This section discusses the evolution of a diffusing cloud once it encounters a boundary. Emphasis is placed on two common types of boundaries, namely those that are perfectly absorbing and those through which there is no flux. The theory section describes how the use of image sources allows us to correctly model the concentration profile of the cloud in the presence of a boundary. The animation compares the effect that no-flux and perfectly absorbing boundaries have on a diffusing cloud, highlighting the progression to a well-mixed condition in the presence of parallel no-flux boundaries.

4. Boundary Conditions

When a diffusing cloud encounters a boundary, its further evolution is affected by the condition of the boundary. The mathematical expressions of four common boundary conditions are described below.

Specified Flux: In this case the flux per area, $(q/A)_n$, across (normal to) the boundary is specified. The subscript 'n' indicates the direction of the outward facing normal, such that $(q/A)_n$ is understood as the flux leaving the fluid domain. The specified flux boundary condition is then written,

(1) $[CV_n - D_n \partial C/\partial n]_{\text{at the boundary}} = (q/A)_n$ = flux leaving fluid domain at boundary

Specified Constant Concentration: In this case the concentration at the boundary is given. This boundary condition is covered in Chapter 7, Spatially Distributed Sources.

(2) $C_{\text{at the boundary}} = \text{constant}$

No-flux boundary: This is a special case of the specified flux condition given above, with $(q/A)_n = 0$. The most general condition is,

(3a) $[CV_n - D_n \partial C/\partial n]_{\text{at the boundary}} = 0.$

Again, the subscript 'n' indicates the outward facing normal. For no flux, the advective and diffusive fluxes must exactly balance. If the boundary is solid, then the velocity normal to it is zero, and the constraint is reduced to,

(3b) $\partial C/\partial n = 0$ at boundary.

When the source is located on the boundary (3b) is somewhat misleading, because the symmetry of the Gaussian curve about its center allows (3b) to be satisfied even as mass leaves the real domain. This exception is explained below.

Perfectly Absorbing: Any chemical molecule that touches this boundary is instantly absorbed, and thus removed from the fluid. The concentration in the fluid at this boundary must be zero.

(4) $C_{\text{at the boundary}} = 0$

No-Flux Boundary Condition:
Analytical solutions that satisfy the no-flux boundary condition are found using the principle of superposition. The method requires that the transport equation,

(5) $$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} + w\frac{\partial C}{\partial z} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \pm S$$

be linear. This is generally the case, unless the specific form of the source or sink (±S) is non-linear. If the equation and boundary conditions are linear, then one can superpose (add together) any number of individual solutions to create a new solution that fits the desired initial or boundary condition. The method is demonstrated here for a one-dimensional system in x, into which mass, M, is released at x = 0 and t = 0. For simplicity, velocity is assumed to be zero everywhere in the system. The cross-sectional area perpendicular to the x-direction is A_{yz}. A solid boundary exists at x = -L. Specifically, we wish to solve:

(6a) $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

(6b) Initial Condition (t = 0): C(x) = Mδ(x)
Boundary Condition: $\partial C/\partial x = 0$ at x = -L.

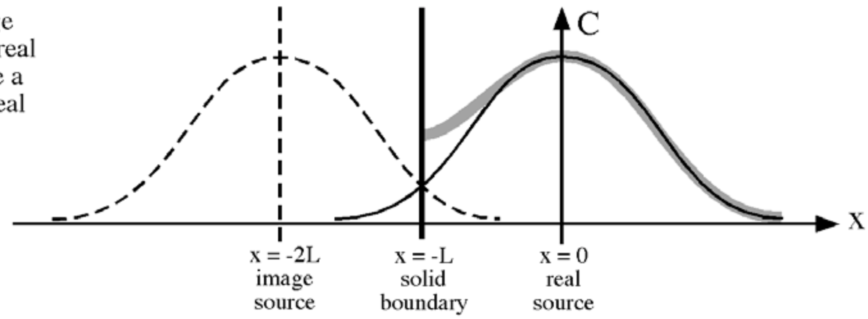
The system's transport equation and initial condition are satisfied by the one-dimensional solution for an instantaneous, point release located at the real source position:

(7) $$C_{real}(x,t) = \frac{M}{A_{yz}\sqrt{4\pi\, Dt}} \exp\left(-x^2/4Dt\right).$$

However, this solution, shown as a solid black line in the following figure, does not satisfy the no-flux condition at x = -L. Specifically, $\partial C/\partial x > 0$ at x = -L. In addition, (7) allows the mass $\int_{-\infty}^{-L} C(x)dx$ to cross the boundary x = -L. This mass can be exactly replaced within the real domain (x > -L) by adding a new, identical source at x = -2L. The additional source is located at the mirror image to the original source, with the mirror located at the no-flux boundary x = -L. So, we call the added source an image source. The mass distribution for the image source, $C_i(x,t)$, is shown as a dashed line. Its shape is identical to the original source, C(x,t), but its peak is shifted from x = 0 to x = -2L. The shift is accomplished by forcing the exponential term to be one at x = -2L, *i.e.* making the argument zero at x = -2L.

(8) $$C_{image}(x,t) = \frac{M}{A_{yz}\sqrt{4\pi\, Dt}} \exp\left(-(x+2L)^2/4Dt\right)$$

Figure 1. Add an image source (dashed) to the real source (black) to create a solution (gray) in the real domain (x > -L) that satisfies the boundary condition, $\partial C/\partial x = 0$ at x = -L.



The superposition (sum) of the original and image sources is shown within the flow domain (x > -L) as a thick, gray line. Note, specifically that this curve satisfies the condition $\partial C/\partial x = 0$ at x = 0, as stated in (6). The solution is thus the sum of (7) and (8),

$$(9) \qquad C(x,t) = C_{real} + C_{image} = \frac{M}{A_{yz}\sqrt{4\pi Dt}}\left(\exp\left(-x^2/4Dt\right) + \exp\left(-(x+2L)^2/4Dt\right)\right)$$

Perfectly Absorbing Boundary Condition:
The method of superposition can also be used to satisfy a perfectly absorbing boundary condition. Consider again the one-dimensional system described above, with the boundary at x = - L acting as a perfect absorber. We then seek a solution to,

$$(10a) \qquad \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

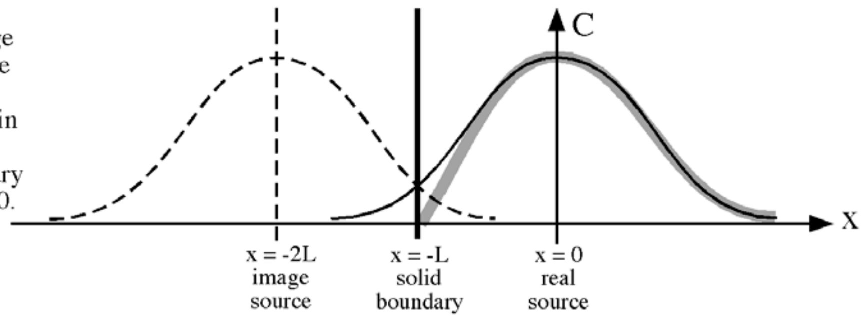
(10b) Initial Condition (t = 0): $C(x) = M\delta(x)$
Boundary Condition: C (x=-L, t) = 0.

As above, the basic solution within the flow domain will be that for an instantaneous release of mass at a discrete point, namely (7). To satisfy the boundary condition, we now subtract, rather than add, the image source.

$$(11) \qquad C(x,t) = C_{real} - C_{image} = \frac{M}{A_{yz}\sqrt{4\pi Dt}}\left(\exp\left(-x^2/4Dt\right) - \exp\left(-(x+2L)^2/4Dt\right)\right).$$

By subtracting the image source (dashed line) from the real source (solid black line), the concentration at the boundary is fixed at zero. Note that the superposed solution (heavy gray line) indicates a flux into the boundary at x = -L, i.e. $\partial C/\partial x > 0$, which is consistent with an absorbing boundary. Also note that the solution (11) gives negative concentrations for the region x < -L, which is physically unrealistic. However, this region is outside the real flow domain (x > -L), so that the unrealistic values are unimportant. We only require the solution within the real domain (x > -L) to be physically reasonable, and it is.

Figure 2. Subtract image source (dashed) from the real source (black) to create a solution (gray) in the real domain (x > -L) that satisfies the boundary condition, C(x= -L,t) = 0.



Multiple Boundaries:
If there is more than one boundary, additional image sources will be required. Continuing with the same one-dimensional system describe above, we now consider boundaries at both x = -L and x = +L.

(12a) $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

(12b) Initial Condition (t = 0): $C(x) = M\delta(x)$
Boundary Condition: $\partial C/\partial x = 0$ at x = -L and x = +L

To satisfy a no-flux condition at x = -L, we add an image source at x = -2L, as above. To satisfy a no-flux condition at x = +L, we need an image source at x = +2L. These two image sources are depicted in figure 3.

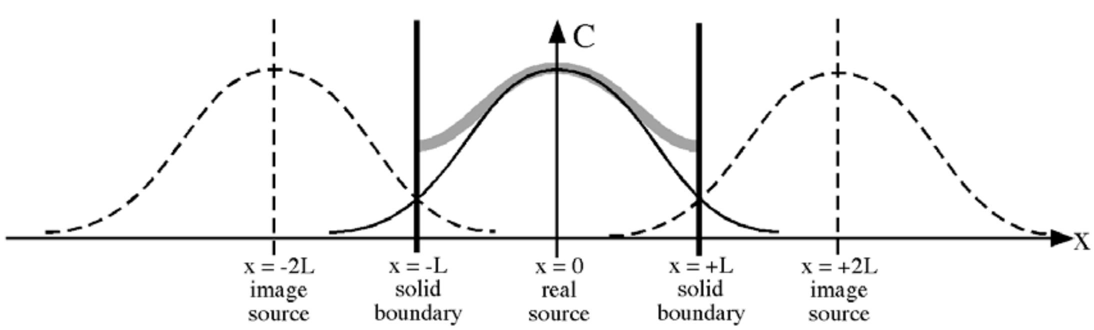


Figure 3. To satisfy the no-flux condition at both boundaries, two image sources (dashed) are added to the real source (black). For short time, the sum of these three sources (gray) is sufficient to satisfy $\partial C/\partial x = 0$ at $x = \pm L$. However, at later time each image source will begin to lose mass across its opposite boundary, and the no-flux condition will no longer be satisfied. Ultimately, images will be needed at $x = \pm 2nL$, for all integer n.

Figure 3 depicts the concentration field for small time. At longer time, one anticipates that, for example, the image source originating at x = -2L will reach and begin to cross the opposite boundary at x = +L and mass will again be lost from the real domain. To balance the loss, an additional image is needed at x = +4L, *i.e.* at the image of x = -2L across a 'mirror' located at the boundary x = +L. Similarly, the image source at x = +2L requires its own image across the x = -L boundary, *i.e.* at x = -4L. Taking this reasoning further, we ultimately need an infinite number of images, just as an object between parallel mirrors generates an infinite number of images. The solution to (12) is then,

$$(13) \quad C(x,t) = \frac{M}{A_{yz}\sqrt{4\pi\, Dt}} \sum_{n=-\infty}^{\infty} \left(\exp\left(-(x+2nL)^2/4Dt\right)\right).$$

Similarly, if the boundaries at x = ±L are perfect absorbers, we must solve

$$(14a) \quad \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

(14b) Initial Condition (t = 0): C(x) = Mδ(x)
Boundary Condition: C = 0 at x = -L and x = +L.

Simple geometric reasoning will show that negative images are needed at x = ± 2L and positive images at x = ±4L, and continuing thusly in an alternating fashion. That is,

$$(15) \quad C(x,t) = \frac{M}{A_{yz}\sqrt{4\pi\, Dt}} \sum_{n=-\infty}^{\infty} \left(\underbrace{-\exp\left(-\frac{(x+(4n-2)L)^2}{4Dt}\right)}_{\text{negative image}} + \underbrace{\exp\left(-\frac{(x+4nL)^2}{4Dt}\right)}_{\text{positive image}} \right).$$

Boundaries in two- and three-dimensional systems:
The method of superposition described above for one-dimensional systems is readily extended to two- and three-dimensional systems. As an example, consider a three-dimensional domain filled with a stagnant fluid (zero current). The system is bounded below by a solid plane at y = 0, such that the domain of interest occupies y ≥ 0. The system is unconstrained in the x-z plane. A slug of mass, M, is released at the point (x, y, z)=0 at the time t = 0. Diffusion is isotropic and homogeneous. Note that because the source is located on the boundary, the gradient condition (3b) is insufficient to inhibit loss of mass from the real domain (y≥0). A more general boundary condition is used,

$$(16a) \quad \frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right)$$

(16b) Initial Condition (t = 0): C(x) = M δ(x) δ(y) δ(z)
Boundary Condition: no-flux out of fluid domain at y = 0.

A general solution that satisfies the stated transport equation and initial condition is given by equation (25) in chapter 3, and repeated here for convenience.

$$C(x,y,z,t) = \frac{M}{(4\pi t)^{3/2}\sqrt{D_x D_y D_z}} \exp\left(-\frac{x^2}{4D_x t} - \frac{y^2}{4D_y t} - \frac{z^2}{4D_z t} \right)$$

In fact, this solution also satisfies the gradient expression for a no-flux boundary condition, *e.g.* as given in (3b). However, this solution does not conserve mass within the real domain, but rather allows half of the mass to diffuse into the region $y < 0$, violating the no-flux boundary condition. To satisfy the no-flux condition at $y = 0$, we must add an image source. The image of the real source, located at $y = 0$, across the plane $y = 0$ will also be located at $y = 0$. Since the real and image sources are co-located, we need only add a factor of 2 to the solution given above. Additionally noting that the diffusion is isotropic ($D_x = D_y = D_z = D$), the solution to (16) is,

(17) $$C(x,y,z,t) = 2\,\frac{M}{(4\pi D t)^{3/2}} \exp\left(-\frac{x^2+y^2+z^2}{4Dt} \right).$$

As a final case, we consider parallel boundaries in a three-dimensional system. The fluid domain is unconstrained in the x-z plane, but constrained in the y-direction by solid, planar boundaries located at $y = \pm L$. There is no current and the diffusion is isotropic and homogeneous. An instantaneous release of mass, M, occurs at $x = y = z = t = 0$. The appropriate transport equation and initial conditions are,

(18) $$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right), \text{ with } C(x, y, z, t{=}0)) = M\,\delta(x)\,\delta(y)\,\delta(z).$$

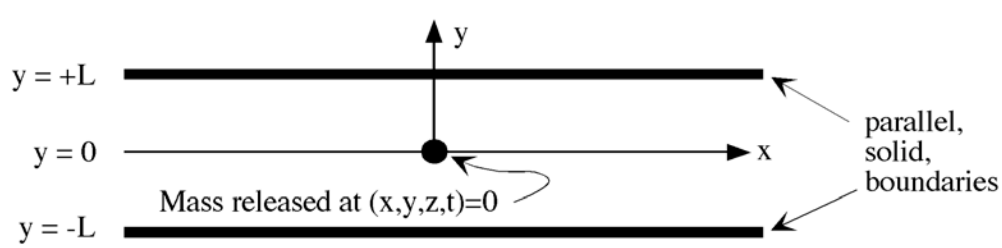


Figure 4. Mass released mid-way between parallel, solid boundaries. System is unconfined in x and z.

To satisfy either a no-flux or perfectly absorbing boundary condition, we will add image sources at positions corresponding to the mirror images of the real source across the planes $y = \pm L$. The real source is located at (x=0, y=0, z=0). The image sources must be then be located at (x=0, y=2nL, z=0) with $n = \pm 1, \pm 2, \pm 3$ upward to $\pm$ infinity. If the boundaries at y = ± L permit no flux, the image sources will all be positive, and the concentration field is described by,

$$(19) \quad C(x,y,z,t) = \frac{M}{(4\pi\, Dt)^{3/2}} \sum_{n=-\infty}^{\infty} \exp\left(-\frac{x^2 + (y+2nL)^2 + z^2}{4Dt}\right)$$

If the boundaries at y = ± L are perfect absorbers, both positive and negative image sources will be needed. The concentration field is can then be described by,

$$(20) \quad C(x, y, z, t) =$$

$$\frac{M}{(4\pi\, Dt)^{3/2}} \sum_{n=-\infty}^{\infty} \left(-\exp\left(-\frac{x^2 + (y+(4n-2)L)^2 + z^2}{4Dt}\right) + \exp\left(-\frac{x^2 + (y+4nL)^2 + z^2}{4Dt}\right)\right).$$

Animation - Perfectly Absorbing and No-Flux Boundaries

The following animation examines the evolution of concentration after a slug mass is released mid-way between solid, parallel boundaries, as in Figure 4. Two scenarios are considered, perfectly absorbing and no-flux boundaries, using the solutions (19) and (20) above. For each system the concentration field is displayed in the plane z = 0. In addition, the concentration profile C(x=0, y, z=0) for each system is plotted for comparison on a single graph.

Before you view the animation answer the following questions.

1. The parallel boundaries are located at y = ± 70 cm, and the diffusivity is D = 1 cm^2s^{-1}. Estimate the time at which the boundaries will begin to impact the evolution of the diffusing cloud.
2. For which boundary condition will peak concentrations decrease more rapidly? Why?
3. What will be the final concentration in each system?

As you view the animation consider the following.

4. Based on the profiles at (x=0, y, z=0), at what time do the boundary conditions begin to impact the concentration field? How does this compare to your prediction in 1)?
5. If the two profiles C(x=0, y, z =0) were not labeled, how would you identify the profile evolving with a no-flux boundary? with an absorbing boundary?
6. Finally, consider the system with no-flux boundaries. Note that over time the profile perpendicular to the boundaries, C(y), becomes increasingly uniform. Eventually, this profile will be sufficiently uniform to consider the system well mixed in this dimension. Evolution of the cloud beyond this point in time will proceed as if the system were two-dimensional in x and z. This is discussed in more detail below.

To view animation and this text simultaneously, open animation from chapter home page.

Answers.

1. A common length scale for a diffusing patch defines the edge of the cloud at 2σ from the centroid (chapter 1). Based on this definition, the cloud edge touches the boundary when $L = 2\sigma = 2\sqrt{2Dt}$. With L = 70 cm and D = $1 cm^2 s^{-1}$, t = 613 s. But, the 2σ delineation of the cloud edge encompasses only 95% of the total mass in the cloud, such that at t = 613 s 5% of the mass has already reached and passed the boundary. A more conservative estimate would define the cloud edge at 3σ, for which the edge of the cloud will touch the boundary at $t = L^2/(18D)$ = 270 seconds. At this time, only 0.3% of the mass has reached the boundary (chapter 1).
2. The peak concentration should decay more rapidly in the system with absorbing boundaries, because the boundaries permit flux, and thus additional dilution, compared to the no-flux boundaries.
3. Since each system is unconfined in x and z, the final concentration will be zero.
4. Based on the animation, the two curves begin to diverge at about 250 seconds. This reasonably agrees with the time estimated for $L = 3\sigma$.
5. The boundary conditions are reflected in the profile shape at the boundary. For the absorbing boundary condition, $\partial C/\partial y > 0$ at y = -L and < 0 at y = +L, both of which indicate flux into the boundary. For the no-flux boundary, $\partial C/\partial y = 0$ at both boundaries.

Time-scale for achieving a uniform condition between boundaries.
We saw in chapter 3 that the transport equation is simpler in systems that may be approximated in reduced dimensions, *e.g.* two rather than three dimensions. When one first considers a system, it is therefore useful to determine whether a reduction in dimensions is possible. To eliminate a given dimension, *e.g.* y, one must show that the concentration is uniform in y, that is $\partial C/\partial y = 0$. If $\partial C/\partial y = 0$, then both the diffusive flux ($D\, \partial^2 C/\partial y^2$) and the advective flux ($v\, \partial C/\partial y$) in y are eliminated,

$$(21) \qquad \frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\cancel{\frac{\partial C}{\partial y}} + w\frac{\partial C}{\partial z} = D\left[\frac{\partial^2 C}{\partial x^2} + \cancel{\frac{\partial^2 C}{\partial y^2}} + \frac{\partial^2 C}{\partial z^2}\right]$$

reducing the transport equation to two-dimensions in x and z. For example, consider the system represented in the above animation with parallel, no-flux boundaries at $y = \pm L$. Initially, the concentration field is three-dimensional with gradients in x, y, and z. Over time the profile perpendicular to the boundaries, C(y), becomes uniform. A temporal progression of C(y) is shown in Figure 5 below. The basic unit of time, L^2/D, is selected from dimensional reasoning. From Figure 5, one sees that the system is uniform in y, i.e. perpendicular to the boundaries, at $t = t_y = (2L)^2/4D$, which is called the mixing-time.

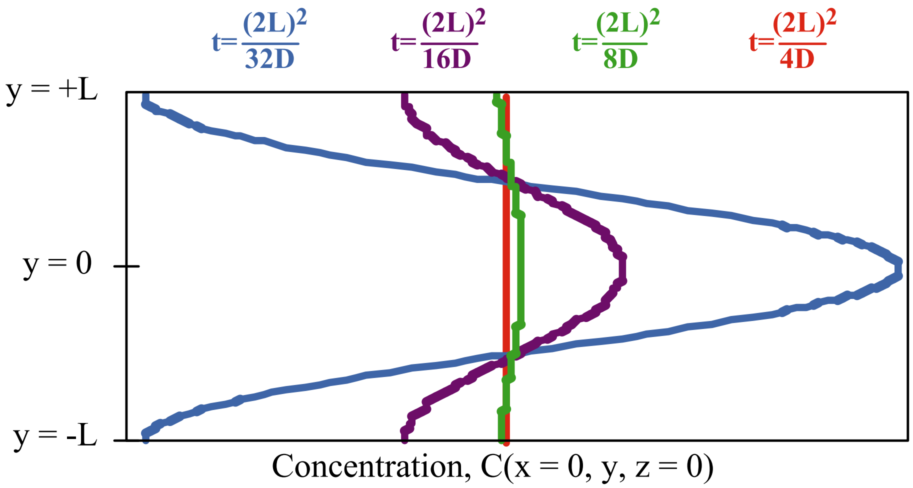


Figure 5. A slug of mass is released at (x, y, z, t)=0 into a fluid domain that is unconstrained in the x-z plane, but is constrained by parallel, no-flux boundaries at y = +L and -L. The profiles of concentration, C(x=0, y, z=0), are plotted for several times after the release. The system is fully mixed (uniform) across the y-domain in a time $t = (2L)^2/4D$.

At times greater than the mixing time $\partial C/\partial y = 0$, and the system can be considered in two-dimensions (x and z) only. That is, for $t > t_y$, the transport equation reduces to,

$$(22) \qquad \frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial z^2}\right],$$

and the evolution of concentration is described by the solution for an instantaneous, point-release in *two-dimensions* (see chapter 3), that is for $t > t_y$

$$(23) \qquad C(x,z,t) = \frac{M}{(2L)\,4\pi Dt}\exp\left(-\frac{x^2 + z^2}{4Dt}\right),$$

where (2L) is the length-scale of the now neglected dimension.

Definition of Mixing Time

For a generic system, we define the length-scale of interest as the full width of the domain in a given direction, e.g. L_x, L_y, L_z. If mass is released in the center of the domain, the time-scales required to achieve uniform conditions in each dimension is,

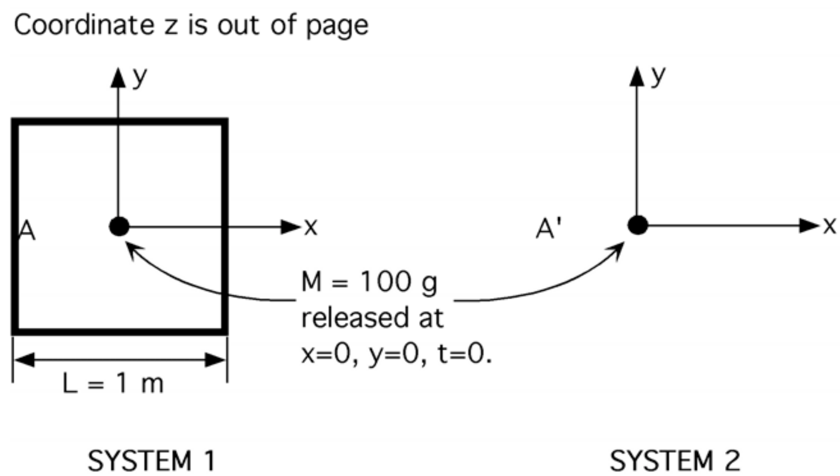
(24) Mixing Time $\qquad t_i = L_i^2/4D_i$, where i = x, y, z.

While the above time scale is a standard definition, from Figure 5, we can see that nearly uniform conditions are approximated at the shorter time $L_i^2/8D_i$.

Example Problem with Animation

Consider the two systems shown below. System 1 is a box with dimensions 1m x 1m x 0.1m. System 2 is defined by parallel, horizontal boundaries at z = ± 0.1 m, but is otherwise unconstrained. All boundaries are no-flux. Both systems have isotropic diffusion, $D = 2\ cm^2 s^{-1}$. At t = 0 a mass, M = 100g, is released into both systems at x=0, y=0, z=0. A concentration probe is located in each system, denoted A and A', at the position (x = -0.5 m, y = 0, z = 0). The detection limit of each probe is 10 ppm (gm^{-3}).

(a) Estimate the time at which the concentration measured at A and A' begin to diverge?
(b) What is the final concentration measured in each system, and when is it achieved?
(c) Confirm your estimates from a) and b) by plotting the concentrations at A and A'.



(a) Estimate the time at which the concentration at A and A' begin to diverge?
The concentrations at A and A' diverge when the boundary impacts the solution in System 1. This occurs when the diffusing cloud reaches the boundary. Estimate this time by equating the edge of the cloud with the length scale 3σ. That is, the cloud will touch the boundary when $3\sigma = 3\sqrt{2Dt} = 50\text{cm}$, such that $t = (50\text{cm})^2 / 18 \bullet 2\text{cm}^2\text{s}^{-1} = 70$ seconds.

(b) What is the final concentration measured at A (A'), and when is it achieved?
The final concentration in **System 1** will be C = (100g)/ (1m x 1m x 0.1m) = 1000 ppm. It is achieved when the mass is fully mixed across the domain. Using the largest dimension to estimate this time-scale, $t = (L)^2/(4\ D) = 1250$ s. As noted above, this is a conservative estimate, and $t = (L)^2/(8\ D) = 625$ s, is also reasonable. Because **System 2** is unbounded, infinite dilution is possible and the final concentration will be C = 0 ppm. Theoretically, this will take infinite time. But, because the probe has a detection limit of 10 ppm, zero concentration will be recorded by the probe for any concentration less than 10 ppm, which occurs in a finite time.

*(c) Confirm your estimate from a) and b) by plotting concentrations at A and A'***.**
In both systems the concentration is uniform in z at t = $(10\text{cm})^2/(4\text{x}2\ \text{cm}^2\text{s}^{-1})$=12.5 sec after the release. Because this is short relative to other time scales of interest (1250 sec), we can neglect the three-dimensional phase of the cloud and use a two-dimensional solution. For System 1, an infinite number of image sources are needed to satisfy the no-flux boundaries. Following **equation 4.19,**

$$C1(x,y,t) = \frac{M}{L_z\, 4\pi\, Dt}\left[\exp\left(-\frac{x^2+y^2}{4Dt}\right) + \sum_{n=1}^{\infty}\exp\left(-\frac{x^2 + (y\pm 2nL)^2}{4Dt}\right) + \sum_{n=1}^{\infty}\exp\left(-\frac{(x\pm 2nL)^2+y^2}{4Dt}\right)\right]$$

real source images along y axis images along x axis

In practice an infinite number of images is not needed. For time less than required to reach a well-mixed condition between the boundaries ($t < L^2/4D$), three images per boundary is sufficient to approximate the full solution with infinite images. Beyond this time, the concentration is steady and uniform, and the detailed solution above is no longer needed. System 2 is described by a simple two-dimensional slug-release (**eq. 3.23**),

$$C2(x,y,t) = \frac{M}{L_z\, 4\pi D\, t}\exp\left(-\frac{x^2+y^2}{4Dt}\right).$$

Using C1 and C2 the concentration at A (A') is plotted in an **animation** in this section. Compare the time scales estimated above with the full solution presented in the animation.
Specifically, the concentration at A and A' diverge at **70 seconds**. The final, steady state concentration is reached in **System 1** between **600 and 1200 seconds**.