CHAPTER 3
DIFFUSION AND ADVECTION-DIFFUSION PROCESSES

3.1 INTRODUCTION

3.2. Molecular Diffusion and Fick’s Law.

3.3. Statistical Theory of Diffusion

3.4. Brownian Motion

3.5. Random Walk Analysis

3.6. Diffusion Equation and Its Analytical Solutions

3.7. Advection-Diffusion Equation and Its Analytical Solutions.

Reference: Mixing in Inland and Coastal Water by Fischer, et al., 1979, Chapter 2.

3.2. MOLECULAR DIFFUSION AND FICK'S LAW

Consider a portion of a water tank contains blue water and the other portion, yellow water, separated by an impermeable membrane. If the membrane is suddenly removed, we will observe the formation of a greenish mixing zone at the interface of the two waters.

As time progresses, the width of the mixed zone grows. Say, δ, is a half the width of the mixing zone. If we plot the square of δ as a function of time, we will observe a linear trend as shown in the figure. The slope of the linear trend, $\Delta\delta^2/\Delta t$, indicates the rate of the growth of the mixing zone. A constant slope or a linear relationship between δ^2 and t implies that the mixing zone grows at a constant rate. The rate of growth generally depends on the temperature of the fluid and its molecular weight.

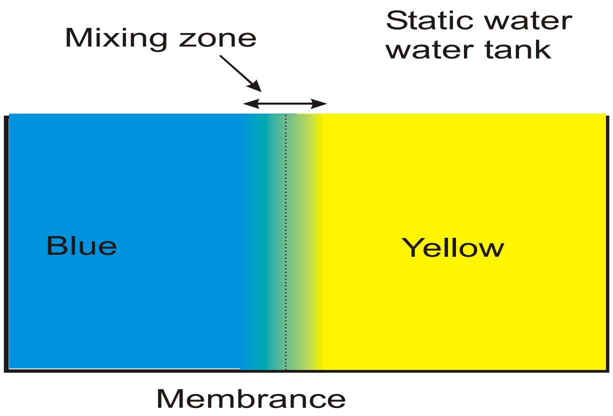


Figure 3.1 A mixing experiment in a static water tank.

The growth of the zone implies increase in mixing. The cause of mixing is attributed to the kinetic activity of molecules, which results in "random" motion of the molecules, and in turn, mixing. This mixing process is generally called "Diffusion". We use the word "random motion" to reflect the fact that we can not describe the motion of each individual molecule in a simple mathematical manners and the fact that we are generally not interested in the behavior of each individual molecule (i.e., microscopic behavior).

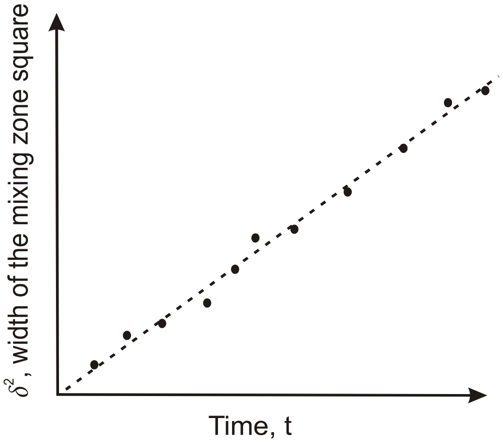


Figure 3.2 Growth of the mixing zone square as a function of time.

Diffusion or smearing is a macroscopic scale phenomenon. It is a result of observation of fluid behavior averaged over a volume. In fact, at microscopic scale level, each blue molecule is still a blue molecule; each yellow molecule is still yellow. The change of color simply is a reflection of the presence of different numbers of blue and yellow molecules in a given volume greater than a molecule itself.

From the water tank experiment, we observe that the blue fluid move into the yellow fluid where the blue is absent or yellow is dominant. Thus, it is logical to conclude that the diffusion takes place from a high concentration region to a low concentration region, depending on the concentration gradient. To quantify this conjecture, a mathematical analysis is presented as follows. Consider the movement of particles at the interface. At a given time interval, Δt, the mass flux per area crossing the interface from blue fluid to the yellow fluid is q_1 and from yellow to blue is q_2. Then the net mass flux per unit interfacial area, ρq [M/L^2T], at the interface is given by:

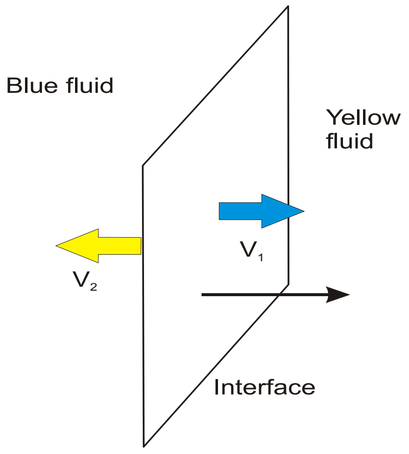


Figure 3.3 Interfacial processes

$$\rho\vec{q} = \rho C_1\vec{v}_1 - \rho C_2\vec{v}_2 \qquad (3.1)$$

Note the concentration is defined as mass per mass (ppm); the average velocity of blue molecules crossing the interface is denoted by v_1; that of yellow molecules is v_2; ρ is the density of the fluid.

If the temperature of the fluid is constant (i.e., isothermal conditions), we may assume that magnitudes of the velocity of yellow and blue molecules are the same although they have different signs

$$|v_m| = |v_1| = |v_2| \qquad (3.2)$$

where | | denotes the magnitude of the velocity. Then the net flux across the interface can be calculated by the formula:

$$\rho\vec{q} = \rho\left(C_1 - C_2\right)\vec{v}_m \qquad (3.3)$$

If we say the C_1 and C_2 are the average concentrations at locations at the opposite side of the interface, separated by a distance ℓ, their coordinates are $x+\ell$ and x, respectively. The net mass flux can be written as

$$\rho\vec{q} = \rho\left(C(x+l) - C(x)\right)\vec{v}_m \qquad (3.4)$$

Applying a first-order Taylor's series approximation, the difference in concentration at $x+\ell$ and x can be written as the product of the concentration gradient and the distance ℓ. That is,

$$\rho\frac{\left(C(x+l) - C(x)\right)}{l} \simeq -\rho\frac{\partial C}{\partial \vec{n}} = -\rho\frac{\partial C}{\partial x} \qquad (3.5)$$

where n is the normal vector to the cross-section. As a result, the net flux vector is given by

$$\rho\vec{q} = -\rho\vec{v}_m l\frac{\partial C}{\partial \vec{n}} \qquad (3.6)$$

If we define $D = V_m l$ and call it the diffusion coefficient, we then have **Fick's law** for diffusion.
That is,

$$\vec{q} = -D\nabla C \qquad (3.7)$$

Fick's Law states that the flux of solute mass (the mass of a solute crossing a unit area per unit time in a given direction) is proportional to the gradient of solute concentration in that direction. This is a general form of Fick's Law. The dimension of D is always $[L^2/T]$. The dimension of q is [L/T] if the concentration is defined as [mass/mass, ppm]. It is $[M/L^2T]$ if the dimension of the concentration is $[M/L^3]$.

3.3 STATISTICAL THEORY OF DIFFUSION

Reference. G.T. Csandady, 1973, Turbulent Diffusion in the Environment.

Previously established Fick's law is a macroscopic law, which describes the diffusion process using an observation-based approach in terms of the average motion of a large number of molecules in a volume. Certainly, the diffusion process can be examined at microscopic level as well. As mentioned previously, the movement of individual molecules, however, is hard to describe. Alternative to studying the movement of individual molecules using a deterministic approach, we may treat it as a random process or stochastic process such that the movement can be described in a statistical or probabilistic framework. This means that we will consider the velocity or displacement of a molecule as a function of time, but its value for any given time is random and may only be specified in terms of a probability distribution. Note that when the probability distribution is not a function of time, the process is known as a "stationary process". Otherwise, it is a non-stationary process and it is "evolutionary".

If we consider the velocity of the molecule as a stochastic process in time and it is a stationary process (i.e., second-order stationary process), the velocity should have the following properties:

$$E\left[v(t)\right]=0 \quad \text{and} \quad E\left[v^2(t)\right]=\sigma_V{}^2 \qquad (3.15)$$

where E represents the expected value (the average value over the ensemble). That is, the mean velocity of a particle is zero and its variance is fixed and does not change.

$$E\left[V(t)V(t+\tau)\right]=\operatorname{cov}(V(t),V(t+\tau)) \qquad (3.16)$$

Where cov[v(t), v(t+τ)] = C(τ) is called the velocity covariance function that depends on the separation time, τ, only. The covariance function is a statistical measure of the persistence of the velocity of a molecule (linear relation between the molecule velocity at two different times, separated by τ). A higher value of the covariance implies higher similarity between the two velocities. If the separation time is zero, τ=0, the covariance is the variance ($C(\tau) = C(0) = \sigma^2_v$).

We can also define an autocorrelation function based on the covariance as

$$\rho(\tau)=c(\tau)/\sigma_V{}^2 \qquad (3.17)$$

The velocity autocorrelation function is assumed to have the following properties:

1) when $\tau=0$, $\rho(\tau)=1$ and
2) when $\tau=\infty$, $\rho(\tau)=0$.
3) The autocorrelation function is bounded by +1 and -1. That is,

$$-1\le\rho(\tau)\le 1$$

Physically, these properties mean that the velocity at any given time is perfectly correlated with itself but is uncorrelated with the velocity at time separated by a large time lag. In addition, the correlation can be either negatively or positively correlated.

Now, we will examine the displacement of a particle over a time interval from 0 to t:

$$x(t) = \int_0^t V(\eta)d\eta \tag{3.18}$$

where η is a dummy integration variable. The rate of change of $x^2(t)$ then can be defined as

$$\frac{d\left[x^2(t)\right]}{dt} = 2x\frac{dx}{dt} = 2\int_0^t V(\eta)d\eta \bullet V(t) = 2\int_0^t V(t)V(\eta)d\eta \tag{3.19}$$

Since the velocity of the molecule is a stochastic process, implying an infinite number of possible velocity values, there will be an infinite number of possible displacements and in turn $x^2(t)$ values. To obtain an average $x^2(t)$ value, we will take the ensemble average (i.e., taking expect value), which results in

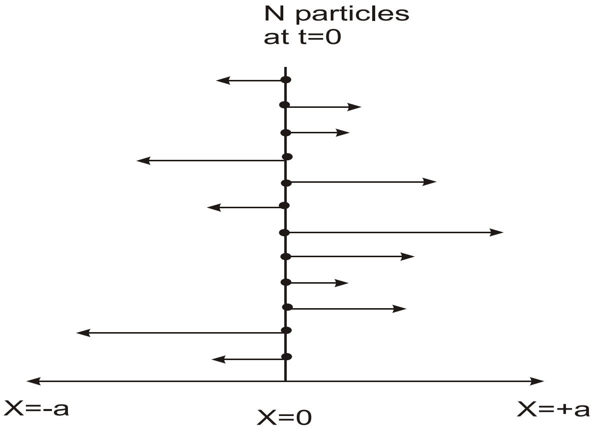


Figure 3.4 A schematic illustration of diffusion concept using movements of a large number of particles.

$$\frac{dE\left[x^2\right]}{dt} = 2\int_0^t E\left[V(t)V(\eta)\right]d\eta = 2\sigma^2{}_V\int_0^t \rho(\tau)d\tau \tag{3.20}$$

Notice that $E[v(t)v(\eta)]=c(t-\eta)=c(\tau)=\sigma^2{}_v\,\rho(\tau)$. Physically, this means that the rate of change in the average square of the displacement of the molecule can be related to the covariance function of its velocity.

This analysis can also be visualized in a different way. Consider an infinite number of molecules exercising random movement, starting from x=0 over a given period from 0 to t. Each molecule has a different velocity.

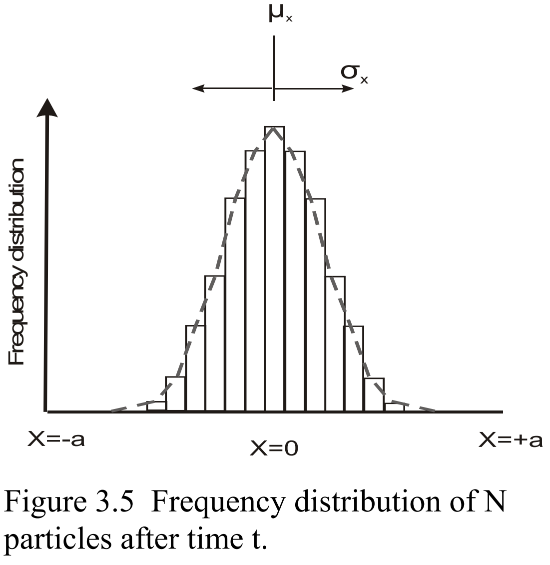


Figure 3.5 Frequency distribution of N particles after time t.

After a period of time, we count the number of molecule at each location x and plot the frequency distribution as illustrated in the figure below. The fraction of the number of molecules at a given location, to the total number of molecules can be defined the frequency, f. Thus, the mean of the distribution will represent the average displacement, μ_x, of the molecules. Then, we define σ_x as a measure of "spread" along the x axis around the mean position. Mathematically,

$$E[x(t)] = \mu_x = \int_{-\infty}^{\infty} x f(x) dx \qquad (3.21)$$

The spread of the molecules is then defined by a spatial variance

$$\sigma_x^2(t) = \int_{-\infty}^{\infty} x^2 f(x,t) dx = E\left[x^2(t)\right] \qquad (3.22)$$

If we say the number of molecules at a given x is the concentration C(x), then the frequency f(x) is the ratio of C(x) to the total number of molecules, C(x)dx. The spatial variance then becomes

$$\sigma_x^2(t) = \int_{-\infty}^{\infty} x^2 c(x,t) dx \Big/ \int_{-\infty}^{\infty} c(x,t) dx \qquad (3.23)$$

If we are interested in the rate of change of the variance, from equation (3.3.6) we have

$$\frac{d\sigma_x^2}{dt} = 2\sigma_V^2 \int_0^t \rho(\tau) d\tau \qquad (3.24)$$

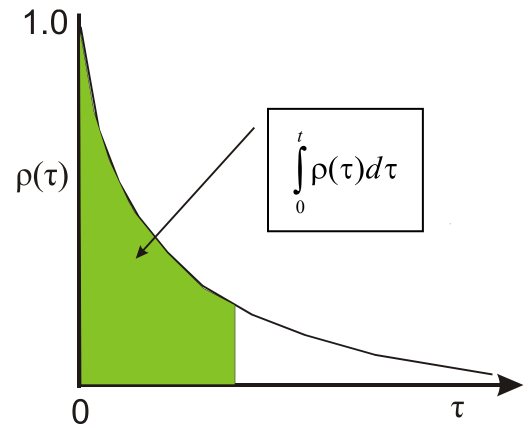


Figure 3.6 The velocity correlation function.

This is known as the G.I. Taylor's theorem, an important theory in studies of diffusion, turbulence, and dispersion process. The theorem states that the rate of spread will depend on the variance of velocity of molecules and their sum of the autocorrelation function over the time period. It is logical to assume that the autocorrelation function of the velocity decays exponentially as shown in the figure (3.3.3). This assumption implies that if a molecule starts with a given velocity, it cannot retain the same velocity after a period of time due to collision with other molecules. Thus, we expect that at large times, its velocity no longer resembles the original given velocity.

Under this condition, it is easy to see that the integral of the autocorrelation function will reach an asymptotic constant value as time approaches infinity. That is,

$$\int_0^t \rho(\tau)d\tau = \text{constant} \qquad (3.25)$$

when t approaches ∞. If this is the case, the rate of the spreading (equation (3.3.3)) will also approach an asymptotic value as t becomes large.

$$\frac{d\sigma_x^2}{dt} = \text{constant} \qquad (3.26)$$

The constant value implies that the size of the cloud of molecules (standard deviation, σ_x) at large times grows at a rate proportional to the square root of time. That is,

$$\frac{\partial \sigma}{\partial t} = \frac{\text{constant}}{\sqrt{t}} \qquad (3.27)$$

According to the above analysis, the size of a dispersive cloud can be determined by

$$\sigma_x^2(t) = 2\sigma_V^2 \int_0^t \int_0^{t'} \rho(\tau)d\tau dt' = 2\sigma_V^2 \int_0^t (t-\tau)\rho(\tau)d\tau \qquad (3.28)$$

Based on the statistical approach, we lean that we can quantify the diffusion process using a spatial mean to describe its mass center and the spread of molecules using the spatial variance. The rate of spreading is a function of time and can reach an asymptotic value, and it is controlled by the molecule velocity covariance function.

Notes:

The above double integration is carried by the following procedure. Supposed we have

$$\int_0^T \int_0^T c(t-s)dtds \qquad (3.29)$$

Let $w=t-s$, then we have $dw = dt$ and change the limits of the integral to obtain

$$\int_0^T \int_{-s}^{T-s} c(w)dwds \qquad (3.30)$$

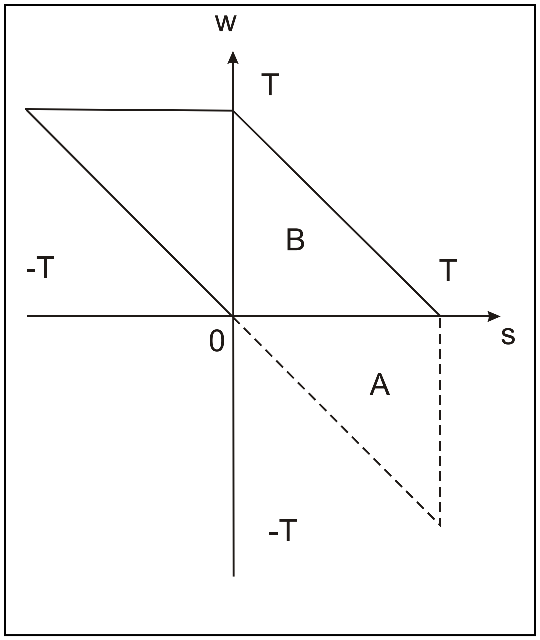


Figure 3.7 Diagram showing an integration procedure.

Next, we can exchange the order of integration due to the same limits for both integrals.

$$\int_{0}^{T}\int_{-w}^{T-w} c(w)\,ds\,dw \qquad (3.31)$$

The above integration can be decomposed into two parts as shown in the figure.

$$= \int_{-T}^{0}\left[\int_{-w}^{T} c(w)\,ds\right]dw + \int_{0}^{T}\left[\int_{0}^{T-w} c(w)\,ds\right]dw \qquad (3.32)$$

Furthermore,

$$= \int_{-T}^{0} (T+w)c(w)\,dw + \int_{0}^{T} (T-w)c(w)\,dw \qquad (3.33)$$

Finally, we have

$$= 2\int_{0}^{T} (T-w)c(w)\,dw \qquad (3.34)$$

3.4 BROWNIAN MOTION

The previous section shows that the spreading of a dispersive cloud of molecules can be related to the velocity covariance function of molecules. However, we have no way to determine the velocity covariance function. The Brownian motion to be discussed below may shed some light on this issue. Brownian motion refers to the irregular motion of small grains or particles of colloidal size immersed in a static fluid. Botanist Robert Brown (1826) observed this phenomenon with the aid of a microscope. Its nature remained a puzzle for a long time. Finally, a paper by Einstein (1905) unraveled this mystery and showed "Brownian Motion" is maintained by collisions with the molecules of the surrounding fluid. Under normal conditions in a liquid, it suffers on the order of 10^{21} collisions per second. Such impulses produce random wanderings of the particles and result in the particles' dispersal.

3.4.1 Dynamic Hypothesis for Brownian motion.

Before we analyze the Brownian motion, we will assume that the Brownian particle is much larger than the molecular structure of the surrounding fluid. Therefore, it must experience a viscous resistance force per unit mass, which will be proportional to its velocity:

$$R = -\beta \vec{U} \tag{3.35}$$

where β is a friction constant, [1/T]. Based on Stoke's law, we know for a spherical particle, $\beta=(6\pi\mu a)/m$, where μ is the viscosity of the fluid, a, and m are the radius and mass of the particle, respectively.

We also will assume that the Brownian particle is small enough to be affected by molecular collisions. In other words, if the particle, moving at a velocity, u, is subject to the random collision of surrounding molecules, it will undergo an acceleration, A(t), which is equal to the force exerting by the molecules divided by the mass of the Brownian particle.

Now we consider the balance of these two forces on a Brownian particle. The net force per unit mass then represents the net acceleration, dU/dt. That is,

$$\frac{d\vec{U}}{dt} = -\beta \vec{U} + \vec{A}(t) \tag{3.36}$$

This equation is known as the Langevin's Equation in fluid dynamics. It has a solution,

$$\vec{U}(t) = U_0 e^{-\beta t} + e^{-\beta t}\int_0^t e^{\beta t} A(\tau) d\tau \tag{3.37}$$

where U_o is the velocity of the particle at time $t = 0$. According to the solution, we see that the velocity of the particle consists of two additive components. The first is the velocity component that depends on the initial velocity (i.e., $U_o e^{-\beta t}$) and the random acceleration, $A(t)$, which is independent of the initial velocity. The strength of the first velocity component will decay exponentially as time increases. When $t >> 1/\beta$ or $\beta t >> 1$, $U_o e^{-\beta t}$ approaches 0. The reduction of this component implies that the particle is no longer dependent on the initial velocity U_o, i.e. the particle "forgot" its initial velocity. In other words, the contribution that depends on U_o has decayed to zero. The remaining component is the end-result of a large number of independent, random impulses.

3.4.2 Autocorrelation function of the Brownian Particle Velocity

The above analysis of the velocity allows us to evaluate the autocorrelation function of the velocity of Brownian particle, required in the evaluation of the rate of spreading of the particles. The autocorrelation function is

$$\rho(\tau) = E\left[U(0)U(\tau)\right]/\sigma_U^2 = e^{-\beta\tau} \tag{3.38}$$

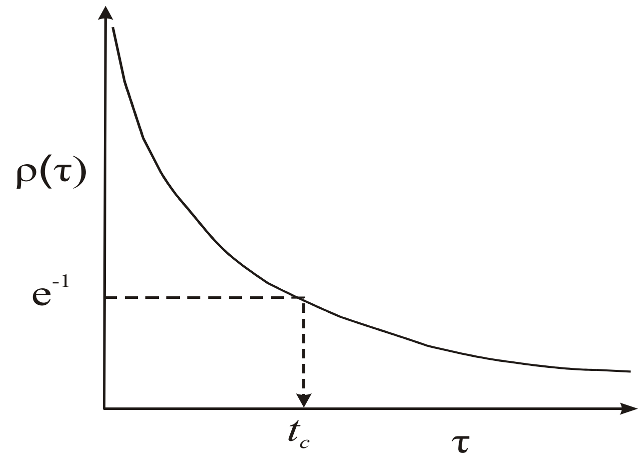


Figure 3.8 Velocity persistent time.

The behavior of the velocity autocorrelation function is illustrated in Fig. 3.8. Based on the figure, we may define a persistent time, $t_c = \beta^{-1}$, at which the autocorrelation of the velocity drops to e^{-1} level. This time scale is equivalent to the correlation scale we discussed previously. It is the time interval beyond which the velocity of the particle is no longer related to its initial velocity. Substituting the correlation function into Taylor's Theorem, we have an expression of the variance of the cloud as a function of time.

$$\sigma_x^2(t) = 2\sigma_V^2 \int_0^t (t-\tau)\rho(\tau)d\tau = 2\sigma_V^2\left[tt_c - t_c^2\left(1-e^{-t/t_c}\right)\right] \tag{3.39}$$

Notice that when $t >> t_c = \beta^{-1}$, the first term in the bracket will be greater than the second term, i.e., $tt_c \gg t_c^2(1-e^{-t/t_c})$. As a result, the variance becomes

$$\sigma_x^2 = \frac{2\sigma_V^2}{\beta}t \tag{3.4.6}$$

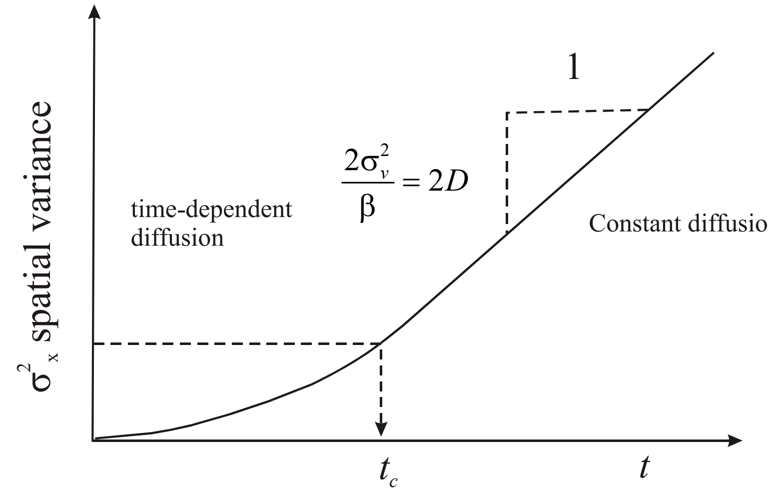


Figure 3.9 Schematic illustration of temporal behavior of the spatial variance of a diffusing plume.

The rate of spreading then is given by

$$\frac{\partial\sigma_x^2}{\partial t} = \frac{2\sigma_V^2}{\beta} = \text{const.} \tag{3.39}$$

The behavior of the spatial variance is depicted in Figure 3.9

According to this figure, at early times ($t<<t_c$), the rate of change in σ_x^2 varies with time (time-dependent diffusion). At time that is greater than t_c, this rate approach to a constant value. This constant value is directly related to the diffusion coefficient in Fick's Law as shown later.

Now, one may ask how long it will take to reach the region where the diffusion coefficient is constant. In other words, what is the persistent time t_c ? To answer this question, we will use Stoke's Law to determine t_c.

$$t_c = \frac{1}{\beta} = \frac{m}{6\pi a \mu} \qquad (3.40)$$

Suppose we consider dispersal spherical particles of a radius a = 10^{-4} cm (the limit of visibility) in the air. Assume a spherical particle of density approximately equal to 1 g/cm^3, floating in air which has a viscosity 16x10^{-2} g/s/cm. Based on Stoke's law the persistent time, t_c, is approximately equal to 1.4x10^{-8} seconds. That is, at time less than 1.4x10^{-8} seconds, the rate of dispersal of the particles is time-dependent; if time is greater than 1.4x10^{-8} seconds, the rate is constant, which can be related to the diffusion coefficient. For most cases our observation time interval is much larger than 1.4x10^{-8} seconds, we certainly will not observe the time-dependent portion of the process. As a result, the time-dependent diffusion phenomenon is often neglected and the diffusion coefficient is assumed to be a constant. In other words, while the diffusion process always undergoes a time-dependent behavior, **our observation scale (the scale of our interest) is much larger than the correlation scale of the velocity variation. Subsequently, for practical purposes we may regard the diffusion coefficient to be a constant.**

3.4.4 Relationship between Diffusion Coefficient and Spatial Concentration Variance.

In the previous analysis, we assume the rate of change in the spatial concentration variance is related to the diffusion coefficient. Here, we will provide a mathematic proof based on the diffusion equation.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (3.41)$$

Multiply the above equation with x^2 and integrate the equation over x from $+\infty$ to $-\infty$, we have

$$\int_{-\infty}^{\infty} \frac{\partial c}{\partial t} x^2 dx = \int_{-\infty}^{\infty} D x^2 \frac{\partial^2 c}{\partial x^2} dx \qquad (3.42)$$

The right-hand side of the equation can be derived by integration by parts (see next page) and then we have

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty} c x^2 dx = 2D\int_{-\infty}^{\infty} c dx \qquad (3.43)$$

Therefore,

$$\frac{\partial}{\partial t}\left[\int_{-\infty}^{\infty} c x^2 dx \Big/ \int_{-\infty}^{\infty} c dx\right] = 2D \qquad (3.44)$$

The term inside the bracket is the expression of the spatial variance. As a result, we demonstrate that

$$\frac{\partial \sigma_x^2}{\partial t} = 2D \qquad (3.45)$$

Notes: Integration by parts:

$$\int x^2 \frac{\partial^2 c}{\partial x^2} dx$$

To integrate the above equation, we will use the formula:

$$\int UdV = UV - \int VdU$$

and let:

$$U = x^2 \qquad dV = \frac{\partial^2 c}{\partial x^2} dxU = x^2$$

Then

$$dU = 2xdx \quad \text{and } V = \frac{\partial c}{\partial x}$$

Therefore, we have:

$$= x^2 \frac{\partial c}{\partial x} - 2\int \frac{\partial c}{\partial x} 2xdx$$

Now, let U = x, and $dV = \frac{\partial c}{\partial x} dx$

Then, dU = dx and V = c:

$$= x^2 \frac{\partial c}{\partial x} - 2\left[xc - \int cdx \right]$$

$$= x^2 \frac{\partial c}{\partial x}\bigg|_{-\infty}^{\infty} - 2xc\big|_{-\infty}^{\infty} + 2\int cdx$$

$$= (\infty)^2 (0) - 2(\infty)(0) + 2\int 0dx$$

3.4.5 Evaluation of diffusion coefficient from snapshot of plumes.

According to the above analysis, suppose that we have several snapshots of a concentration plume (plots of concentration as function of spatial coordinates) at different times. Then, we can hypothetically use the following formulas to evaluate their first and second moments and determine the molecular diffusion coefficient.

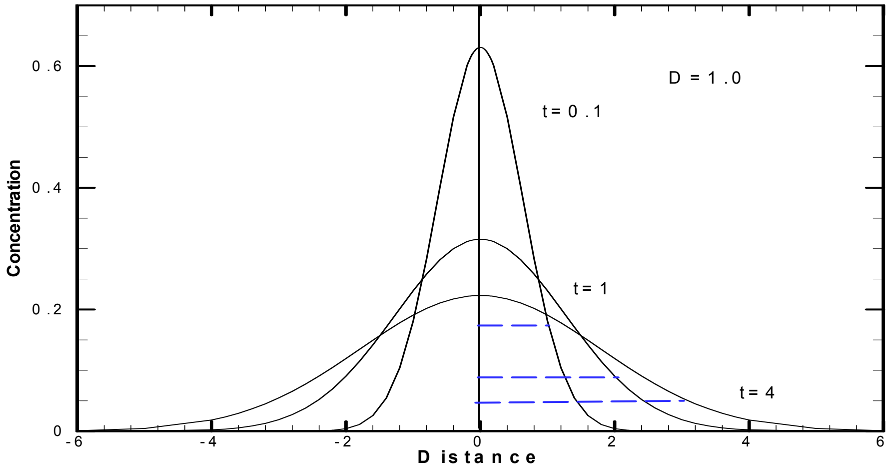


Figure 3.10 An illustration of concentration distributions at various times of an impulse input and square-root of their spatial variances (blue dashed lines).

The first moment can be estimated by

$$\bar{x} = \sum_{t=1}^{n} x_t C_t / \sum_{t=1}^{n} C_t \qquad (3.46)$$

The first moment represents the mean position of the plume. The total number of concentration measurements is n; x_i is the location of measurement C_i. The estimate of second moment can be expressed as:

$$\sigma_x^2 = \frac{\sum_{t=1}^{n} (x_t - \bar{x})^2 C_t}{\sum_{t=1}^{n} C_t} \qquad (3.47)$$

Estimation of Diffusion Coefficient, D

1. Calculate σ_x^2 at different times, using the above formulas.
2. Plot σ_x^2 v.s. time as illustration in the figure above and find a best-fit line that goes through the origin.
3. Determine the slope of the best-fit line. The slope is equal to two times the diffusion coefficient.

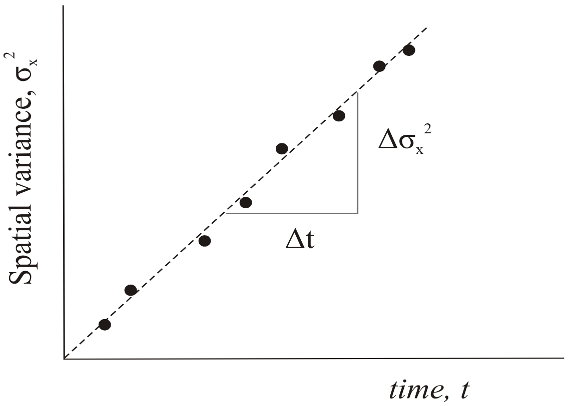


Figure 3.11 A plot of the spatial variances vs. time, for estimating the diffusion coefficient.

3.5 RANDOM WALK ANALYSIS

Reference: Fischer et al. 2.2.1.; Csandy 2.6

From the previous Brownian motion analysis, we have demonstrated two aspects of a concentration displacement probability distribution, $f(x, t)$, or $C(x, t)$ due to diffusion:

a. 1st. moment of the C(x, t)

$E[x(t)] = 0$

b. 2nd. moment at $t >> t_c = 1/\beta$

$\sigma_x^2 = E\left[x^2(t)\right] = 2Dt$

In other words, the concentration spatial variance, σ_x^2, is linearly proportional to time at large times. The standard deviation is then proportional to the square root of time.

$\sigma_x \propto \sqrt{t}$

However, the analysis did not reveal the shape of the plume or concentration distribution as a function of time. Therefore, our next task is to examine the distribution at the large times ($t >> t_c = 1/\beta$).

For molecules, we can see that $t_c << 1$ second. That is, a molecule "forgets" its initial velocity after 1 second or less. Since our observation time interval Δt for diffusion is much larger than one second, the diffusion process that we observe essentially is under the situation that the movement of molecules is uncorrelated. Each step of the molecule is effectively taken at random, independent of any previous step or the particle executes a "random walk". Based on this conclusion, a theoretical analysis of the distribution of molecules, using a random walk analysis, becomes suitable.

To simplify our analysis, we restrict our analysis to random walk along a straight line. This assumption simply focuses us on a one-dimensional analysis. To further simplify our analysis, we will assume that

1. Each Δt, a molecule walks a unit step length.
2. The probability of either a forward or a backward step is ½, analogous to coin tossing experiment.

Based on this assumption, after N steps, the particle could locate at any point from -N to +N:

- N, - N + 1, - N + 2, ..., - 1, 0, 1, ...N - 1, N

if the particle is released at the origin. Then, we ask what is the probability that a particle reach a given point - N < m < + N ?

Let us examine a simple experiment that involves only three steps. Assume that a forward step is represent by + and a backward step by -. Then, we ask ourselves: what is the probability of finding the particle at the location one forward step from the origin? To answer this question, we see that three steps must consist of two forward steps and one backward step (+, +, -) to reach that given location. The probability of obtaining two forward steps and one backward step in the three steps is 1/8. That is,

$$P(+, +, -) = P(+)\,P(+)\,P(-) = ½ \times ½ \times ½ = 1/8$$

In addition to this possible permutation of the forward and backward steps, we must also consider the other possible permutations: we may get one backward step first and then two forward steps follow (- , +, +), or one forward step, one backward step, and one forward step (+, -, +). The net result of these two permutations of steps will also lead the particle to the same location.

Consequently, we must consider the different permutation of these steps or different possible sequences of the steps, which will lead to the same result. The total number of possible sequences of the two forward steps and one backward step can be evaluated as

$$\frac{3!}{1!2!} = 3$$

Finally, the probability that a particle moves to one step forward from the origin after three steps is

3 x ⅛ = ⅜

If we extend this analysis to N steps, the probability of a particle moving to position m after N steps for a given sequence is $(\frac{1}{2})^N$. Then, we shall consider the number of sequences of these N steps that will lead the particle to m.

Number of forward steps = *f*

Number of backward steps = b

$f + b = N$

$f - b = m$

$f = (N + m)/2 \qquad b = (N - m)/2$

Then, the number of different sequences consisting of exactly *f* forward and b backward steps is:

$$\frac{N!}{f!b!} \qquad (3.48)$$

Thus, the probability that a particle reaches a given point, - N < m < N, is

$$P(m,N) = \left[\frac{N!}{f!b!}\right](\frac{1}{2})^N = \frac{N!}{(\frac{N+m}{2})!(\frac{N-m}{2})!}(\frac{1}{2})^N \qquad (3.49)$$

This is basically a binomial probability distribution in the discrete case. If N >> m, we can extend this result to the continuous case. The distribution function thus becomes:

$$P(m,N) = \sqrt{\frac{2}{\pi N}}\exp\left(-\frac{m^2}{2N}\right) \qquad (3.50)$$

If we compare this result to a normal (Gaussian) distribution with mean (μ) equals to zero,

$$P(x;\sigma^2,\mu) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{x^2}{2\sigma^2}\right) \qquad (3.51)$$

We see that σ must equal to $\sqrt{N}$. That is, if N is large, the probability distribution for the particle to be located at location m approaches a normal or Gaussian distribution.

The above analysis tells us the probability distribution of finding a particle located at location, m, after N steps. You then would ask how this probability distribution is related to the concentration distribution *C(x, t)* caused by diffusion or Brownian motion. To establish the relation between *P(m, N)* and *C(x,t)*, we consider the case where ℓ is the step length and x denotes the distance from the origin. Then, the number of steps to x is

m = x/ℓ ;
The probability to find a particle at $m_1 < x < m_2$ is given by

$$\int_{m_1}^{m_2} P(\gamma, N)d\gamma = P(m,N)\cdot\left[\frac{m_1-m_2}{2}\right] = P(m,N)\left[\frac{x_1}{\ell}-\frac{x_2}{\ell}\right]/2 = P(m,N)\frac{\Delta x}{2\ell} \qquad (3.52)$$

The total mass between m_1 and m_2 is given as

$$\Delta M = M \times P(m,N)\frac{\Delta x}{2\ell} \qquad (3.53)$$

where M is the total mass under the entire curve. If we define the concentration as mass per unit length, then we have

$$\frac{\Delta M}{\Delta x} = \frac{M}{2\ell}P(m,N) \qquad (3.54)$$

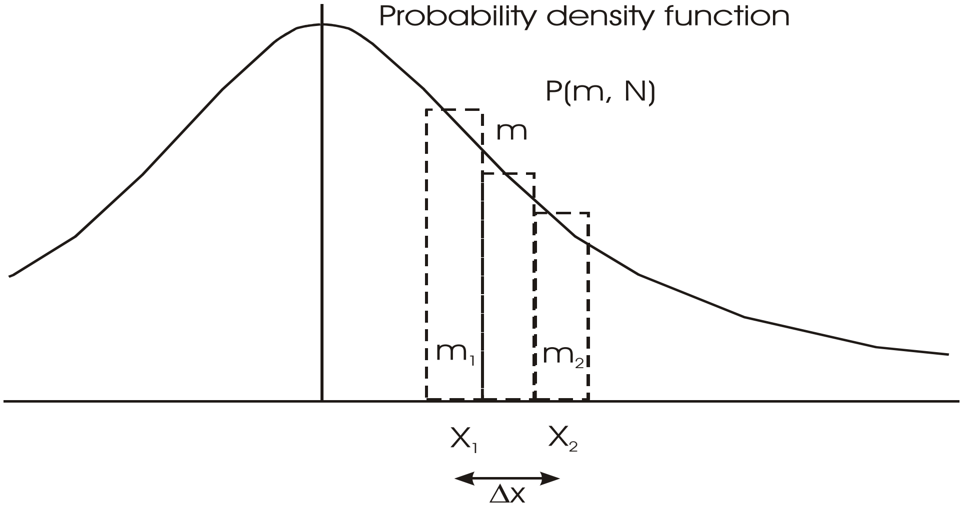


Figure 3.12 A schematic illustration of the concept for relating probability density function used to concentration distribution.

If N approaches ∞, we then have a continuous probability function and the concentration becomes

$$\frac{\Delta M}{\Delta x} = \frac{M}{2\ell}\sqrt{\frac{2}{\pi N}}\exp\left(-\frac{m^2}{2N}\right) = \frac{M}{2}\sqrt{\frac{2}{\pi N \ell^2}}\exp\left(-\frac{m^2}{2N}\right) \qquad (3.55)$$

If we define

$D = \frac{1}{2} n\ell^2$, and $t = \frac{N}{n}$,

where n is the number of displacement per unit time and recall that $m = \frac{x}{\ell}$, we then have:

$$C(x,t) = \frac{M}{2\sqrt{\pi D t}} \exp(-\frac{x^2}{4Dt}) \qquad (3.56)$$

This is exactly the solution of a one-dimensional diffusion equation with an impulse input. Again compare this to the normal probability distribution,

$$P(x,t) = \frac{1}{\sigma\sqrt{2\pi}} \exp(-\frac{x^2}{2\sigma^2}) \qquad (3.57)$$

We see that $\sigma^2 = 2Dt$ and this implies

$$\frac{\partial \sigma^2}{\partial t} = 2D \qquad (3.58)$$

According to the above analysis, we learn that if $t >> t_c$, molecules exercise independent random walk, which leads to a constant rate of spreading, and thus, a constant diffusion coefficient. At the same time the concentration distribution approaches a normal or Gaussian distribution if a slug input is considered. In fact, this distribution is identical to the solution of the classical diffusion equation, implying the diffusion equation is valid for describing diffusion processes if $t >> t_c$. On the other hand, at time less than t_c, we know that the rate of spreading of a solute continuously increase in a nonlinear fashion, but we do not know what the distribution should be. The diffusion equation may then be valid in the ensemble mean sense (i.e., it describes the average of many possible behaviors of diffusion process). More specifically, we do not have an equation to describe the diffusion process at time less than t_c. For molecular diffusion, the time, t_c, however is in the order of thousands of a second and our observation time scale is much greater than that. As a consequence, the classical diffusion equation and its solution are valid for the scale of our observation of molecular diffusion.

3.6 DIFFUSION EQUATION

Consider the equation of mass conservation of the tracer. The continuity equation states that divergence ($\nabla\bullet$) of the mass flux equals change in mass in a control volume:

$$-\nabla\bullet\rho\vec{q} = \frac{\partial\rho C}{\partial t} \tag{3.59}$$

If we assume that ρ is constant in time and space, the continuity equation can be written as

$$-\nabla\bullet\vec{q} = \frac{\partial C}{\partial t} \tag{3.60}$$

Using Fick's Law for $\vec{q}$, we have a general diffusion equation:

$$\nabla\bullet(D\nabla C) = \frac{\partial C}{\partial t} \tag{3.61}$$

If D is constant, the diffusion equation is given as

$$D\nabla^2 C = \frac{\partial C}{\partial t} \tag{3.62}$$

The diffusion coefficient theoretically is a tensor. However, little information about its tensor property is available. For most cases, we assume it is a scalar.

The diffusion equation written in the Cartesian coordinate system: in a three-dimensional system

$$D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) = \frac{\partial C}{\partial t} \tag{3.63}$$

In a two-dimensional x-y space,

$$D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) = \frac{\partial C}{\partial t} \tag{3.64}$$

In a one-dimensional x coordinate system, we have

$$D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \tag{3.65}$$

3.6.1 Analytical Solutions of the Diffusion Equation for Various Initial and Boundary Conditions

To illustrate the behavior of the solution to the diffusion equation, we will concentrate on the one-dimensional diffusion equation only. The procedures in general can be extended to multidimensional problems. Now consider a one-dimensional diffusion process in an infinite domain. The governing equation is

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (3.66)$$

Boundary conditions are $c(-\infty,t)=0$, and $c(+\infty,t)=0$, at all *t*, and an initial condition, $c(x,0)=0$ at all x. The solution to the governing equation depends on the form of input. Here we will consider two cases: 1) a spatial distribution of the input concentration is specified at t = 0, and 2) a concentration at a fixed point is specified as a function of time. Solution techniques are available in many reference books such as Conduction of Heat in Solids by Carslaw and Jaeger (1959), and Diffusion by Crank, J.C. (1956). In the following sections we will present the solution without introducing techniques for solving the equation.

3. 6.1 Spatial distribution of input concentration is specified. Here we will examine the solution for a) an impulse, b) an arbitrary, and c) a step input.

(A) An impulse input or slug input. At t = 0, a tracer of mass, M, is suddenly released at the point x = ξ. For example, a drop of red ink was released to a cup of static and clean water and we would like to quantify the concentration of the red ink in time and space. Mathematically,

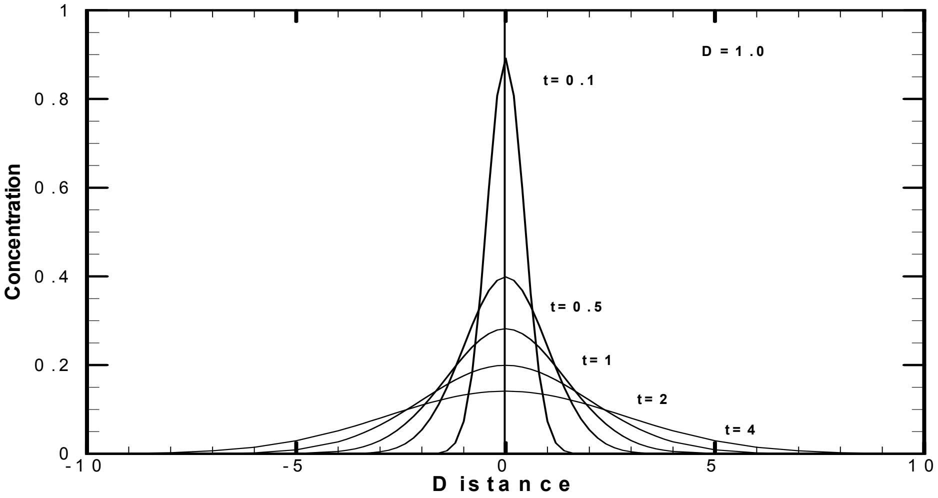


Figure 3.13 Spatial concentration distributions at different time due to a relase of an impulse input.

this input can be specified as $C(x,0)=\frac{M}{\rho A}\delta(x-\xi)$ where δ is a delta

$$\text{function}\begin{cases}\int_{\xi^-}^{\xi^+}\delta(x-\xi)dx=1\\ \delta(x-\xi)=0 \qquad x\neq\xi\end{cases}$$

The solution corresponding to this case is:

$$C(x,t)=\frac{M}{\rho A\sqrt{4\pi Dt}}\exp\left[\frac{-(x-\xi)^2}{4Dt}\right]$$

Notice the concentration has the dimension [mass/mass, ppm]; A is the cross-sectional area [L^2]; the delta function has a dimension [1/L].

A graph of the solution as a function of x for different times is shown in the figure below.This figure shows that the concentration distribution is always symmetric (a bell-shape). This distribution is called a Gaussian distribution or normal distribution, the same as in statistics.

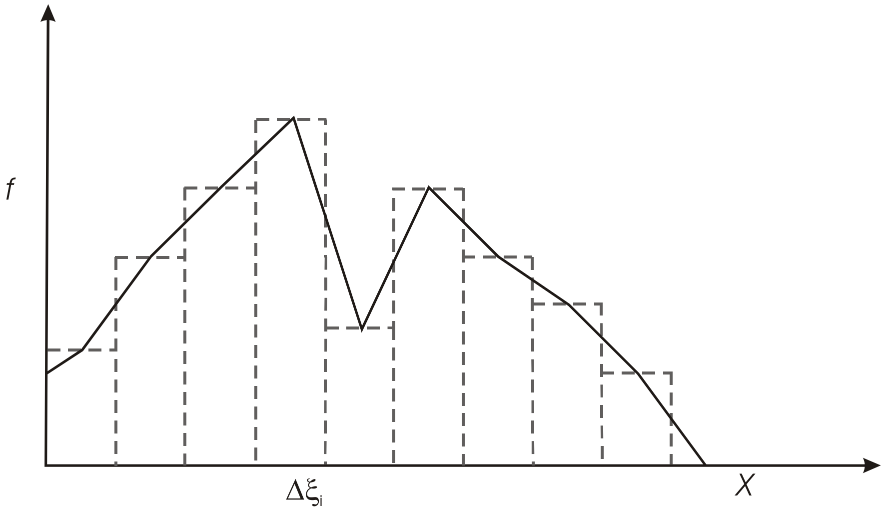


Figure 3.14 Descritization of an arbitrary input in space.

Initially, the distribution is narrow and with a high peak concentration. As time progresses, the peak value decreases and the base of the distribution broadens. The area under the distribution at different times must be the same due to conservation of mass.

(B) Arbitrary Input, Suppose now that the input concentration is specified as $C(x,0)=f(x)$ at $-\infty<x<\infty$, where *f*(x) is some arbitrary function. In spite of the form of the arbitrary function, a *f*(x) function can be represented by a series of separated slugs (or impulse inputs, say, 1, 2, …n, see Figure). Each individual slug has a finite width dξ and a mass *f*(ξ) dξ. That is,

$$M(\xi)=f(\xi)d\xi=\left[\frac{M}{L}\right][L]$$

The solution for each slug *i* is given by

$$C_i(x,t) = \frac{f(\xi_i)d\xi_i}{\rho A\sqrt{4\pi Dt}}\exp\left[\frac{-(x-\xi_i)^2}{4Dt}\right]$$

which represents the contribution to the solution due to the ith slug. Then, the total contribution at a given x and t from all such slugs then becomes

$$C(x,t) = \sum_{i=1}^{n}\frac{f(\xi_i)\Delta\xi_i}{\rho A\sqrt{4\pi Dt}}\exp\left[\frac{-(x-\xi_i)^2}{4Dt}\right]$$

If the we allow the width of the slug to be infinitesimally small, a continuous solution is given as

$$C(x,t) = \int_{-\infty}^{\infty}\frac{f(\xi)}{\rho A\sqrt{4\pi Dt}}\exp\left[\frac{-(x-\xi)^2}{4Dt}\right]d\xi$$

C) Step Input. This input describes a section of the domain being imposed with a given concentration everywhere at time equals zero (e.g., at t=0, a concentration of *C₀* is released over a segment of the domain x<0—analogous to the sudden removal of the membrane in the water tank experiment). We want to find the concentration spatial and temporal distributions. Mathematically, the step input take the following form:

$$C(x,0) = \begin{Bmatrix} 0, x>0 \\ C_0, x<0 \end{Bmatrix} = \frac{f(x)}{\rho A}$$

Solution to the diffusion with this type of step input can be obtained by using the solution developed previously for arbitrary input and setting the arbitrary input function to the step input. That is,

$$C(x,t) = \int_{-\infty}^{0}\frac{C_0}{\sqrt{4\pi Dt}}\exp\left[\frac{-(x-\xi)^2}{4Dt}\right]d\xi + \int_{0}^{\infty}0\exp\left[\frac{-(x-\xi)^2}{4Dt}\right]d\xi$$

which leads to

$$C(x,t) = \frac{C_0}{\sqrt{\pi}}\int_{-\infty}^{0}\exp\left[-\left(\frac{(x-\xi)}{\sqrt{4Dt}}\right)^2\right]\frac{d\xi}{\sqrt{4Dt}}$$

After transformation using $u = (x-\xi)/\sqrt{4Dt}$, we have

$$C(x,t) = -\frac{C_0}{\sqrt{\pi}}\int_{\infty}^{x/\sqrt{4Dt}}\exp\left[-u^2\right]du$$

$$= \frac{C_0}{\sqrt{\pi}}\left(\int_{-\infty}^{0}\exp\left[-u^2\right]du - \int_{0}^{x/\sqrt{4Dt}}\exp\left[-u^2\right]du\right)$$

$$= \frac{C_0}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{2} - \int_{0}^{x/\sqrt{4Dt}}\exp\left[-u^2\right]du\right]$$

$$= \frac{C_0}{2}\left[1 - erf\left[\frac{x}{\sqrt{4Dt}}\right]\right] = \frac{C_0}{2}erfc\left[\frac{x}{\sqrt{4Dt}}\right]$$

where *erf* is the error function, which is

$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\xi^2) d\xi$ and $erfc(z) = 1 - erf(z)$, called the complimentary error function. Tabulation of values of error function and approximation are available (see handout). Properties of the error function are $erf(-z) = -erf(z)$, $erf(0) = 0$, $erf(\infty) = +1.0$, and $erf(-\infty) = -1.0$ and the behavior of the function is shown below.

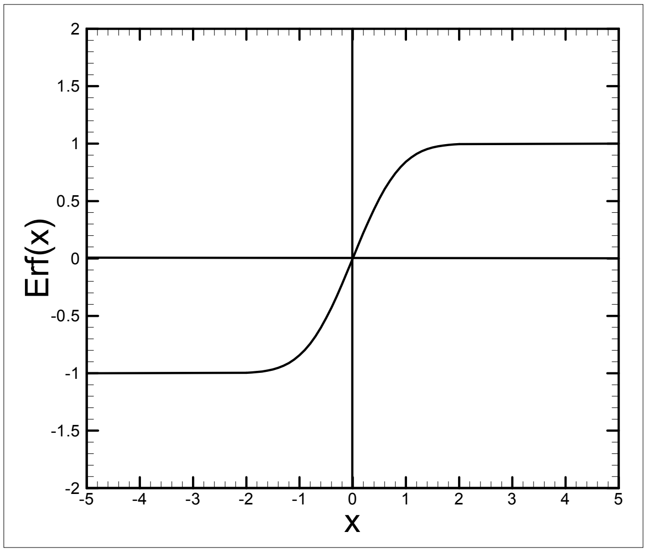
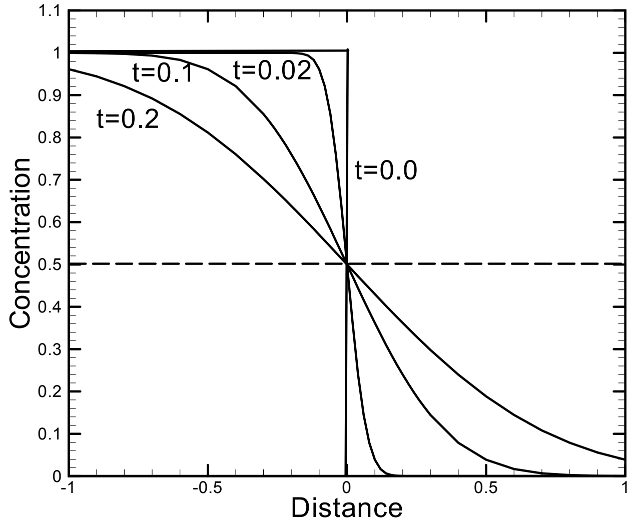


Figure 3.15 The behavior of erf function

Solutions to the diffusion equation at t=0.02, 0.1, and 0.2 for the step input, C_0=1.0 and D=1, are shown in the figure below. Notice that at time approaches infinite, the finial concentration approaches 0.5 everywhere in the solution domain.

Figure 3.16 Spatial concentration distribution at different times



3. 6.2 Input concentration specified as a function of time at a fixed location.

Figure 3.17

In stead of specifying input spatial concentration distribution at time equal to zero, we will show next the solution for the case where input concentration is specified as a function of time at a fixed location. Without loss of generality, we will assume the domain is infinite and unbounded and at initial time t=0, the concentration is zero everywhere along the x axis. We want to find the concentration distribution, $C(x,t)$, if the concentration is suddenly raised to C_0 at all time at the point x=0. This is a step input in time and the solution is given as

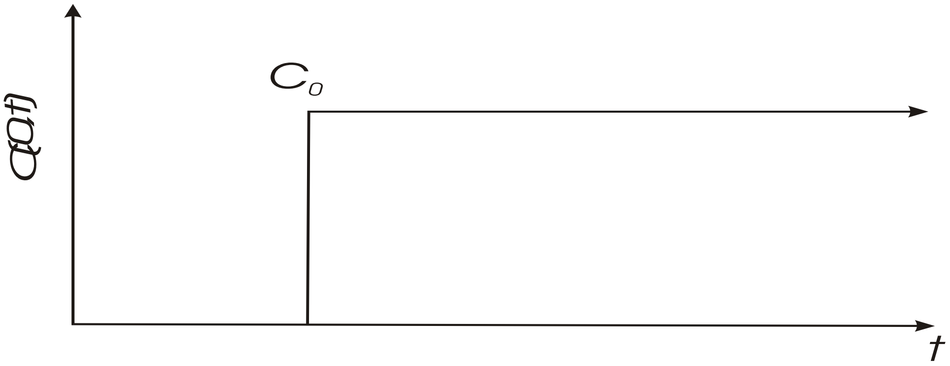


Figure 3.17 An illustration of a step input function at x =0

$$C(x,t) = C_0\left[1 - erf\left(\frac{x}{\sqrt{4Dt}}\right)\right] = C_0 erfc\left[\frac{x}{\sqrt{4Dt}}\right] \text{ for } x>0,$$

and for x<0,

$$C(x,t) = C_0\left[1 - erf\left(\frac{x}{\sqrt{4Dt}}\right)\right]$$

The solution for this problem is graphed below, for C_0=1.0, t=0, 0.02, 0.1, and 0.2 at various distances. Notice that when time approaches infinity, the concentration should approaches unity everywhere.

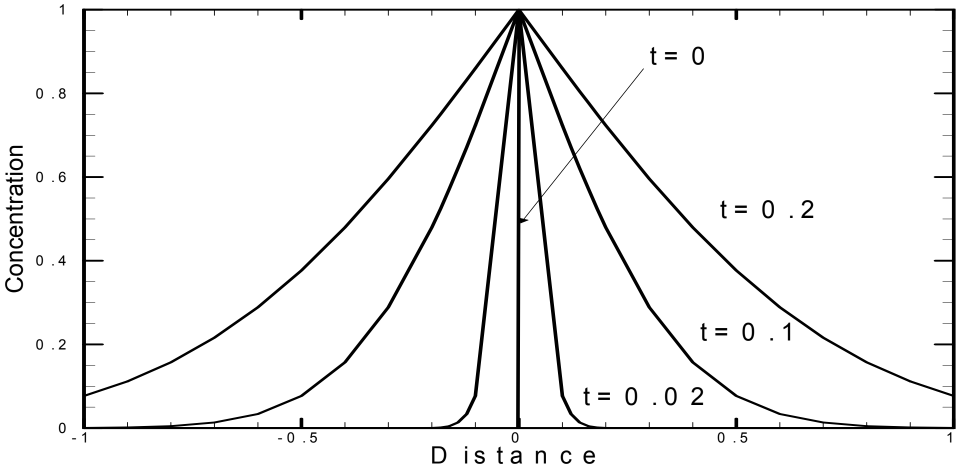


Figure 3.18 Plot of the spatial concentration distribution at different time for a step input at location x=0.

3.7. ADVECTION-DIFFUSION PROCESS

While the previous section discusses diffusion in a static fluid, we now investigate the diffusion process in a fluid moving at a uniform velocity, u, which is constant in time. Under this condition, the total mass flux (q_T) crossing a unit area perpendicular to the flow direction will consist of convective (uc) and diffusive (q_D) fluxes. The convective flux is caused by the bulk movement of the fluid and the diffusive flux is attributed to the random motion of fluid molecules. That is,

$$\vec{q}_T = \vec{q}_D + \vec{u}C \tag{7.1}$$

Again, the continuity equation states that

$$-\nabla \bullet \vec{q}_T = \frac{\partial C}{\partial t} \tag{7.2}$$

Using the expression for q_T, we have

$$-\nabla \bullet (\vec{q}_D + \vec{u}C) = \frac{\partial C}{\partial t} \tag{7.3}$$

Expanding the divergence of the product of velocity and concentration, the above equation becomes

$$-\nabla\bullet\vec{q}_D - \vec{u}\nabla C - C\nabla\vec{u} = \frac{\partial C}{\partial t} \qquad (7.4)$$

Now, we consider the conservation of mass for the pure fluid (i.e., not tracers or chemicals). The continuity equation states that

$$-\nabla\bullet\rho\vec{u} = \frac{\partial\rho}{\partial t} \qquad (7.5)$$

If the fluid is homogeneous (ρ is constant in space) and incompressible (ρ is constant in time), we then have

$$\nabla\bullet\vec{u} = 0 \qquad (7.6)$$

As a result, the term, $C\nabla\vec{u}$, is zero and the equation becomes

$$-\nabla\bullet\vec{q}_D - \vec{u}\nabla C = \frac{\partial C}{\partial t} \qquad (7.7)$$

Substituting Fick's Law for the diffusive flux, we have the advection-diffusion equation,

$$D\nabla^2 C - \vec{u}\nabla C = \frac{\partial C}{\partial t} \qquad (7.8)$$

Where the first term in the equation represents the diffusion flux per volume of the fluid and the second term denotes the advective flux per volume of the fluid. The advection-diffusion equation expressed in Cartesian coordinates is

$$D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) - \left(u_x\frac{\partial C}{\partial x} + u_y\frac{\partial C}{\partial y} + u_z\frac{\partial C}{\partial z}\right) = \frac{\partial C}{\partial t} \qquad (7.9)$$

where u_x, u_y, and u_z are the velocity components in the x, y, and z direction, respectively.

Figure 3.19

3.7.1. Analytical Solution of Advection - Diffusion Equation

Without loss of generality, we will consider one-dimensional problem where the advection takes place in the x>0 direction. Again, the initial concentration along the domain is assumed to be zero everywhere at the initial time, t=0. The governing equation is

$$D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

To solve this equation, we will employ the logic that if we imagine ourselves as observers traveling along with the fluid at the fluid velocity *u*, we then observe the diffusion process only. If this logic is correct, we then can apply the solutions of the diffusion equation that we obtained earlier to this situation. As a consequence, we will define a new coordinate system, η, (convective coordinates or Lagrangian Coordinates):

$\eta = x - ut$

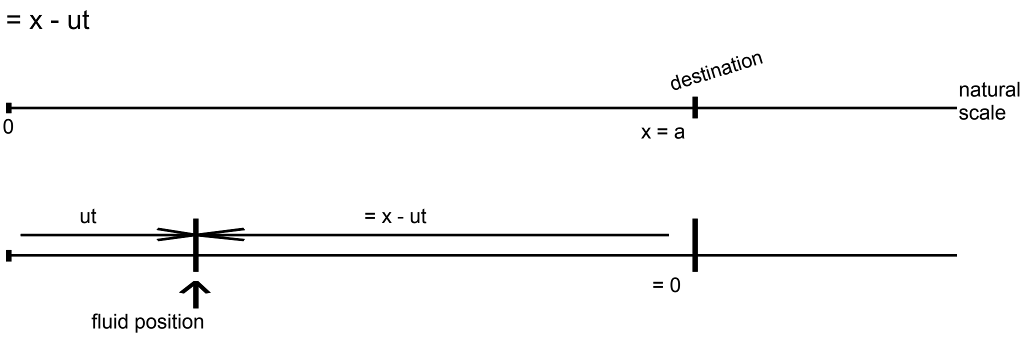
This coordinate system, in essence, translates any given fixed location, x, to the distance between the fixed location and the observer's location, which is described by *ut*.

In addition, we will let $\tau = t$ and then $C(x, t)$ becomes $C(\eta, \tau)$. Using the chain rule, we have

$$\frac{\partial C}{\partial x} = \frac{\partial \eta}{\partial x}\frac{\partial C}{\partial \eta} + \frac{\partial \tau}{\partial x}\frac{\partial C}{\partial \tau} = \frac{\partial C}{\partial \eta}$$

and

$$\frac{\partial^2 C}{\partial x^2} = \frac{\partial^2 C}{\partial \eta^2}$$



Similarly, the time derivative term can be expressed as

$$\frac{\partial C}{\partial t} = \frac{\partial \eta}{\partial t}\frac{\partial C}{\partial \eta} + \frac{\partial \tau}{\partial t}\frac{\partial C}{\partial \tau} = -u\frac{\partial C}{\partial \eta} + \frac{\partial C}{\partial \tau}$$

Substitution of the above expressions to the advection-diffusion equation leads to the following expression:

$$D\frac{\partial^2 C}{\partial \eta^2} - u\frac{\partial C}{\partial \eta} = -u\frac{\partial C}{\partial \eta} + \frac{\partial C}{\partial \tau}$$

which leads to a final form

$$D\frac{\partial^2 C}{\partial \eta^2} = \frac{\partial C}{\partial \tau}$$

After the coordinate transformation, we show that the advection-diffusion equation becomes exactly the same as the diffusion equation, supporting our earlier logic. Therefore, solutions for advection-diffusion equations are the same as those for diffusion equations of various initial and boundary conditions with the exception that we must replace η by $(x - ut)$. The following two examples show how this technique works.

Example 1.

In the case of an impulse input, the solution to the diffusion equation is

$$C(\eta,\tau)=\frac{M}{\rho A\sqrt{4\pi D\tau}}\exp\left[\frac{-(\eta-\xi)^2}{4D\tau}\right]$$

where ξ is the location the slug is released. Then we use the following relation,

$\eta = x - ut$ and $\tau = t$

Therefore, the solution of the advection-diffusion Equation becomes

$$C(x,t)=\frac{M}{\rho A\sqrt{4\pi Dt}}\exp\left[\frac{-[(x-ut)-\xi]^2}{4Dt}\right]$$

This solution here is valid for unbounded domain. Solutions that consider boundary effects can be obtained by the image method as in well hydraulics.

The solution can be plotted in two ways:

1. Spatial distribution, C-x plot, at a given time (called snapshots), which are always symmetric.

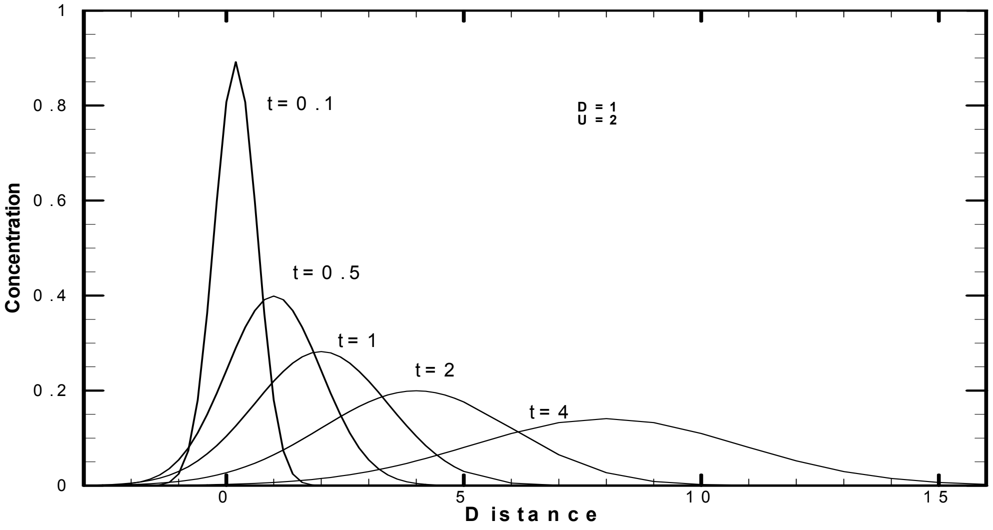


Figure 3.20 Plots of spatial concentration distribution, *C(x)*, at different times.

2. Temporal distribution of the concentration at a given location, C vs t plot, called a breakthrough curve. In this case, the concentration profile is always skewed at small time and becomes almost symmetric at large time.

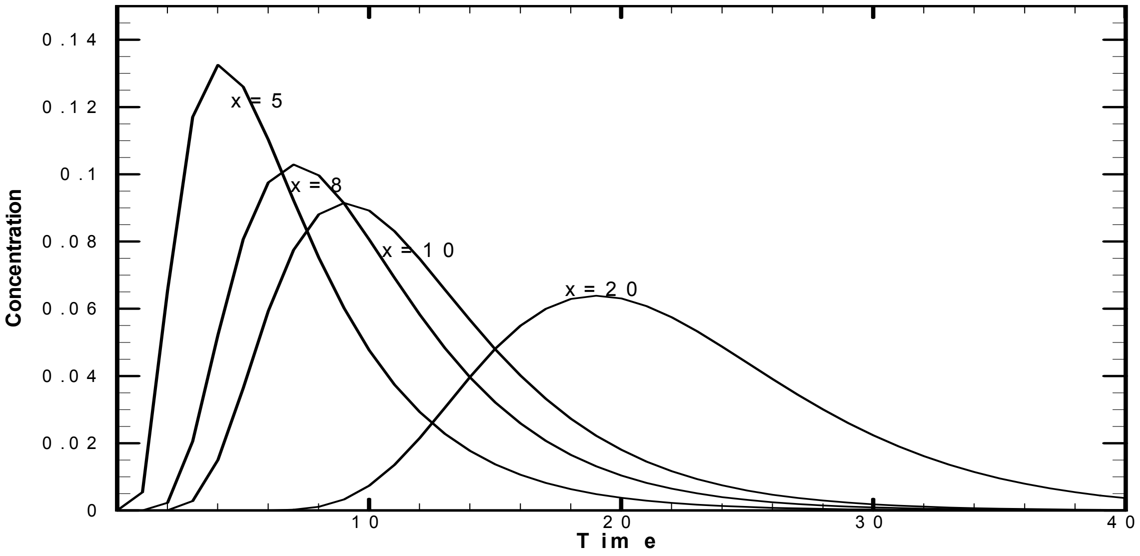


Figure 3.21 Plots of breakthrough curves, *C(t)*, at different distances from the injection point.

The skew distribution is analogous to the Doppler effect of sound in your elementary physics.

Consider one-dimensional problem, where advection takes place from left to right of the figure below with u=1 and D=1. Suppose the concentration at everywhere in the solution domain is zero at the initial time, t=0. An impulse input of a concentration, C_0, is suddenly released at x=0 at time t=0. Find a breakthrough curve (C vs. t) observed at x=6.

Instead of solving an advection-diffusion equation to find the breakthrough curve, we can solve the diffusion equation for the impulse input first and then move the observation location successively toward the diffusion plume. For example, concentration distributions resulting from diffusion alone at eleven different times (t=1, 2, 3, … 11) are plotted in the figure below. To take the advection into consideration, we will move the observation location, x=6, toward the release point according to the velocity, u, and the time after the release. That is, at t=1, we will move the observation location from x=6 to x=5; at the new location we determine the concentration value resulting from the diffusion at that location and time (the circle shown at x=5). At t=2, we again move the observation location from x=5 to x=4 by 1 and then record the concentration value resulting from the diffusion equation corresponding to t=2 (the circle shown at x=4). By successively moving the observation point toward the diffusing plume, we will obtain a temporal concentration distribution (the thick solid line shown in the figure), which is in essence the solution to the advection-diffusion equation at x=5.

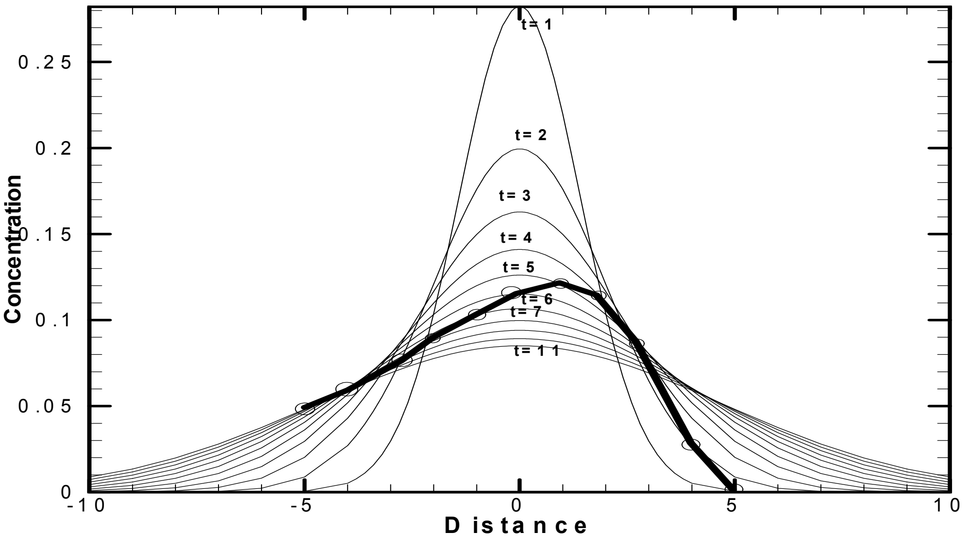


Figure 3.22 A schematic illustration of the physics causing skewness of a breakthrough curve.

The resulting breakthrough curve is skewed: a sharp raising concentration front and a long-tailing recession front. Physical reasoning for this skewed distribution is analogous to the Doppler effects in the sound wave propagation. As the center of the concentration plume moves toward the observation location, we records concentration due to both the advection and diffusion effects moving toward us. Thus, we see rapid arising concentration profile. On the other hand, when the center of the plume passes the observation point, we do not observed the concentration caused by the advection anymore but the concentration diffusing backward from the plume. We consequently observe the long-tailing effect of the plume. Therefore, we can conclude that a breakthrough curve resulting from the classical advection-diffusion equation is always skewed.

Example 2.

Consider the problem of a pipe filled with one fluid and being displaced by a mean flow velocity *u* by another fluid with a tracer in concentration C_o. At time t=0 there is a sharp front so that,

$$C(x,0)=\begin{cases} 0, x>0 \\ C_0, x<0 \end{cases}$$

The solution is already available in the diffusion equation. We merely have to adjust for the moving coordinates and we have,

$$C(x,t)=\frac{C_0}{2}\left[1-erf\left[\frac{(x-ut)}{\sqrt{4Dt}}\right]\right]$$

The solution is graphed in Fig. 3.23.

Figure 3.23
a and b

Example 3.

Consider the problem of a pipe with a constant flow of water and a steady concentration C_o is introduced at the origin of the coordinate system at time t=0 and continued. The solution corresponds to this situation is given by,

$$C(x,t)=\frac{C_0}{2}\left[erfc\left[\frac{x-ut}{\sqrt{4Dt}}\right]+erfc\left[\frac{x+ut}{\sqrt{4Dt}}\right]\exp(\frac{ux}{D})\right]$$

3.7.2. Solutions 3-D Advection-Diffusion

The followings are analytical solutions to three-dimensional diffusion equation for various input types.

1. Instantaneous source of mass *M* at point (*x, y,* z) and *U, D_x, D_y,* and D_Z are constants.

$$C(x,y,z,t)=\frac{M}{\rho(4\pi t)^{2/3}(D_xD_yD_z)^{1/2}}\exp-\left\{\frac{\left[(x-x_1)-ut\right]^2}{4D_xt}+\frac{(y-y_1)^2}{4D_yt}+\frac{(Z-Z_1)^2}{4D_Zt}+kt\right\}$$

2. Instantaneous line source of mass/length, *M* (constant.) at $x_1, y_1, -l\le z\le l$

$$C(x,y,z,t)=\left[\frac{M}{\rho 4\pi t(D_x D_y)^{1/2}}\exp-\left\{\frac{\left[(x-x_1)-ut\right]^2}{4D_x t}+\frac{(y-y_1)^2}{4D_y t}+kt\right\}\right]$$

$$\left[erf\,\frac{(Z+l)}{\sqrt{4D_Z t}}-erf\,\frac{(Z-l)}{\sqrt{4D_Z T}}\right]^{1/2}$$

3. A continuous source of mass (*f* = mass/time) at point (x_1, y_1, z_1).

$$C=\int_0^t\frac{f(\tau)e^{-k(t-\tau)}}{4\pi(t-\tau)^{2/3}(D_x D_y D_Z)^{1/2}}\exp-\left\{\frac{\left[(x-x_1)-u(t-\tau)\right]^2}{4D_x(t-\tau)}+\frac{(y-y_1)^2}{4D_y(t-\tau)}+\frac{(Z-Z_1)^2}{4D_Z(t-\tau)}\right\}d\tau$$

$steady(f = Const.)$

$$C=\frac{f}{4\pi\rho(D_y D_Z)^{1/2}x}\exp-\left\{\frac{uy^2}{4D_y x}+\frac{uZ^2}{4D_Z x}+\frac{kx}{u}\right\}$$

$x_1 = y_1 = Z_1 = 0; ux/D_y \gg 1$

etc.

4. Continuous line source (g = mass/time length); steady g = const.

$$C\cong\frac{g}{\gamma\sqrt{4\pi D_y ux}}\exp-\left[\frac{y^2u}{4D_y x}+\frac{kx}{u}\right]\qquad \text{if } \frac{D_y}{ux},\frac{D_x k}{u^2}\ll 1$$

See Fried [5.3.6, 7]; Wilson and Miller, *Proc. Hydraulic Div. ASCE,* 503-14, April 1978.

5. Continuous "line" source in 2-D, R = mass/time area = constant.

$$C=\int_{y_1=-l/2}^{l/2}\frac{\mathrm{Re}^{-kx/u}}{\rho\sqrt{4\pi D_y u_x}}\exp-\frac{(y-y_1)^2}{4D_y x/u}dy$$

$$C=\frac{R}{\rho u}e^{-kx/u}\frac{1}{2}\left[erf\left(\frac{y+l/2}{\sqrt{4D_y x/u}}\right)-erf\left(\frac{y-l/2}{\sqrt{4D_y x/u}}\right)\right]$$