

# Transient solute transport with sorption in Poiseuille flow

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Previous work on solute transport with sorption in Poiseuille flow has reached contradictory conclusions. Some have concluded that sorption increases mean solute transport velocity and decreases dispersion relative to a tracer, while others have concluded the opposite. Here we resolve this contradiction by deriving a series solution for the transient evolution that recovers previous results in the appropriate limits. This solution shows a transition in solute transport behaviour from early to late time that is captured by the first- and zeroth-order terms. Mean solute transport velocity is increased at early times and reduced at late times, while solute dispersion is initially reduced, but shows a complex dependence on the partition coefficient  $k$  at late times. In the equilibrium sorption model, the time scale of the early regime and the duration of the transition to the late regime both increase with  $\ln k$  for large  $k$ . The early regime is pronounced in strongly sorbing systems ( $k \gg 1$ ). The kinetic sorption model shows a similar transition from the early to the late transport regime and recovers the equilibrium results when adsorption and desorption rates are large. As the reaction rates slow down, the duration of the early regime increases, but the changes in transport velocity and dispersion relative to a tracer diminish. In general, if the partition coefficient  $k$  is large, the early regime is well developed and the behaviour is well characterized by the analysis of the limiting case without desorption.

**Key words:** laminar reacting flows, microfluidics, mixing and dispersion

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## 1. Introduction

Reactive solute transport with surface reaction is common in natural and engineering applications such as solute separation in chromatography (Hlushkou *et al.* 2014), contaminant transport in porous media (Hesse *et al.* 2010) and particle transport in biological systems (Shipley & Waters 2012). Solute transport in a channel with Poiseuille flow and sorbing boundaries provides a simplified model system that allows an understanding of the effect of reactions on the macroscopic transport

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velocity and dispersion of the solute. This two-dimensional configuration resembles some microfluidic systems used in chromatography and biomaterial delivery and provides insight of solute transport in fractures (Wels, Smith & Beckie 1997). In these systems, the macroscopic properties are given by transverse averaging. In the absence of surface reactions, the solute is a tracer and the average transport velocity of the tracer is identical to the mean flow velocity and its dispersion is given by Taylor's analysis (Taylor 1953). However, previous work has reached contradictory conclusions as to the effect of sorption on solute transport velocity and dispersion.

For channel flow with first-order, irreversible adsorption reaction, previous analyses have shown that adsorption increases transport velocity and decreases the dispersion of the solute relative to a tracer in the asymptotic regime (Sankarasubramanian & Gill 1973; De Gance & Johns 1978*a,b*; Lungu & Moffatt 1982; Smith 1983; Barton 1984; Shapiro & Brenner 1986; Balakotaiah & Chang 1995; Mikelić, Devigne & van Duijn 2006; Biswas & Sen 2007). The solute velocity increases because adsorption removes solutes from the slow-moving fluid near the wall so that the solute preferentially samples the fast-moving fluid in the centre of the channel. This can increase the transport velocity by up to 30% with increasing adsorption in planar Poiseuille flow (Lungu & Moffatt 1982).

However, this is in contrast to the results in chromatography showing that adsorption reduces the transport velocity due to the continuous removal of the solute from the concentration front (Golay 1958; Khan 1962). The chromatographic analysis considers a reversible reaction that allows both adsorption and desorption. In this case, the transport of solute is determined by the partition coefficient  $k$ , the ratio of adsorbed mass over aqueous mass. Concretely, the transversely averaged transport velocity will be reduced by a factor of  $1/(1+k)$  relative to the mean flow velocity. Similarly, different results have been reached with respect to the effect of adsorption on the dispersion coefficient. Chromatographic analysis shows a complex dependence of dispersion on  $k$  while dispersion is reduced in the former case.

The main difference between these two contrasting analyses is that one only considers adsorption (e.g. Lungu & Moffatt 1982) while the other considers both adsorption and desorption (e.g. Khan 1962). One might therefore expect that the reversible analysis recovers the results of the irreversible one in the limit of negligible desorption. However, in this limit the discrepancy between the two analyses is the largest. The transport velocity vanishes in the reversible case while it is finite in the irreversible case. This apparent contradiction may be reconciled by the observation that solute transport undergoes a transition from an early regime characterized by increased solute velocity to a late regime characterized by decreased solute velocity (Paine, Carbonell & Whitaker 1983; Balakotaiah & Chang 1995).

Here we present an analysis that demonstrates that the transition in solute transport behaviour reconciles the reversible and irreversible analyses. To this end, we study solute transport in a two-dimensional straight channel with adsorption onto and desorption from the walls. We use the method of moments in combination with the Laplace transform to derive a set of series solutions for zeroth-, first- and second-order longitudinal moments valid for all times. It is shown that the zeroth-order terms in the series solution corresponds to the late-time behaviour, while the first-order terms corresponds to the early-time behaviour. This analysis recovers both the previous results and therefore reconciles them. Moreover, it allows us to quantify the transition for equilibrium and kinetic sorption models. The paper is structured as follows: the problem is formulated in § 2 and solved in § 3, followed by a discussion of the transport regimes in § 4.

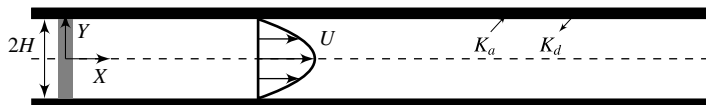


FIGURE 1. In an infinitely long channel, a slender, transversely uniform strip of solute (grey area) is released in the fluid and transported by Poiseuille flow with adsorption on and desorption from the walls.

### 2. Problem formulation

We model single-component solute transport in a two-dimensional straight channel with surface adsorption and desorption, which is illustrated in figure 1. The width of the channel is  $2H$  in the  $Y$  direction and the length is assumed to be infinite in the  $X$  direction. The velocity field is given by an ideal Poiseuille flow,  $U(Y) = (3/2)U_0(1 - Y^2/H^2)$ , where  $U_0$  is the mean flow velocity. Adsorption onto and desorption from the walls allow exchange of mass between the solid surface and the fluid.

The mass transport of solute in the fluid is given by the advection–diffusion equation,

$$\frac{\partial C}{\partial T} + U(Y)\frac{\partial C}{\partial X} = D \left( \frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} \right), \tag{2.1}$$

where  $T$  is the dimensional time [T],  $C$  the dimensional solute concentration [ $ML^{-3}$ ] and  $D$  the diffusion coefficient [ $L^2T^{-1}$ ].

Since the channel is assumed to be infinite, the concentration and any order of its derivative must vanish as  $X \rightarrow \pm\infty$ . Because of the symmetry along the centreline,  $\partial C/\partial Y = 0$ , and only the upper half of the domain is considered.

The adsorbed concentration on the wall is assumed to form an infinitely thin and static surface layer without longitudinal diffusion. The exchange of mass between the wall and the fluid is given as

$$-D\frac{\partial C}{\partial n} = \frac{\partial \Gamma}{\partial T}, \tag{2.2}$$

where  $n$  denotes the outward normal direction of the wall and  $\Gamma$  is the dimensional surface concentration [ $ML^{-2}$ ]. Adsorption and desorption are assumed to be described by first-order reactions, so that the change of surface concentration is given by

$$\frac{\partial \Gamma}{\partial T} = K_a C - K_d \Gamma, \tag{2.3}$$

where  $K_a$  and  $K_d$  are the dimensional adsorption and desorption rate constants, with dimensions of [ $LT^{-1}$ ] and [ $T^{-1}$ ], respectively (Khan 1962). When  $K_d = 0$ , the linear kinetic model reduces to a first-order, irreversible adsorption reaction. When both  $K_a$  and  $K_d$  are large, the reaction approaches local chemical equilibrium. At equilibrium, the surface concentration is linearly proportional to solute concentration,

$$\Gamma = KC, \tag{2.4}$$

where  $K = K_a/K_d$  is the dimensional partition coefficient. Equation (2.4) is also referred to as a linear isotherm (Golay 1958).

Initially, the solute has a uniform transverse distribution at  $X = 0$  with no mass adsorbed on the wall and is assumed to be a  $\delta$ -function in the  $X$  direction so that

$$C(X, Y, 0) = \frac{M_I}{A} \delta(X) \quad \text{and} \quad \Gamma(X, 0) = 0, \quad (2.5a, b)$$

where  $M_I$  represents the total mass in the system [M] and  $A$  is the cross-sectional area of the channel [ $L^2$ ]. A characteristic concentration is chosen as  $C_0 = M_I/(HA)$  to simplify the formulation in dimensionless form. This initial condition, which has been used in previous work, assumes that the system is not in local chemical equilibrium. We note that the transient solute transport behaviour is very sensitive to the initial condition, and further analysis of the effect of the initial condition is provided in appendix A.

The following characteristic quantities are chosen to non-dimensionalize the problem:

$$\left. \begin{aligned} x = X/H, \quad y = Y/H, \quad u = U/U_0, \\ c = C/C_0, \quad \gamma = \Gamma/(C_0H), \quad t = T/(H^2/D). \end{aligned} \right\} \quad (2.6)$$

Note that we choose  $C_0H$  as characteristic surface concentration and the diffusive time scale  $H^2/D$  as the characteristic time scale. Consequently, the dimensionless formulation of the problem is written as

$$\frac{\partial c}{\partial t} + Pe u \frac{\partial c}{\partial x} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}, \quad (2.7a)$$

$$-\frac{\partial c}{\partial y} = \frac{\partial \gamma}{\partial t} \quad \text{at } y = 1, \quad (2.7b)$$

$$\frac{\partial c}{\partial y} = 0 \quad \text{at } y = 0, \quad (2.7c)$$

$$c = \delta(x) \quad \text{at } t = 0, \quad (2.7d)$$

$$\gamma = 0 \quad \text{at } t = 0. \quad (2.7e)$$

If the surface reaction is modelled by the linear kinetic model,

$$\frac{\partial \gamma}{\partial t} = k_a c - k_d \gamma, \quad (2.8)$$

there will be three dimensionless groups in (2.7) and (2.8):

$$Pe = \frac{U_0 H}{D}, \quad k_a = \frac{K_a H}{D}, \quad k_d = \frac{K_d H^2}{D}. \quad (2.9a-c)$$

Physically, the Péclet number,  $Pe$ , represents the ratio of the transverse diffusive time scale to the longitudinal advective time scale and the Damköhler numbers,  $k_a$  and  $k_d$ , represent the ratio of the transverse diffusive time scale to the adsorption and desorption time scales, respectively.

Otherwise, if the equilibrium sorption model is used,

$$\gamma = kc, \quad (2.10)$$

the number of dimensionless groups reduces to two by replacing  $k_a$  and  $k_d$  with

$$k = \frac{k_a}{k_d}. \quad (2.11)$$

In this work,  $k_a$ ,  $k_d$  and  $k$  are all assumed to be constants. A value of 10 is chosen for  $Pe$  to limit the longitudinal domain size required in numerical simulation. This choice will not affect the key results, which are independent of  $Pe$ . In the following, we deal with the more general linear kinetic sorption model analytically, and results will be given for both the kinetic and equilibrium model in §4.

### 3. Solution for the longitudinal moments

Following the classical, transverse-averaging idea introduced by Taylor (1953) to reduce the dimension of the problem, we consider the transverse-averaged concentration  $\bar{c} = \int_0^1 c \, dy$ , and the distribution of  $\bar{c}$  is described by its longitudinal moments  $m_n = \int_{-\infty}^{\infty} x^n \bar{c} \, dx$ , where  $n$  is the order of the moment. The lower-order moments, e.g. zeroth-, first- and second-order moments, are of most interest to us. Furthermore, we define the normalized longitudinal moments of zeroth, first and second order as

$$M_0 = \frac{m_0}{m_l}, \quad M_1 = \frac{m_1}{m_0}, \quad M_2 = \frac{m_2}{m_0} - \left(\frac{m_1}{m_0}\right)^2, \quad (3.1a-c)$$

where  $m_l$  is the dimensionless initial mass, which is unity here. The fraction of solute in the fluid is given by  $M_0$ . The centre of mass and the variance of the solute distribution in the fluid are given by  $M_1$  and  $M_2$ , respectively. Thus, the dimensionless transport velocity and longitudinal dispersion coefficient are

$$v = \frac{dM_1}{dt} \quad \text{and} \quad D_L = \frac{1}{2} \frac{dM_2}{dt}. \quad (3.2a,b)$$

In the following, analytical solutions are derived for lower-order moments  $m_n$  ( $n = 0, 1, 2$ ) in the form of series solutions.

#### 3.1. Moment equation and solution in the Laplace space

Firstly, following the method of moments developed by Aris (1956), multiply (2.7a) by  $x^n$  and integrate in the  $x$  direction to obtain the equation for  $c_n^*(y, t)$ ,

$$\frac{\partial c_n^*}{\partial t} + Pe u \int_{-\infty}^{\infty} x^n \frac{\partial c}{\partial x} \, dx = \int_{-\infty}^{\infty} x^n \frac{\partial^2 c}{\partial x^2} \, dx + \frac{\partial^2 c_n^*}{\partial y^2}, \quad (3.3)$$

where  $c_n^* = \int_{-\infty}^{\infty} x^n c \, dx$  is the  $n$ th longitudinal moment of concentration in the filament through  $y$ , which is not yet transversely averaged. The moments  $m_n$  introduced above are the transverse averages of  $c_n^*$ . After integration by parts and noting that the concentration and all of its derivatives vanish at infinity, we have

$$\frac{\partial c_n^*}{\partial t} - nPe u c_{n-1}^* = n(n-1)c_{n-2}^* + \frac{\partial^2 c_n^*}{\partial y^2}, \quad (3.4a)$$

where  $c_{-1}^* = c_{-2}^* = 0$ . Similarly, the boundary conditions (2.7b) and (2.7c) give

$$-\frac{\partial c_n^*}{\partial y} = \frac{\partial \gamma_n^*}{\partial t} = k_a c_n^* - k_d \gamma_n^* \quad \text{at } y = 1, \quad (3.4b)$$

$$\frac{\partial c_n^*}{\partial y} = 0 \quad \text{at } y = 0, \quad (3.4c)$$

where  $\gamma_n^*$  is defined as the  $n$ th longitudinal moment of the surface concentration.

Laplace transformation in time reduces (3.4) to a system of ordinary differential equations (ODEs) involving only the transformed variable,

$$\hat{c}_n^*(y, s) = \mathcal{L}\{c_n^*\}(s) = \int_0^\infty c_n^* e^{-st} dt, \quad (3.5)$$

because the transformed longitudinal moments of surface concentration  $\hat{\gamma}_n^* = \mathcal{L}\{\gamma_n^*\}$  in the boundary condition can be eliminated. In Laplace space, (3.4) are given by

$$\frac{\partial^2 \hat{c}_n^*}{\partial y^2} = s\hat{c}_n^* - c_n^*(t=0) - nPe u \hat{c}_{n-1}^* - n(n-1)\hat{c}_{n-2}^*, \quad (3.6a)$$

$$-\frac{\partial \hat{c}_n^*}{\partial y} = s\hat{\gamma}_n^* - \gamma_n^*(t=0) = k_a \hat{c}_n^* - k_d \hat{\gamma}_n^* \quad \text{at } y = 1, \quad (3.6b)$$

$$-\frac{\partial \hat{c}_n^*}{\partial y} = 0 \quad \text{at } y = 0. \quad (3.6c)$$

Since no mass is adsorbed on the wall initially,  $\gamma_n^*(t=0) = 0$ . A discussion of the more general initial conditions is given in appendix A. Note that the second equality in (3.6b) can be solved for  $\hat{\gamma}_n^*$  as

$$\hat{\gamma}_n^* = \frac{k_a}{k_d + s} \hat{c}_n^*, \quad (3.7)$$

so that (3.6b) turns into a Robin-type boundary condition,

$$-\frac{\partial \hat{c}_n^*}{\partial y} = \frac{k_a s}{k_d + s} \hat{c}_n^* \quad \text{at } y = 1. \quad (3.8)$$

The  $\delta$ -function initial distribution of solute leads to the following initial conditions:

$$c_0^* = 1, \quad c_1^* = c_2^* = 0 \quad \text{at } t = 0. \quad (3.9a,b)$$

Therefore, (3.6a), together with boundary conditions (3.6c) and (3.8), gives the following system of ODEs for  $\hat{c}_0^*$ ,  $\hat{c}_1^*$  and  $\hat{c}_2^*$ :

$$\frac{d^2 \hat{c}_0^*}{dy^2} = s\hat{c}_0^* - 1, \quad (3.10a)$$

$$\frac{d^2 \hat{c}_1^*}{dy^2} = s\hat{c}_1^* - Pe u \hat{c}_0^*, \quad (3.10b)$$

$$\frac{d^2 \hat{c}_2^*}{dy^2} = s\hat{c}_2^* - 2Pe u \hat{c}_1^* - 2\hat{c}_0^*, \quad (3.10c)$$

with boundary conditions

$$\frac{d\hat{c}_n^*}{dy} = -\frac{k_a s}{k_d + s} \hat{c}_n^* \quad \text{at } y = 1, \quad (3.11a)$$

$$\frac{d\hat{c}_n^*}{dy} = 0 \quad \text{at } y = 0, \tag{3.11b}$$

for  $n = 0, 1, 2$ .

However, it is not the analytical solutions of  $\hat{c}_n^*(y, s)$  but the transverse-averaged moments  $\hat{m}_n(s) = \int_0^1 \hat{c}_n^* dy$  that are of interest here. For instance,  $\hat{m}_0$  has the form

$$\hat{m}_0 = \frac{1}{s} - \frac{k_a \sinh(\sqrt{s})}{\sqrt{s}(k_a s \cosh(\sqrt{s}) + \sqrt{s} \sinh(\sqrt{s})(k_d + s))}. \tag{3.12}$$

The analytical forms of  $\hat{m}_1$  and  $\hat{m}_2$  are complex (given in the supplementary materials available at <https://doi.org/10.1017/jfm.2017.546>), but both of them and  $\hat{m}_0$  can be written in a general form as

$$\hat{m}_n(s) = \frac{N_n(s)}{E(s)^{(n+1)}} \quad \text{for } n = 0, 1, 2, \tag{3.13}$$

where the denominator  $E(s)$  is given by

$$E(s) = k_a s \cosh(\sqrt{s}) + (k_d + s)\sqrt{s} \sinh(\sqrt{s}), \tag{3.14}$$

which is a transcendental function of  $s$  and includes all the singularities of the moments. The numerators  $N_n(s)$  are complex functions of  $s$  obtained by a computer algebra system (MathWorks 2012). The transcendental function  $E(s)$  has two important properties:

- (i) There are only first-order singularities in  $E(s)$ , and thus  $\hat{m}_0$ ,  $\hat{m}_1$  and  $\hat{m}_2$  have only first-, second- and third-order singularities, respectively. This helps to employ the residue theorem for the inverse Laplace transform.
- (ii) All the singularities of  $E(s) = 0$  fall along the negative axis, and thus substituting  $s = -p^2$ , where  $p$  is a real positive number, leads to a transcendental equation of  $p$  in real space (where  $\tanh(ip) = i \tan(p)$  is used),

$$\tan(p)(p^2 - k_d) - k_a p = 0. \tag{3.15}$$

Equation (3.15) has an infinite number of roots  $p_k$ ,  $k = 0, 1, \dots, \infty$ . These roots  $p_k$  correspond to characteristic decay rates of the moments, and the lowest-order term with the smallest root, i.e.  $p_0 = 0$ , dominates the behaviour at late times.

### 3.2. Inverse Laplace transform by the residue theorem

The inverse Laplace transform of the moments can be written as the Bromwich integral,

$$m_n(t) = \frac{1}{2\pi i} \int_{\mathcal{C}} \hat{m}_n(s) e^{st} ds, \tag{3.16}$$

where  $i = \sqrt{-1}$  and  $\mathcal{C}$  is a contour chosen so that all the singularities of  $\hat{m}_n(s)$  are to the left of it. Further, if we apply the residue theorem to the above integral, we have

$$m_n(t) = \sum_{k=0}^{\infty} R_k, \tag{3.17}$$

where  $R_k$  are the residues of  $\hat{m}_n e^{st}$  and can be calculated as

$$R_k = \frac{1}{(l-1)!} \lim_{s \rightarrow s_k} \frac{d^{l-1}}{ds^{l-1}} (\hat{m}_n e^{st} (s - s_k)^l), \tag{3.18}$$

where  $l$  is the order of the  $k$ th singularity or pole  $s_k$ .

Since  $\hat{m}_0$ ,  $\hat{m}_1$  and  $\hat{m}_2$  have only first-, second- and third-order singularities, respectively, we have

$$m_0(t) = \sum_{k=0}^{\infty} \lim_{s \rightarrow s_k} (s - s_k) \hat{m}_0 \exp(st) = \sum_{k=0}^{\infty} a_k \exp(-p_k^2 t), \tag{3.19a}$$

$$m_1(t) = \sum_{k=0}^{\infty} \lim_{s \rightarrow s_k} \frac{d}{ds} [(s - s_k)^2 \hat{m}_1 \exp(st)] = \sum_{k=0}^{\infty} b_k^{(1)} \exp(-p_k^2 t) + b_k^{(2)} t \exp(-p_k^2 t), \tag{3.19b}$$

$$\begin{aligned} m_2(t) &= \sum_{k=0}^{\infty} \frac{1}{2} \lim_{s \rightarrow s_k} \frac{d^2}{ds^2} [(s - s_k)^3 \hat{m}_2 \exp(st)] \\ &= \sum_{k=0}^{\infty} c_k^{(1)} \exp(-p_k^2 t) + c_k^{(2)} t \exp(-p_k^2 t) + c_k^{(3)} t^2 \exp(-p_k^2 t), \end{aligned} \tag{3.19c}$$

where

$$a_k = \lim_{s \rightarrow s_k} (s - s_k) \hat{m}_0, \tag{3.20a}$$

$$b_k^{(1)} = \lim_{s \rightarrow s_k} \frac{d}{ds} [(s - s_k)^2 \hat{m}_1], \tag{3.20b}$$

$$b_k^{(2)} = \lim_{s \rightarrow s_k} (s - s_k)^2 \hat{m}_1, \tag{3.20c}$$

$$c_k^{(1)} = \frac{1}{2} \lim_{s \rightarrow s_k} \frac{d^2}{ds^2} [(s - s_k)^3 \hat{m}_2], \tag{3.20d}$$

$$c_k^{(2)} = \lim_{s \rightarrow s_k} \frac{d}{ds} [(s - s_k)^3 \hat{m}_2], \tag{3.20e}$$

$$c_k^{(3)} = \frac{1}{2} \lim_{s \rightarrow s_k} (s - s_k)^3 \hat{m}_2. \tag{3.20f}$$

In order to remove the limit operator and give an explicit form of the coefficients in (3.20), the general form of moments in Laplace space (3.13) are substituted into (3.20). The fractional forms of  $\hat{m}_0$ ,  $\hat{m}_1$  and  $\hat{m}_2$  allow us to apply L'Hospital's rule and obtain the explicit form of the coefficients,

$$a_k = \frac{N_0}{T_1}, \tag{3.21a}$$

$$b_k^{(1)} = \frac{T_1 N_1' - 2T_2 N_1}{T_1^3}, \tag{3.21b}$$

$$b_k^{(2)} = \frac{N_1}{T_1^2}, \tag{3.21c}$$

$$c_k^{(1)} = \frac{(12T_2^2 - 6T_1 T_3) N_2 - 6T_1 T_2 N_2' + T_1^2 N_2''}{2T_1^5}, \tag{3.21d}$$



$$c_k^{(2)} = \frac{T_1 N'_2 - 3T_2 N_2}{T_1^4}, \tag{3.21e}$$

$$c_k^{(3)} = \frac{N_2}{2T_1^3}, \tag{3.21f}$$

where  $N'_n = dN_n/ds$ ,  $N''_n = d^2N_n/ds^2$  at  $s = s_k$  and  $T_n = E^{(n)}/n!$  is the  $n$ th-order Taylor expansion coefficient of  $E(s)$  at  $s = s_k$ . These coefficients can also be expressed in terms of  $p_k$  by substituting  $s_k = -p_k^2$ . The analytical expressions of  $a_k$ ,  $b_k^{(1)}$ ,  $b_k^{(2)}$ ,  $c_k^{(1)}$ ,  $c_k^{(2)}$  and  $c_k^{(3)}$  are given in the supplementary materials.

To summarize, for a given  $k_a$  and  $k_d$ , (3.15) is first solved for a series of  $p_k$ , which are substituted into (3.21) to obtain the coefficients  $a_k$ ,  $b_k$  and  $c_k$ . The normalized longitudinal moments  $M_0$ ,  $M_1$  and  $M_2$ , the transport velocity  $v$  and the dispersion coefficient  $D_L$  are then determined by definitions (3.1) and (3.2).

### 3.3. Reduction to previous results

In the long-time limit, when the zeroth-order terms dominate, the transport velocity and dispersion coefficient are

$$v_0 = \frac{b_0^{(2)}}{a_0} = Pe \frac{k_d}{k_a + k_d} = Pe \frac{1}{k + 1}, \tag{3.22a}$$

$$D_0 = \frac{1}{2} \left( \frac{c_0^{(2)}}{a_0} - \frac{2b_0^{(1)}b_0^{(2)}}{a_0^2} \right) = \frac{1}{1+k} + Pe^2 \frac{2}{105} \frac{1+9k+25.5k^2}{(1+k)^3} + \frac{Pe^2}{k_d} \frac{k}{(1+k)^3}, \tag{3.22b}$$

which are consistent with the results obtained in chromatography (Khan 1962). For  $k > 0$ , the transport velocity of the solute is slower than the mean flow velocity at late times.

At early but finite time, the first-order terms dominate and lead to an asymptotic velocity  $v_1$  and dispersion coefficient  $D_1$  given as

$$v_1 = \frac{b_1^{(2)}}{a_1} \quad \text{and} \quad D_1 = \frac{1}{2} \left( \frac{c_1^{(2)}}{a_1} - \frac{2b_1^{(1)}b_1^{(2)}}{a_1^2} \right). \tag{3.23a,b}$$

In the limiting case of  $k_d = 0$  analysed by Lungu & Moffatt (1982), the zeroth-order coefficients of the moments vanish, i.e.  $a_0 = b_0^{(2)} = b_0^{(1)} = c_0^{(3)} = c_0^{(2)} = c_0^{(1)} = 0$ . Therefore, the first-order terms dominate and lead to the following asymptotic transport velocity and dispersion coefficient,

$$v_{LM} = \frac{Pe(4k_a^2 p_1^2 + 3k_a^2 + 3k_a + 4p_1^4 - 3p_1^2)}{4p_1^2(k_a^2 + k_a + p_1^2)}, \tag{3.24a}$$

$$D_{LM} = 1 + (Pe^2(-8k_a^6 p_1^4 + 150k_a^6 p_1^2 - 315k_a^6 - 56k_a^5 p_1^4 + 750k_a^5 p_1^2 - 945k_a^5 - 24k_a^4 p_1^6 + 282k_a^4 p_1^4 + 555k_a^4 p_1^2 - 945k_a^4 - 192k_a^3 p_1^6 + 1560k_a^3 p_1^4 - 540k_a^3 p_1^2 - 315k_a^3 + 24k_a^2 p_1^8 - 78k_a^2 p_1^6 + 1455k_a^2 p_1^4 - 495k_a^2 p_1^2 - 136k_a p_1^8 + 810k_a p_1^6 + 225k_a p_1^4 - 8p_1^{10} - 210p_1^8 + 585p_1^6)) / (160p_1^6(k_a^2 + k_a + p_1^2)^3), \tag{3.24b}$$

where  $p_1$  is determined by solving (3.15). Equations (3.24) are consistent with (3.4) and (3.11) given in Lungu & Moffatt (1982), except for a difference in notation. For  $k_a > 0$ , the asymptotic transport velocity of the solute is faster than the mean flow velocity. Note that the early and late transport velocities  $v_1$  and  $v_0$  have linear dependence on  $Pe$ , and the early and late dispersion coefficients  $D_1$  and  $D_0$  (excluding the contribution from pure diffusion) have quadratic dependence on  $Pe$ , so that the normalized ones defined in (4.1) below are generally independent of  $Pe$ .

### 3.4. Equilibrium sorption model

If the kinetics of the reactions are fast enough that local chemical equilibrium is valid, the linear kinetic sorption model reduces to the linear isotherm (i.e. equilibrium sorption model)  $\gamma = kc$ , with  $k = k_a/k_d$ . For the equilibrium sorption model, (3.15) becomes

$$\tan(p) = -kp, \quad (3.25)$$

which can be solved for a series of  $p_k$ . Taking the limit  $k_a \rightarrow \infty$ ,  $k_d \rightarrow \infty$  of (3.21) while keeping  $k_a/k_d = k$ , the coefficients become functions of only the partition coefficient  $k$ , as expected.

### 3.5. First-order approximation of the series solution

For the general case when  $k_d$  is not zero, the fast transport described by (3.24) may survive at early times before desorption has come into play. In this case, the general series solution of the moments (3.19) allows us to study the transition from fast transport at early times described by first-order terms to slow transport at late times described by zeroth-order terms.

The zeroth- and first-order terms correspond to the residues  $R_0$  and  $R_1$  in (3.17). Figure 2(a,b) shows the comparison of the zeroth-order approximation  $R_0$  and first-order approximation  $R_0 + R_1$  with the numerical inversion of the Laplace transform using Talbot's method (Abate & Whitt 2006; McClure 2013). As expected, the first-order approximation  $R_0 + R_1$  captures the solution at both the early and late times, while the zeroth-order approximation  $R_0$  only describes the late-time behaviour. Additional tests show that the first-order approximation is sufficient to describe the solution for a large range of  $k_a$  and  $k_d$  after a short initial time. Therefore, we truncate the series solution (3.19) by retaining only the zeroth- and first-order terms,

$$m_0 = a_0 + a_1 \exp(-p_1^2 t), \quad (3.26a)$$

$$m_1 = (b_0^{(1)} + b_0^{(2)} t) + (b_1^{(1)} + b_1^{(2)} t) \exp(-p_1^2 t), \quad (3.26b)$$

$$m_2 = (c_0^{(1)} + c_0^{(2)} t + c_0^{(3)} t^2) + (c_1^{(1)} + c_1^{(2)} t + c_1^{(3)} t^2) \exp(-p_1^2 t), \quad (3.26c)$$

where the higher-order terms describing the very early-time behaviour are ignored.

## 4. Regimes of transport

In this section, we discuss the transition from the early fast transport to the late slow transport. Numerical simulations of the full two-dimensional problem illustrate the physical mechanism that leads to this transition. The truncated analytical solution provides the estimates of the associated time scales. First, we will use the simpler equilibrium sorption model to discuss the regime transition, followed by the more general kinetic case.

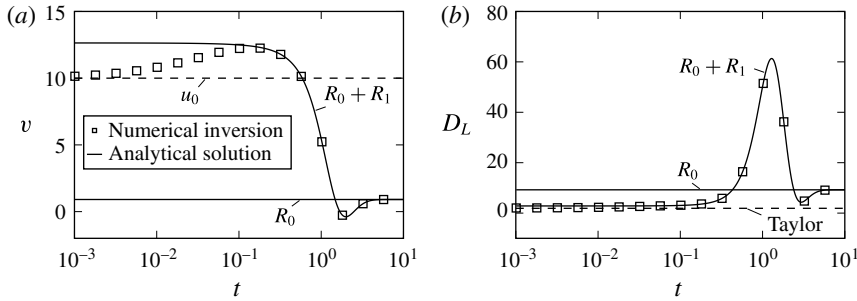


FIGURE 2. Comparison of the zeroth-order approximation ( $R_0$ ) and the first-order approximation ( $R_0 + R_1$ ) with the numerical inversion of the Laplace transform (squares) using Talbot’s method.  $R_0$  and  $R_1$  are the zeroth and first residues of the moments defined in (3.17) and (3.18). Results are shown for  $Pe = 10$ ,  $k_a = 10$  and  $k_d = 1$ . (a) The transport velocity  $v$ , where the mean flow velocity  $u_0 = U_0H/D = Pe$ . (b) The dispersion coefficient  $D_L$ , where the dashed line labelled as Taylor denotes the Taylor dispersion  $2/105Pe^2$ .

4.1. Two-dimensional simulations

Figure 3 shows two-dimensional simulations of the solute concentration at different times for  $Pe = 10$ ,  $k_a = 50$  and  $k_d = 1$ . The full problem is numerically solved by the lattice Boltzmann method (LBM) (Chen & Doolen 1998; Wang & Kang 2010; Zhang & Wang 2015). The  $\delta$ -function initial condition is approximated by a piecewise-constant function that is non-zero in a small interval around the origin. This approximation of the initial condition only affects the results in a short diffusive transient and the results agree well with the analytical solution (figure 3f–h).

Initially, the strong adsorption removes the solute from the slow-moving fluid near the wall. The remaining solute in the centre of the channel forms a fast-moving pulse (figure 3b,c), particularly evident in the transversely averaged concentration shown in figure 3(e). This corresponds to the increased solute transport velocity in the irreversible sorption case (Lungu & Moffatt 1982). This regime persists as long as adsorption dominates.

However, the fast-moving pulse decays rapidly and eventually desorption releases solute in its wake (figure 3d). As the amount of desorbed solute in the slow-moving fluid near the wall increases, the solute transport velocity declines. This process continues until desorption at the back balances adsorption at the front. The transport velocity and dispersion coefficient will approach the slow transport described by the one-dimensional model of the transversely averaged concentration in the reversible sorption case (Khan 1962).

4.2. Equilibrium sorption model

Following the solution procedure in § 3.4, this section presents results and analysis for equilibrium sorption model,  $\gamma = kc$ . To demonstrate the different transport behaviours, we define a normalized transport velocity  $\mathcal{V}$  and a normalized dispersion coefficient  $\mathcal{D}$  as

$$\mathcal{V} = \frac{v}{Pe} \quad \text{and} \quad \mathcal{D} = \frac{D_L - 1}{D_t}, \tag{4.1a,b}$$

where  $D_t = 2/105Pe^2$  is the Taylor dispersion coefficient for a tracer in Poiseuille flow and the unit contribution of diffusion has been subtracted in the numerator of (4.1b).

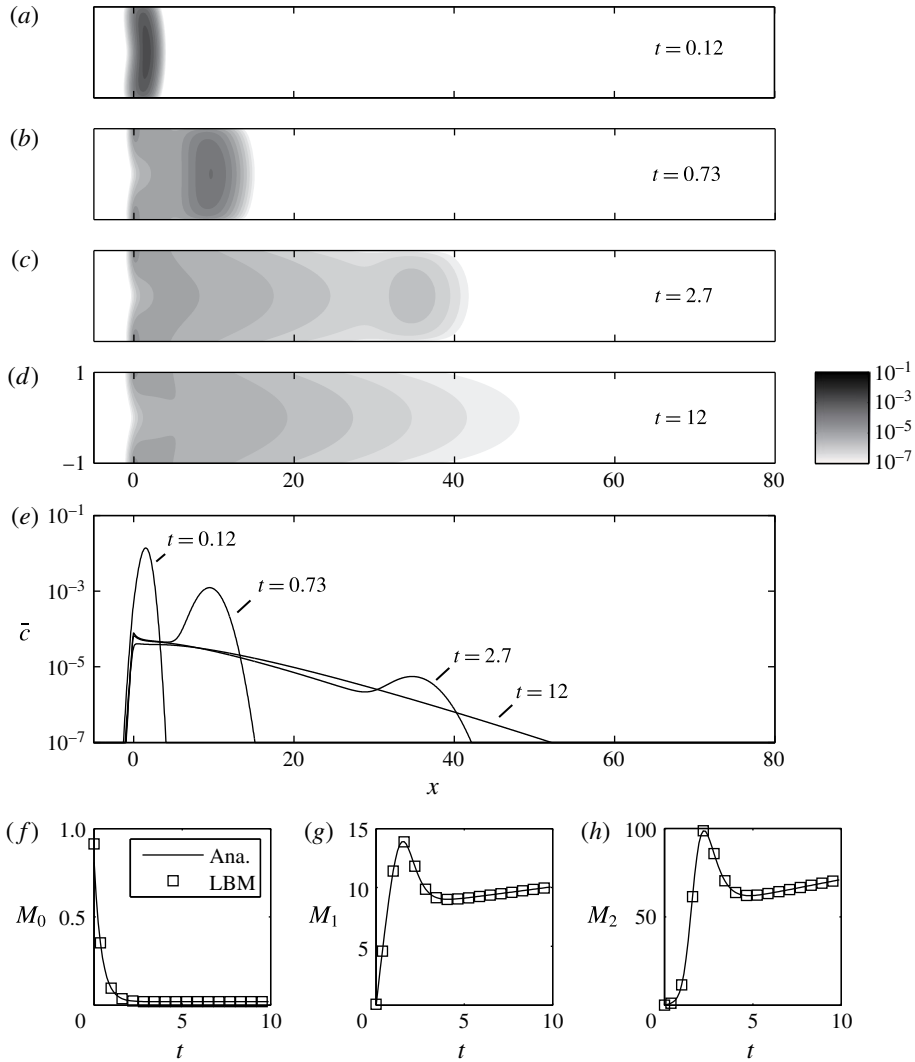


FIGURE 3. Two-dimensional simulation of solute transport with sorption in Poiseuille flow with  $Pe = 10$ ,  $k_a = 50$  and  $k_d = 1$ . (a–d) Concentration distribution and (e) transversely averaged concentration profile at  $t = 0.12, 0.73, 2.7, 12$ . (f–h) The evolution of the zeroth-, first- and second-order moments and comparison of the numerical simulation (LBM) with the first-order approximation of the analytical solution (Ana.).

In this way,  $\mathcal{V} > 1$  ( $\mathcal{D} > 1$ ) means increased velocity (dispersion) relative to a non-reactive tracer while  $\mathcal{V} < 1$  ( $\mathcal{D} < 1$ ) means decreased velocity (dispersion).

Figure 4 shows the evolution of the position of the centre of mass  $M_1$  and the normalized transport velocity  $\mathcal{V}$  for different partition coefficients. For  $k > 10$ , a linear region emerges at early times in figure 4(a), corresponding to an initial plateau in figure 4(b). This corresponds to the well-developed early regime characterized by fast transport, approaching an asymptotic velocity  $1 + 3/\pi^2 \approx 1.3$ . This is consistent with the results in an adsorption-only case with  $k_a \rightarrow \infty$  (Lungu & Moffatt 1982).

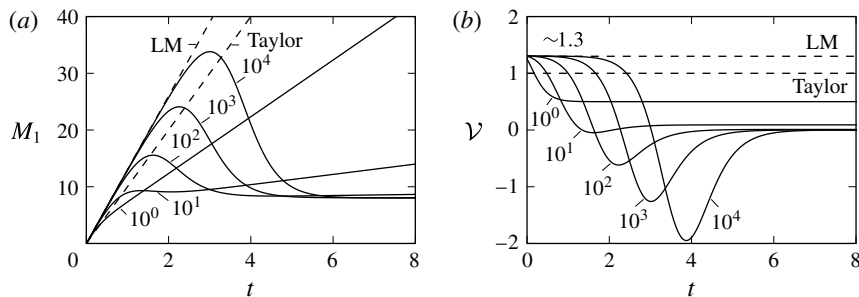


FIGURE 4. Evolution of (a) centre of mass  $M_1$  and (b) normalized transport velocity  $\mathcal{V}$  for different partition coefficients  $k$ . Dashed lines with labels LM and Taylor stand for the asymptotic regime of an adsorption-only case (Lungu & Moffatt 1982) and the asymptotic regime of a non-reactive tracer, respectively.

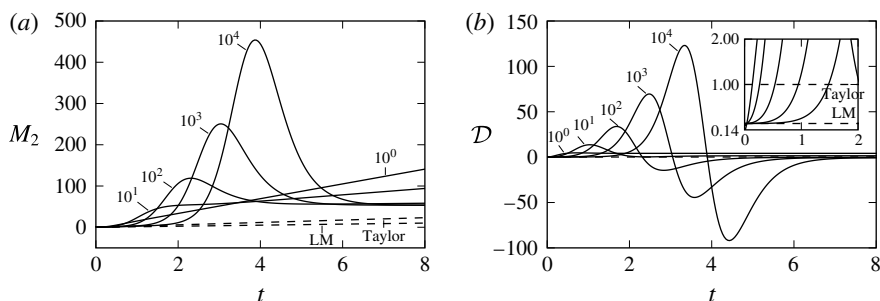


FIGURE 5. Evolution of (a) variance of solute mass distribution  $M_2$  and (b) the normalized dispersion coefficient  $\mathcal{D}$  for different partition coefficients  $k$ . Dashed lines with labels LM and Taylor stand for the asymptotic regime of an adsorption-only case (Lungu & Moffatt 1982) and the asymptotic regime of a non-reactive tracer, respectively.

After a transition period, a second linear region at late times appears, corresponding to the decreased transport velocity  $1/(1+k)$ .

Figure 5 shows similar behaviours of the variance of solute mass in the fluid  $M_2$  and the normalized dispersion coefficient  $\mathcal{D}$ . In the early regime, the dispersion coefficient is reduced relative to a tracer with  $\mathcal{D} \sim 0.14$ , which also agrees with the adsorption-only case with  $k_a \rightarrow \infty$ . In the late regime, the dispersion coefficient is given by the first two terms of (3.22b), first obtained by Golay (1958).

Between the early and late times, there is a drastic transition of the transport behaviour. Especially when  $k$  is large, both  $M_1$  and  $M_2$  decrease after reaching maxima during the transition, and this leads to negative velocity and dispersion coefficient. Physically, it means that desorption near the origin dominates over the fast-moving pulse in figure 3 so that the centre of mass shifts backwards and the variance reduces because the transversely averaged concentration distribution changes from a bimodal type (one peak near the origin and the other at the pulse front) to a unimodal type (single peak near the origin).

To compare the early and late behaviours as a function of  $k$ , we define the normalized early and late velocities as

$$\mathcal{V}_e = \frac{v_1}{Pe} \quad \text{and} \quad \mathcal{V}_l = \frac{v_0}{Pe}, \tag{4.2a,b}$$

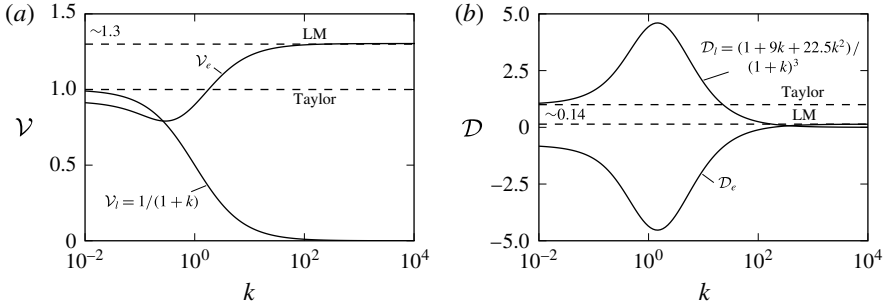


FIGURE 6. (a) Normalized early velocity  $\mathcal{V}_e = v_1/Pe$  and late velocity  $\mathcal{V}_l = v_0/Pe$  and (b) normalized early dispersion coefficient  $\mathcal{D}_e = (D_1 - 1)/D_t$  and late dispersion coefficient  $\mathcal{D}_l = (D_0 - 1/(1+k))/D_t$  as functions of partition coefficient  $k$ .

and similarly we define the normalized early and late dispersion coefficients as

$$\mathcal{D}_e = \frac{D_1 - 1}{D_t} \quad \text{and} \quad \mathcal{D}_l = \frac{D_0 - 1/(1+k)}{D_t}, \tag{4.2c,d}$$

where  $v_0, D_0$  and  $v_1, D_1$  are obtained from the zeroth- and first-order terms of the solution, the equilibrium limits of (3.22) and (3.23). Note that at early times the effective diffusion is not affected by sorption while it is reduced by a factor of  $1/(1+k)$  at late times.

As shown in figure 6, for large  $k$  the difference of normalized transport velocity between  $\mathcal{V}_e$  and  $\mathcal{V}_l$  is the largest and the normalized early-time dispersion coefficient  $\mathcal{D}_e$  asymptotes to 0.14. The normalized late-time dispersion coefficient  $\mathcal{D}_l$  first increases with  $k$ , then reduces towards 0. For small  $k$ , the early velocity  $\mathcal{V}_e$  and dispersion coefficient  $\mathcal{D}_e$  do not reach the asymptotic values 1.3 and 0.14. In this case, the early regime is not well developed and the first-order terms of the solution are not dominant. Therefore,  $\mathcal{V}_e$  and  $\mathcal{D}_e$  do not represent the transport behaviour in this case.

For a tracer in Poiseuille flow, the pre-asymptotic transport before equilibrium has been studied extensively (e.g. Gill & Sankarasubramanian 1970; Haber & Mauri 1988; Mercer & Roberts 1990; Latini & Bernoff 2001; Dentz & Carrera 2007; Bolster *et al.* 2011; Wang *et al.* 2012). Typically, diffusion dominates when  $t \ll t_d = Pe^{-2/3}$ ; and after the characteristic equilibrium time scale,  $t = 1$ , solute transport can be described by the transversely averaged model with the mean flow velocity and the dispersion coefficient  $D_t$ . However, for a reactive case considered here, the time scale to reach equilibrium can be quite different from the tracer case because surface reactions introduce additional characteristic time scales.

In the first-order approximation (3.26), a series of time scales can be defined by comparing the zeroth-order and first-order terms. Taking  $m_0$  as an example, by comparing  $a_0$  and  $a_1 \exp(-p_1^2 t)$ , we can define a time scale as

$$t_1 = \frac{1}{p_1^2} \ln \frac{a_1}{a_0} = \frac{1}{p_1^2} \ln \frac{2k^2(k+1)}{k^2 p_1^2 + k + 1}. \tag{4.3}$$

This time scale indicates the transition from the early regime when the transport is dominated by the first-order terms to the late regime dominated by the zeroth-order

terms. Similarly, other time scales can be determined by comparing  $b_k$  and  $c_k$ . We notice that the coefficients in the series solution have the property

$$\frac{a_1}{a_0} < \frac{b_1^{(2)}}{b_0^{(2)}} \sim \frac{c_1^{(2)}}{c_0^{(2)}} < \frac{c_1^{(3)}}{c_0^{(3)}}, \tag{4.4}$$

which means that  $t_1$  will give the smallest time scale. At the same time, since the time scales for the velocity determined by  $b_1^{(2)}/b_0^{(2)}$  and the dispersion coefficient determined by  $c_1^{(2)}/c_0^{(2)}$  have the same scaling, we can choose

$$t_2 = \frac{1}{p_1^2} \ln \frac{b_1^{(2)}}{b_0^{(2)}} = \frac{1}{p_1^2} \ln \frac{k^2(k+1)^2(4k^2p_1^4 + 3k^2p_1^2 - 3k + 4p_1^2 - 3)}{2p_1^2(k^2p_1^2 + k + 1)^2} \tag{4.5}$$

as a critical time scale, after which the zeroth-order terms dominate and the late-time behaviour emerges. Note that the two time scales are not dependent on  $Pe$ . Consequently, the transient solute transport with sorption can be divided into the following three regimes:

- (I)  $0 < t < t_1$  – early regime with fast transport;
- (II)  $t_1 < t < t_2$  – transition period;
- (III)  $t_2 < t$  – late regime with slow transport.

As shown in figures 4 and 5, the duration of the early regime, as well as the transition period, increase with increasing  $k$ . In the limit of large  $k$ , we have

$$\lim_{k \rightarrow \infty} t_1 = \frac{4}{\pi^2} \ln k \quad \text{and} \quad \lim_{k \rightarrow \infty} t_2 = \frac{8}{\pi^2} \ln k, \tag{4.6a,b}$$

where we have used  $\lim_{k \rightarrow \infty} p_1 = \pi/2$ . Equations (4.6) predict a linear relationship between  $t_1$ ,  $t_2$  and  $\ln k$  when  $k$  is large and  $t_2 \sim 2t_1$ . Figure 7 compares results from the numerical inverse Laplace transform with these analytically determined time scales as a function of  $k$ . When  $k \gg 1$ ,  $t$  scales with  $\ln k$ , as predicted by (4.6). For small  $k$ , the early regime is so short that it is generally not observed.

### 4.3. Kinetic sorption model

In the kinetic sorption model, there are two additional governing parameters, namely, the dimensionless adsorption rate constant  $k_a$  and the dimensionless desorption rate constant  $k_d$ . Generally, a similar transition from early to late behaviour can be observed and the equilibrium results are recovered when kinetics are fast, i.e.  $k_a \gg 1$  and  $k_d \gg 1$ .

Similar to the way that the time scales are determined for the equilibrium model, we can obtain  $t_1$  and  $t_2$  for the kinetic model using (4.3) and (4.5),

$$t_1 = \frac{1}{p_1^2} \ln \frac{2k_a^2(k_a + k_d)}{k_d(p_1^4 + (k_a^2 + k_a - 2k_d)p_1^2 + k_a k_d + k_d^2)}, \tag{4.7a}$$

$$t_2 = \frac{1}{p_1^2} \ln \frac{k_a^2(k_a + k_d)^2(4p_1^6 + (4k_a^2 - 8k_d - 3)p_1^4 + (3k_a^2 + 3k_a + 4k_d^2 + 6k_d)p_1^2 - 3k_a k_d - 3k_d^2)}{2k_d^2 p_1^2 (p_1^4 + (k_a^2 + k_a - 2k_d)p_1^2 + k_a k_d + k_d^2)^2}, \tag{4.7b}$$

which are shown in figure 8.

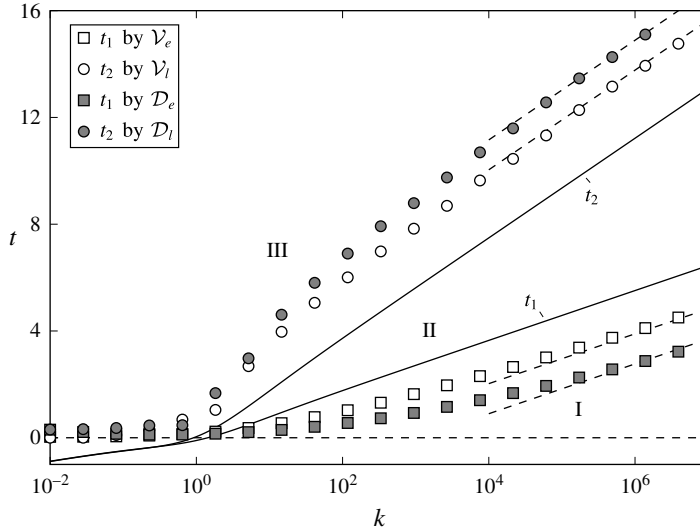


FIGURE 7. Variation of the early time scale  $t_1$  and the late time scale  $t_2$  as functions of partition coefficient  $k$ . The solid lines show  $t_1$  and  $t_2$  from (4.3) and (4.5), respectively, and the dashed lines indicate the scalings for large  $k$  given by (4.6), which have been shifted to match the symbols determined by the numerical inverse Laplace transform. White symbols are determined by velocity and grey symbols are determined by dispersion coefficient. The transient solute transport with sorption is divided into three regimes: (I) early regime with fast transport; (II) transition period; and (III) late regime with slow transport.

The early regime is only observed when  $k_a$  exceeds  $k_d$ . In all other cases, transition occurs from the very beginning followed by a dominated late regime. When both  $k_a$  and  $k_d$  are large, the time scales of the kinetic model recover those of the equilibrium model.

However, if the rates decrease, the kinetic time scales become longer. In this case, the root  $p_1$  of (3.15) can be approximated by  $p_1^2 \approx k_a + k_d$  using Taylor expansion for  $\tan(p)$ . Then the ratios  $a_1/a_0$  and  $b_1^{(2)}/b_0^{(2)}$  used to obtain the time scales simplify to

$$\frac{a_1}{a_0} = \frac{2k_a}{k_d(k_a + 2)} \quad \text{and} \quad \frac{b_1^{(2)}}{b_0^{(2)}} = \frac{k_a^2(4k_a + 4k_d + 7)}{2k_d^2(k_a + 2)^2}. \tag{4.8a,b}$$

This analysis shows that both time scales increase dramatically in the lower left region where  $k_a$  and  $k_d$  are small in figure 8. In this region, the duration of the early regime is long, but the deviations of velocity and dispersion coefficient from the tracer case are minor, as the limiting values given by the adsorption-only case approach unity with small  $k_a$ . Physically, this region corresponds to a kinetically slow-sorbing ( $k_a, k_d \ll 1$ ) solute with a large partition coefficient  $k \gg 1$ .

The analytical solution presented in § 3.3 recovers the previous analysis in the limit of  $k_d = 0$  (Lungu & Moffatt 1982). This limiting solution puts an upper bound on the transport velocity and a lower bound on the dispersion coefficient in the early regime. If the early regime is well developed, the limiting solution given by Lungu & Moffatt (1982) provides a good approximation for finite  $k_d$  (see figure 8c). The well-developed early regime is indicated by grey shadings in figure 8(a), where the early-time asymptotic transport velocity and dispersion coefficient given by (3.23) are



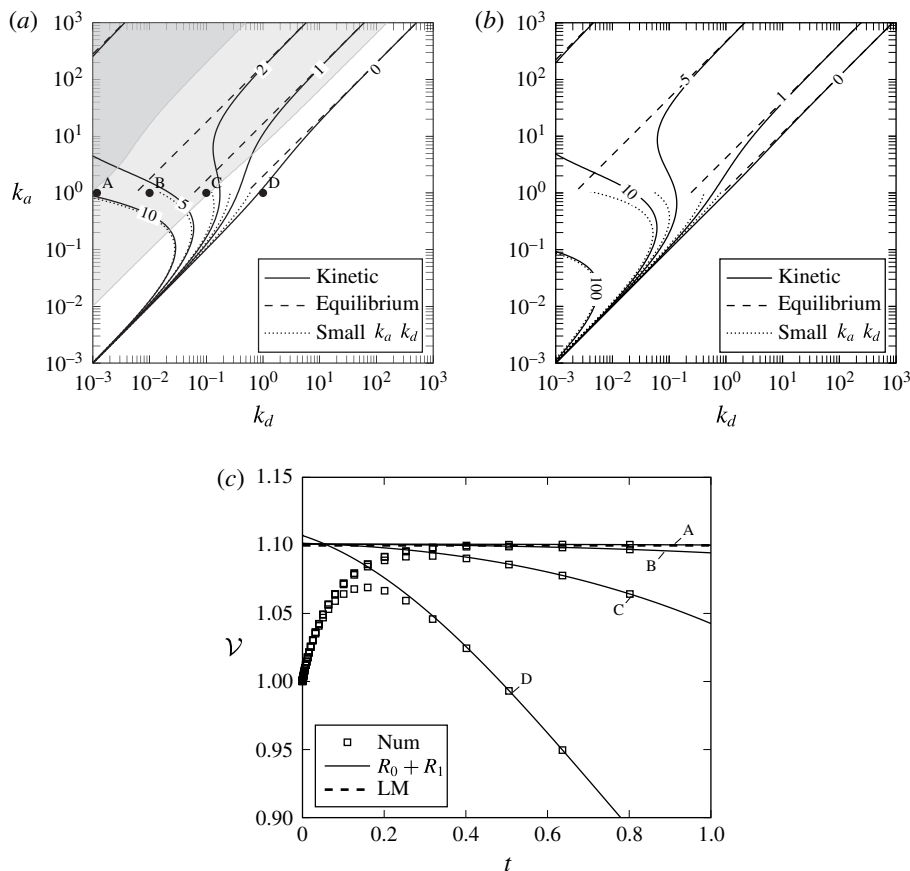


FIGURE 8. Contour lines of (a) the early time scale  $t_1$  and (b) the late time scale  $t_2$  for the kinetic sorption model. Dashed lines represent the time scales obtained from the equilibrium sorption model for large  $k_a$  and  $k_d$  and dotted lines represent approximations for small  $k_a$  and  $k_d$ , given by (4.8a,b). The shaded area in (a) represents the region where the early regime is well developed, i.e. the velocity (light shaded area) and dispersion coefficient (dark shaded area) are close to the limiting values given by the adsorption-only case. (c) The evolution of velocity at early time for the conditions labelled as A, B, C and D in (a). Symbols are the results from full numerical inverse Laplace transform, solid lines are first-order approximation of the analytical solution and dashed line is the asymptotic value for  $k_d = 0$  at  $k_a = 1$ , given by Lungu & Moffatt (1982).

within 10% of the limiting values given by Lungu & Moffatt (1982). Cases A, B and C give examples of the well-developed early regime, while the velocity does not reach the asymptotic value in case D. Generally, if  $k > 10$  ( $k > 1000$ ), the early-time velocity (dispersion coefficient) is well developed. Note that the first-order analytical solution for transport velocity ( $R_0 + R_1$ ) shown in figure 8(c) is computed by (3.2) and (3.26).

### 5. Conclusion

In this work, we reconcile two different analyses of solute transport with sorption in Poiseuille flow that reached apparently contradictory conclusions. We show that these two analyses capture different regimes of the transport. Generally, the solute

experiences an early regime with fast transport velocity if adsorption dominates desorption. At late times, when desorption becomes important, the solute transport slows down. This leads to a regime transition that scales as  $\ln k$  for the equilibrium sorption model, where  $k$  is the dimensionless partition coefficient. Therefore, the early regime is more pronounced when  $k$  is large. In the kinetic sorption model, the early regime is also observed if the kinetics are slow and the dimensionless adsorption rate constant  $k_a$  exceeds the dimensionless desorption rate constant  $k_d$ . As long as  $k_a \gg k_d$ , the early regime is well developed, and the transport velocity and the dispersion coefficient in this early regime are well approximated by the analysis of Lungu & Moffatt (1982) in the limit of  $k_d = 0$ .

The time scales presented in this work allow the determination of the dominant transport behaviour for a given application. Experience shows that the late regime dominates the subsurface transport of sorbing contaminants in fractures. However, the early regime may be important in biomedical applications where transport occurs over smaller distances. Our analysis may also allow a design of chromatography columns that can achieve opposite separation results.

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### Supplementary materials

Supplementary materials are available at <https://doi.org/10.1017/jfm.2017.546>.

### Appendix A. Effect of initial condition

The initial distribution of solute mass manifests itself either as a source term,  $c_n^*(t=0)$ , or as a constant in the boundary condition,  $\gamma_n^*(t=0)$ , in the ODE system (3.10). These effects can be important in our problem in the sense that they may affect the form of the solutions of the moments. A general discussion on this topic is beyond the scope of this paper, and we show a special case as an example.

In the previous formulation, we assume initially there is no mass adsorbed on the wall,  $\gamma_n^*(t=0) = 0$ . In this section, we change the initial condition by retaining the uniform release in the fluid, but assuming the mass distribution between the wall and the bulk has reached equilibrium, namely,  $c(t=0) = \delta(x)/(1+k)$ ,  $\gamma(t=0) = \delta(x)k/(1+k)$ . Following the same procedure as in §§ 3.1 and 3.2, we find that the moments in Laplace space  $\hat{m}_0$ ,  $\hat{m}_1$ ,  $\hat{m}_2$  are no longer in the form of (3.13), but show a slight difference, i.e.

$$\hat{m}_0(s) = \frac{Q_0(s)}{s}, \quad (\text{A } 1a)$$

$$\hat{m}_1(s) = \frac{Q_1(s)}{sE(s)}, \quad (\text{A } 1b)$$

$$\hat{m}_2(s) = \frac{Q_2(s)}{sE^2(s)}, \quad (\text{A } 1c)$$

where  $Q_0$ ,  $Q_1$  and  $Q_2$  are different from  $N_0$ ,  $N_1$  and  $N_2$ . In fact,  $Q_0 = 1/(1+k)$ . Essentially, the order of all the singularities, other than the zeroth-order one, reduce by one in the solutions. Therefore, the series solutions obtained by the residue theorem are written as

$$m_0(t) = a_0, \quad (\text{A } 2a)$$

$$m_1(t) = b_0^{(1)} + b_0^{(2)}t + \sum_{k=1}^{\infty} \tilde{b}_k^{(1)} \exp(-p_k^2 t), \quad (\text{A } 2b)$$

$$m_2(t) = c_0^{(1)} + c_0^{(2)}t + c_0^{(3)}t^2 + \sum_{k=0}^{\infty} \tilde{c}_k^{(1)} \exp(-p_k^2 t) + \tilde{c}_k^{(2)} t \exp(-p_k^2 t), \quad (\text{A } 2c)$$

where  $\tilde{b}_k^{(1)}$ ,  $\tilde{c}_k^{(1)}$  and  $\tilde{c}_k^{(2)}$  are different from  $b_k^{(1)}$ ,  $c_k^{(1)}$  and  $c_k^{(2)}$ . Note that the long-time velocity and dispersion coefficient determined by  $a_0$ ,  $b_0^{(2)}$  and  $c_0^{(2)}$  do not change. However, since  $b_k^{(2)}$  diminishes, the early regime will not be well developed in this case. Physically, the solute that is initially adsorbed onto the wall begins to desorb much earlier, and hence reduces the duration of the early regime. In the limit of  $k_d = 0$ ,  $k \rightarrow \infty$ , and the initial solute mass in the fluid  $c(t=0)$  vanishes so that the results by Lungu & Moffatt (1982) cannot be properly recovered in this case.

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