Multi-mode Low-dimensional Models for Real Time Simulation of Catalytic and Multiphase Reactors

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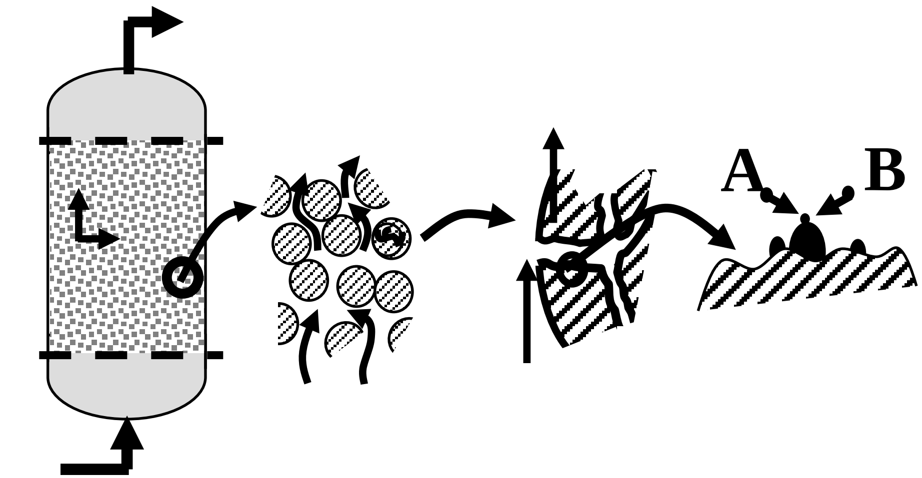
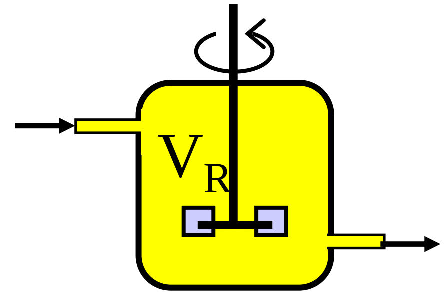
Models of Homogeneous & Catalytic Reactors

Packed-Bed Catalytic Reactor



L(m)	***1***	***10^{-3}***	***10^{-6}***	***10^{-9}***
t(s)	***10-10^{3}***	***1***	***10^{-5}***	***10^{-7}***

Homogeneous Tank Reactor



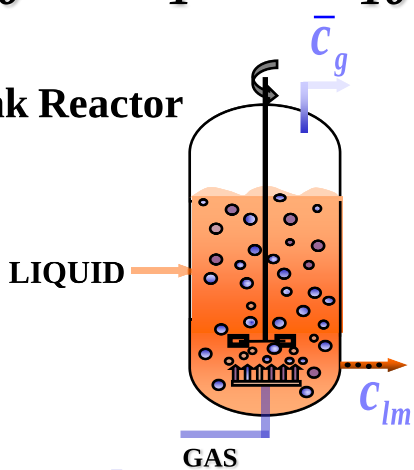
Detailed Model:

$$\mathbf{C}\frac{\partial \mathbf{u}}{\partial t} = \mathbf{F}(\mathbf{x},\mathbf{u},\nabla\mathbf{u},\nabla^2\mathbf{u},\mathbf{p}); \quad \mathbf{x} \text{ in } \Omega, t > 0$$

$$\text{I.C.}: \Gamma(\mathbf{x},\mathbf{u},\nabla\mathbf{u},\mathbf{p}) = 0 \text{ in } \Omega, t = 0$$

$$\text{B.C.}: \text{B}(\mathbf{x},\mathbf{u},\nabla\mathbf{u},\mathbf{p}) = 0 \text{ in } \partial\Omega, t > 0$$

Gas-Liquid Tank Reactor



Ideal CSTR Model:

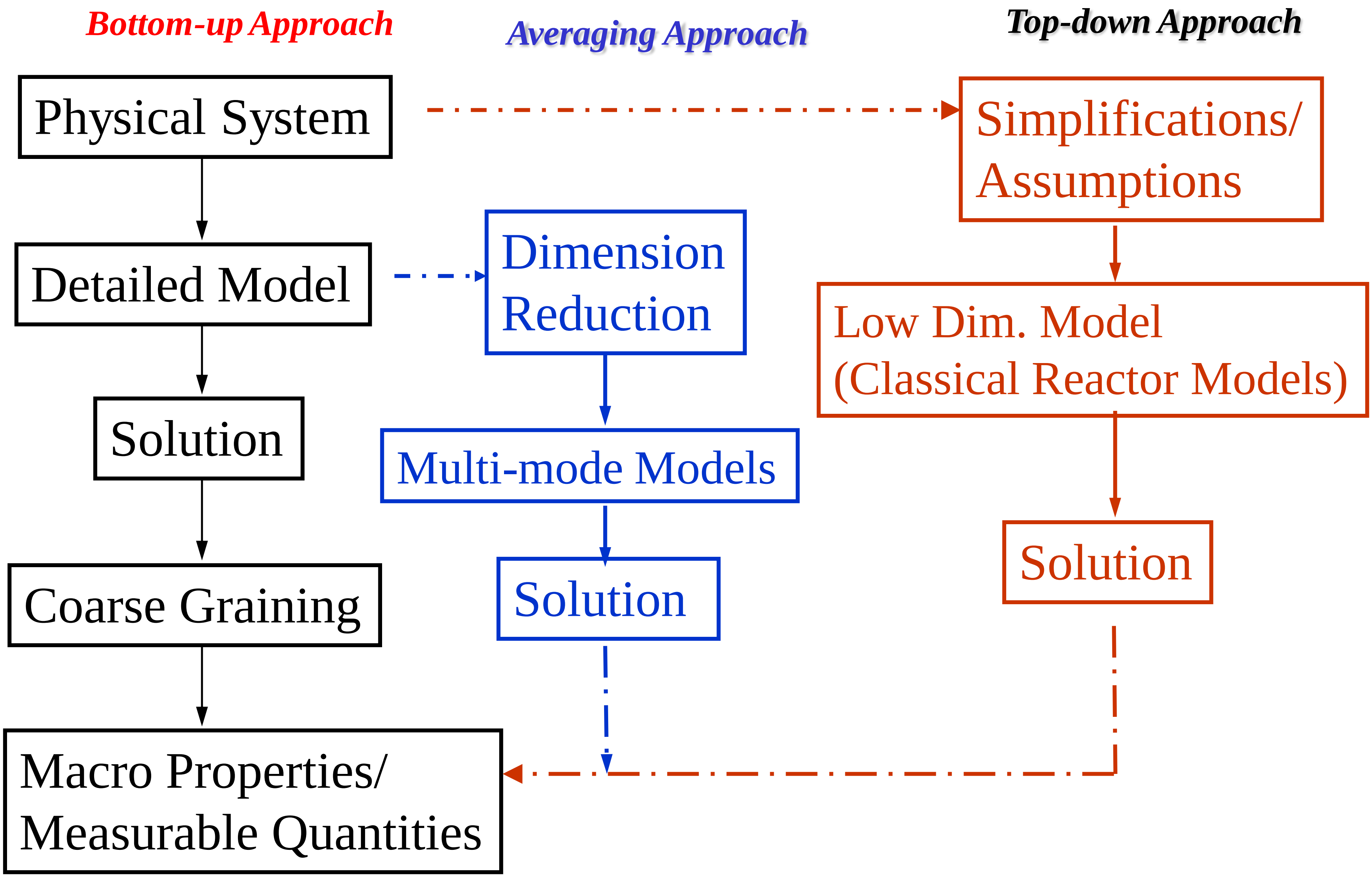
(Bodenstein & Wolgast, 1908)

$$\frac{d\bar{C}}{dt} = \frac{1}{\tau}(C_{in} - \bar{C}) - R(\bar{C}); \quad t > 0$$

$$I.C.: \bar{C}(t=0) = \bar{C}_0$$

<u>Objective</u>: Develop accurate low-dimensional models (in terms of average/measurable quantities) ***without losing any important physics at small length/time scales*****.**

Approaches to Averaging/Dimension Reduction



Averaging/Dimension Reduction Techniques

(i) Method of Multiple Scales
(multiple length/time scales involving a small parameter)

(ii) The Krylov-Bogoliubov Technique
(averaging method for periodically forced systems)

(iii) Method of Moments (Aris, 1956; Brenner,1994)
(uses spatial moments/theory of Brownian motion)

(iv) Volume Averaging using Divergence/Transport Theorems
(Slattery,1969; Whitaker,1967; Anderson & Jackson,1967)

(v) Long-Wave (Lubrication) Method
(used extensively in the fluid mechanics literature)

(vi) Center & Invariant Manifold Theories
(Carr, 1981; Roberts, 1990; Balakotaiah & Chang, 1995)
Elimination of slave modes by asymptotic expansion around a steady-state (or trivial state)

Plus

Many others (e.g. Reynolds' averaging, Renormalization, POD, Inertial Manifolds, etc.)

New Spatial Averaging Method

Liapunov-Schmidt Technique
(Balakotaiah & Chang, 2003; Balakotaiah &Chakraborty, 2002)
perturbation expansion around zero eigenvalue (s)

The Liapunov-Schmidt (L-S) Method for Local Bifurcations

Golubitsky and Schaeffer (1985); Balakotaiah et. al (1985)

$$\mathbf{F}(\mathbf{u},\lambda):\mathbf{R}^{\mathbf{n}}\times\mathbf{R}^{p}\rightarrow\mathbf{R}^{\mathbf{n}}$$

$$\mathbf{F}(\mathbf{0},\mathbf{0})=\mathbf{0}$$

$$\mathbf{L}=D_u\mathbf{F}(\mathbf{0},\mathbf{0})$$

$$\dim(\ker\mathbf{L})=1$$

$$\mathbf{L}\mathbf{y}_{\mathbf{0}}=\mathbf{0}$$

$$\mathbf{L}^{*}\mathbf{v}_{\mathbf{0}}=\mathbf{0};\ \langle\mathbf{y}_{\mathbf{0}},\mathbf{v}_{\mathbf{0}}\rangle=1$$

$$\mathbf{u}=x\,\mathbf{y}_{\mathbf{0}}+\mathbf{w}$$

$$\mathbf{F}=\mathbf{0}\ \Rightarrow\begin{cases}\mathbf{E}\mathbf{F}(x\,\mathbf{y}_{\mathbf{0}}+\mathbf{w},\lambda)=\mathbf{0} & ;\Rightarrow\mathbf{w}=\mathbf{W}(x\,\mathbf{y}_{\mathbf{0}},\lambda)\\(\mathbf{I}-\mathbf{E})\mathbf{F}(x\,\mathbf{y}_{\mathbf{0}}+\mathbf{w},\lambda)=\mathbf{0}\end{cases}$$

Branching Equation:

$$g(x,\lambda)=\langle\mathbf{v}_{\mathbf{0}},(\mathbf{I}-\mathbf{E})\mathbf{F}(x\,\mathbf{y}_{\mathbf{0}}+\mathbf{W}(x\,\mathbf{y}_{\mathbf{0}},\lambda),\lambda)\rangle=0$$

The Liapunov-Schmidt (L-S) Method for Spatial Averaging of Convection-Diffusion-Reaction (CDR) Models

Balakotaiah and Chakraborty; Chem. Eng. Sci.,57,2545-2564 (2002)
Balakotaiah & Chang; SIAM J. Appl. Math., 63,1231-1258 (2003)

Observations:

- Diffusion is dominant at small length scales
- Local Diffusion operator of the CDR equation (with a periodic/ Neumann & Robin BCs has a zero eigenvalue with a constant eigenfunction.
- Spatial degrees of freedom (small length scales) can be eliminated near the zero eigenvalue (small parameter).

Procedure:

- Write the detailed (microscopic) model
- Identify the smallest length/time scale (expressed in terms of a small parameter, say p)
- Express all other parameters (λ_i) as $\lambda_i = \alpha_i p^n$, where α_i is O(1) & $n = 1, 0, -1, \ldots$
- Apply the L-S reduction (eliminate spatial degrees of freedom)

The L-S procedure is equivalent to a Taylor series expansion of the detailed model

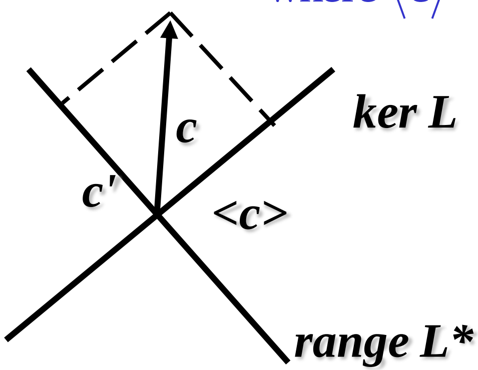
Cross-sectional Averaging by the L-S method (Details)

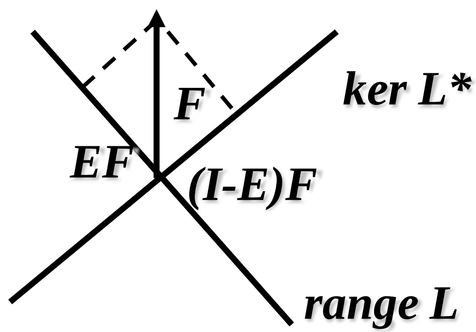
$$F(c,p) \equiv \underbrace{\nabla^2 c}_{\text{Local Diffusion Operator}} - p\, \underbrace{f(x,y,z,t,c,\lambda_i)}_{\text{Large Scale Mixing/Diffusion, Convection \& Reaction}} = 0$$

1. Split the state variable into orthogonal components:

$$c(x,y,z,t) = \langle c\rangle(x,t)\,\psi_0 + c'(x,y,z,t),$$

$$\text{where } \langle c\rangle = \frac{1}{A_\Omega}\iint_\Omega c(x,y,z,t)\,dx\,dy;\ \ \&\ \ c' \perp \langle c\rangle.$$





$$L\psi \equiv -\mu\psi \text{ in } \Omega,$$

$$\text{with } \nabla\psi\cdot n = 0 \text{ in } \partial\Omega.$$

2. Project the governing equation(s) onto complementary function spaces:

(I-E)F=0 → **Global / Averaged equation**

$$\left\langle f\left(\langle c\rangle\psi_0 + c'\right)\psi_0\right\rangle = 0$$

EF=0 → **Local equation**

$$Lc' = pf\left(\langle c\rangle\psi_0 + c'\right) - p\left\langle f\left(\langle c\rangle\psi_0 + c'\right)\psi_0\right\rangle\psi_0$$

Averaging Procedure (Contd.)

3. Solve the reaction-diffusion equation at the local scale by perturbation expansion:

$$c' = \sum_{i=1}^{\infty} p^i c_i \quad \rightarrow$$

$$Lc_1 = f(\langle c\rangle \psi_0) - \langle f(\langle c\rangle \psi_0), \psi_0\rangle \psi_0; \ \langle c_1\rangle = 0,$$

$$Lc_2 = D_c f(\langle c\rangle \psi_0) c_1 - \langle D_c f(\langle c\rangle \psi_0) c_1, \psi_0\rangle \psi_0; \ \langle c_2\rangle = 0, \ldots$$

where $D_c f$ and $D^2_{cc} f$ are Fre′chet derivative s of f.

4. Averaged Model (single equation representation):

$$\langle f(\langle c\rangle \psi_0), \psi_0\rangle + p\langle D_c f(\langle c\rangle \psi_0) c_1, \psi_0\rangle + p^2\left[\langle D_c f(\langle c\rangle \psi_0) c_2, \psi_0\rangle + \frac{1}{2!}\langle D^2{}_{cc} f(\langle c\rangle \psi_0)(c_1, c_1), \psi_0\rangle\right] + O(p^3) = 0$$

5. Write the averaged model Two-Mode/Multi-mode form (in terms of physical variables:

Global Equation:

$$G(\langle c\rangle, c_m) = \langle f(c), \psi_0\rangle$$

$$c_m = \langle c(x, y, z, t)\, u(x, y), \psi_0\rangle$$

Local Equation:

$$c_m(x, t) - \langle c\rangle(x, t) = \langle u\, c', \psi_0\rangle$$

6. If necessary, regularize the averaged model (to expand the range of validity)

Averaged Model in Two-mode and Multi-mode Form

$$c(x,y,z,t) = \langle c \rangle (x,t) + c'(x,y,z,t) \quad \text{such that} \quad c' \perp \langle c \rangle .$$

Project the CDR equation (i.e. F) on two complementary function spaces.

Global Equation

$$G(\langle c \rangle, c_m) = 0$$

$$c_m = \langle c \rangle + \langle u c' \rangle,$$

c_m is the mixing - cup conc.

Local Equation

Solve for c at the local scale, through perturbation expansion

$$\nabla^2 c' = p\, f(\langle c \rangle + c'), \quad \text{with } c' = \sum_{i=1}^{\infty} p^i c_i$$

Spatially Averaged / Two-Mode Models.

Two Modes: ***C_m*** *and* **<C>**

Low-Dimensional Models for Diffusion-Convection-Reaction Problems using the L-S Method

Examples:

1. Transient Heat Conduction Problem
2. Dispersion and Transfer Coefficients
3. Low-D Models for Homogeneous Reactors
4. Low-D models for real time simulation of TWCs

Averaging by L-S Method
1. Transient Heat Conduction in a Slab

$$Bi\frac{\partial\theta}{\partial t}=\frac{\partial^2\theta}{\partial x^2};0<x<1,t>0$$

$$\text{BC1}: \frac{\partial\theta}{\partial x}(0,t)=0$$

$$\text{BC2}: \frac{\partial\theta}{\partial x}(1,t)+Bi\,\theta(1,t)=0$$

$$\text{IC}: \theta(x,0)=f(x)$$

$$Bi=\frac{t_D}{t_E};\ t_D=\frac{a^2}{[k/(\rho c_p)]};\quad t_E=\frac{a(\rho c_p)}{h}$$

$$t=\frac{t'}{t_E};\ \tau=\frac{t'}{t_D}\qquad t=Bi\,\tau$$

$$\text{Lumped Model}(Bi\to 0):$$

$$\bar{\theta}(t)=\int_0^1\theta(x,t)dx$$

$$\frac{d\bar{\theta}}{dt}=-\bar{\theta}$$

$$\text{IC}:\bar{\theta}(0)=\bar{f}$$

$$\frac{\partial^2\theta}{\partial x^2}=Bi\left(\frac{\partial\theta}{\partial t}-\delta(t)f(x)\right);0<x<1,t>0$$

$$\text{BC1}: \frac{\partial\theta}{\partial x}(0,t)=0$$

$$\text{BC2}: \frac{\partial\theta}{\partial x}(1,t)+Bi\,\theta(1,t)=0$$

Averaging by L-S Method
(Transient Heat Conduction in a Slab)

$$\frac{\partial^2\theta}{\partial x^2} = Bi\left(\frac{\partial\theta}{\partial t} - \delta(t) f(x)\right); 0 < x < 1, t > 0$$

$$\text{BC1}: \frac{\partial\theta}{\partial x}(0,t) = 0$$

$$\text{BC2}: \frac{\partial\theta}{\partial x}(1,t) + Bi\,\theta(1,t) = 0$$

Global Equation

$$Bi\left[\frac{d\bar{\theta}}{dt} - \delta(t)\bar{f} + \theta(1,t)\right] = 0$$

$$\frac{d\bar{\theta}}{dt} = -\theta(1,t)$$

$$\bar{\theta}(0) = \bar{f}$$

Local Equation:

$$\theta(x,t) = \bar{\theta}(t) + \theta'(x,t)$$

$$\frac{\partial^2\theta'}{\partial x^2} = Bi\left[\frac{\partial\theta'}{\partial t} - \delta(t)\left(f(x) - \bar{f}\right) - \bar{\theta}(t) - \theta'(1,t)\right]$$

$$\frac{\partial\theta'}{\partial x}(0,t) = 0; \frac{\partial\theta'}{\partial x}(1,t) + Bi\bar{\theta}(t) + Bi\,\theta'(1,t) = 0$$

$$\theta'(x,t) = \sum_{k=1}^{\infty} Bi^k \theta_k(x,t)$$

Averaging by L-S Method
(Transient Heat Conduction in a Slab)

Global Equation

$$\frac{d\bar{\theta}}{dt} = -\theta_s(t) = -\theta(1,t)$$

$$\bar{\theta}(0) = \bar{f}$$

Local Equation

$$\theta_s(t) = \bar{\theta} - \frac{Bi}{3}\bar{\theta} + \frac{Bi}{3}\bar{f}\delta(t) + Bi\,\delta(t)[\bar{g} - g(1)] + O(Bi^2)$$

$$g(x) = \int_0^x \int_0^\xi f(\eta)\,d\eta\,d\xi$$

For $f(x) = 1,$

$$\frac{d\bar{\theta}}{dt} = -\bar{\theta}\left[1 - \frac{Bi}{3} + \frac{4}{45}Bi^2 + O(Bi^3)\right]$$

$$\bar{\theta}(t=0) = 1 - \frac{1}{45}Bi^2 + O(Bi^3)$$

$$Bi = 1 \Rightarrow \quad \bar{\theta} = 0.978\exp[-0.756t]$$

$$Exact\ solution:\ \bar{\theta} = 0.986\exp[-0.740t] + \bar{\theta} = 0.0124\exp[-11.74t] + ..$$

Regularized model,

$$\frac{d\bar{\theta}}{d\tau} = -Bi\frac{\bar{\theta}}{\left(1 + \frac{Bi}{3}\right)} \quad ; t = Bi\,\tau$$

$$\bar{\theta}(\tau = 0) = 1$$

2. Dispersion and Transfer Coefficients

(A) Transfer Coefficient Concept

Film Model for Heat Transfer (W. K. Lewis, 1916)

Film Model for Mass Transfer (W. G. Whitman, 1923)

Boundary Layer Concept (Prandtl, 1904; von Karman, 1934)

(B) Eddy Diffusion/Dispersion Coefficient Concept

B1: Eddy Diffusion Coefficient

Eddy viscosity (J. Boussinesq, 1877)

Turbulent diffusivity/Conductivity (Prandtl,1910)

B2: Dispersion Coefficient

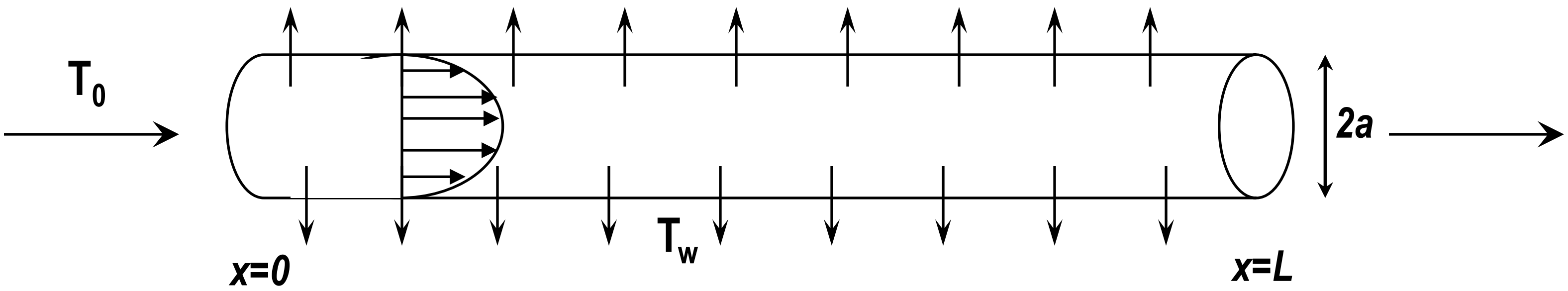
Taylor dispersion coefficient (Taylor,1953;Aris,1956)

These concepts

(i) Eliminate local spatial degrees of freedom (small scales) and coarse-grain the governing equations to obtain averaged/low-dimensional models.

(ii) Express the detailed information contained in the governing equations in terms of a single coefficient (data compression)

Averaging / Coarse-graining (Heat/Mass Transfer Coefficient Concept)



$$2\langle u_x\rangle\left(1-\frac{r^2}{a^2}\right)\frac{\partial T}{\partial x}=\frac{k_f}{\rho_f C_{pf}}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right);$$

$$\text{B.C. \& I.C.}: T(x=0,r)=T_0,\quad T(x,r=a)=T_w.$$

$0 < x < L;$
$0 < r < a;$
$L/a >> 1.$

Local heat transfer coefficient:

$$h(x)=\frac{-k_f\left.\frac{\partial T}{\partial r}\right|_{r=a}}{T_m-T_w}$$

$$T_m = \text{cup-mixing temperature}$$

$$=\int_0^a 2\pi r\, u(r)\, T(x,r)\, dr \,/\, \left(\pi a^2\langle u_x\rangle\right)$$

Coarse-grained / Low-dimensional Model

$$\langle u_x\rangle\rho_f C_{pf}\frac{dT_m}{dx}=a_V q,\quad \text{with}\ T_m(x=0)=T_0;$$

$$q=h(x)\left(T_w-T_m\right)$$

Global Equation $(a_v=2/a)$

Local Equation

$$\frac{h_\infty 2a}{k_f}=Nu_\infty=\frac{48}{11}$$

Averaging / Coarse-graining (Dispersion Coefficient Concept)

Inert Tracer diffusion in laminar flow in a tube

$$\frac{\partial C}{\partial t} + 2\langle u_x \rangle \left(1 - \frac{r^2}{a^2}\right)\frac{\partial C}{\partial x} = D_m\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C}{\partial \varphi^2} + \frac{\partial^2 C}{\partial x^2}\right];$$

$$I.C.\ \&\ BCs.: C(x, r, \varphi, t = 0) = C_0(x, r, \varphi); \quad \frac{\partial C}{\partial r}(r = a) = 0$$

$-\infty < x < \infty;$
$0 < r < a$

Taylor (1953), Taylor-Aris dispersion (Aris, 1956)

Coarse-grained / Low-dimensional Model

$$\frac{\partial \langle C \rangle}{\partial t} + \langle \mathbf{u_x} \rangle \frac{\partial \langle C \rangle}{\partial x} = D_e \frac{\partial^2 \langle C \rangle}{\partial x^2},$$

$$D_e = D_m + \frac{\langle \mathbf{u_x} \rangle^2 a^2}{48 D_m}$$

Generalizations:

Finite systems: $0<x<L$
turbulent flows,
packed-beds,
bubble columns,
Reacting flows, etc

Some Conceptual Difficulties with the Taylor Dispersion Coefficient Concept

- Upstream diffusion even in convection dominated systems
- Diffusion is symmetric (Gaussian) about mean flow
- Infinite speed of propagation of signals even in convection dominated systems
- Validity of downstream BC, especially for large axial Pe
- Dependence of dispersion coefficient on kinetics
- Inability to describe systems whose RTD curve has long tails associated with stagnant (zero velocity) regions and/or bypass behavior, or near segregated flow limit, etc

Key Observations: (i) single concentration is used
(ii) transfer between scales is represented in terms of gradient based on large scale (in contrast to gradient across eliminated length scale)
(ii) Transfer/exchange between scales is not necessarily local

Taylor Dispersion Theory (Revised)

$$\langle C \rangle = \frac{\int_0^{2\pi}\int_0^{a} C(x,r,\varphi,t)\, r\,dr\,d\varphi}{\int_0^{2\pi}\int_0^{a} r\,dr\,d\varphi} = \text{spatial ave. conc.}$$

$$C_m = \frac{\int_0^{2\pi}\int_0^{a} u(r) C(x,r,\varphi,t)\, r\,dr\,d\varphi}{\int_0^{2\pi}\int_0^{a} u(r)\, r\,dr\,d\varphi} = \text{cup-mixing conc.}$$

Local Eqn.:

$$C_m - \langle C \rangle = \sum_{i=1}^{\infty} \gamma_i \left(t_D\right)^i \frac{\partial^i \langle C \rangle}{\partial t^i}$$

Truncated Local Eqn.

$$C_m - \langle C \rangle \approx \left(t_D\right) \frac{\partial \langle C \rangle}{\partial t} \qquad \left(\gamma_1 = 1\right)$$

Averaged model (single mode form):
(with transfer/exchange time)

$$\frac{\partial C_m}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} + \langle u \rangle t_D \frac{\partial^2 C_m}{\partial x \partial t} = 0; t > 0, x > 0$$

$$I.C: C_m(x, t=0) = C_{m0}(x)$$

$$B.C: C_m(x=0, t) = C_{m,in}(t)$$

Averaged model is hyperbolic!

Truncated Averaged model
(two-mode form with transfer coefficient)

$$\frac{\partial \langle C \rangle}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} = 0; \quad \text{Global Eqn.}$$

$$\frac{\partial \langle C \rangle}{\partial t} = k_c a_v \left(C_m - \langle C \rangle\right); \quad \text{Local Eqn.;}$$

$$a_v = \frac{2}{a}; \quad k_c = \frac{24 D_m}{a}$$

$$t_D = \frac{a^2}{48 D_m} = \text{local transfer/ exchange time}$$

The Liapunov-Schmidt (L-S) Method for Exact Spatial Averaging of the Convective-Diffusion Equation

[SIAM J. Appl. Math., 63,1231-1258 (2003); Chem. Eng. Sci.,57,2545-2564 (2002)]

L-S method:

(i) Spatial degrees of freedom (small length scales) can be eliminated near zero eigenvalues (small parameter)

(ii) The L-S method is equivalent to (exact) Taylor expansion of the detailed model in terms of the small parameter (in the function space)

(iii) Easily applied to linear as well as nonlinear models

e.g. classical Taylor problem

Averaged model to all orders

$$\frac{\partial\langle C\rangle}{\partial t} + \langle u\rangle \frac{\partial C_m}{\partial x} = 0; \quad \text{Global Eqn.}$$

$$C_m - \langle C\rangle = \sum_{i=1}^{\infty} \gamma_i (t_D)^i \frac{\partial^i \langle C\rangle}{\partial t^i}; \quad \text{Local Eqn.}$$

Convergence criterion

$$t_D = \frac{a^2}{48 D_m}; \quad \ell_D = \langle u\rangle t_D$$

$$t_D \omega_t < 0.858$$

$$I.C: C_m(x, t=0) = C_{m,0}(x);$$

$$B.C: C_m(x=0, t) = C_{m,in}(t)$$

Comparison of Parabolic and Hyperbolic Models

Taylor's model

$$\frac{\partial C_m}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} = D_e \frac{\partial^2 C_m}{\partial x^2}; D_e = \frac{a^2 \langle u \rangle^2}{48 D_m}$$

Taylor-Aris Parabolic Model

$$\frac{\partial C_m}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} = D_e \frac{\partial^2 C_m}{\partial x^2};$$

$$D_e = D_m + \frac{a^2 \langle u \rangle^2}{48 D_m}$$

+ 2 BCs for finite domains

Hyperbolic model

$$\frac{\partial C_m}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} + \langle u \rangle t_D \frac{\partial^2 C_m}{\partial x \partial t} = 0$$

Leading Order Approximation

$$\frac{\partial \langle C \rangle}{\partial t} = -\langle u \rangle \frac{\partial \langle C \rangle}{\partial x}; \ \langle C \rangle = C_m$$

$$\Rightarrow \ \mathrm{D_e} = \langle u \rangle^2 t_D$$

Hyperbolic models

$$\frac{\partial C_m}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} + \frac{\langle u \rangle a^2}{48 D_m} \frac{\partial^2 C_m}{\partial x \partial t} = D_m \frac{\partial^2 C_m}{\partial x^2}$$

$$\frac{\partial C_m}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} + \langle u \rangle t_D \frac{\partial^2 C_m}{\partial x \partial t} = 0; \quad t_D = \left(\frac{a^2}{48 D_m} + \frac{D_m}{\langle u \rangle^2} \right)$$

Hyperbolic model is a Cauchy Problem while Parabolic one is a BVP

Comparison of Parabolic and Hyperbolic Models

Hyperbolic Model

$$\frac{\partial C_m}{\partial t}+\frac{\partial C_m}{\partial z}+P\frac{\partial^2 C_m}{\partial z\partial t}=0;\ \ P=\beta_1 p=\frac{t_D\langle u\rangle}{L}\quad ;$$

$$I.C: C_m(z,t=0)=C_{m,0}(z);$$

$$B.C: C_m(z=0,t)=C_{m,in}(t);$$

Parabolic Model

$$\frac{\partial C}{\partial t}+\frac{\partial C}{\partial z}=\frac{1}{Pe}\frac{\partial^2 C}{\partial z^2};0<\mathrm{z}<1;\mathrm{Pe}=\frac{\langle \mathrm{u}\rangle L}{D_e}$$

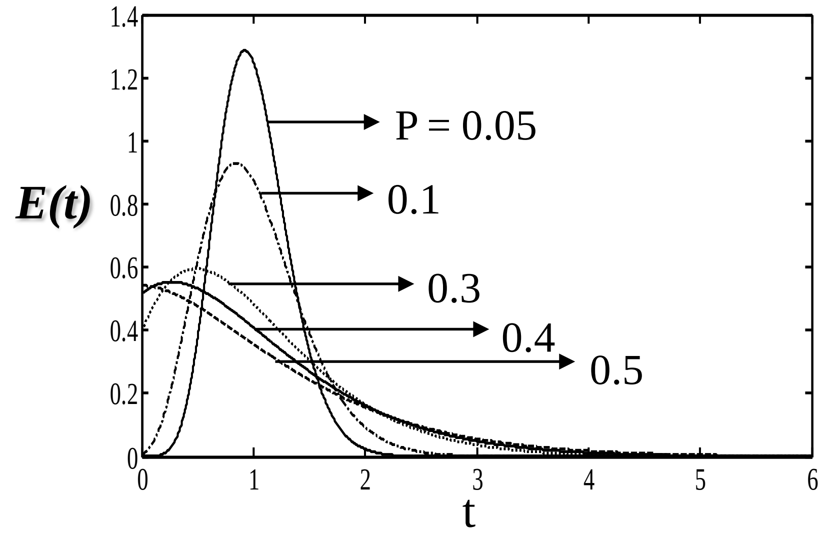
$$BCs:\frac{1}{Pe}\frac{\partial C}{\partial z}=C-C_{in}(t)\text{ at } z=0;\quad \frac{\partial C}{\partial z}=0\ \text{ at } z=1$$

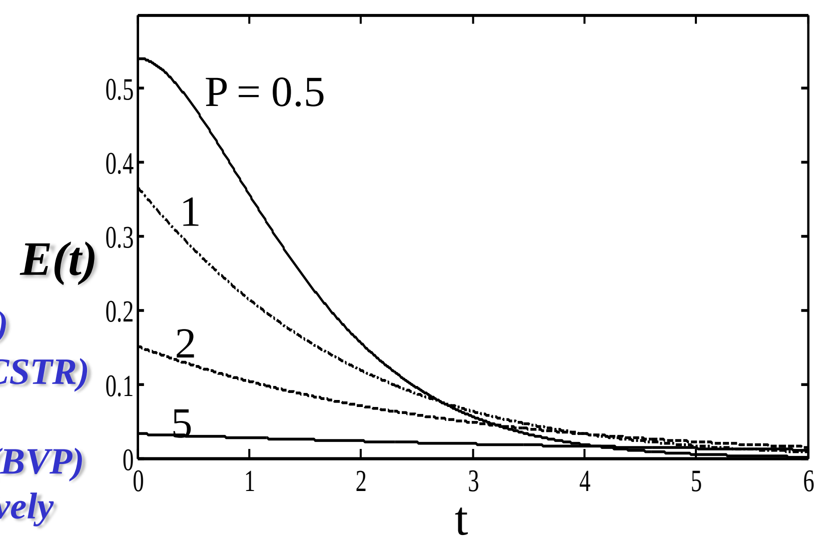
$$IC: C(z,=0)=C_0(z)$$

Observations:

- *Both models predict the same dispersion curves for Pe>>1 (P<<1)*
- *For parabolic model the variance is bounded in 0 (PFR) and 1 (CSTR) while the hyperbolic model has a much larger range of validity*
- *Hyperbolic model is easier to solve (IVP) compared to Parabolic (BVP)*
- *Hyperbolic model has no physical inconsistencies and is qualitatively correct even in the limit of P→∞*

Dispersion curves predicted by the hyperbolic model



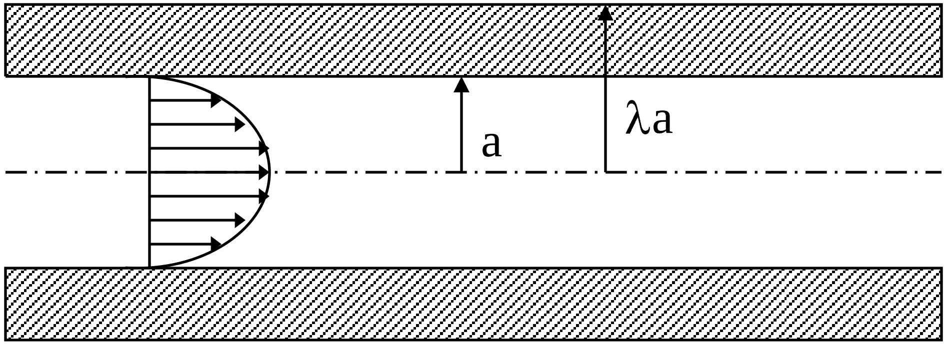


Other Thermal/Solutal Dispersion Problems:

Heat and Mass transfer coefficients in ducts
Thermal Dispersion in Packed Beds
(Universal scaling for disparate capacitances)

Balakotaiah & Chang; SIAM J. Appl. Math., 63,1231-1258 (2003)

Thermal/Solutal dispersion with diffusion into the wall



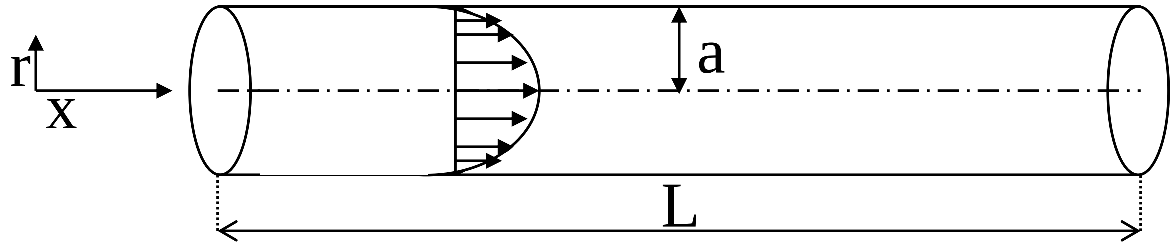
Hyperbolic model can give rise to large Second moment (long tail)

$$\frac{\partial C_m}{\partial t} + \langle u \rangle \frac{\partial C_m}{\partial x} + \langle u \rangle t_D \frac{\partial^2 C_m}{\partial x \partial t} = 0;\ t >> t_D;\ x >> \ell_D (= \langle u \rangle t_D)$$

$$t_D = \frac{a^2}{D_m}\left[\frac{1}{48}\varepsilon(6\varepsilon^2 - 16\varepsilon + 11) + \frac{\mu}{8}\varepsilon(4\varepsilon - \varepsilon^2 - 3 - 2\ln(\varepsilon))\right]$$

$$\varepsilon = \text{porosity};\ \mu = \frac{D_m}{D_s}$$

3. Spatial Averaged Two-mode Models for Homogeneous Tubular Reactors



$$\alpha = \frac{a}{L}$$

CDR Eqn.:

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial c}{\partial \xi}\right) + \frac{1}{\xi^2}\frac{\partial^2 c}{\partial \varphi^2} = p\left[\frac{\partial c}{\partial t} - \frac{p}{Pe_r^{\,2}}\frac{\partial^2 c}{\partial z^2} + u(\xi)\frac{\partial c}{\partial z} + Da\, r(c)\right]$$

Local / Small-scale Diffusion

Macro-scale
Accumulation-Diffusion-Convection-Reaction

B.C.s & I.C:

$$\frac{p}{Pe_r^{\,2}}\frac{\partial c}{\partial z} = u(\xi)\left[c - c_{in}\right] @\ z = 0;\quad \frac{\partial c}{\partial z} = 0\ @\ z = 1;\quad \frac{\partial c}{\partial \xi} = 0\ @\ \xi = 1;\quad c(\varphi) = c(\varphi + 2\pi\pi)\ c(t = 0) = c_0(\xi, z)$$

Dimensionless Parameters:

$p = \frac{a^2 \bar{u}}{L D_\perp} = \frac{t_D}{\tau_C}$,	$Pe_r = \frac{\bar{u} a}{D_x}$,	$Da = \frac{L R(C_R)}{D_x C_R} = \frac{\tau_C}{t_R}$,	$Pe = \frac{Pe_r^2}{p}$.
Transverse/Local Peclet Number	Radial Peclet Number	Damköhler Number	Axial Peclet Number

Spatial averaging is possible when p << 1, *Da* ~ O(1), &
(a) Pe_r ~ O(1/p) or (b) Pe_r ~ O(1) or (c) Pe_r ~ O(p)

Two-Mode Models for Homogeneous Tubular Reactors

Case (a) $Pe_r = O(1/p)$

$$c_m = \frac{\int_{\xi=0}^{\xi=1} \int_{\varphi=0}^{\varphi=2\pi} c\, u(\xi)\, 2\xi \, d\varphi \, d\xi}{2\pi \int_{\xi=0}^{\xi=1} u(\xi)\, 2\xi \, d\xi}$$

Cup-mixing

$$\langle c \rangle = \frac{1}{2\pi} \int_{\xi=0}^{\xi=1} \int_{\varphi=0}^{\varphi=2\pi} c\, 2\xi \, d\varphi \, d\xi .$$

Average

Averaged/Reduced Model (to order p)

$$\frac{\partial c_m}{\partial t} + \frac{\partial c_m}{\partial z} + \beta_1 p \frac{\partial^2 c_m}{\partial z \partial t} + Da\, r(\langle c \rangle) = 0$$

Global Eqn.

$$\beta_1 p \frac{\partial c_m}{\partial z} = \langle c \rangle - c_m \; ; \beta_1 = \frac{1}{48}$$

Local Eqn.

BC and I.C: $c_m = c_{m,in}(t)$, @ $z = 0$; $\langle c \rangle = \langle c_0 \rangle(z)$ @ $t = 0$

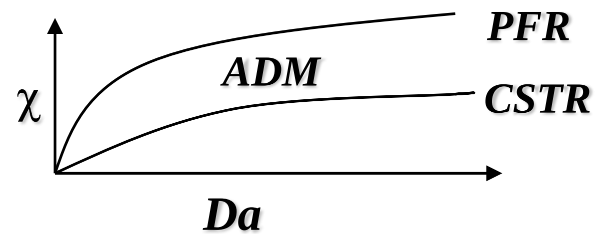
Averaged Model can be written in terms of a single Concentration (c_m) but this leads to transport coefficients dependent on kinetics.

Special cases

- $p = 0 \Rightarrow$ **plug flow model (zeroth order)**
- **Steady state and** $Pe_r >> 1 \Rightarrow$ **two-mode homogeneous tubular reactor model**

$$\frac{dc_m}{dz} = -\frac{(c_m - \langle c \rangle)}{\beta_1 p}; \quad c_m(z=0) = c_{m,in}$$

$$c_m - \langle c \rangle = \beta_1 p Da\, r(\langle c \rangle)$$



Two-Mode Models for Homogeneous Tubular Reactors

Case (b) $Pe_r = O(1)$

Reduced Model (to order p)

Hyperbolic Model

$$\frac{\partial c_m}{\partial t} + \frac{\partial c_m}{\partial z} + \beta_1 p \frac{\partial^2 c_m}{\partial z \partial t} - \frac{p}{Pe_r^2}\frac{\partial^2 \langle c \rangle}{\partial z^2} + Da\, r(\langle c \rangle) = 0$$

Global Eqn.

$$\beta_1 p \frac{\partial c_m}{\partial z} = \langle c \rangle - c_m \;\; ; \beta_1 = \frac{1}{48}$$

Local Eqn.

BCs and I.C : $\frac{p}{Pe_r^2}\frac{\partial \langle c \rangle}{\partial z} = c_m - c_{m,in}$, @ $z = 0$; $\quad \frac{\partial \langle c \rangle}{\partial z} = 0$, @ $z = 1$; $\quad \langle c \rangle = \langle c_0 \rangle$ @ $t = 0$

Special cases

- $p = 0 \Rightarrow$ **plug flow model (zeroth order)**
- **Steady state two-mode model**

$$\frac{dc_m}{dz} + Da\, r(\langle c \rangle) = \frac{p}{Pe_r^2}\frac{d^2 \langle c \rangle}{dz^2}; \quad \langle c \rangle - c_m = \beta_1 p \frac{dc_m}{dz}$$

+ above BCs

- ***No reaction case***

$$\frac{\partial c_m}{\partial t} + \frac{\partial c_m}{\partial z} + \underbrace{\beta_1 p \frac{\partial^2 c_m}{\partial z \partial t} - \frac{p}{Pe_r^2}\frac{\partial^2 \langle c \rangle}{\partial z^2}}_{\text{dispersion terms}} = 0$$

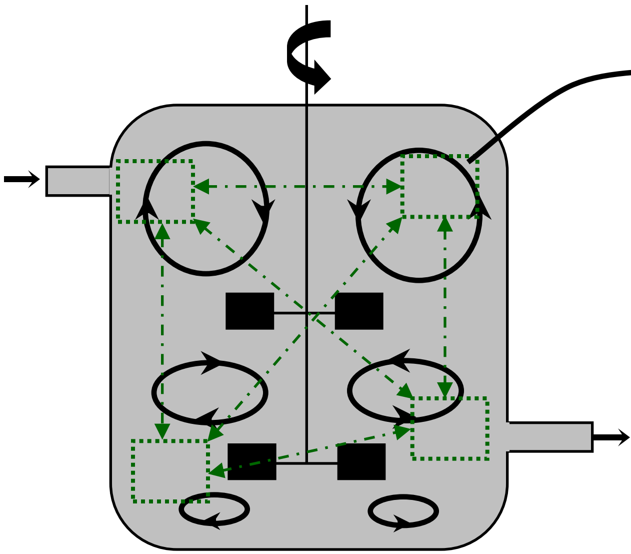
$$-(\beta_1 p + \frac{p}{Pe_r^2})\frac{\partial^2 C_m}{\partial z^2} \quad \text{[Taylor - Aris Parabolic Model]}$$

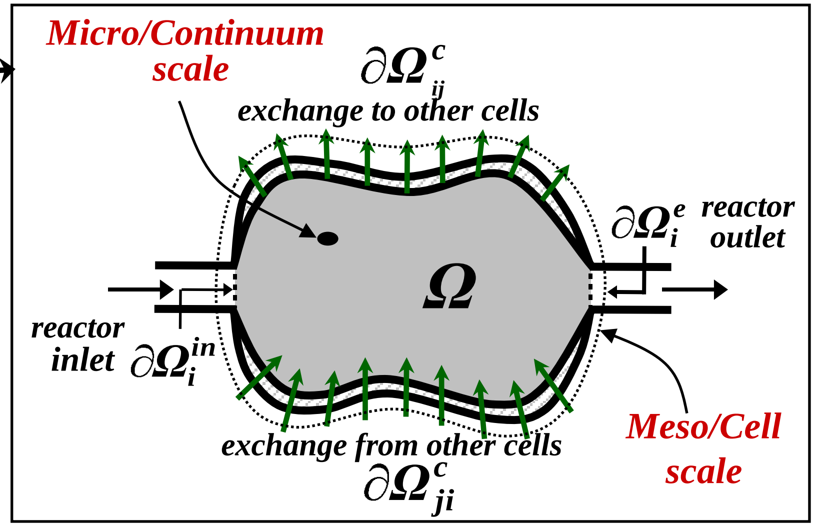
$$(\beta_1 p + \frac{p}{Pe_r^2})\frac{\partial^2 C_m}{\partial z \partial t} \quad \text{[Hyperbolic Model]}$$

Two-mode Models for Homogeneous Reactors

(c) $Pe_r = O(p)$

Micro-Scale reduction : Meso-Micro coupling

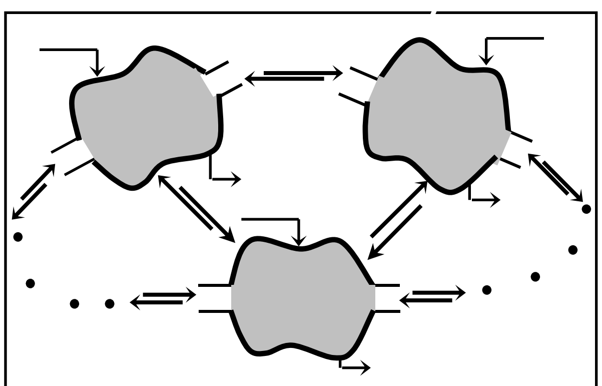




CDR equation

$$\frac{\partial C_i}{\partial t} + \mathbf{U}_i(x,y,z)\cdot\nabla C_i = \nabla\cdot(D\nabla C_i) - R(C_i)$$

three mode meso-scale equation



n-interacting cells

$1 < n < \infty$

exchange between the cells

$$V_i\left[\frac{\partial\langle C_i\rangle}{\partial t} + R(\langle C_i\rangle)\right] = q_i^{in} C_{i,m}^{in} - q_i^{e} C_{i,m}^{e} + \sum_{j=1, j\neq i}^{n}\left(q_{ji}^{c} C_{j,m}^{c} - q_{ij}^{c} C_{i,m}^{c}\right)$$

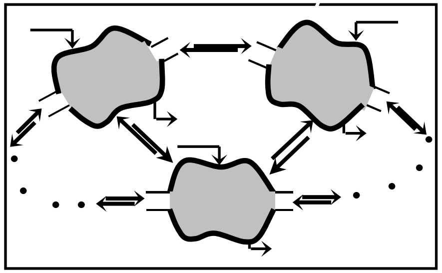
$$C_{i,m}^{e} - \langle C_i\rangle = Pe_{\Omega_i}\left[\chi_i\left(C_{i,m}^{in} - C_{i,m}^{e}\right) + \sum_{j=1, j\neq i}^{n}\chi_{ji}\left(C_{j,m}^{c} - C_{i,m}^{c}\right)\right]$$

$$C_{i,m}^{c} - \langle C_i\rangle = Pe_{\Omega_i}\left[\omega_i\left(C_{i,m}^{in} - C_{i,m}^{e}\right) + \sum_{j=1, j\neq i}^{n}\varpi_{ji}\left(C_{j,m}^{c} - C_{i,m}^{c}\right)\right]$$

Two-Mode Model for Homogeneous Tank Reactors

Meso-Macro Coupling

3n equations



Two-mode reactor scale model

$$\frac{d\langle C\rangle}{dt} + R(\langle C\rangle) = \frac{1}{\tau}\left(C_m^{in} - C_m\right)$$

$$C_m - \langle C\rangle = \frac{1}{\tau}\left(t_{mix,2}C_m^{in} - t_{mix,1}C_m\right)$$

$$\langle C\rangle = \sum_{i=1}^{n} V_i\langle C_i\rangle \Big/ \sum_{i=1}^{n} V_i$$

$$C_m = \sum_{i=1}^{n} q_i^e C_{i,m}^e \Big/ \sum_{i=1}^{n} q_i^e$$

$$C_m^{in} = \sum_{i=1}^{n} q_i^{in} C_{i,m}^{in} \Big/ \sum_{i=1}^{n} q_i^{in}$$

$$t_{mix,1} = \tau_E\left\langle(\alpha^e-\beta)\,Inv(\alpha^E)(\alpha^{in}-\beta)\,y_0, y_0\right\rangle + \tau_d\left(\left\langle\alpha^e(Pe-Pe_c)\,y_0, y_0\right\rangle + \left\langle\beta Pe_c y_0, y_0\right\rangle\right)$$

$$t_{mix,2} = \tau_E\left\langle(\alpha^e-\beta)\,Inv(\alpha^E)\left[\frac{1}{C_m^{in}}\alpha^{in}C^{in} - \beta\right]y_0, y_0\right\rangle + \tau_d\left(\left\langle\frac{1}{C_m^{in}}\alpha^e(Pe-Pe_c)\,c^{in}, y_0\right\rangle + \left\langle\frac{1}{C_m^{in}}\beta Pe_c c^{in}, y_0\right\rangle\right)$$

$$\tau_d = l_d^2 / D$$

$$\tau_E = V/Q$$

$$\tau = V/q$$

macromixing effect — *micromixing effect*

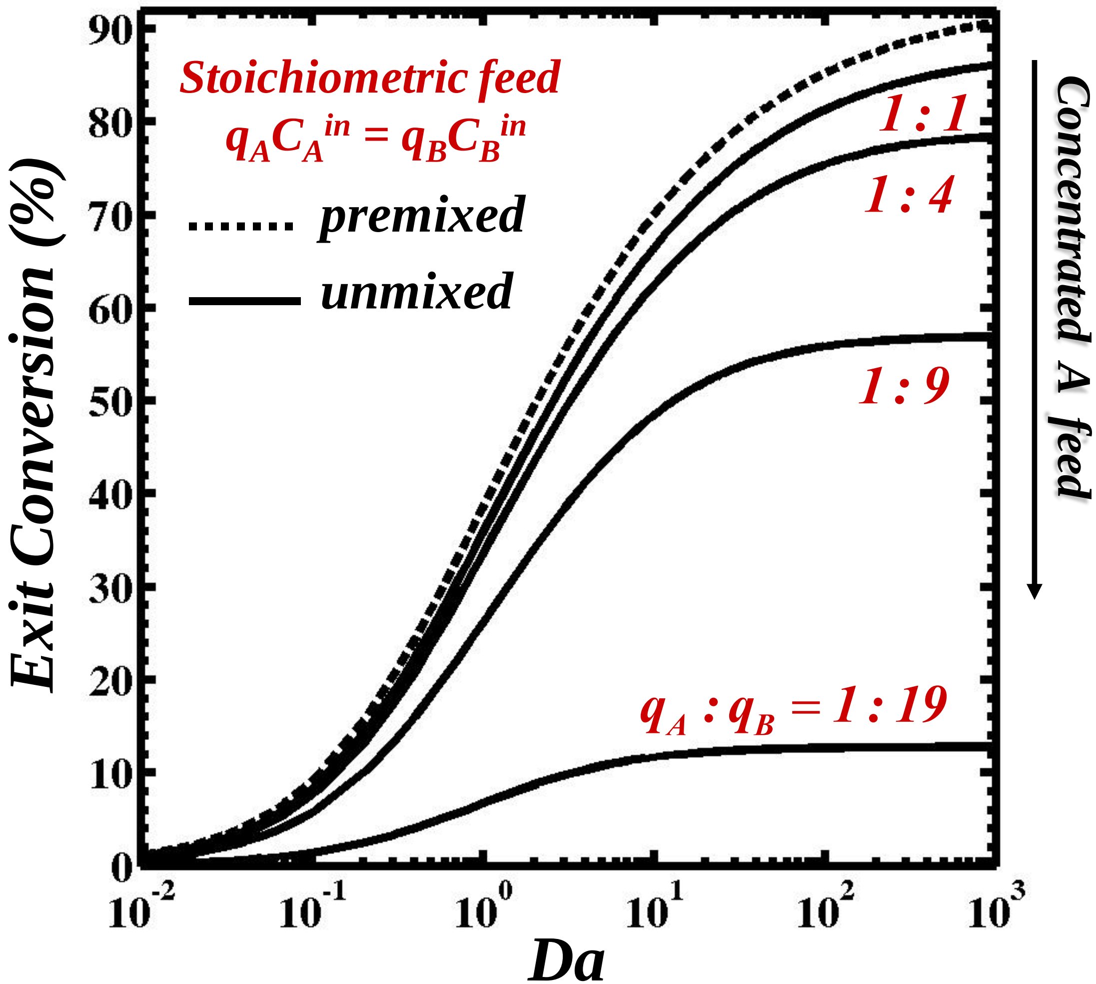
$$t_{mix,1} = f\left(\frac{1}{r.p.m}\right) g_1(\text{feed distribution, reactor geometry}) + f\left(\frac{l_d^2}{D}\right) g_2(\text{feed distribution, reactor geometry})$$

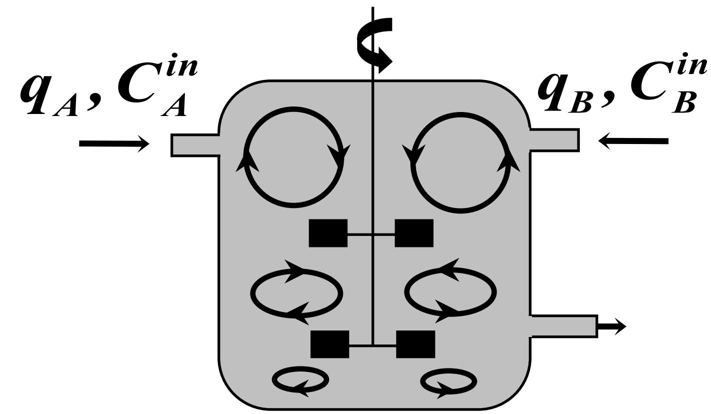
$$t_{mix,2} = f\left(\frac{1}{r.p.m}\right) g_3(\text{feed distribution \& composition, reactor geometry}) + f\left(\frac{l_d^2}{D}\right) g_4(\text{feed distribution \& composition, reactor geometry})$$

For premixed feed $t_{mix,1} = t_{mix,2}$

Effect of feeding on Bimolecular 2nd Order Reaction

$$A+B \rightarrow P$$



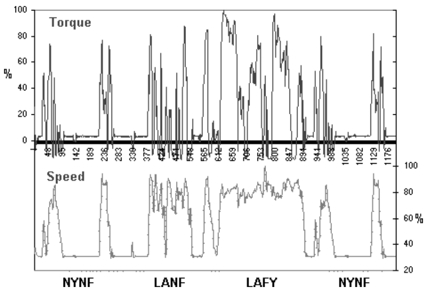


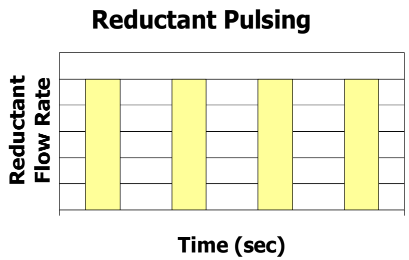
$t_{mix,2}$ is higher for concentrated species

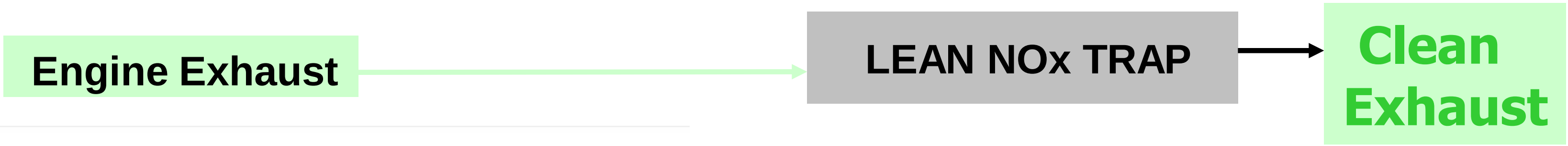
$\tau_E/\tau = 0.1, \quad \tau_d/\tau = 0.1$

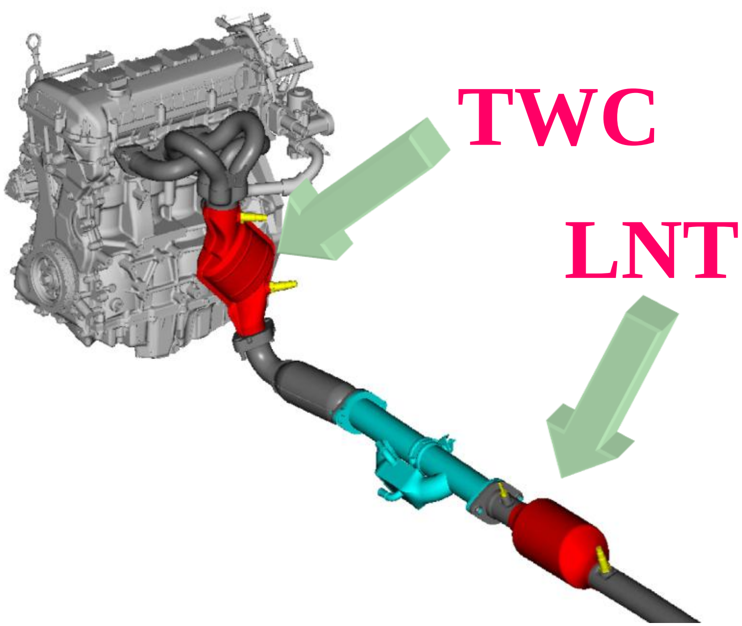
q_A/q_B	$t^A_{mix,1}/\tau$	$t^B_{mix,1}/\tau$	$t^A_{mix,2}/\tau$	$t^B_{mix,2}/\tau$
premixed	0.1	0.1	0.1	0.1
1:1	0.1028	0.1028	0.1417	0.0833
1:4	0.1090	0.1090	0.2350	0.0775
1:9	0.1160	0.1160	0.4800	0.0756
1:19	0.1203	0.1203	0.9775	0.0751

4. Low-D Models for Three-Way Converters(TWCs) & Lean NOx Traps(LNTs)



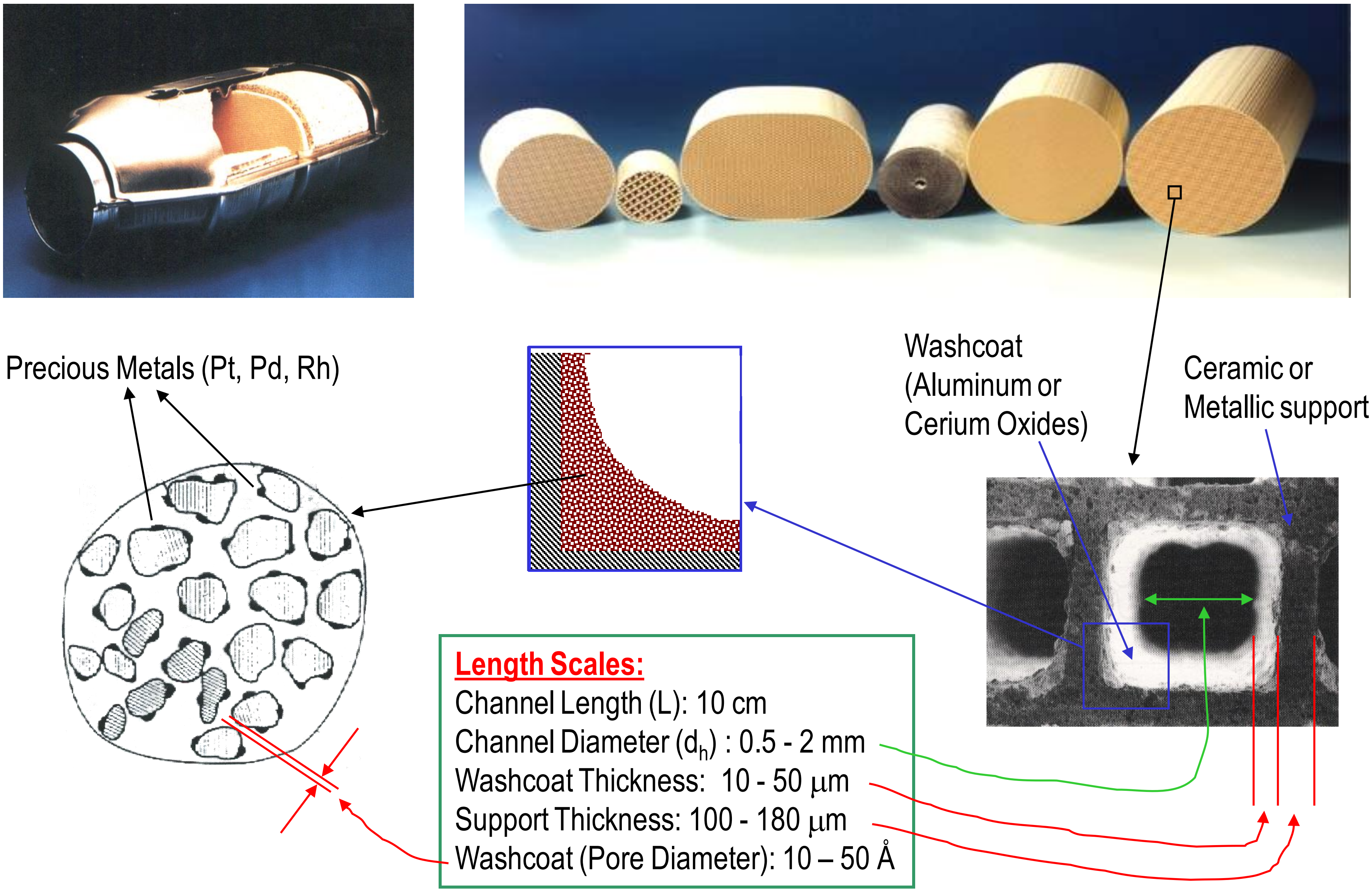




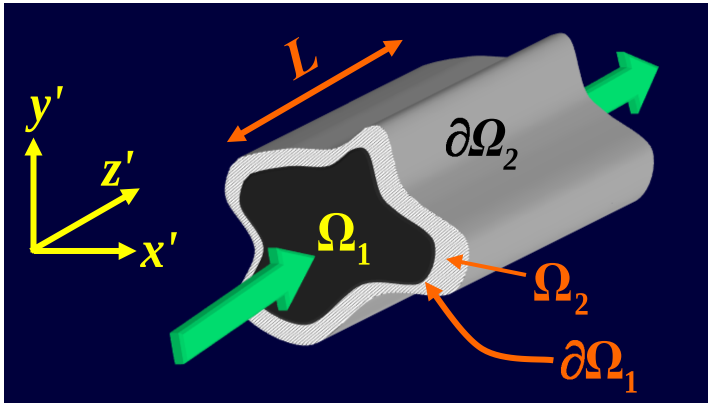


– Challenges
  - Maximize NOx conversion
  - Maximize reductant conversion
  - Minimize fuel penalty
  - Minimize deactivation
  - Achieve robust control

Catalytic Monolith Converter



Low-dimensional Model for a Catalytic Monolith Reactor



Shape Normalized Lengths

$$R_{\Omega_1} = \frac{A_{\Omega_1}}{P_{\Omega}}$$

fluid

$$R_{\Omega_2} = \frac{A_{\Omega_2}}{P_{\Omega}}$$

washcoat

Steady State Balance Equations

$$\underbrace{\frac{\partial C_f}{\partial t} + u(x',y')\frac{\partial C_f}{\partial z'}}_{\text{convection}} = \underbrace{D_m\left(\nabla_*^2 C_f + \frac{\partial^2 C_f}{\partial z'^2}\right)}_{\text{diffusion}}, \ (x',y') \in \Omega_1$$

$$\frac{\partial C_s}{\partial t} + \underbrace{R(C_s)}_{\text{reaction}} = \underbrace{D_e\left(\nabla_*^2 C_s + \frac{\partial^2 c_s}{\partial z'^2}\right)}_{\text{diffusion}}, \ (x',y') \in \Omega_2$$

Coupled PDEs in (x', y', z')

interfacial coupling

Boundary Conditions

$$\left.\begin{aligned} n.D_m \nabla_* C_f &= n.D_e \nabla_* C_s \\ C_f &= C_s \end{aligned}\right\}, \ (x',y') \in \partial\Omega_1$$

$$n.D_e \nabla_* C_s = 0, \ (x',y') \in \partial\Omega_2$$

$$D_m \frac{\partial C_f}{\partial z'} = u(x',y')(C_f - C_{in}(t)) \ \& \ \frac{\partial C_s}{\partial z'} = 0, \ @ z' = 0$$

$$\frac{\partial C_f}{\partial z'} = \frac{\partial C_s}{\partial z'} = 0, \ @ z' = L$$

Low-Dimensional Model for a TWC

Species conservation

$$\frac{\partial C_{fm_j}}{\partial t} = -\bar{u}\frac{\partial C_{fm_j}}{\partial x} - \frac{2k_{ce,j}}{R}\left(C_{fm_j} - C_{s_j}\right)$$

$$\frac{\partial \langle C_{wc}\rangle_j}{\partial t} = \frac{k_{ci,j}}{\delta_c}\left(C_{s_j} - \langle C_{wc}\rangle_j\right) + \sum_{i=1}^{N}\nu_{ij}R_i\left(\langle C_{wc}\rangle_1, \langle C_{wc}\rangle_2 \ldots \langle C_{wc}\rangle_s, Ts\right)$$

$$k_{ce,j}\left(C_{fm_j} - C_{s_j}\right) = k_{ci,j}\left(C_{s_j} - \langle C_{wc}\rangle_j\right)$$

$$k_{ce,j} = \frac{Sh_e D_{m,j}}{4R_\Omega} \qquad k_{ci,j} = \frac{Sh_i D_{s,j}}{\delta_w}$$

j=1,2 …. S (species); N reactions

+ IC + BCs

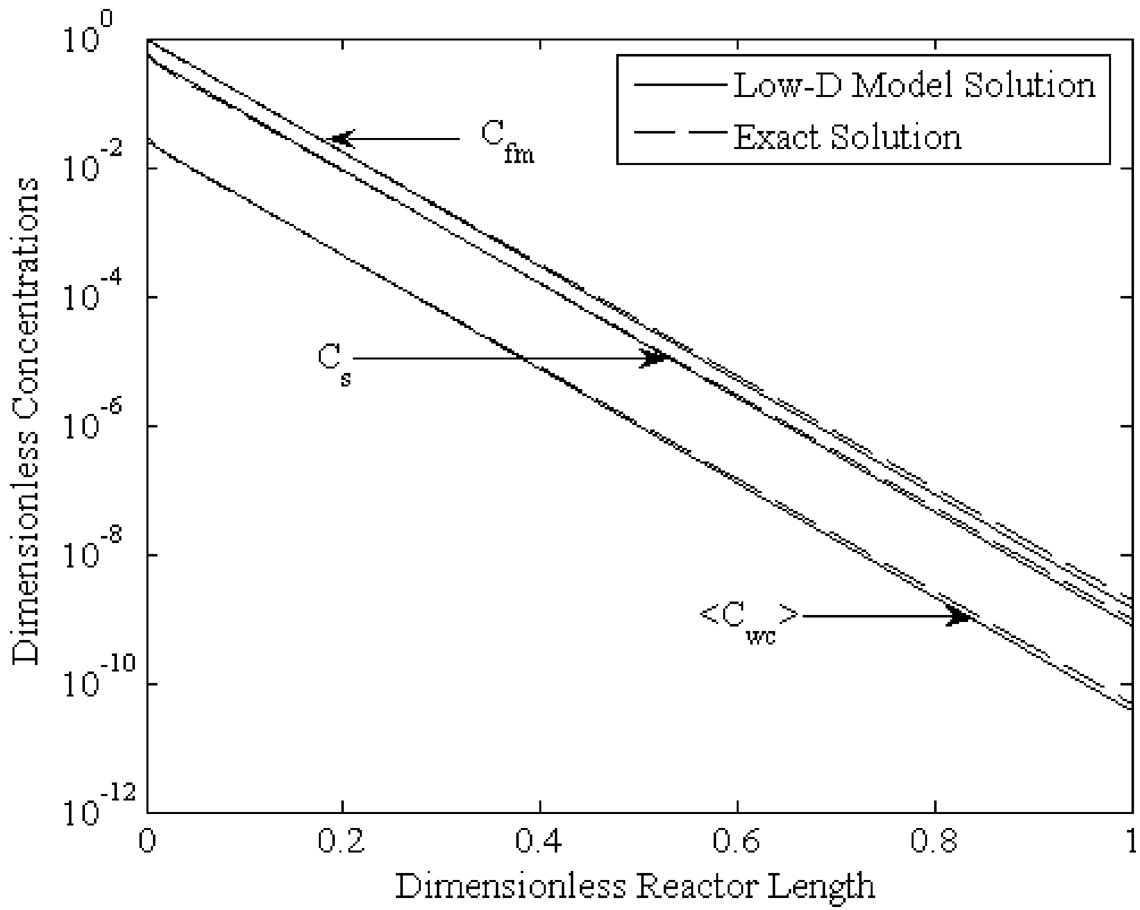
Energy balance

$$\rho_f c_{pf}\frac{\partial T_f}{\partial t} = -\bar{u}\rho_f c_{pf}\frac{\partial T_f}{\partial x} - h(x)a_v\left(T_f - T_s\right)$$

$$\delta_w \rho_w c_{pw}\frac{\partial T_s}{\partial t} = \delta_w k_w \frac{\partial^2 T_s}{\partial x^2} + h(x)\left(T_f - T_s\right) + \delta_c \sum_{j=1}^{N} R_j\left(\langle C_{wc}\rangle_1, \langle C_{wc}\rangle_2, \ldots \langle C_{wc}\rangle_s, T_s\right)\left(-\Delta H_j\right)$$

$$T_f = T_{fin}(t) \text{ @ } x = 0;\ T_s(x,t=0) = T_{s0}(x);\ T_f(x,t=0) = T_{f0}(x);\ \frac{\partial T_s}{\partial x} = 0 \text{ @ } x = 0, L$$

Comparison of Accuracy of Low-D Model for Linear Kinetics, Single Reaction and Isothermal Case:



Overall reactions in TWC

1. $CO + \frac{1}{2}O_2 \rightarrow CO_2$

2. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

3. $CH_y + \frac{4+y}{4}O_2 \rightarrow CO_2 + \frac{y}{2}H_2O$

4. $NO + CO \rightarrow CO_2 + N_2$

$$R_{CO} = \frac{k_1 \hat{X}_{CO} \hat{X}_{O_2}}{F(\underline{\hat{X}}, T_s)}$$

$$R_{H_2} = \frac{k_1 \hat{X}_{H_2} \hat{X}_{O_2}}{F(\underline{\hat{X}}, T_s)}$$

$$R_{HC} = \frac{k_3 \hat{X}_{HC} \hat{X}_{O_2}}{F(\underline{\hat{X}}, T_s)}$$

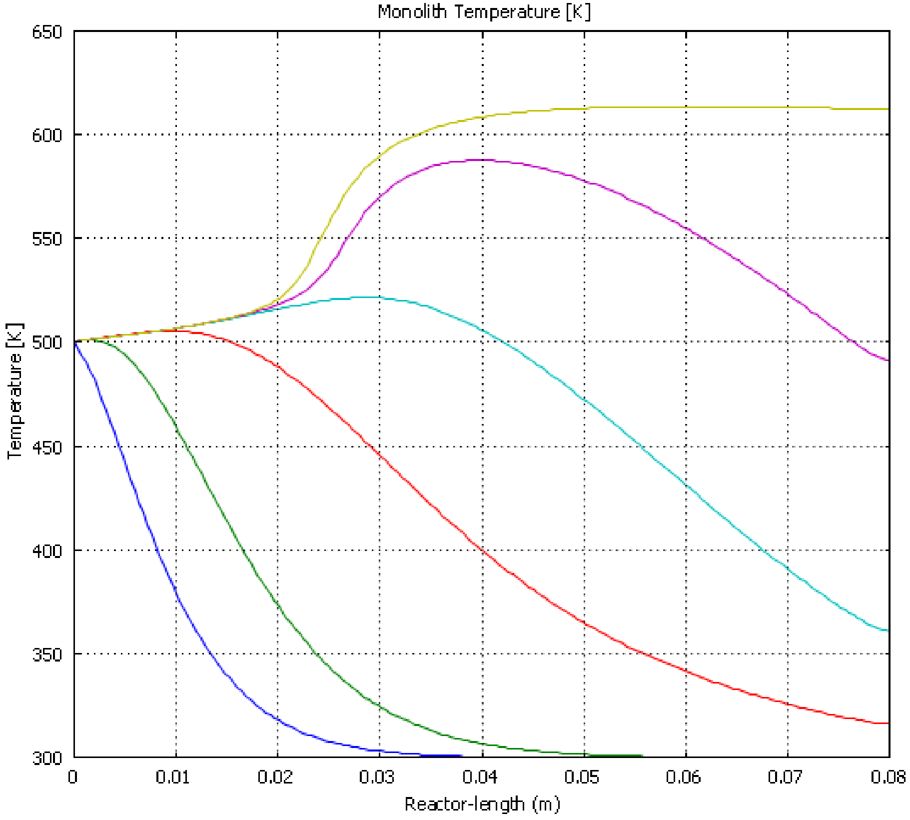
$$R_{NO} = \frac{k_4 \hat{X}_{CO}^{1.4} \hat{X}_{O_2}^{0.3} \hat{X}_{NO}^{0.13}}{T_s^{-0.17}(T_s + ka_5 \hat{X}_{CO})^2}$$

$$F(\underline{\hat{X}}, T_s) = T_s(1 + ka_1 \hat{X}_{CO} + ka_2 \hat{X}_{HC})^2 (1 + ka_3 \hat{X}_{CO}^2 \hat{X}_{HC}^2)(1 + ka_4 \hat{X}_{NO}^{0.7})$$

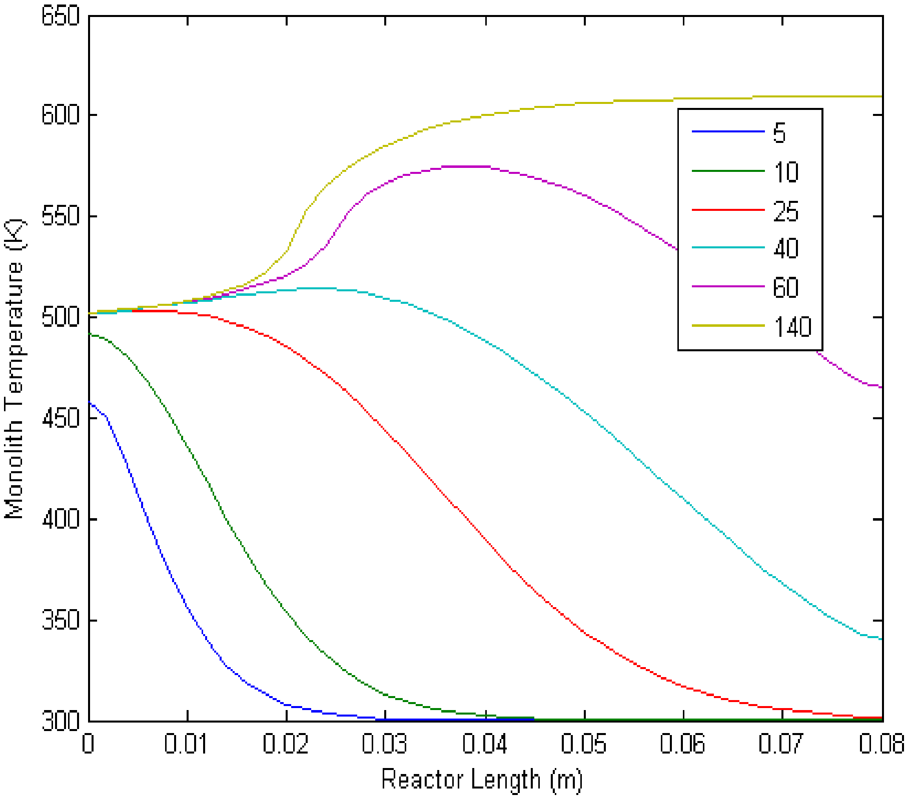
$$k_i = A_i e^{-\frac{E_i}{T_s}} \qquad i = 1, 3, 4$$

$$ka_i = A_{ii} e^{-\frac{E_{ii}}{T_s}} \qquad i = 1 - 5$$

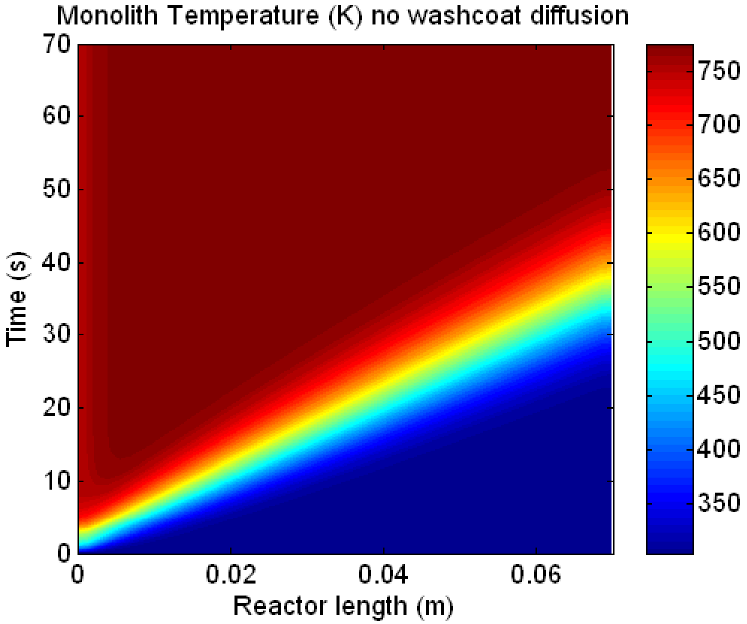
Monolith Temperature

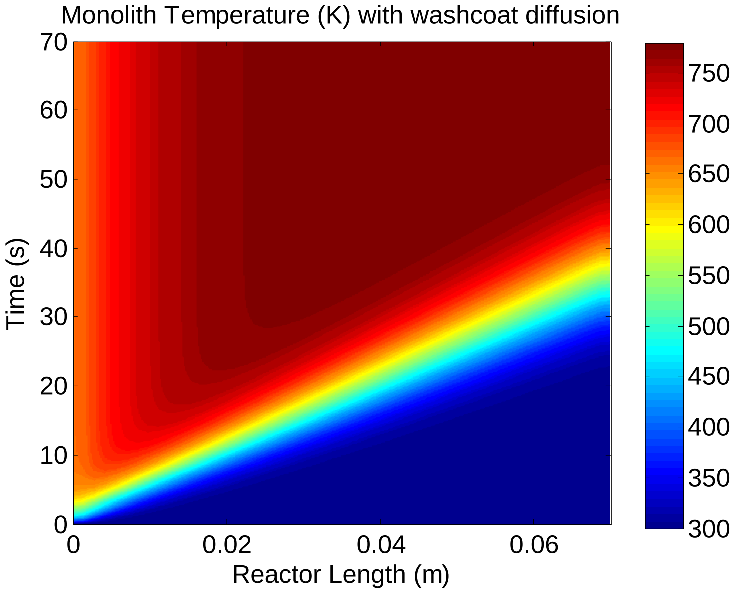


COMSOL SOLUTION



LOW-D MODEL SOLUTION





Transient simulation showing front end ignition (a) monolith temperature without washcoat diffusion (b) monolith temperature with washcoat diffusion

Table : Cumulative emissions

	With washcoat diffusion (g)	Washcoat diffusion neglected (g)
CO	1.0033	0.5646
HC	0.0743	0.0385
NOx	0.0166	0.0149

Summary/Conclusions

- ***The Liapunov-Schmidt Method is an excellent technique for model reduction.***

- ***Multi-mode averaged/coarse-grained models developed by the L-S method describe the system behavior qualitatively and quantitatively.***

- ***Transfer/exchange coefficient concept (hyperbolic) is more physical than dispersion coefficient (parabolic). Multi-mode form of the averaged models with transfer coefficient have a larger domain of validity.***

- ***Convergence of the reduced order models depends on the spatio-temporal frequencies present in the inlet/initial conditions.***

- ***Whenever the local equation/expansion of the L-S method fails to converge, patterned solutions with fine scale structure exist.***

References: (i) Balakotaiah & Chakraborty; Chem. Engng. Sci.,57,2545(2002)
(ii) Balakotaiah & Chang; SIAM J. Appl. Math.,63,1231(2003)
(iii) Chakraborty and Balakotaiah, Advances in Chem. Engng., 2005, Academic Press
(iv) Balakotaiah and Chang, "Applied Nonlinear Methods for Engineers", CUP, 2009