

Perturbation Solution to the Convection–Diffusion Equation with Moving Fronts

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Electrophoresis of a solute through a column in which its transport is governed by the convection–diffusion equation is described. Approximate solutions to the convection–diffusion equation in the limit of small diffusion are developed using perturbation methods. The diffusion coefficient and velocity are assumed to be functions of space and time such that both undergo a sudden change from one constant value to another within a thin transition zone that itself translates with a constant velocity. Two cases are considered: (1) the thickness ϵ_f of the transition zone is negligible compared to the diffusional length scale, so the zone may be treated as a singular boundary across which the diffusion constant and velocity suffer discontinuous changes; (2) the transition zone is considerably wider than the diffusional length scale, so the diffusion coefficient and velocity, although sharply varying, are smooth functions of position and time. A systematic perturbation expansion of the concentration distribution is presented for case 1 in terms of the small parameter $\epsilon = 1/Pe$. A lowest order approximation is given for case 2. A suitably configured system analyzed here can lead to progressive accumulation, or focusing, of the transported solute. The degree of focusing in case 1 scales with ϵ^{-1} , whereas in case 2 it scales with $(\epsilon_f \epsilon)^{-1/2}$, and thus increases much more weakly with increasing Pe . A separation based on this concept requires development of materials and devices that allow dynamic tuning of the mass-transport properties of a medium. This would make it possible to achieve progressive focusing and separation of solutes, such as proteins and DNA fragments, in electrophoretic media with an unprecedented degree of control.

Introduction

Internal boundaries

Convective-diffusive mass transport is central to many problems in physics, chemistry, and engineering (van Kampen, 1981; Gardiner, 1983), and it is of particular importance to separation processes such as electrophoresis (Masoliver and Weiss, 1996). Analytical solutions to the governing equations are well established for many specific geometries and boundary conditions (e.g., Brenner, 1962; Novy et al., 1990), provided that the diffusion coefficient and velocity are constant in space and time. Variable transport coefficients introduce considerable complexity in the treatment of convective-diffusive transport, but progress has been made. In particular, several groups (Ramkrishna and Amundson, 1974; Locke and Arce, 1993; Locke et al., 1993; Vaidya et al., 1996a) have developed analytical solutions in cases where the transport properties are piecewise constant. Such systems are found in many practical situations (e.g., electrophoretic trans-

port through a multilayer composite membrane), and interesting features arise in their transport behavior. The key feature of these systems is the presence of an internal boundary, or “front,” at which the transport properties change abruptly. The existing studies of convective-diffusive transport in the presence of a front are limited to systems in which the front (or fronts) is (1) static, that is, the location of the front does not change as the transport proceeds; and (2) singular, that is, the transport properties change discontinuously. In this article we relax these restrictions, and in doing so are able to demonstrate and analyze several new qualitative effects.

Small diffusion

It is common in many electrophoretic applications to find that the contribution to the solute flux due to diffusion is

very small in comparison with that due to convection. The importance of convection relative to diffusion is quantified by the Péclet number

$$Pe = \frac{\bar{v}L}{\bar{D}}, \quad (1)$$

where L , $\bar{v}$, $\bar{D}$ are characteristic values of the length scale, electrophoretic velocity, and diffusion coefficient, respectively. The Péclet number for electrophoretic flow through a porous matrix is typically of order 10^5 . For example (Locke and Carbonell, 1989), using the data for ferritin undergoing electrophoresis through BioGel A-5 in a column of length 10 cm, with mobility of $8.3 \times 10^{-5} \text{ cm}^2/\text{V s}$, and diffusion coefficient of $3.5 \times 10^{-7} \text{ cm}^2/\text{s}$ in response to an applied electric field of about 60 V/cm, the Péclet number is

$$Pe = \frac{(8.3 \times 10^{-5} \times 60)(10)}{3.5 \times 10^{-7}} = 1.4 \times 10^5. \quad (2)$$

For smaller molecules, the mobility would be higher, but so would the diffusion coefficient, and we expect that the same order of magnitude of Pe would be maintained.

Purely numerical methods suffer in this regime—finite difference techniques require extremely fine meshes (of size $< 1/Pe$) for accurate determination of the concentration profile near an interface; stability of such schemes then demands very small time steps. Thus, to obtain accurate results extremely large computation times are required. Even if an exact solution is available, it can be very difficult to implement in the large- Pe regime because of terms that depend exponentially on Pe (in fact, implementation can become problematic for Pe as small as 100—see, e.g., Vaidya et al., 1996a). Nevertheless, these otherwise intractable transport problems can be made amenable to treatment by exploiting the disparity between the transport mechanisms. The most effective approaches take the form of asymptotic solutions that become valid in the limit $Pe \rightarrow \infty$.

Asymptotic treatments are elementary for the case of constant transport coefficients. The corresponding case where the diffusion coefficient and/or velocity are functions of position only has been extensively studied by Gitterman and Weiss (Gitterman and Weiss, 1993, 1994; Weiss and Gitterman, 1995). However, their methods are restricted to transport in the absence of fronts. The case of convection-dominated transport in the presence of a stationary singular front was recently addressed by the authors (Vaidya et al., 1996a). A systematic expansion in $\epsilon = 1/Pe$ for the concentration distribution on either side of the boundary was developed and was found to be in excellent agreement with numerical results for $Pe > 200$. A point to be noted is that although diffusion is small away from the singular surface, it plays a key role within a boundary layer in satisfying the requirement of continuity of flux across the singular surface at all times.

Moving fronts

Large- Pe applications are particularly interesting when one examines moving fronts. To show why, we first review large- Pe

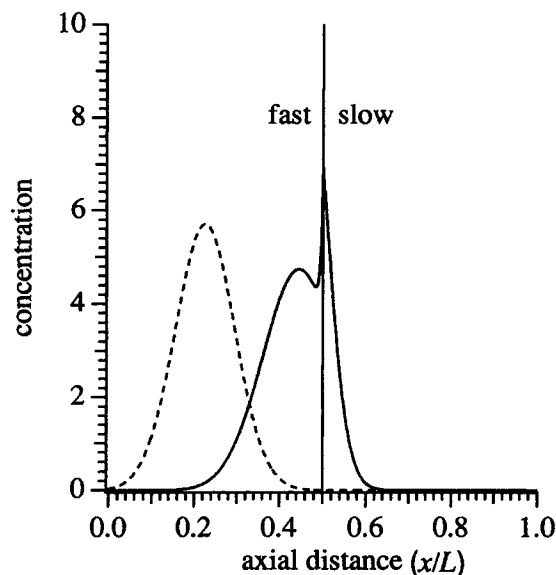
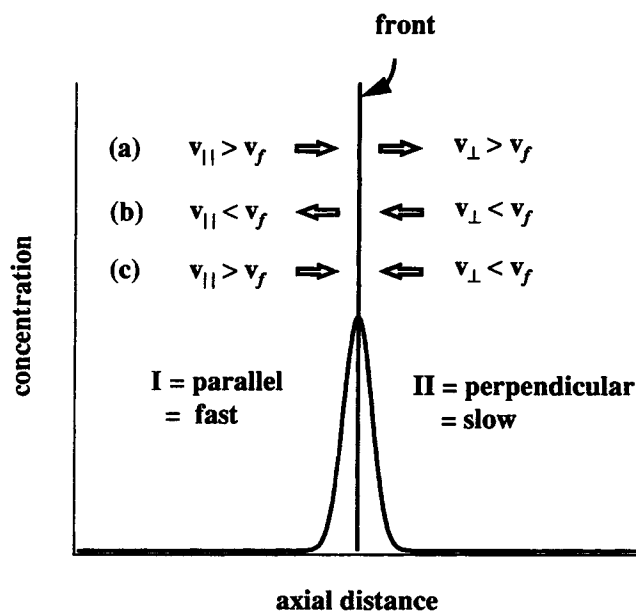


Figure 1. Increase in concentration of solute within the boundary layer on migrating from a fast into a slow domain across a stationary front.

The dashed curve is the initial distribution, and the solid curve is the distribution at a subsequent time. The vertical line represents the front.

transport through a stationary front (Vaidya et al., 1996a). Illustrated in Figure 1 are concentration profiles for a solute undergoing convection–diffusion across a stationary, singular front into a domain where its velocity (and diffusivity) decreases. Near the interface the concentration profile develops a sharp rise to maintain continuity of flux at the front. For a fixed interface this increase in concentration is restricted to the short period during which the solute distribution passes through the front. Thereafter, the solute peak spreads out by diffusion.

Now consider a column containing an electrophoretic medium that is dynamic and tunable in the sense that the transition zone between the domains can be made to move at any prescribed velocity. In such a medium the solute can be made to experience the presence of the interface for a longer period, thereby leading to a progressive concentration increase at the front. Taking the velocity upstream of the front as v^I and that downstream as v^{II} ($v^I > v^{II}$), three possibilities arise for the choice of the velocity of the front v_f : (a) $v_f < v^{II} < v^I$, (b) $v^{II} < v^I < v_f$, and (c) $v^{II} < v_f < v^I$. Figure 2 illustrates the velocity vectors relative to the moving front for these three cases. Case (a) is similar in qualitative behavior to the stationary front (corresponding to the special case $v_f = 0$), and therefore suffers from the same limitation of a short time of interaction between the solute and the front. The same is true of case (b). In case (c) there is incoming flux at the interface from both upstream and downstream domains. In the absence of substantial diffusion, mass conservation would require that the concentration continually increase within a thin layer at the interface. Eventually, the entire solute content would be trapped within the boundary layer, and would elute in a very sharp peak as the front reaches the exit. Ultimately, however, diffusion becomes important enough to limit this progression, and a steady state is reached. A key quantity at



$\Rightarrow$ denotes solute motion relative to front

Figure 2. Principle of dynamic separations using a moving front.

When the front moves with a velocity that is intermediate to the upstream (high) and the downstream (low) values, there is progressive accumulation of the solute at the moving boundary.

the steady state is the characteristic width δ of the concentration distribution. This quantity describes the extent to which the peak can be focused by the moving front.

One might conceive of several types of materials that would be candidates for a tunable medium. Liquid crystals (LCs), for example, are composed of molecules that tend to align spontaneously, forming phases that display anisotropic transport properties. Moreover, on the application of an external field such as a voltage gradient, the molecules switch their direction of alignment to one that is parallel to that of the applied field (de Gennes and Prost, 1993). An externally controlled front can be created with such materials as follows (see Figure 3). Imagine a horizontal capillary filled with a liquid crystalline material such that the spontaneous molecular alignment is parallel to the longitudinal axis of the tube. The capillary is lined along its outer surface with a number of electrodes that can create a transverse voltage gradient within the column. If the electrodes along the right half of the column were switched on while those on the other half were kept off, the molecules in the right half would align perpendicular to the capillary axis, whereas those on the left half would continue to remain parallel to the axis, thus creating a front halfway through the column. By controlling which electrodes go off and which remain on over a period of time, the location of the front could be externally controlled. Alternatively, one might consider materials that respond to other types of external stimuli, such as magnetic fields or light. For example, Ikeda and Tsutsumi (1995) have recently reported azobenzene-based polymeric liquid crystals that switch between an isotropic and a molecularly ordered phase when subjected to a laser pulse with a response time of 200 μ s.

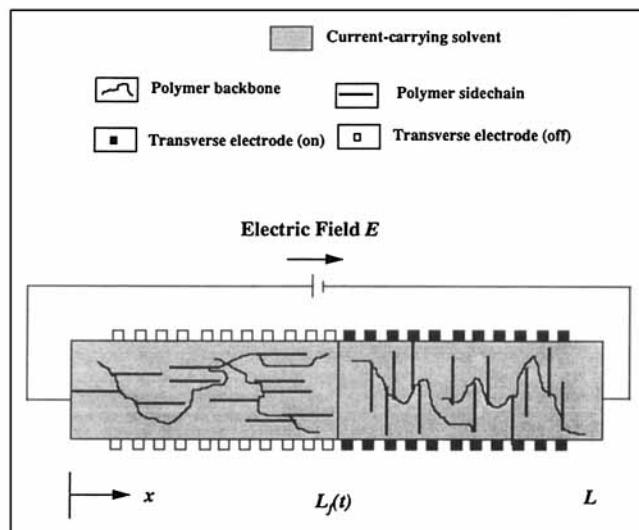


Figure 3. Hypothetical tunable electrophoretic device using liquid crystal polymer.

In addition to the axial DC electric field, the column contains a series of transverse electrode pairs (TEPs). The polymer side chains orient themselves along the axis of the column in the absence of a transverse field, but switch to a perpendicular orientation when the TEPs are turned on. Initially, all the TEPs are turned off. A front can be created at a desired location by turning on all the TEPs downstream of that location. The front can be moved downstream (upstream) by turning the nearest downstream (upstream) TEP off (on).

The specific purpose of this study is to derive a perturbation approximation for the problem of a front that moves with a velocity intermediate between the solute velocities in the upstream and downstream domains (case c). Real materials generally do not exhibit a discontinuous change in transport properties; rather, these properties vary continuously over a small but finite length scale $\epsilon_f L$. We therefore consider both the case of a discontinuous transition and the case of a smooth variation between upstream and downstream values of D and v .

Mathematical Formulation

Transport equations and boundary conditions

The general equation governing one-dimensional convective-diffusive transport of a solute present at dilute concentrations through an electrophoretic column is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D(x, t) \frac{\partial c}{\partial x} \right] - \frac{\partial}{\partial x} [v(x, t)c], \quad (3)$$

where c denotes the concentration of solute, x denotes the axial coordinate measured relative to a space-fixed origin, and t denotes time. We will use superscript $i = I$ for the left (upstream) region ($x < L_f$), where $D = D^I$ and $v = v^I$, and $i = II$ for the righthand (downstream) domain ($L_f < x$), where $D = D^{II}$ and $v = v^{II}$. The line of demarcation between the upstream and downstream domains—the front—moves with a uniform velocity v_f . Thus the location of the front at any time t is given by

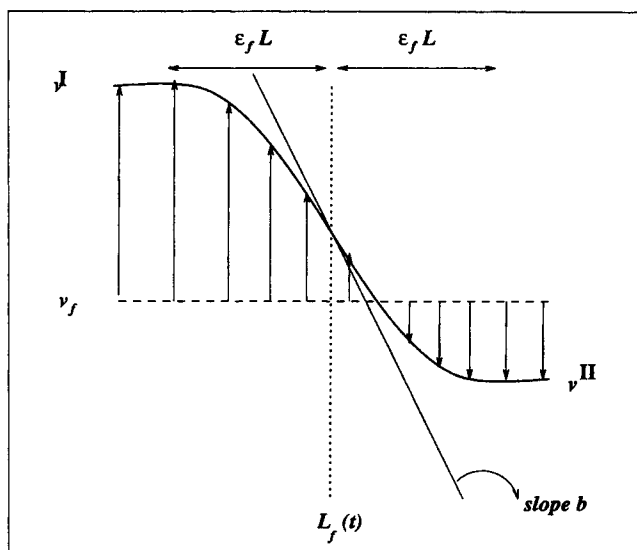


Figure 4. Finite-width front of width $2\epsilon_f L$.

The vertical line defines the "front" and the horizontal line denotes its velocity. The upward arrows indicate a positive value, while the downward arrows indicate a negative value for the velocity of the solute relative to the front.

$$L_f(t) = L_{f_0} + v_f t, \quad (4)$$

where L_{f_0} is the initial position of the front. The case of a stationary front (Locke and Arce, 1993; Locke et al., 1993; Vaidya et al., 1996a) is recovered by setting $v_f = 0$.

The "location" of a singular front is unambiguous, and the definition of L_f is therefore clear in this case. For the case of a continuous transition, it is appropriate to locate L_f at the midpoint of the transition zone as shown in Figure 4. If the velocity of the front is chosen as the arithmetic mean between the upstream and downstream values, this location also corresponds to the point where the velocity of the solute relative to the front vanishes. This is not true, however, for any other choice of v_f .

$$D(x,t) = \begin{cases} D^I, & x < L_f(t) - \epsilon_f L, \\ D^{II}, & x > L_f(t) + \epsilon_f L, \\ D^{II} + (D^I - D^{II}) \cos^2[\theta(x,t)], & L_f(t) - \epsilon_f L < x < L_f(t) + \epsilon_f L. \end{cases} \quad (13)$$

We assume that at time $t = 0$ the column contains a prescribed initial distribution of the solute $F(x)$. At all positive times, there is no solute flux entering the column from upstream. The section of the column beyond $x = L$ is both infinite in length and well-mixed, so that Danckwerts' boundary conditions hold (Danckwerts, 1953; Brenner, 1962; Novy et al., 1990). Therefore,

$$c(x,0) = F(x), \quad (5)$$

$$-D^I \frac{\partial c(0,t)}{\partial x} + v^I c(0,t) = 0, \quad t > 0, \quad (6)$$

$$\frac{\partial c(L,t)}{\partial x} = 0, \quad t > 0. \quad (7)$$

We will be working with the small parameter $\epsilon = 1/Pe$, and we introduce the coordinate $x - L_f(t)$ giving position relative to the moving front. We then cast Eqs. 3-7 in the dimensionless form

$$\frac{\partial c}{\partial \tau} = \epsilon \frac{\partial}{\partial \xi} \left[\phi(\xi) \frac{\partial c}{\partial \xi} \right] - \frac{\partial}{\partial \xi} [\mu(\xi) c], \quad (8)$$

$$c(\xi,0) = f(\xi), \quad (9)$$

$$-\epsilon \phi(\xi_1) \frac{\partial c(\xi_1, \tau)}{\partial \xi} + \mu(\xi_1) c(\xi_1, \tau) = 0, \quad (10)$$

$$\frac{\partial c(\xi_2, \tau)}{\partial \xi} = 0, \quad (11)$$

where

$$\begin{aligned} \tau &= \frac{t \bar{v}}{L}, & \xi &= \frac{x - L_f(t)}{L}; \\ Pe &= \frac{\bar{v} L}{D}, & \epsilon &= \frac{1}{Pe}, \\ \phi &= \frac{D}{\bar{D}}, & \mu &= \frac{v - v_f}{\bar{v}}; \\ \omega_f &= \frac{v_f}{\bar{v}}, & \xi_{f_0} &= \frac{L_{f_0}}{L}. \end{aligned} \quad (12)$$

The quantities $\bar{D}$ and $\bar{v}$ represent characteristic values for the diffusivity and velocity, respectively (e.g., $\bar{D} = D^I$, and $\bar{v} = v^I$). Also, $\xi_1 = -\xi_{f_0} - \omega_f \tau$ and $\xi_2 = 1 - \xi_{f_0} - \omega_f \tau$.

Modeling of the finite-width front

The front is represented by the following specification of the solute diffusivity as a function of position and time

Note that D^I and D^{II} can be interpreted as the diagonal components of the diffusivity tensor with respect to a coordinate system fixed with an LC particle. The dependence of the axial component of the diffusivity tensor on the orientation angle θ follows from the coordinate transformation associated with the rotation of the particle (cf. de Gennes and Prost, 1993). The preceding equation is exact for monomeric LC materials where $\theta(x,t)$ refers to the average orientation of the LC molecules with respect to the axis of the column. The expression is a qualitative description for a polymeric medium where $\theta(x,t)$ refers to the average orientation of the side chains. The value $\theta = 0$ describes the upstream mode, while

$\theta = \pi/2$ refers to the downstream mode. The variation of velocity is given by an analogous formula with v^I and v^{II} as the upstream and downstream values, respectively. The orientation distribution in the transition zone is approximated by the arbitrary but reasonable functional form

$$\theta(x, t) = \frac{\pi}{2}(3\eta^2 - 2\eta^3) \quad (14)$$

where η is given by

$$\eta = \frac{x - L_f(t) + \epsilon_f L}{2\epsilon_f L}, \quad (15)$$

which ensures that the solute diffusivity within the transition zone reaches its upstream and downstream values with zero slope. This smoothness condition at the beginning and end of the transition zone is imposed to maintain stability of the numerical scheme used in evaluating the exact solution. Note that any other sigmoidal variation satisfying the zero slope condition could also be used. The effect of assuming the drastically simpler linear transition zone is discussed later in the article. Recasting the diffusivity variation in nondimensional variables defined in Eq. 12, we see that the dimensionless solute diffusivity varies as

$$\phi(\xi) = \begin{cases} \phi^I, & \xi_1 < \xi < -\epsilon_f, \\ \phi^{II}, & \epsilon_f < \xi < \xi_2, \\ \phi^{II} + (\phi^I - \phi^{II})\cos^2[\theta(\xi)], & -\epsilon_f < \xi < \epsilon_f, \end{cases} \quad (16)$$

where $\theta(\xi)$ is given by Eq. 14 with η rewritten as

$$\eta = \frac{\xi + \epsilon_f}{2\epsilon_f}. \quad (17)$$

The velocity variation $\mu(\xi)$ is given by an analogous equation. Thus the transition zone stretches from $\xi = -\epsilon_f$ to $\xi = \epsilon_f$.

Modified formulation for a singular front

The boundary layer in the solute concentration is not necessarily confined to the front *per se*. For $\epsilon_f \ll \epsilon$ the boundary layer will spill over into the region where the transport properties are constant. It is shown in the next section that when $\epsilon_f \ll \epsilon$, the steady-state thickness is given by $\delta = \epsilon$ and thus is independent of the actual width of the front. The finite width of the transition zone can therefore be neglected, and the variation of transport parameters can be treated as a discontinuity. The governing equations are written in terms of upstream and downstream concentration fields (c^I and c^{II} , respectively). The transport equation (Eq. 8) becomes

$$\frac{\partial c^i}{\partial \tau} = \epsilon \phi^i \frac{\partial^2 c^i}{\partial \xi^2} - \mu^i \frac{\partial c^i}{\partial \xi}, \quad i = I, II, \quad (18)$$

and the boundary conditions at the entrance and exit of the column can be written as

$$-\epsilon \phi^I \frac{\partial c^I}{\partial \xi}(\xi_1, \tau) + \mu^I c^I(\xi_1, \tau) = 0, \quad (19)$$

$$\frac{\partial c^{II}}{\partial \xi}(\xi_2, \tau) = 0. \quad (20)$$

In addition, we need to impose two auxiliary conditions expressing local equilibrium and continuity of flux at the front, namely

$$c^I(0, \tau) = K_{eq} c^{II}(0, \tau), \quad (21)$$

$$-\epsilon \phi^I \frac{\partial c^I}{\partial \xi}(0, \tau) + \mu^I c^I(0, \tau) = -\epsilon \phi^{II} \frac{\partial c^{II}}{\partial \xi}(0, \tau) + \mu^{II} c^{II}(0, \tau). \quad (22)$$

Details of the reduction of Eqs. 8–11 to 18–22 are provided in the Appendix.

Steady-State Width of Concentration Profile

Perturbation methods proceed by recognizing the difference between the correct dynamical length scales in regions near and far away from a boundary (cf. van Dyke, 1975). In the present problem, there is a nontrivial steady state brought about by the balance between convection and diffusion near the front. The correct dynamical length scale near the front is therefore the width of the concentration profile at the steady state. Let δ denote the appropriate dynamical length scale necessary to achieve the balance between convection and diffusion. Since for large Pe the solute accumulates tightly about the center of the front, the spatial variation of its diffusivity and relative velocity can be approximated by linear forms

$$\mu(\xi) = b\xi, \quad (23)$$

$$\phi(\xi) = \phi_0 + \hat{b}\xi, \quad (24)$$

where ϕ_0 is the value of the diffusivity at $\xi = 0$, b is the gradient of the relative velocity, and $\hat{b}$ the gradient of diffusivity at that point. Note that b is of order $1/\epsilon_f$ and can be written as μ_Δ/ϵ_f , where μ_Δ is a number of order unity. Likewise, $\hat{b}$ may be represented as ϕ_Δ/ϵ_f , where ϕ_Δ is a number of order unity. For the specific sigmoidal variation assumed in Eqs. 16 and 17, we have

$$\begin{aligned} \mu_\Delta &= -\frac{3\pi(\mu^I - \mu^{II})}{8}; \\ \phi_\Delta &= -\frac{3\pi(\phi^I - \phi^{II})}{8}. \end{aligned} \quad (25)$$

Since concentration variation near the front is expected to occur over the new characteristic length scale δ , we introduce a stretched coordinate $\zeta = \xi/\delta$. The steady-state equa-

tion written in terms of the stretched coordinate becomes at lowest order,

$$\frac{\mu_\Delta}{\epsilon_f} \frac{d}{d\zeta} [\zeta c_s] = \frac{\epsilon}{\delta^2} \frac{d}{d\zeta} \left[\left(\phi_0 + \frac{\phi_\Delta}{\epsilon_f} \delta \zeta \right) \frac{dc_s}{d\zeta} \right] \quad (26)$$

$$\approx \frac{\epsilon}{\delta^2} \phi_0 \frac{d^2 c_s}{d\zeta^2}, \quad (27)$$

where $c_s(\zeta)$ denotes the steady-state concentration profile. As will become clear in the following subsections, the magnitude of the length scale δ depends on the relative values of the two small parameters involved, viz., ϵ and ϵ_f . Two limiting cases are (1) a singular front, for which $\epsilon_f \ll \epsilon$, and (2) a finite-width front, for which $\epsilon_f \gg \epsilon$.

Singular front

In this case, there arise in turn two possibilities for the way the solute concentration may get distributed in the steady state: (i) the entire solute mass is contained in the transition zone, or (ii) the solute content spills and spreads outside the transition zone.

Consider case (i), where the solute accumulates in the transition zone of thickness (ϵ_f). According to Eq. 27, in order that the convection term balance the diffusion term, the dynamical length scale must be

$$\delta = \sqrt{\epsilon \epsilon_f}. \quad (28)$$

However, since $\epsilon \gg \epsilon_f$, this implies that $\delta \gg \epsilon_f$. In other words, the solute does not accumulate entirely in the transition zone. This is a contradiction to the premise of case (i) and must therefore be rejected.

Now consider case (ii). By spilling outside the transition zone, the solute does not sample the velocity gradient and therefore experiences the constant upstream velocity. Hence the steady-state transport equation at lowest order can be written as

$$\frac{\mu^I}{\delta} \frac{dc_s}{d\zeta} \approx \frac{\epsilon}{\delta^2} \phi_0 \frac{d^2 c_s}{d\zeta^2}. \quad (29)$$

This gives

$$\delta = \epsilon, \quad (30)$$

which is much greater than ϵ_f and is therefore consistent with the premise of case (ii). Therefore it is the correct choice for the steady-state thickness of the concentration boundary layer at a singular interface.

Finite-width front

For a finite-width interface, a similar analysis can be carried out bearing in mind that $\epsilon_f \gg \epsilon$. When the width of the transition zone is greater than the reciprocal of Pe , the solute does indeed accumulate within the transition zone. The dynamical length δ obtained from Eq. 28 is consistent with the previously mentioned assumptions and is therefore the correct choice for this case.

Concentration Profiles for a Singular Front

As noted in the previous section, the characteristic length scale over which concentration gradients occur near the front becomes independent of the actual thickness of the transition zone. The analysis therefore reduces to one in which there is only one small parameter (viz., ϵ), and can therefore be formulated within the framework similar to that in Vaidya et al. (1996a). We thus proceed by dividing the domain of transport into two subdomains, depending on the relative importance of the diffusional term. In the following sections, we outline the methodology of deriving perturbation approximations to the concentration profile. Most algebraic details of derivation have been omitted here for conciseness but can be found in Vaidya (1996).

Outer solution

For large Pe , diffusional effects are negligible away from the interface. Here the solute never samples the gradient in μ and ϕ , and its concentration never increases drastically. Hence in the outer region the solution may be expanded in a regular perturbation series

$$c^{i,out}(\xi, \tau) = c_0^{i,out}(\xi, \tau) + \epsilon c_1^{i,out}(\xi, \tau) + \mathcal{O}(\epsilon^2) + \dots \quad (31)$$

We can express the given arbitrary initial distribution as

$$f^i(\xi) \equiv F[x(\xi)] = f_0^i(\xi) + \epsilon f_1^i(\xi) + \mathcal{O}(\epsilon^2) + \dots \quad (32)$$

The perturbation series for $c^{i,out}(\xi, \tau)$ is substituted in Eq. 18, and on comparing zeroth- and first-order quantities on both sides of the equation, we obtain simplified partial differential equations for successive terms. Each of these equations is solved subject to the initial condition by equating each term of the series $c^{i,out}(\xi, \tau)$ with its corresponding term in the series for $f^i(\xi)$.

Inner solution

In the region near the interface, concentration changes are expected to occur over distances of order ϵ . To resolve this boundary-layer structure, we introduce the stretched coordinate $\zeta = \xi/\epsilon$, in terms of which Eq. 18 becomes

$$\epsilon \frac{\partial c^i}{\partial \tau} = \phi^i \frac{\partial^2 c^i}{\partial \zeta^2} - \mu^i \frac{\partial c^i}{\partial \zeta}. \quad (33)$$

Note that, $\mu^I > 0$ and $\mu^{II} < 0$, and the resultant incoming convective flux from both upstream and downstream domains leads to successive accumulation of solute at the interface. In order for the area under the concentration curve (representing the total mass of solute) to remain unchanged, the leading term of the inner solution must be of order ϵ^{-1} . Therefore, the inner solution takes the form:

$$c^{i,in}(\zeta, \tau) = \frac{1}{\epsilon} c_{-1}^{i,in}(\zeta, \tau) + c_0^{i,in}(\zeta, \tau) + \epsilon c_1^{i,in}(\zeta, \tau) + \mathcal{O}(\epsilon^2) + \dots \quad (34)$$

Collecting terms of order ϵ^{-1} and ϵ^0 , we obtain the successive differential equations for each term in the inner expansion. The form of the inner expansion (Eq. 34) is substituted in the auxiliary conditions of fast equilibrium and continuity of flux expressed by Eqs. 21 and 22, and terms of like order in ϵ are equated. The resultant set of equalities (two for each order of ϵ) provide the boundary conditions necessary to solve each of the successive partial differential equations for the inner expansion.

The general solutions of the preceding equations, subject at most to the requirements of algebraic divergence as $\zeta \rightarrow \pm\infty$, are

$$c_{-1}^{i,\text{in}}(\zeta, \tau) = q^i(\tau) + r^i(\tau) \exp(\nu^i \zeta), \quad (35)$$

$$c_0^{i,\text{in}}(\zeta, \tau) = - \left[\frac{\dot{q}^i(\tau)}{\mu^i} \right] \left(\zeta + \frac{1}{\nu^i} \right) + \dot{r}^i(\tau) \zeta \exp(\nu^i \zeta) - \frac{p^i(\tau)}{\nu^i} + m^i(\tau) \exp(\nu^i \zeta), \quad (36)$$

$$c_1^{i,\text{in}}(\zeta, \tau) = \left(\frac{1}{\mu^i} \right) \left[\frac{\ddot{q}^i(\tau)}{2\mu^i} \left(\frac{1}{\nu^i} \left(\zeta + \frac{1}{\nu^i} \right)^2 + \frac{2}{\nu^i} \left(\zeta + \frac{2}{\nu^i} \right) \right) + \frac{\ddot{r}^i(\tau)}{\mu^i} \left(\zeta - \frac{1}{\nu^i} \right)^2 \exp(\nu^i \zeta) + \frac{\dot{p}^i(\tau)}{\nu^i} \left(\zeta + \frac{1}{\nu^i} \right) + \dot{m}^i(\tau) \zeta \exp(\nu^i \zeta) \right] - \frac{\dot{n}^i(\tau)}{\nu^i} + k^i(\tau) \exp(\nu^i \zeta). \quad (37)$$

Here $k^i(\tau)$, $m^i(\tau)$, $n^i(\tau)$, $p^i(\tau)$, $q^i(\tau)$, and $r^i(\tau)$ represent as yet unknown functions of time τ ; the single dot and double dots, respectively, denote the first and second derivatives with respect to the argument τ ; and $\nu^i = \mu^i/\phi^i$.

Matching of inner and outer solutions

The perturbation analysis is completed by matching the outer and inner solutions to the left and right of the interface. Thus, in the dual limit as $\zeta \rightarrow \pm\infty$, and $\xi \rightarrow 0$ we must have

$$\epsilon^{-1} c_{-1}^{i,\text{in}} + c_0^{i,\text{in}} + \epsilon c_1^{i,\text{in}} + \dots \rightarrow \epsilon^{-1}(0) + c_0^{i,\text{out}} + \epsilon c_1^{i,\text{out}} + \dots. \quad (38)$$

The inner expansion through first order in ϵ varies as

$$\frac{1}{\epsilon} c_{-1}^{i,\text{in}} + c_0^{i,\text{in}} + \epsilon c_1^{i,\text{in}} \sim \frac{1}{\epsilon} q^i(\tau) - \frac{p^i(\tau)}{\nu^i} + \epsilon \left[\frac{\ddot{p}^i(\tau)}{\mu^i \nu^i} \zeta - \frac{n^i(\tau)}{\nu^i} + \frac{\ddot{q}^i(\tau)}{2(\mu^i)^2} \zeta^2 + \frac{\ddot{q}^i(\tau)}{2\nu^i(\mu^i)^2} \zeta \right] \quad (39)$$

in the limit $\zeta \rightarrow \pm\infty$. This behavior is reproduced by the outer solution, $c_0^{i,\text{out}} + \epsilon c_1^{i,\text{out}}$, as can be seen from its Taylor expansion

$$c_0^{i,\text{out}} + \epsilon c_1^{i,\text{out}} \sim c_0^{i,\text{out}}(0, \tau) + \left[\frac{\partial c_0^{i,\text{out}}}{\partial \xi} \right]_{\xi=0} \xi + \epsilon c_1^{i,\text{out}}(0, \tau), \quad (40)$$

valid near $\zeta = 0$. Noting that $\zeta = \xi/\epsilon$, and matching quantities of like order in ϵ in the preceding equation, we find that

$$q^i(\tau) = 0, \quad (41)$$

$$\dot{q}^i(\tau) = 0, \quad (42)$$

$$p^i(\tau) = -\nu^i c_0^{i,\text{out}}(0, \tau), \quad (43)$$

$$\dot{p}^i(\tau) = \nu^i \mu^i \left[\frac{\partial c_0^{i,\text{out}}}{\partial \xi} \right]_{\xi=0}, \quad (44)$$

$$\dot{n}^i(\tau) = -\nu^i c_1^{i,\text{out}}(0, \tau). \quad (45)$$

The remaining boundary conditions that determine the inner solution are furnished by the auxiliary conditions at the interface $\zeta = 0$. Implementing the condition of rapid equilibrium term by term in ϵ gives

$$r^I(\tau) = K_{\text{eq}} r^{II}(\tau), \quad (46)$$

$$-\frac{p^I(\tau)}{\nu^I} + m^I(\tau) = K_{\text{eq}} \left[-\frac{p^{II}(\tau)}{\nu^{II}} + m^{II}(\tau) \right], \quad (47)$$

$$\begin{aligned} & \frac{\ddot{r}^I(\tau)}{(\mu^I \nu^I)^2} + \frac{\dot{p}^I(\tau)}{\mu^I (\nu^I)^2} - \frac{\dot{n}^I(\tau)}{\nu^{II}} + k^I(\tau) \\ &= K_{\text{eq}} \left[\frac{\ddot{r}^{II}(\tau)}{(\mu^{II} \nu^{II})^2} + \frac{\dot{p}^{II}(\tau)}{\mu^{II} (\nu^{II})^2} - \frac{\dot{n}^{II}(\tau)}{\nu^{II}} + k^{II}(\tau) \right]. \end{aligned} \quad (48)$$

Continuity of flux for the leading-order term is automatically satisfied. The condition of continuity of flux for the zeroth- and first-order terms gives

$$\mu^I c_0^{I,\text{out}}(0, \tau) - \mu^{II} c_0^{II,\text{out}}(0, \tau) = \frac{\dot{r}^I(\tau)}{\nu^I} - \frac{\dot{r}^{II}(\tau)}{\nu^{II}}, \quad (49)$$

$$\begin{aligned} & -\frac{\ddot{r}^I(\tau)}{(\mu^I \nu^I)^2} + \frac{\dot{m}^I(\tau)}{\nu^I} + \phi^I n^I(\tau) \\ &= -\frac{\ddot{r}^{II}(\tau)}{(\mu^{II} \nu^{II})^2} + \frac{\dot{m}^{II}(\tau)}{\nu^{II}} + \phi^{II} n^{II}(\tau). \end{aligned} \quad (50)$$

Simultaneous solutions to Eqs. 46–50 using Eqs. 41–45 yield

$$\begin{aligned} r^{II}(\tau) &= r^{II}(0) + \left[\frac{K_{\text{eq}}}{\nu^I} - \frac{1}{\nu^{II}} \right]^{-1} \\ &\times \left[\mu^I \int_0^\tau c_0^{I,\text{out}}(0, s) ds - \mu^{II} \int_0^\tau c_0^{II,\text{out}}(0, s) ds \right], \end{aligned} \quad (51)$$

$$m^{II}(\tau) = m^{II}(0) + \left[\frac{K_{eq}}{\nu^I} - \frac{1}{\nu^{II}} \right]^{-1} \times \left[c_0^{I,out}(0,\tau) - K_{eq} c_0^{II,out}(0,\tau) + \frac{\dot{r}^I(\tau)}{\mu^I(\nu^I)^2} - \frac{\dot{r}^{II}(\tau)}{\mu^{II}(\nu^{II})^2} + \mu^{II} \int_0^\tau c_1^{II,out}(0,s) ds - \mu^I \int_0^\tau c_1^{I,out}(0,s) ds \right], \quad (52)$$

$$n^{II}(\tau) = n^{II}(0) - \nu^{II} \int_0^\tau c_1^{II,out}(0,s) ds, \quad (53)$$

$$r^I(\tau) = K_{eq} r^{II}(\tau), \quad (54)$$

$$m^I(\tau) = K_{eq} m^{II}(\tau) + K_{eq} c_0^{II,out}(0,\tau) - c_0^{I,out}(0,\tau), \quad (55)$$

$$n^I(\tau) = n^I(0) - \nu^I \int_0^\tau c_1^{I,out}(0,s) ds. \quad (56)$$

Equation 49 is the equivalent of the *jump mass balance condition* for a singular interface when there is accumulation near the front in the presence of small diffusional effects. The terms $r^i(\tau)$ and $n^i(\tau)$ represent the zeroth- and first-order concentration at the interface at a given instant in time τ . Hence, $r^i(0)$ and $n^i(0)$ are specified by the initial concentration distribution.

Note that $r^i(\tau)$, which appears in the inner solution of order ϵ^{-1} , cannot be evaluated until the outer solution is resolved through zeroth (ϵ^0) order (see Eq. 49). Similarly, $m^i(\tau)$, which appears in the inner solution for order ϵ^0 term, can only be determined after resolving the equations of first order. This is in contrast to the case for a stationary front (Vaidya et al., 1996a), where terms of a particular order in ϵ are fully determined from outer and inner equations at the same order. For large Péclet numbers, it is adequate to truncate the inner expansion after terms of order ϵ^0 . Hence explicit determination $k^i(\tau)$ has not been attempted and $c_1^{i,in}$ has therefore not been evaluated in the present analysis.

Concentration profiles

The outer concentration variation can be solved by the method of characteristics (Carrier and Pearson, 1976; Locke and Carbonell, 1989) to yield

$$c_0^{i,out}(\xi, \tau) = f_0^i(\xi - \mu^I \tau), \quad (57)$$

$$c_1^{i,out}(\xi, \tau) = \phi^i \tau \dot{f}_0^i(\xi - \mu^I \tau) + f_1^i(\xi - \mu^I \tau). \quad (58)$$

The inner solution is obtained by substitution of these expressions for the outer solution into Eqs. 41–45 and Eqs. 51–56. The complete concentration profile is obtained by evaluating the composite solution:

$$c^i(\xi, \tau) = c^{i,out}(\xi, \tau) + c^{i,in}(\xi, \tau) - c^{i,match}(\xi, \tau) \quad (59)$$

where $c^{i,match}$ represents the limiting behavior of the concentration distribution in the transition from the inner to the outer region and is given by

$$c^{i,match}(\xi, \tau) = \lim_{\xi \rightarrow 0} c^{i,out}(\xi, \tau) = c_0^{i,out}(0, \tau) + \left[\frac{\partial c_0^{i,out}}{\partial \xi} \right]_{\xi=0} \xi + \epsilon c_1^{i,out}(0, \tau). \quad (60)$$

Concentration Profiles for a Finite-width Front

The case of $\epsilon \ll \epsilon_f \ll 1$ is considered next. In this case, the width of the steady-state concentration profile depends on both small parameters ϵ and ϵ_f . The formulation of a systematic perturbation expansion incorporating the two small parameters is problematic. In the present article, we restrict ourselves to deriving only the leading approximation to the concentration profile. This is not entirely unreasonable since, despite the square-root scaling of the steady-state width of the concentration profile with Pe , for the large values of Pe of interest the next correction term would be more than an order of magnitude smaller. In the case of a finite-width front, we must incorporate some detail about the transition zone, as it is no longer infinitesimally thin and its character does influence the evolution of the concentration profile. Nevertheless, its thinness (compared to unity) does permit us to treat it in a simple fashion. Thus we ignore the fine detail of its structure (which is practically unknowable in real applications anyway), and consider only the slope of the variation of the transport properties.

We again must consider “outer” and “inner” solutions, but in the present context they will have unusual connotations. Essentially, the approximate solution can be derived by viewing the solute transport process in terms of a succession of events enumerated below. We shall consider the general case in which the front is placed a fair distance ($> \epsilon_f$) away from the peak in the initial concentration distribution, so that the solute experiences the presence of the front only after catching up to it over a finite time interval. Transport occurs as follows (see Figure 5):

1. (Time interval defined as $0 < \tau < \tau_1$.) The initial concentration distribution evolves in the absence of diffusion. The concentration profile is convected to a point where it is partially or entirely within the width of the front. The negative gradient in the velocity within the front begins to narrow the concentration distribution.

2. (Time interval defined as $\tau_1 < \tau < \tau_0$.) Peak sharpening continues, causing diffusion to become increasingly important. The concentration profile is not entirely within the front, or is not sufficiently sharp to permit the front to be modeled by a linear variation in transport properties.

3. (Time interval defined as $\tau_0 < \tau < \infty$.) The solute concentration peak is now sufficiently sharp that diffusion is important, and the velocity variation is well described by a linear form. Focusing continues until diffusion balances convection and a steady state is attained.

In the following sections, step 1 is termed the outer solution and step 3 the inner solution, while step 2 is the transition. Thus the outer and inner solutions are divided not only on the basis of spatial proximity to the front but also in terms of the time intervals over which each describes the concentration profile. The inner and outer regions each exhibit simplifying features that make them amenable to analysis. The

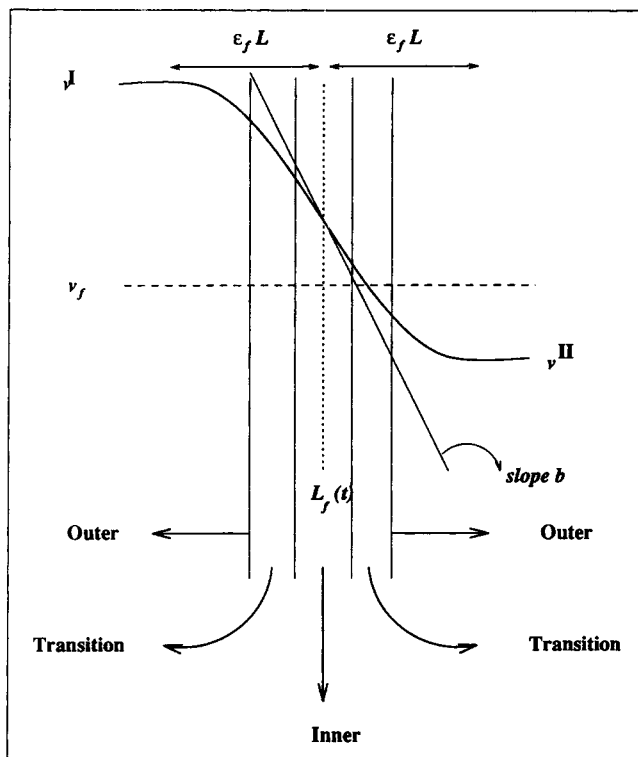


Figure 5. Definition of the “outer” and “inner” region for a finite-width front, with the transition region in between.

transition (step 2) does not. In this regime, the smallness of ϵ is not useful because peak sharpening is making diffusion important, while the smallness of ϵ_f is not yet helpful because the concentration profile is not sufficiently concentrated within the front. We treat step 2 as an extension of the outer solution. Our approach thus in principle shows errors in the concentration profiles at intermediate times. However, we are able to minimize these errors by proper selection of the transition time between the inner and outer solutions. The treatment nevertheless yields the correct steady-state distribution, which is important for practical applications.

Outer solution

To resolve the concentration profile at lowest order the transport equation is reduced to

$$\frac{\partial c}{\partial \tau} = -\frac{\partial}{\partial \xi} [\mu(\xi)c] \quad (61)$$

by neglecting diffusion. This equation is solved numerically by the method of characteristics. Note that if the front is located appreciably far away from the initial solute peak (say a distance $> 2\sigma_0 + \epsilon_f$ from the mean position for an initial Gaussian distribution of standard deviation σ_0), the solute experiences convection under a constant velocity μ^I for a certain interval of time τ_r .

Transition from outer to inner solution

Here sufficient time τ_l has evolved so that some of the solute content is in the linear part of the velocity profile,

$$\mu(\xi) \sim b\xi, \quad (62)$$

and the magnitude of diffusion is still negligible in comparison with convection. The subsequent evolution of concentration is governed by the equation

$$\frac{\partial c}{\partial \tau} = -\frac{\partial}{\partial \xi} [b\xi c], \quad (63)$$

subject to the condition that

$$c(\xi, \tau_l) = \varphi_0(\xi, \tau_l), \quad (64)$$

where $\varphi_0(\xi, \tau_l)$ is the solution to Eq. 61 at $\tau = \tau_l$. The evolution of solute concentration in the linear regime is given by

$$c \sim \varphi(\eta_1) \exp[-b(\tau - \tau_l)], \quad (65)$$

where

$$\eta_1 = \xi \exp[-b(\tau - \tau_l)]. \quad (66)$$

For diffusion to be insignificant compared to convection, we must have

$$\left| \epsilon \frac{\partial^2 c}{\partial \xi^2} \right| \ll \left| \frac{\partial}{\partial \xi} [b\xi c] \right|, \quad (67)$$

from which it follows that

$$\frac{1}{\sigma_0^2} \left(\frac{\epsilon}{-b} \right) \exp[-b(\tau - \tau_l)] \ll 1. \quad (68)$$

This suggests a logarithmic time scale, and hence we introduce a modified time variable defined as

$$\Gamma = \frac{1}{\sigma_0^2} \left(\frac{\epsilon}{-b} \right) \exp[-b(\tau - \tau_r)]. \quad (69)$$

(The significance of choosing a slightly different time scale of the form

$$\Gamma = \frac{1}{\sigma_0^2} \left(\frac{\epsilon}{-b} \right) \exp[-kb(\tau - \tau_r)], \quad (70)$$

where k is a real number not necessarily equal to 1, is addressed in the “Results and Discussion” section.) Note that the interval τ_r , preceding the exponential rise in concentration, has been subtracted in the modified time scale.

We expect diffusion to be negligible for times τ for which $\Gamma \ll 1$. For time scales Γ much greater than unity, one needs to take into account the contribution of diffusion. This is obtained by evaluating the inner solution.

Inner solution

In this region, concentration gradients occur over the much smaller length scale $\delta = \sqrt{\epsilon \epsilon_f}$, so that diffusion can no longer be neglected. In addition to the new time scale Γ , we also introduce the stretched spatial coordinate, $\zeta = \xi/\delta$. The concentration distribution can then be empirically written as

$$c^{\text{in}}(\zeta, \tau) = \frac{1}{\delta} c_{-1}^{\text{in}}(\zeta, \tau) + \mathcal{O}(1). \quad (71)$$

Additionally, the solute has piled up sufficiently close to the front, so that the velocity profile is effectively linear. The convection-diffusion equation (Eq. 8) for the leading-order term of the approximate solution can be rewritten as

$$\Gamma \frac{\partial c_{-1}^{\text{in}}}{\partial \Gamma} = \frac{\partial(\zeta c_{-1}^{\text{in}})}{\partial \zeta} + \frac{1}{\nu_\Delta} \frac{\partial^2 c_{-1}^{\text{in}}}{\partial \zeta^2}, \quad (72)$$

where $\nu_\Delta = (-\mu_\Delta)/\phi_0$. This equation must be solved subject to the condition that

$$c_{-1}^{\text{in}}(\zeta, \Gamma_0) = \psi[\xi(\zeta), \tau_0(\Gamma_0)], \quad (73)$$

where $\psi(\xi, \tau_0)$ is the solution to Eq. 61 at time $\tau = \tau_0$, which corresponds to the value

$$\Gamma_0 = \frac{1}{\sigma_0^2} \left(-\frac{\epsilon}{-b} \right) \exp[-b(\tau_0 - \tau_r)]. \quad (74)$$

All terms in Eq. 72 are of order unity. This equation can be therefore easily integrated numerically using a central difference scheme. Alternatively, it can be cast in the form of the well-known equation of Orstein-Uhlenbeck describing motion of a harmonically bound Brownian particle (Uhlenbeck and Orstein, 1930) after introducing the modified variables

$$\Sigma = \ln(\Gamma/\Gamma_0), \quad (75)$$

$$\Lambda = \zeta \sqrt{\nu_\Delta}. \quad (76)$$

The solution to the resultant equation can be obtained by the method of Green's functions (see, e.g., Weiss and Gitterman, 1995) as

$$c_{-1}^{\text{in}}(\Lambda, \Sigma) = \int_{-\infty}^{\infty} G(\Lambda, \Sigma, \Lambda_0) \Phi(\Lambda_0) d\Lambda_0, \quad (77)$$

where

$$G(\Lambda, \Sigma, \Lambda_0) =$$

$$\frac{1}{\sqrt{2\pi[1 - \exp(-2\Sigma)]}} \exp \left\{ -\frac{[\Lambda - \Lambda_0 \exp(-\Sigma)]^2}{2[1 - \exp(-2\Sigma)]} \right\}. \quad (78)$$

Thus, the steady-state profile in terms of the modified variables can be written as

$$c_{-1}^{\text{in}}(\Lambda, \infty) \rightarrow \frac{1}{\sqrt{2\pi}} \exp \left\{ -\frac{\Lambda^2}{2} \right\}. \quad (79)$$

Changing it to variables fixed with the moving front, we get

$$c_s(\xi) \equiv c(\xi, \infty) \frac{1}{\delta} \sqrt{\frac{\nu_\Delta}{2\pi}} \exp \left\{ -\frac{\nu_\Delta \xi^2}{2\delta^2} \right\}. \quad (80)$$

Therefore the steady-state profile is a Gaussian distribution with standard deviation $\delta/\sqrt{\nu_\Delta}$ (or $\sqrt{\phi_0 \epsilon/b}$), and with the mean position located at the front. Note that this profile is independent of the initial distribution, depending only on the transport parameters, and is thus a characteristic of the solute. This fact is relevant in utilizing the solute focusing ability of a moving front for separation of the components of a binary mixture (Vaidya et al., 1996c).

Concentration profiles

Sigmoidal Front. Let the front be located at a point L_{f_0} at time $t = 0$ downstream of the entire initial solute distribution. We choose the upstream transport properties as the reference values, that is, $\bar{D} \equiv D^I$ and $\bar{v} \equiv v^I$, and define the following variables

$$\alpha = (D^{II}/D^I), \quad (81)$$

$$\beta_f = (v_f/v^I). \quad (82)$$

The parameter α quantifies the anisotropy of the medium for the solute and the parameter β_f represents the dimensionless velocity of the front relative to the reference value. For the purpose of illustration, we can assume α to also denote the ratio of solute velocity in the downstream domain to that in the upstream domain, that is, $\mu^i = \phi^i - \beta_f$. Note that this assumption does not restrict the validity of the proposed mathematical formulation. In situations where (v^{II}/v^I) does not equal (D^{II}/D^I) the velocity ratio has to be specified explicitly, but the procedure for determining the concentration profiles is exactly as illustrated here.

We know that the solute will accumulate in the form of a steady-state distribution at the front, as long as the front moves with a velocity v_f that is intermediate to the upstream and downstream values, v^I and v^{II} , respectively. (It has been found in Vaidya et al. (1996b) that when the front moves with the same velocity as the downstream (upstream) solute velocity, there is no accumulation of solute at long times. This is because in this situation the incoming convective flux from the downstream (upstream) domain vanishes. Thus there is no restoring force to balance the outgoing diffusional flux. Consequently, more and more solute spills over to the downstream (upstream) side and undergoes diffusional spreading. The peak height decreases and over a large period of time goes to zero.) The optimum value for the front velocity is the arithmetic mean of the upstream velocities, that is, $\beta_f = (1 + \alpha)/2$. Note that this fact was tacitly assumed in the theoretical analysis by assuming that the point where relative velocity of the solute vanishes is exactly halfway through the transition zone ($\xi = 0$) (see, e.g., Eq. 23).

In order to determine empirically the exact solution to the convection–diffusion problem for high- Pe solute transport (Eqs. 8, 12 and 13), the finite difference scheme QUICKEST (Leonard, 1979) was employed with a smooth transition between zones I and II (Eqs. 16 and 17). Accurate resolution of the concentration within the front ($\Delta\xi < \delta$) was accomplished with a mesh size $\Delta\xi$ of 5.0×10^{-5} for $Pe = 10^5$ and transition zone of half-width $\epsilon_f = 0.05$; the entire transition zone (of thickness $2\epsilon_f$) was thus discretized over 2,000 nodes. In order to save on the number of nodes needed to determine the concentration profiles, we employed a traveling grid covering only the region where the initial concentration profile is significant and moving with the same speed v_f as the front. For a Gaussian initial distribution, about 99.99% of the mass is included within four standard deviations ($4\sigma_0$) from the mean. We therefore chose a 4,000-node traveling grid spanning a length $L_x > 10\sigma_0$. The time step chosen was $\Delta\tau = 1.0 \times 10^{-6}$. The initial distribution of the solute was chosen to be a Gaussian with its mean location at $\xi_0 = x/L = 0.05$ and a dimensionless standard deviation $\sigma_0 = 0.007$. The initial location of the front was at $\xi_{f_0} = L_{f_0}/L = 0.175$, so as to ensure that the solute experiences convection at constant velocity for a nonnegligible interval of time. The parameter α was set to 0.5.

The asymptotic solution is determined by integrating Eq. 61 numerically along the characteristics using a fourth-order Runge-Kutta method. The time over which it is valid is obtained empirically by comparison with the exact finite difference solution. This interval $\tau_0 = 0.4$ is then translated to its corresponding value of Γ_0 on the logarithmic time scale. We check that the value of $\Gamma_0 = 0.8$ thus obtained is not too small or large compared to unity, as should be the case for the transition from the outer solution to the inner solution. The evolution of solute concentration after time Γ_0 is evaluated using Eq. 77. The initial distribution taken is the output of the asymptotic convection equation at time τ_0 . All concentration profiles preserve the area under the curve to within 0.1%.

Approximation as a Linear Ramp. It is interesting to compare the evolution of the outer concentration under a sigmoidal variation in transport properties with that of one under a perfectly linear variation. The smooth functional form assumed is not sacrosanct since, in real materials, the exact shape of the transition zone cannot be determined with certainty. A linear variation is analytically tractable and reveals the essential qualitative features of the solute transport process. Thus, we also study a velocity profile of the form

$$\mu(\xi) = \begin{cases} \mu^I, & \xi_1 < \xi < -\hat{\epsilon}_f, \\ \mu^{II}, & \hat{\epsilon}_f < \xi < \xi_2, \\ b\xi, & -\hat{\epsilon}_f < \xi < \hat{\epsilon}_f, \end{cases} \quad (83)$$

where $\xi = 0$ is the location of the midpoint of the transition zone (also the position where the relative velocity vanishes for a front velocity equal to the arithmetic mean of the upstream and downstream solute velocities) and b is the gradient of the relative velocity at $\xi = 0$. Note that we have assumed the same slope of the velocity variation at the front as that in the sigmoidal variation. This means that the thickness of the linear ramp has to be adjusted from ϵ_f to $\hat{\epsilon}_f$ in order to maintain the same maximum and minimum values for the

transport parameters. Let us assume that the initial location of the front is downstream of the initial concentration distribution $f(\xi)$. Let $\hat{c}^I(\xi, \tau)$ describe the approximation to the actual concentration profile upstream of the linear ramp, where the solute velocity relative to the front is constant, and $\hat{c}^r(\xi, \tau)$ represent the approximate concentration profile within the linear ramp. The governing equations for the leading order term (ignoring diffusion) then become

$$\frac{\partial \hat{c}^I}{\partial \tau} + \mu^I \frac{\partial \hat{c}^I}{\partial \xi} = 0, \quad -\infty < \xi < -\hat{\epsilon}_f, \quad (84)$$

$$\frac{\partial \hat{c}^r}{\partial \tau} + \frac{\partial}{\partial \xi} [b\xi \hat{c}^r] = 0, \quad -\hat{\epsilon}_f < \xi < \hat{\epsilon}_f. \quad (85)$$

Note that in the absence of diffusion, the solute peak reaches the front at $\xi = 0$ only at infinite time, hence the domain $\xi = [\hat{\epsilon}_f, \infty]$ need not be considered. The upstream concentration distribution $\hat{c}^I$ is solved subject to the initial concentration profile $f(\xi)$. The concentration variation $\hat{c}^r$ is solved subject to the condition that at the “corner” of the linear variation, the concentration profile should be continuous, that is, $\hat{c}^r(-\hat{\epsilon}_f, \tau) = \hat{c}^I(-\hat{\epsilon}_f, \tau)$. The solution is obtained by the method of characteristics as

$$\hat{c}^I = f(\eta_2), \quad (86)$$

$$\hat{c}^r = \left(\frac{-\epsilon_f}{\xi} \right) f(\eta_3), \quad (87)$$

where

$$\eta_2 = \xi - \mu^I \tau, \quad (88)$$

$$\eta_3 = -\hat{\epsilon}_f - \frac{\mu^I}{b} \ln \left(\frac{-\hat{\epsilon}_f}{\xi} \right) - \mu^I \tau. \quad (89)$$

Figure 6 shows the solutions for piecewise linear and smooth variations of the solute velocity, and thereby illustrates the variations in solute concentration that may arise owing to differences in the precise structure of the front.

Results and Discussion

Singular front

Unlike the case for smooth variation of D and v , where the peak in the solute concentration scales as $\epsilon^{-1/2}$ (Gitterman and Weiss, 1993, 1994), for a singular front it scales as ϵ^{-1} . This means that, for a discontinuous variation in transport properties, the solute can be focused extremely sharply by making Pe extremely large. The validity of the perturbation analysis was tested indirectly by deriving Eq. 49 via an integral balance not presented here. It is very difficult to get the exact solution by finite difference calculations for $Pe = 10^5$. This is because for the sake of the stability of the numerical scheme, the discontinuity of a singular interface must be approximated with a suitable sigmoidal ramp. If one were to assume $\epsilon_f = 10^{-6}$ (higher limit of the inequality $\epsilon_f \ll \epsilon$ required for a singular interface), we would require a mesh size $\Delta\xi = 10^{-7}$ to accurately resolve the structure of the bound-

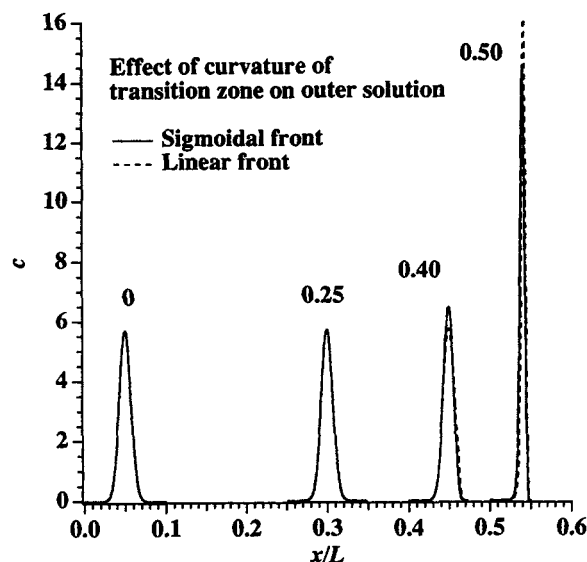


Figure 6. Effect of curvature of the front; comparison of solutions by sigmoidal and perfectly linear transition zone at $Pe = 10^5$.

any layer within thickness ϵ_f within 10 nodes. The resultant small time step $\Delta\tau$ would translate to a tremendous amount of cpu time.

Finite-width front

Figure 7 compares the concentration profiles approximated by the outer solution of the asymptotic theory with the finite-difference solution for two different values of Pe , viz., 10^4 and 10^5 , respectively. Some of the numerical parameters were modified for $Pe = 10^4$ as follows: $\Delta\xi = 1.0 \times 10^{-4}$, $\xi_0 = 0.20$, and $\xi_{f0} = 0.325$. The agreement is poorer for the lower Pe , thus identifying the practical limit of “large Pe ” below which the asymptotic analysis becomes very inaccurate. All subsequent calculations have therefore been based on the value for $Pe = 10^5$. The time interval τ_r is taken as the time required by the mean position of the concentration profile to reach the trailing edge of the sigmoidal ramp, that is,

$$\tau_r = \frac{\xi_{f0} - \epsilon_f - \xi_0}{\mu^1} \quad (90)$$

The gradient of the velocity at the front given by Eqs. 16 and 17 is $b = \mu_\Delta/\epsilon_f$. The dimensionless interval over which the velocity is roughly linear could therefore be taken as

$$\hat{\epsilon}_f = \frac{\epsilon_f}{[3\pi(\mu^1 - \mu^{11})/4]} \quad (91)$$

The time τ_0 at which the solute enters the linear regime (also taken as the time after which diffusion begins to become appreciable) can be estimated as the time it takes for the mean position to reach within a distance $\hat{\epsilon}_f$ of the front assuming constant convection, that is,

$$\xi_0 - \xi_{f0} + \mu^1(1 - \beta_f)\tau_0 = -\hat{\epsilon}_f \quad (92)$$

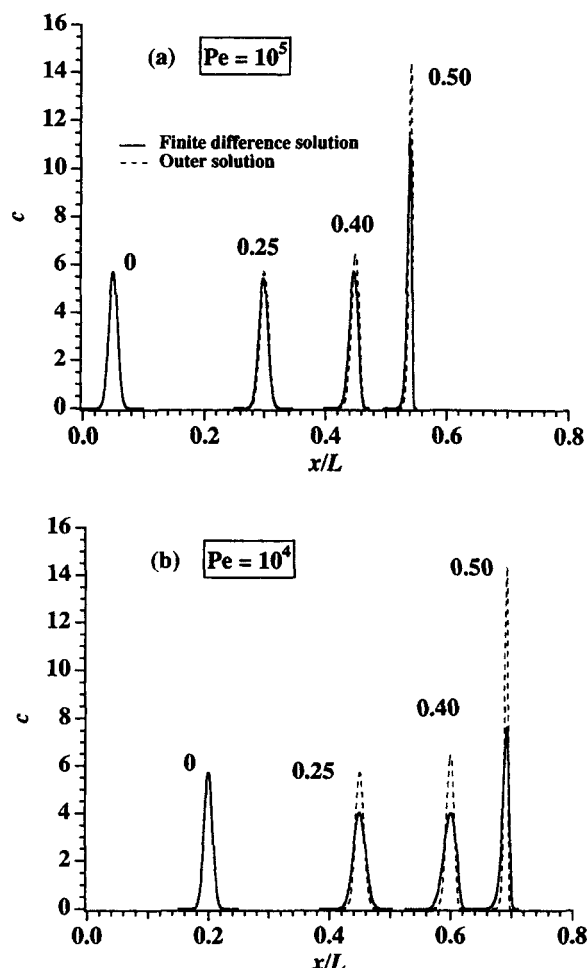


Figure 7. Comparison of convection without diffusion for a sigmoidal front with the finite difference solution for (a) $Pe = 10^5$ and (b) $Pe = 10^4$.

The times τ_r and τ_0 are estimated as 0.075 and 0.4, respectively. The time of switching over between the asymptotic solution neglecting diffusion and the convection-diffusion equation with linear velocity therefore is (Eq. 74) estimated empirically as $\Gamma_0 = 0.8$. As can be seen from Figure 8, this is the point where appreciable deviations from the asymptotic convection solution are beginning to occur. These deviations occur because the analog of the matching and composite solutions formulated for the singular-front problem—which serve to smooth out the transition between outer and inner solutions—are not obvious for this case. Instead, a sudden switch between the complementary formulations valid far away from and near the front has to be made. Once the switching time is determined in terms of the dimensionless group Γ_0 , with its dependence on ϵ and ϵ_f , we believe this criterion can be used for higher values of Pe and larger transition-zone thicknesses. The concentration profile for subsequent time has been determined on the basis of Eq. 77.

The perturbation approach is valid for small times and long times. It suffers from inaccuracies at intermediate intervals near the switching time Γ_0 . If time were to be modified as in Eq. 70, it would result in a modified convection-diffusion as follows:

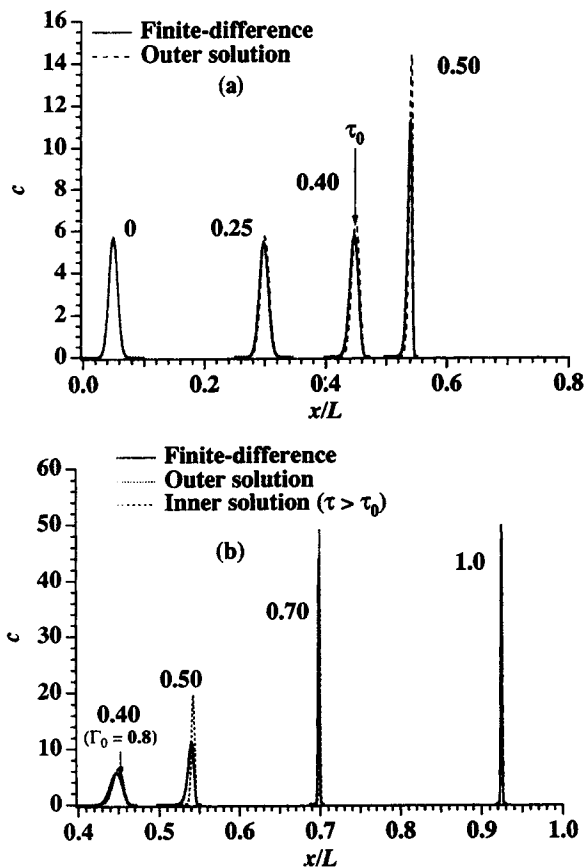


Figure 8. Comparison of asymptotic convection plus modified convection-diffusion with exact solution.

(a) Diffusion is ignored until time τ_0 (or Γ_0), after which (b) the solution is evaluated based on the Orstein-Uhlenbeck equation.

$$k\Gamma \frac{\partial c_{-1}^{\text{in}}}{\partial \Gamma} = \frac{\partial(\zeta c_{-1}^{\text{in}})}{\partial \zeta} + \frac{1}{\nu_\Delta} \frac{\partial^2 c_{-1}^{\text{in}}}{\partial \zeta^2}, \quad (93)$$

which is not fundamentally different from Eq. 72. This change may affect the inaccuracies at intermediate times, but will not affect the prediction of the steady-state concentration profile.

The effect of details of the structure of the front is illustrated in Figure 6, and is not great. From a practical viewpoint, it is easier to approximate the smooth variation in transport properties as piecewise linear variation because the solute concentration can be obtained analytically instead of numerically.

To obtain better quantitative agreement for smaller Pe , the next-order correction is needed. Unfortunately, since the problem involves two small parameters ϵ and ϵ_f , a form of the correction term is not obvious.

Concluding Remarks

Analytical solutions formulated for convection-diffusion phenomena with singular boundaries are not easily applied at Péclet numbers encountered in electrophoresis. Perturbation methods asymptotically valid at high Pe are available but they

are typically formulated for uninterrupted domains. A step toward incorporating near-interface dynamics in the presence of stationary internal boundaries using perturbation methods was taken by Vaidya et al. (1996a). The present article presents the perturbation solution for convection-diffusion with moving boundaries. The specific form of the variation of velocity and diffusion coefficient assumed gives rise to a well-defined steady state whereby the entire solute content accumulates in the boundary-layer region. Since the steady state is nontrivial, the transient perturbation solutions derived are valid at long times. The main conclusion of this work relating to practical application of focusing solutes within thin regions is that there are diminishing returns on increasing Pe for a fixed transition zone thickness ϵ_f , since the concentrating effect goes from a ϵ^{-1} dependence to a $\epsilon^{-1/2}$ dependence as $1/Pe$ becomes $\ll \epsilon_f$.

We intend to follow up this investigation with a theoretical study on how the focusing effect studied here can be exploited to enhance a separation process (Vaidya et al., 1997).

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Notation

E = electric-field strength, V/m
 F = initial concentration distribution, kg/m³
 f = initial concentration distribution, dimensionless
 K_{eq} = equilibrium constant, dimensionless
 L_f = location of interface from column entrance, m
 Γ = logarithmic time scale, dimensionless
 Λ = modified coordinate, dimensionless
 Σ = modified time scale, dimensionless
 η = coordinate in the transition zone, dimensionless
 ϵ = inverse Péclet number, dimensionless
 ϵ_f = half-width of transition zone, dimensionless
 ϕ = diffusion coefficient, dimensionless
 μ = velocity of solute relative to the front, dimensionless
 ξ = coordinate fixed at the front, dimensionless
 ζ = stretched coordinate, dimensionless

Subscripts

$\parallel$ = parallel (fast) mode
 $\perp$ = perpendicular (slow) mode
 match = matching solution

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Appendix

As shown in the subsection titled "Modified Formulations for a Singular Front," for the case where $\epsilon_f \ll \epsilon$, the actual thickness of the transition zone is not relevant in determining the width of the final concentration peak. Thus, the analysis can be simplified by formulating the problem in terms of a nonzero ϵ_f and extrapolating the results in the limit as $\epsilon_f \rightarrow 0$. In other words, a discontinuity is the limiting case of a linear ramp, as the width of the ramp goes to zero. To begin with, the velocity and diffusivity profiles may be written as

$$\mu(\xi) = \frac{\mu^I + \mu^{II}}{2} + \left(\frac{\mu^{II} - \mu^I}{2} \right) \frac{\xi}{\epsilon_f}, \quad (\text{A1})$$

$$\phi(\xi) = \frac{\phi^I + \phi^{II}}{2} + \left(\frac{\phi^{II} - \phi^I}{2} \right) \frac{\xi}{\epsilon_f}. \quad (\text{A2})$$

Integrating Eq. 8 over $[-\epsilon_f, \epsilon_f]$ we get

$$\begin{aligned} \frac{\partial}{\partial \tau} \int_{-\epsilon_f}^{\epsilon_f} c \, d\xi + \left[\left(\frac{\mu^I + \mu^{II}}{2} \right) + \left(\frac{\mu^{II} - \mu^I}{2} \right) \frac{\xi}{\epsilon_f} \right] c \Big|_{-\epsilon_f}^{\epsilon_f} \\ = \epsilon \left[\left(\frac{\phi^I + \phi^{II}}{2} \right) + \left(\frac{\phi^{II} - \phi^I}{2} \right) \frac{\xi}{\epsilon_f} \right] \frac{\partial c}{\partial \xi} \Big|_{-\epsilon_f}^{\epsilon_f}. \end{aligned} \quad (\text{A3})$$

The concentration has a well-defined one-sided derivative at $\xi = 0$. Thus, it may be expanded in a Taylor series around $\xi = 0$ to give

$$c(\xi, \tau) = c(0^-, \tau) + c'(0^-, \tau)\xi + c''(0^-, \tau)(\xi^2)/2 + \dots \quad (\xi < 0), \quad (\text{A4})$$

$$= c(0^+, \tau) + c'(0^+, \tau)\xi + c''(0^+, \tau)(\xi^2)/2 + \dots \quad (\xi > 0), \quad (\text{A5})$$

where the primes denote partial derivatives with respect to ξ . Splitting the interval of integration in Eq. A3 into $[-\epsilon_f, 0]$ and $[0, \epsilon_f]$ and substituting Eqs. A4 and A5 for the appropriate domain, we get

$$\begin{aligned} \dot{c}(0^-, \tau)(-\epsilon_f) + \dot{c}'(0^-, \tau)(-\epsilon_f)^2/2 + \dots \\ + \dot{c}(0^+, \tau)(\epsilon_f) + \dot{c}'(0^+, \tau)(\epsilon_f^2)/2 + \dots \\ + \mu^{II}c(\epsilon_f, \tau) - \mu^Ic(-\epsilon_f, \tau) \\ = \epsilon \left[\phi^{II} \frac{\partial c(\epsilon_f, \tau)}{\partial \xi} - \phi^I \frac{\partial c(-\epsilon_f, \tau)}{\partial \xi} \right], \end{aligned} \quad (\text{A6})$$

where the dot denotes the derivative with respect to time τ . On taking the limit as $\epsilon_f \rightarrow 0$ and rearranging we find that at $\xi = 0$,

$$-\epsilon \phi^I \frac{\partial c^I}{\partial \xi} + \mu^I c^I = -\epsilon \phi^{II} \frac{\partial c^{II}}{\partial \xi} + \mu^{II} c^{II}, \quad (\text{A7})$$

which is the statement of continuity of flux at a singular front. The reason why the concentration may not be continuous is because of a change in porosity. This condition relates the concentrations on either side of the front through an equilibrium constant, and that gives us our other auxiliary condition

$$c^I(0, \tau) = K_{eq} c^{II}(0, \tau). \quad (\text{A8})$$

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