The Dispersion Model

Chapter 13

Choice of Models

Models are useful for representing flow in real vessels, for scale up, and for diagnosing poor flow.

We have different kinds of models depending on whether flow is close to plug, mixed, or somewhere in between.

Chapters deal primarily with small deviations from plug flow.

There are two models for this: the dispersion model and the tanks-in-series model.

They are roughly equivalent. These models apply to turbulent flow in pipes, laminar flow in very long tubes, flow in packed beds, shaft kilns, long channels, screw conveyers, etc.

For laminar flow in short tubes or laminar flow of viscous materials these models may not apply, and it may be that the parabolic velocity profile is the main cause of deviation from plug flow.

We treat this situation, called the pure convection model, in Chapter 15.

If you are unsure which model to use go to the chart at the beginning of Chapter 15.

It will tell you which model should be used to represent your setup.

AXIAL DISPERSION

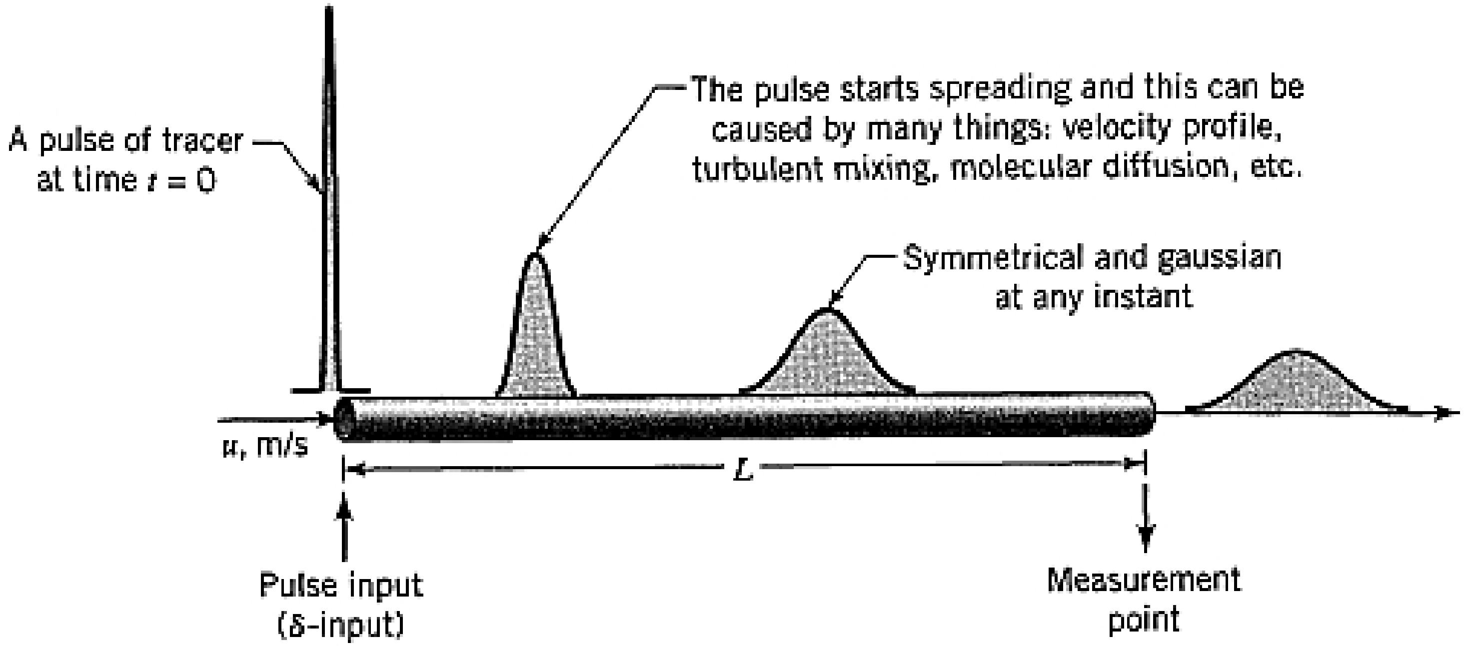
Suppose an ideal pulse of tracer is introduced into the fluid entering a vessel.

The pulse spreads as it passes through the vessel, and to characterize the spreading according to this model (see Fig.), we assume a diffusion-like process superimposed on plug flow.

We call this dispersion or longitudinal dispersion to distinguish it from molecular diffusion.

The dispersion coefficient D (m^2/s) represents this spreading process. Thus

- Large D means rapid spreading of the tracer curve
- small D means slow spreading
- D = 0 means no spreading, hence plug flow



$\left(\dfrac{\mathbf{D}}{uL}\right)$ is the dimensionless group characterizing the spread in the whole vessel.

We evaluate **D** or $\mathbf{D}/uL$ by recording the shape of the tracer curve as it passes the exit of the vessel. In particular, we measure

$\bar{t}$ = mean time of passage, or when the curve passes by the exit

σ^2 = variance, or a measure of the spread of the curve

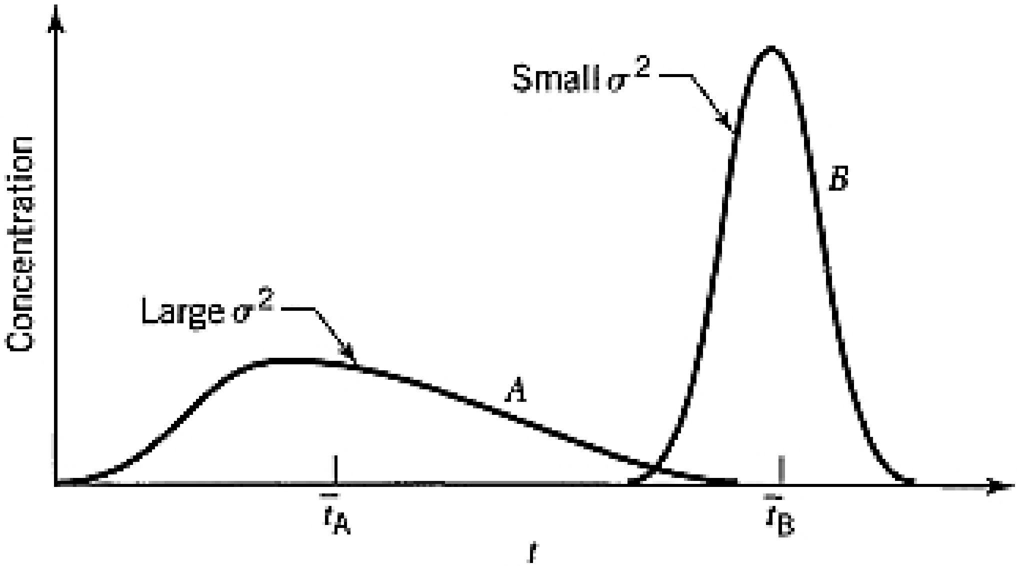
These measures, $\bar{t}$ and σ^2, are directly linked by theory to **D** and $\mathbf{D}/uL$. The mean, for continuous or discrete data, is defined as

$$\bar{t} = \frac{\int_0^\infty t\,C\,dt}{\int_0^\infty C\,dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i}$$

$$\sigma^2 = \frac{\int_0^\infty (t-\bar{t})^2 C\,dt}{\int_0^\infty C\,dt} = \frac{\int_0^\infty t^2 C\,dt}{\int_0^\infty C\,dt} - \bar{t}^2 \qquad \sigma^2 \cong \frac{\sum (t_i-\bar{t})^2 C_i \Delta t_i}{\sum C_i \Delta t_i} = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2$$

The variance represents the square of the spread of the distribution as it passes the vessel exit and has units of $(\text{time})^2$.

It is particularly useful for matching experimental curves to one of a family of theoretical curves



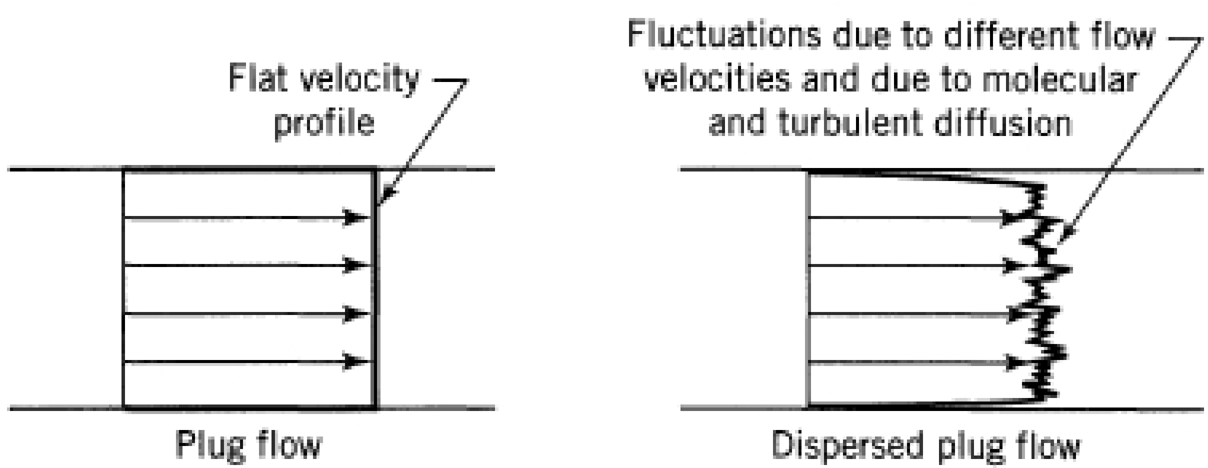
- Consider plug flow of a fluid, on top of which is superimposed some degree of backmixing, the magnitude of which is independent of position within the vessel.
- This condition implies that there exist no stagnant pockets and no gross bypassing or short-circuiting of fluid in the vessel.
- This is called the dispersed plug flow model, or simply the **dispersion model.**

- For molecular diffusion in the x-direction the governing differential equation is given by Fick's law:

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

where D, the coefficient of molecular diffusion, is a parameter which uniquely characterizes the process.
In an analogous manner we may consider all the contributions to intermixing of fluid flowing in the x-direction to be described

Representation **of** the dispersion (dispersed plug flow) model.



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

where the parameter D, which we call the longitudinal or axial dispersion coeficient, uniquely characterizes the degree of backmixing during flow.

- We use the terms longitudinal and axial because we wish to distinguish mixing in the direction of flow from mixing in the lateral or radial direction, which is not our primary concern.
- These two quantities may be quite different in magnitude.
- For example, in streamline flow of fluids through pipes, axial mixing is mainly due to fluid velocity gradients, whereas radial mixing is due to molecular diffusion alone.

In dimensionless form where $z = (ut + x)/L$ and $\theta = t/\bar{t} = tu/L$, the basic differential equation representing this dispersion model becomes

$$\frac{\partial C}{\partial \theta} = \left(\frac{\mathbf{D}}{uL}\right) \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z}$$

where the dimensionless group $\left(\frac{\mathbf{D}}{uL}\right)$, called the vessel dispersion number, is the parameter that measures the extent of axial dispersion. Thus

$$\frac{\mathbf{D}}{uL} \to 0 \quad \text{negligible dispersion, hence plug flow}$$

$$\frac{\mathbf{D}}{uL} \to \infty \quad \text{large dispersion, hence mixed flow}$$

This model usually represents quite satisfactorily flow that deviates not too greatly from plug flow, thus real packed beds and tubes (long ones if flow is streamline).

Fitting the Dispersion Model for Small Extents of Dispersion, D/uL < 0.01

- If we impose an idealized pulse onto the flowing fluid then dispersion modifies this pulse.
- For small extents of dispersion (if D/uL is small) the spreading tracer curve does not significantly change in shape as it passes the measuring point (during the time it is being measured).
- Under these conditions the solution to Eq is not difficult and gives the symmetrical curve.

$$C = \frac{1}{2\sqrt{\pi(\mathbf{D}/uL)}} \exp\left[-\frac{(1-\theta)^2}{4(\mathbf{D}/uL)}\right]$$

The equations representing this family are

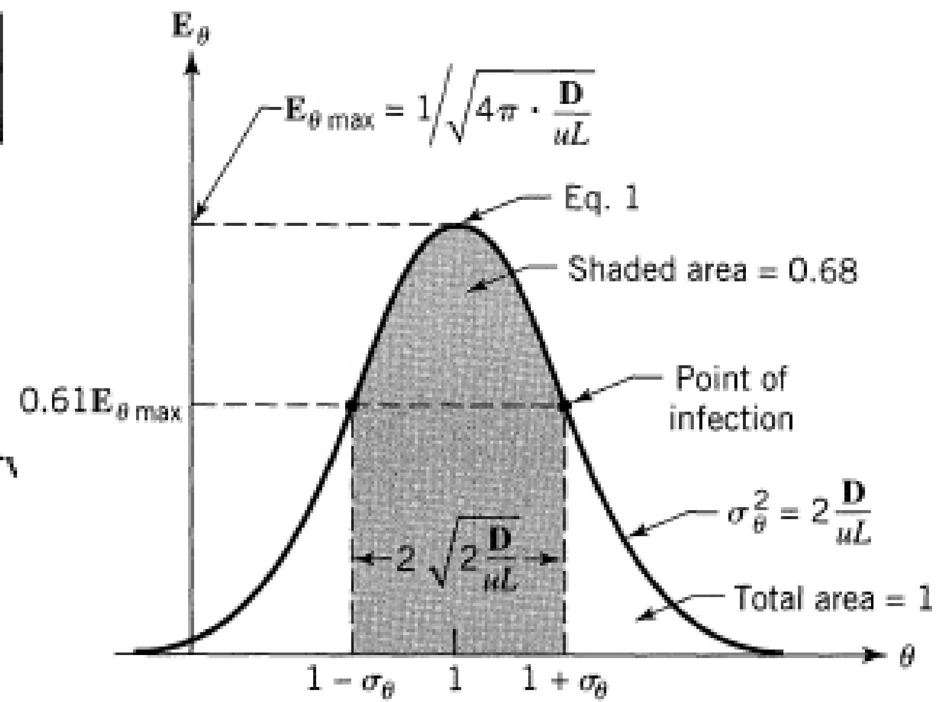
$$\mathbf{E}_\theta = \bar{t} \cdot \mathbf{E} = \frac{1}{\sqrt{4\pi(\mathbf{D}/uL)}} \exp\left[-\frac{(1-\theta)^2}{4(\mathbf{D}/uL)}\right]$$

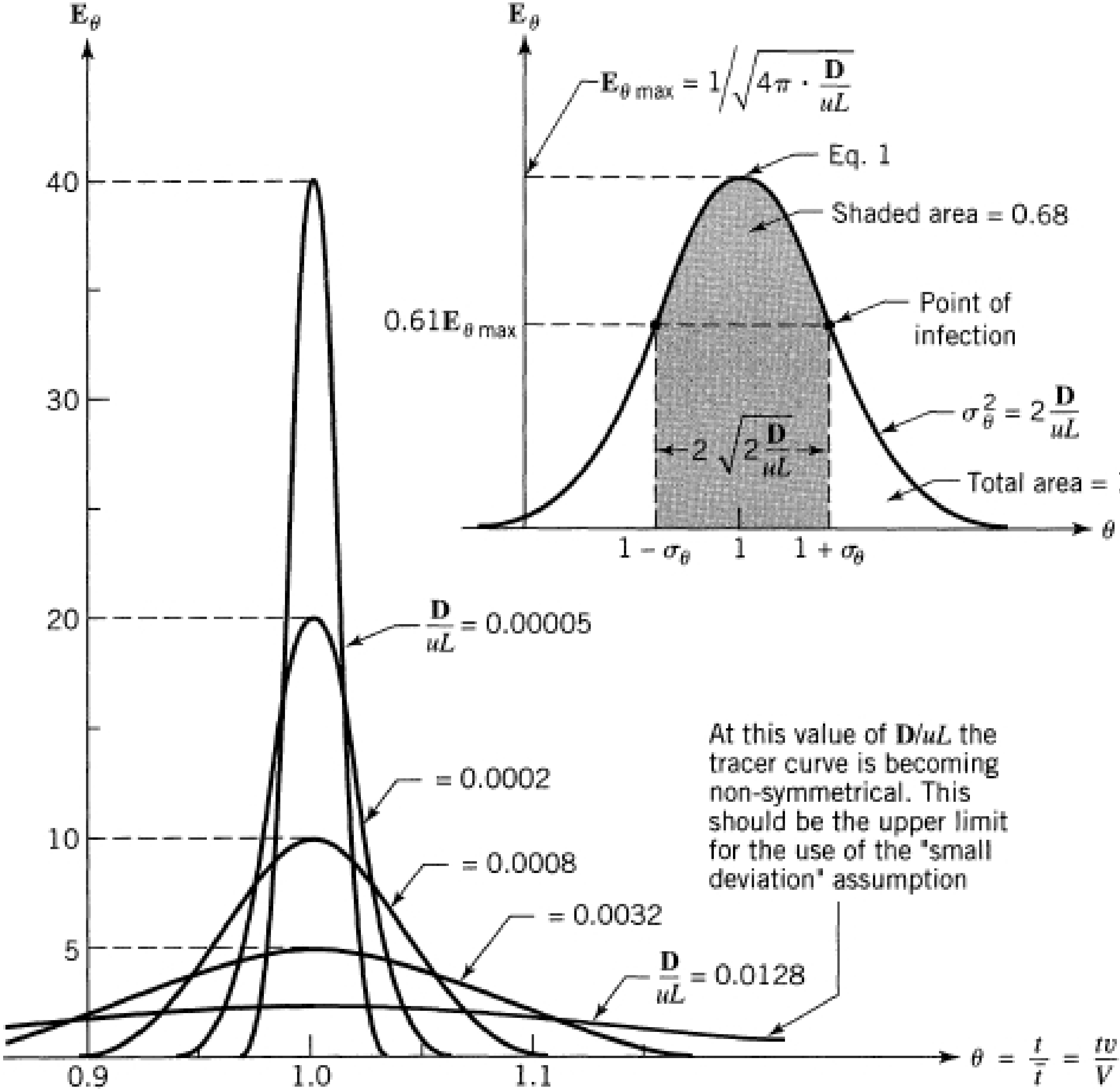
$$\mathbf{E} = \sqrt{\frac{u^3}{4\pi \mathbf{D} L}} \exp\left[-\frac{(L-ut)^2}{4\mathbf{D}L/u}\right]$$

$$\bar{t}_{\mathbf{E}} = \frac{V}{v} = \frac{L}{u} \quad \text{or} \quad \bar{\theta}_{\mathbf{E}} = 1$$

mean of **E** curv

$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = 2\left(\frac{\mathbf{D}}{uL}\right) \quad \text{or} \quad \sigma^2 = 2\left(\frac{\mathbf{D}L}{u^3}\right)$$

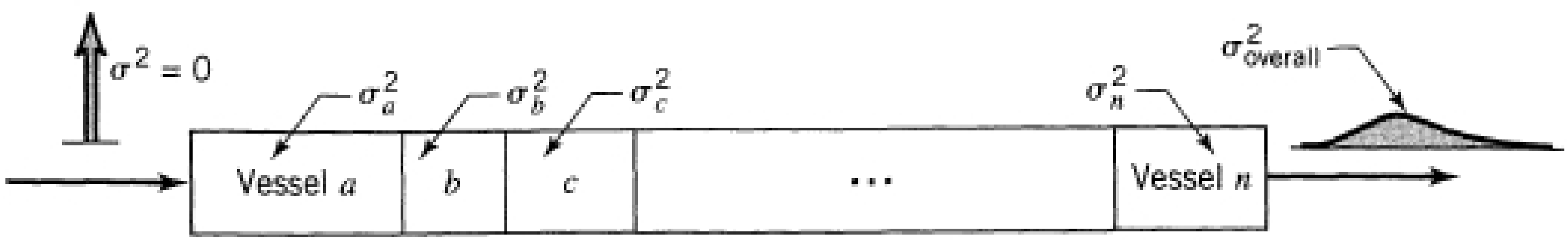




E_θ
40
30
20
10
5
0.9
1.0
1.1
$\theta = \frac{t}{\bar{t}} = \frac{tv}{V}$
$\frac{D}{uL} = 0.00005$
= 0.0002
= 0.0008
= 0.0032
$\frac{D}{uL} = 0.0128$
At this value of D/uL the tracer curve is becoming non-symmetrical. This should be the upper limit for the use of the "small deviation" assumption
E_θ
$E_{\theta\,max} = 1\Big/\sqrt{4\pi \cdot \frac{D}{uL}}$
Eq. 1
Shaded area = 0.68
$0.61E_{\theta\,max}$
Point of infection
$\sigma_\theta^2 = 2\frac{D}{uL}$
$2\sqrt{2\frac{D}{uL}}$
Total area = 1
$1 - \sigma_\theta$
1
$1 + \sigma_\theta$
θ

- Note that D/uL is the one parameter of this curve. Figure shows a number of ways to evaluate this parameter from an experimental curve: by calculating its variance, by measuring its maximum height or its width at the point of inflection, or by finding that width which includes 68% of the area.
- Also note how the tracer spreads as it moves down the vessel. From the variance expression of Eq. 8 we find that

$$\sigma^2 \propto L \qquad \text{or} \qquad \left(\begin{matrix}\text{width of tracer}\\ \text{curve}\end{matrix}\right)^2 \propto L$$



additivity of means and of variances of the E curves of vessels ***a,b,.*** . . ,*n.*

Fortunately, for small extents of dispersion numerous simplifications and approximations in the analysis of tracer curves are possible.
First, the shape of the tracer curve is insensitive to the boundary condition imposed on the vessel, whether closed or open .So for both closed and open vessels

$$C_{\text{pulse}} = \mathbf{E} \text{ and } C_{\text{step}} = \mathbf{F}.$$

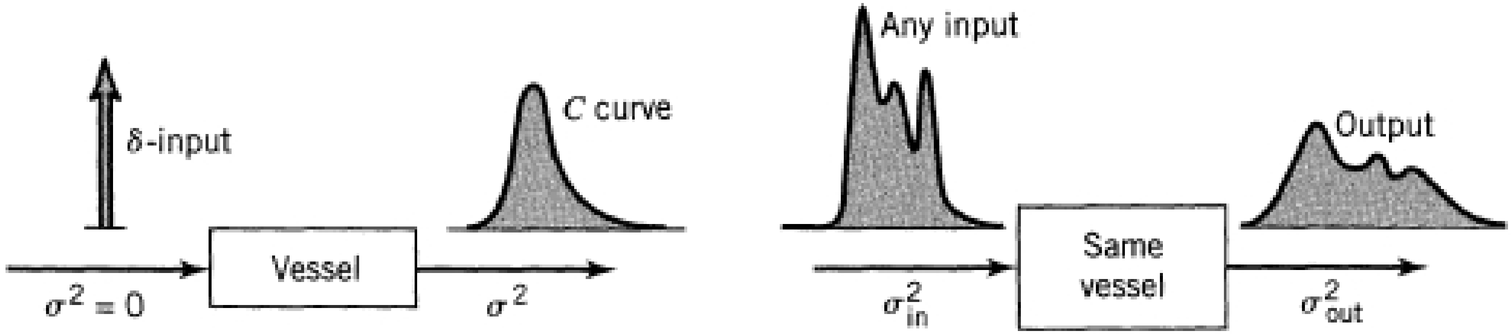
For a *series of vessels* the $\bar{t}$ and σ^2 of the individual vessels are additive, thus,

$$\bar{t}_{\text{overall}} = \bar{t}_a + \bar{t}_b + \cdots = \frac{V_a}{v} + \frac{V_b}{v} + \cdots = \left(\frac{L}{u}\right)_a + \left(\frac{L}{u}\right)_b + \cdots$$

$$\sigma^2_{\text{overall}} = \sigma^2_a + \sigma^2_b + \cdots = 2\left(\frac{\mathbf{D}L}{u^3}\right)_a + 2\left(\frac{\mathbf{D}L}{u^3}\right)_b + \cdots$$

- The additivity of times is expected, but the additivity of variance is not generally expected.
- This is a useful property since it allows us to subtract for the distortion of the measured curve caused by input lines, long measuring leads, etc.
- This additivity property of variances also allows us to treat any one-shot tracer input, no matter what its shape, and to extract from it the variance of the E curve of the vessel.

$$\Delta\sigma^2 = \sigma^2_{\text{out}} - \sigma^2_{\text{in}}$$



$$\frac{\sigma^2_{out} - \sigma^2_{in}}{(\bar{t}_{out} - \bar{t}_{in})^2} = \frac{\Delta\sigma^2}{(\Delta\bar{t})^2} = \Delta\sigma^2_\theta = 2\left(\frac{\mathbf{D}}{uL}\right)$$

- Thus no matter what the shape of the input curve, the *D/uL* value for the vessel can be found.
- The goodness of fit for this simple treatment can only be evaluated by comparison with the more exact but much more complex solutions.

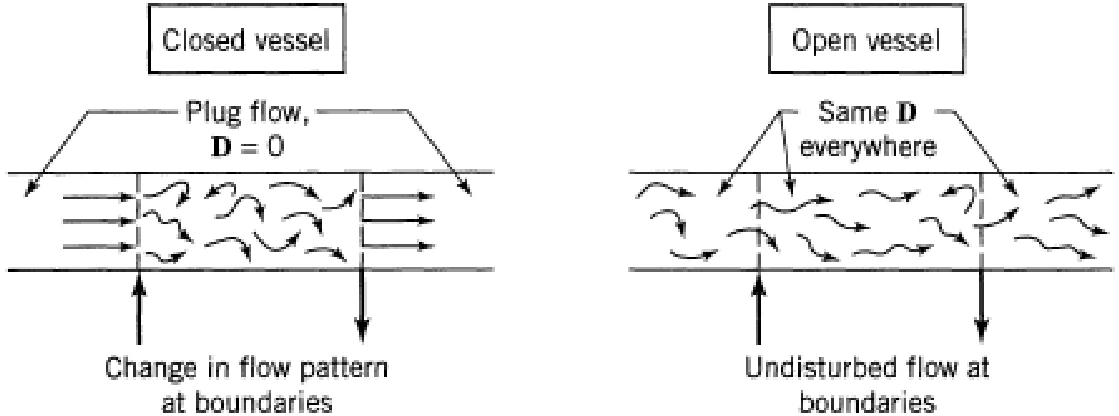
- From such a comparison we find that the maximum error in estimate of *D/uL* is given by

$$\text{error} < 5\% \text{ when } \frac{\mathbf{D}}{uL} < 0.01$$

Large Deviation from Plug Flow, $D/UL > 0.01$

- Here the pulse response is broad and it passes the measurement point slowly enough that it changes shape-it spreads-as it is being measured.
- This gives a non symmetrical E curve.
- An additional complication enters the picture for large *D/uL:*

  What happens right at the entrance and exit of the vessel strongly affects the shape of the tracer curve as well as the relationship between the parameters of the curve and *D/uL.*
- Let us consider two types of boundary conditions: either the flow is undisturbed as it passes the entrance and exit boundaries (we call this the open b.c.),
- or you have plug flow outside the vessel up to the boundaries (we call this the closed b.c.).
- This leads to four combinations of boundary conditions, closed-closed, open-open, and mixed.



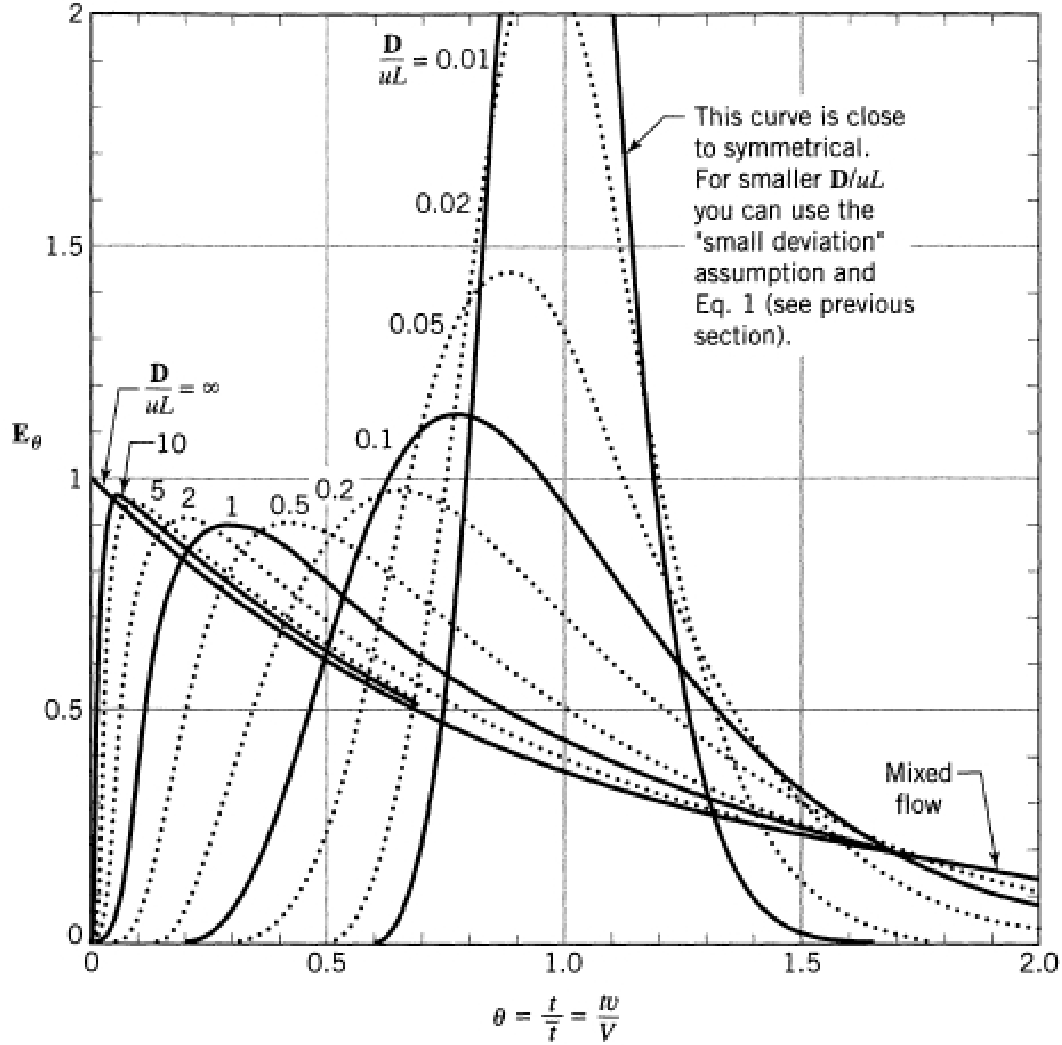
- Figure illustrates the closed and open extremes, whose RTD curves are designated as E_{cc} and E_{bc}.
- Now only one boundary condition gives a tracer curve which is identical to the E function and which fits all the mathematics of Chapter 11, and that is the closed vessel.
- For all other boundary conditions you do not get a proper RTD.
- In all cases you can evaluate *D/uL* from the parameters of the tracer curves; however, each curve has its own mathematics.
- Let us look at the tracer curves for closed and for the open boundary conditions.

Tracer response curves for closed vessels and large deviations from plug flow.

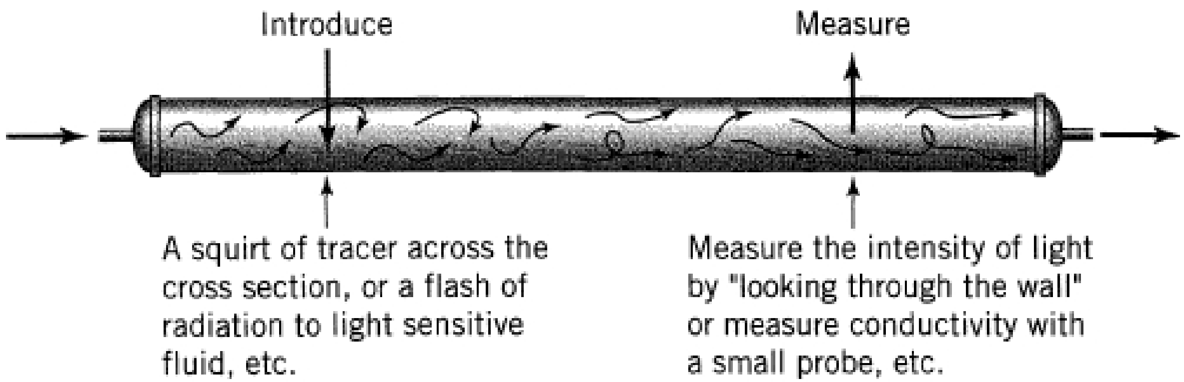
Closed Vessel. Here an analytic expression for the E curve is not available. However, we can construct the curve by numerical methods, see Fig., or evaluate its mean and variance exactly, as was first done by van der Laan (1958). Thus

$$\bar{t}_{\mathbf{E}} = \bar{t} = \frac{V}{v} \quad \text{. . . or . . .} \quad \bar{\theta}_{\mathbf{E}} = \frac{\bar{t}_{\mathbf{E}}}{\bar{t}} = \frac{\bar{t}_{\mathbf{E}}\, v}{V} = 1$$

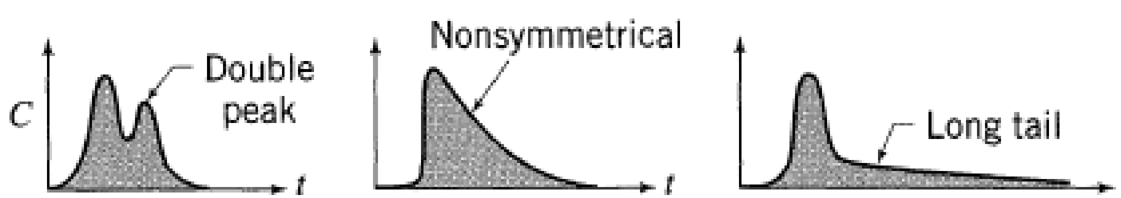
$$\sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = 2\left(\frac{\mathbf{D}}{uL}\right) - 2\left(\frac{\mathbf{D}}{uL}\right)^2 \left[1 - e^{-uL/\mathbf{D}}\right]$$

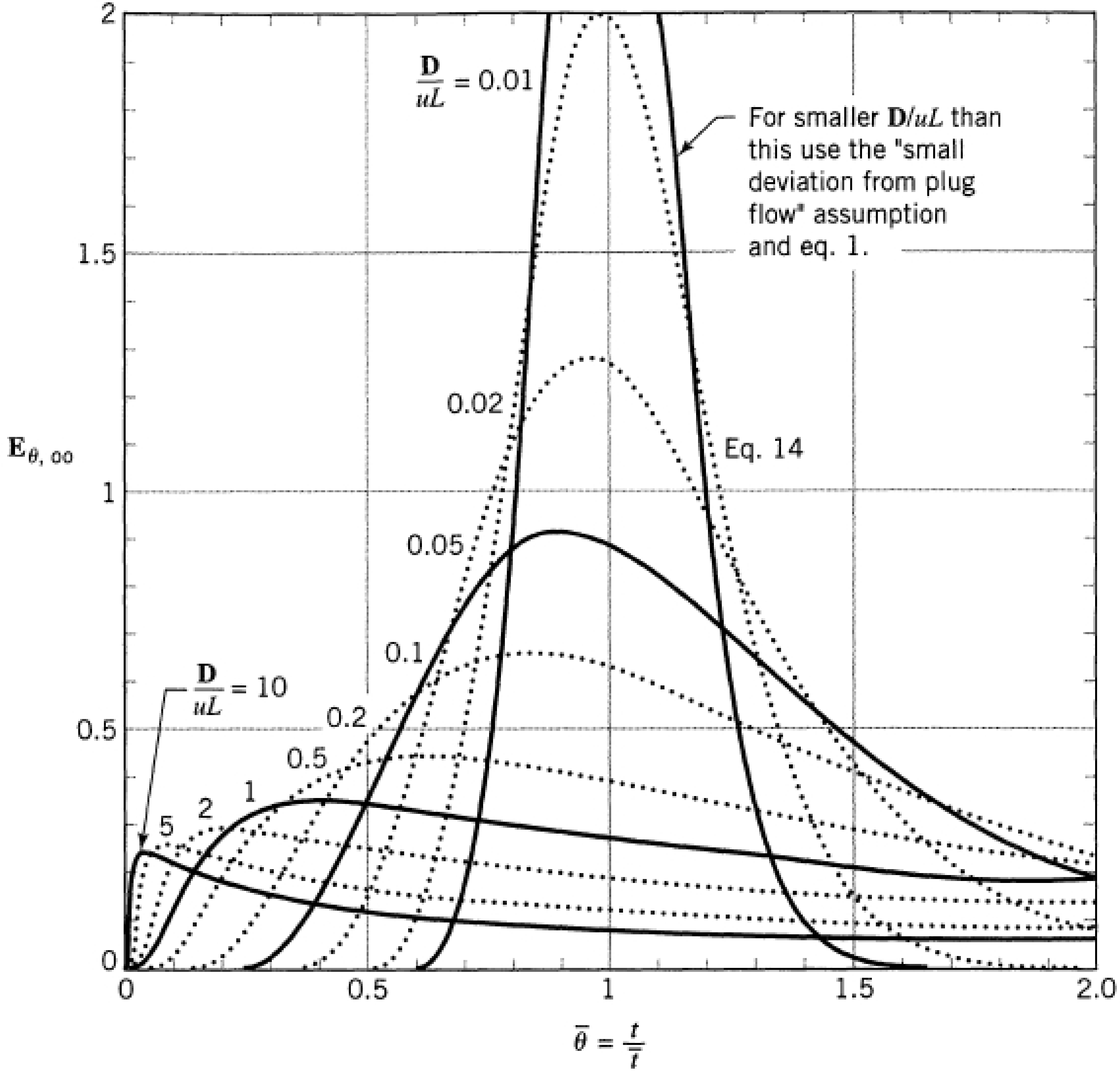


Open Vessel. This represents a convenient and commonly used experimental device, a section of long pipe (see Fig. 13.9).



- It also happens to be the only physical situation (besides small ***D/uL)*** where the analytical expression for the E curve is not too complex.
- The results are given by the response curves shown in fig.
- the following equations, first derived by Levenspiel and Smith





2
1.5
1
0.5
0
0
0.5
1
1.5
2.0
$\mathbf{E}_{\theta,\,oo}$
$\bar{\theta} = \frac{t}{\bar{t}}$
$\frac{\mathbf{D}}{uL} = 0.01$
For smaller $\mathbf{D}/uL$ than this use the "small deviation from plug flow" assumption and eq. 1.
0.02
Eq. 14
0.05
0.1
$\frac{\mathbf{D}}{uL} = 10$
0.2
0.5
1
2
5

$$\mathbf{E}_{\theta,oo} = \frac{1}{\sqrt{4\pi(\mathbf{D}/uL)}} \exp\left[-\frac{(1-\theta)^2}{4\theta(\mathbf{D}/uL)}\right]$$

$$\mathbf{E}_{t,oo} = \frac{u}{\sqrt{4\pi \mathbf{D} t}} \exp\left[-\frac{(L-ut)^2}{4\mathbf{D}t}\right]$$

$$\bar{\theta}_{\mathbf{E},oo} = \frac{\bar{t}_{\mathbf{E}oo}}{\bar{t}} = 1 + 2\left(\frac{\mathbf{D}}{uL}\right) \quad \text{...or...} \quad t_{\mathbf{E}oo} = \frac{V}{v}\left(1 + 2\frac{\mathbf{D}}{uL}\right)$$

open-open vessel

$$\sigma^2_{\theta,oo} = \frac{\sigma^2_{t,oo}}{\bar{t}^2} = 2\frac{\mathbf{D}}{uL} + 8\left(\frac{\mathbf{D}}{uL}\right)^2$$

Comments

(a) For small $\mathbf{D}/uL$ the curves for the different boundary conditions all approach the "small deviation" curve of Eq. 8. At larger $\mathbf{D}/uL$ the curves differ more and more from each other.

(b) To evaluate $\mathbf{D}/uL$ either match the measured tracer curve or the measured σ^2 to theory. Matching σ^2 is simplest, though not necessarily best; however, it is often used. But be sure to use the right boundary conditions.

(c) If the flow deviates greatly from plug ($\mathbf{D}/uL$ large) chances are that the real vessel doesn't meet the assumption of the model (a lot of independent random fluctuations). Here it becomes questionable whether the model should even be used. I hesitate when $\mathbf{D}/uL > 1$.

(d) You must always ask whether the model should be used. You can always match σ^2 values, but if the shape looks wrong, as shown in the accompanying sketches, don't use this model, use some other model.

(e) For large $\mathbf{D}/uL$ the literature is profuse and conflicting, primarily because of the unstated and unclear assumptions about what is happening at the vessel boundaries. The treatment of end conditions is full of mathematical subtleties as noted above, and the additivity of variances is questionable. Because of all this we should be very careful in using the dispersion model where backmixing is large, particularly if the system is not closed.

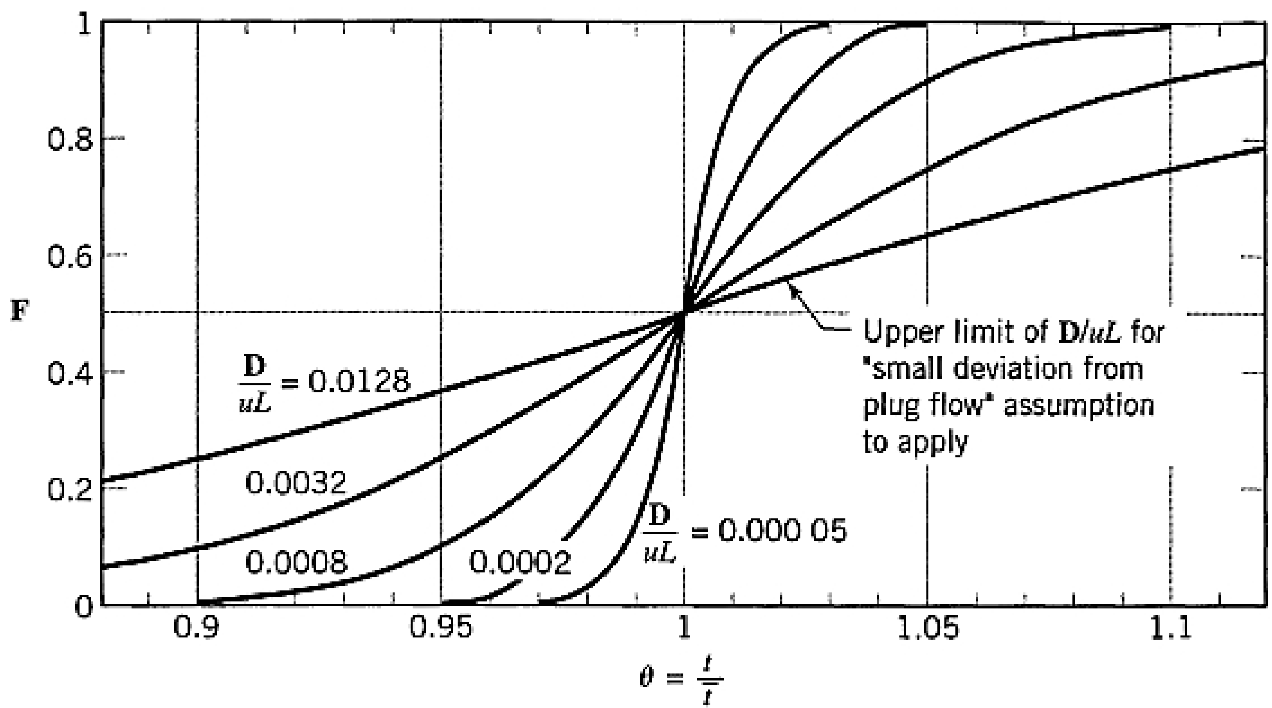
(f) We will not discuss the equations and curves for the open-closed or closed-open boundary conditions. These can be found in Levenspiel (1996).

Step Input of Tracer

- Here the output F curve is S-shaped and is obtained by integrating the corresponding E curve. Thus at any time *t* or ***θ***

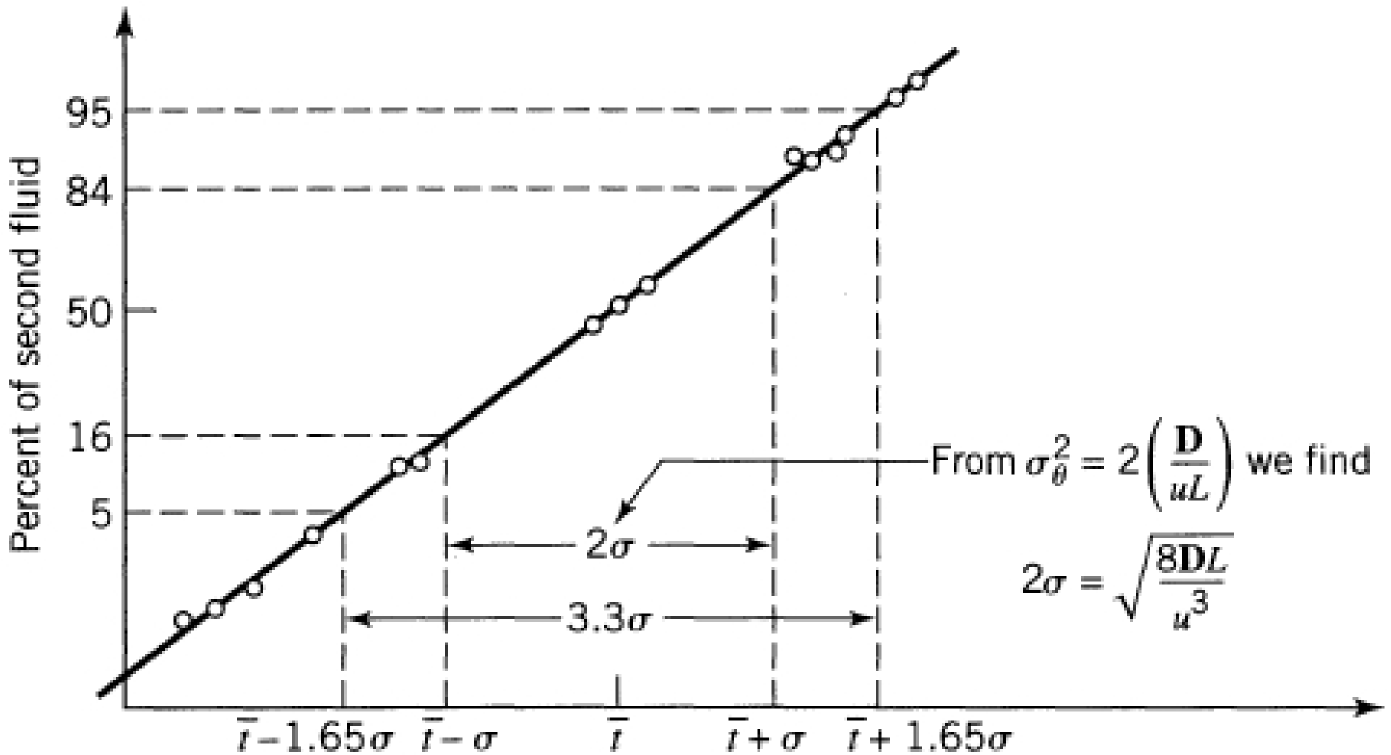
$$\mathbf{F} = \int_0^\theta \mathbf{E}_\theta \, d\theta = \int_0^t \mathbf{E} \, dt$$

The shape of the **F** curve depends on D/uL and the boundary conditions for the vessel.
Analytical expressions are not available for any of the F curves



Small Deviation from Plug Flow, D/uL < 0.01

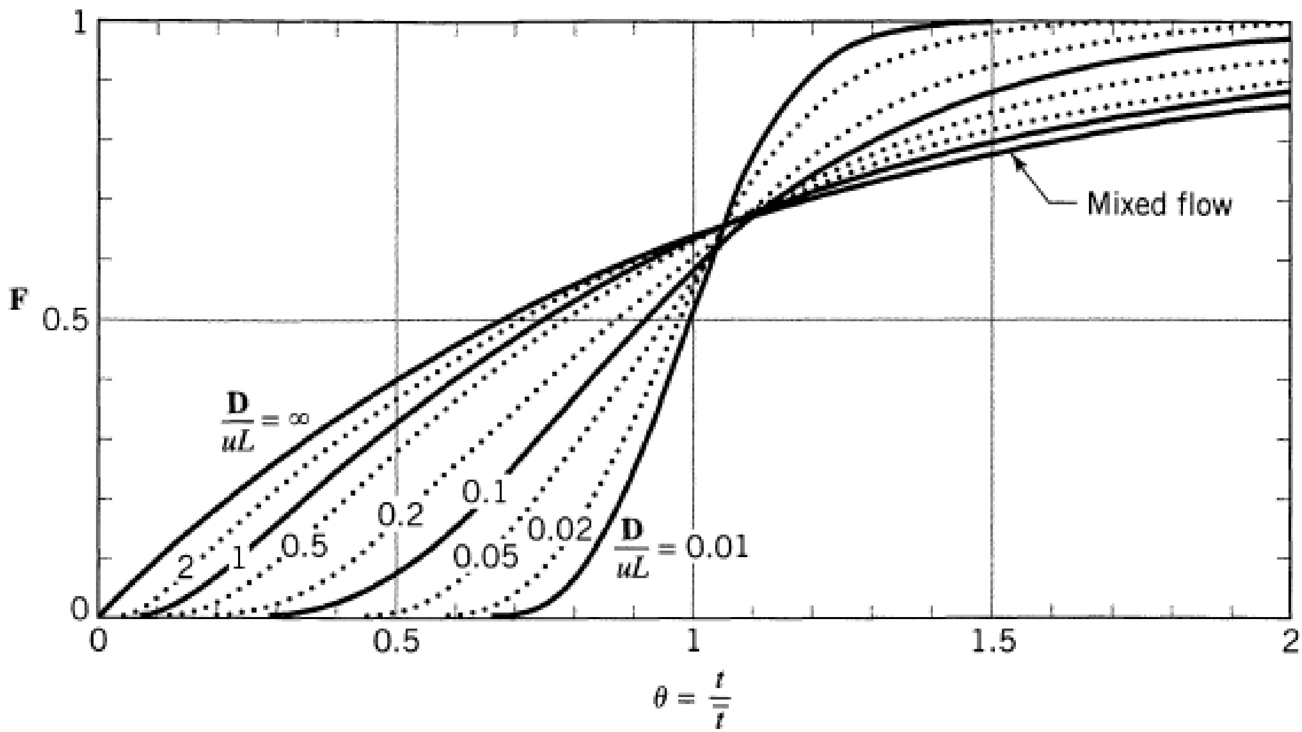
- From Eqs. we can find the curves of Fig.
- For these small deviations from plug flow we can find **D/uL** directly by plotting the experimental data on probability graph paper as indicated in Fig. .



Probability plot **of** a step response signal. From this we find D/uL directly.

Step Response for Large Dispersion, D/uL > 0.01.

- For large deviations from plug flow, the problem of boundary conditions must be considered, the resulting S-shaped response curves are not symmetrical, their equations are not available, and they are best analyzed by first differentiating them to give the corresponding Cpulse curve. Figure shows an example of this family of curves.
- Step response curves for large deviations from plug flow in closed vessels.



(a) One direct commercial application of the step experiment is to find the zone of intermixing-the contaminated width-between two fluids of somewhat similar properties flowing one after the other in a long pipeline.

Given ***D/uL*** we find this from the probability plot of Fig. Design charts to ease the calculation are given by Levenspiel (1958a).

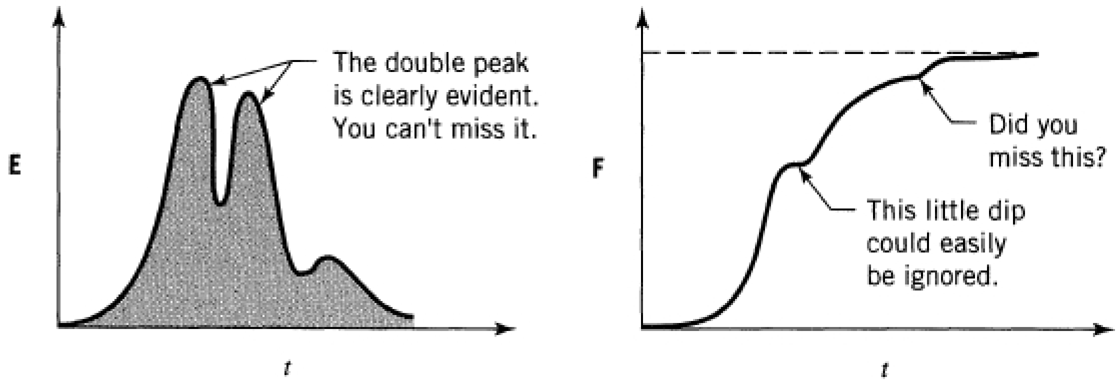
(b) Should you use a pulse or step injection experiment?

Sometimes one type of experiment is naturally more convenient for one of many reasons. In such a situation this question does not arise

But when you do have a choice, then the pulse experiment is preferred because it gives a more "honest" result.

The reason is that the F curve integrates effects; it gives a smooth good-looking curve which could well hide real effects.

- For example, Fig. shows the corresponding E and F curves for a given vessel.



Sensitivity of the E and F curves for the same flow.

D/uL FROM AN **F *CURVE***

On the assumption that the closed vessel of Example *11.1,* Chapter *11,* is well represented by the dispersion model, calculate the vessel dispersion number ***D/uL.*** The *C* versus *t* tracer response of this vessel is

t, min	0	5	10	15	20	25	30	35
C_{pulse}, gm/liter	0	3	5	5	4	2	1	0

Since the C curve for this vessel is broad and unsymmetrical, see Fig. 11.E1, let us guess that dispersion is too large to allow use of the simplification leading to Fig. 13.4. We thus start with the variance matching procedure of Eq. 18. The mean and variance of a continuous distribution measured at a finite number of equidistant locations is given by Eqs. 3 and 4 as

$$\bar{t} = \frac{\sum t_i C_i}{\sum C_i} \qquad \sigma^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \bar{t}^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \left[\frac{\sum t_i C_i}{\sum C_i}\right]^2$$

$$\sum C_i = 3 + 5 + 5 + 4 + 2 + 1 = 20$$

$$\sum t_i C_i = (5 \times 3) + (10 \times 5) + \cdots + (30 \times 1) = 300 \text{ min}$$

$$\sum t_i^2 C_i = (25 \times 3) + (100 \times 5) + \cdots + (900 \times 1) = 5450 \text{ min}^2$$

$$\bar{t} = \frac{300}{20} = 15 \text{ min}$$

$$\sigma^2 = \frac{5450}{20} - \left(\frac{300}{20}\right)^2 = 47.5 \text{ min}^2$$

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} = \frac{47.5}{(15)^2} = 0.211$$

Now for a closed vessel Eq. 13 relates the variance to $\mathbf{D}/uL$. Thus

$$\sigma_\theta^2 = 0.211 = 2\frac{\mathbf{D}}{uL} - 2\left(\frac{\mathbf{D}}{uL}\right)^2 (1 - e^{-uL/\mathbf{D}})$$

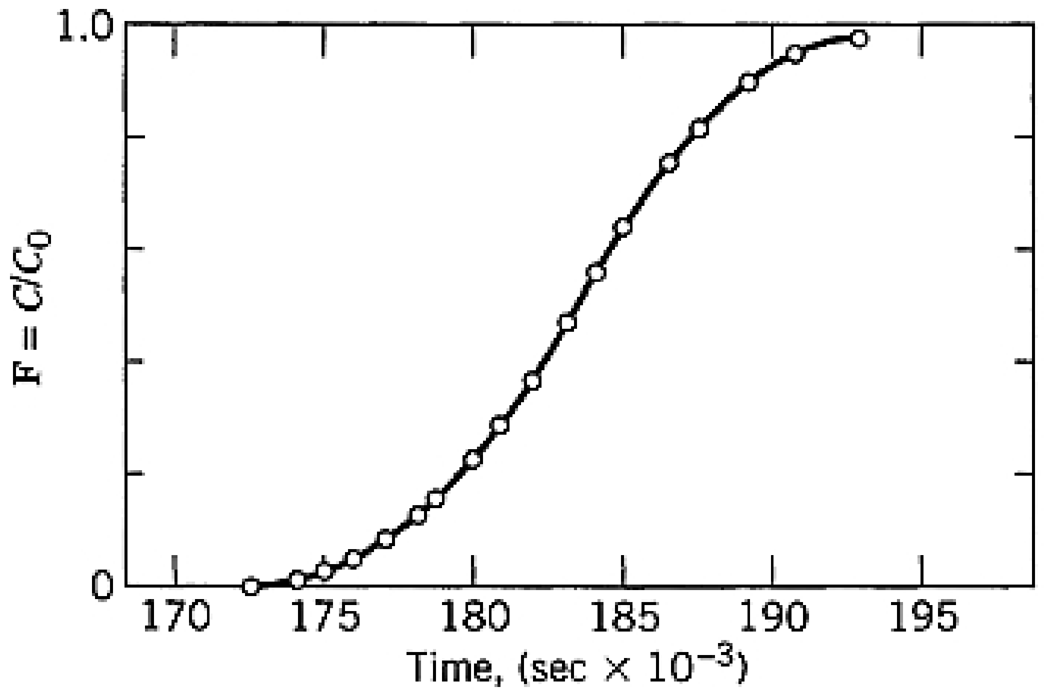
Ignoring the second term on the right, we have as a first approximation

$$\frac{\mathbf{D}}{uL} \cong 0.106$$

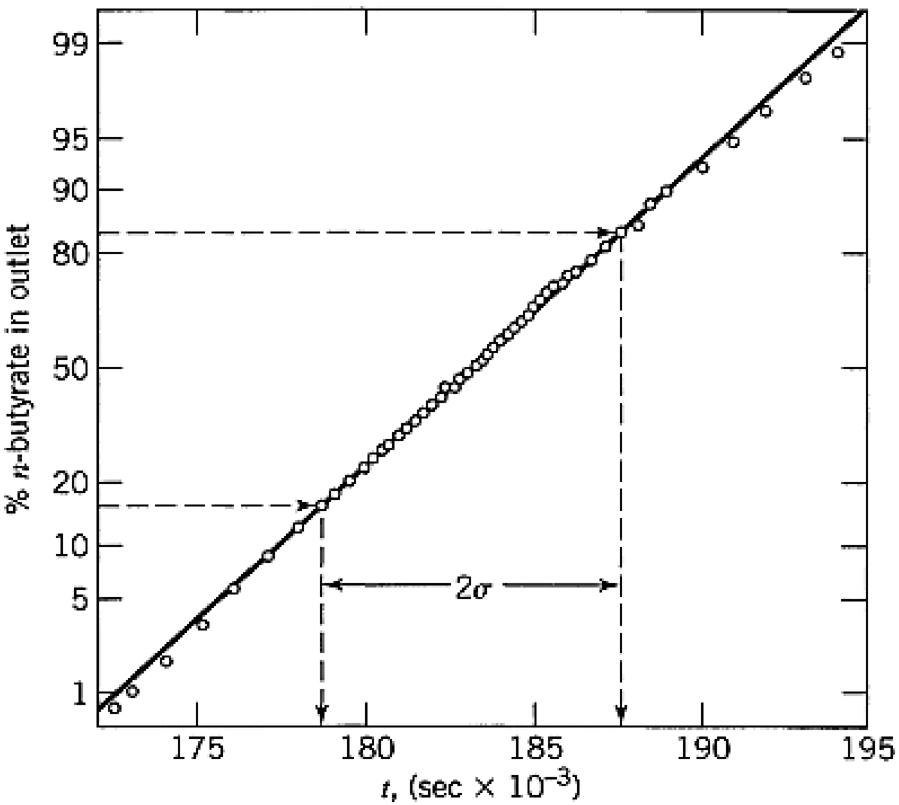
Correcting for the term ignored we find by trial and error that

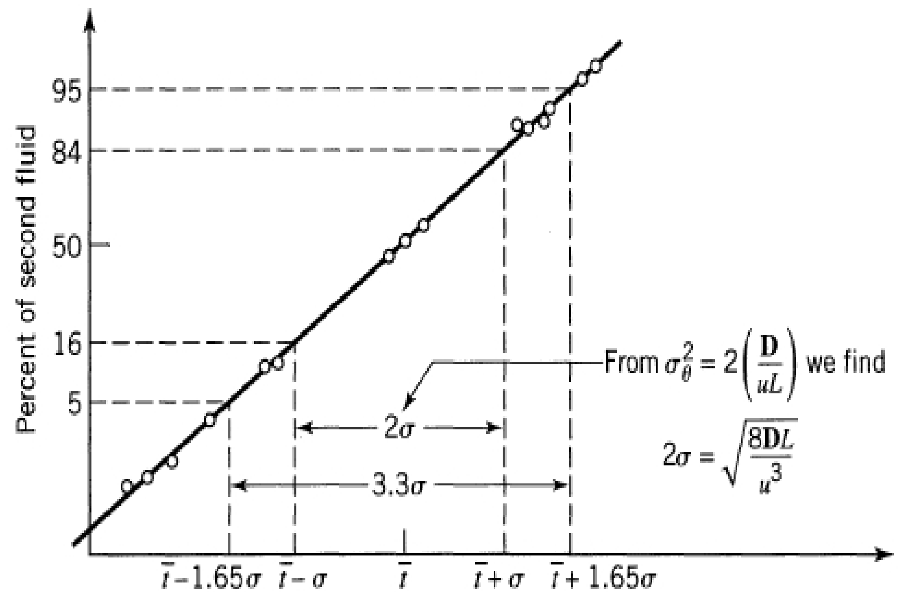
$$\frac{\mathbf{D}}{uL} = \underline{\underline{0.120}}$$

- von Rosenberg (1956) studied the displacement of benzene by n-butyrate in a 38 mm diameter packed column 1219 mm long, measuring the fraction of ***n-***butyrate in the exit stream by refractive index methods.
- When graphed, the fraction of n-butyrate versus time was found to be S-shaped. This is the **F** curve, and it is shown in Fig. for von Rosenberg's run at the lowest flow rate,where u = 0.0067 mm/s, which is about 0.5 m/day. Find the vessel dispersion number of this system.



- Instead of taking slopes of the **F** curve to give the E curve and then determining the spread of this curve, let us use the probability paper method. So, plotting the data on this paper does actually give close to a straight line, as shown in





- To find the variance and *D/uL* from a probability graph is a simple matter.
- Just follow the procedure illustrated in Fig.. Thus Fig. shows that the 16th percentile point falls at *t* = 178 550 s

  the 84th percentile point falls at *t* = 187 750 s

  and this time interval represents *2u.*

Therefore the standard deviation is

and this time interval represents 2σ. Therefore the standard deviation is

$$\sigma = \frac{187\,750 - 178\,500}{2} = 4600 \text{ s}$$

We need this standard deviation in dimensionless time units if we are to find **D**. Therefore

$$\sigma_\theta = \frac{\sigma}{\bar{t}} = (4600 \text{ s})\left(\frac{0.0067 \text{ mm/s}}{1219 \text{ mm}}\right) = 0.0252$$

$$\sigma_\theta^2 = (0.0252)^2 = 0.00064$$

$$\frac{\mathbf{D}}{uL} = \frac{\sigma_\theta^2}{2} = \underline{\underline{0.00032}}$$

Note that the value of $\mathbf{D}/uL$ is well below 0.01, justifying the use of the gaussian approximation to the tracer curve and this whole procedure.

[redacted]

D/uL FROM A ONE-SHOT INPUT

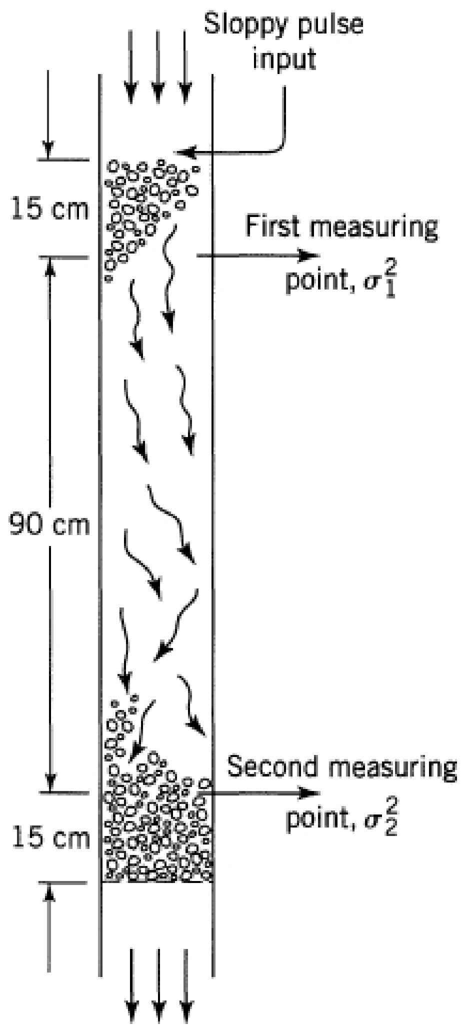
- Find the vessel dispersion number in a fixed-bed reactor packed with 0.625-cm catalyst pellets.
- For this purpose tracer experiments are run in equipment shown in Fig. E13.3.
- The catalyst is laid down in a haphazard manner above a screen to a height of 120 cm, and fluid flows downward through this packing.

A sloppy pulse of radioactive tracer is injected directly above the bed, and output signals are recorded by Geiger counters at two levels in the bed 90 cm apart.

The following data apply to a specific experimental run.

Bed voidage = 0.4,superficial velocity of fluid (based on an empty tube) = 1.2 cm/sec, and variances of output signals are found to be

$\sigma_1^2 = 39\ \text{sec}^2$ and $\sigma_2^2 = 64\ \text{sec}^2$. Find $\mathbf{D}/uL$.



$$\Delta\sigma^2 = \sigma_2^2 - \sigma_1^2 = 64 - 39 = 25\ \text{sec}^2$$

$$\Delta\sigma_\theta^2 = \Delta\sigma^2\left(\frac{v}{V}\right)^2 = (25\ \text{sec}^2)\left[\frac{1.2\ \text{cm/sec}}{(90\ \text{cm})(0.4)}\right]^2 = \frac{1}{36}$$

from which the dispersion number is

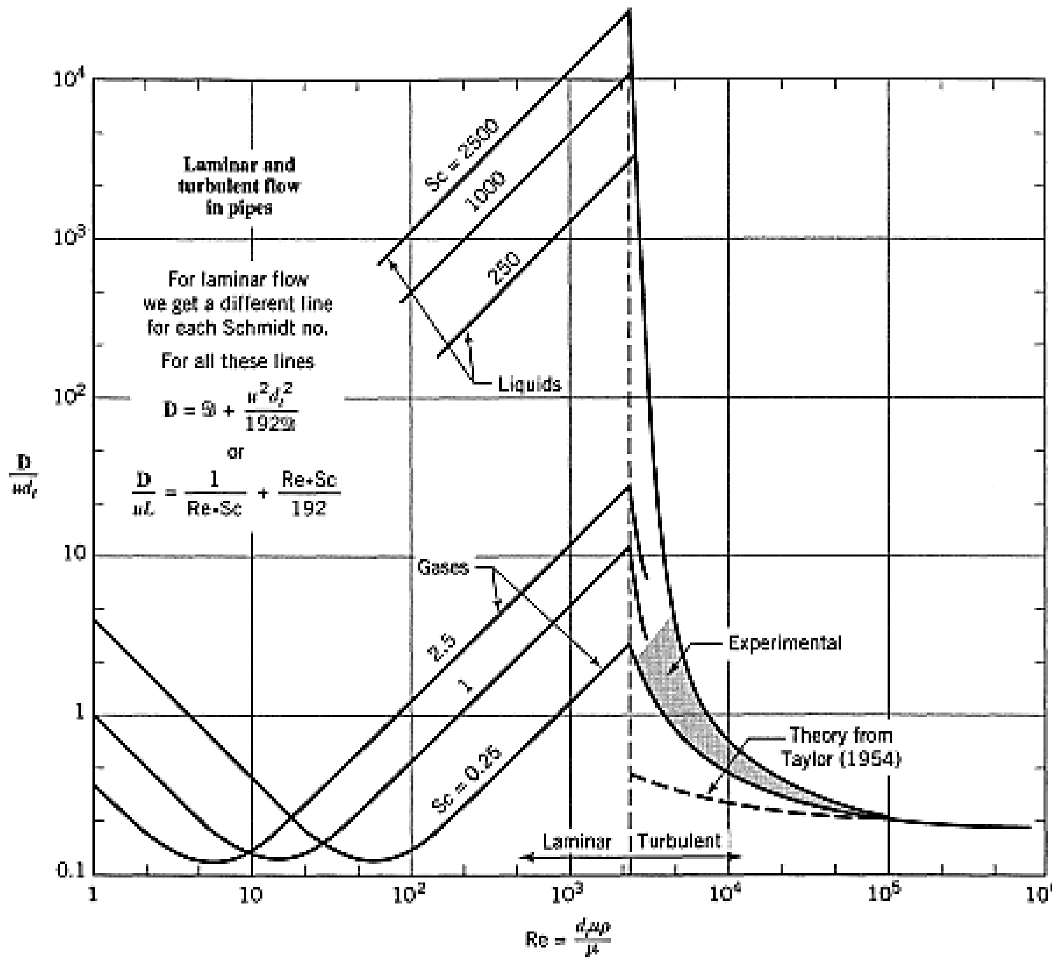
$$\frac{\mathbf{D}}{uL} = \frac{\Delta\sigma_\theta^2}{2} = \underline{\underline{\frac{1}{72}}}$$

CORRELATIONS FOR AXIAL DISPERSION

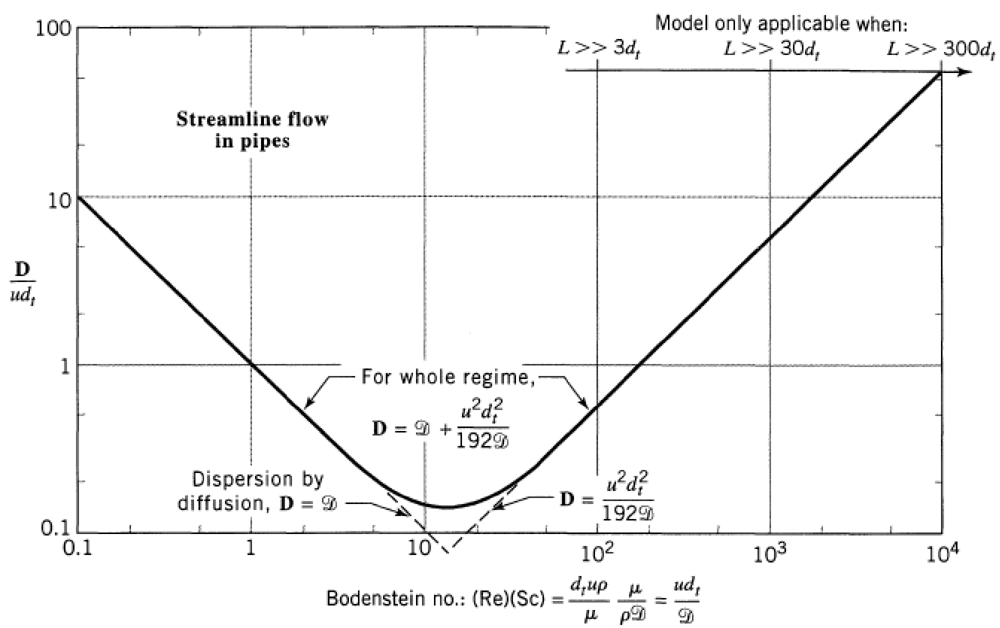
The vessel dispersion number $\mathbf{D}/uL$ is a product of two terms

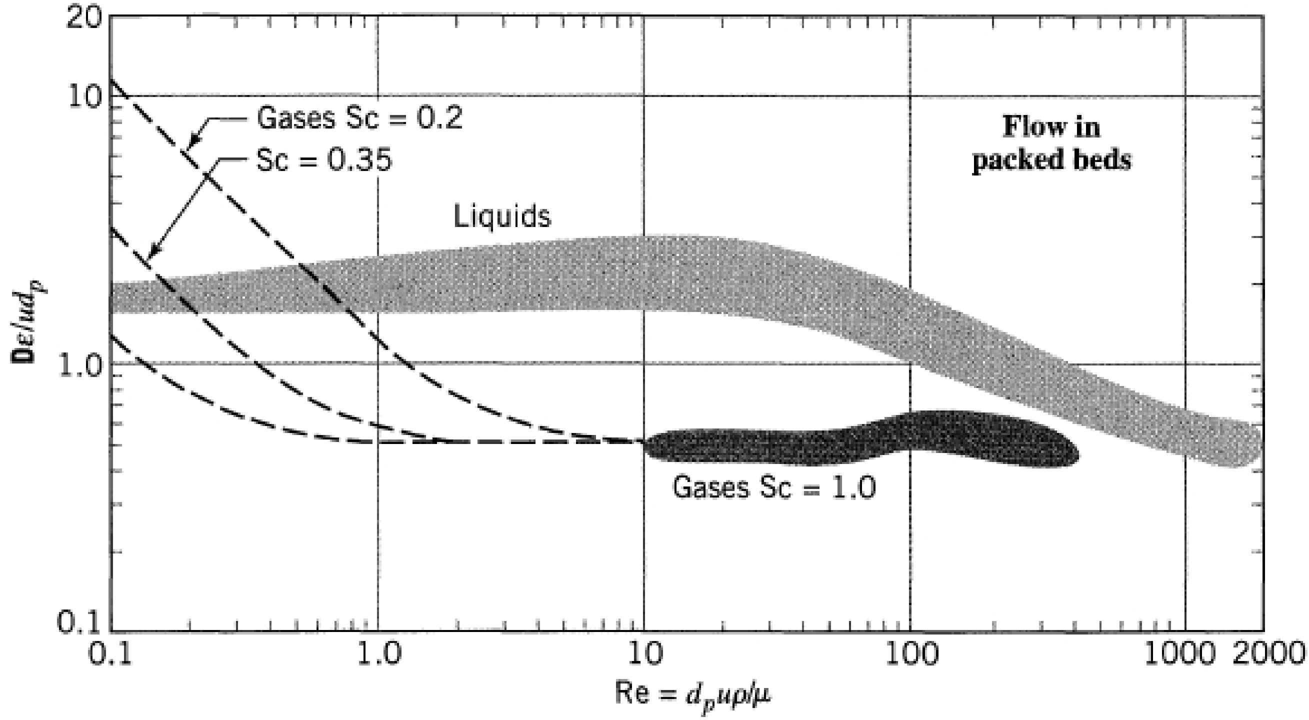
$$\frac{\mathbf{D}}{uL} = \begin{pmatrix}\text{intensity of}\\ \text{dispersion}\end{pmatrix}\begin{pmatrix}\text{geometric}\\ \text{factor}\end{pmatrix} = \left(\frac{\mathbf{D}}{ud}\right)\left(\frac{d}{L}\right)$$

$$\frac{\mathbf{D}}{ud} = f\begin{pmatrix}\text{fluid}\\ \text{properties}\end{pmatrix}\begin{pmatrix}\text{flow}\\ \text{dynamics}\end{pmatrix} = f\left[\begin{pmatrix}\text{Schmidt}\\ \text{no.}\end{pmatrix}\begin{pmatrix}\text{Reynolds}\\ \text{no.}\end{pmatrix}\right]$$



- Figures show the findings for flow in pipes. This model represents turbulent flow, but only represents streamline flow in pipes when the pipe is long enough to achieve radial uniformity of a pulse of tracer.
- For liquids this may require a rather long pipe, Note that molecular diffusion strongly affects the rate of dispersion in laminar flow.
- At low flow rate it promotes dispersion; at higher flow rate it has the opposite effect.
- Correlations similar to these are available or can be obtained for flow in beds of porous and/or adsorbing solids, in coiled tubes, in flexible channels, for pulsating flow, for non-Newtonians, and so on.





Experimental findings on dispersion of fluids flowing with mean axial velocity ***u*** in packed beds.

CHEMICAL REACTION AND DISPERSION

Our discussion has led to the measure of dispersion by a dimensionless group *D/uL.*

Let us now see how this affects conversion in reactors.

Consider a steady-flow chemical reactor of length L through which fluid is flowing at a constant velocity *u,* and in which material is mixing axially with a dispersion coefficient D.

Let an n^th^-order reaction be occurring.

$$A \rightarrow \text{products}, \quad -r_A = kC_A^n$$

By referring to an elementary section of reactor as shown in Fig., the basic material balance for any reaction component

input = output + disappearance by reaction + accumulation

becomes for component A, at steady state,

$(\text{Out-in})_{\text{bulk flow}}$ + $(\text{out-in})_{\text{axial dispersion}}$ + disappearance by reaction + accumulation = o

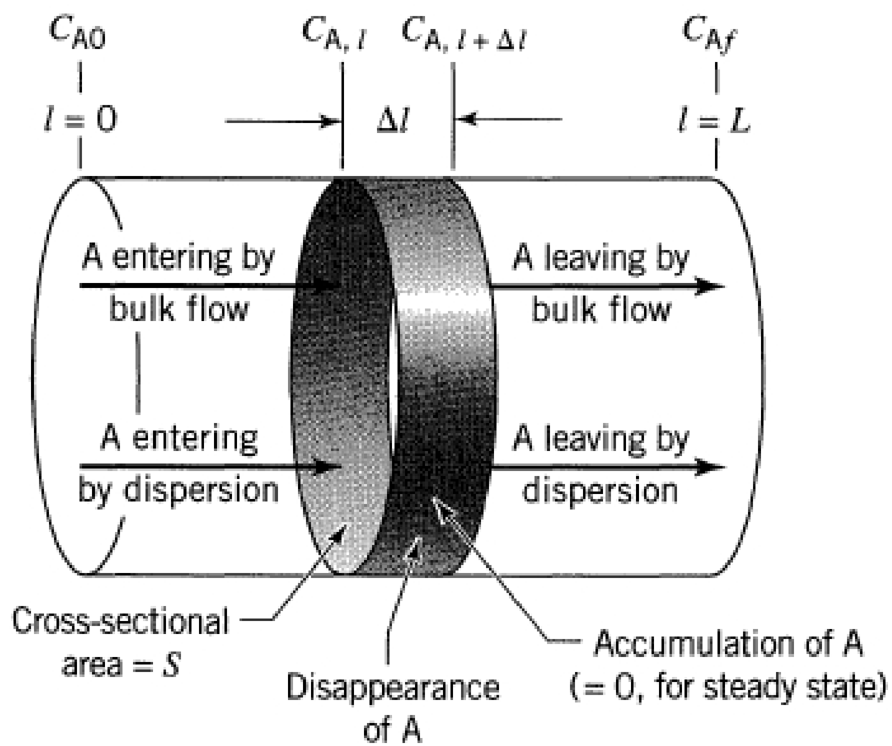
The individual terms (in moles A/time) are as follow

$$\text{entering by bulk flow} = \left(\frac{\text{moles A}}{\text{volume}}\right)\left(\begin{array}{c}\text{flow}\\ \text{velocity}\end{array}\right)\left(\begin{array}{c}\text{cross-sectional}\\ \text{area}\end{array}\right)$$

$$= C_{\mathrm{A},l}uS, \quad [\text{mol/s}]$$

$$\text{leaving by bulk flow} = C_{\mathrm{A},l+\Delta l}uS$$

$$\text{entering by axial dispersion} = \frac{dN_\mathrm{A}}{dt} = -\left(\mathbf{D}S\,\frac{dC_\mathrm{A}}{dl}\right)_{l+\Delta l}$$



leaving by axial dispersion $= \frac{dN_A}{dt} = -\left(\mathbf{D} S \frac{dC_A}{dl}\right)_{l+\Delta l}$

disappearance by reaction $= (-r_A)\, V = (-r_A) S\, \Delta l, \quad$ [mol/s]

$$u \frac{(C_{A,l+\Delta l} - C_{A,l})}{\Delta l} - \mathbf{D} \frac{\left[\left(\frac{dC_A}{dl}\right)_{l+\Delta l} - \left(\frac{dC_A}{dl}\right)_l\right]}{\Delta l} + (-r_A) = 0$$

$$\lim_{l_2 \to l_1} \frac{Q_2 - Q_1}{l_2 - l_1} = \lim_{\Delta l \to 0} \frac{\Delta Q}{\Delta l} = \frac{dQ}{dl}$$

So taking limits as $\Delta l \to 0$ we obtain

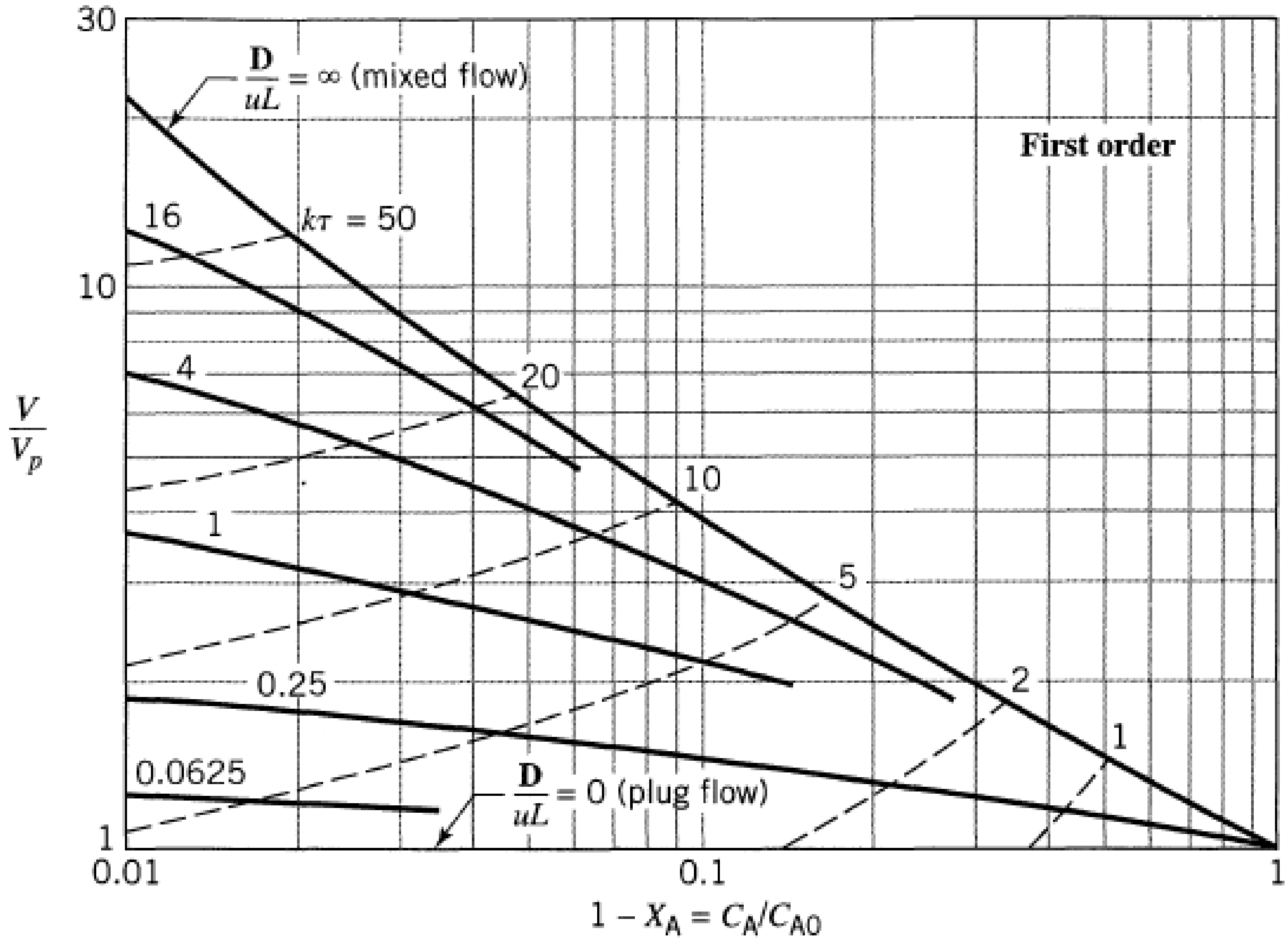
$$u \frac{dC_A}{dl} - \mathbf{D} \frac{d^2 C_A}{dl^2} + kC_A^n = 0$$

In dimensionless form where $z = l/L$ and $\tau = \bar{t} = L/u = V/v$, this expression becomes

$$\frac{\mathbf{D}}{uL} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} - k\tau C_A^n = 0$$

$$\frac{\mathbf{D}}{uL} \frac{d^2 X_A}{dz^2} - \frac{dX_A}{dz} + k\tau C_{A0}^{n-1} (1 - X_A)^n = 0$$

First-Order Reaction



- Exit conditions the solution is

$$\frac{C_A}{C_{A0}} = 1 - X_A = \frac{4a \exp\left(\frac{1}{2}\frac{uL}{\mathbf{D}}\right)}{(1+a)^2 \exp\left(\frac{a}{2}\frac{uL}{\mathbf{D}}\right) - (1-a)^2 \exp\left(-\frac{a}{2}\frac{uL}{\mathbf{D}}\right)}$$

$$a = \sqrt{1 + 4k\tau(\mathbf{D}/uL)}$$

Figure is a graphical representation of these results in useful form, prepared by combining, and allows comparison of reactor sizes for plug and dispersed plug flow. For *small deviations* ***from*** *plug* ***flow*** *D/uL* becomes small, the E curve approaches gaussian;
hence, on expanding the exponentials and dropping higher
order terms Eq. 19 reduces to

$$\frac{C_A}{C_{A0}} = \exp\left[-k\tau + (k\tau)^2 \frac{\mathbf{D}}{uL}\right]$$

$$= \exp\left[-k\tau + \frac{k^2\sigma^2}{2}\right]$$

- compares the performance of real reactors which are close to plug flow with plug flow reactors.
- Thus the size ratio needed for identical conversion is given by

$$\frac{L}{L_p} = \frac{V}{V_p} = 1 + (k\tau)\frac{\mathbf{D}}{uL} \qquad \text{for same } C_{A\,\text{out}}$$

$$\frac{C_A}{C_{Ap}} = 1 + (k\tau)^2\frac{\mathbf{D}}{uL} \qquad \text{for same } V \text{ or } \tau$$

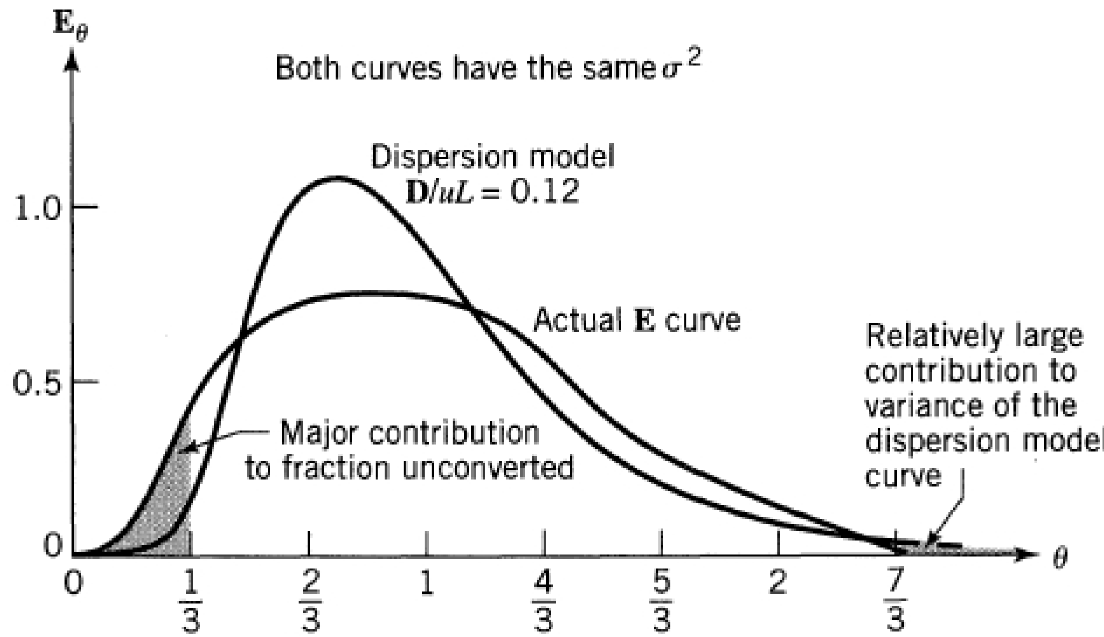
CONVERSION FROM THE DISPERSION MODEL

$$\frac{\mathbf{D}}{uL} = 0.12$$

Conversion in the real reactor is found from Fig. 13.19. Thus moving along the $\boldsymbol{k\tau}$ = (0.307)(15) = 4.6 line from C/C_o = 0.01 to D/uL = 0.12, we find that the fraction of reactant unconverted is approximately

$$\frac{C}{C_0} = 0.035, \qquad \text{or} \qquad \underline{\underline{3.5\%}}$$

Comments. Figure shows that except for a long tail the dispersion model curve has for the most part a greater central tendency than the actual curve. On the other hand, the actual curve has more short-lived material leaving the vessel



$$\left(\frac{C}{C_0}\right)_{\text{actual}} = 4.7\% > \left(\frac{C}{C_0}\right)_{\substack{\text{dispersion}\\ \text{model}}} = 3.5\%$$

13.3. RTD studies were carried out by Jagadeesh and Satyanarayana (IEC/PDD **11** 520, 1972) in a tubular reactor (L = 1.21 m, 35 mm ID). A squirt of NaCl solution (5 N) was rapidly injected at the reactor entrance, and mixing cup measurements were taken at the exit. From the following results calculate the vessel dispersion number; also the fraction of reactor volume taken up by the baffles.

t, sec	NaCl in sample
0–20	0
20–25	60
25–30	210
30–35	170
35–40	75
40–45	35
45–50	10
50–55	5
55–70	0

(v = 1300 ml/min)

13.3 From experiment:

t, sec	$\bar{t}$, sec	C
0-20	10	0
20-25	22.5	60
25-30	27.5	210
30-35	32.5	170
35-40	37.5	75
40-45	42.5	35
45-50	47.5	10
50-55	52.5	5
55-70	62.5	0

Calculate D/uL:

$\Sigma C = 565$

$\Sigma tC = 17687.5$

$\Sigma t^2 C = 573781.25$

$$\bar{t} = \frac{\Sigma tC}{\Sigma C} = 31.31 \text{ sec}$$

$$\sigma^2 = \frac{\Sigma t^2 C}{\Sigma C} - (\bar{t})^2 = 35.52 \text{ sec}^2$$

$$\frac{D}{uL} = \frac{\sigma^2}{2(\bar{t})^2} = 0.018 \leftarrow$$

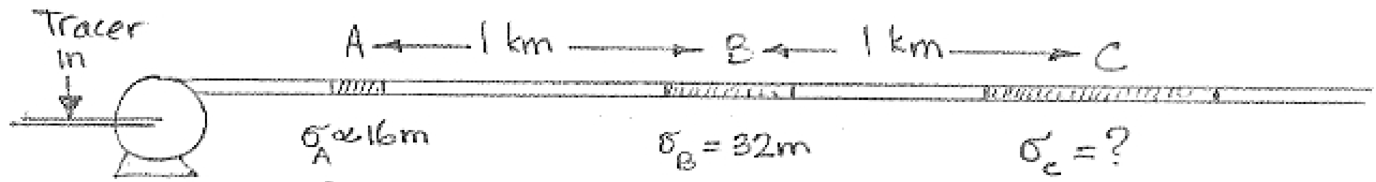
Now calculate the volume of the baffles

From mat. balance
$$\left.\begin{array}{l} V = (1.21\times10^2)(\pi\times1.75^2) = 1164 \text{ cm}^3 \\ v = 1300 \text{ cm}^3/\text{min} = 21.67 \text{ cm}^3/\text{s} \end{array}\right\} \bar{t} = \frac{1164}{21.67} = 53.72 \text{ sec}$$

$$\therefore \text{Volume of baffles} = \frac{53.72-31.31}{53.72}(1164) = 486 \text{ cm}^3 \leftarrow$$

13.5. An injected slug of tracer material flows with its carrier fluid down a long, straight pipe in dispersed plug flow. At point *A* in the pipe the spread of tracer is 16 m. At point *B*, 1 kilometer downstream from A, its spread is 32 m. What do you estimate its spread to be at a point *C*, which is 2 kilometers downstream from point A?

13.5



$\sigma_A \propto 16\text{m}$ $\qquad$ $\sigma_B = 32\text{m}$ $\qquad$ $\sigma_C = ?$

$\sigma_A^2 \propto 256$ $\qquad$ $\sigma_B^2 \propto 1024$ $\qquad$ $\sigma_C^2 \propto ?$

Let us solve this with the dispersion model. We could also do this with the tanks-in-series model.

Then from Eq 8 $\quad \sigma^2 = 2(DL/u^3)$

or $\sigma^2 \propto L$ ... or $(\text{spread})^2 \propto L$

So $\quad \sigma_C^2 - \sigma_B^2 = \sigma_B^2 - \sigma_A^2$

or $\quad \sigma_C^2 - 1024 = 1024 - 256$

or $\sigma_C^2 = 1792$ $\qquad$ or Width $= k\,\sigma_C = 42.3\text{m}$ ←

13.7. Kerosene and gasoline are pumped successively at 1.1 m/s through a 25.5-cm ID pipeline 1000 km long. Calculate the 5/95%–95/5% contaminated width at the exit of the pipe given that the kinematic viscosity for the 50/50% mixture is

$$\mu/\rho = 0.9 \times 10^{-6}\ \mathrm{m^2/s}$$

13.7 First find the σ^2 for this flow

$$Re = \frac{du\rho}{\mu} = (0.255)(1.1)/0.9\times10^{-6} = 3.12\times10^{5}$$

From Fig 15: $D/ud_t = 0.22$

From Eq 8: $\frac{D}{uL} = \left(\frac{D}{ud_t}\right)\left(\frac{d_t}{L}\right) = 0.22\left(\frac{0.255}{1000\,000}\right) = 5.61\times10^{-8}$

$$\frac{\sigma^2}{\bar{t}^2} = \sigma_\theta^2 = 2\left(\frac{D}{uL}\right) = 2\,(5.61\times10^{-8}) = 11.22\times10^{-8}$$

$$\therefore \sigma = (11.22\times10^{-8})^{1/2}\ \frac{1000\,000}{1.1} = 304.5\ \text{sec}$$

$\therefore$ the width at $1\sigma = (304.5)(1.1) = 335$ m

From 5/95 to 95/5 Fig 12 shows that this includes

$(1.655\times2)\,\sigma$ of width

$\therefore$ the 5/95 to 95/5% width is

$(335\text{m})(1.655\times2) = 1105$ m ←

↖ width of one σ^2

13.11. The kinetics of a homogeneous liquid reaction are studied in a flow reactor, and to approximate plug flow the 48-cm long reactor is packed with 5-mm nonporous pellets. If the conversion is 99% for a mean residence time of 1 sec, calculate the rate constant for the first-order reaction

(a) assuming that the liquid passes in plug flow through the reactor

(b) accounting for the deviation of the actual flow from plug flow

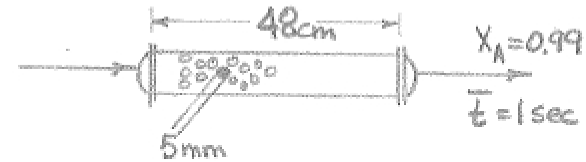
(c) What is the error in calculated k if deviation from plug flow is not considered?

Data: Bed voidage $\varepsilon = 0.4$

Particle Reynolds number $Re_p = 200$

13.11 First calculate k assuming plug flow, then account for dispersion

a) Find k assuming plug flow



For a 1st order reaction, $\varepsilon_A = 0$, we have

$$k\tau = \ln \frac{C_{A0}}{C_A} \quad \cdots \quad k_{plug} = \frac{1}{\tau} \ln \frac{C_{A0}}{C_A} = \frac{1}{(1\,sec)}(4.6) = 4.6\,sec^{-1}$$ a)

13.11 (continued) b) Find k accounting for deviation from plug flow according to the dispersion model

From the curve of Fig 17 we find for $Re_p = 200$ & $\epsilon = 0.4$

$$\frac{D\epsilon}{ud_p} = 1 \quad \text{... thus} \quad \frac{D}{ud_p} = 2.5$$

The size ratio of real to plug flow reactor, or what is equivalent, the ratio of the corresponding rate constants is found either from Fig 19 or from Eq 22 if the k ratio or the L ratio is close to unity. Use Eq. 22. Then

$$\frac{L}{L_p} = \frac{k_{true}}{k_{measured}} = 1 + k\tau\left(\frac{D}{uL}\right) = 1 + k\tau\left(\frac{D}{ud_p}\right)\left(\frac{d_p}{L}\right)$$

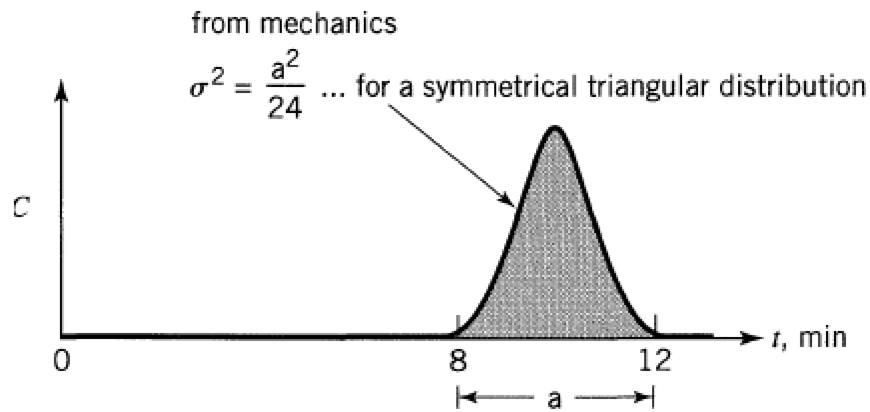
$$= 1 + 4.6(2.5)\left(\frac{5\,mm}{480\,mm}\right) = 1.1198$$

$$\therefore k_{true} = (4.6\,sec^{-1})(1.1198) = 5.15\,sec^{-1}$$ ← b)

Note: Direct use of Eq. 19 pg 314 (trial & error unfortunately) would give a more accurate answer.
Also, are you sure that $k_{true} > k_{plug}$? Convince yourself.

c) Error in assuming plug flow $= \left(\frac{5.15 - 4.60}{5.15}\right) \times 100 = 11\%$ underestimate ← c)

13.13. Calculations show that a plug flow reactor would give 99.9% conversion of reactant which is in aqueous solution. However, our rector has an RTD somewhat as shown in Fig. P13.13. If $C_{A0} = 1000$, what outlet concentration can we expect in our reactor if reaction is first order? From mechanics $\sigma^2 = a^2/24$ for a symmetrical triangle with base a, rotating about its center of gravity.



13.13 For plug flow with $X_A = 0.999$, or $C_A = 1.000$ and $C_{A0} = 1000$

$$\frac{C_A}{C_{A0}} = e^{-k\bar{t}} \quad \ldots \text{ or } k\bar{t} = \ln\frac{1000}{1} = 6.9078 \quad \ldots \text{ or } k = 0.69078$$

From Fig P13 $\quad \sigma^2 = \frac{4^2}{24} = \frac{2}{3}$

So from Eq 21

$$\frac{C_A}{C_{A0}} = \exp\left[(-k\bar{t}) + \frac{k^2\sigma^2}{2}\right] = \exp\left[-6.9078 + \frac{(0.69078)\frac{2}{3}}{2}\right]$$

or $\quad = 0.001172$

$\therefore C_A = 1.17$ ←