

Chapter 2

Reaction–Advection– Dispersion Equation

A problem of great importance in environmental science is to understand how chemical or biological contaminants are transported through subsurface aquifer systems. In this chapter we consider the transport of a chemical or biological tracer carried by water through a uniform, one-dimensional, saturated, porous medium, and we derive simple mathematical models based on mass balance that incorporate advection, dispersion, and adsorption. Thus, we extend the ideas in the Chapter 1, where we focused only on the diffusion process with no flow.

The approach we take is the traditional continuum mechanics approach. Each variable, for example, density, is viewed in a mathematical sense as an idealized point function over the domain of interest. Both physically and mathematically, the values these point functions take are regarded as averages over small elementary, or representative, volume elements. The models we develop are also highly deterministic. This means they contain coefficients and functions that are regarded as completely known. In fact, the opposite may be true. There is a natural variability of nature that lends itself to an alternate approach, namely, a stochastic approach. For example, the soil conductivity, which characterizes how fast fluid can be transported through the soil fabric, is a highly variable quantity because of the ever present heterogeneities in the subsurface; one could view it as a random variable with a constant mean value over which is superimposed random spatial “noise.” But this will not be the view here; this kind of random variability is not in deterministic models. Continuum-based, deterministic models include some variability, but it is disguised in through phenomenological equations obtained by the averaging process.

A complicating factor in subsurface modeling is the variability caused by the presence of several spatial scales. Aquifers can be of the order of 10^4 meters, or larger, while heterogeneities within the aquifer can range over $10^{-2} - 10^2$

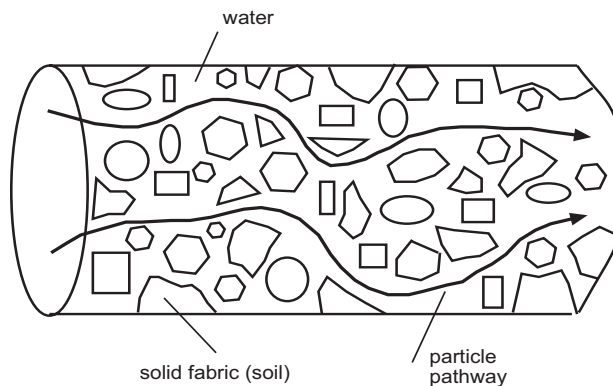


Figure 2.1: A one-dimensional porous medium showing the solid fabric, or grains, and the interstitial spaces, or pores.

meters. The pores themselves can be as small as 10^{-4} meters, while adhesive water layers, important in adsorption, may be 10^{-7} meters thick. Whether a stochastic or deterministic model is more valid is not the issue; rather, the goal is to develop a predictive model that captures the essential features of the physical processes involved.

2.1 Mass Balance

We imagine that water is flowing underground through a fixed soil or rock matrix; this soil or rock matrix, which is composed of solid material, will also be referred to as the **fabric** that makes up the porous medium. In any fixed volume, the fraction of space, called the pore space, available to the water is assumed to be ω , which is called the **porosity** of the medium. Clearly, $0 < \omega < 1$. In general, the porosity can vary with position, or even pressure, but in this chapter we assume ω is constant throughout the medium. When we say the porosity is constant, that means we are observing from a distance where there is uniformity in the porosity. If we looked on a small scale, the porosity would be either zero or one; but here we assume the representative volume element is on an order where averages of percentage pore space are constant over the entire medium. Furthermore, we assume that the flow is **saturated**, which means that all of the available pore space is always filled with fluid. There are, of course, many fuzzy issues here; for example, do we count dead end pores, where the water is trapped, as part of the pore space? Generally, no; the pore space is that space where there is mobile water. We will refer this, and other similar questions, to texts on hydrogeology [see, e.g., deMarsily (1986)]. Again, our goal is to develop simple, phenomenological mathematical models, and often some of the fine detail is omitted.

We will assume that the flow is one-dimensional, in the x -direction, and takes place in a tube of cross-sectional area A (see figure 2.1). Assuming the areal porosity is the same as the volume porosity, the cross-sectional area actually available for flow is ωA . Now let $C(x, t)$ be the concentration, measured in mass per unit volume of water, of a chemical or biological tracer dissolved in the liquid, and let $Q(x, t)$ denote its **flux**, or the rate per unit area that the contaminant mass crosses a cross section at x . We are assuming that the contaminant, for example, ions, has no volume itself and therefore does not affect the volume of the carrying liquid. We further assume that the tracer is created or destroyed with rate $F(x, t)$, measured in mass per unit volume of porous medium, per unit time. For example, F , which we call a **reaction term** or **source term**, can measure an adsorption rate, a decay rate, a rate of consumption in a chemical reaction, or even a growth or death rate if the tracer is biological. Note that the source Q can depend upon x and t through its dependence on C , i.e., $F = F(C)$. Finally, we denote by V the specific discharge, or the volume of water per unit area per unit time that flows through the medium. Note that V has velocity units, and for the present discussion we assume V is *constant*. Later we investigate the driving mechanism of the flow and set aside this constant assumption; for now we assume there is a driving mechanism that is able to maintain a constant velocity flow. We call V the **Darcy velocity**. The velocity $v \equiv V/\omega$ is called the **average velocity**; v is the velocity that would be measured by a flow meter in the porous domain. Clearly, the average velocity exceeds the Darcy velocity. Subsequently, in a constitutive equation, we shall relate the flux to the Darcy velocity. Note that we have taken the concentration to be measured in mass per unit volume. The reader should be aware that in other contexts the concentration could be measured in molarity (moles per unit volume of fluid) or molality (moles per unit mass of fluid). Recall that a mole is the mass unit equal to the molecular weight.

The basic physical law for flow in a porous medium is derived from mass balance of the chemical tracer. Mass balance states that the rate of change of the total mass in an arbitrary section of the medium must equal the net rate that mass flows into the section through its boundaries, plus the rate that mass is created, or destroyed, within the section. Therefore, consider an arbitrary section $a \leq x \leq b$ of the medium. Mass balance, written symbolically, leads directly to the integral conservation law

$$\frac{d}{dt} \int_a^b C(x, t) \omega A dx = Q(a, t)A - Q(b, t)A + \int_a^b F(x, t) A dx. \quad (2.1)$$

The term on the left-side is the rate of change of the total amount of tracer in the section, and the first two terms on the right measure the rate that the tracer flows into the section at $x = a$ and the rate that it flows out at $x = b$; the last term is the rate that the tracer is created in the section. We assume that C and ϕ are continuously differentiable functions; thus, we may bring the time derivative under the integral sign and appeal to the fundamental theorem

of calculus to write the mass balance law as

$$\int_a^b (\omega C_t + Q_x - F) dx = 0.$$

Because the interval of integration $[a, b]$ is arbitrary, the integrand must vanish and we obtain the mass balance law in the local, differential form

$$\omega C_t + Q_x = F. \quad (2.2)$$

Some treatments on hydrogeology measure F in units of mass per time per unit volume of water, rather than per unit volume of porous medium; then there will be an ωF term on the right-side of (2.2).

At this point, a constitutive relation, usually based in empirics, must be postulated regarding the form of the flux Q . We should ask how dissolved particles get from one place to another in a porous medium. There are three generally accepted ways. One way is by **advection**, which means that particles are simply carried by the bulk motion of the fluid. This leads us to define the **advective flux** $Q^{(a)}$ by

$$Q^{(a)} = VC,$$

which is just the product of the velocity and concentration. Another method of transport is by **molecular diffusion**. This is the spreading caused by the random molecular motion and collisions of the particles themselves. This is precisely the type of diffusion discussed in Chapter 1; there we stated that this type of motion is driven by concentration gradients and the flux due to diffusion is given by Fick's law. We call this the **molecular diffusion flux** $Q^{(m)}$ and we take

$$Q^{(m)} = -\omega D^{(m)} C_x.$$

$D^{(m)}$ is the **effective molecular diffusion coefficient** in the porous medium. The diffusion occurs in a liquid phase enclosed by the solid porous fabric. The solid boundaries hinder the diffusion, and therefore $D^{(m)}$ is smaller than the usual molecular diffusion coefficient D_0 that one would measure in an immobile liquid with no solid boundaries. The reduction in the diffusion coefficient is therefore caused by the structure of the porous fabric and the presence of the tortuous flow paths available to the fluid. The ratio $D^{(m)}/D_0$ is often called the **tortuosity** of the medium and varies roughly from 0.1 to 0.7. Molecular diffusion is present whether or not the fluid is moving.

There is a third contribution to the particle flux called **kinematic** (or, **mechanical**) **dispersion**. This is the spreading, or mixing phenomenon, caused by the variability of the complex, microscopic velocities through the pores in the medium. So, it is linked to the heterogeneities present in the medium and is present only if there is flow. The idea is that different flow pathways have different velocities and some have a greater than average velocity to carry the solutes ahead of a position based only on the mean velocity. The mathematical form of the dispersion flux $Q^{(d)}$ is taken to be Fickian and given by

$$Q^{(d)} = -\omega D^{(d)} C_x,$$

where $D^{(d)}$ is the **dispersion coefficient**. Thus, the net flux is given by the sum of the advective, molecular, and dispersion fluxes:

$$\begin{aligned} Q &= Q^{(a)} + Q^{(m)} + Q^{(d)} \\ &= VC - \omega(D^{(m)} + D^{(d)})C_x. \end{aligned}$$

If we define the **hydrodynamic dispersion coefficient** D by

$$D = D^{(m)} + D^{(d)},$$

then the net flux is given simply as

$$Q = VC - \omega DC_x.$$

The Fickian term $-\omega DC_x$ is termed the **hydrodynamic dispersion**. It consists of molecular diffusion and kinematic dispersion.

To summarize, when there is no flow velocity, the only flux is molecular diffusion. When there is flow, we get advection and dispersion as well. So, if there is a “plume” of contaminant in the subsurface, we expect it to advect with the bulk motion of the fluid and spread out from diffusion and dispersion. Thus, dispersion adds a spreading effect to the diffusional effects. Generally, it is observed in three dimensions that the spreading caused by dispersion is greater in the direction of the flow than in the transverse directions. If no dispersion were present, a spherical plume would just spread uniformly as it advected with the flow. This means that in a higher-dimensional formulation of the equations, the hydrodynamic dispersion would be different in different directions.

Because dispersion is present in moving fluids, it has been an important exercise to determine how the dispersion coefficient depends on the velocity of the flow. Experiments have identified several flow regimes where different mechanisms dominate. These flow regimes are usually characterized by the Peclet number

$$Pe = \frac{|V|l}{\omega D_0},$$

where l is an intrinsic length scale, say the mean diameter of pores. For very low velocity flows, i.e., very small Peclet numbers, molecular diffusion dominates dispersion. As the Peclet number increases, both processes are comparable until dispersion begins to dominate and diffusion becomes negligible; this occurs for approximately $Pe > 10$. Generally, for many velocities of interest, experimenters propose, in the direction of the flow, the linear constitutive relationship

$$D^{(d)} = \alpha_L |V|,$$

where α_L is the **longitudinal dispersivity**. In transverse directions to the flow, the dispersion coefficient is taken to be $\alpha_T |V|$, where the transverse dispersivity α_T is roughly an order of magnitude smaller than the longitudinal dispersivity. If we make these assumptions, the hydrodynamic dispersion coefficient in one-dimensional flow can be written

$$D = D^{(m)} + \alpha_L |V|.$$

When the velocity is small, the dispersion is negligible, and when the velocity is large, the dispersion will dominate the diffusion. Details of experiments and numerical values of the Peclet number ranges and dispersivities can be found in hydrogeology texts [see deMarsily (1986) or Domenico and Schwartz (1990)].

Combining the constitutive relations with the mass balance law (2.2) gives the fundamental **reaction-advection-dispersion equation**

$$\omega C_t = (\omega DC_x)_x - VC_x + F. \quad (2.3)$$

If D is constant, then D can be pulled out of the derivative and we can write

$$C_t = DC_{xx} - vC_x + \omega^{-1}F.$$

We remark that geologists, civil engineers, mathematicians, and so on, frequently use different terminology in describing the phenomena embodied in equation (1.3). Thus, advection is often termed convection, and dispersion is replaced with diffusion. The reaction term F is a source. Therefore, equation (2.3) is sometimes called a reaction-convection-diffusion equation, or a convection-diffusion equation with sources.

Observe that special cases of equation (2.3) are the **dispersion (or diffusion) equation**,

$$C_t = DC_{xx},$$

which was the subject of Chapter 1, and the simple **advection equation**

$$C_t = -vC_x.$$

The advection equation has a general solution of the form of a **right-traveling wave**

$$C(x, t) = U(x - ct),$$

where U is an arbitrary function. These types of solutions are the subject of Chapter 3.

Example 28 *If the tracer is radioactive with decay rate λ , then $F = -\lambda\omega C$ and we obtain the linear **advection-dispersion-decay equation***

$$C_t = DC_{xx} - vC_x - \lambda C.$$

A change of dependent variable to $w = Ce^{\lambda t}$ leads to an equation without the decay term, and a transformation of independent variables to $\tau = t$, $\xi = x - vt$ eliminates the advection term. Hence, the advection-dispersion-decay equation can be transformed into a simple diffusion equation. The complete transformation is

$$c(x, t) = w(x, t)e^{\frac{v}{2D}(x-vt) - \lambda t},$$

which gives $w_t = Dw_{xx}$.

Example 29 If the tracer is a biological species with **logistic growth** rate $F = rC(1 - C/K)$, where r is the growth constant and K is the carrying capacity, then

$$C_t = DC_{xx} - vC_x + \frac{r}{\omega}C \left(1 - \frac{C}{K}\right),$$

which is an advection-dispersion equation with growth.

2.2 Several Dimensions

Now let us consider a porous domain Ω in \mathbb{R}^3 . Before stating the mass balance law we briefly review some notation. Points in \mathbb{R}^3 are denoted by $x = (x_1, x_2, x_3)$ or just (x, y, z) . Because of the context, there should be no confusion in using x sometimes as a point and other times as a coordinate. A volume element is $dx = dx_1 dx_2 dx_3$. Volume integrals over Ω are denoted by

$$\int_{\Omega} f(x) dx,$$

and flux integrals over the surface $\partial\Omega$ of Ω are denoted by

$$\int_{\partial\Omega} Q \cdot ndA.$$

Here, f is a scalar function, Q is a vector function,¹ and n is the outward unit normal. Note that we are dispensing with writing triple and double integrals.

If we apply mass balance to an arbitrary ball (spherical region) Ω' in Ω , the integral conservation law takes the form

$$\frac{d}{dt} \int_{\Omega'} \omega C dx = - \int_{\partial\Omega'} Q \cdot ndA + \int_{\Omega'} F dx, \quad (2.4)$$

where $\partial\Omega'$ denotes the surface of the ball Ω' . Here, n is the outward unit normal vector the concentration is $C = C(x, t)$, where $x \in \mathbb{R}^3$, and the flux vector is Q . As in one dimension, equation (2.4) states that the rate of change of solute in the ball equals the net flux of solute through the surface of the ball plus the rate that solute is produced in the ball. The divergence theorem allows us to rewrite the surface integral and (2.4) becomes

$$\frac{d}{dt} \int_{\Omega'} \omega C dx = - \int_{\Omega'} \nabla \cdot Q dx + \int_{\Omega'} F dx.$$

Owing to the arbitrariness of the domain Ω' , we obtain the local form of the conservation law as

$$(\omega C)_t = -\nabla \cdot Q + F, \quad x \in \Omega.$$

¹We shall not use special notation for vectors; whether a quantity is a vector or scalar will be clear from the context.

Here we are assuming that the functions are sufficiently smooth to allow application of the divergence theorem and permit pulling the time derivative inside the integral. As in the one-dimensional case we have too many unknowns, and so additional equations, in the form of constitutive relations, are needed. In particular, we assume that the vector flux is made up of a dispersive-diffusion term and an advective term and is thus related to the concentration via

$$Q = -\omega D \nabla C + CV,$$

where V is the vector Darcy velocity and D is the hydrodynamic dispersion coefficient. Then the mass balance law becomes

$$\omega C_t = \nabla \cdot (\omega D \nabla C) - \nabla \cdot (CV) + F.$$

If the flow is incompressible, then $\nabla \cdot V = 0$ and we obtain

$$\omega C_t = \nabla \cdot (\omega D \nabla C) - V \cdot \nabla C + F, \quad (2.5)$$

which is the **reaction–advection–dispersion equation** in three dimensions. If the dispersion coefficient D is a pure constant, then it may be brought out of the divergence and we obtain the equation in the form

$$C_t = D \Delta C - v \cdot \nabla C + \omega^{-1} F,$$

where Δ is the three-dimensional Laplacian operator (recall the vector identity $\Delta C = \nabla \cdot \nabla C$) and $v = V/\omega$ is the average velocity vector.

In general, the dispersion coefficient D in (2.5) is not constant; in fact, usually $D = D(x, C)$, which means that it may depend on position if the medium is nonhomogeneous or even the concentration. Furthermore, it may have different values in different directions if the medium is not isotropic. In the special case that the hydrodynamic dispersion coefficient varies in the coordinate directions we have

$$D = \text{diag}(D^{(x)}, D^{(y)}, D^{(z)}),$$

which is a diagonal matrix. Then the mass balance law is expanded to

$$\omega C_t = (\omega D^{(x)} C_x)_x + (\omega D^{(y)} C_y)_y + (\omega D^{(z)} C_z)_z - V \cdot \nabla C + F.$$

In many hydrogeological applications the flow field and geometry lends itself to a description in cylindrical coordinates. This occurs, for example, in the pumping of wells and boreholes. In cylindrical geometry the mass balance equation (2.5) can be written as

$$C_t = \frac{1}{r} (r D^{(r)} C_r)_r + \frac{1}{r^2} (D^{(\theta)} C_\theta)_\theta + (D^{(z)} C_z)_z - \nabla \cdot (Cv) + \omega^{-1} F,$$

where we have used the fact that the gradient operator is

$$\nabla = (\partial_r, \frac{1}{r} \partial_\theta, \partial_z),$$

and the average velocity is $v = (v^{(r)}, v^{(\theta)}, v^{(z)})$ in cylindrical coordinates. The quantities $D^{(r)}, D^{(\theta)}, D^{(z)}$ represent the hydrodynamic dispersion coefficients in the coordinate directions. [Expressions for the divergence, gradient, and Laplacian in various coordinate systems can be found in many calculus texts, texts in fluid mechanics or electromagnetic theory. A good reference is Bird, Stewart, and Lightfoot (1960). See also Sun (1995) for a general formulation in orthogonal curvilinear coordinates].

An important case of this latter equation occurs when the velocity field is radial, i.e., $v = (v^{(r)}, 0, 0)$, and there is negligible dispersion in the vertical or angular directions, i.e., $D^{(z)} = D^{(\theta)} = 0$. Then we obtain the radial reaction-advection-dispersion equation

$$C_t = \frac{1}{r}(rD^{(r)}C_r)_r - v^{(r)}C_r - \frac{C}{r}(rv^{(r)})_r + \omega^{-1}F.$$

Specifically, if the radial velocity is

$$v^{(r)} = \frac{a}{r},$$

then the velocity field is divergence-free and the radial equation becomes

$$C_t = \frac{1}{r}(rD^{(r)}C_r)_r - \frac{a}{r}C_r + \omega^{-1}F.$$

Using the constitutive assumption that the kinematic dispersion coefficient is proportional to the magnitude of the velocity and diffusion is negligible, that is, $D^{(r)} = \alpha_r||v|| = a\alpha_r/r$, we have

$$C_t = \frac{a\alpha_r}{r}C_{rr} - \frac{a}{r}C_r + \omega^{-1}F. \quad (2.6)$$

We can think of equation (2.6) as modeling the transport of a contaminant in a radial flow field. If $a < 0$, then the flow is toward an extraction well and the equation models a **remediation process**; if $a > 0$, then the flow is radially outward from a well and the process is a **contamination process**. The value of a depends on the pumping rate. In Section 2.5 we solve a special radial dispersion problem.

Boundary conditions on the concentration are also a necessary ingredient in model formulation. We discuss different types of boundary conditions in Section 2.7.

2.3 Adsorption Kinetics

Several geochemical mechanisms can change the character of transported substances through porous domains. One such important mechanism is **adsorption**. Adsorption is a process, often brought on by ion exchange, that causes the mobile tracer, or solute, to adhere to the surface of the solid porous fabric, and thus become immobile. To model such processes in one dimension we let

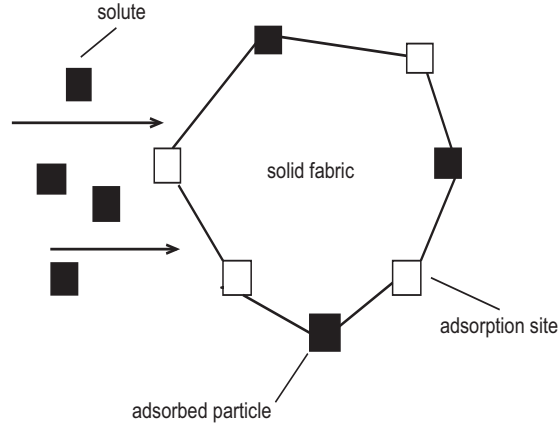


Figure 2.2: Solute-site-adsorbed particle reaction.

$S = S(x, t)$ denote the amount of solute adsorbed. Because the solutes become attached to mineral particles, this amount S of solute adsorbed is usually measured in mass of solute per unit mass of soil. The mass of soil per unit volume of porous medium is $\rho(1 - \omega)$ and therefore the rate of adsorption is given by

$$F = -\rho(1 - \omega)S_t.$$

Consequently, under the assumption of constant D , the mass balance equation (2.3) becomes

$$C_t = DC_{xx} - vC_x - \frac{\rho(1 - \omega)}{\omega}S_t, \quad (2.7)$$

which is the **adsorption-advection-dispersion** equation. In Chapter 5 we examine different kinds of geochemical reactions, namely, those that change the mineralogy of the host rock and even change the porosity of medium.

2.3.1 Instantaneous Kinetics

In the simplest case we can envision the adsorption process as a reversible chemical reaction where one adsorption site on the solid reacts with a solute particle to produce an adsorbed particle. The reversibility of the reaction means that, in a strict sense, the process is an adsorption-desorption process. A schematic is shown in figure 2.2, and we represent the reaction as



Here σ denotes the density of adsorption sites on the immobile solid fabric.

If the number of adsorption sites is large, then we may take σ to be constant. Then the law of mass action states that the reaction rate is

$$r = k_f \sigma C - k_b S,$$

where k_f and k_b are the forward and backward rate constants, respectively. If we assume that the reaction equilibrates on a fast time scale compared to that of dispersion and advection, then the reaction is always in equilibrium ($r \equiv 0$), or

$$S = K_d C, \quad (2.8)$$

where $K_d \equiv k_f \sigma / k_b$. Thus, there is an instantaneous, algebraic, linear relation between the concentration of solute and the concentration of adsorbed particles. Equation (2.8) is called a **linear adsorption isotherm** and K_d is the **distribution constant** (a typical value is $K_d = 0.476 \mu\text{gm/gm}$). Substituting (2.8) into (2.7) yields, after rearrangement, an advection–dispersion equation

$$R_f C_t = DC_{xx} - vC_x, \quad (2.9)$$

where R_f is the **retardation constant** given by

$$R_f = 1 + \frac{\rho K_d (1 - \omega)}{\omega}.$$

Thus, a linear adsorption process reduces the apparent speed of advection to v/R_f . The literature in hydrogeology is full of closed-form, or analytic, solutions to this equation with various initial and boundary data.

If there is a limited number of adsorption sites with density σ_0 , then

$$S + \sigma = \sigma_0,$$

and the equilibrium condition is $R = k_f(\sigma_0 - S)C - k_b S = 0$, or

$$S = \frac{k_f \sigma_0 C}{k_f C + k_b}. \quad (2.10)$$

This relationship is the **Langmuir adsorption isotherm**. Now the mass balance equation (2.7) is nonlinear and given by

$$\left(C + \frac{\rho(1 - \omega)}{\omega} \frac{k_f \sigma_0 C}{k_f C + k_b} \right)_t = DC_{xx} - vC_x. \quad (2.11)$$

In general, if the reaction equilibrates on a time scale that is fast compared to that of advection and dispersion, then we assume an algebraic relationship between the solute concentration C and the adsorbed concentration S . Such relations, which hold in an equilibrium state, are said to be instantaneous and define the adsorption kinetics. The algebraic relationship, called the **adsorption isotherm**, often takes the form

$$S = f(C), \quad (2.12)$$

where the function f usually has the properties:

$$f \in C^2(0, \infty); \quad f(0) = 0; \quad f'(C) > 0, \quad f''(C) < 0 \text{ for } C > 0. \quad (2.13)$$

For some isotherms $f'(0)$ may not exist, as in the case of the Freundlich isotherm below.

In addition to the linear and the Langmuir isotherms, (2.8) and (2.10), respectively, other adsorption isotherms are suggested in the literature. A partial list is the following:

$$\begin{aligned} S &= K_d C, && \text{(linear)} \\ S &= \frac{k_f \sigma_0 C}{k_f C + k_b} && \text{(Langmuir)} \\ S &= k C^{1/n}, \quad n > 1 && \text{(Freundlich)} \\ S &= k_1 C - k_2 C^2 && \text{(quadratic)} \\ S &= \frac{k_1 C^m}{1 + k_2 C^m} && \text{(generalized Langmuir)} \\ S &= k_1 e^{-k_2/C} && \text{(exponential)} \end{aligned}$$

The Freundlich isotherm is one widely applied to the adsorption of various metals and organic compounds in soils. Unfortunately there is no upper limit to the amount of solute that can be adsorbed, so the Freundlich isotherm must be used with caution in experimental studies.

In summary, with kinetics given by (2.12), the mass balance equation takes the form

$$(C + \beta f(C))_t = DC_{xx} - vC_x,$$

or, equivalently,

$$(1 + \beta f'(C))C_t = DC_{xx} - vC_x, \quad (2.14)$$

where $\beta = \rho(1 - \omega)/\omega$ and f satisfies the conditions (2.13).

2.3.2 Noninstantaneous Kinetics

If the reaction proceeds so slowly that it does not have time to come to local chemical equilibrium, then the kinetics of adsorption-desorption is not instantaneous and requires a dynamic rate law for its description. Such a law has the form

$$S_t = F(S, C). \quad (2.15)$$

So the rate of adsorption depends on both C and S . We could reason, for example, that the adsorption rate should increase as the concentration C of solute increases ($F_C \geq 0$); but, as more and more chemical is adsorbed, the ability of the solid to adsorb additional chemical will decrease ($F_S \leq 0$). The simplest such model with these characteristics is

$$S_t = F(S, C) = k_1 C - k_2 S, \quad k_1, k_2 > 0.$$

For nonequilibrium adsorption–desorption, solute–soil reactions, the coupled pair of equations

$$C_t = DC_{xx} - vC_x - \frac{\rho(1-\omega)}{\omega}S_t, \quad (2.16)$$

$$S_t = F(S, C) \quad (2.17)$$

form a general model. We shall always assume that

$$F_C \geq 0, \quad F_S \leq 0. \quad (2.18)$$

Exercise 30 For the linear system

$$C_t = DC_{xx} - vC_x - \beta S_t, \quad \beta \equiv \frac{\rho(1-\omega)}{\omega} \quad (2.19)$$

$$S_t = k_1 C - k_2 S, \quad (2.20)$$

eliminate S to obtain a single equation for C by the following scheme. Substitute (2.20) into (2.19) and then take the time derivative to get

$$C_{tt} = DC_{xxt} - vC_{xt} - \beta(k_1 C_t - k_2 S_t).$$

Then multiply (2.19) by k_2 and subtract the result from the last equation to obtain

$$C_{tt} + (\beta k_1 - k_2)C_t = DC_{xxt} - k_2 DC_{xx} - vC_{xt} + vk_2 C_x.$$

This is a third-order differential equation for the concentration C . It can be compared with the wave equation with internal damping

$$u_{tt} = c^2 u_{xx} + au_{xxt}$$

[see, for example, Guenther and Lee (1991)].

Example 31 In the case that the transported particles are colloids, Saiers, et al. (1994) have given a kinetics law of the form

$$S_t = \frac{\omega K_d}{\rho_b} C \frac{a-S}{a} - kS,$$

where ρ_b is the bulk density of the solid fabric, k is the entrainment coefficient, a is the colloidal retention capacity. [A mathematical analysis of this model can be found in Cohn and Logan (1995)].

2.3.3 Multiple-Site Kinetics

In some cases attachment of the solute to soil particles can occur in different ways with different kinetics. For example, such differences can arise because of different adsorption behavior of planar sites and edge sites on the soil. Or, different adsorption sites may have different accessibility. Let us assume there

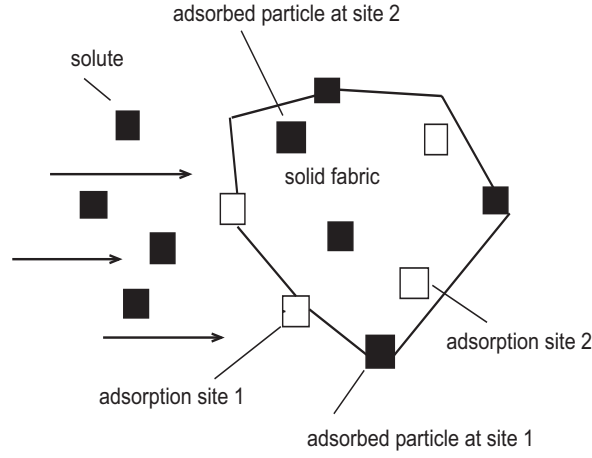
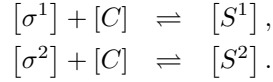


Figure 2.3: Solute-particle reaction for multiple sites represented schematically by interior and surface locations.

are two ensembles of adsorption sites represented by densities σ^1 and σ^2 . See figure 2.3.

Let $S^1 = S^1(x, t)$ and $S^2 = S^2(x, t)$ denote the concentrations of adsorbed material at sites 1 and 2, respectively. The reaction can be represented symbolically by



The net rate of adsorption is $S_t = (S^1 + S^2)_t$ and therefore the adsorption-advection-dispersion equation becomes

$$C_t = DC_{xx} - vC_x - \frac{\rho(1-\omega)}{\omega}(S_t^1 + S_t^2).$$

In the case both reactions are in local chemical equilibrium we supplement this equation with the two isothermal relations

$$S^1 = f_1(C), \quad S^2 = f_2(C).$$

If both are slow to equilibrate, then we have

$$S_t^1 = F_1(C, S^1), \quad S_t^2 = F_2(C, S^2).$$

In the mixed case where the first reaction equilibrates rapidly and the second equilibrates slowly, we have

$$S^1 = f_1(C), \quad S_t^2 = F_2(C, S^2).$$

2.4 Dimensionless Equations

Generally, in applied mathematics we study equations in their dimensionless form. Not only does the dimensionless model usually contain fewer parameters, but in applying perturbation methods to obtain approximations it is essential to scale the problem properly so that small parameters are correctly placed in the governing equations [see Lin and Segel (1989) or Logan (1997c) for a general discussion of the importance of scaling and dimensional analysis]. If L is some length scale for the problem, then, unless otherwise noted, we select the time scale to be L/v , which is the **advection time scale**. Other time scales can be chosen, for example, one based on diffusion or one based on the reaction rate. Concentrations can be scaled by some reference concentration C_0 , which could be the maximum initial or boundary concentration at an inlet. Therefore, we introduce dimensionless space, time, and concentration variables via

$$\xi = \frac{x}{L}, \quad \tau = \frac{t}{L/v}, \quad u = \frac{C}{C_0}.$$

Then the reaction–advection–dispersion model

$$C_t = DC_{xx} - vC_x + \omega^{-1}F$$

becomes

$$u_\tau = \alpha u_{\xi\xi} - u_\xi + f,$$

where

$$\alpha \equiv Pe^{-1} = \frac{D}{vL}, \quad q \equiv \frac{L}{\omega v C_0} F$$

are dimensionless quantities. Here, α is the reciprocal of what is called the **Peclet number**, which measures the ratio of advection to dispersion; q is the source term and u is the dimensionless concentration. Usually, we will just use x and t for the dimensionless spatial and time variables in place of ξ and τ and write the **reaction–advection–dispersion model** as

$$u_t = \alpha u_{xx} - u_x + q. \quad (2.21)$$

In the same manner, we will write the **equilibrium model** (2.7) and (2.12) in dimensionless form as

$$u_t = \alpha u_{xx} - u_x - \beta s_t, \quad (2.22)$$

$$s = f(u). \quad (2.23)$$

Here s is the dimensionless adsorbed concentration (scaled by C_0) and $\beta > 0$ is a dimensionless constant. The dimensionless **nonequilibrium model** (2.16)–(2.17) is

$$u_t = \alpha u_{xx} - u_x - \beta s_t, \quad (2.24)$$

$$s_t = F(u, s). \quad (2.25)$$

Observe that the equilibrium equation is of the form

$$g(u)_t = \alpha u_{xx} - u_x,$$

where $g(u) = u + \beta f(u)$. Because $g'(u) > 0$, we may define the one-to-one transformation $w = g(u)$. Then, if $u = h(w)$ is the inverse transformation, we have $u_x = h'(w)w_x$ and the equation may be written

$$w_t = \alpha(h'(w)w_x)_x - h'(w)w_x.$$

Thus we have succeeded in transforming the equilibrium equation to a uniformly parabolic equation.

Much is known about nonlinear **reaction–diffusion equations**, without advection, of the form

$$u_t = (k(u)u_x)_x + F(u).$$

For example, they are discussed in detail in Samarski *et al.* (1995). Such nonlinear models are commonplace in population dynamics and in combustion theory.

2.5 Nonlinear Equations

In the preceding sections we developed some of the basic nonlinear mathematical models in contaminant transport. We now illustrate, by way of examples, some of the elementary properties of nonlinear equations and techniques used to study them. These techniques include comparison methods, similarity methods, and energy methods. Later, in Chapter 3, we study traveling waves.

The partition of differential equations into linear and nonlinear models is a significant one. Linear equations are sometimes solvable; in any case, they have a form that permits the vast tools of linear analysis, or functional analysis, to be applied to determine their behavior and solution structure. Nonlinear equations are nearly always unsolvable by analytic methods, and to obtain specific solutions we nearly always resort to numerical methods. Generally, the tools of nonlinear analysis are not so nearly well-developed and all-encompassing as in linear analysis. Nevertheless, there are some general principles and techniques that are available that take us beyond just *ad hoc* methods.

We emphasize again that we are studying model equations. Using the term “model” helps us realize the distinction between reality and theory. Models do not include all of the details of the physical reality. In the best of all possible worlds, the model should give a reasonable description of some part of reality. This is why we often separate out the mechanisms and study equations only with diffusion or only with advection. Understanding the behavior of these simple models can then give us clues into the behavior of more general problems. For example, if we can show that some simple, model, nonlinear reaction–advection–dispersion equation has solutions that blow up (go to infinity, or have their derivatives go to infinity) at a finite time, then we have succeeded in creating a healthy skepticism about such equations. Therefore,

when we as applied scientists or mathematicians develop detailed descriptions of other, more complicated, systems, we will have insights into their behavior and may not unconsciously believe that our model has solutions that exist for all time. It is always tempting (and dangerous!) to believe that our descriptions of reality automatically lead to well-posed problems.

2.5.1 A Comparison Principle

In Section 1.5 we stated and proved a comparison principle for a linear parabolic equation. Such results extend to nonlinear equations. We begin with some terminology. Consider the partial differential equation

$$u_t = F(x, t, u, u_x, u_{xx}). \quad (2.26)$$

For notational simplicity, we denote $p = u_x$, $r = u_{xx}$, and we write the function F as $F = F(x, t, u, p, r)$. We assume that F is a continuously differentiable function of its five variables. We say the function F is **elliptic** with respect to a function $u = u(x, t)$ at a point (x, t) if

$$F_r(x, t, u, p, r) > 0 \quad \text{at } (x, t). \quad (2.27)$$

The function F is elliptic in a domain D of space time if it is elliptic at each point of D . If F is elliptic in D , then we say that equation (2.26) is **parabolic** in D . We say the function F is **uniformly elliptic** with respect to a function $u = u(x, t)$ in D if F_r is bounded away from zero; that is, there exists a positive constant μ such that

$$F_r(x, t, u, p, r) \geq \mu > 0 \quad \text{for all } (x, t) \in D. \quad (2.28)$$

In this case we say that equation (2.26) is **uniformly parabolic** in D . Although D may be quite general, we usually take $D = I \times (0, T)$, where I is an open interval in \mathbb{R} (possibly unbounded).

For example, if $D(u)$ is a nonnegative, continuously differentiable function and $H(u)$ is continuously differentiable, then the nonlinear advection–dispersion equation

$$u_t = (D(u)u_x)_x + H(u)_x \quad (2.29)$$

is parabolic for all functions u ; the parabolicity condition (2.27) becomes simply $D(u) > 0$. If the dispersion coefficient is bounded away from zero, that is, $D(u) \geq d_0 > 0$, then it is uniformly parabolic; in this case we say the equation (2.26) is **nondegenerate**. If the diffusion coefficient satisfies only the condition $D(u) > 0$, then we say the advection–dispersion equation (2.28) is **degenerate**.

Another example is the equilibrium model

$$g(u)_t = \alpha u_{xx} - u_x, \quad g(u) \equiv u + \beta f(u), \quad (2.30)$$

where the isotherm is positive, increasing, and concave downward, and $f(0) = 0$. As noted in Section 2.2, we can transform this equation to standard parabolic

form by letting $w = g(u)$. This mapping is one-to-one and invertible; we denote the inverse transformation by $u = h(w)$. Then the model (2.28) becomes

$$w_t = (\alpha h'(w)w_x)_x - h'(w)w_x,$$

where

$$h'(w) = \frac{1}{g'(u)} = \frac{1}{1 + \beta f'(u)}, \quad u = h(w).$$

Clearly, if $f'(0^+) = +\infty$, then $h'(0^+) = 0$ and the equation is degenerate.

Exercise 32 In the case of a Freundlich isotherm $f(u) = \sqrt{u}$, we have $f'(0^+) = 0$ and equation (2.30) is degenerate. Show that

$$h(w) = (\sqrt{(\beta/2)^2 + w} - \beta/2)^2,$$

which gives

$$h'(w) = \frac{\sqrt{\beta^2 + 4w} - \beta}{\sqrt{\beta^2 + 4w}}.$$

Note that $h'(0) = 0$.

Exercise 33 In the case of a Langmuir isotherm $f(u) = \frac{u}{1+u}$, show that

$$h'(w) = \frac{(1+u)^2}{\beta + (1+u)^2}.$$

Check that $h'(v) \geq 1/(1+\beta)$, so the equation (2.30) is nondegenerate.

Nonlinear parabolic equations of the form (2.26) admit what is called a **comparison principle**, which allows us to compare solutions to similar problems, say, differing only in their initial or boundary data. If one of the problems can be solved, then a comparison principle can give bounds on the solution to the problem that perhaps cannot be solved. This information can be used, for example, to prove positivity of solutions, to obtain asymptotic estimates of the behavior of solutions for large times, or produce a priori bounds that guarantee existence of solutions.

The basic comparison result can be stated as follows [see Protter and Weinberger (1967)]:

Theorem 34 Let I be a bounded spatial interval in \mathbb{R} and let $D = I \times (0, T]$, and let L denote the operator defined by

$$Lu \equiv u_t - F(x, t, u, u_x, u_{xx}).$$

Suppose that u, w , and W are continuous on the closure of D and twice continuously differentiable on D . Furthermore, assume that F is elliptic on D with respect to the functions $\theta w + (1-\theta)u$ and $\theta W + (1-\theta)u$ for all $0 \leq \theta \leq 1$. If

$$Lw \leq Lu \leq LW \quad \text{in } D,$$

and

$$w(x, 0) \leq u(x, 0) \leq W(x, 0) \quad x \in I,$$

and

$$w(x, t) \leq u(x, t) \leq W(x, t) \quad x \in \partial I, 0 \leq t \leq T,$$

then

$$w(x, t) \leq u(x, t) \leq W(x, t) \quad \text{in } D.$$

Example 35 Consider the initial boundary value problem

$$u_t = (D(u)u_x)_x - u_x, \quad x \in (a, b), t > 0, \quad (2.31)$$

$$u(x, 0) = u_0(x), \quad x \in (a, b), \quad (2.32)$$

$$u(a, t) = u_1(t), \quad u(b, t) = u_2(t), \quad t > 0, \quad (2.33)$$

where u_1, u_2 , and u_0 are nonnegative. Taking w to be the identically zero function $w \equiv 0$ shows that $u(x, t) \geq 0$, giving a positivity result for a classical solution $u(x, t)$.

Exercise 36 Consider the equilibrium model

$$g(u)_t = \alpha u_{xx} - u_x, \quad x \in (a, b), t > 0, \quad (2.34)$$

$$u(x, 0) = u_0(x), \quad x \in (a, b), \quad (2.35)$$

$$u(a, t) = u_1(t), \quad u(b, t) = u_2(t), \quad t > 0, \quad (2.36)$$

where $g(u) \equiv u + \beta f(u)$ and where u_0, u_1 , and u_2 are nonnegative. Show that this problem can be transformed into

$$w_t = (\alpha h'(w)w_x)_x - h'(x)w_x, \quad x \in (a, b), t > 0, \quad (2.37)$$

$$w(x, 0) = w_0(x), \quad x \in (a, b), \quad (2.38)$$

$$w(a, t) = ww_1(t), \quad w(b, t) = w_2(t), \quad t > 0, \quad (2.39)$$

where $w_0 = u_0 + \beta f(u_0) \geq 0, w_1 = u_1 + \beta f(u_1) \geq 0, w_2 = u_2 + \beta f(u_2) \geq 0$. Use the comparison principle to show that $w(x, t)$, and hence $u(x, t)$, is nonnegative.

The comparison principle can also be applied to prove a maximum principle for the equilibrium model (2.37)–(2.39). Let $m > 0$ be the maximum of the data $\{w_0, w_1, w_2\}$ for $x \in [a, b]$ or $t \in [0, T]$. Then, if w is a classical solution to (2.37)–(2.39), then

$$Lw \equiv w_t - (\alpha h'(w)w_x)_x + h'(x)w_x = 0 \leq L(m) = 0.$$

This implies $w(x, t) \leq m$ in $[a, b] \times [0, T]$.

2.5.2 Similarity Solutions

In Chapter 1 we observed that the classical, linear diffusion equation has solutions that are smooth, even when the boundary and initial data are discontinuous. The diffusion equation smooths out solutions. When the diffusion is nonlinear, however, this smoothing property no longer holds; nonlinear diffusion or dispersion equations can propagate piecewise smooth solutions in much the same manner as a wave-like equation. This type of phenomenon occurs when the equation is degenerate, i.e., when the dispersion coefficient $D = D(u)$ can vanish. Intuitively, one can think physically that when the dispersion coefficient vanishes, then dispersion is not present to smooth out irregularities in the solution.

We illustrate this type of behavior using a standard technique for obtaining solutions to nonlinear parabolic problems on unbounded domains. Let us consider the equilibrium model on a semi-infinite domain with no advection:

$$(u + \beta f(u))_t = \alpha u_{xx}, \quad x > 0, t > 0, \quad (2.40)$$

$$u(0, t) = 1, \quad t > 0, \quad (2.41)$$

$$u(x, 0) = 0, \quad x > 0, \quad (2.42)$$

$$u(x, t) \rightarrow 0 \text{ as } x \rightarrow \infty, \quad (2.43)$$

where f satisfies the conditions $f(0) = 0$, $f \in C^1[0, \infty) \cup C^2(0, \infty)$, with $f > 0$, $f' > 0$, $f'' < 0$. The similarity method is a general method to construct solutions when the differential equation is invariant under a local Lie group of transformations. These internal symmetries lead to classes of invariant solutions called **similarity solutions**. We refer the reader to one of the following references for a general discussion of the similarity method: Dresner (1983), Logan (1987, 1994). Here, motivated by the form of solutions to the classical, linear heat equation, we shall attempt a solution of the form

$$u(x, t) = y(s),$$

where the similarity variable s is given by

$$s = \frac{x}{\sqrt{t}}.$$

Substituting the expression for u into the PDE gives an ordinary differential equation for the function y , namely,

$$-\frac{s}{2} \frac{d}{ds}(y + \beta f(y)) = \alpha \frac{d^2 y}{ds^2}.$$

The initial and boundary conditions force

$$y(0) = 1, \quad y(+\infty) = 0.$$

Integrating the differential equation with respect to s and using the boundary condition at $s = +\infty$ to evaluate the constant of integration yields

$$\frac{dy}{ds} = -\frac{s}{2\alpha}(y + \beta f(y)).$$

Separating variables and integrating gives the formal, implicit solution to (2.40)–(2.43) as

$$\int_1^y \frac{dw}{w + \beta f(w)} = -\frac{s^2}{4\alpha},$$

or, in original variables,

$$\int_1^u \frac{dw}{w + \beta f(w)} = -\frac{x^2}{4\alpha t}.$$

Exercise 37 As an example of the preceding calculation, verify the details of the following special case. Consider the case of a Langmuir isotherm where

$$f(u) = \frac{k_1 u}{k_2 + u}.$$

A partial fractions expansion gives

$$\int \frac{dw}{w + \beta f(w)} = \ln(w^a (w + A)^b),$$

where $a = k_2/A$, $b = 1 - k_2/A$, $A = \beta k_1 + k_2 > 0$. Moreover, $0 < a < 1$ and $b > 0$. Therefore,

$$\ln(w^a (w + A)^b) \Big|_1^y = -\frac{s^2}{4\alpha},$$

or

$$s^2 = -4\alpha \ln \left(y^a \left(\frac{y + A}{1 + A} \right)^b \right).$$

This equation defines, implicitly, a solution $u(x, t) = y(x/\sqrt{t})$.

To illustrate another property of nonlinear diffusion equations, consider

$$u_t = (uu_x)_x, \quad x \in \mathbb{R}, \quad t > 0. \quad (2.44)$$

This is a special case of the **porous media equation**

$$u_t = (u^n u_x)_x,$$

which occurs in many contexts. In (2.44) the flux is $Q = -D(u)u_x$, where the dispersion coefficient $D(u) = u$ depends on the concentration. We say the equation is degenerate because the dispersion coefficient has the property that $D(u) \rightarrow 0$ as $u \rightarrow 0$; it is not bounded away from zero. This degeneracy gives the equation distinctive properties that do not occur if $D(u) \geq \epsilon > 0$. We append to (2.44) the conditions

$$u(x, 0) = 0, \quad x \neq 0, \quad (2.45)$$

$$\int_{\mathbb{R}} u(x, t) dx = 1, \quad t \neq 0. \quad (2.46)$$

These conditions represent the release of a unit amount of contaminant at the origin at $t = 0$ [in other symbols, $u(x, 0) = \delta(x)$, the delta distribution]. This problem admits a similarity solution of the form

$$u = t^{-1/3}y(s), \quad s = x/t^{1/3},$$

where

$$(yy')' + \frac{1}{3}(sy)' = 0.$$

Integrating once gives

$$y(y' + \frac{s}{3}) = 0.$$

We have set the constant of integration to equal zero because $y(\pm\infty) = 0$. It follows that

$$y = 0 \quad \text{or} \quad y = \frac{1}{6}(s_0^2 - s^2),$$

where s_0 is an arbitrary constant. Neither solution alone can satisfy the conditions (2.45)–(2.46) on \mathbb{R} , so we piece together these two solutions to obtain

$$u(x, t) = 0, \quad |s| > s_0; \quad u(x, t) = \frac{1}{6}(s_0^2 - s^2)t^{-1/3}, \quad |s| < s_0.$$

We choose s_0 so that

$$\int_{\mathbb{R}} y(s) dx = 1,$$

which gives $s_0 = 3^{2/3}/2^{1/3}$. Consequently,

$$u(x, t) = 0, \quad |x| > s_0 t^{1/3}; \quad u(x, t) = \frac{t^{-1/3}}{6} \left(s_0^2 - \frac{x^2}{t^{2/3}} \right), \quad |x| < s_0 t^{1/3}. \quad (2.47)$$

Figure 2.4 shows several time snapshots of the concentration. The solution is continuous, but u_x is not continuous. There are sharp “wavefronts” propagating along the spacetime loci $|x| = s_0 t^{1/3}$, much like one can observe in a hyperbolic problem. Thus, this is not a solution in the classical sense; it is an example of a *weak* solution.

Exercise 38 Find solutions of the equation

$$xu_t = u_{xx}, \quad x, t > 0$$

of the form $u = t^\gamma F(x/t^{1/3})$. Obtain the solution $u = t^{-2/3} \exp(-x^3/9t)$.

2.5.3 Blowup of Solutions

Another characteristic phenomenon often occurring in nonlinear parabolic problems is blow up of solutions in finite time. In other words, the growth of the solution, measured in some manner, becomes infinite at a finite time. This reminds us of similar behavior for ordinary differential equations. For example,

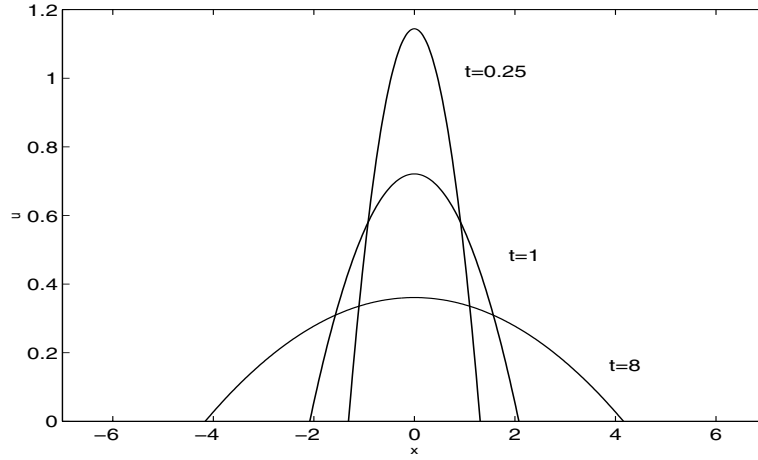


Figure 2.4: Time snapshots of the solution (2.47).

the initial value problem $y' = 1 + y^2$, $y(0) = 0$, has solution $y(t) = \tan t$, which blows up at $t = \pi/2$. To illustrate this type of behavior we consider the semilinear reaction-diffusion equation

$$u_t = u_{xx} + u^3, \quad x \in (0, \pi), \quad t > 0, \quad (2.48)$$

$$u(0, t) = u(\pi, t) = 0, \quad t > 0, \quad (2.49)$$

$$u(x, 0) = u_0(x), \quad x \in (0, \pi). \quad (2.50)$$

The initial datum u_0 is assumed to be continuous and nonnegative on $(0, \pi)$, and

$$\int_0^\pi u_0(x) \sin x \, dx > 2.$$

From the comparison principle we observe that the solution is nonnegative so long as it exists. We define

$$s(t) = \int_0^\pi u(x, t) \sin x \, dx.$$

Using integration by parts,

$$\begin{aligned} s'(t) &= \int_0^\pi u_t(x, t) \sin x \, dx \\ &= \int_0^\pi (u_{xx}(x, t) \sin x + u^3 \sin x) dx \\ &= -s(t) + \int_0^\pi u^3(x, t) \sin x \, dx. \end{aligned}$$

Now we apply Holder's inequality² with $p = 3$ and $q = 3/2$ to obtain

$$\begin{aligned} s(t) &= \int_0^\pi u \sin x \, dx = \int_0^\pi \sin^{2/3} x \, u \sin^{1/3} x \, dx \\ &\leq \left(\int_0^\pi (\sin^{2/3} x)^{3/2} \, dx \right)^{2/3} \left(\int_0^\pi (u \sin^{1/3} x)^3 \, dx \right)^{1/3} \\ &\leq 2^{2/3} \left(\int_0^\pi u^3 \sin x \, dx \right)^{1/3}. \end{aligned}$$

In other words,

$$s(t) \leq 4 \left(\int_0^\pi u^3 \sin x \, dx \right)^{1/3},$$

and therefore

$$s'(t) \geq -s(t) + \frac{s(t)^3}{4}, \quad t > 0, \quad s(0) > 2.$$

This inequality will imply that $s(t) \rightarrow \infty$ at a finite time t . To show this is the case let $v = 1/s^2$. Then the differential inequality becomes

$$v'(t) \leq 2v(t) - \frac{1}{2}.$$

Multiplying by $\exp(-2t)$ and integrating gives

$$v(t) \leq \frac{1}{4}(1 - e^{-2t}) + v(0)e^{2t}.$$

Consequently,

$$s(t) \geq \left(e^{2t} \left(\frac{1}{s(0)^2} - \frac{1}{4} \right) + \frac{1}{2} \right)^{-2}.$$

Because $s(0) > 2$, the right-side of this inequality goes to infinity at a finite value of t . Therefore the solution blows up in finite time.

Reaction-diffusion equations can have this type of behavior where solutions only exist locally, for finite times. The situation would not improve if we added a linear advection term. This type of phenomenon is characteristic for some equations containing reaction terms. In (2.48)–(2.50) the presence of diffusion, or dispersion, does not cause decay; reaction wins the competition and the solution blows up. Blow up for reaction diffusion equations is discussed thoroughly in Samarski *et al* (1995).

2.5.4 Stability of the Zero Solution

Another method to aid in understanding the behavior of nonlinear evolution equations is to inquire about the linearized stability of steady-state solutions. This study is really about the permanence of steady solutions when they are

²If $1/p + 1/q = 1$, then $\int |fg| dx \leq (\int |f|^p dx)^{1/p} (\int |g|^q dx)^{1/q}$.

subjected to small perturbations. Let us consider the equilibrium model on a bounded domain:

$$(u + \beta f(u))_t = \alpha u_{xx} - u_x, \quad 0 < x < 1, \quad t > 0, \quad (2.51)$$

$$u(0, t) = u(1, t) = 0, \quad t > 0, \quad (2.52)$$

where f satisfies the conditions $f(0) = 0$, $f \in C^1[0, \infty) \cup C^2(0, \infty)$, with $f > 0$, $f' > 0$, $f'' < 0$. It is clear that $u \equiv 0$ is a steady-state solution to the problem. If $w = w(x, t)$ represents a small perturbation to the zero solution, then $f(w) = f(0) + f'(0)w + \frac{1}{2}f''(\tilde{w})w^2$, where $0 < \tilde{w} < w$, and the perturbation w satisfies the linearized problem

$$(w + \beta f'(0)w)_t = \alpha w_{xx} - w_x, \quad 0 < x < 1, \quad t > 0, \quad (2.53)$$

$$w(0, t) = w(1, t) = 0, \quad t > 0. \quad (2.54)$$

The linearized equation (2.53) can be written

$$w_t = dw_{xx} - aw_x, \quad 0 < x < 1, \quad t > 0,$$

where $d = \alpha/(1 + f'(0))$ and $a = 1/(1 + f'(0))$. To analyze this equation we use an **energy method**. First multiply the equation by w and then integrate over $0 < x < 1$ to get

$$\int_0^1 ww_t dx = \int_0^1 dw w_{xx} dx - \int_0^1 aw w_x dx.$$

Now observe that $2ww_t = (w^2)_t$, $2ww_x = (w^2)_x$, and integrate the first term on the right-side by parts. We obtain

$$\frac{d}{dt} \int_0^1 w^2 dx = 2dww_x \Big|_0^1 - \int_0^1 w_x^2 dx - w^2 \Big|_0^1.$$

But the boundary conditions (2.54) force the two boundary terms to vanish and we obtain

$$\frac{d}{dt} \int_0^1 w^2 dx = -2d \int_0^1 w_x^2 dx.$$

Therefore

$$\frac{d}{dt} \|w(\cdot, t)\|^2 \leq 0,$$

where

$$\|w(\cdot, t)\| = \left(\int_0^1 w^2 dx \right)^{1/2}$$

is the $L^2[0, 1]$ or energy norm. Therefore, the energy norm of small perturbations remain bounded for all $t > 0$.

The previous calculation shows that small perturbations stay under control when a linearized analysis is performed. We can sometimes analyze the nonlinear equation in the same manner, using an energy method. Note that the nonlinear equation can be written

$$g(u)_t = \alpha u_{xx} - u_x,$$

where $g(u) = u + \beta f(u) > 0$. Multiplying by $g(u)$ and integrating from over $0 < x < 1$ yields

$$\begin{aligned} \frac{d}{dt} \|g(u(\cdot, t))\|^2 &= 2\alpha \int_0^1 g(u) u_{xx} dx - 2 \int_0^1 g(u) u_x dx \\ &= 2\alpha g(u) u_x \Big|_0^1 - 2\alpha \int_0^1 g'(u) u_x^2 dx - 2 \int_0^1 g(u) u_x dx \\ &= -2\alpha \int_0^1 g'(u) u_x^2 dx - 2 \int_0^1 g(u) u_x dx. \end{aligned}$$

Because $g'(u) = 1 + f'(u) > 0$, the first term on the right is nonpositive. To estimate the second term let $G(u)$ be the antiderivative of g , i.e., $G(u) = \int_0^u g(y) dy$. Then

$$\int_0^1 g(u) u_x dx = \int_0^1 G(u)_x dx = G(u) \Big|_0^1 = 0.$$

Therefore

$$\frac{d}{dt} \|g(u(\cdot, t))\|^2 = -2\alpha \int_0^1 g'(u) u_x^2 dx \leq 0,$$

and so the norm of $g(u)$ stays under control. Thus $\|u(\cdot, t)\|$ remains bounded and the energy stays under control.

Arguments like those given above are predicated on the assumption that solutions exist and are called *a priori* estimates.

2.6 The Reaction–Advection Equation

2.6.1 Semilinear Equations

For completeness, we now examine some properties of the preceding equations when dispersion is absent, i.e., $\alpha = 0$, and when the reaction term is given by $\Phi = \Phi(u)$. In deep bed filtration theory (Chapter 3), we shall observe that the dispersion term is neglected in some models. With neglect of dispersion, equation (2.3) becomes the **reaction–advection equation**

$$u_t + v u_x = \Phi(u), \tag{2.55}$$

which is, in general, a semilinear hyperbolic equation. Therefore, this equation is not parabolic at all and we do not have some of the properties expected

in parabolic equations. To solve reaction-advection equations we introduce a moving coordinate system, or characteristic coordinates, defined by

$$\xi = x - vt, \quad \tau = t.$$

Then the equation becomes

$$U_\tau = \Phi(U),$$

where $U(\xi, \tau) = u(\xi + v\tau, \tau)$. (Easily, by the chain rule for derivatives, the advection operator $\partial_t + v\partial_x$ simplifies to just ∂_τ in characteristic coordinates.) Therefore,

$$\int^U \frac{dw}{\Phi(w)} = \tau + \psi(\xi),$$

where ψ is an arbitrary function. Thus, the equation

$$\int^u \frac{dw}{\Phi(w)} = t + \psi(x - vt)$$

defines, implicitly, the general solution of (2.55). The arbitrary function is determined specifically by initial or boundary data. The following exercise and example give two illustrations: a Cauchy problem with initial datum given on the entire real line and a Cauchy-Dirichlet problem where initial datum is given on a half line and a Dirichlet condition is prescribed at the boundary.

Exercise 39 Consider the Cauchy problem for the reaction-advection equation with Langmuir kinetics:

$$u_t + vu_x = -\frac{k_1 u}{k_2 + u}, \quad x \in \mathbb{R}, \quad t > 0, \quad (2.56)$$

$$u(x, 0) = u_0(x), \quad x \in \mathbb{R}, \quad (2.57)$$

where $u_0(x) \geq 0$. Show that the solution is given implicitly by

$$-t = \int_{u_0}^u \left(\frac{k_2}{k_1 w} + \frac{1}{k_1} \right) dw,$$

or, after simplification,

$$u - k_1 t - u_0 = k_2 \ln(u/u_0).$$

Using graphical techniques show that for each x and $t > 0$ there is a unique value $u = u(x, t) < u_0(x)$. For $t > 0$ the single root at $t = 0$ bifurcates into two roots, the smaller of which is the solution. As $t \rightarrow 0+$ it is clear that $u \rightarrow 0$. Therefore show that the Cauchy problem (2.56)–(2.57) has a global solution.

Example 40 Consider the Cauchy-Dirichlet problem for the reaction-advection equation with Freundlich-type kinetics:

$$u_t + vu_x = -\sqrt{u}, \quad x > 0, \quad t > 0, \quad (2.58)$$

$$u(x, 0) = u_0(x), \quad x > 0, \quad (2.59)$$

$$u(0, t) = g(t), \quad t > 0, \quad (2.60)$$

where $u_0(x) \geq 0$ and $g(t) \geq 0$. In characteristic coordinates the equation becomes

$$U_\tau = -\sqrt{U}.$$

Integration yields the general solution

$$\sqrt{U} = -\frac{\tau}{2} + \psi(\xi)$$

or

$$\sqrt{u} = -\frac{t}{2} + \psi(x - vt) \quad (2.61)$$

where ψ is an arbitrary function. Because signals in this system travel at speed v , we treat the regions $x > vt$ and $x < vt$ separately. The region $x > vt$, which is ahead of the leading signal $x = vt$, is influenced by the initial data (2.59) along $t = 0$. Thus, applying the initial condition to the general formula for u gives

$$\sqrt{u_0(x)} = \psi(x),$$

thereby determining the arbitrary function for this region. Therefore

$$\sqrt{u} = -\frac{t}{2} + \sqrt{u_0(x - vt)}, \quad x > vt.$$

For the region $0 < x < vt$ we apply the boundary condition to the general solution to get

$$\sqrt{g(t)} = -\frac{t}{2} + \psi(-vt).$$

Thus, replacing $-vt$ by $t - x/v$,

$$\psi(x - vt) = \frac{t - x/v}{2} + \sqrt{g(t - x/v)}.$$

Therefore,

$$\sqrt{u} = -\frac{x}{2v} + \sqrt{g(t - x/v)}, \quad 0 < x < vt.$$

We observe that these solution formulas hold only for those times for which the right-hand sides are nonnegative. For times greater than the loci where the right-hand sides vanish, we set $u(x, t) \equiv 0$.

2.6.2 Quasilinear Equations

In the absence of dispersion, the equilibrium model (2.22)–(2.23) becomes

$$(1 + \beta f'(u))u_t + u_x = 0. \quad (2.62)$$

Unlike a semilinear equation where the nonlinearity appears in the reaction, or source term, this equation is quasilinear and the nonlinearity occurs in the differential operator. We can anticipate the development of singularities (shocks) as a solution propagates in time.

We rewrite (2.62) as

$$u_t + c(u)u_x = 0,$$

where

$$c(u) = \frac{1}{1 + \beta f'(u)}.$$

Observe, from the assumptions on the isotherm f , that

$$c(u) > 0 \quad c'(u) > 0.$$

Thus we have a standard kinematic wave equation. The analysis of such equations is straightforward and can be found in many texts [e.g., see Logan (1997c, 1994), Whitham (1974), or Smoller (1994)].

To illustrate the analysis, let us consider the Cauchy problem, or the pure initial value problem on \mathbb{R} . We impose the initial concentration

$$u(x, 0) = u_0(x), \quad x \in \mathbb{R}.$$

We define the characteristic curves as solutions of the equation

$$\frac{dx}{dt} = c(u(x, t)).$$

On these curves the PDE becomes

$$\frac{du}{dt} = 0 \quad \text{or} \quad u = \text{const.}$$

From the calculation

$$\frac{d^2x}{dt^2} = \frac{d}{dt}c(u) = c'(u)\frac{du}{dt} = 0,$$

it follows that the characteristic curves are straight lines. If (x, t) is an arbitrary point in spacetime, then the characteristic line connecting (x, t) to a point $(\xi, 0)$ on the x axis has speed $c(u_0(\xi))$ and is given by

$$x - \xi = c(u_0(\xi))t. \tag{2.63}$$

By the constancy of u on the characteristic, the solution u at (x, t) is given by

$$u(x, t) = u_0(\xi). \tag{2.64}$$

The two equations (2.63)–(2.64) define the solution, if it exists; the solution is (2.64) where $\xi = \xi(x, t)$ is defined implicitly by (2.63). To determine the validity of the solution, let us calculate the partials u_x and u_t . We have

$$u_x = u'_0(\xi)\xi_x = \frac{u'_0(\xi)}{1 + tc'(u_0(\xi))u'_0(\xi)},$$

where ξ_x was computed from (2.63). A similar calculation shows

$$u_t = u'_0(\xi)\xi_t = -\frac{c(u_0(\xi))u'_0(\xi)}{1 + tc'(u_0(\xi))u'_0(\xi)}.$$

It is easy to verify that $u_t + c(u)u_x = 0$, provided the denominator in the expression for the derivatives never vanishes, i.e.,

$$1 + tc'(u_0(\xi))u'_0(\xi) \neq 0.$$

Because $c'(u) > 0$, if the initial concentration $u_0(x)$ is nondecreasing, then the denominator is always positive and the solution to the Cauchy problem exists for all time. On the other hand, if there is a value of x_0 where $u'_0(x_0) < 0$, then there will be two characteristic lines that cross, contradicting the constancy of u on the characteristics. In this case the solution will blow up and a “gradient catastrophe” will occur in finite time; at this time the classical solution must terminate. At this blowup time a shock will form and a weak solution will be propagated.

2.7 Examples

2.7.1 Advection–Dispersion Equation

In Chapter 1 we discussed several properties of the diffusion, or dispersion, equation. In this section we solve some sample problems associated with the advection-dispersion equation

$$C_t = DC_{xx} - vC_x \quad (2.65)$$

and some of its variants. As we have noted, the equation can be put into dimensionless form

$$u_t = \alpha u_{xx} - u_x, \quad (2.66)$$

where α is the inverse of the Peclet number, i.e., $\text{Pe} = \alpha^{-1} = Lv/D$, where L is a length for the problem.

As in the case of the dispersion equation we can inquire about plane wave solutions of (2.66) of the form $u = e^{i(kx - \omega t)}$. Substituting into the equation (2.66) we find that the wave number k and frequency ω are related by the dispersion relation $\omega = k - \alpha k^2 i$. Therefore, plane wave solutions have the form

$$u(x, t) = e^{-\alpha k^2 t} e^{ik(x-t)},$$

which are oscillatory, decaying, waves moving at the unit advection speed.

The fundamental solution of the advection-dispersion equation (2.66) is the solution of the Cauchy problem

$$u_t = \alpha u_{xx} - u_x, \quad x \in \mathbb{R}, \quad t > 0 \quad (2.67)$$

$$u(x, 0) = \delta(x), \quad x \in \mathbb{R}, \quad (2.68)$$

where δ is the delta distribution. Hence, it is the response to a unit, point source at $x = 0$ applied at the time $t = 0$. The simplest way to solve (2.67)–(2.68) is to transform to characteristic, moving coordinates $\xi = x - t$, $\tau = t$. Then the problem becomes

$$u_\tau = \alpha u_{\xi\xi}, \quad \xi \in \mathbb{R}, \quad t > 0, \quad (2.69)$$

$$u(\xi, 0) = \delta(\xi), \quad \xi \in \mathbb{R}, \quad (2.70)$$

which is the Cauchy problem for the diffusion equation. By the results in Section 1.1 we have

$$u(\xi, \tau) = g(\xi, \tau),$$

where g is the fundamental solution of the diffusion equation. Consequently, the fundamental solution of the advection-dispersion equation is

$$u(x, t) = g(x - t, t) = \frac{1}{\sqrt{4\pi\alpha t}} e^{-(x-t)^2/4\alpha t}.$$

By superimposing the responses caused by a distributed initial source ϕ , we can obtain the solution to the general Cauchy problem

$$u_t = \alpha u_{xx} - u_x, \quad x \in \mathbb{R}, \quad t > 0, \quad (2.71)$$

$$u(x, 0) = \phi(x), \quad x \in \mathbb{R}, \quad (2.72)$$

as

$$u(x, t) = \int_{-\infty}^{\infty} \frac{1}{\sqrt{4\pi\alpha t}} e^{-(x-y-t)^2/4\alpha t} \phi(y) dy. \quad (2.73)$$

Exercise 41 In the case where the initial condition is Gaussian, i.e., $\phi(x) = e^{-x^2/a}$, show that the integral in (2.73) can be calculated in analytic form to obtain

$$u(x, t) = \frac{\sqrt{a}}{\sqrt{a + 4\alpha t}} e^{-(x-t)^2/(a+4\alpha t)}.$$

Conclude that, as time increases, the Gaussian concentration profile decays, advects to the right with speed one, and spreads outward.

Exercise 42 If the initial condition is a step function $\phi(x) = 1 - H(x)$, where H is the Heaviside function, show that the solution to (2.71)–(2.72) is

$$u(x, t) = \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{t-x}{\sqrt{4\alpha t}} \right) \right), \quad x < t,$$

and

$$u(x, t) = \operatorname{erfc} \left(\frac{x-t}{\sqrt{4\alpha t}} \right), \quad x > t,$$

where $\operatorname{erfc} = 1 - \operatorname{erf}$.

2.7.2 Boundary Conditions

Problems with boundaries require boundary data. In addition to the usual Dirichlet condition, where the concentration is specified on a boundary, there are other important boundary conditions that arise from the fact that the flux has two parts, an advective part caused by the bulk flow and a dispersive part caused by diffusion and mechanical dispersion. Every problem must be analyzed carefully to determine which condition best models the physical situation.

An important boundary condition at an inlet boundary arises naturally for the advection–dispersion equation (2.65). Assume that the problem is defined on a semi-infinite domain $x > 0$ with inlet boundary at $x = 0$. The flux is given by $Q \equiv -DC_x + vC$, and if we require that the flux be continuous across the boundary, we have

$$-DC_x(0^+, t) + vC(0^+, t) = -DC_x(0^-, t) + vC(0^-, t),$$

where 0^+ and 0^- denote the right and left limits, respectively. If the region to the left of the boundary is a reservoir (e.g., a well or a lake) where the chemical has concentration $C_0(t)$ and is perfectly stirred, then there are no gradients and we have

$$C_x(0^-, t) = 0, \quad C(0^-, t) = C_0(t).$$

Thus, we obtain the **Fourier boundary condition**

$$-DC_x(0, t) + vC(0, t) = vC_0(t), \quad t > 0.$$

If $x = l$ is an outflow boundary, we can make a similar argument as in the last example and equate the flux on both sides of the boundary, or

$$-DC_x(l^+, t) + vC(l^+, t) = -DC_x(l^-, t) + vC(l^-, t).$$

Assuming the region to the right of $x = l$ is a perfectly stirred reservoir and that its concentration is the same as the concentration exiting the domain, then we get the condition

$$C_x(l, t) = 0, \quad t > 0.$$

Observe that this is *not* a no-flux condition; it must be remembered that the flux involves an advection term that is not zero. This boundary condition is called a zero-gradient condition.

Exercise 43 *The advection–dispersion equation (2.65) on a bounded domain can be solved by the eigenfunction expansion method (see Chapter 1). Consider the problem with Dirichlet boundary conditions:*

$$\begin{aligned} C_t &= DC_{xx} - vC_x, & 0 < x < l, & t > 0, \\ C(0, t) &= C(l, t) = 0, & t > 0, \\ C(x, 0) &= f(x), & 0 < x < l. \end{aligned}$$

Show that the associated Sturm–Liouville problem is

$$Dy'' - vy' = \lambda y, \quad 0 < x < l; \quad y(0) = y(l) = 0,$$

and that the eigenvalues and eigenfunctions are given by

$$\lambda_n = -\frac{v^2 l^2 + 4n^2 \pi^2 D^2}{4Dl^2}, \quad y_n(x) = e^{vx/2D} \sin \frac{n\pi x}{l}, \quad n = 1, 2, \dots$$

Thus, obtain the solution

$$u(x, t) = \sum_{n=1}^{\infty} a_n e^{\lambda_n t} e^{vx/2D} \sin \frac{n\pi x}{l},$$

where

$$a_n = \frac{(f, y_n)}{\|y_n\|^2}.$$

In Chapter 1 we introduced a pure boundary value problem associated with the diffusion equation. Such a problem models the flow in a half-space when boundary conditions are imposed for a long time. We can proceed in the same manner for more general equations. Consider the two boundary value problems

$$c_t = Dc_{xx} - vc_x - \lambda c, \quad x > 0, t \in \mathbb{R}, \quad (2.74)$$

$$-Dc_x(0, t) + vc(0, t) = vf(t), \quad t \in \mathbb{R}, \quad (2.75)$$

and

$$u_t = Du_{xx} - vu_x - \lambda u, \quad x > 0, t \in \mathbb{R}, \quad (2.76)$$

$$u(x, 0) = f(t), \quad t \in \mathbb{R}, \quad (2.77)$$

where the first has a Fourier boundary condition and the second has a Dirichlet condition. It is straightforward to verify that bounded solutions to the two problems are connected by the relation

$$c(x, t) = \frac{v}{D} e^{vx/D} \int_x^{\infty} u(y, t) e^{-vy/D} dy,$$

which effectively allows the reduction of a problem with a Fourier condition to one with a Dirichlet condition. The connection is also defined by the differential relation

$$vu(x, t) = -Dc_x(x, t) + vc(x, t).$$

It is well-known [e.g., see Guenther and Lee (1996)] that the solution to (2.76)–(2.77) is

$$u(x, t) = \frac{2}{\sqrt{\pi}} e^{vx/2D} \int_0^{\infty} e^{-y^2 - \frac{(\lambda + v^2/4D)x^2}{4Dy^2}} f\left(t - \frac{x^2}{4Dy^2}\right) dy.$$

Observe that if f is a periodic function, then so is u . Further results on periodic boundary conditions and other references can be found in Logan and Zlotnik (1995).

Exercise 44 Verify the details in the last few paragraphs.

2.7.3 A Perturbation Problem

Perturbation methods provide a powerful technique to obtain approximate solutions to difficult problems when a large or small parameter is present. In the next few paragraphs we use perturbation methods to analyze a simple problem that can be solved analytically by other methods. Consider the problem

$$C_t = DC_{xx} - vC_x - \lambda C, \quad x > 0, t > 0, \quad (2.78)$$

$$C(0, t) = C_b(t), \quad t > 0, \quad (2.79)$$

$$C(x, 0) = 0, \quad x > 0, \quad (2.80)$$

that models the advection, dispersion, and decay of a chemical tracer on the semi-infinite domain $x > 0$, with a given Dirichlet boundary condition. Furthermore, assume that the dispersion constant is small in some sense (which we clarify later). We have already observed that this problem can be transformed into one involving the diffusion equation by letting

$$C(x, t) = u(x, t)e^{vx/2D - (\lambda + v^2/4D)t}.$$

Then u satisfies

$$u_t = Du_{xx}, \quad x > 0, t > 0,$$

$$u(0, t) = h(t) \equiv C_b(t)e^{(\lambda + v^2/4D)t}, \quad t > 0,$$

$$u(x, 0) = 0, \quad x > 0.$$

Using Laplace transforms, the solution to this problem is

$$u(x, t) = -2D \int_0^t g_x(x, t - \tau)h(\tau)d\tau,$$

where $g(x, t)$ is the fundamental solution. Therefore we have obtained the exact solution to the problem, but it is somewhat obscured because of the complicated integral formula. We can often get a better idea of the behavior of the solution using a singular perturbation method. Such a strategy is common; asymptotic methods are often preferred over difficult integral representations (which, by the way, usually require asymptotic approximations anyway). The reader unfamiliar with singular perturbation methods can consult Kevorkian and Cole (1981), Lin and Segel (1989), or Logan (1997c).

First we recast the problem into dimensionless form. Scaling t by λ^{-1} , x by v/λ , and C by the maximum value of $C_b(t)$, we obtain the model

$$c_t = \epsilon c_{xx} - c_x - c, \quad x > 0, t > 0, \quad (2.81)$$

$$c(0, t) = c_b(t), \quad t > 0, \quad (2.82)$$

$$c(x, 0) = 0, \quad x > 0, \quad (2.83)$$

where

$$\epsilon = \frac{\lambda D}{v^2}.$$

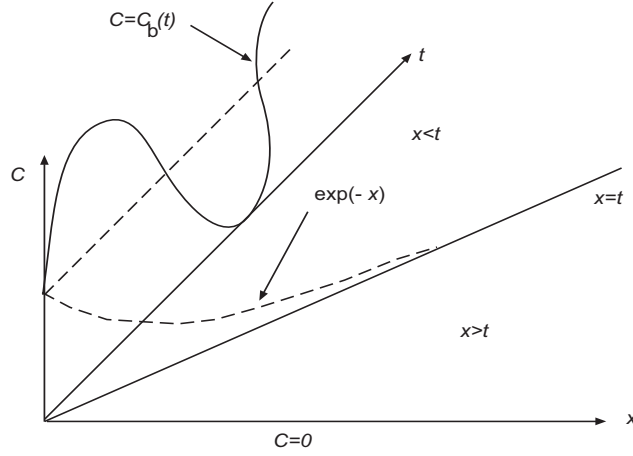


Figure 2.5: Spacetime diagram.

The assumption that the dispersion constant is small means precisely that $\epsilon \ll 1$, or the constant D is small compared to v^2/λ .

When we set $\epsilon = 0$, we obtain the **outer problem**

$$c_{0t} = -c_{0x} - c_0,$$

which is a hyperbolic equation. The general solution to this simple advection equations is (see Section 2.4)

$$c_0(x, t) = G(x - t)e^{-t},$$

where G is an arbitrary function. In the domain $x > t$, i.e., ahead of the leading signal from the boundary, we clearly have

$$c_0(x, t) = 0, \quad x > t.$$

Behind the wave, i.e., for $0 < x < t$ we apply the boundary condition to determine $G(t) = c_b(-t)e^{-t}$. Therefore, behind the wave we have

$$c_0(x, t) = c_b(t - x)e^{-x}, \quad 0 < x < t.$$

Thus, the outer solution is defined in two pieces. Along the leading edge $x = t$ we expect exponential decay because $c_0(t^-, t) = c_b(0)e^{-x} = e^{-x}$. But we note that the two solutions do not match along the line $x = t$. It is here, in a neighborhood of $x = t$, that we require an “inner” approximation that will tie together the two pieces of the outer approximation. Figure 2.5 shows depicts the situation geometrically.

To find the inner approximation we change to characteristic coordinates: $\eta = x$, $\tau = t - x$. In these variables the PDE becomes

$$c_{\eta\eta} - 2\epsilon c_{\eta\tau} + \epsilon c_{\tau\tau} - c_{\eta} - c = 0,$$

and the inner region, or boundary layer, is now along $\tau = 0$. Selecting a new scaled variable

$$\xi = \tau/\sqrt{\epsilon},$$

we obtain

$$\epsilon c_{\eta\eta} - 2\sqrt{\epsilon}c_{\eta\xi} + c_{\xi\xi} - c_{\eta} - c = 0,$$

which is the **inner problem**. The dominant balance must be among the last three terms. Thus, to leading order,

$$c_{\xi\xi}^i - c_{\eta}^i - c^i = 0,$$

where c^i denotes the leading-order inner approximation. Letting $u = c^i e^{\eta}$ then transforms the last equation into the diffusion equation

$$u_{\eta} = u_{\xi\xi}.$$

Matching the inner approximation with the two outer approximation gives the boundary conditions

$$c^i \rightarrow 0 \quad \text{as } \xi \rightarrow -\infty$$

and

$$c^i \rightarrow e^{-\eta} \quad \text{as } \xi \rightarrow +\infty.$$

Thus, $u \rightarrow 0$ as $\xi \rightarrow -\infty$ and $u \rightarrow 1$ as $\xi \rightarrow +\infty$. Therefore, the solution to the u problem is

$$u(\xi, \eta) = \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{\xi}{\sqrt{4\eta}} \right) \right).$$

Hence

$$c^i(\tau, \eta) = \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{\tau/\sqrt{\epsilon}}{\sqrt{4\eta}} \right) \right) e^{-\eta}.$$

Returning to the original coordinates, we have inner approximation

$$c^i(x, t) = \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{t-x}{\sqrt{4\epsilon x}} \right) \right) e^{-x}.$$

This is the approximation that joins the two pieces of the outer approximation.

Finally, we can form a uniform approximation by adding the inner and outer approximations and then subtracting their common limit. We obtain

$$\begin{aligned} c(x, t) &= \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{t-x}{\sqrt{4\epsilon x}} \right) \right) e^{-x}, \quad x > t, \\ c(x, t) &= c_b(t-x)e^{-x} + \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{t-x}{\sqrt{4\epsilon x}} \right) \right) e^{-x} - e^{-x}, \quad 0 < x < t. \end{aligned}$$

Exercise 45 Find bounded solutions to the following model with spatially dependent dispersion:

$$\begin{aligned} c_t &= ((a+vx)c_x)_x - vc_x - \lambda c, \quad x > 0, \quad t \in \mathbb{R}, \\ c(0, t) &= \sin \omega t, \quad t \in \mathbb{R}, \end{aligned}$$

and describe how the amplitude and phase depend on ω . *Hint: assume that $c = \phi(x)e^{i\omega t}$ and then change the independent variable to $\xi = a + vx$.*

2.7.4 Radial Dispersion

The one-dimensional advection–dispersion equation in the semi-infinite domain $x > 0$ is

$$u_t = \alpha u_{xx} - u_x, \quad x > 0, \quad t > 0.$$

With initial and boundary conditions given by

$$u(x, 0) = 0, \quad x > 0; \quad u(0, t) = u_0 = \text{const.},$$

it is well-known [e.g., see Sun (1995)] that the solution is given by

$$u(x, t) = \frac{u_0}{2} \left(\text{erf } c \left(\frac{x-t}{\sqrt{4\alpha t}} \right) + e^{x/\alpha} \text{erf } c \left(\frac{x+t}{\sqrt{4\alpha t}} \right) \right).$$

Here, $\text{erf } c$ is the complementary error function defined by $\text{erf } c(z) = 1 - \text{erf}(z)$, where $\text{erf}(z)$ is the error function. For each fixed x , the second term in the solution becomes negligible quickly and so the solution is often approximated by first term.

The solution to the one-dimensional advection–dispersion equation with decay, subject to the same initial and boundary data, can be found in, for example, de Marsily (1986). Many other solutions are given Sun (1995). Most of these analytic solutions are found using transform methods. A compendium is given in van Genuchten and Alves (1982).

In the next few paragraphs we examine a simple advection–dispersion equation in radial geometry:

$$c_t = \frac{\alpha a}{r} c_{rr} - \frac{a}{r} c_r, \quad r > r_0, \quad t > 0, \quad (2.84)$$

$$c(r, 0) = 0, \quad r > r_0, \quad c(r_0, t) = c_0, \quad t > 0. \quad (2.85)$$

We assume that solutions remain bounded as $r \rightarrow 0$. Rescaling the problem via

$$\bar{r} = \frac{r}{\alpha}, \quad \bar{t} = \frac{t}{\alpha^2/a}, \quad u = \frac{c}{c_0}$$

gives, upon dropping the overbars, the dimensionless model

$$u_t = \frac{1}{r} u_{rr} - \frac{1}{r} u_r, \quad r > R, \quad t > 0, \quad (2.86)$$

$$u(r, 0) = 0, \quad r > R, \quad u(R, t) = 1, \quad t > 0, \quad (2.87)$$

where $R \equiv r_0/\alpha$.

Now let $U(r, s)$ denote the Laplace transform of $u(r, t)$. Then, taking Laplace transforms of the PDE and boundary condition gives

$$U'' - U' - srU = 0, \quad U(R, s) = \frac{1}{s},$$

where prime denotes the r derivative. The first derivative term can be eliminated by making a transformation of the dependent variable to

$$W = Ue^{-r/2}.$$

Then the differential equation becomes

$$W'' - \left(\frac{1}{4} + sr\right)W = 0.$$

Changing the independent variable to

$$z = \left(\frac{1}{4} + sr\right)/s^{2/3}$$

transforms the equation into **Airy's equation**

$$\frac{d^2W}{dz^2} - zW = 0.$$

Here we have used the same symbol for the dependent variable W . The general solution to Airy's equation is [see Abramowitz and Stegun (1962)]

$$W(z, s) = c_1(s) \text{Ai}(z) + c_2(s) \text{Bi}(z).$$

To keep solutions bounded we must set $c_2(s) = 0$. Hence,

$$W(r, s) = c_1(s) \text{Ai}\left(\frac{0.25 + sr}{s^{2/3}}\right),$$

or

$$U(r, s) = c_1(s)e^{r/2} \text{Ai}\left(\frac{0.25 + sr}{s^{2/3}}\right).$$

Finally we apply the boundary condition $U(R, s) = 1/s$ and we obtain the solution to the problem (2.86)–(2.87) in the transform domain:

$$U(r, s) = \frac{1}{s} e^{(r-R)/2} \text{Ai}\left(\frac{0.25 + sr}{s^{2/3}}\right) / \text{Ai}\left(\frac{0.25 + sR}{s^{2/3}}\right).$$

Although the inversion appears formidable (and it is in the analytic sense), it is relatively easy if carried out numerically. There are several numerical algorithms available to invert Laplace transforms, and two of them are discussed briefly in Appendix C. Here we use the **Stehfest algorithm**. The Maple V (version 5) worksheet, presented in Appendix C, can produce the plots shown in figure 2.6, which are two profiles of the concentration $u(r, t)$. The scaled well radius is $R = 1$.

Exercise 46 *Exercise 47* Consider the model advection-adsorption-dispersion-decay model

$$\begin{aligned} u_t &= au_{xx} - u_x + s - c, \\ s_t &= u - s, \end{aligned}$$

on the domain $x, t > 0$ with $u(x, 0) = s(x, 0) = 0$ and $u(0, t) = u_0$. Take Laplace transforms and show that the bounded solution in the transform domain is

$$U(x, p) = \frac{u_0}{p} e^{mx},$$

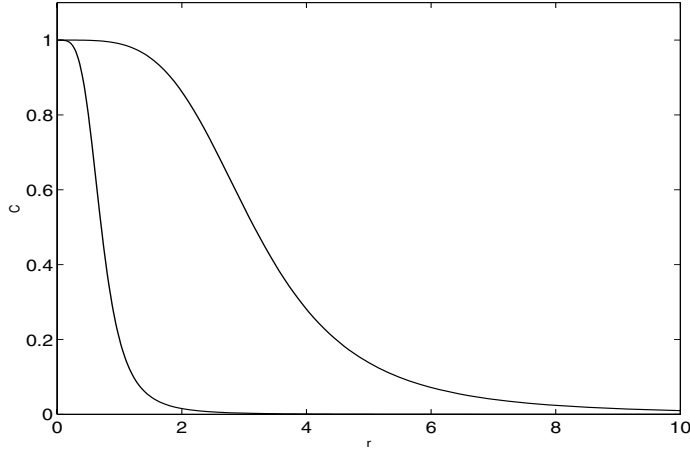


Figure 2.6: Two radial concentration profiles showing how a solute disperses and advects from a well.

where

$$m = \frac{1}{2a} - \frac{1}{\sqrt{a}} \sqrt{\frac{1}{4a} + \frac{p(p+2)}{p+1}}.$$

Obtain an approximation for $t \gg 1$ (large t) and for $t \ll 1$ (small t) by considering $p \ll 1$ and $p \gg 1$, respectively. Show that

$$U(x, p) \sim \frac{u_0}{p} e^{x/2a} e^{-\frac{x}{\sqrt{a}} \sqrt{\frac{1}{4a} + ks}},$$

where $k = 1$ for $p \gg 1$ and $k = 2$ for $p \ll 1$. Thus, show

$$u(x, t) \sim \frac{u_0}{2\pi i} e^{x/2a} \int_B e^{-\frac{x}{\sqrt{a}} \sqrt{\frac{1}{4a} + ks}} e^{pt} dp,$$

where $k = 1$ for $t \ll 1$ and $k = 2$ for $t \gg 1$. Here, B is a Bromwich path. Finally, use a table of Laplace transforms to invert the last expression, obtaining the approximation

$$u(x, t) \sim \frac{u_0}{2} \left\{ \operatorname{erfc} \left[\frac{1}{2\sqrt{a}} \left(x\sqrt{\frac{k}{t}} - \sqrt{\frac{t}{k}} \right) \right] + e^{x/a} \operatorname{erfc} \left[\frac{1}{2\sqrt{a}} \left(x\sqrt{\frac{k}{t}} + \sqrt{\frac{t}{k}} \right) \right] \right\}$$

where $k = 1$ for small t and $k = 2$ for large t .

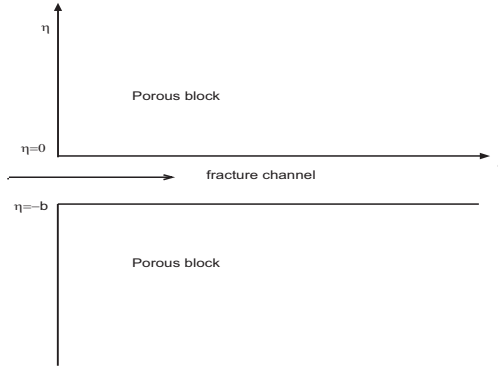


Figure 2.7: Single-fracture medium.

2.7.5 Fractured Media

Fractures in porous media are rapidly conducting pathways that channel the water through the domain. The presence of fractures in the porous fabric can have a significant influence on groundwater transport. For example, it is reported in the literature that fracture networks can significantly retard the transport of migrating radionuclides through the medium. Unfortunately, the structure of fracture systems can be quite complex and difficult to model. Therefore, many of the mathematical models developed in the literature apply only to idealized conditions and fracture geometries. These studies using simplified fissure structures are often considered worst-case scenarios in that, for example, a porous region with a single fracture will retain more of a decaying contaminant than will a complicated fracture network and will therefore lead to an overestimate of the retardation capacity of the porous blocks.

The simplified geometry we consider (figure 2.7) is the same as that studied by Tang *et al.* (1981) and others, namely a single fracture channel of width b in an infinite porous domain [also see Sun (1995), p. 69]. For the final form of the model, in the fracture we consider advection, decay, linear adsorption to the fracture surface, and loss to the fabric; in the porous blocks, or fabric, that bound the channel we impose unidirectional dispersion, perpendicular to the fracture channel, linear adsorption, and decay. This mathematical model leads to a single, degenerate, parabolic problem in a quarter-space with evolutionary, oblique boundary data and source terms.

To fix the notation, let $m(\xi, \eta, \tau)$ denote the concentration of a chemical contaminant (mass per unit volume of water) in the porous block $\xi, \eta > 0$. Here, τ is time. For the present, the contaminant is assumed to diffuse in both the ξ and η directions, and it experiences first-order decay and linear adsorption throughout the region. In the standard way, mass balance of the contaminant gives the governing equation

$$\omega m_\tau = D_1 m_{\xi\xi} + D_2 m_{\eta\eta} - \omega \Lambda m - \rho_b s_\tau,$$

where ω is the constant porosity, D_1 and D_2 are the molecular diffusion constants in the ξ and η directions, Λ is the decay constant, $\rho_b = \rho(1 - \omega)$ is the bulk density of the solid porous matrix, and $s = s(\xi, \eta, \tau)$ is the sorbed concentration given in mass per unit mass of solid fabric. We assume linear adsorption, that is, $s = K_d m$, where K_d is the distribution constant. We may combine the conditions above to write the mass balance equation in the porous domain as

$$R' m_\tau = D' m_{\xi\xi} + D'' m_{\eta\eta} - \Lambda m, \quad \xi, \eta > 0, \quad \tau > 0, \quad (2.88)$$

where $R' = 1 + \rho_b K_d / \omega$ is the retardation constant, $D' = D_1 / \omega$, $D'' = D_2 / \omega$. It is clearly sufficient, by our symmetry assumption, to formulate and solve the problem in the quarter-space $\xi > 0, \eta > 0$.

In the fracture channel $-b < \eta < 0$, $\xi > 0$, the concentration, measured in mass per unit volume of water, is given by $c(\xi, \tau)$. Thus, we are assuming no variation in the concentration across the fracture. To derive the governing equation in the fracture we take a small section of the fracture channel of length $\Delta\xi$, width b , and unit thickness. Mass balance applied to this section yields

$$\frac{\partial}{\partial t}(cb\Delta\xi) = b(\phi(\xi, \tau) - \phi(\xi + \Delta\xi, \tau)) - (b\Delta\xi)\Lambda c - (2\Delta\xi)Q - (2\Delta\xi)s'_t.$$

The left-hand side is the time rate of change of the mass in the section; the first term on the right-hand side is the net flux through the cross sections at ξ and $\xi + \Delta\xi$ (ϕ is the flux); the second term is the decay rate and the third term is rate of loss of contaminant to the porous blocks through the upper and lower faces [$Q = Q(\xi, \tau)$ is measured in mass per unit area per unit time]; the last term is the rate of adsorption to the fracture walls, with $s' = s'(\xi, \eta, \tau)$ given in mass of contaminant per unit area. We assume linear adsorption, i.e., $s' = K'_d c$, and we assume that the loss term is proportional to the concentration gradient in the porous block, i.e., we assume the constitutive relation

$$Q = -D''\omega m_\eta(\xi, 0, \tau).$$

The constitutive relation for the flux ϕ consists of a dispersive flux term and a convection term; that is,

$$\phi = -Dc_\xi + Vc,$$

where D is the constant dispersivity and V is the Darcy velocity. Upon dividing the mass balance law by $b\Delta\xi$, taking the limit as $\Delta\xi$ goes to zero, and using the definitions above, we obtain the mass balance equation in the fracture channel in the form

$$Rc_\tau = Dc_{\xi\xi} - Vc_\xi - \Lambda c + \frac{2\omega D''}{b}m_\eta(\xi, 0, \tau), \quad (2.89)$$

where R is a surface retardation factor in the fracture given by $R = 1 + 2K'_d/b$. Note that our assumption is that the fracture is a channel; that is, we have chosen the porosity to be unity.

Along the interface $\eta = 0$ between the fracture and the porous block we assume that the concentration is continuous, i.e.,

$$m(\xi, 0, \tau) = c(\xi, \tau).$$

Thus, also, $m(\xi, -b, \tau) = c(\xi, \tau)$ along the lower fracture interface.

There are several characteristic times that could be used to rescale the problem and reduce it to dimensionless form. For example, there are time scales for convection, diffusion, and for the rate that contaminant is being injected at the input boundary. We shall scale time on the basis of convection, which is reasonable because the intended observations will often involve measuring contaminant output from the fracture at some distance downstream. Let L be a length scale in the ξ direction, and let $T = L/V$ be the time scale. We take the η length scale to be $Y = \sqrt{D''T}$. For simplicity we assume the retardation parameters to be unity, i.e., $R = R' = 1$. Then, a change to dimensionless variables x, y , and t defined by

$$x = \frac{\xi}{L}, \quad y = \frac{\eta}{Y}, \quad t = \frac{\tau}{T},$$

transforms (2.88) and (2.89) into

$$m_t = \epsilon m_{xx} + m_{yy} - \lambda m, \quad (2.90)$$

$$c_t = \alpha c_{xx} - c_x - \lambda c + \gamma m_y(x, 0, t), \quad (2.91)$$

where

$$\epsilon \equiv \frac{D'}{VL}, \quad \alpha \equiv \frac{D}{VL},$$

and

$$\gamma \equiv \frac{2\omega\sqrt{LD''/V}}{b}.$$

Here, $\lambda = L\Lambda/V$. At the inlet boundary of the fracture we assume a Dirichlet condition

$$c(0, t) = c_0(t), \quad t > 0,$$

where c_0 is a given continuous function representing an input concentration, and $c_0(0) = 0$. Initially we assume the absence of contaminant, or

$$m(x, y, 0) = 0, \quad x, y \geq 0; \quad c(x, 0) = 0, \quad x \geq 0.$$

Along the boundary $x = 0$ we impose a no-flux condition

$$m_x(0, y, t) = 0, \quad y, t > 0. \quad (2.92)$$

Our basic assumptions to simplify the model are

$$\epsilon \ll 1, \quad \alpha \ll 1, \quad \gamma = 0(1).$$

So, on a convection time scale, diffusion in the ξ direction in the porous block is assumed to be small. Furthermore, the smallness of α imposes the condition that dispersion can be neglected in the fracture; such an assumption is valid when the advective flux in the fracture is large [Sudicky and Frind (1982)].

Therefore, the simplified model equations ($\alpha = \epsilon = 0$) become

$$m_t = m_{yy} - \lambda m, \quad (2.93)$$

$$c_t = -c_x - \lambda c + \gamma m_y(x, 0, t). \quad (2.94)$$

We now observe that, because $m(x, 0, t) = c(x, t)$, (2.94) can be regarded as an evolutionary boundary condition on m along the fracture interface $y = 0$. Thus, we write (2.94) as

$$m_t(x, 0, t) = -m_x(x, 0, t) - \lambda m(x, 0, t) + \gamma m_y(x, 0, t).$$

Furthermore, one can remove decay from the preceding equations by the transformation $u(x, y, t) = m(x, y, t)e^{\lambda t}$. Then the final form of the boundary value problem becomes

$$u_t = u_{yy}, \quad x, y > 0, \quad t > 0, \quad (2.95)$$

$$u_t + u_x = \gamma u_y, \quad x, t > 0, \quad y = 0, \quad (2.96)$$

$$u(0, 0, t) = u_0(t), \quad t > 0, \quad (2.97)$$

$$u(x, y, 0) = 0, \quad x, y \geq 0, \quad (2.98)$$

where $u_0 \equiv c_0 e^{\lambda t}$.

Observe that the no-flux boundary condition (2.92) has not been included in the problem (2.95)–(2.98). Indeed, neglecting diffusion in the porous block in the x direction precludes a boundary condition along $x = 0$; otherwise we obtain an ill-posed problem. This means that, in the simplified model, there can be contaminant flux along the boundary $x = 0$. [Logan, Ledder, and Homp (1998) have shown that this problem (2.95)–(2.98) is the leading order problem corresponding to a singular perturbation problem (2.90)–(2.91) with $\alpha = O(\sqrt{\epsilon})$, with a boundary layer in the gradient along $x = 0$.]

Using Laplace transforms we now obtain the solution to (2.95)–(2.98). We proceed formally. Let $\psi(x, t)$ denote the (unknown) value of the concentration u along $y = 0$, and consider the following boundary value problem in y and t :

$$u_t = u_{yy}, \quad y > 0, \quad t > 0, \quad (2.99)$$

$$u(x, 0, t) = \psi(x, t), \quad t > 0, \quad (2.100)$$

$$u(x, y, 0) = 0, \quad y > 0, \quad (2.101)$$

where $x > 0$ is regarded as a parameter. From the results in Chapter 1 we know that the solution to (2.99)–(2.101) is given by the convolution integral

$$u(x, y, t) = h(y, \cdot) \star \psi(x, \cdot) = \int_0^t h(y, t-s) \psi(x, s) ds, \quad (2.102)$$

where h is given by

$$h(y, t) = \frac{y e^{-y^2/4t}}{\sqrt{4\pi t^3}}.$$

If $U(x, y, p)$ and $\Psi(x, p)$ denote the Laplace transforms (on t) of u and ψ , respectively (here, we use the symbol p is the transform variable, rather than s), then applying the convolution theorem to (2.102) gives

$$U(x, y, p) = e^{-y\sqrt{p}}\Psi(x, p). \quad (2.103)$$

Now take the Laplace transform of (2.96) to obtain

$$pU(x, 0, p) = -U_x(x, 0, p) + \gamma U_y(x, 0, p),$$

or

$$\Psi_x(x, p) = -(p + \gamma\sqrt{p})\Psi(x, p),$$

which is a differential equation for Ψ . From condition (2.97) we obtain $\Psi(0, p) = U_0(p)$, where U_0 is the transform of u_0 . Thus,

$$\Psi(x, p) = U_0(p)e^{-(p+\gamma\sqrt{p})x}.$$

This gives, from (2.103),

$$U(x, y, p) = U_0(p)e^{-(p+\gamma\sqrt{p})x-y\sqrt{p}},$$

which is the solution to the problem in the transform domain. By the convolution theorem we then obtain

$$u(x, y, t) = u_0(t) \star \frac{H(t-x)(\gamma x + y)}{\sqrt{4\pi}(t-x)^{3/2}} e^{-(\gamma x + y)^2/4(t-x)}, \quad (2.104)$$

where H is the Heaviside function. Here we have used the well-known transform [see, for example, Carslaw and Jaeger (1959)]

$$\mathcal{L}\left(\frac{z}{\sqrt{4\pi}t^{3/2}}e^{-z^2/4t}\right) = e^{-z\sqrt{p}},$$

and the shift theorem

$$\mathcal{L}(H(t-z)f(t-z)) = F(p)e^{-pz}.$$

Equation (2.104) can be written concisely as

$$u(x, y, t) = \int_0^{t-x} h(\gamma x + y, t-s-x)u_0(s)ds,$$

which is the solution to (2.95)–(2.98).

Exercise 48 Follow the ideas presented in this section and formulate a model of flow on the domain $x > 0$ through an infinite system of parallel fractures (parallel to the x -axis), each of width b and each separated by a porous block of width h . Assume zero initial conditions and a periodic boundary condition on the solute concentration at the inlets to the fractures along $x = 0$. Reduce the model to dimensionless form, neglect dispersion in the porous blocks in the x -direction and obtain a solution for the problem. Logan, Zlotnik, and Cohn (1996) can be consulted for details.

2.8 Reference Notes

There are several elementary, hydrogeology books that have a mathematical flavor, for example, de Marsily (1986) and Fetter (1993). Books that discuss mathematical modeling from an advanced viewpoint are Fowler (1997), Lin and Segel (1989), and Logan (1987, 1997c). Accessible texts for the underlying mathematical fluid mechanics are Acheson (1990), Chorin and Marsden (1993), and Bird, Stewart, and Lightfoot (1960). There are many reference texts for nonlinear PDEs; books dealing strictly with the subject are Logan (1994), Smoller (1994), and Whitham (1974). The book by Knobel (2000) is an excellent introduction to nonlinear waves. Gelhar (1993) has an introduction to the stochastic approach to groundwater problems.



<http://www.springer.com/978-0-387-95276-5>

Transport Modeling in Hydrogeochemical Systems

Logan, J.D.

2001, XIII, 225 p., Hardcover

ISBN: 978-0-387-95276-5