

5.3 Determination of Moments

Finally, we show how to determine the moments of an impulse response based on the example of the dispersion model.

For the dispersion model we have that $E_\theta(\theta)$ curve is given by eq (114). Then the moments of the E_θ curve are $\mu_n = \int_0^\infty \theta^n E_\theta(\theta) d\theta$.

Clearly, this would require some lengthy integrations and series manipulations. Instead, we can use the Laplace transform of the $E_\theta(\theta)$ curve $\bar{E}(s)$ given by eq (108) and recall that

$$\mu_n = (-1)^n \left. \frac{d^n \bar{E}}{ds^n} \right|_{s=0} \quad (137)$$

However, differentiating eq (108), although easier than integration and summation of equation (114), is also tedious. We can instead recognize that $\bar{E}(s)$ can be expanded in Taylor series about $s = 0$.

$$\bar{E}(s) = \sum_{n=0}^{\infty} \left. \frac{d^n \bar{E}(s)}{ds^n} \right|_{s=0} \frac{s^n}{n!} \quad (138)$$

If we introduce the moments this gives:

$$\bar{E}(s) = \sum_{n=0}^{\infty} (-1)^n \frac{\mu_n}{n!} s^n = \mu_0 - \mu_1 s + \frac{\mu_2}{2!} s^2 - \frac{\mu_3}{3!} s^3 \quad (139)$$

If we expand eq (108) for small s , and compare term by term with the above expansion given by eq (139), we can readily identify all the moments. Really, we are interested only in the second moment.

$$\bar{E}(s) = \frac{4\sqrt{1 + \frac{4s}{Pe}} e^{\frac{Pe}{2}} e^{-\frac{Pe}{2}\sqrt{1 + \frac{4s}{Pe}}}}{\left(1 + \sqrt{1 + \frac{4s}{Pe}}\right)^2 - \left(1 - \sqrt{1 + \frac{4s}{Pe}}\right)^2 e^{-Pe\sqrt{1 + \frac{4s}{Pe}}}} \quad (108)$$

First by Taylor series:

$$\begin{aligned}
\sqrt{1 + \frac{4s}{Pe}} &= 1 + \frac{2}{Pe}s - \frac{4}{Pe^2} \frac{s^2}{2} + O(s^3) \\
1 + \sqrt{1 + \frac{4s}{Pe}} &= 2 + \frac{2}{Pe}s - \frac{4}{Pe^2} \frac{s^2}{2} + O(s^3) \\
1 - \sqrt{1 + \frac{4s}{Pe}} &= -\frac{2}{Pe}s + \frac{4}{Pe^2} \frac{s^2}{2} + O(s^3) \\
\left(1 + \sqrt{1 + \frac{4s}{Pe}}\right)^2 &= \left(2 + \frac{2}{Pe}s\right)^2 - \frac{16}{Pe^2} \frac{s^2}{2} + O(s^3) \\
&= 4 + \frac{8}{Pe}s + \frac{4}{Pe^2}s^2 - \frac{8}{Pe^2}s^2 + O(s^3) \\
&= 4 + \frac{8}{Pe}s - \frac{4}{Pe^2}s^2 + O(s^3) \\
\left(1 - \sqrt{1 + \frac{4s}{Pe}}\right)^2 &= \frac{4}{Pe^2}s^2 + O(s^3)
\end{aligned}$$

$$\begin{aligned}
e^{-\frac{Pe}{2}\sqrt{1 + \frac{4s}{Pe}}} &= e^{-\frac{Pe}{2} - s + \frac{1}{Pe}s^2} = e^{-\frac{Pe}{2}} e^{-s} e^{\frac{s^2}{Pe}} \\
&= e^{-\frac{Pe}{2}} \left(1 - s + \frac{s^2}{2}\right) \left(1 + \frac{s^2}{Pe}\right) = e^{-\frac{Pe}{2}} \left(1 - s + \left(\frac{1}{2} + \frac{1}{Pe}\right)s^2\right) \\
&= e^{-\frac{Pe}{2}} \left(1 - s + \left(1 + \frac{2}{Pe}\right)\frac{s^2}{2}\right) + O(s^3) \\
e^{-Pe\sqrt{1 + \frac{4s}{Pe}}} &= e^{-Pe - 2s + \frac{2}{Pe}s^2} = e^{-Pe} e^{-2s} \left(1 - \frac{1}{Pe}s\right) \\
&= e^{-Pe} \left(1 - 2s \left(1 - \frac{1}{Pe}s\right) + \frac{4s^2}{2}\right) \\
&= e^{-Pe} \left(1 - 2s + 2\left(\frac{1}{Pe} + 1\right)s^2\right) + O(s^3)
\end{aligned}$$

Combining the above

$$\bar{E}(s) = \frac{4\left(1 + \frac{2}{Pe}s - \frac{2}{Pe^2}s^2\right) e^{\frac{Pe}{2}} e^{-\frac{Pe}{2}} \left(1 - s + \left(1 + \frac{2}{Pe}\right)\frac{s^2}{2}\right)}{4 + \frac{8}{Pe}s - \frac{4}{Pe^2}s^2 - \frac{4}{Pe^2}s^2 e^{-Pe} \left(1 - 2s + 2\left(\frac{1}{Pe} + 1\right)s^2\right)}$$

Keeping only the terms up to and including s^2 we get:

$$\bar{E}(s) = \frac{\left(1 + \frac{2}{Pe}s - \frac{2}{Pe^2}s^2\right)\left(1 - s + \left(\frac{1}{2} + \frac{1}{Pe}\right)s^2\right)}{1 + \frac{2}{Pe}s - \frac{1}{Pe^2}s^2(1 + e^{-Pe})}$$

$$\bar{E}(s) = \frac{1 - \left(1 - \frac{2}{Pe}\right)s + \left(\frac{1}{2} - \frac{1}{Pe} - \frac{2}{Pe^2}\right)s^2}{1 + \frac{2}{Pe}s - \frac{1}{Pe^2}(1 + e^{-Pe})s^2}$$

Expand the denominator by binomial theorem

$$\frac{1}{1-x} = 1 + x + x^2 + \dots \quad \frac{1}{1+x} = 1 - x + x^2 \dots$$

$$\bar{E}(s) = \left[1 - \left(1 - \frac{2}{Pe}\right)s + \left(\frac{1}{2} - \frac{1}{Pe} - \frac{2}{Pe^2}\right)s^2\right]$$

$$\left[1 - \frac{2}{Pe}s + \frac{1}{Pe^2}(1 + e^{-Pe})s^2 + \left(\frac{2}{Pe}s - \frac{1}{Pe^2}(1 + e^{-Pe})s^2\right)^2 \dots\right]$$

$$\bar{E}(s) = 1 - s + \left[\frac{1}{2} + \frac{1}{Pe} - \frac{1}{Pe^2}(1 - e^{-Pe})\right]s^2$$

By comparison with the $\bar{E}(s)$ expansion in its moments we identify:

$$\bar{E}(s) = \mu_0 - \mu_1 s + \frac{\mu_2}{2} s^2$$

$$\mu_0 = 1$$

$$\mu_1 = 1$$

$$\mu_2 = 1 + \frac{2}{Pe} - \frac{2}{Pe^2}(1 - e^{-Pe})$$

$$\sigma_D^2 = \mu_2 - \mu_1^2 = \frac{2}{Pe} - \frac{2}{Pe^2}(1 - e^{-Pe})$$

This is eq (118) in the notes.

5.4 Application of Perturbation Methods to the Dispersion Model for Tubular Reactors

The axial dispersion model for tubular reactors at steady state can be described by the following equations:

$$\frac{1}{Pe} \frac{d^2c}{dz^2} - \frac{dc}{dz} - R_n c^n = 0 \quad (1)$$

$$z = 0 \quad 1 = c - \frac{1}{Pe} \frac{dc}{dz} \quad (2)$$

$$z = 1 \quad \frac{dc}{dz} = 0 \quad (3)$$

where

$c = \frac{C_A}{C_{A_0}}$ = is the dimensionless reactant concentration

$z = \frac{Z}{L}$ = is the dimensionless distance along the reactor measured from the entrance

$Pe = \frac{UL}{D}$ = is the axial dispersion Peclet number

L = total reactor length

$U = \frac{Q}{A}$ = is the linear mean velocity in the reactor (superficial velocity in packed beds)

Q = volumetric flow rate through the reactor

A = cross-sectional area of the reactor

D = dispersion coefficient in the reactor (defined per total cross-sectional area in packed beds).

Note: If D is defined per cross-sectional area unoccupied by solids in packed beds then $D\varepsilon$ will appear in the Pe instead of D . ε is bed porosity.

$R_n = k \tau C_{A_0}^{n-1}$ - dimensionless reaction rate group (Damkohler number).

Note: In packed beds this implies that the rate was defined per unit reactor volume.

$\tau = \frac{L}{U}$ - reactor space time (space time based on superficial velocity).

Equations (1), (2) and (3) describe the behavior of tubular reactors and catalytic packed bed reactors under isothermal conditions, at steady state for an n-th order irreversible, single reaction. Application of these equations to packed bed reactors assumes that external and internal mass transfer limitations (i.e mass transfer from fluid to pellets and inside the pellets) are nonexistent or have been properly accounted for in the overall rate expression.

Solutions to eqs (1-3) for an n-th order reaction ($(n \neq 0, n \neq 1)$) can be obtained only by numerical means. However, the problem is a difficult nonlinear two-point boundary value problem. [See: P.H. McGinnis, Chem. Engr. Progr. Symp. Ser. No 55 Vol 61, p 2 (1968), Lee, E.S., AIChE J., 14(3), 490 (1968), Lee, E.S., Quasilinearization (1969)].

Since in practical applications Pe numbers are quite large ($Pe \geq 5$), and often $Pe = O(10^2)$, it is of interest to develop approximate solutions to the dispersion model for large Pe numbers. Remember, large Pe ($\bar{\sigma}^2 \approx \frac{2}{Pe}$) means small variance and, hence, small variation from plug flow, and is exactly the condition under which the dispersion model is applicable. Such approximate solutions can allow us to estimate well the departure from plug flow performance and will save a lot of effort which is necessary for numerical evaluations of the model.

We are interested in large Pe , then $\frac{1}{Pe} = \varepsilon$ and ε is very small ($\varepsilon \ll 1$).

Equations (1-3) can be written as:

$$\varepsilon \frac{d^2c}{dz^2} - \frac{dc}{dz} - R_n c^n = 0 \quad (1')$$

$$z = 0; \quad 1 = c - \varepsilon \frac{dc}{dz} \quad (2')$$

$$z = 1; \quad \frac{dc}{dz} = 0 \quad (3')$$

A. Outer Solution

Let us assume that a solution of the following form exists:

$$c = F(z) = \sum_{n=0}^{\infty} \varepsilon^n F_n(z) = F_0(z) + \varepsilon F_1(z) + \varepsilon^2 F_2(z) + \dots \quad (4)$$

If we can find such a solution then, due to the fact that $\varepsilon \ll 1$, we can hope that the first few

terms will be adequate to describe our solution. [Strictly speaking this would be true only if the series given by Eq (4) converges fast. Remarkably, a good approximation to the solution is obtained even for divergent series! (For this and further details, see Nayfeh, A.H., Perturbation Methods, Wiley, 1973)

We do need in Eq (1') an expression for c^n . However, as we are going to keep only the first few terms of the series (4) raising it to an n-th power is not that difficult.

$$\begin{aligned}
 c^n &= \left[F_0 + \varepsilon F_1 + \varepsilon^2 F_2 + \varepsilon^3 F_3 + \dots \right] \\
 &= F_0^n + \varepsilon n F_0^{n-1} F_1 + \varepsilon^2 \left[\frac{1}{2} n(n-1) F_0^{n-2} F_1^2 + n F_0^{n-1} F_2 \right] \\
 &+ \varepsilon^3 \left[\frac{1}{6} n(n-1)(n-2) F_0^{n-3} F_1^3 + n(n-1) F_0^{n-2} F_1 F_2 + n F_0^{n-1} F_3 \right] + O(\varepsilon^4) \quad (5)
 \end{aligned}$$

Differentiate eq (4) once and twice and substitute both derivatives and eq (5) into eq (1'):

$$\begin{aligned}
 \varepsilon \left[\frac{d^2 F_0}{dz^2} + \varepsilon \frac{d^2 F_1}{dz^2} + \varepsilon^2 \frac{d^2 F_2}{dz^2} + \varepsilon^3 \frac{d^2 F_3}{dz^2} + \dots \right] - \left[\frac{dF_0}{dz} + \varepsilon \frac{dF_1}{dz} + \varepsilon^2 \frac{dF_2}{dz} + \dots \right] \\
 - R_n \left[F_0^n + \varepsilon n F_0^{n-1} F_1 + \varepsilon^2 \left(\frac{1}{2} n(n-1) F_0^{n-2} F_1^2 + n F_0^{n-1} F_2 + \dots \right) \right] = 0 \quad (6)
 \end{aligned}$$

Substitute also eq (4) and its derivative into eq (2'):

At $z = 0$

$$1 = F_0 + \varepsilon F_1 + \varepsilon^2 F_2 + \dots - \varepsilon \left[\frac{dF_0}{dz} + \varepsilon \frac{dF_1}{dz} + \varepsilon^2 \frac{dF_2}{dz} + \dots \right] \quad (7)$$

Group now the terms with equal powers of ε in eq (6) and eq (7) together, and require that they ?? to zero:

$$\varepsilon^0: \quad \frac{dF_0}{dz} + R_n F_0^n = 0 \quad (8)$$

$$z = 0, \quad F_0 = 1 \quad (8a)$$

$$\varepsilon^1: \quad \frac{dF_1}{dz} + R_n n F_0^{n-1} F_1 = \frac{d^2 F_0}{dz^2} \quad (9)$$

$$z = 0, \quad F_1 = \frac{dF_0}{dz} \quad (9a)$$

$$\varepsilon^2 : \frac{dF_2}{dz} + R_n n F_0^{n-1} F_2 = \frac{d^2 F_1}{dz^2} - \frac{R_n}{2} n(n-1) F_0^{n-2} F_1^2 \quad (10)$$

$$z = 0, \quad F_2 = \frac{dF_1}{dz} \quad (10a)$$

ε^3 : etc.

Notice at this point that the differential equations (D.E.'s) (eq 8-11, etc.) are first order D.E.'s, while the original equation (1') was second order. Eq (8) is first order for F_0 . Once eq (8) is solved and F_0 determined, the right hand side of eq (9) is known and the left hand side is a first order D.E. for F_1 , etc. Thus, we can successively determine all the F_i 's. However, because all of these are first order equations, we can only satisfy one of the original boundary conditions. If we tried to satisfy the boundary condition at the reactor exit, given by eq (3'), we would have that $\frac{dF_i}{dz} = 0$ at $z = 1$ for all i , implying that all F_i 's are constant due to the form of D.E.'s (eq 8-11). Thus, we would not be able to get any information. This indicates that we have to satisfy the condition at the reactor entrance given by eq (2') as indicated by eq (7). This results in a set of conditions given by eqs(8a - 10a).

The solution of eq (8) with I.C. (initial condition) (8a) is readily obtained:

$$F_0(z) = [1 + R_n(n-1)z]^{\frac{1}{1-n}} \quad (11)$$

Verify that this indeed is a concentration profile in a plug flow reactor for an n-th order reaction!

Differentiate eq (11) twice, substitute into eq (9) and solve eq (9) with I.C. eq (9a):

$$F_1(z) = R_n [1 + R_n(n-1)z]^{\frac{n}{1-n}} \left\{ \ell n [1 + R_n(n-1)z]^{\frac{n}{1-n}} - 1 \right\} \quad (12)$$

Differentiate eq (12) twice and substitute together with eq (12) and eq (11) on the right hand side of eq (10). Solve eq (10) with I.C. eq (10a):

$$F_2(z) = \frac{R_n^2 n}{n-1} \left\{ \frac{1-3n}{2} u^{\frac{n}{1-n}} + u^{\frac{2n-1}{1-n}} \left[\frac{n^2}{2(n-1)} \ell n^2 u - 2n \ell n u + \frac{7n-5}{2} \right] \right\} \quad (13)$$

$$\text{where } u = 1 + R_n (n - 1) z \quad (14)$$

Now we have found F_0, F_1, F_2 and we could write our solution as $F_0 + \varepsilon F_1 + \varepsilon^2 F_2$. However, we realize that such a solution only satisfies the B.C. eq (2') at the reactor inlet and does not satisfy condition eq (3') at the reactor outlet. Ultimately we are interested not in the concentration profile along the reactor but in its value (concentration value) at the reactor exit. Since the B.C. at the exit is not satisfied we have a lot of reasons to doubt the validity of our solution at the exit and must find ways of improving it. In perturbation theory the solution given by eq (4) is called an "outer" solution

$$c^0(z) = F_0(z) + \varepsilon F_1(z) + \varepsilon^2 F_2(z) + \varepsilon^3 F_3(z) + \dots c^0 - \text{outer solution} \quad (15)$$

B. Inner Solution

We have seen before that the reason why the "outer" solution cannot satisfy the B.C. at the exit ($z=1$) given by eq (3') is that all the terms F_i 's of the "outer" solution were obtained from first order D.E.s. Now we must expand ("stretch") our coordinate system in such a way that we can take a "closer" look at what happens in the very vicinity (in the "boundary layer") next to $z = 1$.

Let

$$\eta = \frac{1-z}{\varepsilon^\alpha} \quad \alpha > 0 \quad (16)$$

Since $\varepsilon \ll 1$ eq (16) gives reasonably large values of η for z very close to 1. Thus, we are stretching the coordinate system near $z = 1$.

By chain rule we have:

$$\frac{dc}{dz} = \frac{dc}{d\eta} \frac{d\eta}{dz} = -\frac{1}{\varepsilon^\alpha} \frac{dc}{d\eta} \quad (17)$$

$$\frac{d^2c}{dz^2} = \frac{1}{\varepsilon^{2\alpha}} \frac{d^2c}{d\eta^2} \quad (18)$$

Substituting eq (17) and eq (18) into eq (1') we get:

$$\varepsilon^{1-2\alpha} \frac{d^2c}{d\eta^2} + \varepsilon^{-\alpha} \frac{dc}{d\eta} - R_n c^n = 0 \quad (19)$$

We require now that the derivatives should stand by equal powers of ε i.e $1 - 2\alpha = -\alpha$ and plus that we will get a 2nd order D.E. This gives $\alpha = 1$. Hence,

$$\eta = \frac{1-z}{\varepsilon} \quad (20)$$

and

$$\frac{1}{\varepsilon} \frac{d^2 c}{d\eta^2} + \frac{1}{\varepsilon} \frac{dc}{d\eta} - R_n c^n = 0$$

becomes:

$$\frac{d^2 c}{d\eta^2} + \frac{dc}{d\eta} - \varepsilon R_n c^n = 0 \quad (21)$$

We assume now that the solution to eq (21) is the "inner" solution c^i and that it can be represented by a power series in ε :

$$c^i = \sum_{n=0}^{\infty} \varepsilon^n c_n^i = c_0^i + \varepsilon c_1^i + \varepsilon^2 c_2^i + \varepsilon^3 c_3^i + \dots \quad (22)$$

Remember again that we are developing the inner solution in the very vicinity of $z = 1$, so the "outer" solution in that region is so close to 1 that it can be represented by a Taylor series expansion around $z = 1$ i.e $\eta = 0$

$$\begin{aligned} c^o(z) = & F_0(1) + F_0'(1)(z-1) + \frac{F_0''(1)}{2}(z-1)^2 + \dots \\ & + \varepsilon \left[F_1(1) + F_1'(1)(z-1) + \frac{F_1''(1)}{2}(z-1)^2 + \dots \right] \\ & + \varepsilon^2 \left[F_2(1) + F_2'(1)(z-1) + \frac{F_2''(1)}{2}(z-1)^2 + \dots \right] + O(\varepsilon^3) \end{aligned} \quad (23)$$

where $F_i' = \frac{dF_i}{dz}$

Now from eq (20)

$$z-1 = -\varepsilon\eta \quad ; \quad (z-1)^2 = \varepsilon^2\eta^2 \quad (24)$$

Substitute eq (24) into eq (23) and group together the terms with the same powers of ε :

$$\begin{array}{ccc} c_1^{oi} & c_1^{oi} & c_2^{oi} \\ \downarrow & \downarrow & \downarrow \\ c^o(z) = c^{oi}(\eta) = & F_0(1) + \varepsilon[F_1(1) - F_0'(1)\eta] + \varepsilon^2 \left[F_2(1) - F_1'(1)\eta + \frac{1}{2} F_0''(1)\eta^2 \right] \end{array} \quad (25)$$

This is often called an "inner-outer expansion", c^{oi} , i.e the expansion of the outer solution in the inner (boundary) layer.

Now the inner solution given by the series represented by eq (22) can be represented by the sum of two series: one from the inner-outer expansion and the other from the true inner solution undetectable by the outer one.

$$\begin{aligned} c^i(\eta) &= \sum_{n=0}^{\infty} \varepsilon^n c_n^i = \sum_{n=0}^{\infty} \varepsilon^n [c_n^{oi}(\eta) + G_n(\eta)] \\ &= F_0(1) + G_0(\eta) + \varepsilon [F_1(1) - F_0'(1)\eta + G_1(\eta)] \\ &\quad + \varepsilon^2 \left[F_2(1) - F_1'(1)\eta + \frac{1}{2} F_0''(1)\eta^2 + G_2(\eta) \right] + O(\varepsilon^3) \end{aligned} \quad (26)$$

Differentiate eq (26) once and twice, raise it to the n-th power and substitute everything into eq (21) and require that the sum of the terms with equal powers of ε be zero:

$$\frac{d^2 G_0}{d\eta^2} + \frac{dG_0}{d\eta} = 0 \quad (27)$$

$$\frac{d^2 G_1}{d\eta^2} + \frac{dG_1}{d\eta} = F_0'(1) + R_n [F_0(1) + G_0]^n \quad (28)$$

$$\frac{d^2 G_2}{d\eta^2} + \frac{dG_2}{d\eta} = -F_0''(1) + F_1'(1) - F_0''(1)\eta + nR_n [F_0(1) + G_0]^{n-1} [F_1(1) - F_0'(1)\eta + G_1] \quad (29)$$

This is a set of 2nd order D.E.s for the G_i 's. When the G_i 's are determined successively the right hand side of the above equations is always known. For 2nd order equations we need 2 B.C.s.

One B.C. is obtained from eq (3') i.e.

$$\frac{dc^i}{d\eta} = 0 \text{ at } \eta = 0 \quad (30)$$

which leads to

$$\frac{dG_0}{d\eta} = 0 \text{ at } \eta = 0 \quad (27a)$$

$$\frac{dG_1}{d\eta} = F_0'(1) \text{ at } \eta = 0 \quad (28a)$$

$$\frac{dG_2}{d\eta} = F_1'(1) \text{ at } \eta = 0 \quad (29a)$$

Remember that away from the boundary at $z = 1$ we do not sense or detect the G_i 's as F_i 's nicely satisfy the B.C. at $z = 0$ and are probably a good representation of the actual solution for $1 > z \geq 0$ but not at $z = 1$. This implies that as we move away from $z = 1$, i.e as η increases, all G_i 's go to zero. This is the 2nd boundary condition:

$$\eta \rightarrow \infty \quad G_i \rightarrow 0 \quad \text{for } i = 0, 1, 2, 3, \dots \quad (27b, 28b, 29b)$$

The solution of eq (27) with eq (27a) is

$$G_0(\eta) = 0 \quad (31)$$

The solution of eq (28) with eq (28a) and eq (28b) is:

$$G_1(\eta) = R_n \left[1 + R_n(n-1) \right]^{\frac{n}{1-n}} e^{-\eta} \quad (32)$$

The solution of eq (29) with eq (29a) and eq (29b) is:

$$G_2(\eta) = -R_n^2 n \left[1 + R_n(n-1) \right]^{\frac{2n-1}{1-n}} \left\{ 3 + \eta + \ell n \left[1 + R_n(n-1) \right]^{\frac{n}{1-n}} \right\} e^{-\eta} \quad (33)$$

If we substitute eq (20) into eqs (31-33) we will get G_i 's in terms of z .

The concentration profile close to the reactor exit is given by equation (26) (where η can be substituted in terms of z). We are especially interested in the outflow concentration at the exit, i.e at $z = 1$, $\eta = 0$. Since $\varepsilon = 1/Pe$ we get:

$$\begin{aligned} c_{exit} = 1 - x_A &= F_0(z=1) + \frac{1}{Pe} [F_1(z=1) + G_1(\eta=0)] \\ &+ \frac{1}{Pe^2} [F_2(z=1) + G_2(\eta=0)] + O\left(\frac{1}{Pe^3}\right) \end{aligned} \quad (34)$$

Let $\rho_n = [1 + (n-1)R_n]$

$$c_{exit} = 1 - x_A = \rho_n^{\frac{1}{1-n}} + \frac{1}{Pe} \left\{ R_n \rho_n^{\frac{n}{1-n}} \ell n \rho_n^{\frac{n}{n-1}} \right\} + \quad (35)$$

$$\frac{1}{Pe^2} \left\{ \frac{1-3n}{2} \rho_n^{\frac{n}{1-n}} + \rho_n^{\frac{2n-1}{1-n}} \left[\frac{n-1}{2} \left(\frac{n}{1-n} \ell n \rho_n + 1 \right)^2 + 1 \right] \right\} + O\left(\frac{1}{Pe^3}\right) \quad (36)$$

After some additional algebra:

$$c_{exit} = \rho_n^{\frac{1}{1-n}} \left\{ 1 + \frac{1}{Pe} \left[\frac{R_n n}{n-1} \frac{\ell n \rho_n}{\rho_n} \right] + \frac{1}{Pe^2} \frac{R_n^2 n}{2\rho_n^2} \left[\left(\frac{n}{1-n} \ell n \rho_n + 1 \right)^2 - \rho_n - 2(1+nR_n) \right] + O\left(\frac{1}{Pe^3}\right) \right\} \quad (37)$$

where $R_n = k\bar{t}C_0^{n-1}$ and $\rho_n = 1 + (n-1)R_n$

Notice that the leading term is a solution for the plug flow reactor, thus as $Pe \rightarrow \infty$, plug flow occurs. Straightforward algebra (although admittedly tedious), would produce higher order terms $\frac{1}{Pe^3}$, etc. However, there is no need for that. Experience from fluid mechanics, heat transfer, solid mechanics and reaction engineering shows that perturbation series are often not uniformly convergent and that 2nd order perturbation solutions, as the one given by Eq (37), or even first order perturbation solutions (dropping the term with $\frac{1}{Pe^2}$) provide satisfactory answers which are often better at lower Pe than higher order solutions.

The perturbation solution for the dispersion model has been worked out in detail by Burghardt and Zaslowski, Chem. Eng. Sci., 23, 575-591 (1968), but their second order term contains an error due to improper matching of perturbation solutions. See their paper for comparison of approximate perturbation solutions with numerical solutions.

Let us now examine the conditions under which the deviation of the tubular reactor length from the length required by plug flow is less than 5%. In other words we are looking for the conditions under which the tubular reactor, the length of which is within 5% of the PFR, would give the same conversion as the PFR.

$$\frac{L - L_p}{L} = 1 - \frac{L_p}{L} \leq 0.05 \quad (38)$$

For a fixed given flow rate

$$1 - \frac{L_p}{L} = 1 - \frac{\tau_p}{\tau} = 1 - \frac{(R_n)_p}{R_n} = 1 - \frac{(\rho_n)_p - 1}{\rho_n - 1}$$

$$1 - \frac{L_p}{L} = \frac{\rho_n - \rho_{np}}{\rho_n - 1} = \frac{1 - \frac{\rho_{np}}{\rho_n}}{1 - \frac{1}{\rho_n}} \leq 0.05 \quad (39)$$

$$1 - \frac{\rho_{np}}{\rho_n} \leq 0.05 \left(1 - \frac{1}{\rho_n} \right) \quad (40)$$

In the plug flow reactor we have

$$1 - x_{Ap} = \rho_{np}^{1-n} \quad (41)$$

For the axial dispersion model we will use the first order perturbation solution:

$$1 - x_A = \rho_n^{1-n} \left\{ 1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \right\} = 1 - x_{Ap} \quad (42)$$

Therefore:

$$\left(\frac{\rho_{np}}{\rho_n} \right)^{1-n} = 1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n}$$

$$\frac{\rho_{np}}{\rho_n} = \left[1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \right]^{1-n} \quad (43)$$

Then using eq. 40) we get

$$1 - \frac{\rho_{np}}{\rho_n} = 1 - \left[1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \right]^{1-n} \leq 0.05 \left(1 - \frac{1}{\rho_n} \right) \quad (44)$$

$$\left[1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \right]^{1-n} \geq 1 - 0.05 \left(1 - \frac{1}{\rho_n} \right) \quad (45)$$

For $n > 1$

$$\left[1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \right] \leq \left[1 - 0.05 \left(1 - \frac{1}{\rho_n} \right) \right]^{\frac{1}{1-n}} \approx 1 - \frac{0.05 \left(1 - \frac{1}{\rho_n} \right)}{1-n} \quad (46a)$$

For $0 < n < 1$

$$\left[1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \right] \geq \left[1 - 0.05 \left(1 - \frac{1}{\rho_n} \right) \right]^{\frac{1}{1-n}} \approx 1 - \frac{0.05 \left(1 - \frac{1}{\rho_n} \right)}{1-n} \quad (46b)$$

For $n > 1$ (From eq. (46a))

$$\frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \leq \frac{0.05}{n-1} \left(1 - \frac{1}{\rho_n} \right) \quad (47a)$$

For $0 < n < 1$ (From eq. (46b))

$$\frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \geq \frac{0.05}{n-1} \left(1 - \frac{1}{\rho_n} \right) \quad (47b)$$

Multiply (47a) and (47b) on both sides by $(n-1)$. In (47a) $n - 1 > 0$ and the inequality is preserved, in (47b) $n - 1 < 0$ and when multiplying with the negative number the inequality sign is reversed. Thus, for all n , $n \neq 1$.

$$\frac{1}{Pe} R_n n \frac{\ln \rho_n}{\rho_n} \leq 0.05 \left(1 - \frac{1}{\rho_n} \right) \quad (48)$$

which gives

$$Pe \geq \frac{20n}{n-1} \ln \rho_n \quad (49)$$

Thus, when Pe number satisfies inequality (49) the difference in the length of a tubular reactor which can be described by the axial dispersion model and plug flow reactor, both giving the same conversion, will be within 5%.

Eq. (49) may be written as:

$$Pe \geq 20n \ln \rho_n^{\frac{1}{n-1}} \quad (50)$$

In the last approximation (using $1 - x_A \approx \rho_n^{\frac{1}{1-n}}$) we get:

$$Pe \geq 20n \ln \left(\frac{1}{1-x_A} \right) \quad (51)$$

Formula (51) clearly shows that the magnitude of the Pe number which will guarantee small discrepancies between tubular reactors and plug flow depends not only on the reaction order but also on conversion!

For packed beds

$$Bo = \frac{Ud_p}{D} \quad (52)$$

Equations (49) and (51) become:

$$\frac{L}{d_p} \geq \frac{20n}{Bo(n-1)} \ln \rho_n \quad (53)$$

$$\frac{L}{d_p} \geq \frac{20n}{Bo} \ln \left(\frac{1}{1-x_A} \right) \quad (54)$$

How long the reactor should be with respect to the size of packing in order to eliminate dispersion effects is dependent on Bo (Bodenstein) number, reaction order, n , and dimensionless reaction number R_n (Damkohler number) or conversion.

Similarly one may develop a criterion that will show how large Pe should be in order to guarantee that the exit concentration from the tubular reactor will be within 5% of the one predicted by plug flow design.

$$\frac{c_{exit} - c_p}{c_p} \leq 0.05 \quad (55)$$

$$\frac{\rho_n^{\frac{1}{1-n}} \left\{ 1 + \frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \right\} - \rho_n^{\frac{1}{1-n}}}{\rho_n^{\frac{1}{1-n}}} \leq 0.05 \quad (56)$$

$$\frac{1}{Pe} \frac{R_n n}{n-1} \frac{\ln \rho_n}{\rho_n} \leq 0.05$$

$$Pe \geq \frac{20 n R_n}{(n-1) \rho_n} \ln \rho_n \quad (57)$$

The reactor length to particle diameter ratio in packed beds that will guarantee maximum 5% deviation in exit concentration based on plug flow design is:

$$\frac{L}{d_p} \geq \frac{20n R_n}{B_o(n-1)\rho_n} \ell n \rho_n \quad (58)$$

For reference and industrial usage of the above see:

1. D.E. Mears, Chem. Eng. Sci., 26, 1361 (1971)
2. D.E. Mears, Ind. Eng. Chem. Fundamentals, 15, 20 (1976)