Taylor Dispersion in Microchannels

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Front page picture adopted from [5].
# Contents

List of figures ........................................................................... v

1 Introduction ........................................................................... 1

2 Theory ................................................................................... 3
   2.1 The convection-diffusion equation ..................................... 3
   2.2 The moments of concentration ........................................ 6
   2.3 The effective dispersion coefficient ................................... 9
      2.3.1 Long-time regime .................................................... 15
      2.3.2 Short-time regime .................................................. 17

3 Experiments ........................................................................... 19
   3.1 Serpentine channel device .............................................. 19
   3.2 Rotary mixer ..................................................................... 21

4 Conclusion ............................................................................. 23

A Articles ................................................................................ 1

Bibliography ........................................................................... XV
List of Figures

2.1 System geometry. ................................................................. 4

3.1 The serpentine channel device. ........................................... 20
3.2 Experimental results for serpentine channel device. Theoretical values versus measured values. ..................................................... 21
3.3 Schematic of the rotary mixer. ............................................. 21
3.4 Experimental results for Rotary mixer. Theoretical value versus measured values. ................................................................. 22
LIST OF FIGURES
Chapter 1

Introduction

In many microfluidic systems concentration gradients exist which give rise to diffusion. Furthermore, if the fluid is flowing with a non-zero velocity this will cause convection. This convection-diffusion situation is known as Taylor dispersion and is governed by the so-called convection-diffusion equation

\[ \frac{\partial}{\partial t} c + \mathbf{V} \cdot \nabla c = D \nabla^2 c, \]  

(1.1)

where \( c \) is the concentration, \( \mathbf{V} \) is the velocity field and \( D \) is a diffusion coefficient.

In some application the Taylor dispersion is a useful mechanism as it e.g. enhances mixing, compared to mixing by pure diffusion. However, on the other hand, in separation devices this mechanism decreases the resolution.

The Taylor dispersion problem is mostly treated in circular pipes and is for this geometry considered a well-understood mechanism. Unfortunately, this is not a common channel shape in microfluidic systems, where channels, due to fabrication processes, could have a parabolic or rectangular cross-section.

This report deals with Taylor dispersion using two articles written by a French group as inspiration. The first article considers the theory of the Taylor dispersion problem in channels with almost arbitrary constant cross-section, and concludes surprisingly that the dispersion depends on the width of the channel and not on the smallest transverse direction, namely the height. The second article verifies these result experimentally in a serpentine channel device and a rotary mixer.
Chapter 2

Theory

In this section the theory presented in [1] will be discussed. Initially the convection-diffusion equation will be derived followed by the variance, which can be used to calculate the effective dispersion coefficient, an essential parameter in dispersion. The derivation follows the method of moments developed by Aris, [4].

2.1 The convection-diffusion equation

The Taylor dispersion is as mentioned in Chap. 1 governed by the convection-diffusion equation given by Eq. (1.1), which will be derived below.

Conservation of mass can be written as

\[ D_t c(x, y, z, t) + \nabla \cdot J(x, y, z, t) = 0 \quad \Leftrightarrow \quad D_t c(x, y, z, t) = -\nabla \cdot J(x, y, z, t), \]

where \( D_t \) is the material time derivative given by \( D_t = \partial_t + (u \cdot \nabla) \), \( c \) is the concentration and \( J \) is the mass current density. The notation \( \partial_t f(t) \) denotes \( \frac{\partial}{\partial t} f(t) \). The current density \( J \) is given by

\[ J(x, y, z, t) = -D \nabla c(x, y, z, t), \]

where \( D \) is the diffusion coefficient. Inserting Eq. (2.3) in Eq. (2.2) yields

\[ D_t c = -\nabla \cdot (-D \nabla c). \]

Since \( D = \text{const.}, \nabla \cdot \nabla = \nabla^2 \), and the velocity only has a \( z \)-component, \( u \), Eq. (2.4) can be written as

\[ \partial_t c + u \partial_z c = D \nabla^2 c. \]

The velocity averaged in the shortest transverse direction, see Fig. 2.1 keeping in mind that the velocity only depends on \( x \) and \( y \) only, is given by

\[ \bar{u}(x) = \frac{1}{h(x)} \int_0^{h(x)} u(x, y) dy, \]
where $h(x)$ is given by $h(x) = h_0 H\left(\frac{x}{w/2}\right)$, with $H(X)$ being a dimensionless function, which depends on the cross-sectional shape of the microchannel and is given by

$$H(X) = 0 \quad \text{for } X = \pm 1$$

$$0 < H(X) \leq 1 \quad \text{for } X \in [-1; 1]. \quad (2.7)$$

Similarly the averaged concentration can be found as

$$\bar{c}(x, z, t) = \frac{1}{h(x)} \int_0^{h(x)} c(x, y, z, t) \, dy. \quad (2.9)$$

We now want to rewrite Eq. (2.4) in terms of $\bar{v}$ and $\bar{c}$. This is done by integrating on both sides with respect to $y$ from 0 to $h(x)$

$$\int_0^{h(x)} \partial_t c(x, y, z, t) \, dy + \int_0^{h(x)} u(x, y) \partial_z c(x, y, z, t) \, dy = \int_0^{h(x)} D \nabla^2 c(x, y, z, t) \, dy. \quad (2.10)$$

If we start with the first term on the left hand side we may rearrange this to obtain

$$\int_0^{h(x)} \partial_t c(x, y, z, t) \, dy = \partial_t \int_0^{h(x)} c(x, y, z, t) \, dy,$$  

since we are integrating with respect to $y$ and the limits do not have a $t$-dependence. This is recognized as the time derivative of the average concentration $\bar{c}$ times $h(x)$

$$\partial_t \int_0^{h(x)} c(x, y, z, t) \, dy = \partial_t h(x) \bar{c}(x, z, t) = h(x) \partial_t \bar{c}(x, z, t) \quad (2.12)$$

$$\partial_t \int_0^{h(x)} c(x, y, z, t) \, dy = \partial_t h(x) \bar{c}(x, z, t) \quad (2.12)$$

$$= h(x) \partial_t \bar{c}(x, z, t) \quad (2.13)$$
The second term on the left hand side can be calculated using integration by parts
\[
\int_0^{h(x)} u(x, y) \partial_z c(x, y, z, t) dy = \left[ \partial_z c(x, y, z, t) \int_0^{h(x)} u(x, y) dy \right]_{0}^{h(x)} - \int_0^{h(x)} \left[ \partial_y \partial_z c(x, y, z, t) \int_0^{h(x)} u(x, y) dy \right] dy.
\]  
(2.14)

If we interchange the differentiation in the last term on the right hand side, i.e. \( \partial_y \partial_z = \partial_z \partial_y \) and restrict ourselves only to consider time scales longer than \( h_0^2 / D \), i.e. the concentration in the short transverse direction is smeared out due to diffusion, then \( \partial_y c = 0 \). Furthermore due to the smearing the concentration at \( y = h(x) \) and at \( y = 0 \) is approximately \( \bar{c}(x, z, t) \). Eq. (2.14) can therefore be written as
\[
\int_0^{h(x)} u(x, y) \partial_z c(x, y, z, t) dy = \partial_z \bar{c}(x, z, t) \left( \int_0^{h(x)} u(x, y) dy \right)_{h(x)} - \int_0^{h(x)} u(x, y) dy \bigg|_0^{h(x)}.
\]  
(2.15)

The terms in the parentheses are simply the integral of \( u(x, y) \) from 0 to \( h(x) \). Using this and rearranging yields
\[
\int_0^{h(x)} u(x, y) \partial_z c(x, y, z, t) dy = \partial_z \bar{c}(x, z, t) \int_0^{h(x)} u(x, y) dy \Leftrightarrow \int_0^{h(x)} u(x, y) dy = h(x) \bar{u}(x) \partial_z \bar{c}(x, z, t).
\]  
(2.16)

The right hand side is given by
\[
\int_0^{h(x)} D \nabla^2 c(x, y, z, t) dy = \int_0^{h(x)} D (\partial_x^2 + \partial_y^2 + \partial_z^2) c(x, y, z, t) dy.
\]  
(2.17)

Since the upper limit in the integration depends on \( x \) the second derivative with respect to \( x \) cannot simply be put outside the integral. The term can however be rewritten using the following theorem
\[
\partial_z \int_0^{h(x)} f(x, y) dy = \int_0^{h(x)} \partial_z f(x, y) dy + f(x, h(x)) \bar{d}_x h(x) \Leftrightarrow \int_0^{h(x)} \partial_z f(x, y) dy = \partial_z \int_0^{h(x)} f(x, y) dy - f(x, h(x)) \bar{d}_x h(x).
\]  
(2.18)

If we now insert \( \partial_z c(x, y, z, t) \) instead of \( f(x, y) \) we obtain
\[
\int_0^{h(x)} \partial_z \partial_z c(x, y, z, t) dy = \partial_z \int_0^{h(x)} \partial_x c(x, y, z, t) dy - \partial_z c(x, h(x), z, t) \bar{d}_x h(x).
\]  
(2.19)

If we assume no flux boundaries \( \partial_z c(x, h(x), z, t) = 0 \). Using the theorem on the remaining term on the right hand side yields
\[
\partial_x \int_0^{h(x)} \partial_z c(x, y, z, t) dy = \partial_x \left[ \partial_z \int_0^{h(x)} c(x, y, z, t) dy - c(x, h(x), z, t) \bar{d}_x h(x) \right].
\]  
(2.20)
CHAPTER 2. THEORY

The first term in the square brackets is readily recognized as $h(x)$ times the average concentration. Since we are only considering times scales longer than $h_0^2/D$, $c(x, h(x), z, t)$ is approximately $\bar{c}(x, z, t)$. Eq. (2.21) can now be written as

$$\partial_x \int_0^{h(x)} \partial_x c(x, y, z, t) dy \approx \partial_x [\partial_x \{h(x)\bar{c}(x, z, t)\} - \bar{c}(x, z, t) d_x h(x)]. \quad (2.22)$$

The right hand side can be rearranged to yield

$$\partial_x [\partial_x \{h(x)\bar{c}(x, z, t)\} - \bar{c}(x, z, t) d_x h(x)] = \partial_x [d_x h(x)] \bar{c}(x, z, t) + h(x) \partial_x c(x, z, t)$$

$$= \partial_x [h(x) \partial_x \bar{c}(x, z, t)] = [d_x h(x)] \partial_x \bar{c}(x, z, t) + h(x) \partial_x^2 \bar{c}(x, z, t)$$

$$= \partial_x [h(x) \partial_x \bar{c}(x, z, t)]. \quad (2.23)$$

Since we only are considering time scales longer than $h_0^2/D$ the derivative in the $y$-direction is zero, and the second derivative is therefore also zero. The last term of the Laplacian is easily calculated as the integration limits do not depend on $z$, hence

$$\int_0^{h(x)} \partial_x^2 c(x, y, z, t) dy = \partial_x^2 \int_0^{h(x)} c(x, y, z, t) dy \Leftrightarrow$$

$$= h(x) \partial_x^2 \bar{c}(x, z, t). \quad (2.24)$$

We can now write up the convection-diffusion equation in terms of $\bar{u}(x)$ and $\bar{c}(x, z, t)$ using Eqs. (2.13), (2.16), (2.23) and (2.24) divided by $h(x)$

$$\partial_t \bar{c} + \bar{u} \partial_x \bar{c} = D \partial_x^2 \bar{c} + \frac{D}{h(x)} \partial_x [h(x) \partial_x \bar{c}]. \quad (2.25)$$

2.2 The moments of concentration

The moments of concentration are, following Aris’ method of moments [4], given by,

$$c_n(x, t) = \int_{-\infty}^{\infty} \bar{c}(x, z, t)(z - Vt)^n dz, \quad (2.26)$$

where $V$ is the cross-sectionally averaged velocity given by

$$V = \frac{1}{\frac{\sqrt{2}}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} h(x) dx \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \bar{u}(x) dx}. \quad (2.27)$$

If we now consider how $c_0(x, t)$ evolves in time we simply write

$$\partial_t c_0(x, t) = \partial_t \int_{-\infty}^{\infty} \bar{c}(x, z, t)(z - Vt)^0 dz \Leftrightarrow$$

$$= \partial_t \int_{-\infty}^{\infty} \bar{c}(x, z, t) dz. \quad (2.28)$$
2.2. THE MOMENTS OF CONCENTRATION

However, as the integration does not alter the $t$-dependence, the differentiation with respect to $t$ may be put inside the integral

$$\partial_t c_0(x, t) = \int_{-\infty}^{\infty} \partial_t \bar{c}(x, z, t) dz.$$  \hspace{1cm} (2.29)

The expression for $\partial_t \bar{c}(x, z, t)$ is known from Eq. (2.25) and is inserted

$$\partial_t c_0(x, t) = \int_{-\infty}^{\infty} \left[ -\bar{u}(x) \partial_z \bar{c}(x, z, t) + D \partial_z^2 \bar{c}(x, z, t) + \frac{D}{h(x)} \partial_x [h(x) \partial_x \bar{c}(x, z, t)] \right] dz. \hspace{1cm} (2.30)$$

In the following the term $\frac{D}{h(x)} \partial_x [h(x) \partial_x \bar{c}]$ will simply be denoted $\mathcal{D}_x \bar{c}$. If we now start with the first term in the integral

$$- \int_{-\infty}^{\infty} \bar{u}(x) \partial_z \bar{c}(x, z, t) dz = -\bar{u}(x) \int_{-\infty}^{\infty} \partial_z \bar{c}(x, z, t) dz$$

$$= -\bar{u}(x) \left[ \bar{c}(x, z, t) \right]_{-\infty}^{\infty}$$

$$= 0. \hspace{1cm} (2.31)$$

The concentration at $z = \pm \infty$ is obviously zero, hence $\bar{c}(x, z, t)$ is also zero. The second term gives

$$\int_{-\infty}^{\infty} D \partial_z^2 \bar{c}(x, z, t) dz = D \int_{-\infty}^{\infty} \partial_z^2 \bar{c}(x, z, t) dz$$

$$= D \left[ \partial_z \bar{c}(x, z, t) \right]_{-\infty}^{\infty}$$

$$= 0. \hspace{1cm} (2.32)$$

Here the same argument regarding the concentration at $z = \pm \infty$ is used. The last term yields

$$\int_{-\infty}^{\infty} \mathcal{D}_x \bar{c}(x, z, t) dz = \mathcal{D}_x \int_{-\infty}^{\infty} \bar{c}(x, z, t) dz$$

$$= \mathcal{D}_x c_0(x, t). \hspace{1cm} (2.33)$$

The operator $\mathcal{D}_x$ can be put outside the integral since this does not alter the $x$-dependence. The time derivative of $c_0(x, t)$ can therefore be written as

$$\partial_t c_0(x, t) = \mathcal{D}_x c_0(x, t). \hspace{1cm} (2.34)$$

The time evolution of $c_1(x, t)$ may also be found in a similar way. The time derivative of $c_1$ is given by

$$\partial_t c_1(x, t) = \partial_t \int_{-\infty}^{\infty} \bar{c}(x, z, t)(z - Vt) dz$$

$$= \int_{-\infty}^{\infty} \left[ z \partial_t \bar{c}(x, z, t) dz - V \bar{c}(x, z, t) - Vt \partial_t \bar{c}(x, z, t) \right] dz. \hspace{1cm} (2.35)$$
Here we recognize \( \int_{-\infty}^{\infty} \bar{c}(x, z, t) dz = c_0(x, t) \) and \( \partial_t \bar{c}(x, z, t) \) is given by Eq. (2.25)

\[
\partial_t c_1(x, t) = \int_{-\infty}^{\infty} z \left[ -\bar{u}(x) \partial_z \bar{c}(x, z, t) + D \partial_z^2 \bar{c}(x, z, t) + D_x \bar{c}(x, z, t) \right] dz
- V c_0(x, t) - V t \partial_t c_0(x, t).
\]

(2.36)

The first term in the integral gives

\[
- \int_{-\infty}^{\infty} z \bar{u}(x) \partial_z \bar{c}(x, z, t) dz = -\bar{u}(x) \left\{ [\bar{c}(x, z, t)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \bar{c}(x, z, t) dz \right\}
= \bar{u}(x) c_0(x, t).
\]

(2.37)

Here we have used integration by parts and the facts that \( \bar{c}(x, \pm\infty, t) = 0 \) and \( \int_{-\infty}^{\infty} \bar{c}(x, z, t) dz = c_0 \). The second term yields

\[
\int_{-\infty}^{\infty} D_z \partial_z^2 \bar{c}(x, z, t) dz = D \left\{ [z \partial_z \bar{c}(x, z, t)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \partial_z \bar{c}(x, z, t) dz \right\}
= D \left\{ [z \partial_z \bar{c}(x, z, t)]_{-\infty}^{\infty} - [\bar{c}(x, z, t)]_{-\infty}^{\infty} \right\}
= 0.
\]

(2.38)

(2.39)

Once again we have used \( \bar{c}(x, \pm\infty, t) = 0 \) and therefore \( \partial_z \bar{c}(x, \pm\infty, t) = 0 \). The last term gives

\[
\int_{-\infty}^{\infty} D_x \bar{c}(x, z, t) z dz = D_x \int_{-\infty}^{\infty} \bar{c}(x, z, t) z dz
= D_x \int_{-\infty}^{\infty} \bar{c}(x, z, t) (z - V t + V t) dz
= D_x \int_{-\infty}^{\infty} \bar{c}(x, z, t) (z - V t) dz + V t \int_{-\infty}^{\infty} \bar{c}(x, z, t) dz
= D_x [c_1(x, t) + V t c_0(x, t)].
\]

(2.40)

Obviously it is allowed to add and subtract \( V t \) on one side. The time derivative of \( c_1(x, t) \) can now be written as

\[
\partial_t c_1(x, t) = \bar{u}(x) c_0(x, t) + D_x c_1(x, t) + V t D_x c_0(x, t) - V c_0(x, t) - V t \partial_t c_0(x, t)
= \bar{u}(x) c_0(x, t) + D_x c_1(x, t) + V t [D_x c_0(x, t) - \partial_t c_0(x, t)] - V c_0(x, t)
= [\bar{u}(x) - V] c_0(x, t) + D_x c_1(x, t).
\]

(2.41)

Here we have used that \( \partial_t c_0(x, t) = D_x c_0(x, t) \) given by Eq. (2.34).

The moment of concentration \( c_0(x, t) \) will tend towards a constant value, \( c_0^\infty(x) \) for \( t \to \infty \) regardless of the initial conditions. This value \( c_0^\infty \) is simply given by Eq. (2.34) with the left hand side equal to zero

\[
0 = \frac{D}{h(x)} \partial_x (h(x) \partial_x c_0^\infty)
0 = \partial_x (h(x) \partial_x c_0^\infty)
\]

\[
c_0^\infty = \frac{1}{\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} h(x) dx}.
\]

(2.42)
2.3. THE EFFECTIVE DISPERSION COEFFICIENT

As a consequence \( c_1(x, t) \) will also tend towards a constant value for \( t \to \infty \), which can be found using Eqs. (2.42) and (2.41)

\[
D_x c_1^\infty = -c_0^\infty h(x)(\bar{u}(x) - V).
\]  

(2.43)

2.3 The effective dispersion coefficient

The variance may be used to find the effective dispersion coefficient using the following relation, given in [1],

\[
D_{\text{eff}} = \frac{1}{2} d_t \sigma^2(t).
\]  

(2.44)

Intuitively, this relation makes sense, as it may be approximated in the following way

\[
D_{\text{eff}} \approx \frac{1}{2} \left( \frac{\sigma^2(t + \Delta t) - \sigma^2(t)}{\Delta t} \right) \Leftrightarrow 2D_{\text{eff}} \Delta t \approx \sigma^2(t + \Delta t) - \sigma^2(t).
\]  

(2.45)

The right hand side corresponds to the distance a particle is diffused in the period from \( t \) to \( t + \Delta t \). This is also what the left hand side represents.

Hence, the variance of \( z \) must be found in order to find \( D_{\text{eff}} \) and is given by

\[
\sigma^2(t) = \langle (z^2)(t) \rangle - \langle z \rangle^2(t),
\]  

(2.46)

where \( \langle z^n \rangle(t) \) is given by

\[
\langle z^n \rangle(t) = \frac{\int_{-\infty}^{\infty} z^n \left[ \int_{-\frac{w}{2}}^{\frac{w}{2}} \int_{0}^{h(x)} c(x, y, z, t) dy dx \right] dz}{\int_{-\infty}^{\infty} \int_{-\frac{w}{2}}^{\frac{w}{2}} \int_{0}^{h(x)} c(x, y, z, t) dy dx dz}.
\]  

(2.47)

The denominator is easily evaluated

\[
\int_{-\infty}^{\infty} \int_{-\frac{w}{2}}^{\frac{w}{2}} \int_{0}^{h(x)} c(x, y, z, t) dy dx dz = \int_{-\infty}^{\infty} \int_{-\frac{w}{2}}^{\frac{w}{2}} h(x) \bar{c}(x, z, t) dx dz
\]

\[
= \int_{-\frac{w}{2}}^{\frac{w}{2}} h(x) c_0(x, t) dx.
\]  

(2.48)

If the initial concentration is assumed to be normalized i.e.

\[
\int_{-\frac{w}{2}}^{\frac{w}{2}} h(x) c_0(x, t) dx = 1,
\]  

(2.49)

then it will remain so for all times. If we now consider the variance in the moving coordinate system with the \( z \)-coordinate \( z' = z - Vt \) it is simply

\[
\sigma^2(t) = \langle (z - Vt)^2 \rangle(t) - \langle (z - Vt) \rangle^2(t).
\]  

(2.50)
CHAPTER 2. THEORY

In the following only the numerator will be considered. If we start with the first term we obtain

\[
\langle (z - Vt)^2 \rangle (t) = \int_{-\infty}^{\infty} (z - Vt)^2 \left[ \int_{-\frac{x}{x}}^{h(x)} c(x, y, z, t) dy dx \right] dz
\]

\[
= \int_{-\infty}^{\infty} (z - Vt)^2 \left[ \int_{-\frac{x}{x}}^{h(x)} h(x)\bar{c}(x, z, t) dx \right] dz,
\tag{2.51}
\]

where we have used the expression for \( \bar{c}(x, z, t) \) given by Eq. (2.9). As none of the limits in the integration with respect to \( x \) depend on \( z \) it is allowed to interchange the two integrations. Remembering that the concentration is normalized we get

\[
\langle (z - Vt)^2 \rangle (t) = \int_{-\infty}^{\infty} h(x) \left[ \int_{-\infty}^{\infty} \bar{c}(x, y, z, t)(z - Vt)^2 dz \right] dx
\]

\[
= \int_{-\frac{x}{x}}^{h(x)} h(x)c_2(x, t) dx
\tag{2.52}
\]

We now consider the second term

\[
\langle z - Vt \rangle (t) = \langle z \rangle (t) - \langle Vt \rangle (t).
\tag{2.53}
\]

The last term is readily evaluated

\[
\langle Vt \rangle (t) = \int_{-\infty}^{\infty} Vt \left[ \int_{-\frac{x}{x}}^{h(x)} c(x, y, z, t) dy dx \right] dz
\]

\[
= Vt \int_{-\infty}^{\infty} h(x) c(x, y, z, t) dx dy dz
\]

\[
= Vt
\tag{2.54}
\]

The first term is given by

\[
\langle z \rangle (t) = \int_{-\infty}^{\infty} z \left[ \int_{-\frac{x}{x}}^{h(x)} c(x, y, z, t) dy dx \right] dz
\]

\[
= \int_{-\infty}^{\infty} h(x)\bar{c}(x, z, t) dx \int_{-\infty}^{\infty} z\bar{c}(x, z, t) dz.
\tag{2.55}
\]

Since the limits in the integration with respect to \( x \) do not depend on \( z \) it is allowed to interchange the integrations

\[
\langle z \rangle (t) = \int_{-\infty}^{\infty} h(x) \left[ \int_{-\infty}^{\infty} \tilde{c}(x, z, t) dz \right] dx.
\tag{2.56}
\]
2.3. THE EFFECTIVE DISPERSION COEFFICIENT

We now differentiate on both sides with respect to $t$

$$\partial_t \langle z \rangle(t) = \partial_t \int_{-\infty}^{\infty} h(x) \left[ \int_{-\infty}^{\infty} z \bar{c}(x, z, t) \, dz \right] \, dx.$$  (2.57)

The expression for $\partial_t \bar{c}(x, z, t)$, given by Eq. (2.25), is inserted

$$\langle z \rangle(t) = \int_{-\infty}^{\infty} \left[ \bar{u}(x) \partial_z \bar{c}(x, z, t) + D \partial_z^2 \bar{c}(x, z, t) + D_x \bar{c}(x, z, t) \right] \, dz. \quad (2.58)$$

We evaluate each term in the $z$-integral one at a time starting with the first

$$\int_{-\infty}^{\infty} -zu(x) \partial_z \bar{c}(x, z, t) \, dz = -u(x) \left[ \bar{c}(x, z, t) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \bar{c}(x, z, t) \, dz$$

$$= u(x) c_0(x, t). \quad (2.59)$$

Here we have used that $\bar{c}(x, \pm \infty, t) = 0$ and $\int_{-\infty}^{\infty} \bar{c}(x, z, t) \, dz = c_0(x, t)$. The second term is given by

$$\int_{-\infty}^{\infty} zD \partial_z^2 \bar{c}(x, z, t) \, dz = D \left( \left[ z \partial_z \bar{c}(x, z, t) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \partial_z \bar{c}(x, z, t) \, dz \right)$$

$$= D \left( \left[ z \partial_z \bar{c}(x, z, t) \right]_{-\infty}^{\infty} - \left[ \bar{c}(x, z, t) \right]_{-\infty}^{\infty} \right)$$

$$= 0. \quad (2.60)$$

As before $\bar{c}(x, \pm \infty, t) = 0$ and therefore $\partial_z \bar{c}(x, z, t) \big|_{\pm \infty} = 0$. The last term is given by

$$\int_{-\infty}^{\infty} zD_x \bar{c}(x, z, t) \, dz = \left[ zD_x \bar{c}(x, z, t) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \partial_z D_x \bar{c}(x, z, t) \, dz \quad (2.61)$$

One is allowed to interchange $\partial_z$ and $D_x$, hence

$$\int_{-\infty}^{\infty} zD_x \bar{c}(x, z, t) \, dz = \left[ zD_x \partial_z \bar{c}(x, z, t) \right]_{-\infty}^{\infty} - D_x \int_{-\infty}^{\infty} \partial_z \bar{c}(x, z, t) \, dz$$

$$= \left[ zD_x \partial_z \bar{c}(x, z, t) \right]_{-\infty}^{\infty} - \left[ \bar{c}(x, z, t) \right]_{-\infty}^{\infty}$$

$$= 0. \quad (2.62)$$

The same arguments as before are also used here. The time derivative of $\langle z \rangle(t)$ is therefore given by

$$d_t \langle z \rangle(t) = \int_{-\infty}^{\infty} \bar{u}(x) h(x) c_0(x, t) \, dx$$

$$= \frac{\int_{-\infty}^{\infty} h(x) c_0(x, t) \, dx}{\int_{-\infty}^{\infty} h(x) c_0(x, t) \, dx}. \quad (2.63)$$
CHAPTER 2. THEORY

If we now restrict ourselves only to consider time scales longer than $\frac{w^2}{D}$ then $c_0(x, t) = c_0(t)$ since the concentration will be smeared out in the $xy$-plane, i.e. across the channel. In this case Eq. (2.63) will become

$$d_t \langle z \rangle (t) = \frac{c_0(t) \int \frac{w}{2} \bar{u}(x) h(x) dx}{c_0(t) \int \frac{w}{2} h(x) dx}.$$  (2.64)

The cross-sectionally averaged velocity $V$ is given by Eq. (2.27) and can be rewritten to obtain

$$V \int -\frac{w}{2}^w h(x) dx = \int -\frac{w}{2}^w h(x) \bar{u}(x) dx.$$  (2.65)

Inserting this we get

$$d_t \langle z \rangle (t) = \frac{V c_0(t) \int \frac{w}{2} \bar{u}(x) h(x) dx}{c_0(t) \int \frac{w}{2} h(x) dx} = V.$$  (2.66)

The time derivative of $\langle (z - V t) \rangle (t)$ for $t \gg \frac{w^2}{D}$ is therefore

$$d_t \langle (z - V t) \rangle (t) = \partial_t \langle z \rangle (t) - \partial_t \langle V t \rangle (t) = V - d_t V t$$

$$= 0.$$  (2.67)

Hence, in this time regime the variance is given by

$$\sigma^2(t) = \int_{-\infty}^{\infty} h(x) c_2(x, t) dx.$$  (2.68)

If we now consider the time derivative of the variance, it is given by

$$d_t \sigma^2(t) = d_t \langle (z - V t)^2 \rangle (t) = \partial_t \int \frac{w}{2} h(x) c_2(x, t) dx$$

$$= \int \frac{w}{2} h(x) \partial_t c_2(x, t) dx.$$  (2.69)

The expression for $c_2(x, t)$ can be obtained from Eq. (2.26)

$$\partial_t c_2(x, t) = \partial_t \int_{-\infty}^{\infty} \bar{e}(x, z, t)(z - V t)^2 dz$$

$$= \int_{-\infty}^{\infty} \partial_t \bar{e}(x, z, t)(z - V t)^2 dz$$

$$= \int_{-\infty}^{\infty} (z - V t)^2 \partial_t \bar{e}(x, z, t) - 2V \bar{e}(x, z, t)(z - V t) dz$$

$$= \int_{-\infty}^{\infty} (z - V t)^2 \partial_t \bar{e}(x, z, t) dz - 2V c_0.$$  (2.70)
\[ \partial_t \bar{c}(x, z, t) \text{ is known from Eq. (2.25) and is simply inserted} \]

\[
\begin{align*}
\partial_t c_2(x, t) &= \int_{-\infty}^{\infty} (z - Vt)^2 \left[ -\bar{u}(x) \partial_z \bar{c}(x, z, t) + D \partial_z^2 \bar{c}(x, z, t) + D_x \bar{c}(x, z, t) \right] dz \\
&= \int_{-\infty}^{\infty} (z^2 + (Vt)^2 - 2zVt) \left[ -\bar{u}(x) \partial_z \bar{c}(x, z, t) + D \partial_z^2 \bar{c}(x, z, t) \\
&\quad + D_x \bar{c}(x, z, t) \right] dz. \quad (2.71)
\end{align*}
\]

Starting with the terms including \(-\bar{u}(x) \partial_z \bar{c}(x, z, t)\) yields

\[
\begin{align*}
- \int_{-\infty}^{\infty} z^2 \bar{u}(x) \partial_z \bar{c}(x, z, t) dz &= -\bar{u}(x) \int_{-\infty}^{\infty} z^2 \bar{c}(x, z, t) dz \\
&= -\bar{u}(x) \left\{ \left[ z^2 \bar{c}(x, z, t) \right]_{-\infty}^{\infty} - 2 \int_{-\infty}^{\infty} z \bar{c}(x, z, t) dz \right\} \\
&= 2\bar{u}(x) \int_{-\infty}^{\infty} \bar{c}(x, z, t)(z - Vt + Vt) dz \\
&= 2\bar{u}(x) c_1(x, t) + 2\bar{u}(x) Vtc_0(x, t) \quad (2.72)
\end{align*}
\]

\[
\begin{align*}
- \int_{-\infty}^{\infty} (Vt)^2 \bar{u}(x) \partial_z \bar{c}(x, z, t) dz &= -(Vt)^2 \bar{u}(x) \int_{-\infty}^{\infty} \partial_z \bar{c}(x, z, t) dz \\
&= -(Vt)^2 \bar{u}(x) \left\{ \left[ \bar{c}(x, z, t) \right]_{-\infty}^{\infty} \right\} \\
&= 0 \quad (2.73)
\end{align*}
\]

\[
\begin{align*}
\int_{-\infty}^{\infty} 2zVt \bar{u}(x) \partial_z \bar{c}(x, z, t) dz &= 2Vt \bar{u}(x) \int_{-\infty}^{\infty} z \partial_z \bar{c}(x, z, t) dz \\
&= 2Vt \bar{u}(x) \left\{ \left[ z\bar{c}(x, z, t) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \bar{c}(x, z, t) dz \right\} \\
&= -2Vt \bar{u}(x) c_0(x, t) \quad (2.74)
\end{align*}
\]

\[
\begin{align*}
\int_{-\infty}^{\infty} (z - Vt)^2 \bar{u}(x) \partial_z \bar{c}(x, z, t) dz &= 2\bar{u}(x) c_1(x, t). \quad (2.75)
\end{align*}
\]

Here we have integrated by parts and used the fact that \(\bar{c}(x, \pm\infty, t) = 0\). Proceeding with
the terms that include \( D\partial_x^2 \bar{c}(x,z,t) \) gives

\[
\int_{-\infty}^{\infty} z^2 D\partial_x^2 \bar{c}(x,z,t) dz = D \left\{ \left[ z^2 \partial_z \bar{c}(x,z,t) \right]_{-\infty}^{\infty} - 2 \int_{-\infty}^{\infty} z \partial_z \bar{c}(x,z,t) dz \right\} = -2D \left\{ \left[ z \bar{c}(x,z,t) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \bar{c}(x,z,t) dz \right\} = 2Dc_0(x,t)
\]

(2.76)

\[
\int_{-\infty}^{\infty} (Vt)^2 D\partial_z^2 = (Vt)^2 D [\partial_z \bar{c}(x,z,t)]_{-\infty}^{\infty} = 0
\]

(2.77)

\[- \int_{-\infty}^{\infty} 2zVtD\partial_x \bar{c}(x,z,t) dz = -2VtD \left\{ \left[ z \partial_z \bar{c}(x,z,t) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \bar{c}(x,z,t) dz \right\} = 2VtD [\bar{c}(x,z,t)]_{-\infty}^{\infty} = 0
\]

(2.78)

\[
\int_{-\infty}^{\infty} (z - Vt)^2 \partial_t \bar{c}(x,z,t) = 2Dc_0(x,t).
\]

(2.79)

Once again integration by parts has been performed and it has been used that \( \bar{c}(x,\pm\infty, t) = 0 \) and therefore \( \partial_z \bar{c}(x,\pm\infty, t) = 0 \). The last terms including \( D_x \bar{c}(x,z,t) \) is easily evaluated

\[
\int_{-\infty}^{\infty} (z - Vt)^2 D_x \bar{c}(x,z,t) dz = D_x \int_{-\infty}^{\infty} \bar{c}(x,z,t)(z - Vt)^2 dz = D_x c_2(x,t).
\]

(2.80)

The time derivative of the variance may therefore be written

\[
d_t ((z - Vt)^2) = \int_{-\frac{w}{2}}^{\frac{w}{2}} h(x) [2c_1(x,t)(\bar{u}(x) - V) + 2Dc_0(x,t) + D_x c_2(x,t)] dx = 2D \int_{-\frac{w}{2}}^{\frac{w}{2}} c_0(x,t) h(x) dx + 2 \int_{-\frac{w}{2}}^{\frac{w}{2}} c_1(x,t)(\bar{u}(x) - V) h(x) dx + 2 \int_{-\frac{w}{2}}^{\frac{w}{2}} D_x c_2(x,t) h(x) dx.
\]

(2.81)

If we now use the fact that the concentration is normalized i.e.

\[
\int_{-\frac{w}{2}}^{\frac{w}{2}} h(x) \left\{ \int_{-\infty}^{\infty} \bar{c}(x,z,t) dz \right\} dz = \int_{-\frac{w}{2}}^{\frac{w}{2}} h(x)c_0(x,t) dx = 1,
\]

(2.82)

then Eq. (2.81) can be written as

\[
d_t ((z - Vt)^2) = 2D + 2 \int_{-\frac{w}{2}}^{\frac{w}{2}} c_1(x,t)(\bar{u}(x) - V) h(x) dx + \int_{-\frac{w}{2}}^{\frac{w}{2}} D_x c_2(x,t) h(x) dx.
\]

(2.83)
If we now consider the last term and insert the expression for the differential operator given by $D_x f(x) = \frac{D}{h(x)} \partial_x (h(x) \partial_x f(x))$, where $f(x)$ is an arbitrary function of $x$, we get

$$\int_{-\frac{w}{2}}^{\frac{w}{2}} h(x) \frac{D}{h(x)} \partial_x (h(x) \partial_x c_2(x, t)) dx = \int_{-\frac{w}{2}}^{\frac{w}{2}} D \partial_x (h(x) \partial_x c_2(x, t)) \frac{w}{2}$$

$$= D \left[ h(x) \partial_x c_2(x, t) \right] \frac{w}{2}$$

$$= 0. \quad (2.84)$$

Here we have used that the height is zero at the boundaries of the channels in $x$-direction as the function $H(\pm 1) = 0$. The final expression for the time derivative of the variance is therefore given by

$$d_t \langle (z - V t)^2 \rangle(t) = 2D + 2 \int_{-\frac{w}{2}}^{\frac{w}{2}} c_1(x, t)(\bar{u}(x) - V)h(x) dx. \quad (2.85)$$

### 2.3.1 Long-time regime

In the lubrication theory the velocity field is given by $u(x, y) = Ay(h(x) - y)$, where $A$ is a constant proportional to the pressure. This can be used to calculate the averaged velocity in the lubrication theory

$$\bar{u}(x) = \frac{1}{h(x)} \int_0^{h(x)} u(x, y) dy$$

$$= \frac{A}{h(x)} \int_0^{h(x)} y(h(x) - y) dy$$

$$= \frac{A}{h(x)} \left[ \frac{1}{2} h(x)^3 - \frac{1}{3} h(x)^3 \right]$$

$$= Ah(x)^2$$

$$= \frac{Ah(x)^2}{6}. \quad (2.86)$$

If we consider the cross-sectionally averaged velocity this can be written as

$$V = \frac{\int_{-\frac{w}{2}}^{\frac{w}{2}} dx \int_0^{h(x)} dy u(x, y)}{\int_{-\frac{w}{2}}^{\frac{w}{2}} dx \int_0^{h(x)} dy}$$

$$= \frac{A}{6} \int_{-\frac{w}{2}}^{\frac{w}{2}} dx h(x)^3$$

$$h_0 \int_{-\frac{w}{2}}^{\frac{w}{2}} dx \frac{h(x)}{h_0}$$

$$= Ah_0^2 I_3 \Leftrightarrow$$

$$A = \frac{6I_1}{A h_0^2 V}. \quad (2.87)$$
Inserting Eq. (2.87) in Eq. (2.86) we get

\[
\bar{u}(x) = \frac{I_1 h^2(x)}{I_3 h_0^2} V.
\]  

(2.88)

We now introduce an intermediate function, which can be obtained from Eqs. (2.43) and (2.85)

\[
g(x) = \frac{1}{D} \int_{-w/2}^{x} dx' h(x')(\bar{u}(x') - V).
\]  

(2.89)

If we use the intermediate function defined in Eq. (2.89) to rewrite Eq. (2.85) we obtain

\[
d_t \langle (z - V t)^2 \rangle(t) = 2D \left( 1 + \frac{\int_{\frac{w}{2}}^{\frac{w}{2}} dx \left[ g^2(x)/h(x) \right]}{\int_{-\frac{w}{2}}^{\frac{w}{2}} dx h(x)} \right).
\]  

(2.90)

Inserting \( g(x) \), \( \bar{u}(x) \) and \( h(x) = h_0 H\left(\frac{x}{w/2}\right) \) and only considering the numerator of the fraction we get

\[
\int_{-\frac{w}{2}}^{\frac{w}{2}} dx \left[ g^2(x)/h(x) \right] = h_0 V^2 D^2 \int_{-\frac{w}{2}}^{\frac{w}{2}} dx \left[ \left( \frac{\int_{-w/2}^{w/2} dx' H\left(\frac{x'}{w/2}\right) \left( I_1 h_0^2 \left( \frac{x'}{w/2} \right) V - \bar{u}(x') \right)}{h_0 \left( \frac{x'}{w/2} \right)} \right)^2 \right].
\]  

(2.91)

The variable \( x \) is be substituted by \( X \) through the following substitution

\[
X = \frac{x}{w/2} \Leftrightarrow \quad d_x X = \frac{2}{w} dX \Leftrightarrow \quad dx = \frac{w}{2} dX.
\]  

(2.92)

Using this on both the inner and outer integrals yields

\[
\int_{-\frac{w}{2}}^{\frac{w}{2}} dx \left[ g^2(x)/h(x) \right] = h_0 V^2 w^3 \int_{-1}^{1} dX \left[ \left( \frac{\int_{-1}^{1} dX' H(X') \left( I_1 h_0^2 \left( \frac{x}{w/2} \right) - \bar{u}(x') \right)}{H(X')} \right)^2 \right].
\]  

(2.93)
Doing the same substitution in the denominator of the fraction in Eq. (2.90) we get
\[
\int_{-\frac{w}{2}}^{\frac{w}{2}} h(x)dx = \frac{w}{2} h_0 \int_{-1}^{1} H(X) dX
\]
\[= \frac{w}{2} h_0 I_1. \tag{2.94}
\]
Inserting Eqs. (2.93) and (2.94) in Eq. (2.90) we get
\[
d_t \langle (z - V t)^2 \rangle(t) = 2D(1 + \kappa_l P_{e_w}^2), \tag{2.95}
\]
where \(\kappa_l\) is a dimensionless constant, which only depends on the cross-sectional shape of the channel, given by
\[
\kappa_l = \frac{1}{4I_1} \int_{-1}^{1} \frac{1}{H(X)} \left[ \int_{-1}^{X} \left( \frac{H'(X') I_1}{I_3} - 1 \right) H(X') dX' \right]^2 dX, \tag{2.96}
\]
and \(P_{e_w}\) is the Peclet number defined using the width \(w\) given by
\[
P_{e_w} = \frac{wV}{D}. \tag{2.97}
\]
Here it should be noticed that the width and not the height is the relevant length scale, which is quite surprising. As \(\kappa_l\) only depends on the cross-sectional shape of the channel this implies that the height of the channel is not a parameter which affects the effective dispersion coefficient, which is given by
\[
D_{\text{long}}^{\text{eff}}(t) = \frac{1}{2} d_t \sigma^2(t)
\]
\[= 2D(1 + \kappa_l P_{e_w}^2)t. \tag{2.98}
\]
\(\kappa_l\) can be calculated for e.g. a parabolic cross-section with \(H(X) = 1 - X^2\) and yields \(\kappa_l \approx 3.1 \times 10^{-3}\).

2.3.2 Short-time regime

For short times the concentration is homogeneous in the \(y\)-direction but not in the \(x\)-direction. In this time-regime the time derivative of the variance can be written as\(^1\)
\[
d_t \langle (z - V t)^2 \rangle(t) = 2D + 2 \int_{-\frac{w}{2}}^{\frac{w}{2}} dx h(x) (\bar{u}(x) - V)^2 \int_{-\frac{w}{2}}^{\frac{w}{2}} dX h(x) \tag{2.99}
\]
Inserting Eq. (2.86) in Eq. (2.99) yields
\[
D_{\text{short}}^{\text{eff}}(t) = \frac{1}{2} d_t \sigma_{\text{short}}^2(t) \simeq D \left( 1 + \kappa_s P_{e_w}^2 \frac{D t}{w^2} \right), \tag{2.100}
\]
\(^1\)See [1, p. 392] for further details
where $\kappa_s$ is given by

$$\kappa_s = \frac{I_1I_5}{I_3^2} - 1. \quad (2.101)$$

Once again it should be noted that the effective dispersion coefficient does not depend on the height.
Chapter 3

Experiments

In this chapter the experiments discussed in [2] will be compared to the theory given in Chap. 2. Two kind of structures are used for experiments in [2], namely a serpentine channel device, and a rotary mixer. Both of these devices are fabricated out of polydimethylsiloxane (PDMS) using multi-layer soft-lithography, [3]. This makes it possible to use a set of control channels as valves, activated by pressure, for the underlying fluidic channels. The experiments investigates the dispersion of a plug of tracers.

3.1 Serpentine channel device

The serpentine channel device is used to ensure that the concentration is smeared out in the cross-sectional plane. The time scale required to ensure this is $O \left( \frac{w^2}{D} \right)$ which corresponds to a channel length of $O \left( \frac{U w^2}{D} \right)$. For a velocity of $3 \, \text{mm s}^{-1}$, this yields a channel length of approximately 100 mm. A top view of the serpentine channel device is shown in Fig. 3.1A, a cross-sectional view is given in Fig. 3.1D.

For each experiment the device is filled with $10^{-2} \, \text{M NaOH}$. The experiment is conducted by injecting a plug of fluorescein between valve 2 and 4 shown in Fig. 3.1C. Each measurement consists of measuring the intensity of the fluorescein at different positions and estimating the mean velocity by using

$$U = \frac{\text{distance between two consecutive positions, 1 and 2}}{t_{\text{max,2}} - t_{\text{max,1}}},$$  \hspace{1cm} (3.1)

where $t_{\text{max,i}}$ is the position where the intensity at position $i$ reaches its maximum. A Gaussian profile of the form

$$C(t) \approx \frac{1}{\sqrt{4\pi D_{\text{eff}} t_{\text{max}}}} \exp \left( - \frac{U^2 (t_{\text{max}} - t)^2}{4D_{\text{eff}} t_{\text{max}}} \right),$$  \hspace{1cm} (3.2)

is then fitted to these intensity measurements as can be seen in Fig. 3.2(a). The photo-bleaching of the fluorescein is neglected in this experiment as it would mostly affect the height of the Gaussian, which is not related to the effective dispersion coefficient.
It is now possible to deduce the effective dispersion coefficient, which then can be plotted against the theoretical coefficient of dispersion given by

\[ D_{\text{eff}} = D \left( 1 + \frac{kU^2w^2}{D^2} \right), \]  

(3.3)

where \( k \) is a numerical constant, which only depends on the cross-sectional shape of the channel. A plot of the experimental effective dispersion coefficient versus the theoretical effective dispersion coefficient for two different channel widths is show in Fig. 3.2(b), from which is evident that the values indeed agree. This indicates that the theory proposing that the effective dispersion coefficient depends on the width rather than the height is correct.
3.2. ROTARY MIXER

Before each experiment the mixer, which is shown in Fig. 3.3, is filled with $10^{-2}$ M NaOH. After the filling a small plug of fluorescein is injected and mixed by peristaltic mixing using valves 3, 5 and 6. Different frequencies yield different mean velocities.

For small velocities, $U_{\text{min}} = \frac{D}{\sqrt{kw}} < U$, the mixing is dominated by molecular diffusion, whereas for large velocities, $U < \frac{2\pi RD}{w^2} = U_{\text{max}}$ the concentration distribution wraps into itself. Hence the experiments are performed at velocities in the interval $U_{\text{min}} < U < U_{\text{max}}$ as it is the hydrodynamic dispersion which is of interest. For the given geometry

![Figure 3.3: Schematic of the rotary mixer. Fluidic channels, 11 μm high and 100 μm wide, are in black and the control channels are in gray, 20 μm high and 100 μm wide. Mixing is achieved by peristaltic pumping. Picture adopted from [2].]
CHAPTER 3. EXPERIMENTS

Figure 3.4: (a): Intensity versus time for \( U = 0.91 \text{ mms}^{-1} \). The inset is a linear fit of \( \ln \left( \frac{c(t)}{c_b^{\prime}(t)} - 1 \right) \) versus time, where \( c(t) \) is the measured intensity and \( c_b^{\prime}(t) \) is its asymptotic form. The slope of the line is a measurement of the effective long-time dispersion. (b): Theoretical dispersion coefficient versus measured effective dispersion coefficient with \( k = 0.003 \) for a channel with parabolic shape and \( D = 3 \times 10^{-4} \text{ mm}^2 \text{s}^{-1} \). The black solid line is the theoretical prediction for \( D_{\text{eff}} = D + \frac{kU^2}{D} \). The two vertical dashed lines indicate the region in which the mixing is dominated by hydrodynamic dispersion. Pictures adopted from [2].

\( U_{\text{min}} = 5.5 \times 10^{-2} \text{ mm s}^{-1} \) and \( U_{\text{max}} = 7.5 \times 10^{-1} \text{ mm s}^{-1} \). A measurement consists of measuring the intensity and the corresponding time. The time between two consecutive peaks are used to estimate the mean velocity. As each experiment consists of more than two peaks several estimates of the mean velocity can be obtained per experiment, see Fig. 3.4(a).

However, in contrast to the serpentine channel experiments the focus is here on a transient state, why it is not possible simply to fit a given analytical solution. Thus the analysis is performed on the late-time relaxation of the peak values towards the final asymptotic value. This can be seen in the inset of Fig. 3.4(a), where \( \ln \left( \frac{c(t)}{c_b^{\prime}(t)} - 1 \right) \) is plotted versus time, with \( c(t) \) being the measured intensity and \( c_b^{\prime}(t) \) is its asymptotic value, where photobleaching has been taken into account. The slope of this line is a measurement of the effective long-time dispersion.

Once again the measured values of \( D_{\text{eff}} \) for different velocities are compared to the theoretical values as shown in Fig. 3.4(b). It is noticed that the measured values in general are slightly larger than the predicted, which could be caused e.g. by the peristaltic pumping as this might distort the flow when it passes through the active valves.
Chapter 4

Conclusion

The phenomena of Taylor dispersion has been investigated, using two French articles, [1] and [2], as inspiration.

The theory for Taylor dispersion in microchannels is presented yielding a very surprising result. For long times, i.e. where the concentration is homogeneous in the cross-sectional plane, it was found that the effective dispersion coefficient could be written as

$$D_{\text{eff}}^{\text{long}} = D(1 + \kappa_l Pe_w^2), \quad Pe_w = \frac{Vw}{D},$$

(4.1)

where $V$ is the cross-sectionally averaged velocity, $w$ is the width, $D$ is diffusion coefficient and $\kappa_l$ is a dimensionless constant which only depends on the cross-sectional shape of the channel. This implies that the dispersion coefficient does not depend on the shortest transverse direction, namely the height, as one intuitively might expect, but rather the width of the microchannel.

For short times, i.e. where the concentration is homogeneous in the shortest transverse direction, a similar result was found

$$D_{\text{eff}}^{\text{short}} = D \left(1 + \kappa_s Pe_w^2 \frac{Dt}{w^2}\right),$$

(4.2)

where $\kappa_s$ also is a dimensionless constant which only depends on the cross-sectional shape of the channel, which again states that the height is not an important factor.

In [2] these theoretical results were shown to be correct for a serpentine channel device and rotary mixer with parabolic cross-section. It can therefore be concluded that the height is not an important parameter when considering Taylor dispersion in microchannels.
Appendix A

Articles

In this appendix the articles, [1] and [2], are reprinted.
Hydrodynamic Dispersion in Shallow Microchannels: the Effect of Cross-Sectional Shape

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We highlight the fact that hydrodynamic dispersion in shallow microchannels is in most cases controlled by the width of the cross section rather than by the much thinner height of the channel. We identify the relevant time scales that separate the various regimes involved. Using the lubrication approximation, we provide simple formulas that permit a quantitative evaluation of dispersion for most shallow cross-sectional shapes in the “long-time” Taylor regime, which is effectively diffusive. Because of its relevance for microfluidic systems, we also provide results for the short-time “ballistic regime” (for specific initial conditions). The special cases of parabolic and quasi-rectangular shapes are considered due to their frequent use in microsystems.

Hydrodynamic dispersion refers to the inevitable spreading along the flow direction of dissolved or suspended Brownian particles in a flowing fluid, the ultimate origin of the spreading being related to velocity variations in the direction transverse to the mean flow. The effect is particularly significant in laminar flows in channels for which there is generally a gradual change in velocity from zero at the boundary to a maximum value in the center. The dispersion significantly reduces the resolution of analytic studies performed using pressure-driven flow in microfluidic devices and analytical lab-on-a-chip systems (ref 1 and references therein). Such analytic studies include, for example, separating species or determining rates of chemical reactions. Hydrodynamic dispersion also limits the number of samples that can be transported sequentially in a given microchannel and thereby limits the throughput of the device.

Although such (Taylor) dispersion is considered a well-understood phenomenon, it nevertheless remains difficult to quantify in practice for many microchannel configurations, which depart notably from the circular capillary usually described in textbooks. As a consequence, many analyses refer to situations with only one transverse dimension (radius or height), a procedure that we will show can lead to order of magnitude errors in the estimation of dispersion. In principle, the basic procedure for properly quantifying mass transport in laminar pressure-driven flows is well established, and follows the seminal works of Taylor (1) and Aris (2) see also Brenner and Edwards. (3) Either of the two approaches, though somewhat different in detail, allows one to quantify the dispersion for arbitrary channel cross sections. In one recent application, Dutta and Leighton (4) discussed how to limit dispersion in pressure-driven flows by tailoring the cross-sectional shape of the microchannel. For simple shapes of the channel cross section (e.g., two planes, a circle, and an ellipse), analytical results for dispersion are available, while more complicated shapes require numerical analysis (see also ref 6).

In this paper, we provide basic results for describing simply and quantitatively the effect of hydrodynamic dispersion for situations where the microfluidic channel has a slender, shallow cross section with a typical height $h_0$ much smaller than the width $w$ (see Figure 1, top). These situations are numerous in microfluidic devices, partly as a consequence of the various microfabrication methods (see, for example, ref 7 and references therein). Some common cross sections include quasi-rectangular and trapezoidal shapes (e.g., via chemical etching of crystalline silica), quasi-parabolic shapes (e.g., PDMS channels used in multilayer devices), etc.

There are two main contributions in this paper. First, we demonstrate and emphasize that, when $h_0 \ll w$, in almost all cases (i.e., we exclude quasi-rectangular cross sections) hydrodynamic dispersion is controlled by the width $w$, the larger of the two transverse dimensions, and not by the height $h_0$ of the microchannel. This fact is in contrast with calculations of the hydrodynamic dispersion in situations where the microfluidic channel has a slender, shallow cross section with a typical height $h_0$ much smaller than the width $w$. (2)

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dynamic resistance, which is always controlled by the smallest of the two cross-sectional dimensions. Second, we provide simple (user-friendly) formulas for the hydrodynamic dispersion for any shape of the cross section, for the long-time Taylor dispersion regime, and also for the short-time regime of hydrodynamic stretching (focusing on specific initial conditions). Both time regimes are important in the microfluidic context, and our formulas also provide an estimate of the crossover time between the two regimes. These formulas are obtained following Aris’s method of moments adapted to shallow geometries along the lines mentioned above relies on Aris’s “method of moments” formulation as described in the appendix. In the following section, we provide the main results. We provide explicit formulas that exhibit the scaling dependence of the dispersion coefficient on the geometric and flow parameters and the quantitative dependence on the shape of the cross section. Following that, we discuss our results, compute the effective dispersion coefficients that quantify spreading for a variety of cross-sectional shapes, discuss the case of quasi-rectangular shapes, and comment on the implications of our results for microfluidic applications. In the Appendix, we provide the main lines of the derivation, which as mentioned above relies on Aris’s “method of moments” formulation combined with a lubrication description of pressure-driven flow in these geometries.

For the sake of clarity, the paper is organized with the main results clearly identified and mathematical details relegated to the appendix. In the following section, we introduce the nomenclature used, comment on the physical ingredients of the problem, and provide the reader with our main results. We then consider a set of similar particles with a molecular (thermal) diffusivity D and describe their transport by the classical convective–diffusion equation for the concentration field c(x, y, z, t):

\[
\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = D \nabla^2 c
\]

We assume no flux boundary conditions at the walls of the channel, n\cdot\mathbf{v} = 0, where n is the local normal vector at the boundary.

**Basic problem statement.** We consider a sample of particles injected in the channel at time t = 0 and around z = 0 (initial concentration c(x, y, z, t = 0)), and we follow the evolution of this pulse (see Figure 1, bottom). The moments of the concentration distribution quantify the evolution:

\[
\langle \phi(z) \rangle(t) = \frac{\int_0^L \int_0^w \int_0^h \phi(x, y, z, 0) c(x, y, z, t) \, dy \, dz}{\int_0^L \int_0^w \int_0^h c(x, y, z, t) \, dy \, dz}
\]

The innermost integrations in (3) provide the area-averaged concentration, which is often the quantity measured in experiments using a variety of detection schemes (refractometry, fluorescence, etc.). The mean position and variance are then \langle z(t) \rangle and \langle z^2(t) \rangle = \langle z(t) \rangle^2. It is also common to quantify dispersion along the flow direction in terms of the (time-dependent) effective dispersion coefficient, \text{D}_\text{eff}(t), defined as

\[
\text{D}_\text{eff}(t) = \frac{1}{2} \frac{d}{dt} \langle z^2(t) \rangle
\]

The specific “shape” of the cross section by writing h(x) = h_0 f(x/w(z)), where f(0) = 0, is a dimensionless function that is zero for x = ±1 and has a maximum equal to 1 between these two points. We denote by S the constant cross-sectional area, S = \int_0^w h_0 f(x/w(z)) \, dx. We present results valid for the conditions h_0 = w = L, which are generally true for a large number of microfluidic applications.

**Flow and Transport of Particles.** We assume that there is a steady incompressible pressure-driven laminar flow in the channel. The velocity field is directed along the channel axis, \mathbf{u} = u(x, y, z = 0), and this field is independent of z so long as the cross-sectional shape of the channel is constant. The cross-sectionally averaged (mean) velocity V is defined as

\[
V = \frac{1}{3} \int \mathbf{u}(x, y, z) \, dS
\]

We then consider a set of similar particles with a molecular (thermal) diffusivity D and describe their transport by the classical convective–diffusion equation for the concentration field c(x, y, z, t):

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\]

We assume no flux boundary conditions at the walls of the channel, n\cdot\mathbf{v} = 0, where n is the local normal vector at the boundary.

**NOMENCLATURE AND MAIN RESULTS**

Transport Model and Basic Definitions. Geometry. We utilize Cartesian coordinates and consider a straight channel of constant cross-sectional shape, with length L in the flow (z) direction, constant width w in the x direction, and a cross section described by its shape h(x) in the y direction (Figure 1, top). The maximum value of h(x) is denoted h_0. To conveniently discuss the scaling form of our results, we separate the amplitude h_0 from the specific “shape” of the cross section by writing h(x) = h_0 f(x/w(z)), where f(0) is a dimensionless function that is zero for x = ±1 and has a maximum equal to 1 between these two points. We denote by S the constant cross-sectional area, S = \int_0^w h_0 f(x/w(z)) \, dx. We present results valid for the conditions h_0 = w = L, which are generally true for a large number of microfluidic applications.

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\[
\text{D}_\text{eff}(t) = \frac{1}{2} \frac{d}{dt} \langle z^2(t) \rangle
\]

which tends to a constant value at long times.

**Time Scales and Different Regimes for Shallow Channels.** As stated above, we focus on the case where the cross section is shallow, h_0 = w. This induces two typical time scales for the exploration by the solutes of velocity variations perpendicular to the channel axis, exploration that they perform by thermal diffusion. These two time scales separate three regimes (see Figure 2): “very short” times, less than O(h_0^2/D), during which solute only mildly samples the shorter transverse dimension,
"short" times, larger than $O(h_0^2/D)$ but less than $O(w^2/D)$, during which solute, having "equilibrated" in the short dimension starts to sample the longer transverse dimension, and eventually a "long" time regime, i.e., times longer than $O(w^2/D)$. If the thickness of the channel varies progressively along the largest transverse dimension, then the thickness-averaged velocities will vary noticeably from place to place (i.e., at different positions $x$ along the width). These variations induce a hydrodynamic stretching extending throughout the short-time regime that adds up to the one corresponding to velocity heterogeneities in the thickness (Figure 2). Only in the long-time regime can molecular diffusion progressively reduce this "ballistic" hydrodynamic spreading by "averaging" throughout the cross section.

The reason the transverse variations of velocities along the width dominate the overall Taylor dispersivity is because the statistical averaging is poorer in that direction due to the longer diffusion time required. For a quasi-rectangular channel, there is little or no such transverse heterogeneity along the $x$ direction of the height-averaged velocity (except for the vicinity of the side walls), so that this source of dispersion is weak or absent.

Main Results. To substantiate these qualitative statements, we now provide our analytical results, obtained, as detailed in the Appendix, by combining the method of moments applied to shallow channels as described in Aris\(^\text{1}\) with a lubrication description of the flow field. Our results thus hold for smooth shallow cross-sectional shapes. The case of abrupt shape changes, as occurs for nearly rectangular shapes, is discussed in the section entitled Long-Time Dispersion for Quasi-Rectangular Shapes.

Long-Time Dispersion. At long times, i.e., longer than $O(w^2/D)$, the spreading of the sample is effectively diffusive (Taylor–Aris dispersion). The average position is $\langle x \rangle = Vt$ and the variance, $\sigma_{\text{max}}^2(t)$, grows linearly in time

$$\sigma_{\text{max}}^2(t) = \langle (x - \langle x \rangle)^2 \rangle(t) \approx 2D(1 + \epsilon_s Pe_0^2) t$$

where $Pe_0$ is the Peclet number defined using the width $w$ as the relevant length scale (not $h_0$) and $V$ as the mean velocity:

$$Pe_0 = Vw/D$$

This identification of the prominent role of the channel width is the first main point of our paper. The second is an explicit formula for the constant $\epsilon_s$ in (5), which depends only on the nondimensional shape of the cross section as described by the function $H(X)$:

$$\epsilon_s = \frac{1}{4} \int_0^1 \frac{1}{H(X)} \left( \int_0^1 [H'(X)]^2 dX - 1 \right) H(X) dX$$

where we have introduced the short-band notation

$$I_n = \int_0^1 H'(X) dX$$

This long-time behavior is fully described by the effective dispersion coefficient:

$$D_{\text{eff}}(t) = D(1 + \epsilon_s Pe_0^2)$$

We emphasize that remarkably the channel height $h_0$ is completely absent in this long-time limit obtained for a smooth cross section (again abrupt shape changes, such as almost rectangular shapes are not included in this analysis).

Dispersion at Shorter Times. Due to its special relevance for microfluidic systems, we also investigate dispersion at shorter times, although the results are then not universal and depend on the initial distribution of solutes.

Of special interest is the "short" time regime, i.e., times scales longer than the (fast) time scale for molecular diffusion in the $y$ direction but shorter than for that along the width of the channel; i.e., $O(h_0^2/D) < t < O(w^2/D)$. Then, differences along the width $x$ of the height-averaged velocities lead to an effective diffusion coefficient increasing linearly in time. For initial distributions homogeneous along $x$, we explicitly obtain as described in the Appendix

$$D_{\text{eff}}(t) = D + \frac{1}{2} \frac{d}{dt} \sigma_{\text{MAX}}^2(t) = D \left( 1 + \epsilon_s Pe_0^2 \frac{D}{w^2} \right)$$

where $\epsilon_s$ is a dimensionless number that depends only on the nondimensional shape $H$ of the cross section:

$$\epsilon_s = I_3/I_5^2 - 1$$

Again, $h_0$ does not enter the description.

For even shorter times, i.e., shorter than $O(h_0^2/D)$, and for an initial distribution homogeneous in the cross section, a simple calculation using the lubrication description of the flow (eq 25 in the Appendix) yields a diffusivity formally similar to (10), with $\epsilon_s$ replaced by $\epsilon_a = (6I_3/I_5^2)^3 - 1 = \epsilon_s + (I_7/I_5^2)$.

Crossover Time. A useful outcome of the previous analysis is an estimate for the typical crossover time $t_0$ between hydrodynamic stretching and broadening by Taylor–Aris dispersion.
DISCUSSION

For large Péclet numbers \( (Pe \gg 1) \), equating the variance in the two regimes yields this time scale, which as expected scales as

\[
t_\text{xo} = \frac{2κ_2 w^2}{D} = \frac{κ_2 w^2}{V} \tag{12}
\]

the time to diffuse the width, sets the limit of validity of the long-time dispersive regime (eqs 6–10). Once again the channel width \( w \) is the important length scale.

In the above quantitative characterization of the dispersion process, three shape-dependent dimensionless numbers, \( κ_1, κ_2 \), and \( κ_0 \), have been introduced. We calculate and tabulate these numbers for several representative shapes in the next section.

### DISCUSSION

**General Remarks.** As is well known in the literature on hydrodynamic dispersion, the flow contributes a long-time effective diffusion that varies as the square of the average velocity. However, the channel dimension that enters the description is not the height (assuming \( h_0 = h \)), a fact that is generally obscured since most analyses concern effectively two-dimensional situations. Furthermore, it is the shape of that dimension that enters the expression of the long-time Taylor dispersion, so that we are actually arguing that, for channels of aspect ratio, \( w/h_0 \), of order 10, hydrodynamic dispersion is 100 times larger than an analysis based on the height would suggest! It is nevertheless worth noting that if the pressure drop \( Δp \) is specified for a channel of length \( L \), then the mean velocity \( V = (h_0 Δp/12μL) \), where \( μ \) is the viscosity of the fluid; this feature brings the smallest dimension, the height, into the overall description.

The formulas above have been established using the lubrication approximation (see Appendix), so that we expect them to hold for arbitrary smooth and narrow cross sections. Note that although the examples quoted here mostly refer to the format common in microfluidics where one of the surface is flat (as in the examples quoted here mostly refer to the format commonly used to mix materials in one step of their processing in integrated systems using two-layer soft lithography. For such systems, the operation of active elements such as valves is favored by using smooth rounded cross sections, and fabrication often results in parabolic cross-sectional shapes of the channels. A typical microfluidic rotary mixer has a centerline radius \( R = 1000 \mu \text{m} \), width \( w = 100 \mu \text{m} \), height \( h = 10 \mu \text{m} \), and mean velocity \( V = 0.1 \text{ cm/s} \). Therefore, if we take the molecular diffusivity to be \( D = 5 \times 10^{-5} \text{ cm}^2/\text{s} \), then the crossover time for an experiment is typically \( t_\text{c} = 0.0345/\text{D} = 0.7 \text{ s} \). This time scale should be compared with the average circulation time around the rotary mixer \( 2πR/V \approx 6 \text{ s} \). Thus, well before a single revolution, the transport process is characterized by the description of dispersion based on the channel width. Our formulas can thus be used to refine the analysis presented by Squires and Quake,10 where only one dimension was considered, and provides guidance for a complete 3D analysis of the problem along the lines of the 2D analysis presented by Gleeson et al.11

**Other Simple Shapes.** We have also computed the values of the nondimensional parameters \( κ_1, κ_2 \), and \( κ_0 \), for elliptical and triangular cross sections, which are reported alongside those for the parabola in Table 1. The long-time result for the elliptical shape matches the limit of Aris’s exact calculation (p 76 in ref 3).

Focusing on the long-time dispersivity, two facts are immediately apparent and worth emphasizing. First, as is common in such dispersion problems, the numbers are small for prefactors in a scaling theory, i.e., typically of order \( 10^{-2} \)–\( 10^{-3} \). Second, they are smaller (and so is dispersion) for flatter shapes, as is obvious following the sequence triangle \( \to \) parabola \( \to \) ellipse. This result corresponds to more uniform values of the velocity distribution, i.e., smaller gradients of the height-averaged velocities.

An extension of the above argument suggests making a connection to the case of the flattest shapes, i.e., rectangular shapes, for which exact (numerical) results are available. Blindly applying the above results with \( h_0 = h \) leads to numerical values that are exactly zero for both the short- and long-time coefficients, as the height-averaged velocity is uniform. This result is at odds with existing calculations, but is logical in the framework of our approximations as we explain in the next subsection.

### Long-Time Dispersion for Quasi-Rectangular Shapes

To establish the connection between our analysis for smooth shapes and the rectangle (which is not smooth as \( h(x) \) goes abruptly from \( h_0 \) to 0 on the two sides), we consider dispersion in quasi-rectangular channels (Figure 3, top), which are flat for \( |x| < w/2 \), and then monotonically tend to zero over the length \( l \). In addition to providing a connection to the case of a rectangle, the topic is of interest on its own, as this kind of channel shape is indeed found in some microfluidic systems.7 We start by general

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APPENDIX A. ARTICLES

VI

APPENDIX A. ARTICLES

Table 1. Coefficients $\kappa$, $\kappa_s$, and $\kappa_v$ According to the Lubrication Approach for Shallow Cross-Sectional Shapes (Height $h_0$ and Width $w$ with $h_0 \approx w$)

<table>
<thead>
<tr>
<th>Cross-sectional shape</th>
<th>$\kappa$</th>
<th>$\kappa_s$</th>
<th>$\kappa_v$</th>
<th>$D_{\text{disp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>triangle</td>
<td>1/192 = 0.0052</td>
<td>1/3 ≈ 0.333</td>
<td>1/32 = 0.031</td>
<td>$D + 0.0052(\frac{Pe^2}{w})D$</td>
</tr>
<tr>
<td>parabola</td>
<td>3347/104900 = 0.00031</td>
<td>53/289 = 0.178</td>
<td>3347/96460 = 0.0035</td>
<td>$D + 0.0031(\frac{Pe^2}{w})D$</td>
</tr>
<tr>
<td>ellipse</td>
<td>5/2204 = 0.0022</td>
<td>1/9 ≈ 0.111</td>
<td>5/128 = 0.039</td>
<td>$D + 0.0022(\frac{Pe^2}{w})D$</td>
</tr>
</tbody>
</table>

Figure 3. Quasi-rectangular cross-sectional shapes.

Considerations that hold irrespective of the shape of the two (smooth) "wings", before providing an explicit illustration for the case of triangular end pieces (Figure 3, bottom). To be specific, in the discussion below we assume $h_0 \leq \lambda \leq w/2$.

Recall that dispersion is controlled by transverse diffusion, which samples the velocity distribution. For the general quasi-rectangular cross-sectional shape, the depth-averaged velocity is the same throughout the central flat region and variations are restricted to a region of size $\lambda$ near the side walls, which then controls the dispersion. Indeed, the nondimensional coefficient $\kappa_v$ now dependent on $\lambda/w$, can be shown from eq 7 to behave as

\[
\kappa_v(\lambda/w) = \frac{\lambda^2}{w^2} f(\lambda/w),
\]

where $f(\lambda/w)$ is an $O(1)$ function with finite limits for $\lambda/w \to 0$ and $\lambda \to w/2$. Thus, when $\lambda = O(w)$, as outlined above the dispersive correction $O(\kappa_vPe^2)$ is controlled by the width of the channel. In contrast, in the limit $\lambda \ll w$ or $\lambda/w \to 0$, the depth-averaged velocity only varies on a scale $\lambda$ near the boundaries and $\kappa_v = O(\lambda/w)f(0)$. This implies that the dispersion, proportional to $\kappa_vPe^2 = f(0)(V/w)/D$, is independent of the width of the channel and is controlled by the small region of size $\lambda$ in the neighborhood of the corner.

At the limit of validity of our formalism, we take $\lambda = O(h_0 < w)$ and observe that for nearly rectangular channels the dispersive contribution becomes $O(h_0^2)$, where $h_0 = Vh_0/D$; the dispersion now depends completely on the channel height (not the width). This result is known in the literature on dispersion in rectangular channels $D_{\text{disp}} = 8/(1/20)Pe^2$ (e.g., refs 12 and 13), with in that case the side walls yielding only a prefactor change (not a scaling one) to the 2D result $D_{\text{disp}}^2 = (1/20)Pe$.

However, as we have demonstrated in this paper, this is not true for generic shallow microchannels.

To illustrate these points, we consider a special class of shapes that are rectangular in the middle and triangular near the end (see Figure 3). As the triangular region of width $\lambda$ is diminished, the cross section approaches a rectangle of height $h_0$ and width $w$. So, we utilize the dimensionless shape function involving the parameter $\epsilon$, $0 \leq \epsilon = \lambda/(w/2) \leq 1$,

\[
H(\epsilon) = \begin{cases} 
1 & \text{for } 0 \leq |\epsilon| \leq 1 - \epsilon \\
1 - |\epsilon| & \text{for } 1 - \epsilon \leq |\epsilon| \leq 1 
\end{cases}
\]

Each of the necessary integrals in eqs 7 and 8 for the dispersion can now be evaluated; e.g., $I_1 = 2(1 - 1/\epsilon)$, $I_2 = 2(1 - 1/\epsilon)$, etc. After some algebra we find that $\kappa_v(\epsilon)$ has the form

\[
\kappa_v(\epsilon) = \frac{\epsilon^2}{192} \left( \frac{32 - 52\epsilon + 20\epsilon^2 + \epsilon^3}{(2 - \epsilon)(4 - 3\epsilon)^2} \right)
\]

in the limit $\epsilon \to 1$, the cross section is a triangle, and we indeed recover $\kappa_v(\epsilon = 1) = 1/192$ as given in Table 1. In contrast, in the limit $\lambda \ll w$ or $\epsilon = 0$, $\kappa_v = \epsilon^2/192$, or a dispersion for high Péclet numbers that is $\kappa_vPe^2 = 1/48(V/w)/D$. Extrapolating this result to $\lambda = h_0$ provides a result consistent with the magnitude and scaling of the dispersivity for rectangular cross sections. However, here we reach the limits of our approximations, so that to produce exact results for such shapes, the detailed velocity distribution in the corner needs to be known (e.g., refs 12 and 13), and a full three-dimensional analysis is necessary.

ACKNOWLEDGMENT

H.A.S. thanks the Harvard MRSEC for support and the City of Paris and the Laboratoire de Physico-Chimie Théorique of ESPCI for support during a sabbatical visit. We thank the Institut d'Études Scientifiques de Cargese for providing a pleasant and stimulating environment in which this work was initiated.

APPENDIX: MATHEMATICAL DERIVATIONS OF THE MAIN RESULTS BY ARIS’S METHOD OF MOMENTS

In this Appendix, we first outline a procedure already followed by Aris at the end of his seminal paper, which led him to a general formula for the long-time dispersion in shallow channels. We then describe the additional steps we take to obtain the results presented in the text, i.e., making use of the lubrication ap-
proximation and solving for the short-time behavior for a special class of initial conditions.

Starting from the convection–diffusion eq 2, the first step in the analysis of the transport problem is to use the approximation \( h_0 = \infty \) to derive a simplified equation for quantities averaged along the short transverse direction \( y \). It is convenient to define the transverse averages

\[
\bar{u}(x, t) = \frac{1}{h_0} \int_0^{h_0} u(x, y) \, dy
\]  

(17)

\[
\bar{c}(x, y, t) = \frac{1}{h_0} \int_0^{h_0} c(x, y, z, t) \, dy
\]  

(18)

Here we have assumed, as sketched in Figure 1, the most common situation in microfluidics, which is that the channel is closed on one side by a flat plate so that the channel boundaries at \( y = 0 \) and \( y = h_0 \). Any other smooth shape described by \( y_{\text{max}}(x) \) and \( y_{\text{min}}(x) \) with \( y_{\text{max}}(x) - y_{\text{min}}(x) = h(x) \) leads to identical results in the present frame of approximations. The evolution equation for \( \bar{c}(x, y, t) \), which is adequate to describe evolution at time scales longer than \( h_0^2/D \), is

\[
\frac{\partial \bar{c}}{\partial t} + \frac{\partial \bar{c} \bar{u}}{\partial x} = \frac{1}{h_0} \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial h_0} \left( \frac{\partial \bar{c}}{\partial h_0} \right) \right] + \frac{D}{h_0^2} \frac{\partial^2 \bar{c}}{\partial x^2}
\]  

with the boundary conditions \( \partial \bar{c} / \partial y (x = \pm w/2, y, t) = 0 \), and an arbitrary initial condition \( \bar{c}(x, y, t = 0) \), which is normalized for simplicity so that \( \int dx h(x) (\partial \bar{c} / \partial z)(x, y, t = 0) = 1 \) (which then obviously holds for any time).

We can now follow the methods of moments developed by Aris\(^2\) and inspect the evolution of the quantities (or moments), defined as

\[
c_i(x, t) = \int \bar{c}(x, y, t)(z - Vt)^i \, dz
\]  

(20)

In particular, the first two moments evolve according to

\[
\frac{\partial c_0}{\partial t} = \frac{1}{h_0} \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial h_0} \left( \frac{\partial c_0}{\partial h_0} \right) \right] + \frac{D}{h_0^2} \frac{\partial^2 c_0}{\partial x^2}
\]  

(21)

\[
\frac{\partial c_1}{\partial t} = (\bar{u}(x) - V)c_0(x, t) + \frac{1}{h_0} \frac{\partial}{\partial x} \left[ \frac{\partial}{\partial h_0} \left( \frac{\partial c_1}{\partial h_0} \right) \right] + \frac{D}{h_0^2} \frac{\partial^2 c_1}{\partial x^2}
\]  

(22)

with \( \partial c_2 / \partial y \) (at \( y = \pm w/2 \), \( t = 0 \)) = 0. The variance \( \sigma^2(t) \) = \( \langle (z - Vt)^2 \rangle (x, t) \) evolves as

\[
\frac{d}{dt} \langle (z - Vt)^2 \rangle = 2D + 2 \int dx h(x) (\bar{u}(x) - V)c_1(x, t)
\]  

(23)

Whatever the initial conditions, as time goes on, \( c_i(x, t) \) tends toward a constant value \( c_i(t \to \infty) = c_i^\ast = (\partial dx h(x)^{-1}) \), and consequently, \( c_1(x, t) \) tends toward a steady profile \( c_1(x, t \to \infty) = c_1^\ast \) given by this result can be used in (23) to compute the

\[
D \frac{d}{dx} \left( h(x) \frac{d c_1}{dx} \right) = -c_1^\ast h(x) (\bar{u}(x) - V)
\]  

(24)

long-time dispersivity through a shape-dependent integral, as already recognized by Aris (with slightly different notations), and used by him for the case of ellipses. We now take a few additional steps.

(i) The main step is to use the lubrication approximation to relate the flow pattern \( u(x, y) \) to the shape. Within the lubrication approximation \( u(x, y) = Ayh(x - y) \) with \( A \) a constant proportional to the pressure gradient, so that we find

\[
\bar{u}(x) = \frac{I_1 h_0^2}{I_0 h_0^2} \bar{V}
\]  

(25)

where the constants \( I_j \) are defined in eq 8.

(ii) Long-time regime: Then we introduce the intermediate function

\[
g(x) = \int_0^{h_0} d'h(x)(\bar{u}(x') - \bar{V})
\]  

(26)

to obtain from eqs 23 and 24, through an integration by parts (note that \( g(\pm w/2) = 0 \)),

\[
\frac{d}{dt} \langle (z - Vt)^2 \rangle = 2D \left( \int dx h(x)(\sigma^2(x)/h(x)) \right) \int dx h(x)
\]  

(27)

Inserting in this equation the lubrication flow field (25) and extracting from the integrals the dimensional quantities using \( h = hJ(2w/D) \) yields the final results given as eq 7 in the main body of the paper for the long-time regime.

(iii) Shorttime regime: In addition, to get partial insight into the "shorttime" regime where homogenization along \( y \) is effective but not that along \( x \), we focus on a solvable family of cases, namely that of initial conditions independent of \( x \): \( \bar{c}(x, z, t = 0) = f(z) \). In that limit, given the normalization chosen \( c_0(x, t, 0) \) is a constant in space and time \( c_0(x, 0) = (dx h(x)^{-1}) \), and \( c_1(x, t, 0) = 0 \) if the origin of the \( x \) axis is chosen at the initial location of the center of mass of the distribution \( Jdz' = 0 \). Then for times shorter than the diffusion time across the channel \( t < O(w^2/D) \), it is clear that we have the simple approximation \( c_i(x, t) = (dx h(x)^{-1}) (\bar{u}(x) - V) t \). Thus, the evolution of the variance follows from eq 23:

\[
\frac{d}{dt} \langle (z - Vt)^2 \rangle = 2D + 2 \int dx h(x)(\sigma^2(x)/h(x)) \int dx h(x)
\]  

(28)

Inserting the flow field in the lubrication approximation 25 yields the "shorttime" result quoted in the text.

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Experimental characterization of hydrodynamic dispersion in shallow microchannels†

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Hydrodynamic dispersion in shallow microchannels with almost parabolic cross-sectional shapes and with heights much less than their widths is studied experimentally. Both long serpentine channels and rotary mixers are used. The experimental results demonstrate that the dispersion depends on the width rather than the height of the channel. The results are in quantitative agreement with a recently proposed theory of dispersion in shallow channels.

Introduction

In a channel flow, hydrodynamic dispersion refers to the inevitable axial spreading of solute due to transverse velocity variations. Such dispersion plays an important role in microfluidic devices and, depending on the application, it can be an advantage or a drawback. Indeed, in separation devices, dispersion decreases the resolution and limits the throughput whereas in mixing devices, it can increase mixing efficiency. In addition, optimization may be one goal when designing a new device. We recently proposed formulas for dispersion in any shallow geometry with height,  $h$, much smaller than its width, $w$ (Fig. 1).1 The main result is that the long-time dispersivity is controlled by the width of the channel rather than by the height. In this paper, we report experiments, both in long serpentine channels and in a rotary mixer configuration, 2 which validate the formulas we proposed and demonstrate that the long-time dispersivity can be predicted very accurately.

The transport of a plug of tracers by a pressure-driven flow was first studied by Taylor3 and Aris.4 They demonstrated that for long times, the tracer distribution evolves diffusively with a long-time dispersivity $D_{\text{eff}}$, which depends on the cross-sectional shape of the channel. However, analytical results are available only for simple shapes of the cross-section such as a slab geometry (two parallel plates), a circle and an ellipse. In the first two cases, the long-time dispersivity is $D_{\text{eff}} = D + k_0 U^2 h^2 / D$ with $U$ the mean flow velocity, $D$ the thermal diffusion coefficient, $h$ the smallest dimension of the channel (distance between the two plates or radius of the circle) and $k_0$ a constant depending on the shape ($k_0 = 1/210$ for two plates and $k_0 = 1/48$ for circular channels).5 In most common cases, $U/D \gg 1$ and the long-time dispersivity can be predicted using $D_{\text{eff}} = D + k D / U^2$. Because in these two cases the effective dispersivity is controlled by the smallest dimension of the channel, it is often assumed that Taylor dispersion in microfluidic channels is also controlled by the smallest dimension, i.e. the height in most cases. However, this is only true for channels with quasi-rectangular cross-sections. As we have recently pointed out, for shallow smooth microfluidic channels of width, $w$, much greater than the height, $h_0$ (Fig. 1), the long-time dispersivity is controlled by the width of the channel (rather than by the height) with $D_{\text{eff}} = D + k / D$ and $k$ a constant that depends only on the shape of the channel.1 Our recent results are consistent with the results proposed by Aris3 for channels with an elliptical cross-section.

Mixing is another topic of interest in microfluidics. In fact, for many applications such as biological reactions or kinetics studies, the reaction should not be diffusion-limited. Fast homogenization of samples is thus required. Several devices such as the rotary mixer 6 or the herringbone mixer7 have recently been proposed. The rotary mixer (see Fig. 3) is of particular interest to us as it relies, in some regimes of operation, on hydrodynamic dispersion to achieve complete mixing. In fact, such devices are straightforward to fabricate using the multi-layer soft-lithography technique,7 and the associated soft-valve technology allows for precise control of volumes of reagents. Mixing in the rotary mixer has been

\[ D_{\text{eff}} = D + k D / U^2 \]

\[ D_{\text{eff}} = D + k_0 U^2 h^2 / D \]

\[ D_{\text{eff}} = D + k D / U^2 \]

\[ D_{\text{eff}} = D + k_0 U^2 h^2 / D \]

\[ D_{\text{eff}} = D + k D / U^2 \]

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analyzed numerically using two-dimensional models. Yet, to the best of our knowledge, no analyses have taken into account the three-dimensional aspects of the microchannels, and no experimental quantification of mixing time in a rotary configuration as a function of the long-time dispersivity has been reported.

In this paper, we first report experimental data for the long-time dispersivity in long serpentine shallow microchannels and show that they agree with the predictions of Ajdari et al. We then characterize mixing in the rotary configuration and demonstrate that mixing times can again be quantitatively predicted using the same theoretical results.

Materials and methods

Microchip fabrication

Long serpentine channels (Fig. 2) and rotary mixers were fabricated out of polydimethylsiloxane (PDMS) using multi-layer soft-lithography. Each chip consists of two levels of channels: fluids circulate in the bottom channels (fluidic channels), while the channels on top (control channels) operate the pressure-actuated valves. The resist molds used for PDMS casting were obtained using UV optical lithography. The optical masks for the fluidic layer of the serpentine channels were designed using L-Edit CAD software and were fabricated by electron-beam lithography using a Leica EBPG 5000+ nanowriter. The other masks were designed using Adobe Illustrator and were printed on transparencies using a high-resolution printer. Molds for the fluidic channels were made of Shipley SPR 220-7 photoresist coated at 1500 rpm for 60 seconds. Once developed, the resist was heated at 165 °C for 15 minutes to create channels with a parabolic cross-section (the photoresist reflows and channels become rounded). Molds for the control channels were made of SU8-2010 using the MicroChem protocol for 20 μm high channels.

The mold for the control channels was exposed to a vapour of trimethylchlorosilane (TMCS) for 2 minutes. A thick layer of PDMS (a 20 : 1 mixture of monomer (GE RTV 615 component A) and hardener (GE RTV 615 component B)) was then poured onto the mold placed in a Petri dish and left at room temperature for 15 minutes to degas. PDMS was spun-coated at 3000 rpm for 60 seconds onto the mold for making the associated fluidic channels. The two layers were cured for 45 minutes at 78 °C. Holes for the control channels were then punched and the layer for the control channel was aligned to that for the fluidic channel. The two-layer device was cured overnight at 78 °C. Holes for the fluidic channels were then punched. The device was eventually sealed onto a pre-cleaned glass slide after a 1 minute plasma treatment and left overnight at 78 °C. The fluidic channels have an essentially parabolic cross-sectional shape (Fig. 2D) and are 11 μm high. To assess the importance of the cross-sectional geometry, channels of two widths were fabricated: the channels were either 57.5 μm or 100 μm wide (Fig. 2A). The control channels have a rectangular shape and are 20 μm high and 100 μm wide.

Fig. 2  A. Global view of the serpentine device, which has two levels of channels. Fluidic channels, in black, are 11 μm high and either 57.5 μm or 100 μm wide. Control channels, in gray, are 20 μm high and 100 μm wide. The radius of curvature of the turns of the serpentine channel is 150 μm as measured along the centerline. A plug of fluorescein is formed in the injection part of the device (B) and is then transported along the serpentine channel using a pressure-driven flow. B. Injection part of the device, which utilizes two-layer soft-lithography. Upon the opening of valves 1 and 3 and closing of valves 2 and 4, a plug of fluorescein is formed between valves 2 and 4. The plug is 500 μm wide and is transported along the channel by a pressure-driven flow of an aqueous solution of NaOH (10^-2 M) as soon as valves 1 and 3 are closed and valves 2 and 4 are opened. C. Close-up view of the fluidic channels. Alignment ticks, 10 μm wide and spaced every 1 mm (center to center), allow determination of the position along the channel through microscopic observations. D. Experimental cross-sectional shape of the fluidic channel (black line) and the fit by a parabolic shape (gray line).
Methods

A 4.9 × 10^{-5} M solution of fluorescein (Fluka 46955) is obtained by dilution with a freshly prepared 10^{-2} M solution of NaOH. The fluorescein solution is recorded using a CCD camera (Sony DFW-V500) coupled to a microscope and an HBO mercury lamp with a filter set specific to fluorescein (Zeiss filter set 44: BP 475/40 nm, FT 500 nm, BP 530/50 nm).

1. Serpentine channels. In each experiment, a plug of fluorescein is first formed between valves 2 and 4 (Fig. 2B) and this plug is transported by a pressure-driven flow of an aqueous solution of NaOH (10^{-2} M), used to ensure a stable value of the fluorescence and prevent dye adsorption on the channel walls. The position along the channel is determined using tick marks that were placed along the axis (see Fig. 4A). For a given channel width and a given mean flow velocity, several measurements are made at different positions along the length of the channel. Each of these measurements consists in recording the fluorescence intensities as functions of time at two positions falling in the same frame of observation (better understood by looking at Fig. 4A). Several experiments are performed for both channel widths, and for each width two mean flow velocities are investigated.

2. Rotary mixer. For each experiment, the rotary mixer is first filled with a solution of 10^{-2} M NaOH. Then a small plug of fluorescein is injected between valves 3 and 5 (Fig. 3). All the input and output channels are then closed (valves 1, 2, 4 and 7) and mixing of the fluid in the loop is induced by peristaltic pumping (using valves 3, 5 and 6). In all of the rotary mixer experiments, the actuation sequence for peristaltic pumping is [100 010 001], where “1” represents closed and “0” represents open so that, for example, 100 means that valve 3 is closed and valves 5 and 6 are opened. The plug of fluorescein, which is about 400 μm in length, is formed between valves 3 and 5 by closing them, opening valve 4 and flushing the fluorescein in. Fluorescence intensity is observed at the position indicated by the dashed box on the right.

Fig. 3  Schematic of the rotary mixer made of two levels of channels. Fluidic channels, in black, are 11 μm high and 100 μm wide. Control channels, in gray, are 100 μm wide and 20 μm high. The radius of the ring is 1 mm. Valves are pressure-actuated. Mixing is achieved in the ring by peristaltic pumping using valves 3, 5 and 6, while maintaining valves 1, 2, 4 and 7 closed. The sequence of actuation of valves is [100 010 001] where 1 means that the valve is closed (pressure is applied) and 0 means that the valve is opened (e.g. 100 means that valve 3 is closed and 5 and 6 are opened). The plug of fluorescein, which is about 400 μm in length, is formed between valves 3 and 5 by closing them, opening valve 4 and flushing the fluorescein in. Fluorescence intensity is observed at the position indicated by the dashed box on the right.

Fig. 4  A. Typical experimental image. For one experiment, the fluorescence intensity is recorded versus time at two given positions in the device (positions 1 and 2). Images are taken every 200 ms. The black dashed line indicated by the arrow represents a typical slice of the picture on which fluorescence intensity is averaged. B. Typical plots of mean fluorescence intensity versus time at positions 1 and 2 obtained after image analysis using Matlab software. These results are obtained in 57.5 μm wide channels and at low velocity, U = 0.3 mm s^{-1}, on the last loop of the serpentine channel.

932 | Lab Chip, 2006, 6, 930–935 This journal is © The Royal Society of Chemistry 2006
Serpentine channels

Results

Analysis of the fluorescence images is performed using a Matlab code that we developed. For each position (Fig. 4A), the fluorescence intensity is averaged on a slice of an image of height 240 pixels and width 5 pixels centered on the chosen ticks (Fig. 4A). Typical plots of the fluorescence intensity versus time are thus obtained (Fig. 4B). The mean flow velocity, $U$, is estimated using

$$U = \frac{\text{distance between two consecutive positions, 1 and 2}}{\text{time at which the fluorescence intensity at position } i \text{ reaches its maximum.}}$$

where $t_{\text{max},i}$ is the time at which the fluorescence intensity at position $i$ reaches its maximum. The evolution of the tracer profile sufficiently long times (i.e., times greater than $O(\nu/2D)$, when the solute has "equilibrated" in the two transverse dimensions), the solution of the diffusion equation for a one-dimensional profile centered at a location $U t$ is in the Gaussian

$$c(x,t) = \frac{1}{4\pi D_{\text{eff}}t} \exp \left( -\frac{(x-Ut)^2}{4D_{\text{eff}}t} \right)$$

where $D_{\text{eff}}$ is the effective dispersion coefficient, which plays the role of diffusion here. In the long-time regime relevant here, at a given position $x = U t_{\text{max}}$, the concentration of fluorescein versus time is essentially:

$$C(t) \approx \frac{1}{\sqrt{4\pi D_{\text{eff}}t_{\text{max}}}} \exp \left( -\frac{U^2(t_{\text{max}}-t)^2}{4D_{\text{eff}}t_{\text{max}}} \right)$$

where $t_{\text{max}}$ is the time at which the fluorescence intensity reaches its maximum (at this given position). Each individual intensity plot (e.g., Fig. 5), taken as a measure of the concentration, is thus fitted by a Gaussian of the form of eqn (1), $c(t) = (Ac \exp^{-b(x-t^2)/2a})$, using a Matlab curve fitting tool (part of the Matlab toolbox); $c_{\text{gauss}}$ is introduced to account for the baseline signal and any background noise. A typical fit is shown in Fig. 5, which also indicates $t_{\text{max}}$ and $\Delta t$. With $b = t_{\text{max}}$, the effective dispersion coefficient, $D_{\text{eff}}$, is then deduced as $D_{\text{eff}} = abk$. Using this procedure, which involves two intensity plots (Fig. 4B) in each experiment, the mean flow velocity and two measurements of the effective dispersion coefficient are determined. Repeating the experiments at different locations along the channel for the same

Fig. 6 Measured effective dispersivity $D_{\text{eff}}$ versus the theoretical predictions for the effective dispersivity. We used the calculated value $k = 0.003$ for a channel of parabolic shape and $D = 3 \times 10^{-6}$ mm$^2$s$^{-1}$ for the thermal diffusion coefficient of fluorescein. Results for two different channel widths and two different speeds are shown.

mean velocity and channel width we find very consistent data for $D_{\text{eff}}$ (see the clustering of the points on Fig. 6).

We make two additional remarks as to the experimental procedure:

Measurements of $D_{\text{eff}}$ should be made after the transient region in which the solute equilibrates in the two transverse dimensions. The time scale for the sample to diffuse along the width is $O(\nu/2D)$, corresponding to a length along the serpentine channel of $O(Uw/2D)$. For channels of width 100 μm, this length is about 100 mm for $U = 3$ mm s$^{-1}$. This distance is quite big compared to typical lengths of microchannels (a few centimetres). We thus had to design a long serpentine channel so as to measure $D_{\text{eff}}$ on chip.

Also, in principle photobleaching could alter the validity of translating the fluorescence signal into a measure of the concentration field. In these experiments however, the effects of photobleaching of the fluorescein can be neglected. First, given the geometry of the set-up, in each experiment the tracer particles are exposed to light for less than 5 seconds. Second, bleaching would affect mainly the measurement of the height of the Gaussian and much less the measurement of the width of the Gaussian (related to the effective dispersion coefficient $D_{\text{eff}}$).

Discussion

In their theoretical paper describing Taylor dispersion, Ajdari et al$^1$ proposed that in shallow microchannels, the dispersion should be controlled by the width of the channel rather than by the height. In fact, in contrast to quasi-rectangular channels, where there is only a weak variation of the height-averaged velocity along the width of the channel, the transverse variations of velocities along the width dominate the overall Taylor dispersivity in shallow microchannels. Consequently, the long-time dispersion coefficient was predicted to be

$$D_{\text{eff}} = D \left( 1 + \frac{k U^2 w^2}{D^2} \right)$$

where $w = 100$ μm and $w = 57.5$ μm.
where $k$ is a numerical coefficient that depends only on the geometry of the channel’s cross-section.

We now compare our experimental results to these predictions by using $k = 0.003$ as calculated by Ajdari et al. for channels of parabolic shape, $D = 3 \times 10^{-4}$ mm$^2$ s$^{-1}$ for the thermal diffusion coefficient of fluorescein, and the measured values of mean flow velocity. In the present range of velocities, we check that $kU^{2/3} > D$ and thus use a simplified form of eqn (2): $D_{\text{eff}} = kU^{2/3}dD$.

As can be seen in Fig. 6, the values of the effective dispersivity obtained experimentally are in very good agreement with the theoretical predictions, which lends support to the analytical formulas and approach of Ajdari et al. In particular, our results demonstrate that $D_{\text{eff}}$ scales with the square of the width of the channel and certainly not as the square of the height.

**Rotary mixer**

**Measurements**

In the rotary mixer with a channel width $w$ and radius of the ring $R$, three mixing regimes have been identified. Roughly, for $D_{\text{eff}} < U < 2\pi RD/w$, with $k$ the geometric dispersion prefactor in eqn (2), mixing results from the dispersive spreading of the fluorescent plug, and is thus controlled by hydrodynamic dispersion. For small mean speeds, $U < D_{\text{eff}}/w$, mixing is dominated by molecular diffusion. In contrast, for large mean speeds, $U > 2\pi RD/w$, the concentration distribution wraps onto itself and mixing can no longer be described by Taylor-like hydrodynamic dispersion. For the geometry of our rotary mixer, mixing is expected to be dominated by hydrodynamic dispersion for (approximately) $U_{\text{eff}} < U < U_{\text{max}}$ with $U_{\text{max}} = 5.5 \times 10^{-4}$ mm s$^{-1}$ and $U_{\text{max}} = 7.5 \times 10^{-4}$ mm s$^{-1}$. Experiments in the rotary mixer are thus performed in this range of velocities.

Fluorescence intensity is recorded at the position indicated on Fig. 3 and averaged on a slice of each image of height 5 pixels and length 640 pixels. Mean flow velocities are estimated by measuring the time between two consecutive peaks. Since in most experiments, more than two peaks are recorded (see Fig. 7), several measurements of the mean flow velocity are made in each experiment.

The concentration of fluorescein $c(t)$ time in the rotary configuration is modelled using the solution of a one-dimensional convection-diffusion equation (see Supplementary information). However, in contrast to the serpentine channel where we focus on long times, in the rotary mixer the theoretical solution for concentration is strongly dependent on the initial conditions (as we are focusing on a transient state). Since these initial conditions fluctuate experimentally, in part due to the abrupt starting of pumping, the experimental data cannot simply be fitted using the available analytical solution.

Thus, we mostly analyze the late-time relaxation of the peak values of intensity (Fig. 7) towards the final asymptotic value. For sufficiently long times, these extrema have an exponential relaxation towards the asymptotic value and

![Fig. 7 Typical plot of mean fluorescence intensity vs time, as obtained in rotary mixer experiments after image analysis using Matlab software. This plot is obtained at $U = 0.91$ mm s$^{-1}$. The plot in the inset is used to measure the effective dispersivity in this experiment. The values of $\ln[(\text{c}(t)/\text{c}(\infty))]$ are plotted for each extrema of the fluorescence intensity (black dots). These values are then fitted using a linear function. The slope of the line in the inset is a measurement of the effective long-time dispersivity (see Supplementary information for full details).](image-url)

Satisfy $m \approx \exp(-D_{\text{eff}}/R^2)$, with $t_0$ and $m$ denoting, respectively, the time and deviation from the asymptotic value of the extrema, and $D_{\text{eff}}$ the effective dispersion coefficient.

In order to analyze the relaxation of peak values, we have to take into account the photobleaching of the fluorescein, which is significant here. For each mean flow velocity, we thus perform several experiments where we start exposing the sample to light at different times (where $t = 0$ roughly corresponds to the time at which we start pumping). We thus obtain several measurements of the fluorescence intensity, each corresponding to a different exposure time. For each of these experiments, we obtain the bleaching effect with a linear decrease of the signal over time, estimated as described in the Supplementary information. Data are then corrected for the bleaching and we effectively obtain an exponential decay of extrema values vs time. The long-time dispersion coefficient is then estimated for each experiment using the fact that the decay constant of the exponential is $R^2/D_{\text{eff}}$. We compare these experimental values of the effective dispersion coefficient to the theoretical values as predicted using eqn (2), the measured mean flow velocities, $k = 0.003$ for channels of parabolic shape and $D = 3 \times 10^{-4}$ mm$^2$ s$^{-1}$ for the thermal diffusion coefficient of fluorescein. Moreover, as predicted by Ajdari et al. for channels of parabolic shape, the effective
The time scale necessary to mix samples in the transport regime where mixing is dominated by hydrodynamic dispersion (measured effective dispersivity) scales with the width of the channel rather than with the height. It is also to be noted that in nearly rectangular channels, where there is only a weak variation across the width of the height-averaged velocity, in which case the dispersivity varies with the height of the microchannel. Our results quantitatively support our recent theoretical predictions, suggesting that they can be used to quantitatively predict the amount of dispersion in various microfluidic geometries, which could be of great help at the design stage.

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