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On the Two-Domain Equations for Gas Chromatography

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On the Two-Domain Equations for Gas Chromatography

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Abstract

We present an analysis of gas chromatographic columns where the stationary phase is not assumed to be a thin uniform coating along the walls of the cross section. We also give an asymptotic analysis assuming that the parameter $\beta = \frac{KD^{II}\rho^{II}}{D^{I}\rho^{I}}$ is small. Here K is the partition coefficient, and D^i and ρ^i, $i = I, II$ are the diffusivity and density in the mobile ($i = I$) and stationary ($i = II$) regions.

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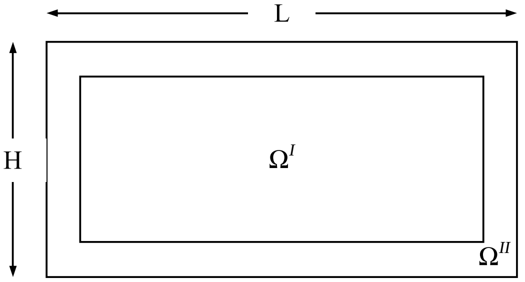
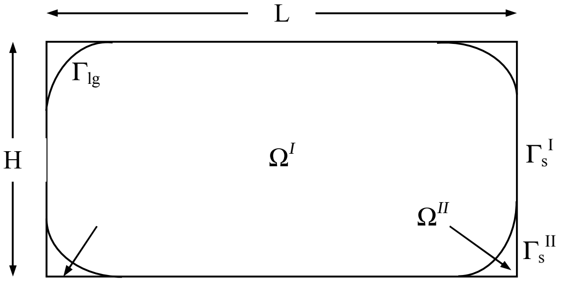
1 Introduction

Chromatography is an analytical technique for the separation of mixtures. In gas chromatography (GC) the sample to be analyzed is transported down a long narrow column by a carrier gas. The column is coated by a static retentative liquid. As the analyte is advected down the column, its molecules are continually adsorbed and desorbed by this liquid, providing resistance to transport. The ease with which any particular component is absorbed by the liquid determines how much time it spends in the stationary liquid phase, and hence how long it takes to pass down the whole length of the column. Each component in the sample has a characteristic separation rate that can be used to identify it, and thus the composition of the original mixture.



(a) Schematic of a GC column. Ω^I denotes the mobile phase and Ω^{II} the stationary phase.



(b) GC column with stationary phase accumulated in corners. The boundary of Ω^I consists of the solid wall Γ_s^I and Γ_{lg}, the interface between the liquid and gas phases. The boundary of Ω^{II} consists of Γ_{lg} and the solid wall Γ_s^{II}.

Figure 1(a) gives a schematic of a cross section of a GC device. The interior region Ω^I containing the carrier gas is referred to as the mobile phase, and the exterior region Ω^{II} containing the retentative liquid is referred to as the stationary phase. We will denote the cross sectional areas of the mobile and stationary phases as A^I and A^{II}, respectively. Let the gas and liquid densities in these two regions be denoted as ρ^I and ρ^{II}, and the diffusivities of the analyte in the two regions as D^I and D^{II}.

The foundations for capillary gas chromatography were laid by Golay in the classic paper [7]. He extended the concept of Taylor-Aris dispersion [15, 2] to analyze the evolution of a gas flowing through a tube coated with a thin layer of a stationary liquid. The primary result in his paper was the prediction of the rates at which an analyte is transported and diffused down the tube. Although presented in a different way, Golay's result was equivalent to showing that the analyte concentration C obeys the one dimensional advection diffusion equation

$$\frac{\partial C}{\partial t} + U_{eff}\frac{\partial C}{\partial z} = D_{eff}\frac{\partial^2 C}{\partial z^2}. \tag{1.1}$$

The coordinate z defines the axial position along the tube, the coefficient U_{eff} tells how fast the analyte moves down the tube, and D_{eff} tells how quickly it spreads as it moves down the tube. Golay showed that the effective velocity could be written as

$$U_{eff} = U_0 \lambda, \qquad \lambda = \frac{1}{1+k_b}, \tag{1.2}$$

where U_0 is the average value of the velocity in the tube, and[1]

$$k_b = \frac{K \rho^{II} \delta}{\rho^I}, \tag{1.3}$$

where

$$\delta = \frac{A^{II}}{A^I} \tag{1.4}$$

is the ratio of the cross sectional area of the stationary phase to that of the mobile phase. Similar to Taylor-Aris diffusion, Golay showed that the effective diffusivity could be written as

$$D_{eff} = D^I \lambda \left(c_0 + c_1 Pe^2 \right), \tag{1.5}$$

where Pe is the Péclet number, which we define to be

$$Pe = \frac{U_0 \sqrt{A^I}}{D^I}. \tag{1.6}$$

Golay gave analytical expressions for c_0 and c_1 for GC columns of circular cross section. The quantity c_0 has a simple analytical expression (see §3), and for GC columns is very close to unity. The modeling challenge is to compute c_1.

Golay's analysis was for GC columns of circular cross section coated with a uniform thin stationary phase. In recent years columns of rectangular, or nearly rectangular cross section have been used in micro-fabricated GC columns. Several authors have analyzed GC columns with rectangular cross sections [8, 14, 5, 6, 1, 10]. However, all of these authors have assumed that the cross sections are *uniformly coated* with a thin layer of stationary phase. As in Golay's paper, this assumption allows them to find the solution by solving the governing equations only in the gas phase, and accounting for the presence of the stationary phase through a reacting side wall boundary condition,

$$D \nabla C \cdot \mathbf{n} = -\frac{k_b}{2} \frac{\partial C}{\partial t}. \tag{1.7}$$

This boundary condition can be derived by writing down the advection diffusion equations in regions Ω^I and Ω^{II}, and considering the asymptotic limit as the thickness of the stationary layer goes to zero.

In practice, when columns of nearly rectangular cross section are coated with a stationary layer, the stationary phase tends to accumulate in the corners. This leads to cross sections as in Figure 1(b). An examination of the justification behind the reacting side wall boundary

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[1] We put the subscript b on k_b to denote that it is related to the reacting side wall boundary condition (1.7), as well as to distinguish it from the Fourier wavenumber k that will be used later in this paper.

condition (1.7) shows that, at the very least, it requires that the radius of curvature of the stationary phase be large compared to its thickness. This is clearly not satisfied for the cross sections in Figure 1(b).

We present a general formulation of gas chromatography that allows us to model cross sections that have arbitrary geometries for the stationary phase. That is, we do not assume that the stationary phase is necessarily a thin layer coating the outer wall. In [13], we apply this theory to the special case of rectangular cross sections with the stationary phase accumulated in the corners. In particular, we will assume that the thickness of the stationary phase is zero except in the corners, as in Figure 1(b). Our analysis shows that for such columns, the scaling laws for the effective diffusivity are quite different than when the stationary phase is spread out over a thin layer. The difference arises not merely because the stationary layer is thick, but because its aspect ratio is order unity.

We now point out the similarities and differences between the general case (Figure 1(b)) and that of thin layers (Figure 1(a)). In [5], the authors generalize the results of Golay by showing that for arbitrary cross sections the constant c_1 in (1.5) can be written as

$$c_1 = \lambda \left((k_b \lambda)^2 g_1 + (k_b \lambda) g_2 + g_3 \right). \tag{1.8}$$

Here the parameters g_k depend only on the geometry of the cross section. In deriving this formula it is assumed tht the stationary layer thin and of uniform thickness, and hence the reacting sidewall boundary condition in Eqn. (1.7) is applicable. [2]

In this paper, we show that when the assumption of a thin and uniform stationary layer is dropped we can write

$$c_1 = \lambda \left(\left(\frac{K \lambda \rho^{II}}{\rho^I} \right)^2 I_1(\beta) + \left(\frac{K \lambda \rho^{II}}{\rho^I} \right) I_2(\beta) + I_3(\beta) \right), \tag{1.9}$$

where

$$\beta = \frac{K D^{II} \rho^{II}}{D^I \rho^I}. \tag{1.10}$$

The functions I_k are dimensionless functions of both the geometry and the parameter β. Unlike the parameters g_k, which depend only on the geometry of Ω^I, the parameters I_k depend on the geometry of both regions Ω^I and Ω^{II}. For typical GC devices β can be assumed to be very small. The value of β varies according to the analyte of interest, but it is generally less than 1.0×10^{-2}. In §4 we show that for $\beta \ll 1$ we have

$$I_1 = \frac{1}{\beta} h_0 + h_1 + O(\beta), \tag{1.11a}$$

$$I_2 = h_2 + O(\beta), \tag{1.11b}$$

$$I_3 = h_3 + O(\beta). \tag{1.11c}$$

Here the h_k are now functions only of the geometry, and are independent of β. We can compute h_0 by solving an equation in Ω^{II}, and h_3 by solving an equation only in Ω^I. To

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[2] The constants of [5] differ from ours. For example, they write $1/105 g_2$ whereas we write g_2.

compute h_1 and h_2 we first solve a Poisson equation in Ω^{II}, and pass the normal derivative along the liquid/gas interface Γ_{lg} to Ω^{I}. Using only this information from Ω^{II}, we then compute h_1 and h_2. In this sense, the small β approximation leaves the equations in two regions weakly coupled.

If the stationary layers are thin and uniform the reacting sidewall boundary condition (1.7) is applicable. Assuming a uniformly thin stationary layer and including a correction term to (1.7) described in Golay(1958), we get

$$h_0 = g_0\delta^3, \tag{1.12a}$$
$$h_1 = g_1\delta^2, \tag{1.12b}$$
$$h_2 = g_2\delta, \tag{1.12c}$$
$$h_3 = g_3. \tag{1.12d}$$

Assuming (1.12) hold and that $\delta/\beta \ll 1$ (as it is for columns of circular cross section), we can ignore the term h_0/β in (1.11a). In this case, (1.8) and (1.9) are identical. However, for concentrated stationary layers, the term h_0/β becomes more important. When the stationary phase is neither thin nor uniform, the term h_0/β becomes the dominant term in c_1.

The small β approximation allows us to compute the terms h_k by solving weakly coupled equations in the regions Ω^I and Ω^{II}. However, more physical insights and simpler computations arise if we can completely decouple these equations. In realistic column geometries, the parameter δ in (1.4) is small. In [13] we use the results of this paper as a starting point for an asymptotic analysis for the case where δ is small. In that paper we also present an analysis for when the aspect ratio of the channel is very large. Both of these analyses simplify the problem, and reduce the number of effective parameters that need to be adjusted when doing numerical computations.

In [13] we show that when the stationary layers are concentrated in the corners, and δ is small, we have

$$h_0 = f_0\delta^2, \tag{1.13a}$$
$$h_1 = \delta^2\left(-\ln(\delta) f_{1,0} + f_{1,1}\right) + o(\delta^2), \tag{1.13b}$$
$$h_2 = \delta f_2 + o(\delta), \tag{1.13c}$$
$$h_3 = f_3 + o(1). \tag{1.13d}$$

Here the functions f_k are independent of δ. The constant f_0 can be computed by solving an equation in the stationary layer alone, and the constants $f_{1,0}$, $f_{1,1}$, f_2, and f_3 can be computed by solving equations over a rectangular cross section and accounting for the stationary phase by putting appropriate sources in the corners.

Note that for the case of sufficiently thin uniform stationary layers, the term h_1 will eventually dominate h_0/β. This will be the case for concentrated stationary layers, but only after δ is as small as $e^{-1/\beta}$. Since β is less than 1.0×10^{-2}, for all practical purposes, this never occurs. However, in [13] we show that the term h_1 grows in importance relative to h_0 as the aspect ratio of the channel becomes larger.

For columns with concentrated stationary layers, the fact that D_{eff} is a strong function of β may have significant impact upon the design of GC columns. If one assumes that the form for thin layers in (1.8) holds, we see that one does not need to be concerned with the value of β, and hence the ratio D^{II}/D^{I} when choosing the materials for a GC device. However, the results in this and the following paper show that this is in fact an important factor in the performance of GC columns with rectangular cross section.

The analysis of rectangular GC columns is accomplished in four steps. First, in §2 and §3 we derive a procedure for computing U_{eff} and D_{eff} for arbitrary cross sections. This procedure makes no assumptions about the size of any of physical parameters or the thickness of the stationary layer other than that the tube is sufficiently long for Taylor-Aris dispersion theory to apply. Next, in §4 we simplify this analysis assuming that the parameter β is small. We illustrate the validity of the small β approximation in §5 with some numerical examples. In [13] we apply this theory to the special case where the stationary phase is confined to small regions in the corners of a rectangular cross section is considered, and then further simplify the analysis by assuming that the aspect ratio of the rectangle is very large.

2 The Two-Domain Equations of Gas Chromatography

Although gas chromatography utilizes both mobile and stationary phases, almost all modeling has been done by approximating the effect of the stationary phase with a reacting side wall boundary condition on the mobile phase. In this section we formulate the equations of gas chromatography so that we can account for arbitrarily thick stationary phases. When numerically solving these equations it is more convenient to formulate the problem in terms of variables that are continuous at the boundary between the two phases. Physically, this could be done using the chemical potential or chemical activity as the unknown variables. However, for our purposes it is simpler to accomplish the same end using a simple mathematical scaling.

We assume that we have an infinitely long straight tube with a constant cross section. We assume that an incompressible fluid flows down Ω^I with a constant pressure gradient, and that there is no slip at the boundary $\partial\Omega^I$. In this case, the velocity $\underline{u} = U_0(0, 0, f(x, y))$ is unidirectional where $f(x, y)$ satisfies

$$\begin{aligned} \nabla_2^2 f &= -K_u \quad && \text{in } \Omega^I, \\ f &= 0 && \text{on } \partial\Omega^I, \end{aligned}$$

and K_u is chosen so that

$$\frac{1}{A^I}\int_{\Omega^I} f(x, y)\,dA = 1. \tag{2.1}$$

Here and in the following we use the notation

$$\nabla_2^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}, \tag{2.2}$$

to represent the two-dimensional Laplacian ignoring the axial derivatives.

In terms of the concentration C of the analyte, the equations for gas chromatography can be written as

$$\rho^I\left(\frac{\partial C^I}{\partial t} + U_0 f(x, y)\frac{\partial C^I}{\partial z}\right) = \kappa^I \nabla^2 C^I \qquad \text{in } \Omega^I, \tag{2.3}$$

$$\rho^{II}\frac{\partial C^{II}}{\partial t} = \kappa^{II}\nabla^2 C^{II} \quad \text{in } \Omega^{II}, \tag{2.4}$$

along with the boundary conditions

$$C^{II} = KC^I \qquad \text{on } \partial\Omega^I, \tag{2.5a}$$

$$\kappa^{II}\frac{\partial C^{II}}{\partial n} = \kappa^I\frac{\partial C^I}{\partial n} \quad \text{on } \partial\Omega^I, \tag{2.5b}$$

$$\frac{\partial C^{II}}{\partial n} = 0 \qquad \text{on } \partial(\Omega^I \cup \Omega^{II}). \tag{2.5c}$$

Equation (2.3) is the advection diffusion equation in the gas phase, and (2.4) is the diffusion equation in the stationary phase. We denote the conductivities in the mobile and stationary phases as $\kappa^I = \rho^I D^I$ and $\kappa^{II} = \rho^{II} D^{II}$, respectively. The boundary condition (2.5a) involves the partition coefficient K, and gives the jump in the concentration at the boundary between the mobile and stationary phases. The boundary conditions (2.5b) and (2.5c) require that the flux of analyte be continuous at the boundary between the phases and zero at the outer wall.

To simplify our later asymptotic analysis, we prefer to work with equations where the dependent variable is continuous at the interface $\partial\Omega^I$. We thus rewrite the equations of chromatography using the rescaled variables $\mathcal{A}^I$ and $\mathcal{A}^{II}$ defined by

$$C^I = B^I \mathcal{A}^I, \qquad C^{II} = B^{II} \mathcal{A}^{II},$$

where

$$B^I = 1, \qquad B^{II} = K. \tag{2.6}$$

In terms of these variables (2.3)-(2.5c) can be rewritten as

$$\rho^I B^I \left(\frac{\partial \mathcal{A}^I}{\partial t} + U_0 f(x,y) \frac{\partial \mathcal{A}^I}{\partial z} \right) = \alpha^I \nabla^2 \mathcal{A}^I \qquad \text{in } \Omega^I, \tag{2.7}$$

$$\rho^{II} B^{II} \frac{\partial \mathcal{A}^{II}}{\partial t} = \alpha^{II} \nabla^2 \mathcal{A}^{II} \quad \text{in } \Omega^{II}, \tag{2.8}$$

with boundary conditions

$$\alpha^I \frac{\partial \mathcal{A}^I}{\partial n} = \alpha^{II} \frac{\partial \mathcal{A}^{II}}{\partial n} \quad \text{on } \partial\Omega^I, \tag{2.9a}$$

$$\mathcal{A}^I = \mathcal{A}^{II} \qquad \text{on } \partial\Omega^I, \tag{2.9b}$$

$$\frac{\partial \mathcal{A}^{II}}{\partial n} = 0 \qquad \text{on } \partial(\Omega^I \cup \Omega^{II}), \tag{2.9c}$$

where

$$\alpha^i = \kappa^i B^i, \qquad i = I, II. \tag{2.10}$$

3 The Effective Velocity and Diffusion Coefficients

The calculation of the effective velocity U_{eff} and effective diffusion coefficient D_{eff} is a straightforward application of the techniques described in [2, 11, 4] and [3, Chapter 12]. For this reason, we will merely state the final answer, leaving the details of the derivation to Appendix A.

The effective velocity is given by (1.2). The effective diffusion coefficient can be written as

$$D_{eff} = D^I \lambda \left(1 + k_b D^{II}/D^I + J\right), \tag{3.1}$$

where λ is defined in (1.2), k_b is defined in (1.3), and $J = c_1 Pe^2$ is given by either of the equivalent expressions

$$J = -\frac{1}{\alpha^I A^I} \sum_i \int_{\Omega^i} \left(\alpha^i \nabla_2^2 \mathcal{A}_1^i\right) \mathcal{A}_1^i dA, \tag{3.2}$$

or

$$J = \frac{1}{\alpha^I A^I} \sum_i \int_{\Omega^i} \alpha^i \left(\nabla \mathcal{A}_1^i \cdot \nabla \mathcal{A}_1^i\right) dA. \tag{3.3}$$

The latter expression for J can be derived from the former through integration by parts and application of appropriate boundary conditions.

The functions $\mathcal{A}_1^I$ and $\mathcal{A}_1^{II}$ satisfy the equations

$$\alpha^I \nabla_2^2 \mathcal{A}_1^I = \rho^I B^I U_0 \left(-\lambda + f(x,y)\right) \quad \text{in } \Omega^I, \tag{3.4a}$$

$$\alpha^{II} \nabla_2^2 \mathcal{A}_1^{II} = -\rho^{II} B^{II} U_0 \lambda \quad \text{in } \Omega^{II}, \tag{3.4b}$$

along with the boundary conditions (2.9).

The term $k_b D^{II}/D^I$ in (3.1) is very small in GC devices. This arises from the fact that D^{II}/D^I is on the order of 1.0×10^{-4}, and k_b is never significantly larger than 10. In terms of (1.5), this is equivalent to saying that $c_0 = 1 + k_b D^{II}/D^I$ is very close to unity. As such, the modeling challenge is to compute c_1. Given J, we can compute D_{eff} through (3.1). To more clearly show the functional dependence of D_{eff} upon the problem parameters, we rewrite J as follows.

We begin by noting that the equations (3.4) are linear, and that the expression for J is is a bilinear functional of $\mathcal{A}^I$, $\mathcal{A}^{II}$. Linearity implies that we can write[3]

$$\mathcal{A}_1^i = \frac{U_0}{D^I} \left(-\frac{\rho^{II} K \lambda}{\rho^I} \phi^i + \psi^i\right), \quad i = I, II, \tag{3.5}$$

---

[3] See Appendix B for details.

where

$$\begin{aligned}
\nabla_2^2\phi^I &= -\frac{A^{II}}{A^I} = -\delta \quad && \text{in } \Omega^I, && (3.6a)\\
\beta\nabla_2^2\phi^{II} &= 1 && \text{in } \Omega^{II}, && (3.6b)\\
\phi^I &= \phi^{II} && \text{on } \partial\Omega^I && (3.6c)\\
\frac{\partial\phi^I}{\partial n} &= \beta\frac{\partial\phi^{II}}{\partial n} && \text{on } \partial\Omega^I, && (3.6d)\\
\frac{\partial\phi^{II}}{\partial n} &= 0 && \text{on } \partial(\Omega^I \cup \Omega^{II}), && (3.6e)
\end{aligned}$$

and

$$\begin{aligned}
\nabla_2^2\psi^I &= f(x,y) - 1 \quad && \text{in } \Omega^I, && (3.7a)\\
\beta\nabla_2^2\psi^{II} &= 0 && \text{in } \Omega^{II}, && (3.7b)\\
\psi^I &= \psi^{II} && \text{on } \partial\Omega^I, && (3.7c)\\
\frac{\partial\psi^I}{\partial n} &= \beta\frac{\partial\psi^{II}}{\partial n} && \text{on } \partial\Omega^I, && (3.7d)\\
\frac{\partial\psi^{II}}{\partial n} &= 0 && \text{on } \partial(\Omega^I \cup \Omega^{II}). && (3.7e)
\end{aligned}$$

When we substitute (3.5) into (3.2) (see Appendix B) we arrive at the expression

$$J = Pe^2\left(\left(\frac{K\rho^{II}\lambda}{\rho^I}\right)^2 I_1(\beta) + \frac{K\lambda\rho^{II}}{\rho^I} I_2(\beta) + I_3(\beta)\right), \tag{3.8}$$

where

$$I_1 = \delta\frac{1}{(A^I)^2}\int_{\Omega^I}\phi^I dA - \frac{1}{(A^I)^2}\int_{\Omega^{II}}\phi^{II} dA, \tag{3.9}$$

$$I_2 = 2\frac{1}{(A^I)^2}\int_{\Omega^I}\phi^I(f-1)dA, \tag{3.10}$$

$$I_3 = -\frac{1}{(A^I)^2}\int_{\Omega^I}\psi^I(f-1)dA. \tag{3.11}$$

Note that the functions I_k are dimensionless. Equation (3.8) is equal to $c_1 Pe^2$, where c_1 is given in (1.9).

4 Small β Approximation

The two-domain equations of gas chromatography described in the previous sections determine solutions on the domains Ω^I and Ω^{II} simultaneously. However, as the parameter β is always small in GC columns, the solutions are only weakly coupled. We will show that this allows us to independently solve for the leading order terms of ϕ^{II} and ψ^{II} in Ω^{II}, and use those solutions to provide boundary conditions when determining the leading order terms of ϕ^I and ψ^I in Ω^{II}.

There are several reasons for considering the limit as $\beta \to 0$. One of the main benefits of taking this limit is that the asymptotic solution for small values of β can be obtained by performing numerical calculations on quantities that depend only on the geometry, not on the values of any of the physical parameters.

In this section we will derive the asymptotic forms given in (1.11), giving explicit expressions for computing h_k. We begin by considering the asymptotic solution for ψ^I, ψ^{II} assuming that $\beta \ll 1$. We suppose that

$$\psi^i = \psi_0^i + \beta\psi_1^i + \dots \quad i = I, II. \tag{4.1}$$

Collecting terms of order one we find that

$$\begin{aligned}
\nabla_2^2\psi_0^I &= f - 1 && \text{in } \Omega^I, && \text{(4.2a)}\\
\frac{\partial\psi_0^I}{\partial n} &= 0 && \text{on } \partial\Omega^I = \Gamma_{lg} \cup \Gamma_s^I, && \text{(4.2b)}\\
\nabla_2^2\psi_0^{II} &= 0 && \text{in } \Omega^{II}, && \text{(4.2c)}\\
\psi_0^{II} &= \psi_0^I && \text{on } \Gamma_{lg}, && \text{(4.2d)}\\
\frac{\partial\psi_0^{II}}{\partial n} &= 0 && \text{on } \Gamma_s^{II}. && \text{(4.2e)}
\end{aligned}$$

Note that the solution ψ_0^I can be determined independently of ψ_0^{II}. Once we know this solution we can solve an elliptic PDE with both Dirichlet and Neumann boundary conditions to determine ψ_0^{II}. However, ψ_0^{II} is not needed to determine the functions I_k to leading order. In particular, substituting our expansion into (3.11) we have $I_3 = h_3 + O(\beta)$, where

$$h_3 = -\frac{1}{(A^I)^2}\int_{\Omega^I}(f-1)\psi_0^I dA. \tag{4.3}$$

A simple argument shows that we can carry out our perturbation expansion to all orders of β.

We now consider the determination of ϕ^I ϕ^{II}. If we assume an expansion as for ψ^i, we find that we cannot get a consistent set of problems. We can get a consistent expansion if we assume that ϕ^{II} is much larger than ϕ^I. Specifically, we assume that

$$\begin{aligned}
\phi^I &= \phi_0^I + \beta\phi_1^I + \dots,\\
\phi^{II} &= \frac{1}{\beta}\left(\phi_{-1}^{II} + \beta\phi_0^{II} + \dots\right).
\end{aligned}$$

Collecting the terms of order $1/\beta$, we find that

$$\nabla_2^2 \phi_{-1}^{II} = 1, \quad \text{in } \Omega^{II}, \tag{4.4a}$$

$$\phi_{-1}^{II} = 0 \quad \text{on } \Gamma_{lg}, \tag{4.4b}$$

$$\frac{\partial \phi_{-1}^{II}}{\partial n} = 0 \quad \text{on } \Gamma_s^{II}. \tag{4.4c}$$

This allows us to solve for ϕ_{-1}^{II}. Collecting the terms of order one in Ω^I we find

$$\nabla_2^2 \phi_0^I = -\frac{A^{II}}{A^I} = -\delta \quad \text{in } \Omega^I, \tag{4.5a}$$

$$\frac{\partial \phi_0^I}{\partial n} = \frac{\partial \phi_{-1}^{II}}{\partial n} \quad \text{on } \Gamma_{lg}, \tag{4.5b}$$

$$\frac{\partial \phi_0^I}{\partial n} = 0 \quad \text{on } \Gamma_s^I. \tag{4.5c}$$

We can now substitute our expansion into (3.10) and obtain $I_2 = h_2 + O(\beta)$, where

$$h_2 = 2\frac{1}{(A^I)^2} \int_{\Omega^I} (f-1)\phi_0^I dA. \tag{4.6}$$

As (4.5) is a pure Neumann boundary value problem, we only know ϕ_0^I up to an arbitrary additive constant. Recalling (2.1), we see that we can add an arbitrary constant to ϕ_0^I without changing the value of h_2 in (4.6).

We now consider the calculation of I_1 as in (3.9). If we are only interested in computing these quantities to $O(1/\beta)$, we only need to know ϕ_{-1}^{II}. We have

$$h_0 = -\frac{1}{(A^I)^2} \int_{\Omega^{II}} \phi_{-1}^{II} dA. \tag{4.7}$$

Substituting our expansion into (3.9), it might first appear that we need to compute both ϕ_0^I and ϕ_0^{II} in order to compute I_1 to zeroeth order in β. However, we can add an arbitrary constant to ϕ^I and ϕ^{II} without changing the value of I_1. We now show that without ever computing ϕ_0^{II} we can determine the constant to add to ϕ_0^I so that the integral of ϕ_0^{II} over region II vanishes. This allows us to determine I_1 without knowing ϕ_0^{II}.

Collecting terms to order one in Ω^{II}, we see that ϕ_0^{II} must satisfy

$$\nabla_2^2 \phi_0^{II} = 0 \quad \text{in } \Omega^{II},$$

$$\phi_0^{II} = \phi_0^I \quad \text{on } \Gamma_{lg},$$

$$\frac{\partial \phi_0^{II}}{\partial n} = 0 \quad \text{on } \Gamma_s^{II}.$$

The solution ϕ_0^{II} is determined uniquely only if ϕ_0^I is given, and we have demonstrated above that we only know ϕ_0^I up to an additive constant. Thus, we also only know ϕ_0^{II} up to the same additive constant, but we are free to choose that constant without altering the value of h_2. We will choose this constant so that $\int_{\Omega^{II}} \phi_0^{II} dA$ conveniently vanishes.

We can write

$$\int_{\Omega^{II}} \phi_0^{II} dA = \int_{\Omega^{II}} \left(\phi_0^{II}\nabla_2^2\phi_{-1}^{II} - \phi_{-1}^{II}\nabla_2^2\phi_0^{II}\right) dA = \int_{\Gamma_{lg}\cup\Gamma_s^{II}} \left(\phi_0^{II}\frac{\partial\phi_{-1}^{II}}{\partial n} - \phi_{-1}^{II}\frac{\partial\phi_0^{II}}{\partial n}\right) dl.$$

Clearly, the last integral vanishes on Γ_s^{II}. Furthermore, we have $\phi_{-1}^{II} = 0$ and $\phi_0^I = \phi_0^{II}$ on Γ_{lg}. It follows that

$$\int_{\Omega^{II}} \phi_0^{II} dA = \int_{\Gamma_{lg}} \phi_0^I \frac{\partial\phi_{-1}^{II}}{\partial n} dl.$$

Thus, if we choose the arbitrary additive constant to ϕ_0^I so that

$$\int_{\Gamma_{lg}} \phi_0^I \frac{\partial\phi_{-1}^{II}}{\partial n} dl = 0, \tag{4.8}$$

we do not need to compute the integral of ϕ_0^{II} over Ω^{II} when determining I_1. This gives us $I_1 = h_0/\beta + h_1$ as in (1.11a), where

$$h_1 = \delta\frac{1}{(A^I)^2}\int_{\Omega^I} \phi_0^I dA. \tag{4.9}$$

It should be noted that the quantities h_k have been defined so they are dimensionless. Thus, if we compute them for two geometrically similar cross sections with different sizes, we will get the same values.

It should be noted that the term h_0/β is on the order of $1/\beta$, while the other terms in c_1 are order unity. However, there are two other small parameters in this problem. In particular, the parameter $\delta = A^{II}/A^I$ is small, and the inverse aspect ratio $\varepsilon = H/L$ is also frequently small. (c.f. Figure 1(b).) As we will see in the following sections, as these parameters go to zero, the term h_0/β does not necessarily dominate the other terms. However, for typical parameters in rectangular GC columns, this term is either dominant, or extremely important.

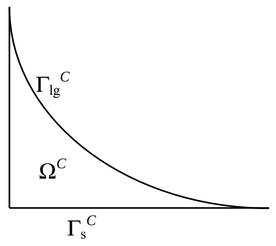

Figure 5.1. Blow up of one corner of column cross section.

5 Numerical Examples Illustrating the Small β Approximation

In this section we present some numerical examples illustrating the validity of the small β approximation. All numerical examples in this section were obtained using Sundance [9], a software system for rapid development of parallel PDE simulation and optimization problems.

Assuming the interface between the gas and stationary phase is in capillary equilibrium, the boundary between these regions must be circular arcs. In rectangular GC devices the contact angle is extremely small, and we will assume that it is zero. Consider any one of the four corners of the column cross section, and let Ω^C denote the domain of the stationary phase in that corner, and let it have area A^C.

As in Figure 5.1, we denote Γ_{lg} as the interface between the liquid and gas regions. Denote the portion of Γ_{lg} in this corner separating Ω^C and Ω^I as Γ_{lg}^C, and denote the portion of Γ_s^{II} in this corner as Γ_s^C. Let the arc Γ_{lg}^C be an arc of a circle of radius r_0.

The computation of the portion of ϕ_{-1}^{II} in this corner requires the solution of

$$\nabla^2 q_{r_0} = 1 \quad \text{in } \Omega^C, \tag{5.1a}$$

$$q_{r_0} = 0 \quad \text{on } \Gamma_{lg}^C, \tag{5.1b}$$

$$\frac{\partial q_{r_0}}{\partial n} = 0 \quad \text{on } \Gamma_s^C. \tag{5.1c}$$

We then compute

$$I_C = (A^C)^2 \mu,$$

where

$$\mu = \frac{1}{(A^C)^2} \int_{\Omega_C} q_{r_0}(x,y) dA. \tag{5.2}$$

Simple scaling arguments show that μ is dimensionless, and without loss of generality we can set $r_0 = 1$ when computing it. Numerical computations show that

$$\mu \approx 0.105331.$$

Method	r_0	I_1	I_2	I_3
Two Domain	0.20	0.203×10^{-2}	0.628×10^{-3}	0.595×10^{-2}
Small β	0.20	0.201×10^{-2}	0.623×10^{-3}	0.590×10^{-2}
Two Domain	0.10	0.125×10^{-3}	0.163×10^{-3}	0.629×10^{-2}
Small β	0.10	0.124×10^{-3}	0.162×10^{-3}	0.620×10^{-2}
Two Domain	0.05	0.773×10^{-5}	0.413×10^{-4}	0.630×10^{-2}
Small β	0.05	0.778×10^{-5}	0.415×10^{-4}	0.630×10^{-2}

Table 5.1. This shows the comparison between the full two domain solution computed with (2.7)-(2.9), and the small β approximation. In this example we are using $\beta = 0.01$, which is a bit bigger than the upper limit of realistic GC columns. This value of β is obtained by using $\kappa^{II}/\kappa^{I} = 0.087$, and $K = 0.1138$. These calculations were done with a rectangular column with an aspect ratio of 4 to 1.

We can now compute h_0 in (4.7) by summing I_C for each of the four corners, and then dividing by $-(A^I)^2$. We emphasize that μ depends only Γ^C_{lg} being the arc of a circle, independent of the radius of that circle, and is thus a constant for all geometries we consider.

In a polar coordinate system, let

$$p_0(\theta) = \frac{\partial q_{r_0}}{\partial n}$$

be the normal derivative as a function of θ. Then we have

$$p_{r_0}(\theta) = r_0 p_1(\theta),$$

where $p_1(\theta)$ is the normal derivative when $r_0 = 1$.

In order to simplify the communication of the normal derivative from Ω^{II} to Ω^{I} for the boundary condition (4.5b) we have done a curve fit to the function $p_1(\theta)$. This curve fit is accurate to about one percent, and is given by

$$p_1(\theta) = 0.31268 \cos\left(\frac{1.0356\,|\sin(\theta)|}{1.0 - 0.76\,|\sin(\theta)|}\right). \tag{5.3}$$

Figure 5.2 shows a plot of the function $p_1(\theta)$ in (5.3), and compares it to the accurate numerical computation of the normal derivative. This figure shows that little error results in passing the data between the two regions using our curve fit.

Table 5.1 shows the comparison between the full two domain solution computed with (2.7)-(2.9), and the small β approximation. In these calculations we have distributed the stationary phase equally in each of the corners, allowing us to use symmetry boundary

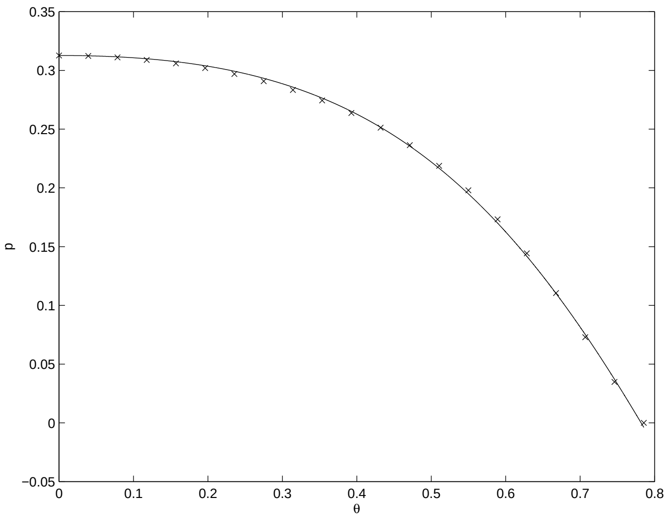

Figure 5.2. This shows the function $p_1(\theta)$, giving the normal derivative of q_1 at the boundary. The continuous curve is the curve fit given by (5.3), and the crosses give the accurate numerical computation of this normal derivative. The maximum error between the two curves is less than 3.0×10^{-3}.

conditions. When computing the small β approximation, we have used the curve fit in (5.3) to pass the data from ϕ^{II}_{-1} to Ω^{I}. For this reason, our answers should not be expected to be better than about one percent accurate (well beyond experimental errors). We believe Table 5.1 illustrates convincingly that little information is lost by making the small β approximation.

We should remark that making the small β approximation has numerous advantages over the full two domain equations. First, the influence of the parameter β is taken into account analytically, giving us one fewer parameter to adjust. Second, we have simplified many of the tasks involved in solving numerical PDES, such as meshing. Finally, we are in a position to gain more insight by further simplifying the problem as we do in [13].

6 Conclusions

Micro-fabricated GC columns have cross sections where the stationary phase does not uniformly coat the walls of the column cross section. In such situations the reacting side wall boundary condition frequently used to analyze the performance of GC columns is not applicable. We have presented an alternative analysis for such situations. We show that the behavior of such GC columns is qualitatively different than for uniformly coated GC columns. In particular, the scaling laws for the two cases are not identical, as seen by comparing the two equations (1.8) and (1.9) for c_1.

We use these results in [13] to make the small δ approximations, where the stationary phase is concentrated in the corners.

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A The Effective Velocity and Diffusion Coefficients

In this appendix we supply the details of the calculation of U_{eff} in (1.2) and D_{eff} and J in (3.1)-(3.3). We will closely follow the approach outlined in [12], which is similar to that given in [4].

We begin by Fourier transforming the governing equations (2.7) and (2.8) in the axial direction (z). For each value of the wavenumber k, this gives us an initial value problem that can be solved using two dimensional eigenmodes that have the temporal behavior $e^{\sigma_m(k)t}$. We can then solve the initial value problem for our original (not Fourier transformed) equations by taking the inverse Fourier transform of an infinite eigenfunction expansion. An asymptotic analysis of this rather messy expression shows that after an initial transient, all but the lowest order mode in our infinite series has decayed rapidly. Thus in order to compute the behavior of our solution, we only need to know the first mode and its corresponding eigenvalue. Furthermore, if we are interested in the long time behavior of our solution, we only need to know the behavior of this eigenvalue for small values of the wavenumber k. That is, we need to determine the expansion

$$\sigma = i\sigma_1 k + \sigma_2 k^2 + \dots. \tag{A1}$$

We then have

$$\sigma_1 = -U_{eff}, \quad D_{eff} = -\sigma_2. \tag{A2}$$

Intuitively, this holds from the fact that using these definitions of U_{eff} and D_{eff}, (1.1) has the same dispersion relation as (A1).

In order to determine σ_1 and σ_2, we carry out Rayleigh-Schrödinger perturbation theory of eigenvalues, with k as the small perturbation parameter. The spatially Fourier transformed eigenvalue problem is given by

$$\rho^I B^I \left(\sigma \mathcal{A}^I + ikU_0 f(x,y)\mathcal{A}^I\right) = \alpha^I \left(\nabla_2^2 \mathcal{A}^I - k^2 \mathcal{A}^I\right) \quad \text{in } \Omega^I, \tag{A3}$$

$$\rho^{II} B^{II} \sigma \mathcal{A}^{II} = \alpha^{II} \left(\nabla_2^2 \mathcal{A}^{II} - k^2 \mathcal{A}^{II}\right) \quad \text{in } \Omega^{II}, \tag{A4}$$

where the functions $\mathcal{A}^I$ and $\mathcal{A}^{II}$ still satisfy the boundary conditions (2.9).

We will expand σ, $\mathcal{A}^I$ and $\mathcal{A}^{II}$ in a Taylor series in k. That is, we will assume that we can write

$$\mathcal{A}^j = \mathcal{A}_0^j + \mathrm{i}\mathcal{A}_1^j k + \mathcal{A}_2^j k^2 + \dots, \quad j = I, II, \tag{A5}$$

as well as also expanding σ as in (A1). In order to carry out this perturbation expansion, we use the fact that we can solve the equations

$$\alpha^i \nabla_2^2 \mathcal{A}^I = F^i(x,y) \quad \text{in } \Omega^i,\ i = I, II \tag{A6}$$

with the boundary conditions (2.9) so long as

$$\int_{\Omega^I} F^I dA + \int_{\Omega^{II}} F^{II} dA = 0 \tag{A7}$$

We refer to (A7) as the *solvability condition.*

A.1 Zeroeth Order

If we substitute (A5) and (A1) into (A3) and (A4), and collect the terms that are order zero in k, we get the equations

$$\alpha^i \nabla_2^2 \mathcal{A}_0^i = 0, \quad i = I, II,$$

along with the boundary conditions (2.9). The only solutions to this equation have $\mathcal{A}_0^I = \mathcal{A}_0^{II} = constant$. Since we are solving an eigenvalue problem, without loss of generality, we can scale our eigenfunctions so that

$$\mathcal{A}_0^I = \mathcal{A}_0^{II} = 1.$$

A.2 First Order - The Effective Velocity U_{eff}

If we collect all of the terms to first order in k, we get

$$\alpha^I \nabla_2^2 \mathcal{A}_1^I = \rho^I B^I \left(\sigma_1 + U_0 f(x,y)\right) \quad \text{in } \Omega^I, \tag{A8a}$$

$$\alpha^{II} \nabla_2^2 \mathcal{A}_1^{II} = \rho^{II} B^{II} \sigma_1 \quad \text{in } \Omega^{II}. \tag{A8b}$$

These equations have the same form at (A6). All of the terms on the right hand side of these equations are known, except for σ_1. Application of the solvability condition (A7) to (A8) uniquely determines σ_1. In particular, we have that

$$\sigma_1 \left(\rho^I B^I A^I + \rho^{II} B^{II} A^{II}\right) + \rho^I B^I A^I U_0 = 0$$

It follows that $\sigma_1 = -U_{eff}$, where

$$U_{eff} = \lambda U_0,$$

and λ is defined in (1.2). In the definition of λ we used k_b from (1.3) and in the definition of k_b we used δ from (1.4). We also used the relation $K = B^{II}/B^I$ from (2.6).

Once we have chosen σ_1 so the compatibility condition is satisfied, we can solve (A8). Using our given value for σ_1 we arrive at (3.4) given in §3. We can add an arbitrary constant to this solution, but it will not effect the next stage of our analysis.

A.3 Second Order - The Effective Diffusion Coefficient

Collecting the terms to order k^2, we get

$$\alpha^I \nabla_2^2 \mathcal{A}_2^I = \sigma_2 \rho^I B^I + \alpha^I - \rho^I B^I \left(\sigma_1 + U_0 f(x,y)\right) \mathcal{A}_1^I \quad \text{in } \Omega^I, \tag{A9a}$$

$$\alpha^{II} \nabla_2^2 \mathcal{A}_2^{II} = \sigma_2 \rho^{II} B^{II} + \alpha^{II} - \rho^{II} B^{II} \sigma_1 \mathcal{A}_1^{II} \quad \text{in } \Omega^{II}. \tag{A9b}$$

All of the terms in the right hand side of this expression are already known, except for σ_2. As we did with σ_1, we can determine σ_2 by applying the solvability conditions (A7) to (A9). After some simple manipulations we get

$$\sigma_2 = -D_{eff},$$

where D_{eff} is as given in (3.1), and J is given by

$$J = -\frac{1}{\alpha^I A^I}\left(\int_{\Omega^I} \rho^I B^I \left(\sigma_1 + U_0 f\right)\mathcal{A}_1^I dA + \int_{\Omega^{II}} \rho^{II} B^{II} \sigma_1 \mathcal{A}_1^{II}\right).$$

Using the fact that $\mathcal{A}_1^I$, $\mathcal{A}_1^{II}$ satisfy (A9), this expression be written as (3.2). If we integrate (3.2) by parts and apply the boundary conditions, we arrive at (3.3).

B The Terms I_1, I_2, I_3

In this appendix we supply the details for the derivation of (3.8) and (3.9)-(3.11).

We begin by rewriting (A8a) as

$$\alpha^I \nabla_2^2 \mathcal{A}_1^I = \rho^I B^I U_0 \left(f(x,y) - 1\right) + \rho^I B^I \left(\sigma_1 + U_0\right) \quad \text{in } \Omega^I. \tag{B1}$$

Application of the solvability condition (A7) to this equation and (A8a) gives the relation $\rho^I B^I \left(\sigma_1 + U_0\right) A^I + \rho^{II} B^{II} \sigma_1 A^{II} = 0$. This allows us to rewrite (A8a) so that equations (A8) become

$$\alpha^I \nabla_2^2 \mathcal{A}_1^I = \rho^I B^I U_0 \left(f(x,y) - 1\right) - \rho^{II} B^{II} \sigma_1 \delta \quad \text{in } \Omega^I, \tag{B2}$$

$$\alpha^{II} \nabla_2^2 \mathcal{A}_1^{II} = \rho^{II} B^{II} \sigma_1 \quad \text{in } \Omega^{II}. \tag{B3}$$

We then split up the solution of this problem into

$$\mathcal{A}_1^i = \frac{\rho^{II} B^{II}}{\alpha^I} \sigma_1 \phi^i + \frac{\rho^I B^I U_0}{\alpha^I} \psi^i = \frac{U_0}{D^I} \left(-\frac{K\lambda \rho^{II}}{\rho^I} \phi^i + \psi^i \right) \quad i = I, II, \tag{B4}$$

where ϕ^i satisfies (3.6), and ψ^i satisfies (3.7). Here we used $\beta = \frac{\alpha^{II}}{\alpha^I}$. Note that both of these sets of equations satisfy the solvability condition (A7).

If we substitute (3.5) into (3.3), we get

$$J = Pe^2 \mathbf{t}^T \mathbf{S} \mathbf{t}, \tag{B5}$$

where the Péclet number Pe is defined in (1.6),

$$\mathbf{S} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}, \qquad \mathbf{t} = \begin{bmatrix} -\frac{\rho^{II} K\lambda}{\rho^I} \\ 1 \end{bmatrix},$$

and

$$\begin{aligned}
(A^I)^2 S_{11} &= \int_{\Omega^I} \left(\nabla \phi^I\right) \cdot \left(\nabla \phi^I\right) dA + \beta \int_{\Omega^{II}} \left(\nabla \phi^{II}\right) \cdot \left(\nabla \phi^{II}\right) dA \\
&= -\int_{\Omega^I} \phi^I \nabla_2^2 \phi^I dA - \beta \int_{\Omega^{II}} \phi^{II} \nabla_2^2 \phi^{II} dA, \\
(A^I)^2 S_{22} &= \int_{\Omega^I} \left(\nabla \psi^I\right) \cdot \left(\nabla \psi^I\right) dA + \beta \int_{\Omega^{II}} \left(\nabla \psi^{II}\right) \cdot \left(\nabla \psi^{II}\right) dA \\
&= -\int_{\Omega^I} \psi^I \nabla_2^2 \psi^I dA - \beta \int_{\Omega^{II}} \psi^{II} \nabla_2^2 \psi^{II} dA, \\
(A^I)^2 S_{12} = (A^I)^2 S_{21} &= \int_{\Omega^I} \left(\nabla \phi^I\right) \cdot \left(\nabla \psi^I\right) dA + \beta \int_{\Omega^{II}} \left(\nabla \phi^{II}\right) \cdot \left(\nabla \psi^{II}\right) dA \\
&= -\int_{\Omega^I} \phi^I \nabla_2^2 \psi^I dA - \beta \int_{\Omega^{II}} \phi^{II} \nabla_2^2 \psi^{II} dA.
\end{aligned}$$

Using the governing equations (3.6) for ϕ and (3.7) for ψ, these expressions can be simplified to

$$S_{11} = I_1, \tag{B6a}$$

$$S_{12} = S_{21} = -\frac{I_2}{2}, \tag{B6b}$$

$$S_{22} = I_3. \tag{B6c}$$

where I_1, I_2 and I_3 are given in (3.9), (3.10), and (3.11).

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