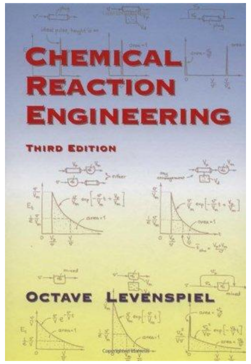
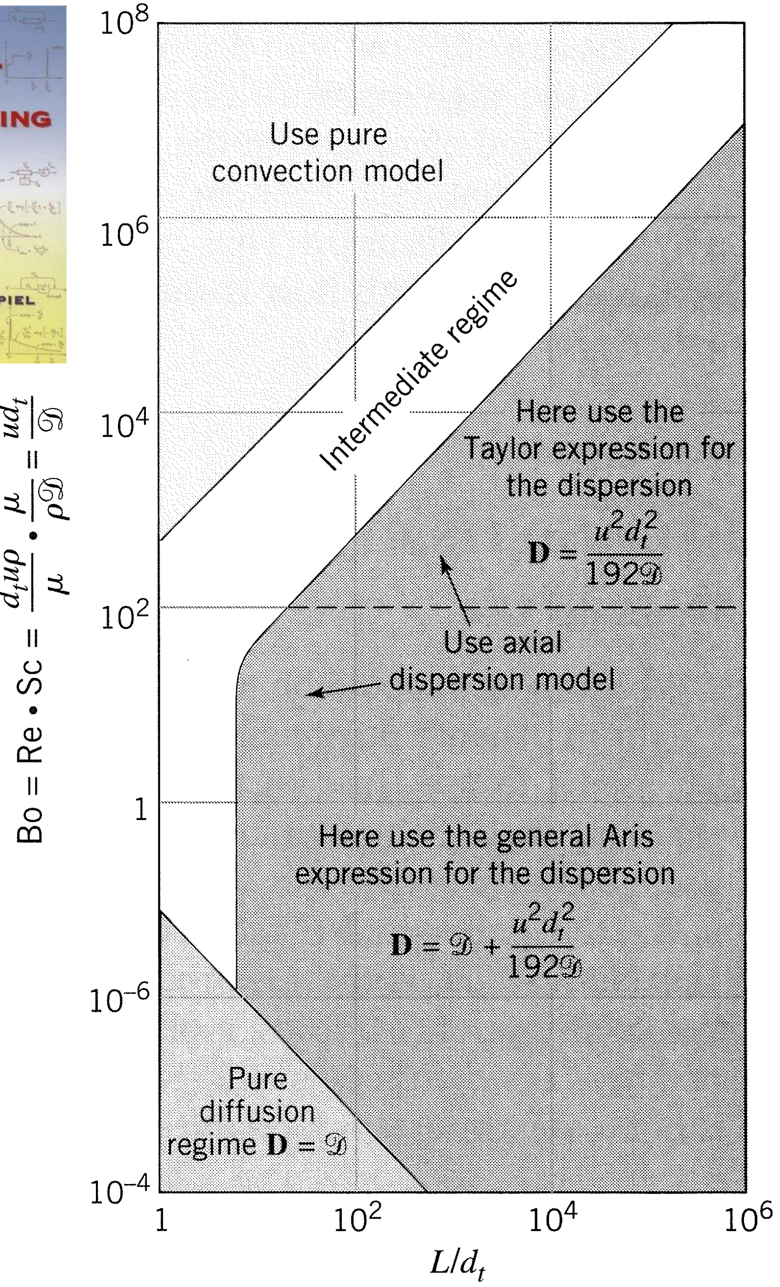




Analytical modelling of solute dispersion in laminar flow

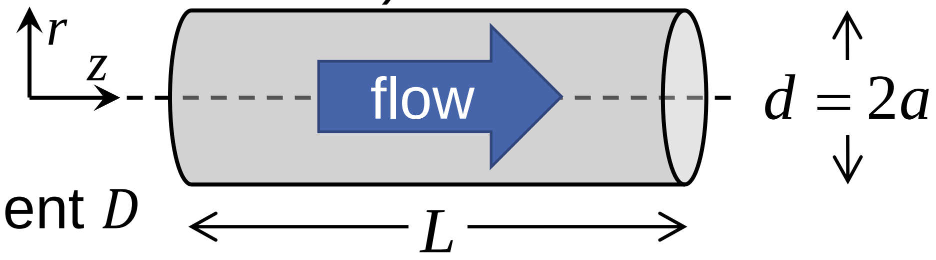
Bridging the gap between pure convection and axial dispersion regimes

Dr.-Ing. Martin Wörner
Karlsruhe Institute of Technology (KIT)
Institute of Catalysis Research and Technology (IKFT)

IMRET-17 | October 27-30, 2024 | Graz, Austria

Dispersion in laminar liquid flow

- Examples where dispersion in laminar flow is important
  - Flow chemistry[1] in milli- and micro reactors
  - Continuous production of nano-materials[2], continuous-flow polymerization[3]
  - Continuous thermal processing of food[4], continuous virus inactivation ...
  - Dispersion/macromixing is characterized by the Residence Time Distribution
- Non-dimensional parameters for solute dispersion in laminar pipe flow
  - Pipe radius a (diameter $d = 2a$)
  - Pipe length L
  - Mean velocity U
  - Diffusion coefficient D



Two dimensionless groups
- $\lambda = L/d$
- Peclet number $Pe = dU/D$

[1] M.B. Plutschack, B. Pieber, K. Gilmore, P.H. Seeberger, The Hitchhiker's Guide to Flow Chemistry, *Chemical Reviews* **117** (2017) 11796-11893
[2] P.R. Makgwane, S.S. Ray, Synthesis of nanomaterials by continuous-flow microfluidics: A review, *J. Nanoscience and Nanotechnology* **14** (2014) 1338-1363
[3] M.H. Reis, T.P. Varner, F.A. Leibfarth, The influence of residence time distribution on continuous-flow polymerization, *Macromolecules* **52** (2019) 3551-3557
[4] A.P. Torres, F.A.R. Oliveira, Residence time distribution studies in continuous thermal processing of liquid foods: a review, *J. Food Eng.* **36** (1998) 1-30

Competition of two time scales

- Dispersion arises from the combined action of convection and diffusion
  - Time scale of longitudinal convection (space time) $\tau_s = L / U$
  - Time scale of transversal diffusion $\tau_d = a^2 / D$

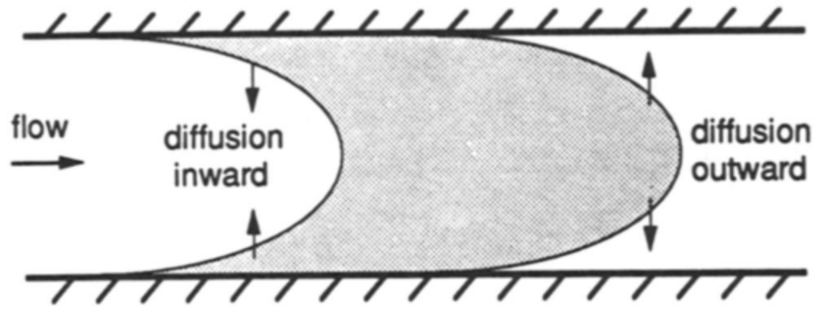
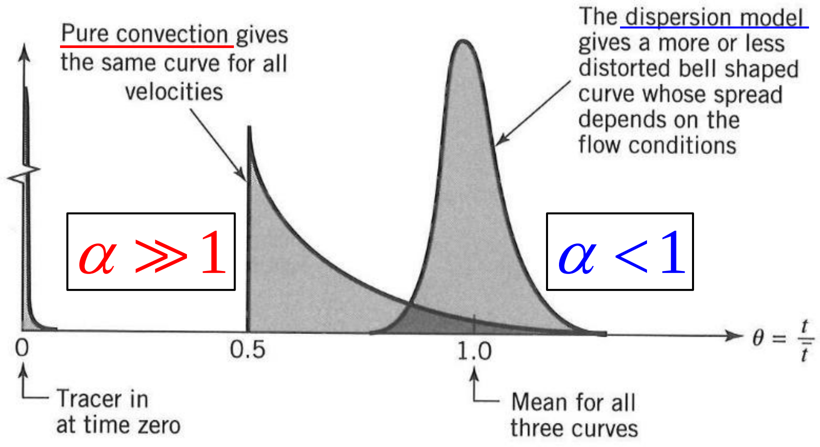


FIGURE 1. Schematic drawing of the shear-augmented dispersion of a bolus in fully developed steady flow.

Image credit: Sharp[5]



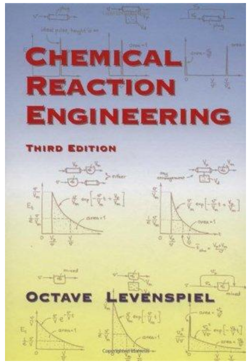
- Solvent: skewed "pure convection" RTD
- Solute: RTD depends on ratio of both time scales

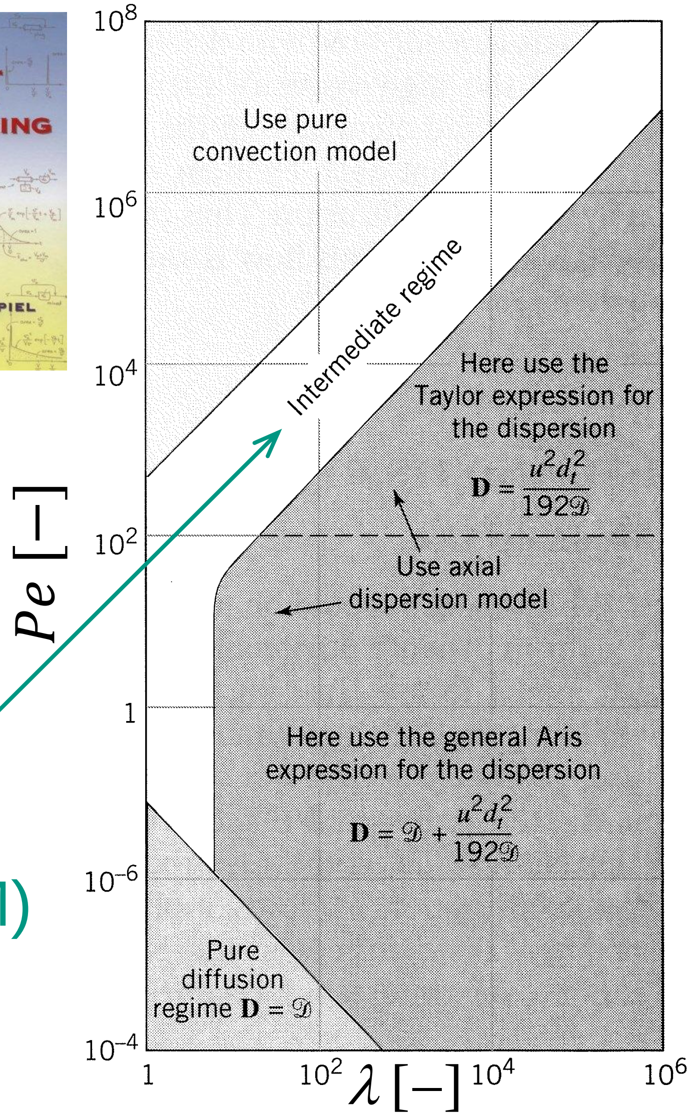
$$\alpha = \frac{\tau_d}{\tau_s} = \frac{a^2 U}{LD} = \frac{Pe}{4\lambda}$$

[5] M.K. Sharp, Shear-augmented dispersion in non-Newtonian fluids, *Annals of Biomedical Engineering* **21** (1993) 407-415

Map of dispersion regimes[6,7]

- Octave Levenspiel[6]:
  “*If your system falls in the no-man’s land between regimes, calculate the reactor behavior based on the two bounding regimes and then try averaging.*”
- OL gives no advice how to average RTDs in practice
  - Linear interpolation[8] is not suitable here
  - Interpolation method of Bursal[9] is only for RTDs with finite variance; variance of PC RTD is infinite
- Strong need for a RTD-model for intermediate regime (IM) (or transition regime TR)

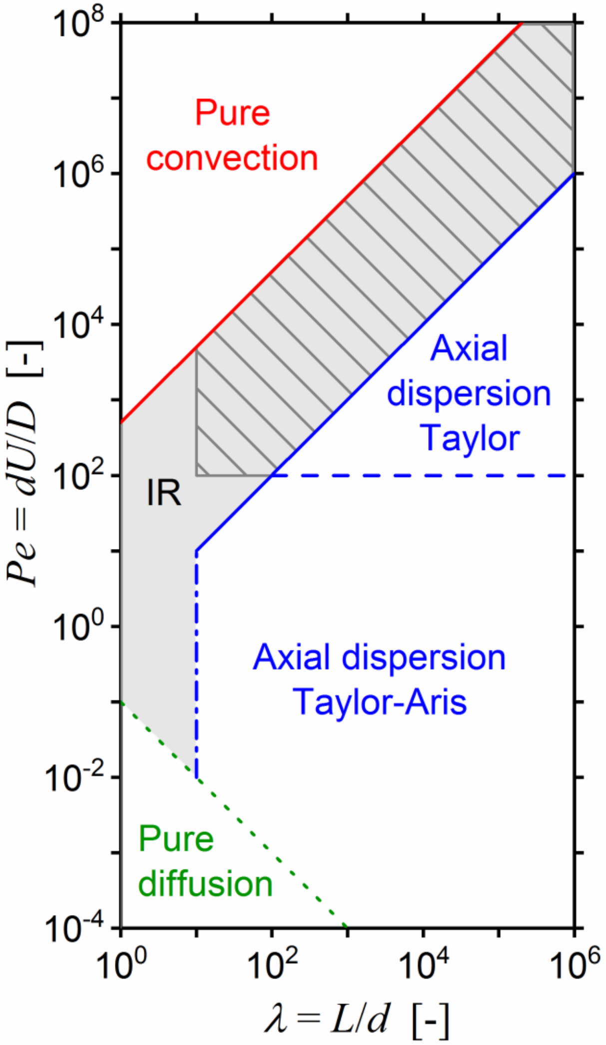




[6] O. Levenspiel, Chemical Reaction Engineering, 3rd ed., John Wiley & Sons, Hoboken, NJ, 1999
[7] V. Ananthakrishnan, W.N. Gill, A.J. Barduhn, Laminar Dispersion in Capillaries. I. Mathematical Analysis, *AIChE J.* **11** (1965) 1063-1072
[8] A.L. Read, Linear interpolation of histograms, *Nuclear Instruments and Methods in Physics Research A* **425** (1999) 357-360
[9] F.H. Bursal, On interpolating between probability distributions, *Applied Mathematics and Computation* **77** (1996) 213-244

Goal: model for RTD in intermediate regime

- Analytical approach for straight tube
  - Derive model from first principles
- Model shall be valid in hatched region
  - Fully developed velocity profile $\lambda \geq 10$
  - Taylor dispersion limit $Pe \geq 100$,
  - AD regime limit $\alpha = Pe/4\lambda \geq \alpha_{AD} = 0.25$
  - PC regime limit $\alpha = Pe/4\lambda \leq \alpha_{PC} = 125$
- Close and test model using RTD data from literature

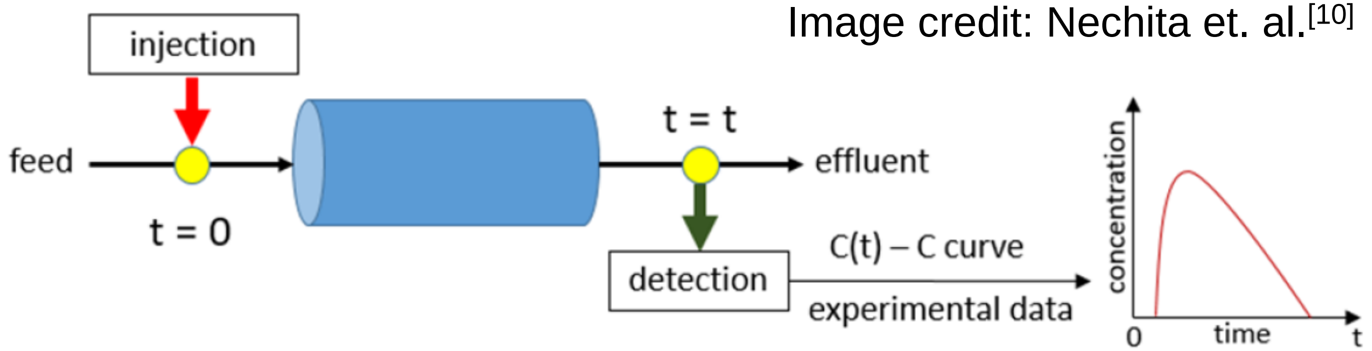


Measurement of RTD by tracer techniques

KIT Karlsruhe Institute of Technology

- Tracer injection at inlet
  - Pulse or step input
  - Tracer mass proportional to local flow rate at each point of the inlet plane (“injection in flow”)
- Tracer detection at outlet
  - “Mixing-cup” measurement (proportional to flow rate)
  - *C*-curve $c_{\text{cup}}(t)$
- Normalization yields RTD
  - *E*-curve $E(t)$
  - Mean and variance of RTD

Image credit: Nechita et. al.[10]



$$E(t) = \frac{c_{\text{cup}}(t)}{\int_0^\infty c_{\text{cup}}(t)\text{d}t} \rightarrow \int_0^\infty E(t)\text{d}t = 1$$

$$\bar{t}_E = \int_0^\infty t \cdot E(t)\text{d}t$$

$$\sigma_E^2 = \int_0^\infty (t - \bar{t}_E)^2 E(t)\text{d}t$$

In numerical simulation:

$$c_{\text{cup}}(t) = \frac{2}{a^2 U}\int_0^a \underbrace{c(r, z = L, t)}_{=c_{\text{outlet}}} \cdot u(r) \cdot r \cdot \text{d}r$$

“Mixing-cup measurement”

[10] M.T. Nechita, G.D. Suditu, A.C. Puitel, E.N. Dragoi, Residence time distribution: Literature survey, functions, mathematical modeling, and case study-diagnosis for a photochemical reactor, *Processes* **11** (2023) 3420

Solute concentration equation

Karlsruhe Institute of Technology

- Convection-diffusion equation for concentration of a passive tracer

$$\frac{\partial c}{\partial t} + \underbrace{2U\left(1-\frac{r^2}{a^2}\right)}_{=u(r)}\frac{\partial c}{\partial z} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)+\frac{\partial^2 c}{\partial z^2}\right]$$

$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0 \quad \text{symmetry b.c.} \qquad \left.\frac{\partial c}{\partial r}\right|_{r=a} = 0 \quad \text{impermeable wall}$$

- No general practical analytical solution is known for $c = c(z,r,t)$
- Solutions for special cases[11,12,13]
  - Solution for $D = 0$ $\quad c_{t=0} = c_{\text{ref}} f(z,r) \rightarrow c(z,r,t>0) = c_{\text{ref}} f(z-u(r)\cdot t, r) \quad c_{\text{ref}} = \frac{m_{\text{tracer}}}{\pi a^2 L}$
  - Asymptotic solution for sufficiently long tubes $L \gg Ua^2/D$ ($\rightarrow$ AD regime)

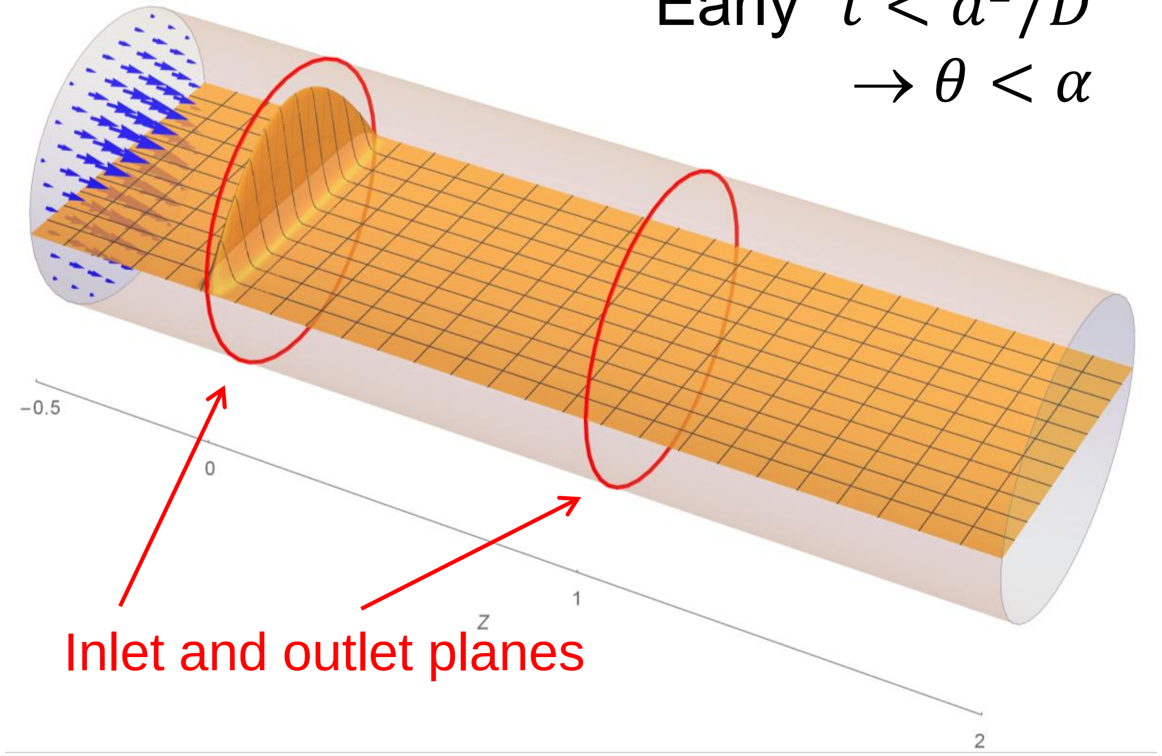
$$c(z,t) = \frac{m_{\text{tracer}}}{Q}\frac{z}{\sqrt{4\pi D_{\text{ax}} t}}\cdot\exp\left(-\frac{(z-U\cdot t)^2}{4D_{\text{ax}}t}\right) \neq c(r) \qquad D_{\text{ax}} = D + \frac{a^2U^2}{48D} = D\left(1+\frac{Pe^2}{192}\right)$$

[11] G.I. Taylor, Dispersion of soluble matter in solvent flowing slowly through a tube, *Proc. Royal Society of London A* **219** (1953) 186-203
[12] R. Aris, On the dispersion of a solute in a fluid flowing through a tube, *Proc. Royal Society of London A* **235** (1956) 67-77
[13] O. Levenspiel, W.K. Smith, Notes on the diffusion-type model for the longitudinal mixing of fluids in flow, *Chem. Eng. Sci.* **6** (1957) 227-233

Two limiting regimes treated by Taylor[11]

"Early" $t < a^2/D$

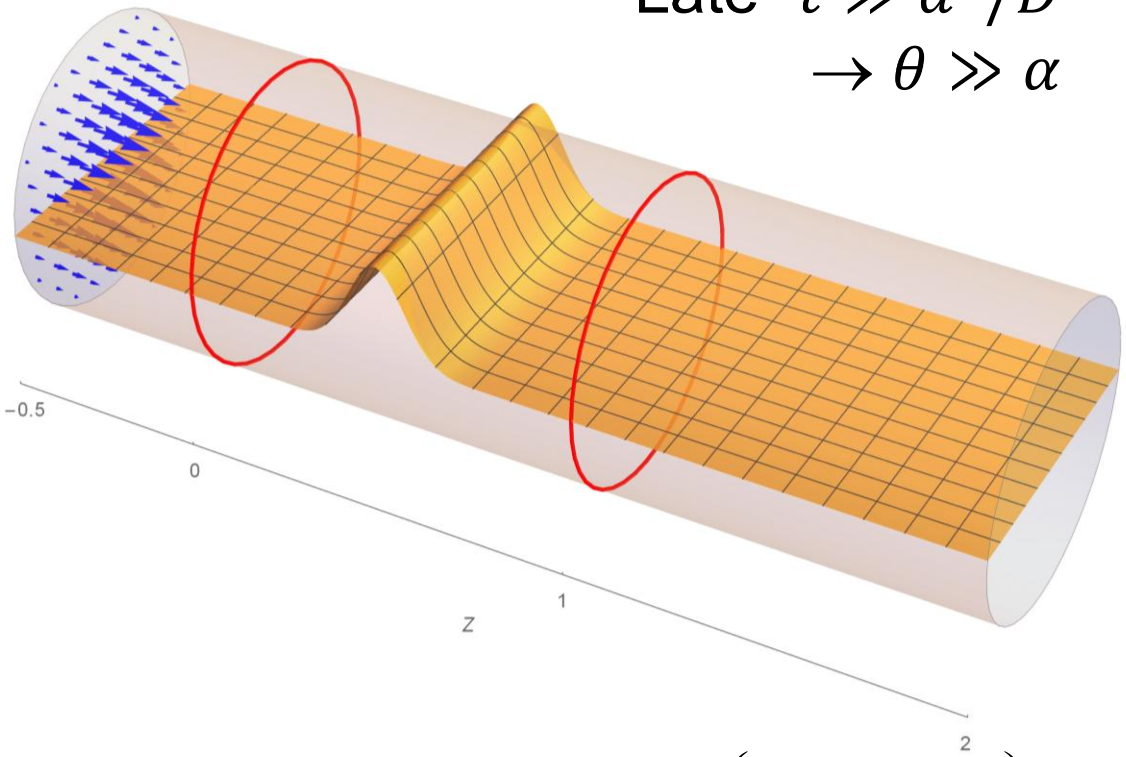
$\rightarrow \theta < \alpha$



$$\frac{c_{t=0}}{c_{\mathrm{ref}}} = u(r)\delta_{\varepsilon}(z) \quad \rightarrow \quad \frac{c(z,r,t>0)}{c_{\mathrm{ref}}} = u(r)\delta_{\varepsilon}(z-u(r)\cdot t)$$

"Late" $t \gg a^2/D$

$\rightarrow \theta \gg \alpha$



$$\frac{c(z,t)}{c_{\mathrm{ref}}} = \frac{L}{U}\frac{z}{\sqrt{4\pi D_{\mathrm{ax}} t}} \cdot \exp\left(-\frac{(z-U\cdot t)^2}{4D_{\mathrm{ax}}t}\right)$$

[11] G.I. Taylor, Dispersion of soluble matter in solvent flowing slowly through a tube, *Proc. Royal Society of London A* **219** (1953) 186-203

Normalized solute concentration equation

Karlsruhe Institute of Technology

- Normalization

$$C = \frac{c}{c_{\mathrm{ref}}} \qquad \theta = \frac{t}{\tau_{\mathrm{s}}} \qquad R = \frac{r}{a} \qquad Z = \frac{z}{L}$$

$\rightarrow$ inlet $Z = 0$, outlet $Z = 1$

- Non-dimensional convection-diffusion equation

$$\frac{\partial C}{\partial \theta} + \underbrace{2(1-R^2)}_{=V(R)} \frac{\partial C}{\partial Z} = \frac{1}{\alpha}\frac{1}{R}\frac{\partial}{\partial R}\left(R\frac{\partial C}{\partial R}\right)$$

$$\alpha = \frac{\tau_{\mathrm{d}}}{\tau_{\mathrm{s}}} = \frac{Pe}{4\lambda}$$

Longitudinal molecular diffusion is neglected

Bodenstein number

$$\rightarrow Bo = \frac{LU}{D_{\mathrm{ax}}} \approx \frac{48}{\alpha}$$

- Pure convection ($D = 0$) $\rightarrow$ RTD can be computed from given velocity profile[14]

$$\alpha = \frac{\tau_{\mathrm{d}}}{\tau_{\mathrm{s}}} \rightarrow \infty$$

$$\frac{\partial C}{\partial \theta} + V(R)\frac{\partial C}{\partial Z} = 0$$

$$E_\theta(\theta) = \begin{cases} 0 & \theta < 0.5 \\ \dfrac{1}{2\theta^3} & \theta \geq 0.5 \end{cases}$$

PC RTD is parameter-free and scale-invariant

[14] M. Wörner, General pure convection residence time distribution theory of fully developed laminar flows in straight planar and axisymmetric channels, *Chem. Eng. Sci.* **122** (2015) 555-564

Strategy for model development

- Novel approach for Mechanistic Transition Regime (MTR) model
  - Determine an approximate outlet concentration for the pure convection (PC) regime (CD = Convection Dominated regime)
  - Combine outlet concentrations of CD and AD regimes with two free parameters to obtain an assumed outlet concentration field for the transition regime (TR)
  - Choose assumed outlet concentration field so that RTD, mean and variance can all be computed analytically (mathematical relations on next slide) $\rightarrow$ unclosed model
- Close model by fixing the two free parameters
  - In the limits the TR RTD should agree with those of the PC and AD regimes
  - Establish relation between the two free parameters by mean value of unclosed RTD
  - Determine model parameters by comparison with numerical RTD data from literature

Computation of RTD for Poiseuille flow

Karlsruhe Institute of Technology

$$c_{\text{cup}}(t) = \frac{2}{a^2}\int_0^a \underbrace{c(r, z = L, t)}_{= c_{\text{outlet}}} \cdot \frac{u(r)}{U} \cdot r \cdot \mathrm{d}r$$

Substitution $r \rightarrow V$

$$\frac{u(r)}{U} = 2\left(1 - \frac{r^2}{a^2}\right) = V$$

$$C_{\text{cup}}(\theta) = \frac{1}{2}\int_0^2 C_{\text{outlet}}(\theta \mid V) \cdot V \cdot \mathrm{d}V$$

V acts as dummy variable

$$E_\theta(\theta) = \tau_s E(t) = \frac{C_{\text{cup}}(\theta)}{\int_0^\infty C_{\text{cup}} \cdot \mathrm{d}\theta} = \frac{C_{\text{cup}}(\theta)}{M_0}$$

$$\bar{\theta}_{E_\theta} = \frac{\bar{t}_E}{\tau_s} = \int_0^\infty E_\theta \cdot \theta \cdot \mathrm{d}\theta = \frac{M_1}{M_0}$$

$$\sigma_\theta^2 = \frac{\sigma_E^2}{\tau_s^2} = \int_0^\infty E_\theta \cdot (\theta - \bar{\theta}_{E_\theta})^2 \cdot \mathrm{d}\theta = \frac{M_2}{M_0} - \frac{M_1^2}{M_0^2}$$

$$M_0 = \int_0^\infty C_{\text{cup}} \cdot \theta^0 \cdot \mathrm{d}\theta = \frac{1}{2}\int_0^2 \left\{\int_0^\infty C_{\text{outlet}}(\theta \mid V) \cdot \theta^0 \cdot \mathrm{d}\theta\right\} \cdot V \cdot \mathrm{d}V$$

$$M_1 = \int_0^\infty C_{\text{cup}} \cdot \theta^1 \cdot \mathrm{d}\theta = \frac{1}{2}\int_0^2 \left\{\int_0^\infty C_{\text{outlet}}(\theta \mid V) \cdot \theta^1 \cdot \mathrm{d}\theta\right\} \cdot V \cdot \mathrm{d}V$$

$$M_2 = \int_0^\infty C_{\text{cup}} \cdot \theta^2 \cdot \mathrm{d}\theta = \frac{1}{2}\int_0^2 \left\{\int_0^\infty C_{\text{outlet}}(\theta \mid V) \cdot \theta^2 \cdot \mathrm{d}\theta\right\} \cdot V \cdot \mathrm{d}V$$

WOLFRAM MATHEMATICA

Convection Dominated outlet concentration

- Make scale-invariant pure convection (PC) RTD scale dependent → CD RTD
- Replace spatial delta function by regularized version ($\varepsilon > 0$) $\quad \delta(z) \;\rightarrow\; \delta_\varepsilon(z\,|\,\varepsilon)$

$$\frac{\partial C}{\partial \theta} + V\frac{\partial C}{\partial Z} = 0 \qquad c(r,z,t=0\,|\,\varepsilon) = \frac{m}{A}\frac{u(r)}{U}\underbrace{\frac{1}{\varepsilon\sqrt{\pi}}\exp\left(-\frac{z^2}{\varepsilon^2}\right)}_{=\delta_\varepsilon(z|\varepsilon)} \qquad \varepsilon = \frac{4\lambda^2 D}{U} \ll 1$$

small length scale

$$C_{\text{outlet}}^{\text{CD}}(\theta\,|\,V,\alpha) \approx \frac{\alpha\cdot V}{\sqrt{\pi\theta}}\cdot\exp\left[-\alpha^2\frac{(1-V\theta)^2}{\theta}\right] \qquad \int_0^\infty C_{\text{cup}}^{\text{CD}}\cdot d\theta = 1 \;\checkmark$$

Entire injected tracer leaves the outlet plane for any value of α

$$E_\theta^{\text{CD}}(\theta\,|\,\alpha) = \frac{1}{2\theta^3}\cdot\left\{\frac{\sqrt{\theta}}{2\sqrt{\pi}\alpha}\left[\exp\left(-\frac{\alpha^2}{\theta}\right)-(1+2\theta)\cdot\exp\left(-\alpha^2\frac{(1-2\theta)^2}{\theta}\right)\right] + \frac{2\alpha^2+\theta}{4\alpha^2}\left[\operatorname{erf}\left(\frac{\alpha}{\sqrt{\theta}}\right)-\operatorname{erf}\left(\alpha\frac{1-2\theta}{\sqrt{\theta}}\right)\right]\right\}$$

$$\lim_{\alpha\to\infty} E_\theta^{\text{CD}}(\theta\,|\,\alpha) = \frac{H(0.5)}{2\theta^3} = E_\theta^{\text{PC}} \;\checkmark$$

MTR – <u>assumed</u> outlet concentration field

- Limiting cases (<u>A</u>xial <u>D</u>ispersion ↔ <u>C</u>onvection <u>D</u>ominated)

$$C_{\text{outlet}}^{\text{AD}}(\theta|\alpha) = \sqrt{\frac{12}{\pi\alpha\theta}} \cdot \exp\left[-\frac{12}{\alpha}\frac{(1-\theta)^2}{\theta}\right] \qquad p=0, \quad S=\frac{\alpha}{24}$$

$$C_{\text{outlet}}^{\text{CD}}(\theta|V,\alpha) = \frac{\alpha \cdot V}{\sqrt{\pi\theta}} \cdot \exp\left[-\alpha^2\frac{(1-V\theta)^2}{\theta}\right] \qquad p=1, \quad S=\frac{1}{2\alpha^2}$$

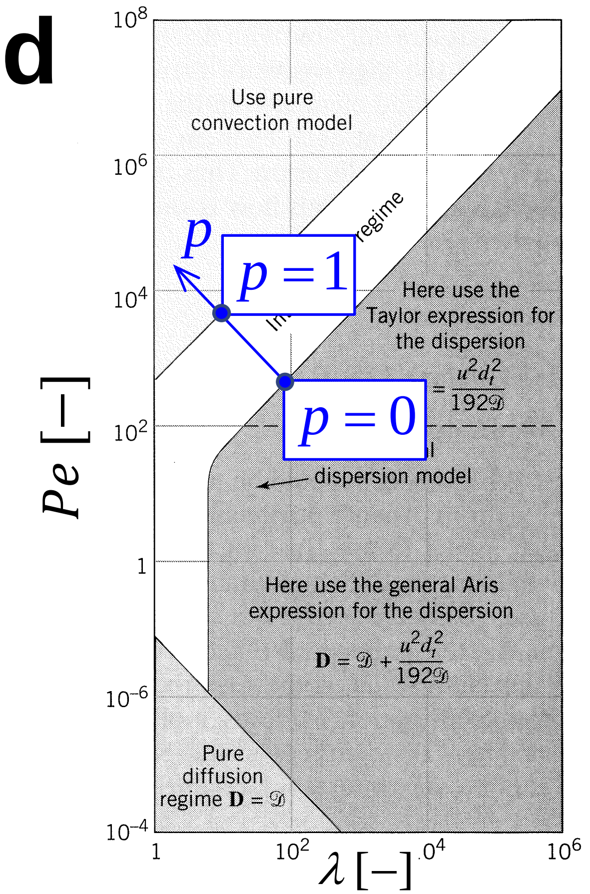
- Both cases are combined by introducing two parameters
  - $p(\alpha)$ models distance from AD and PC regimes
  - $S(\alpha)$ is a model parameter related to the variance
- Assumed $C_{\text{outlet}}^{\text{MTR}}$ enabling the <u>analytical calculation</u> of all integrals

$$C_{\text{outlet}}^{\text{MTR}}(\theta|V,p,S) = \frac{1-p+pV}{\sqrt{2\pi S\theta}} \cdot \exp\left\{-\frac{\left[1-\theta(1-p+pV)\right]^2}{2S\theta}\right\}$$

$$0 < p(\alpha) < 1$$
$$S(\alpha) > 0$$

$$\left.\frac{\partial C_{\text{outlet}}^{\text{MTR}}}{\partial R}\right|_{R=1} \neq 0$$

permeable wall



MTR model – tracer passing outlet plane

$$C_{\text{cup}}^{\text{MTR}}(\theta\,|\,p,S)=\frac{1}{2}\int_0^2 C_{\text{outlet}}^{\text{MTR}}(\theta\,|\,V,p,S)\cdot V\cdot \mathrm{d}V=\frac{1}{2}\int_0^2 \frac{V(1-p+pV)}{\sqrt{2\pi S\theta}}\cdot\exp\left\{-\frac{[1-\theta(1-p+pV)]^2}{2S\theta}\right\}\cdot\mathrm{d}V$$

$$\underbrace{\int_0^\infty C_{\text{cup}}^{\text{MTR}}\cdot\mathrm{d}\theta}_{=M_0^{\text{TR}}}=\frac{1}{2}\int_0^2 V\left\{\int_0^\infty C_{\text{outlet}}^{\text{MTR}}(\theta\,|\,V)\cdot\mathrm{d}\theta\right\}\cdot\mathrm{d}V$$

$$=\frac{1}{2}\int_0^2 V\cdot\underbrace{\left\{\int_0^\infty \frac{1-p+pV}{\sqrt{2\pi S\theta}}\cdot\exp\left\{-\frac{[(1-\theta(1-p+pV)]^2}{2S\theta}\right\}\cdot\mathrm{d}\theta\right\}}_{=1}\cdot\mathrm{d}V=1$$

✓

Entire injected tracer leaves the outlet plane for any value of p and S

$$E_\theta^{\text{MTR}}(\theta\,|\,p,S)=C_{\text{cup}}^{\text{MTR}}(\theta\,|\,p,S)=\frac{1}{2}\int_0^2 \frac{V(1-p+pV)}{\sqrt{2\pi S\theta}}\cdot\exp\left\{-\frac{[1-\theta(1-p+pV)]^2}{2S\theta}\right\}\cdot\mathrm{d}V$$

$$\bar{\theta}_{E_\theta^{\text{MTR}}}=\frac{1}{2}\int_0^2 V\cdot\frac{S+1-p+pV}{(1-p+pV)^2}\cdot\mathrm{d}V,\qquad M_2^{\text{MTR}}=\frac{1}{2}\int_0^2 V\,\frac{1+3S(1+S)-p(1-V)(2+3S)+p^2(1-V)^2}{(1-p+pV)^4}\cdot\mathrm{d}V$$

Unclosed RTD of transition regime (TR)

- Performing the integrations on the previous slide yields
  - Non-dimensional differential solute RTD

$$E_\theta^{\mathrm{MTR}}(\theta\,|\,p,S)=\underbrace{\frac{1}{2\theta^3}}_{E_\theta^{\mathrm{PC}}}\underbrace{\left\{\sqrt{\frac{S\theta}{2\pi}}\frac{\exp(-f_+^2)-(1+2p\theta)\exp(-f_-^2)}{p^2}+\left[1-\theta(1-p-S)\right]\frac{\mathrm{erf}(f_+)-\mathrm{erf}(f_-)}{2p^2}\right\}}_{\text{defines deviation of RTD in transition regime from RTD of pure convection regime}}$$

$$f_\pm=\frac{1-\theta\pm p\theta}{\sqrt{2S\theta}}$$

  - Non-dimensional MRT of solute

$$\bar{\theta}_{E_\theta^{\mathrm{MTR}}}(p,S)=\frac{1+p-S}{p+p^2}-\frac{1-p-S}{p^2}\mathrm{Arctanh}(p)$$

  - Non-dimensional variance of solute RTD

$$\sigma^2_{\theta,\mathrm{MTR}}(p,S)=\frac{\mathrm{Arctanh}(p)}{p^2}+\frac{3pS(1-p^2)+(3-p)pS^2-(1-p^2)^2}{p(1-p)^2(1+p)^3}-\left(\frac{1+p-S}{p+p^2}-\frac{1-p-S}{p^2}\mathrm{Arctanh}(p)\right)^2$$

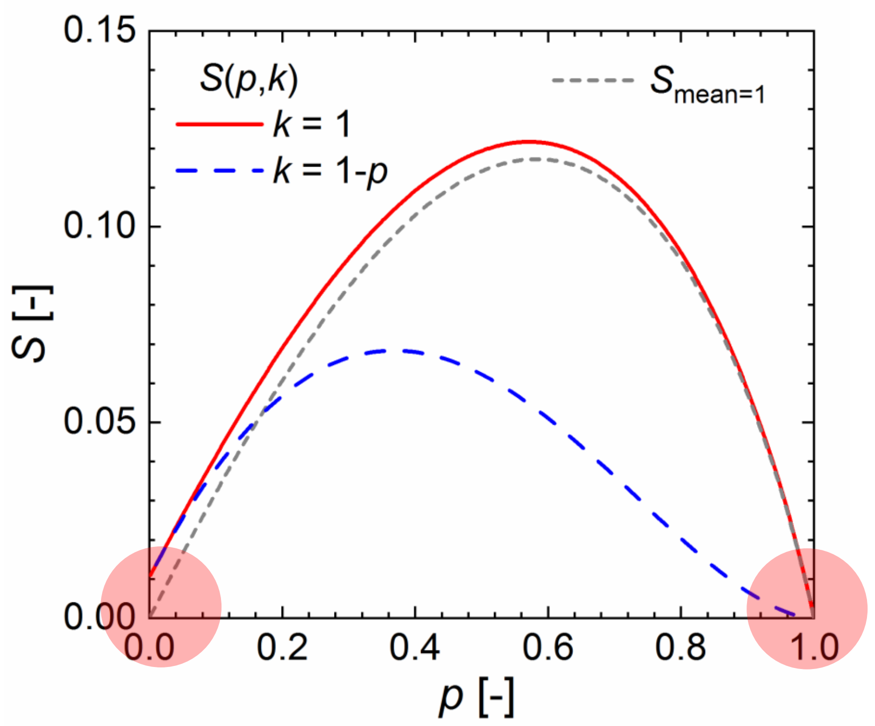
Determining the variance parameter $S(p)$

$$\bar{\theta}_{E_\theta^{TR}} \overset{!}{=} 1 \quad \rightarrow \quad S_{\text{mean}=1}(p) = \frac{(1-p^2)\left[\text{Arctanh}(p) - p\right]}{(1+p)\,\text{Arctanh}(p) - p}$$

$$\lim_{p\to 0} S_{\text{mean}=1}(p) = \lim_{p\to 1} S_{\text{mean}=1}(p) = 0$$

$$S(p=0) = \frac{\alpha_{AD}}{24} > 0, \quad S(p=1) = \frac{1}{2\alpha_{CD}^2} > 0$$

$$\alpha_{AD} = 0.25, \quad \alpha_{CD} = 125$$



$$S(p,k) = \frac{\alpha_{AD}}{24}(1-p) + \frac{p}{2\alpha_{CD}^2} + k \cdot \underbrace{\frac{(1-p^2)\left[\text{Arctanh}(p) - p\right]}{(1+p)\,\text{Arctanh}(p) - p}}_{S_{\text{mean}=1}} > 0$$

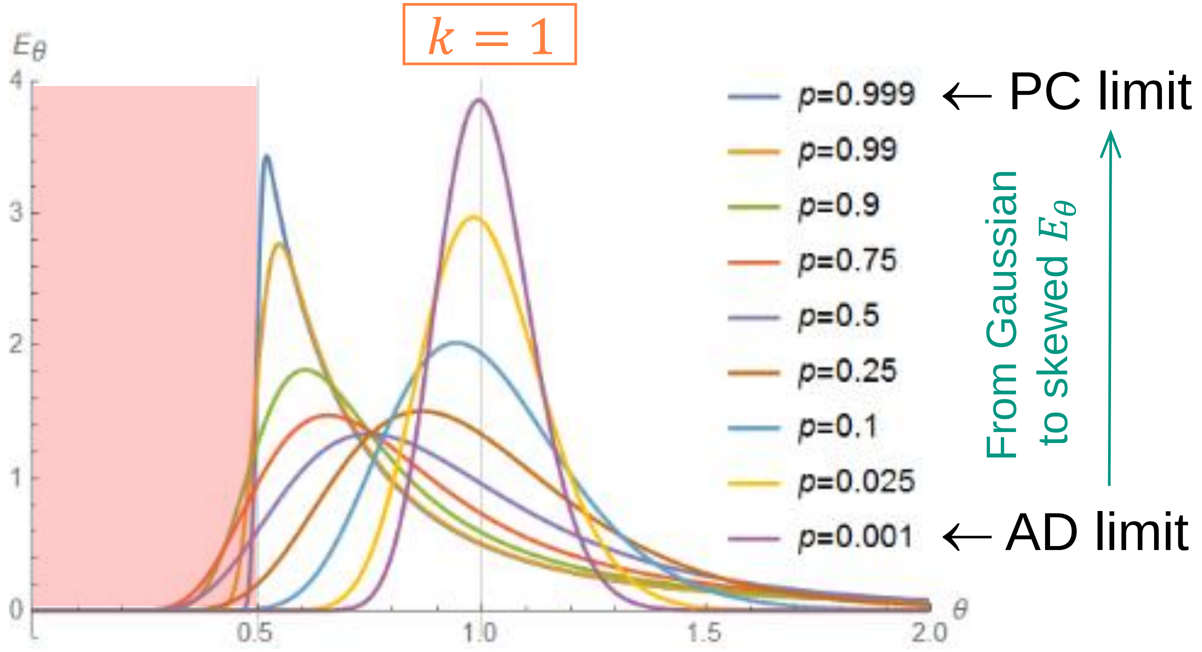
$$k \in \{1, 1-p\}$$

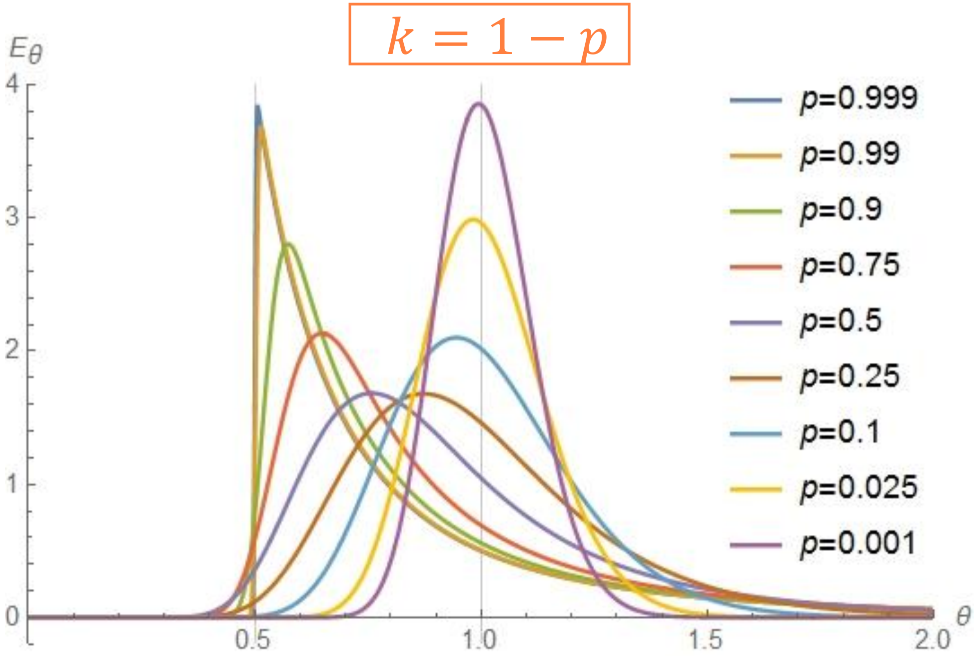
MTR closed in $S = S(p,k)$ but unclosed in p

$$E_\theta^{\mathrm{MTR}}(\theta \mid p) = \underbrace{\frac{1}{2\theta^3}}_{E_\theta^{\mathrm{PC}}} \underbrace{\left\{ \sqrt{\frac{S\theta}{2\pi}} \frac{\exp(-f_+^2) - (1+2p\theta)\exp(-f_-^2)}{p^2} + [1-\theta(1-p-S)] \frac{\mathrm{erf}(f_+) - \mathrm{erf}(f_-)}{2p^2} \right\}}_{\text{defines deviation of RTD in transition regime from RTD of pure convection regime}}$$

$$f_\pm = \frac{1-\theta \pm p\theta}{\sqrt{2S\theta}}$$

$$0 < p < 1$$





- Problem for $k = 1$: some solute is faster than the maximum solvent velocity (unphysical)
- Problem for $k = 1 - p$: mean solute RTD is less than 1 (but above 0.93) for $p \geq 0.2$

Simpler compartment model (→ dTiS model)

- Plug flow reactor (→ delay time) followed by cascade of Tanks-in-Series

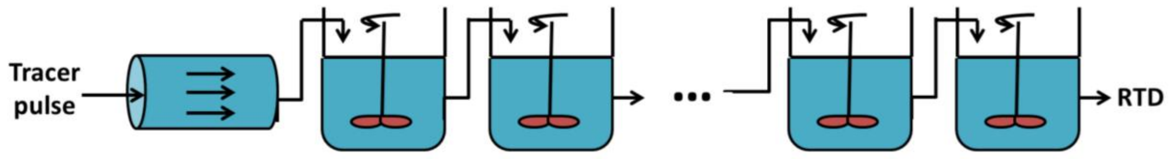


Image credit: Grimard et al.[16]

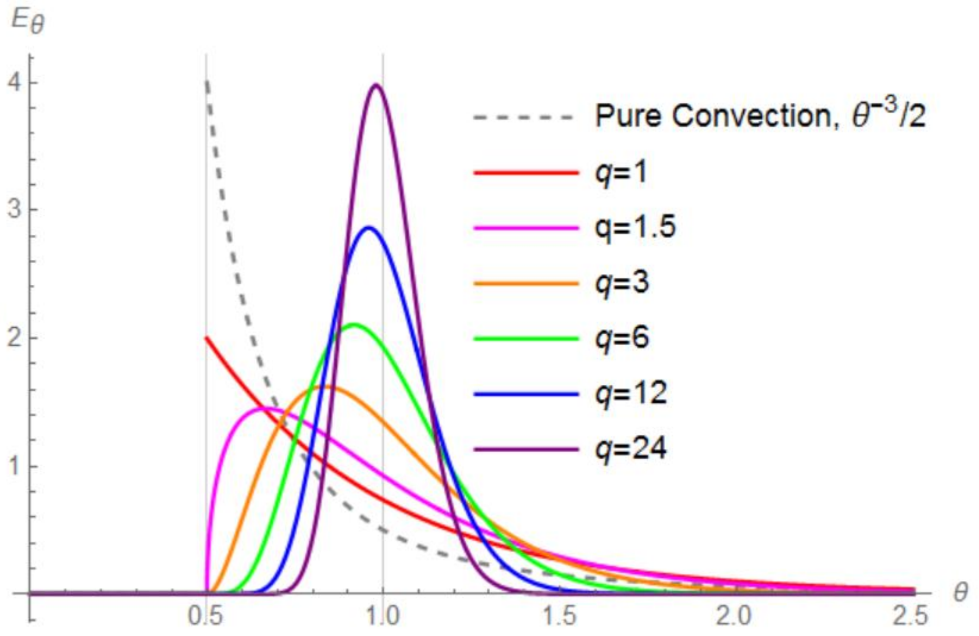
Compartment models are based on the combination of ideal PFR and CSTR arranged in different configurations

$$E_\theta^{\mathrm{dTiS}}(\theta\,|\,q)=\begin{cases}0 & \theta<0.5\\ \dfrac{2q}{\Gamma(q)}\left[q(2\theta-1)\right]^{q-1}\exp\left[-q(2\theta-1)\right] & \theta\geq 0.5\end{cases}$$

$$\bar{\theta}_{\mathrm{dTiS}}=1,\quad \sigma^2_{\theta,\mathrm{dTiS}}=(4q)^{-1},\quad q\in\mathbb{R},\quad q\geq 1$$

Novel model (unclosed)

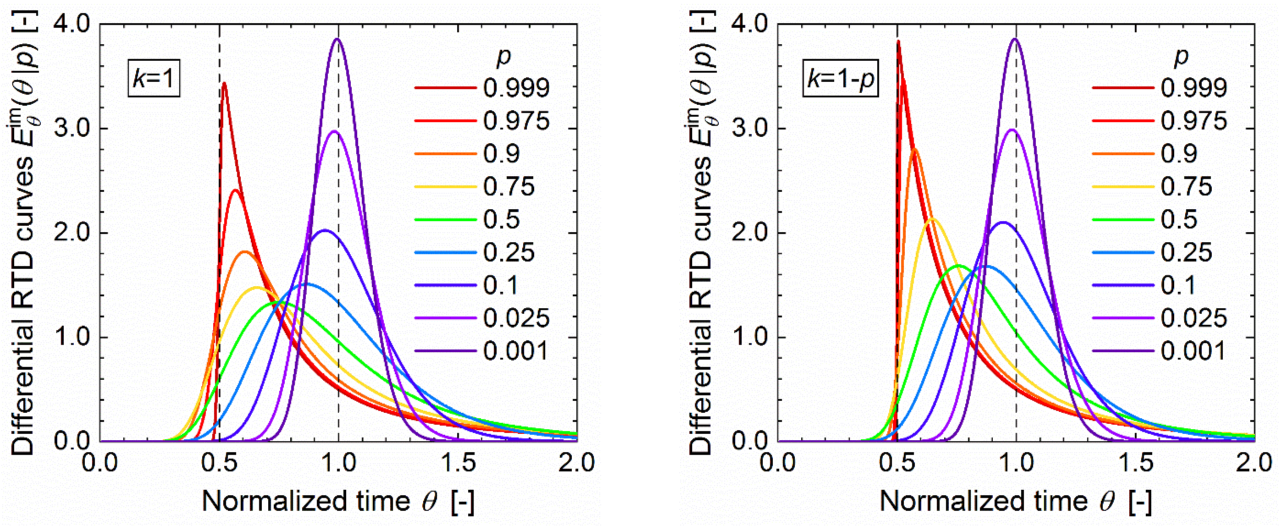
- Model with $q=1$ cannot fit the PC case
- Large q values fit axial dispersion case



[16] J. Grimard, L. Dewasme, A. Vande Wouwer, A review of dynamic models of hot-melt extrusion, *Processes* **4** (2016) 19

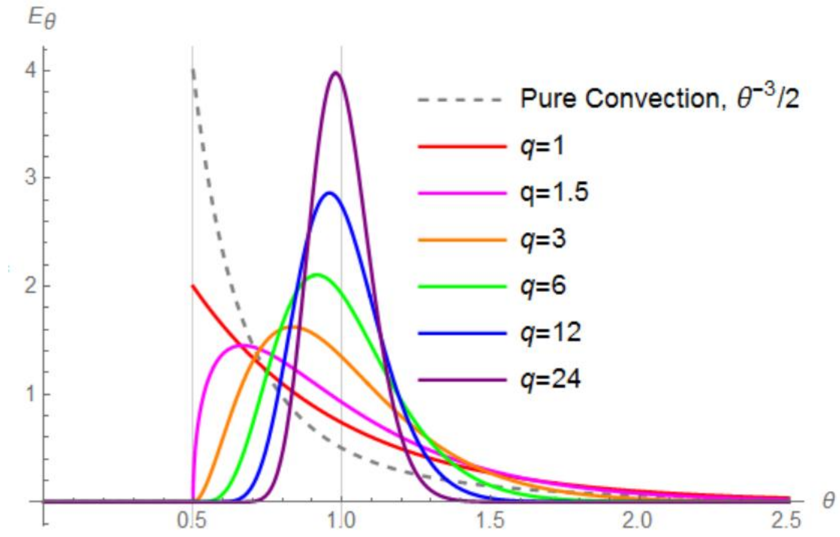
Three continuous families of RTD curves

Mechanistic transition regime (MTR) model



Free parameter $0 < p < 1$

Delayed tank-in-series model



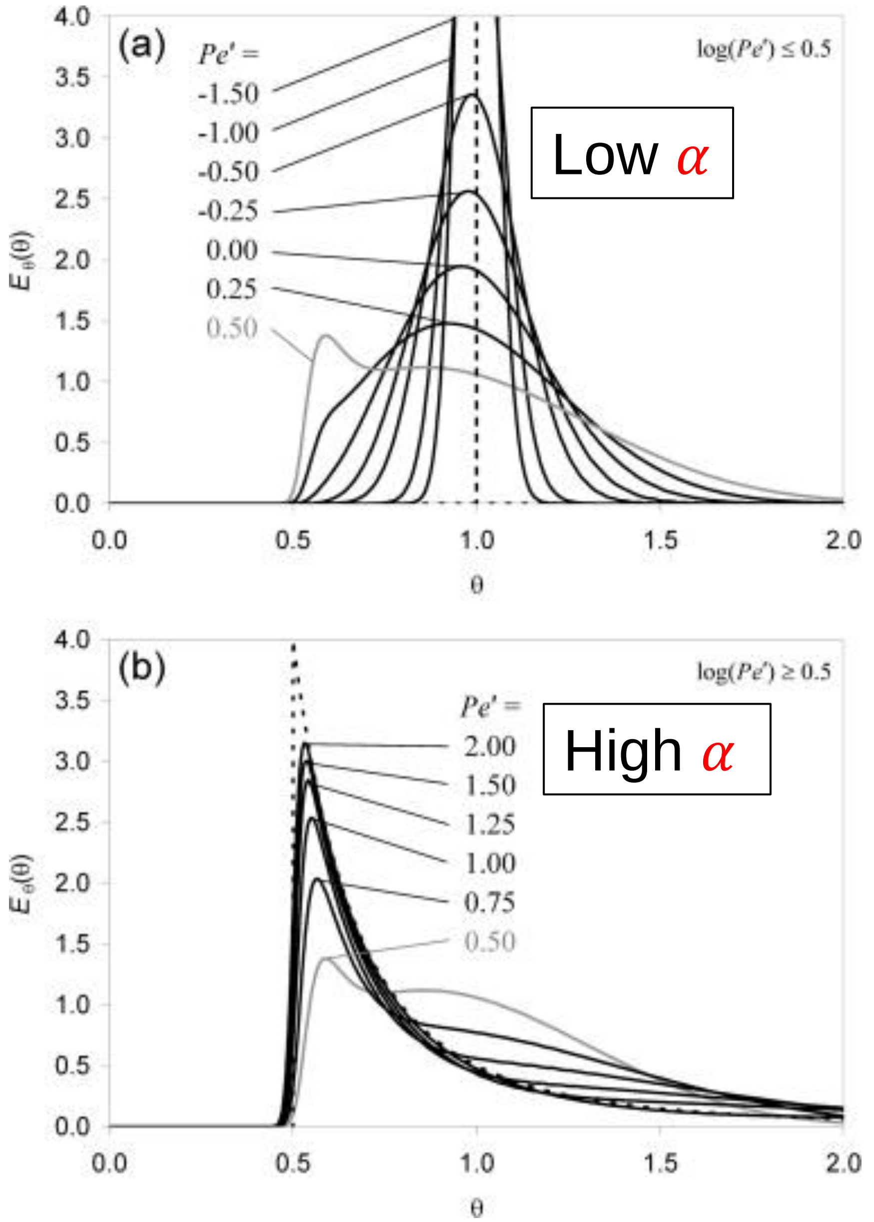
Free parameter $q \geq 1$

Closure by numerical RTD data[17]

- Advection-diffusion equation (dimensionless)

$$\frac{\partial C}{\partial \theta} + \underbrace{2(1-R^2)}_{=V(R)} \frac{\partial C}{\partial Z} = \underbrace{\frac{1}{Pe'}}_{\equiv \alpha} \frac{1}{R} \frac{\partial}{\partial R}\left(R \frac{\partial C}{\partial R} \right)$$

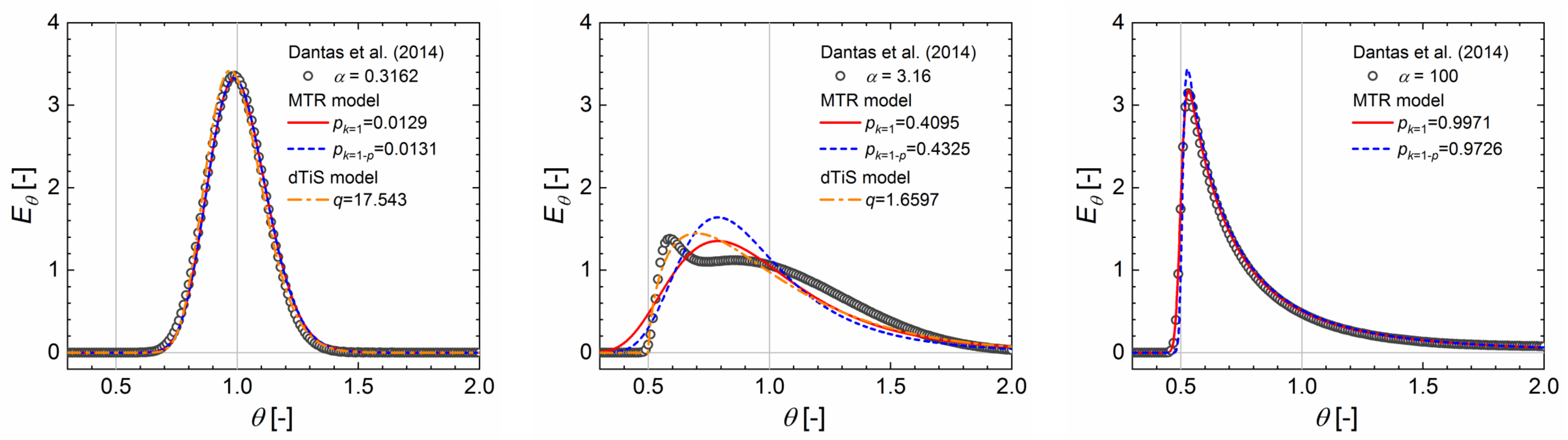
- Solution by finite difference method (1st order)
- Step input of tracer
- Evaluation of cumulative RTD $F(\theta)$
- Derivation yields differential RTD $E_\theta(\theta)$
- Parameter $Pe' \equiv \alpha$ is varried by four orders of magnitude $(0.032 - 316)$
- Special curve $\log Pe' = 0.50 \rightarrow \alpha = 3.16$



[17] J.A.T.A. Dantas, P.R. Pegoraro, J.A.W. Gut, *Int. J. Heat Mass Transf.* **71** (2014) 18-25

Determining model parameters p and q (1/3)

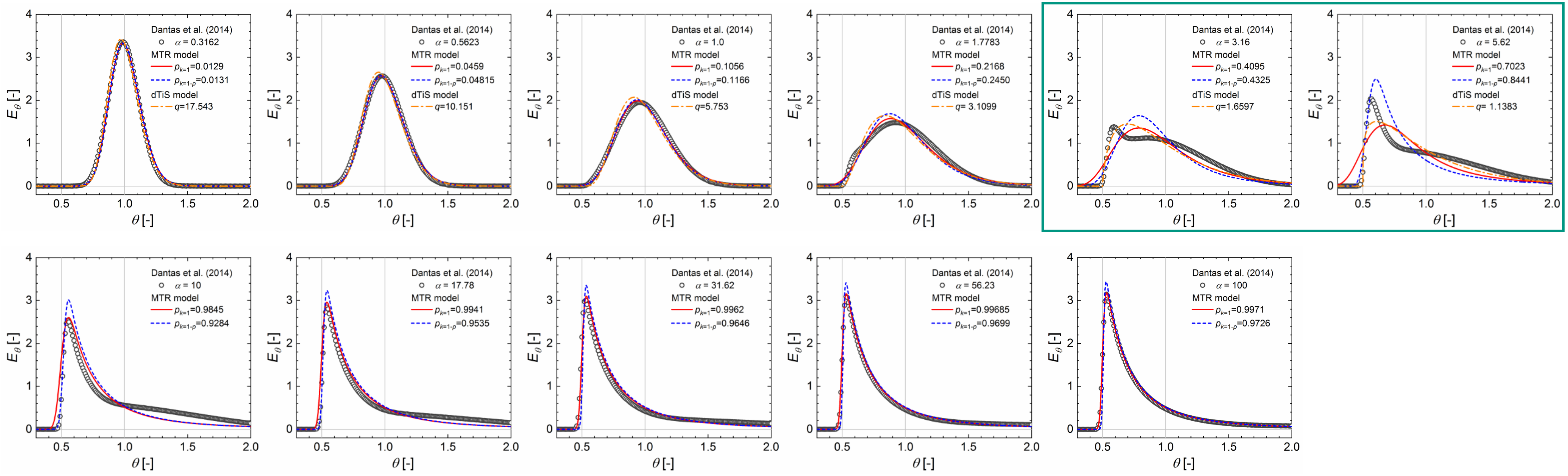
- Least-square fitting of numerical RTD data[17] (dots) by present models (lines)
- Eleven numerical values of α in range $0.3162 \leq \alpha \leq 100$



[17] J.A.T.A. Dantas, P.R. Pegoraro, J.A.W. Gut, Determination of the effective radial mass diffusivity in tubular reactors under non-Newtonian laminar flow using residence time distribution data, *Int. J. Heat Mass Transf.* **71** (2014) 18-25

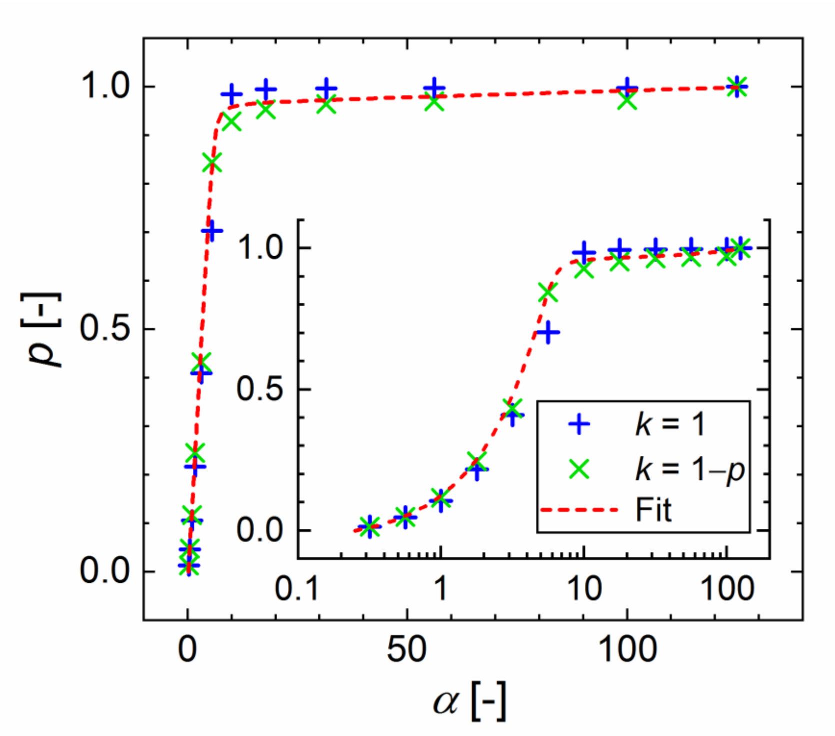
Determining model parameters p and q (2/3)

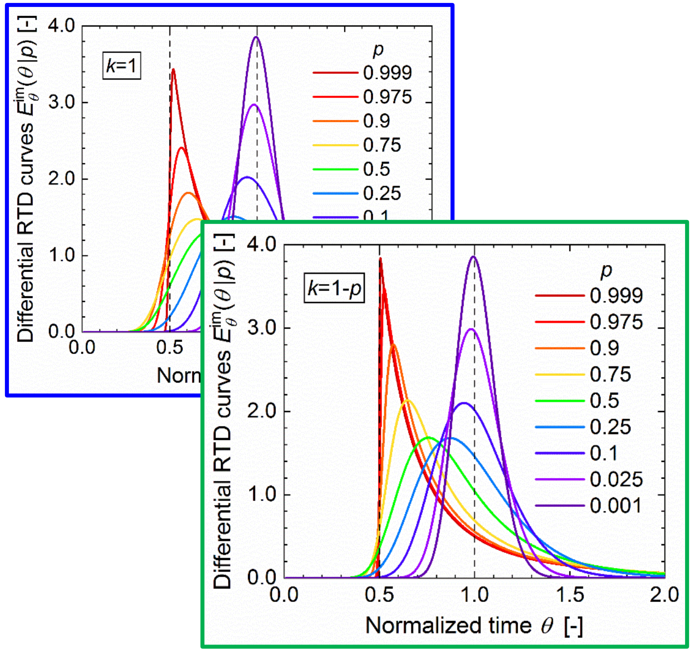
Karlsruhe Institute of Technology

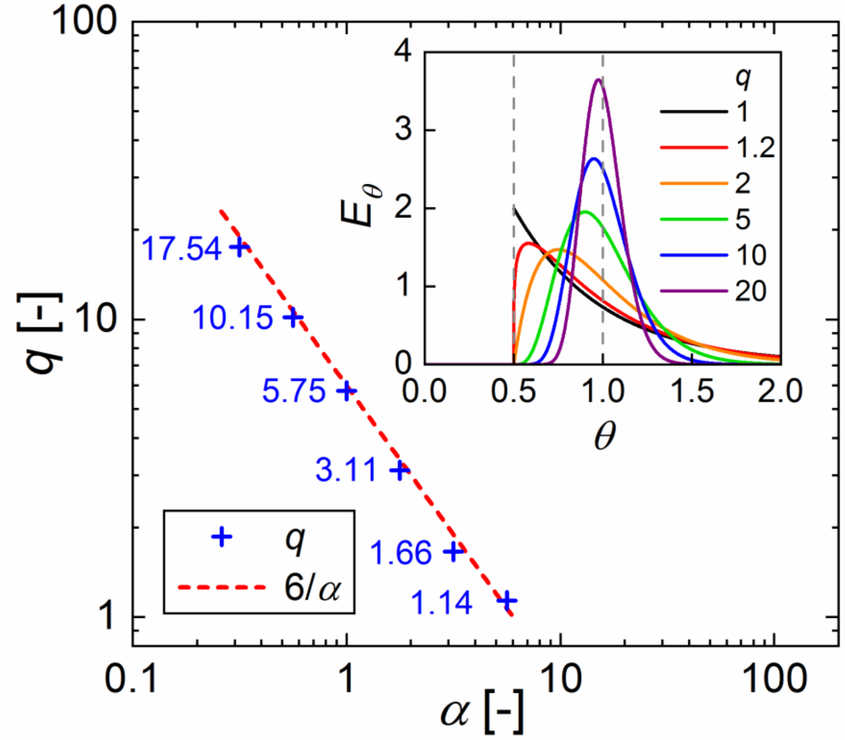


- In range $2 < \alpha < 8$ with plateau the present models don't fit the numerical data well
- Fitting yields eleven discrete values $p_i(\alpha_i)$ and six values $q_i(\alpha_i)$

Determining model parameters p and q (3/3)







$$p(\alpha) = \underbrace{\frac{125\sqrt{545} - \sqrt{14162} - 12}{5988}}_{\approx 0.4655} + \underbrace{\frac{48 + 4\sqrt{14162} - \sqrt{545}}{5988}}_{\approx 0.0836} \cdot \alpha - \frac{\sqrt{1 + (\alpha - 6)^2}}{12}$$

$$q(\alpha) = \frac{6}{\alpha}$$

- Relations $p(\alpha)$ and $q(\alpha)$ are monotonic but non-linear

Summary MTR model (valid for $0.25 < \alpha < 125$)

Karlsruhe Institute of Technology

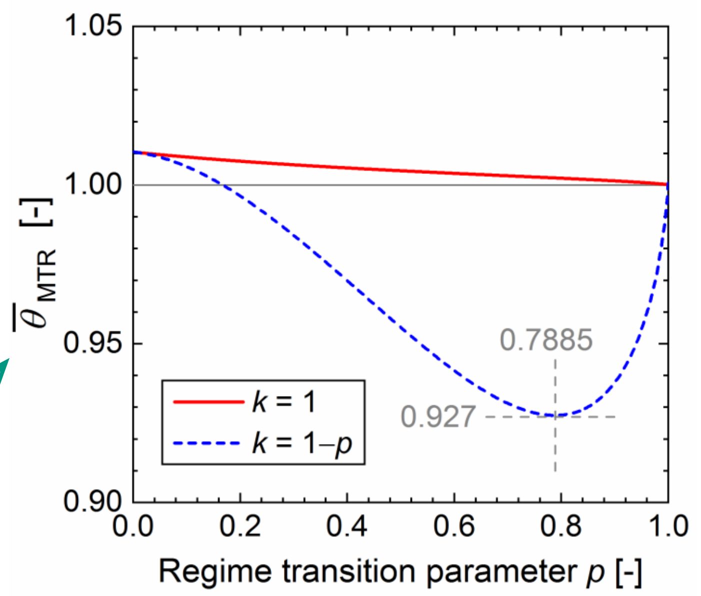
$$E_\theta^{\mathrm{MTR}}(\theta\,|\,p,S) = \frac{1}{2\theta^3}\left\{\sqrt{\frac{S\theta}{2\pi}}\frac{\exp(-f_+^2)-(1+2p\theta)\exp(-f_-^2)}{p^2} + \left[1-\theta(1-p-S)\right]\frac{\mathrm{erf}(f_+)-\mathrm{erf}(f_-)}{2p^2}\right\}$$

$$f_\pm = \frac{1-\theta \pm p\theta}{\sqrt{2S\theta}}$$

$$S(p,k) = \frac{1-p}{96} + \frac{p}{31250} + k\cdot\frac{(1-p^2)\left[\mathrm{Arctanh}(p)-p\right]}{(1+p)\,\mathrm{Arctanh}(p)-p}, \quad k\in\{1, 1-p\}$$

$$p(\alpha) = \underbrace{\frac{125\sqrt{545}-\sqrt{14162}-12}{5988}}_{\approx 0.4655} + \underbrace{\frac{48+4\sqrt{14162}-\sqrt{545}}{5988}}_{\approx 0.0836}\cdot\alpha - \frac{\sqrt{1+(\alpha-6)^2}}{12}$$

$$\overline{\theta}_{\mathrm{MTR}}(p,S) = \frac{1+p-S}{p+p^2} - \frac{1-p-S}{p^2}\mathrm{Arctanh}(p)$$



$$\sigma^2_{\theta,\mathrm{MTR}}(p,S) = \frac{\mathrm{Arctanh}(p)}{p^2} + \frac{3pS(1-p^2)+(3-p)pS^2-(1-p^2)^2}{p(1-p)^2(1+p)^3} - \left(\frac{1+p-S}{p+p^2} - \frac{1-p-S}{p^2}\mathrm{Arctanh}(p)\right)^2$$

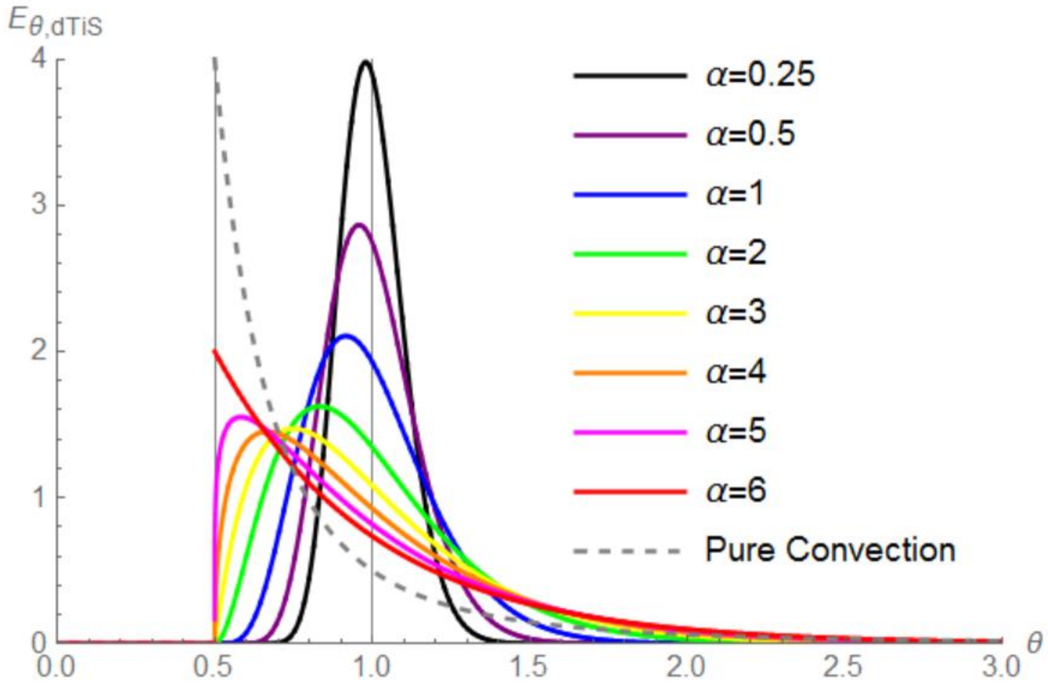
Summary dTiS model (valid for $0.25 \leq \alpha \leq 6$)

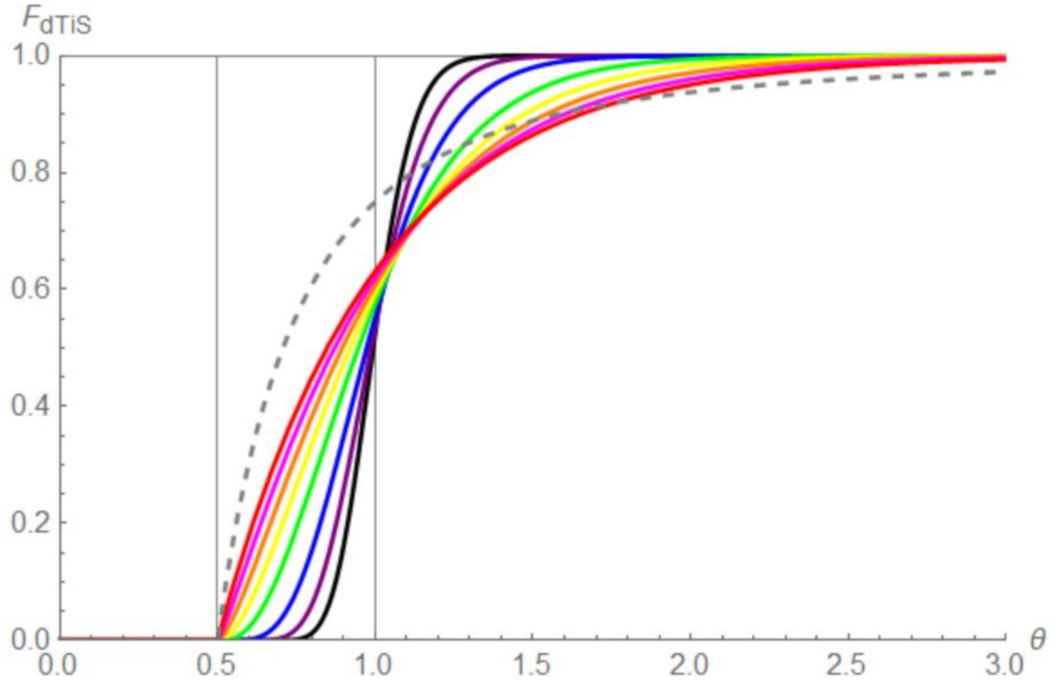
$$E_{\theta,\mathrm{dTiS}}(\theta\,|\,\alpha)=\frac{H(\theta-0.5)}{\Gamma(6/\alpha)}\cdot\frac{12}{\alpha}\cdot\left[\frac{6\cdot(2\theta-1)}{\alpha}\right]^{\frac{6-\alpha}{\alpha}}\cdot\exp\left[-\frac{6\cdot(2\theta-1)}{\alpha}\right]$$

$$F_{\mathrm{dTiS}}(\theta\,|\,\alpha)=H(\theta-0.5)\cdot\left[1-\frac{\Gamma(6/\alpha,6(2\theta-1)/\alpha)}{\Gamma(6/\alpha)}\right]$$

$$\bar{\theta}_{\mathrm{dTiS}}=1$$

$$\sigma^2_{\theta,\mathrm{dTiS}}=\frac{\alpha}{24}$$





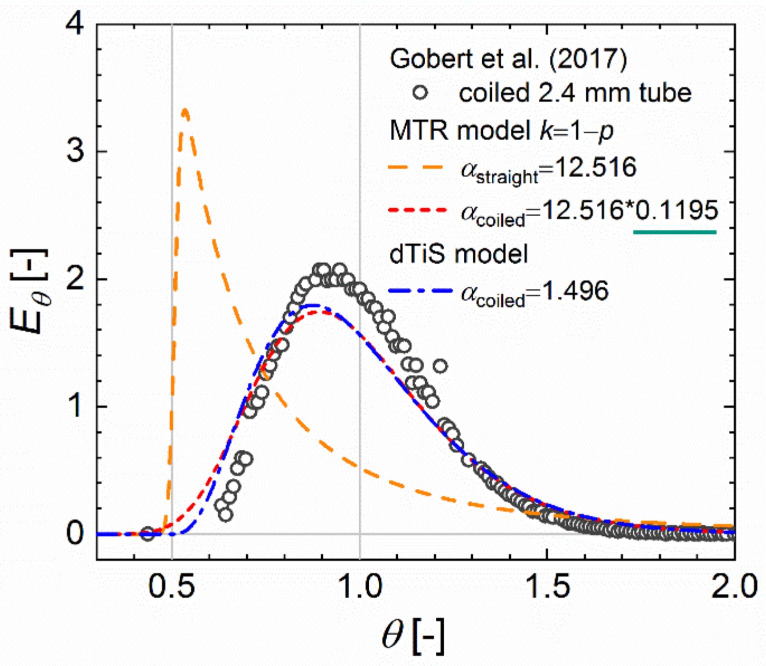
Model application on coiled tubes

- Dispersion regime map is for straight tubes
- Coiling reduces axial dispersion compared to straight tubes
- Correlation[18] for dispersion reduction factor κ, here applied to experimental RTD data of Gobert et al.[19] $(Dn = 11.3)$

$$\kappa = D_{\mathrm{ax,coiled}} / D_{\mathrm{ax,straight}}$$

$$\kappa^{-1} = 1 + 0.9415\left[\log_{10}(520 Dn^2) - 2\right]^{1.983}$$

$$E_\theta^{\mathrm{coiled}} = E_\theta^{\mathrm{MRT}}(\theta \mid \alpha_{\mathrm{coiled}} = \kappa \cdot \alpha_{\mathrm{straigth}})$$



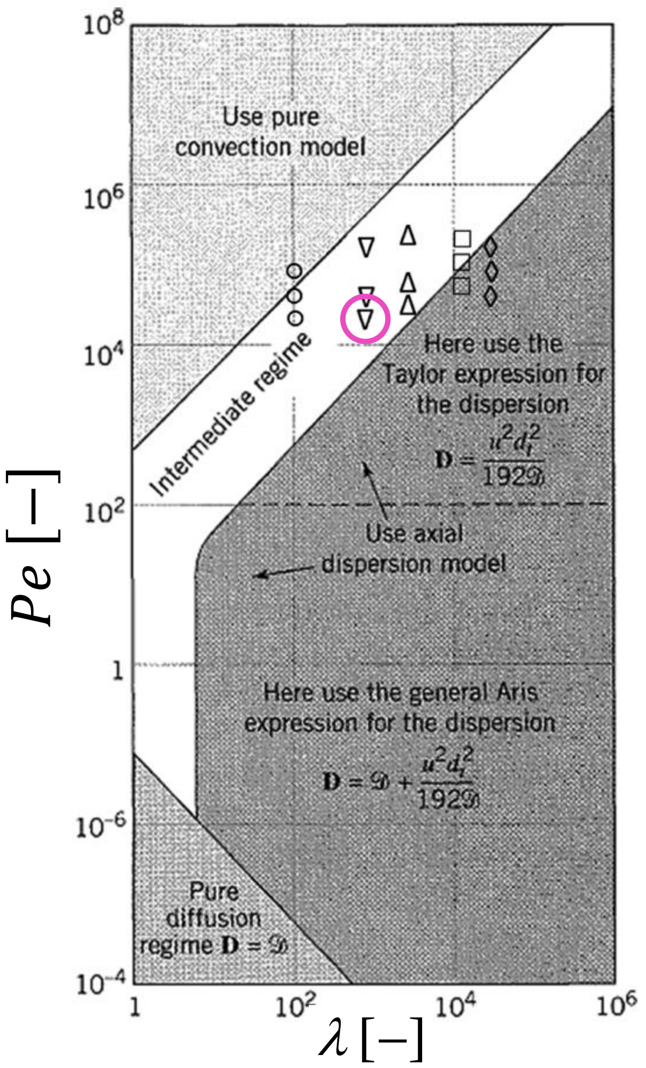


Figure 3. Placement of tubular reactors 0.4 (◇), 0.7 (□), 1.6 (△), 2.4 (▽), and 4.8 (○) mm, within diagram of Levenspiel et al.[7] (Adapted in part with permission from Levenspiel, O. Chemical reaction engineering. *Chemical Engineering Science* 1999, 19. Copyright 1999, John Wiley and Sons).

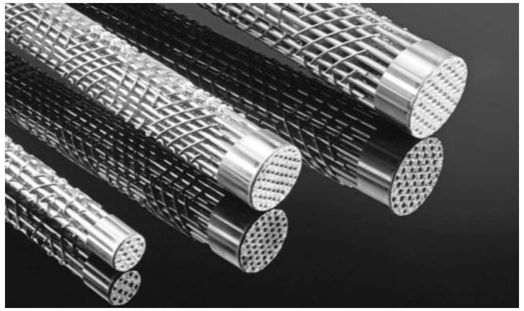
[18] F. Florit, R. Rota, K.F. Jensen, Dispersion in coiled tubular reactors: A CFD and experimental analysis on the effect of pitch, *Chem. Eng. Sci.* **233** (2021) 116393

[19] S.R.L. Gobert, S. Kuhn, L. Braeken, L.C.J. Thomassen, Characterization of milli- and microflow reactors: mixing efficiency and residence time distribution, *Org. Proc. Res. Dev.* **21** (2017) 531-542

Characterizing other laminar microreactors

Karlsruhe Institute of Technology

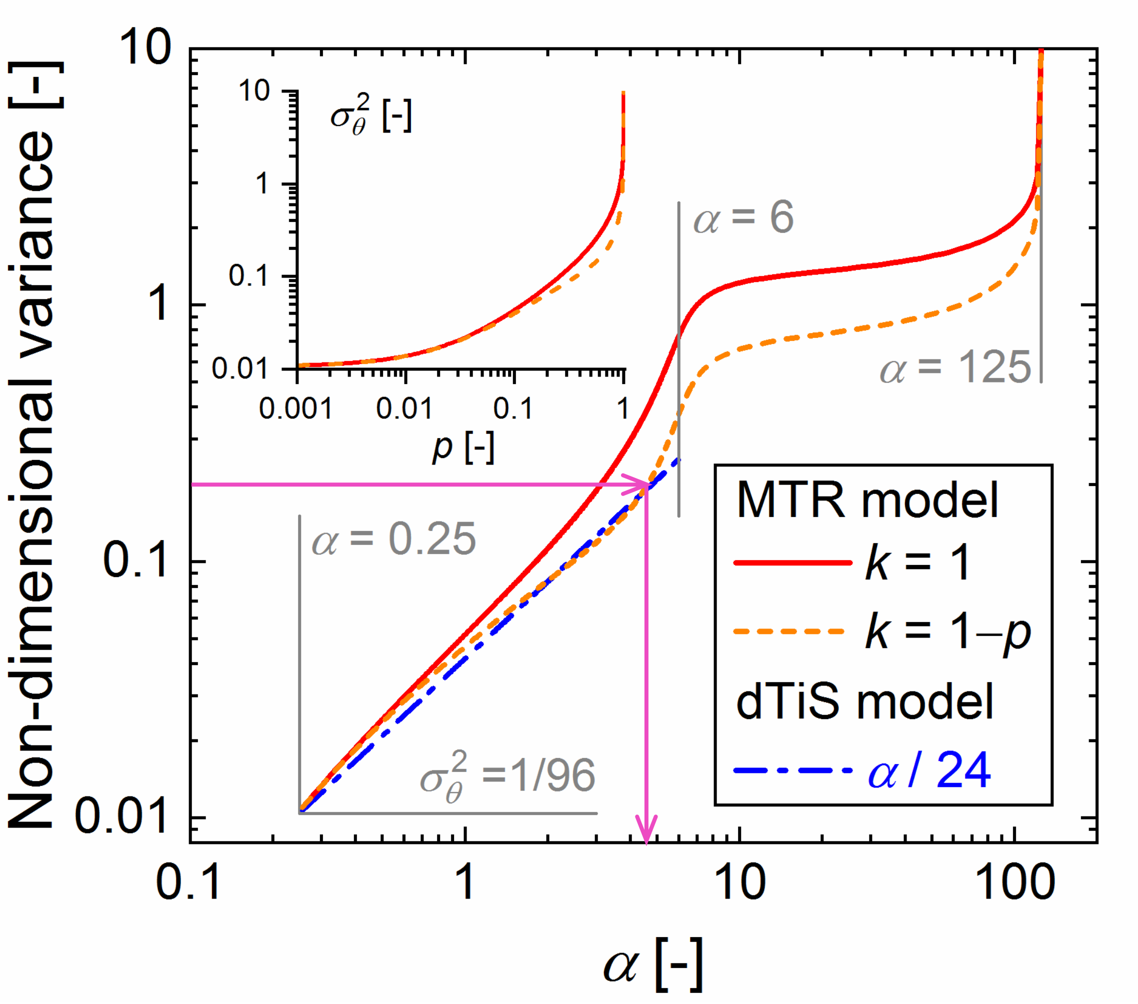
- Static mixers and plate flow reactors



fluitec
mixing+reaction solutions

Halen Technologies
ENGINEERED TO FLOW

- Measured RTDs can be correlated to the present models by means of a weighted least square method using α as fitting parameter



Conclusions

- Development of an original method to model the RTD in the transition regime
  - Models depend solely on the time scale ratio $\alpha = \tau_\mathrm{d}/\tau_\mathrm{s} = Pe/(4\lambda) = a^2U/LD$
  - Mechanistic model (MTR) is valid in entire transition regime $0.25 < \alpha < 125$
  - Compartment model (dTiS) is valid in subsection of transition regime $0.25 \leq \alpha \leq 6$
- For laminar flow in straight and coiled tubes both models are predictive
  - Models can be used to characterize other microreactors by measured tracer variance
- Model limitations
  - MTR model with $k = 1$: breakthrough time by maximum solvent velocity is violated
  - MTR model with $k = 1 - p$: mean solute RT can be lower than mean solvent RT
  - Both models cannot account for plateau or double peak in the range $2 < \alpha < 8$
- Despite these limitations the proposed models are expected to be very useful

Karlsruhe Institute of Technology

Acknowledgements

- Thanks for providing research data
  - Prof. Jorge Gut (University of Sao Paulo, Brazil)
  - Dr. Sven Gobert, Prof. Leen Thomassen (KU Leuven, Belgium)
- Stephen Wolfram's Mathematica Software

WOLFRAM MATHEMATICA

https://www.stephenwolfram.com/

Questions?