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Filtration of nanoparticles: evolution of cake-structure and pressure-drop

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Nanoparticle filtration

- Removal of wanted or unwanted particles
  - E.g. Flame-synthesized catalytic nanoparticles or diesel soot from engines
- Pressure-drop build-up is major parameter
  - Too high ΔP may halt or damage the engine [1]
  - Affects fuel economy
  - Highly related to structure of filter deposit (cake)

Setten et al., (2001), Catalysis Reviews, 43(4), 489-564

Cake formation

Filtration of nanoparticles

Highly porous cake : > 95 % [1,2]

Low penetration into substrate even for particles much smaller than the capillary

Analogous to thermophoretic deposition onto non-porous substrates

Structure determined by Pe [3,4]

Ballistic limit (85% porosity / 15 % **solid volume fraction**, ϕ_{sd}) reached above Pe > 10

At Pe < 10, ϕ_{sd} = f(Pe)

$$\boxed{Pe = \frac{d_p \cdot U}{2D}}$$

d_p: Particle diameter
U: Approach velocity
D: Particle diffusion coefficient

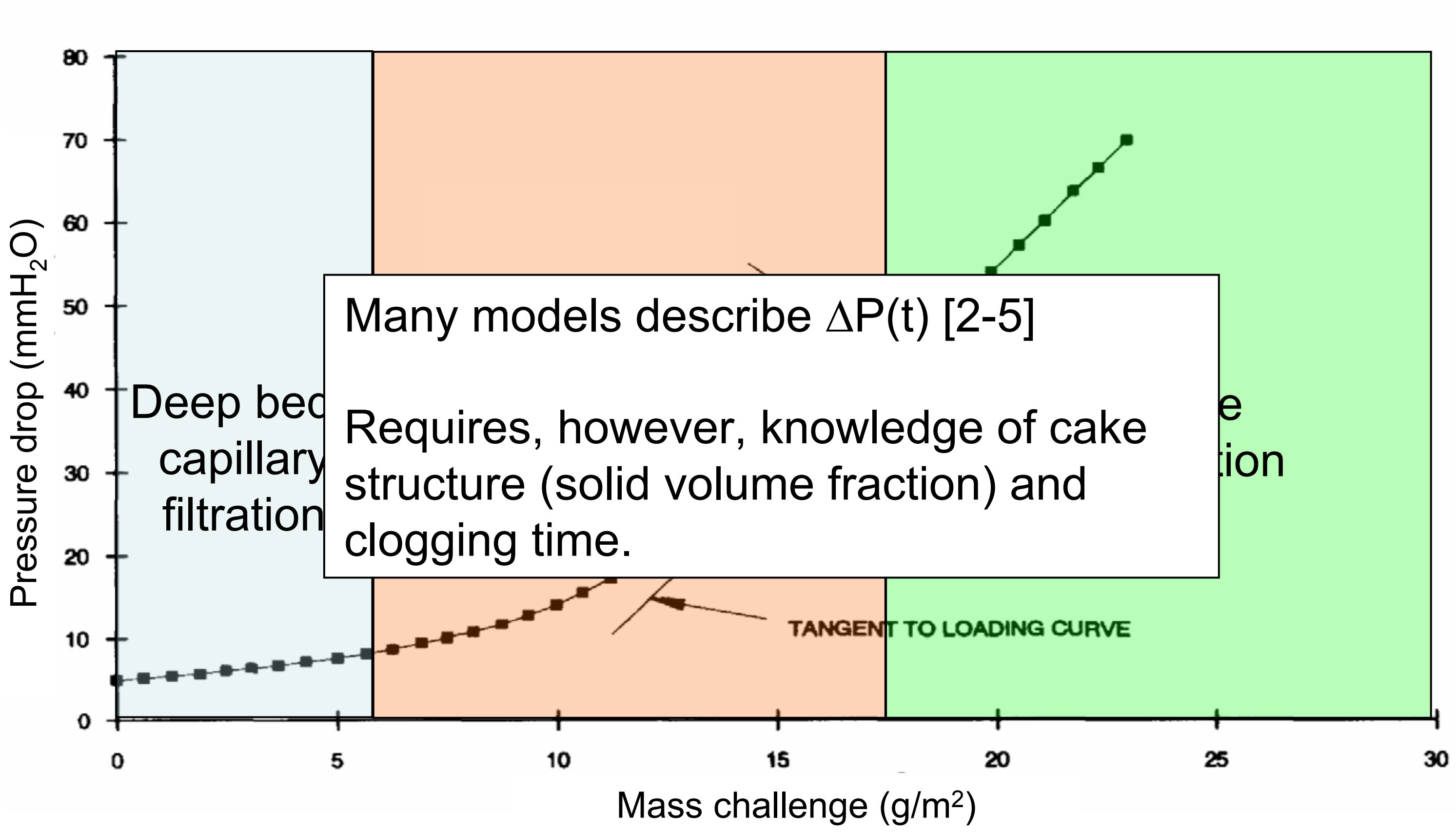
[1] Andersen, S. K., Johannessen, T., Mosleh, M., Wedel, S., Tranto, J. and Livbjerg, H., (2002), *J. Nanopart. Res*., 4(5), 405-416

[2] Elmøe, T.D., (2008), PhD Thesis, Department of Chemical Engineering, Technical University of Denmark, Kgs. Lyngby

[3] Mädler, L., Lall, A. A. And Friedlander, S. K., (2006), *Nanotechnology*, 17(19), 4783-4795

[4] Rodríguez-Pérez, D., Castillo, J. L, and Antoranz, J. C., *Phys. Rev. E*., 72(2), 021403-1 - 021403-9

Filtration regimes



Many models describe ΔP(t) [2-5]

Requires, however, knowledge of cake structure (solid volume fraction) and clogging time.

[1] Japuntich, D. A., Stenhouse, J. I. T., and Liu, B. Y. H., (1994), *J. Aerosol Sci*., 25(2), 385-393
[2] Spurny, K.R., Lodge, J.P., Frank, E.R. And Sheesley, D.C., (1969), *Env. Sci. Technol*., 3(5), 453-464
[3] Davies, C.N., (1970), *Aerosol Sci.,* 1, 35-39
[4] Kirsch, V. A., (1998), *Kolloidn. Zh.*, 60(4), 480-484.
[5] Hinds, W. C. and Kadrichu, N. P., (1997), *Aerosol Sci. Technol.*, 27(2), 162-173.

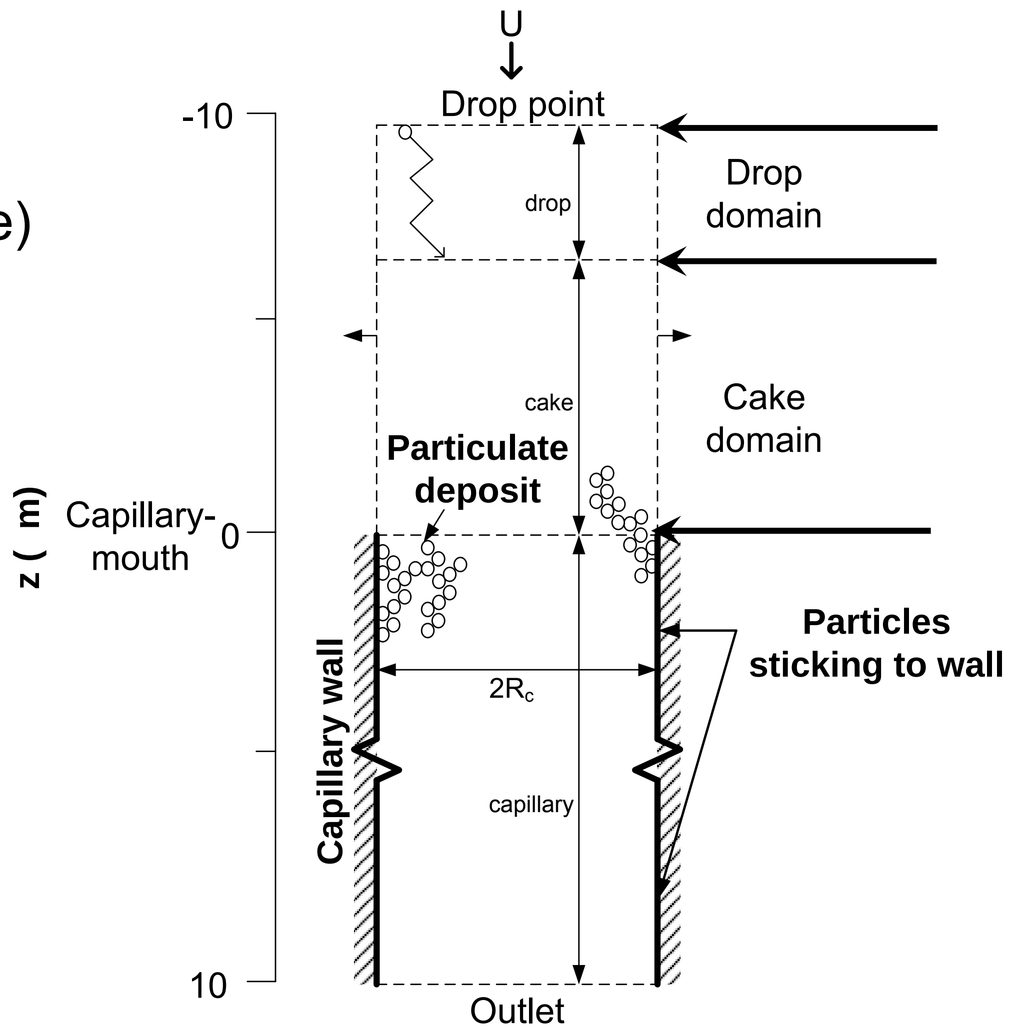
Our approach

Particle (spherical, monodisperse) tracking by Langevin dynamics

Deposition one-at-a-time [1]

Irreversible deposition

No deposition on surface between pores (~ high porosity)



[1] Tassoupolos, M., Obrien, J. A., and Rosner D. E., (1989), *AiChe J.*, 35(6), 967-980

Results

Solid volume fraction profile

$$\phi_{sd}(z) = \frac{V_p(z)}{V_{tot}}$$

$V_p(z)$: Total particle volume at position z

Clogging time, t_{cl}

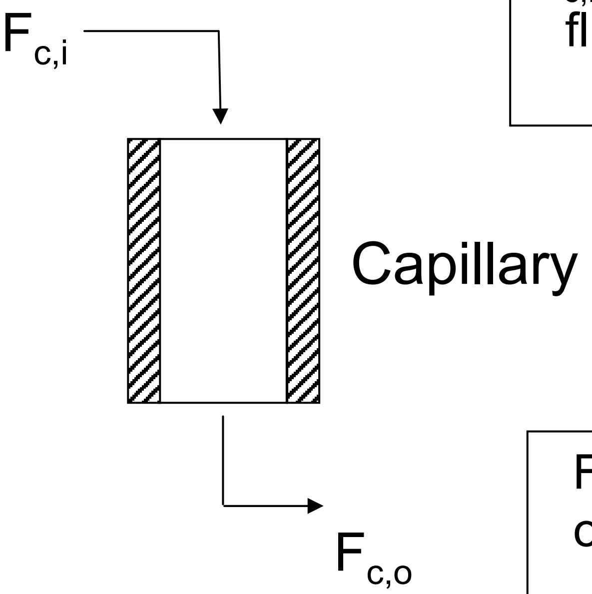
Time until $F_{c,i} = 0$

Filtration efficiency $\eta(t)$

$\eta = 1 - F_{c,o}$

Pressure-drop $\Delta P(t)$

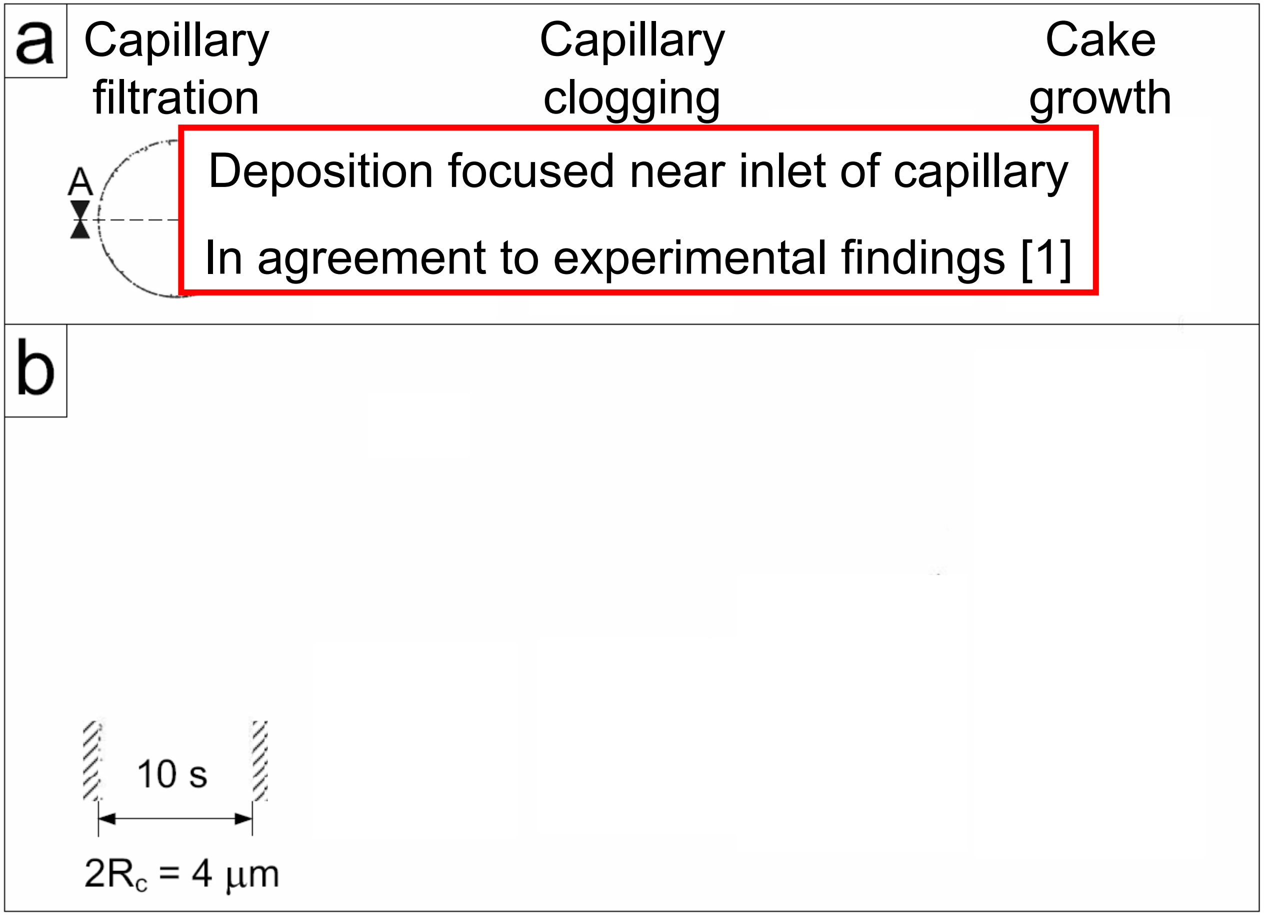
From $\phi_{sd}(z)$



$F_{c,i}$: Fraction of flux entering capillary

$F_{c,o}$: Fraction of flux exiting capillary

Structural evolution at Pe = 1



Deposition focused near inlet of capillary

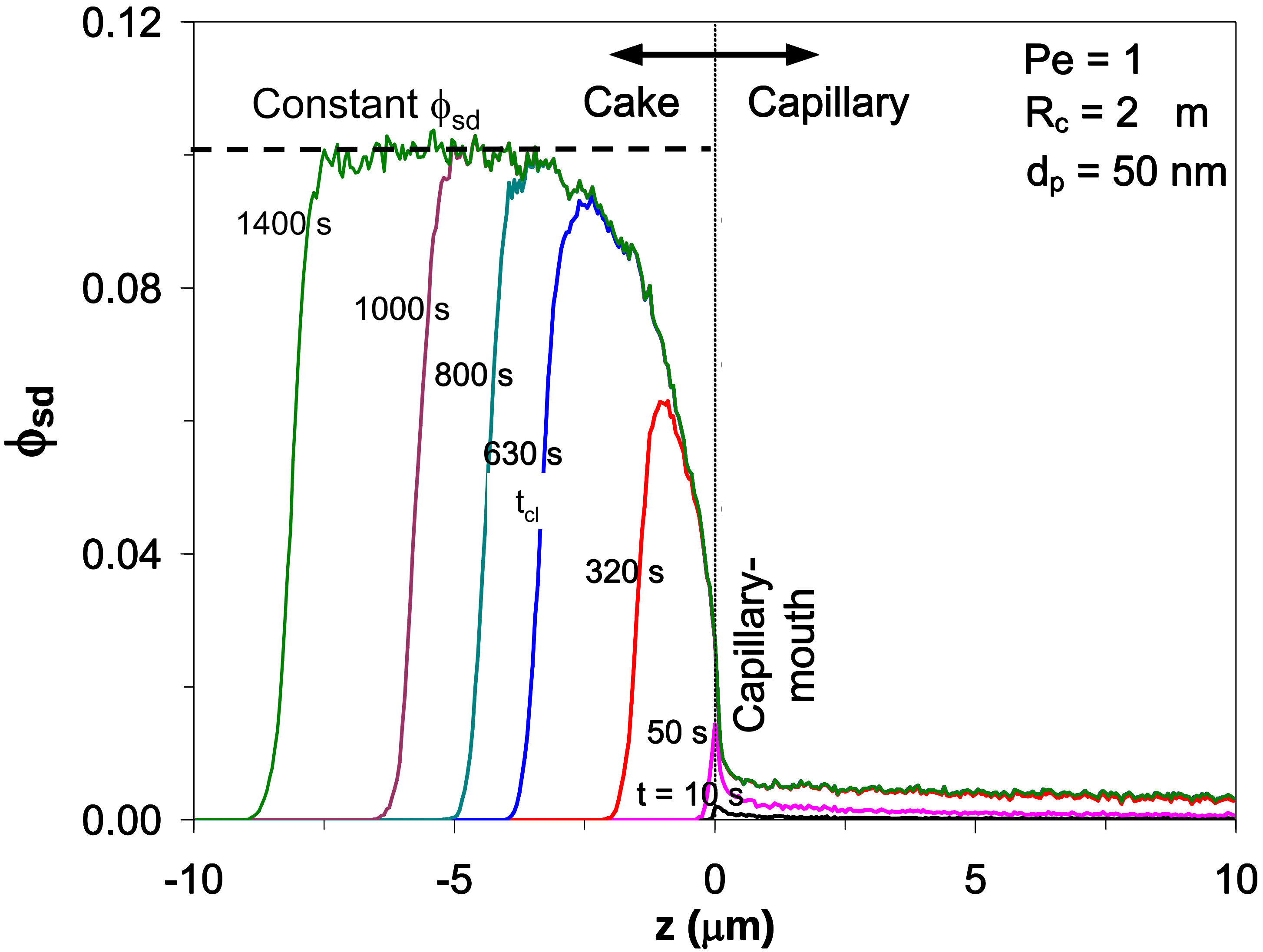
In agreement to experimental findings [1]

$d_p = 50$ nm

$C_0 = 10^{14}$ m^{-3}

[1] Johannessen, T., Jensen, J. R., Mosleh, M., Johansen, J., Quaade, U. And Livbjerg, H., (2004), *Chem. Eng. Res. Des.*, 82(A11), 1444-1452

Solid volume fraction evolution

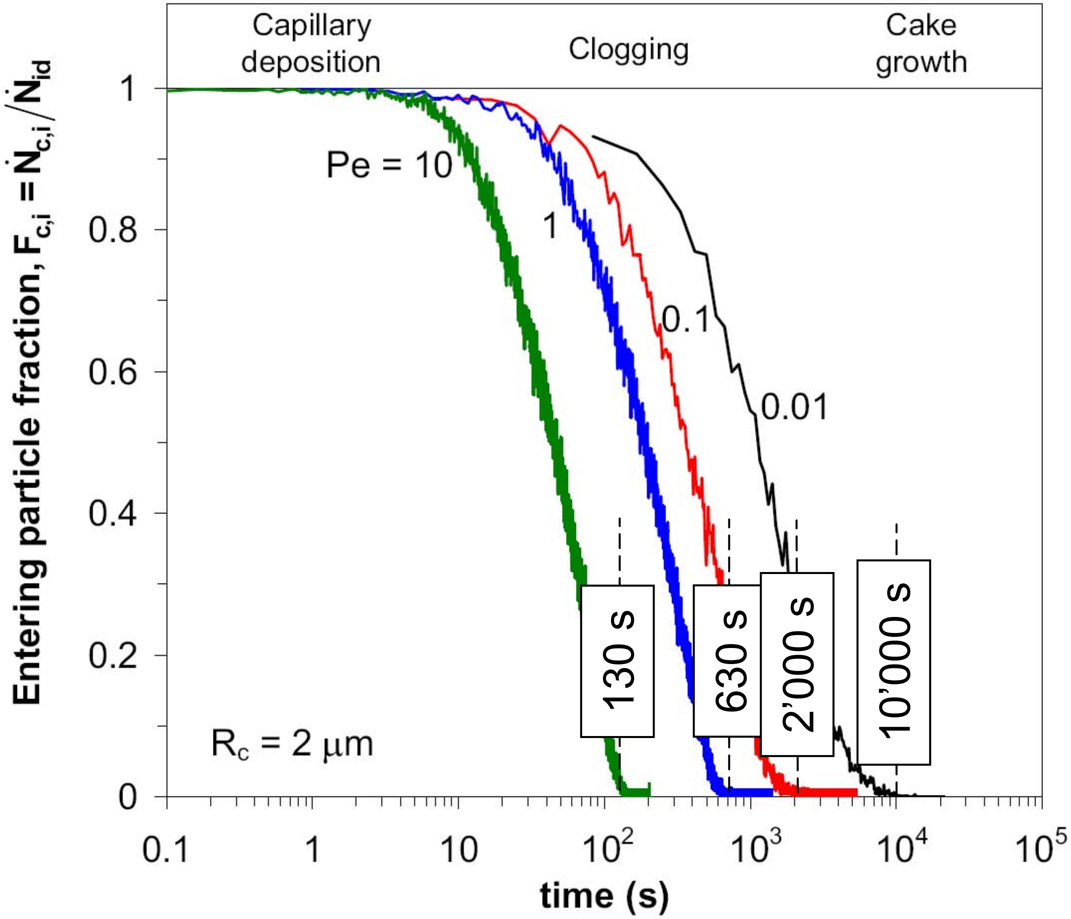


Onset of cake formation

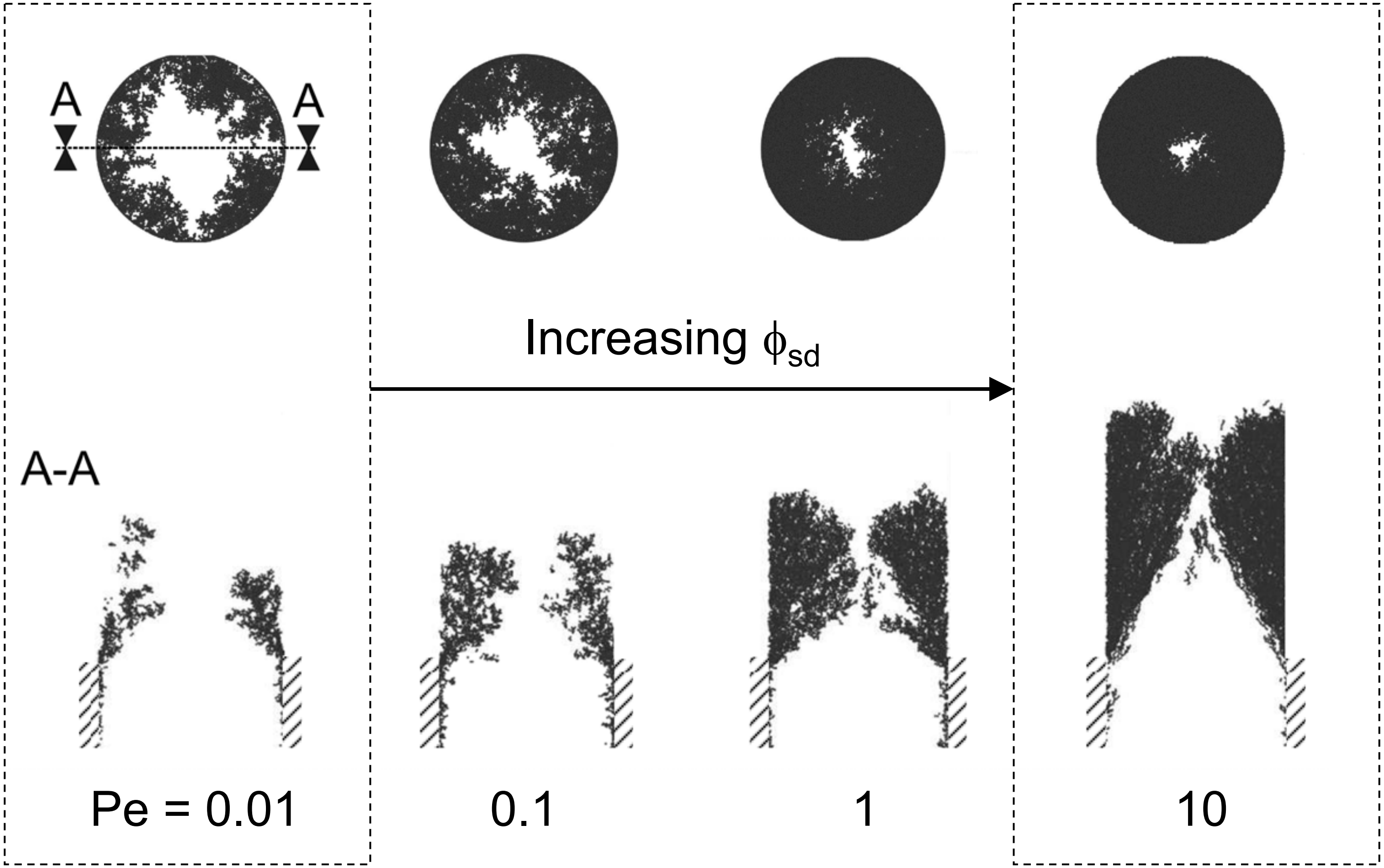
t_{cl} not linear with the particle flux ($\propto$ Pe)

Due to increased packing

↳ Larger ϕ_{sd}



Structures at t_{cl} vs Pe



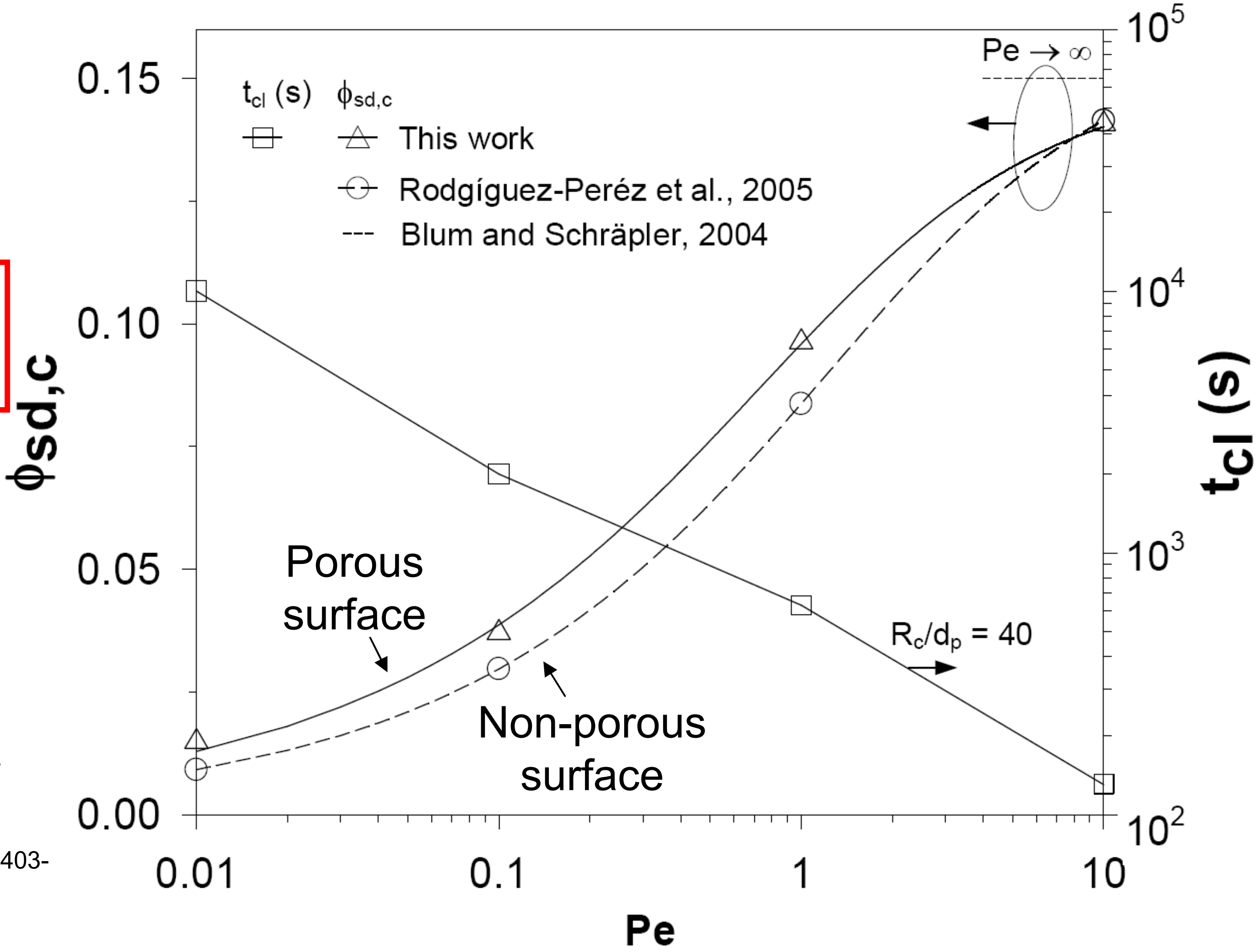
Void conical structure

Cake $\phi_{sd,c}$ and clogging time t_{cl}

$\phi_{sd,c}$ follows s-shaped curve

$$\boxed{\phi_{sd,c} = 0.15\left(1+\frac{1.5}{Pe}\right)^{-0.5}}$$

t_{cl} seems to follow power-law with Pe



Blum J., and Schräpler, R., (2004), *Phys. Rev. Lett.*, 93(11), 115503-1 – 115503-4

Rodríguez-Pérez, D., Castillo, J. L, and Antoranz, J. C., *Phys. Rev. E.*, 72(2), 021403-1 - 021403-9

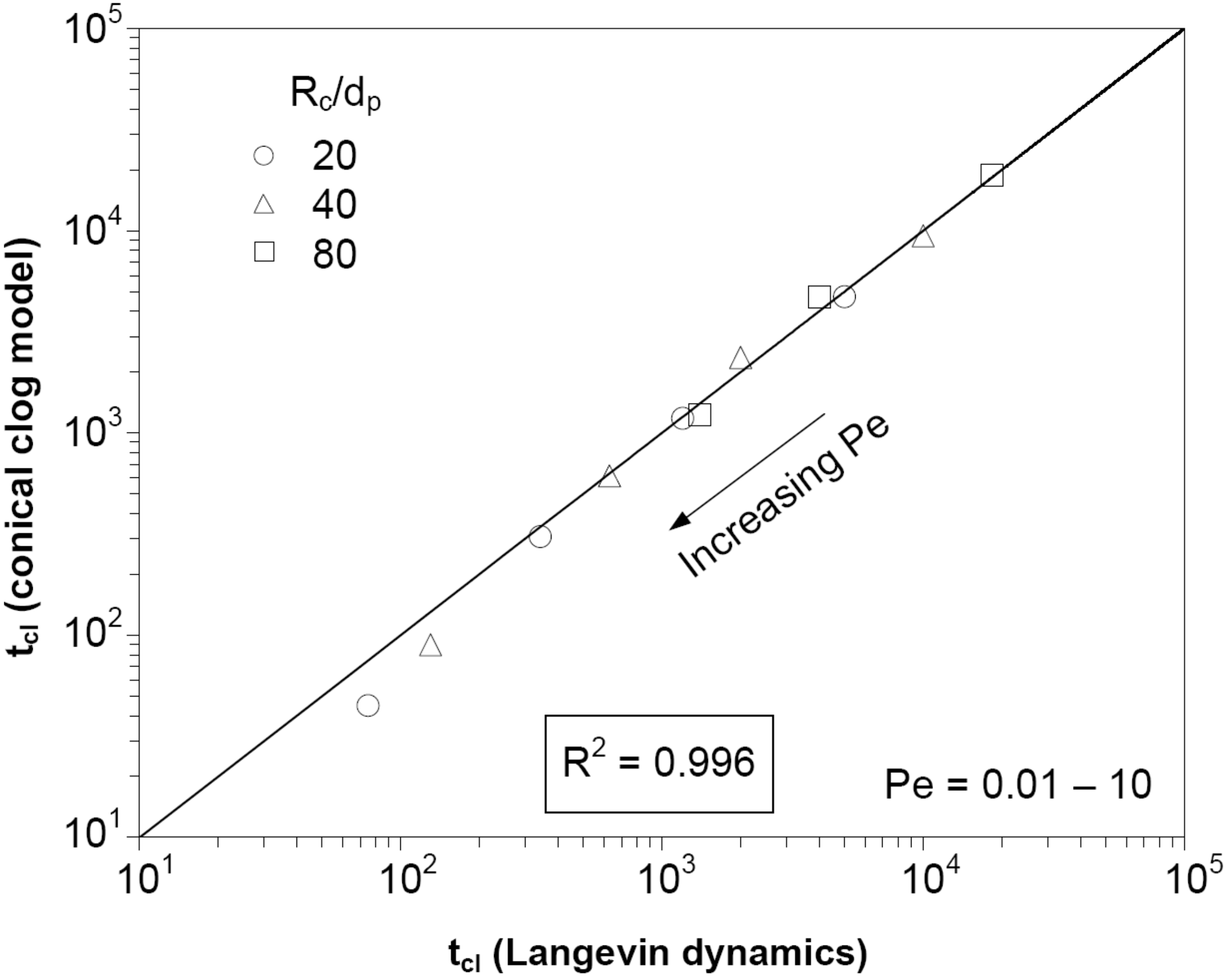
Estimation of clogging time

$$t_{cl} = \frac{2R_c\phi_{sd,c}}{UC_0v_p}$$

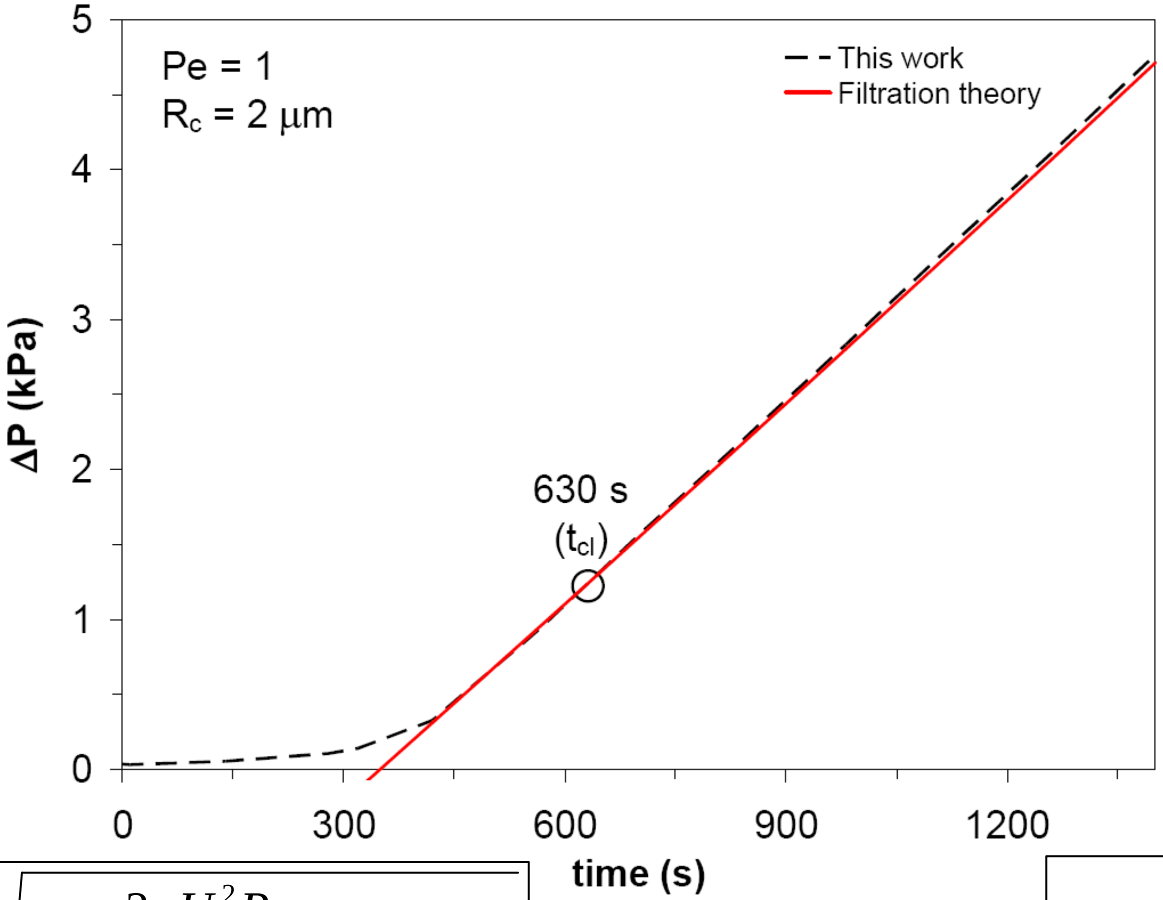
R_c: Capillary radius

C_0: Aerosol concentration

v_p: Volume of single particle



Comparison to filtration theory



d_p = 50 nm

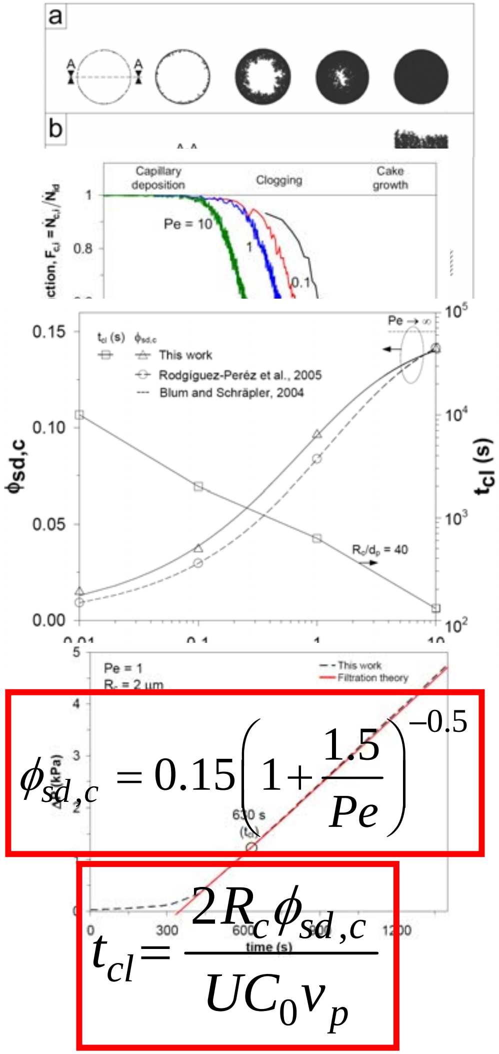
$C_0 = 10^{14}$ m^{-3}

$$\Delta P_{cake}(t) = P_0 - \sqrt{P_0^2 - \frac{2\mu U^2 P_0}{B_{0c}} C_0 v_p (t - t_{cl})}$$

$$B_{0c} = \frac{d_p^2}{150} \frac{\left(1 - \phi_{sd,c}\right)^3}{\phi_{sd,c}^2}$$

Conclusions

- Full transition between capillary and cake filtration studied by first principles
- Deposition focused near capillary inlet
- Capillary clogging followed by cake growth
  - Characterized by the clogging time t_{cl}
  - Constant solid volume fraction $\phi_{sd,c}$ function of Pe
  - Pressure-drop evolution in agreement with cake filtration theory
- Simple correlation derived between process parameters, clogging time and cake solid volume fraction



$$\phi_{sd,c} = 0.15\left(1+\frac{1.5}{Pe}\right)^{-0.5}$$

$$t_{cl} = \frac{2R_c\phi_{sd,c}}{UC_0 v_p}$$

Acknowledgements

- ETH Zürich for use of Gonzales HPC Cluster
- Financial support by The Danish Council of Technological Research, Nanoprim and CCMX-Nancer

Functional nanoparticle films

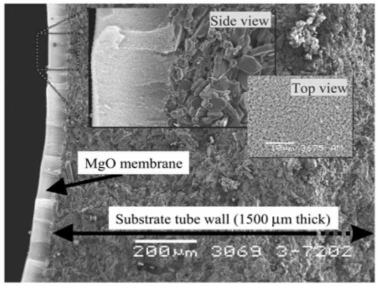
Applications:

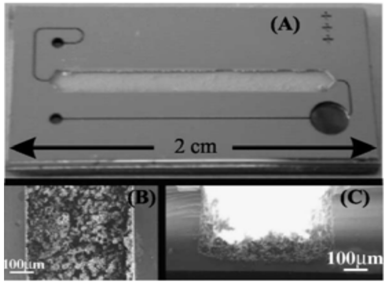
Membrane filters (Andersen et al., 2002)

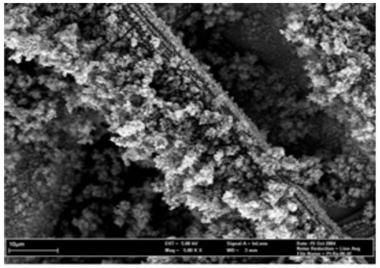
Catalysis (Thybo et al., 2004)

Fuel cells (Chakraborty et al., 2005)

Gas sensors (Mädler et al., 2006a)





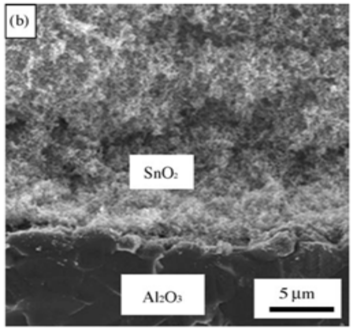


Andersen, S. K., Johannessen, T., Mosleh, M., Wedel, S., Tranto, J. and Livbjerg, H., (2002), *J. Nanopart. Res*., 4(5), 405-416

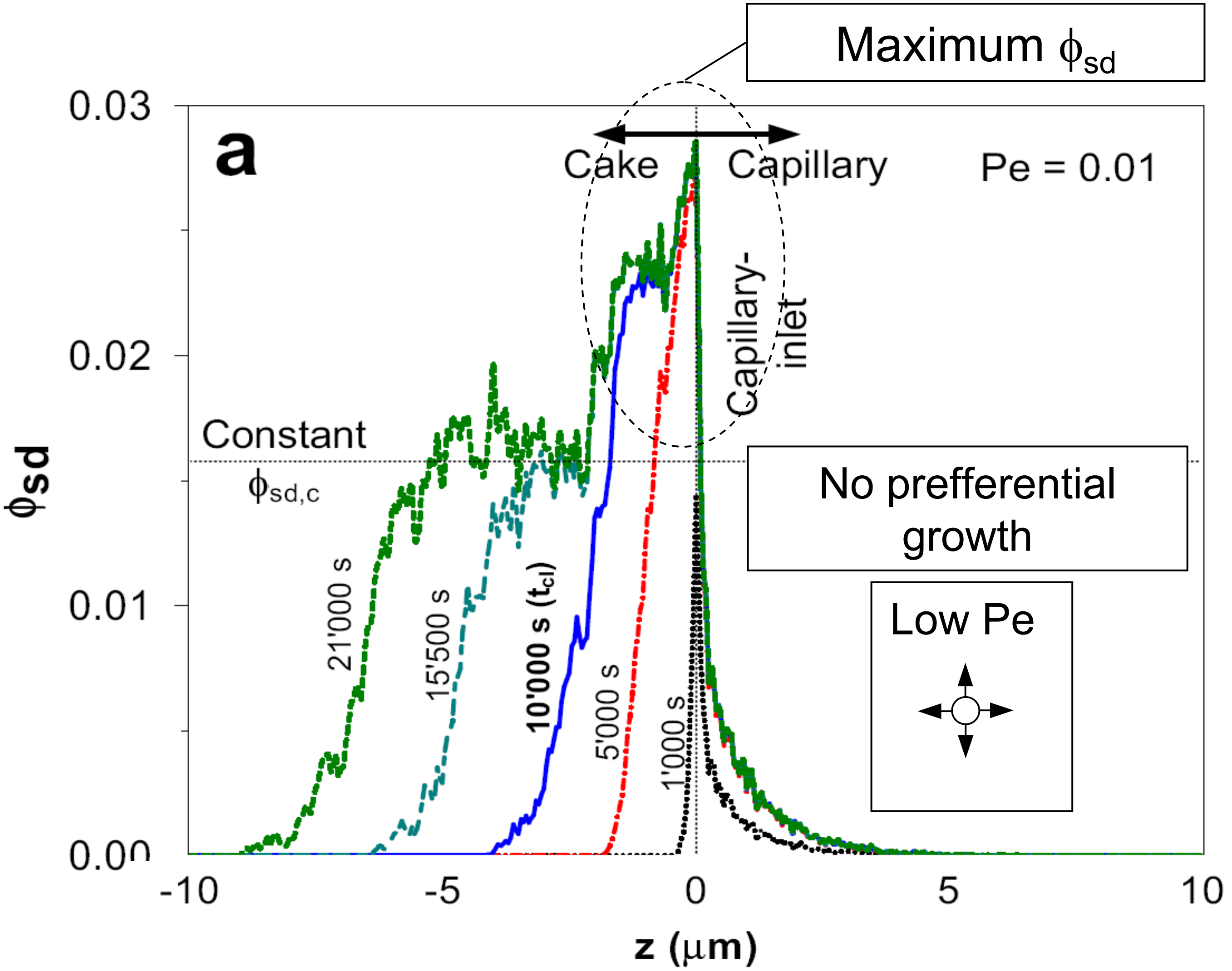
Thybo, S., Jensen, S., Johansen, J., Johannessen, T., Hansen, O. And Quaade, U. J., (2004), *J. Catal*., 223(2), 271-277

Chakraborty, D., Bischoff, H., Chorkendorff, I. And Johannessen, T., (2005), *J. Electrochem. Soc.,* 152(12), A2357-A2363

Mädler, L., Roessler, A., Pratsinis, S. E., Sahm, T., Gurlo, A., Barsan, N. and Weimar, U., (2006a), *Sens. Actuators, B*., 114(1), 283-295



Solid volume fraction evolution at low Pe

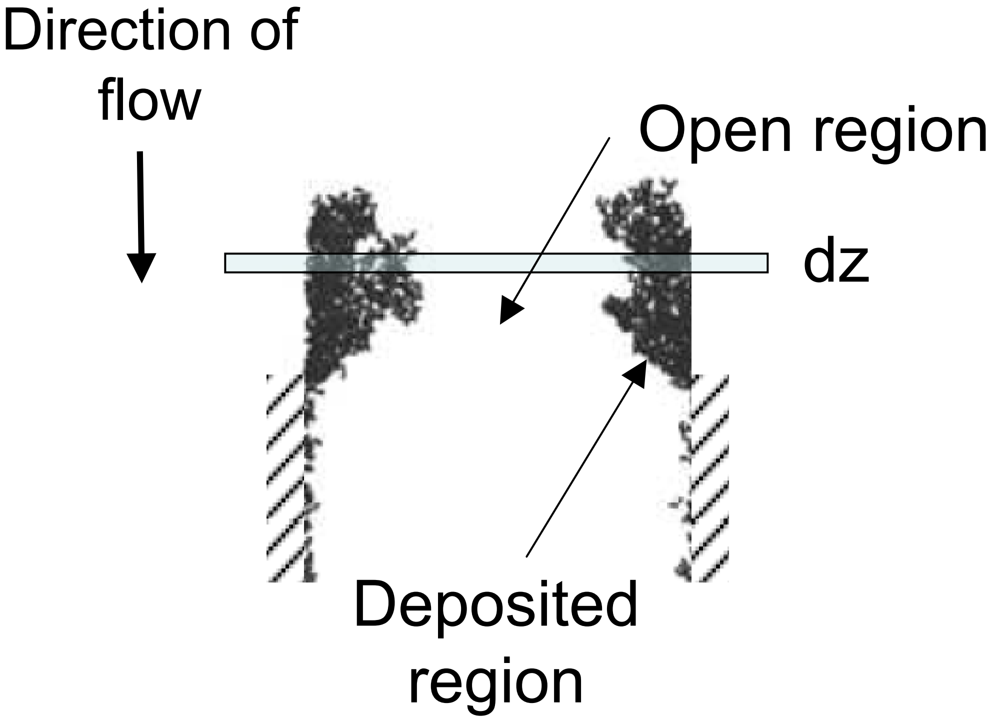


Maximum ϕ_{sd}

No prefferential growth

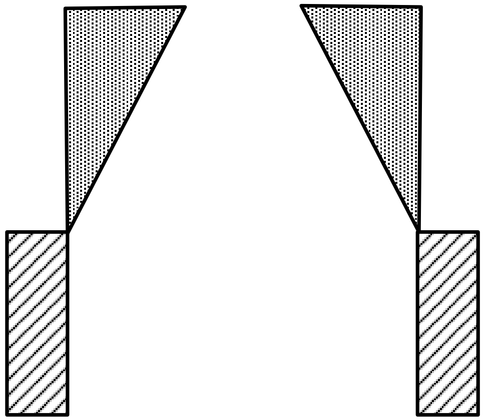
Low Pe

Two region pressure-drop model 1



LD model

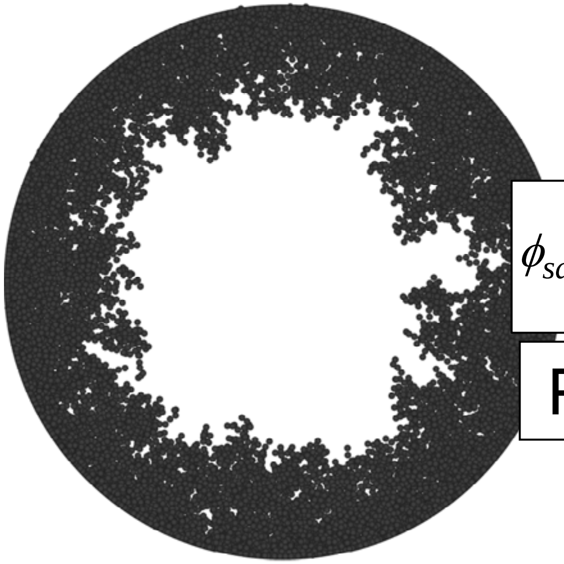
Cross-sectional view



Simplified model

Two region pressure-drop model 2

Slice dz
(top-down view)

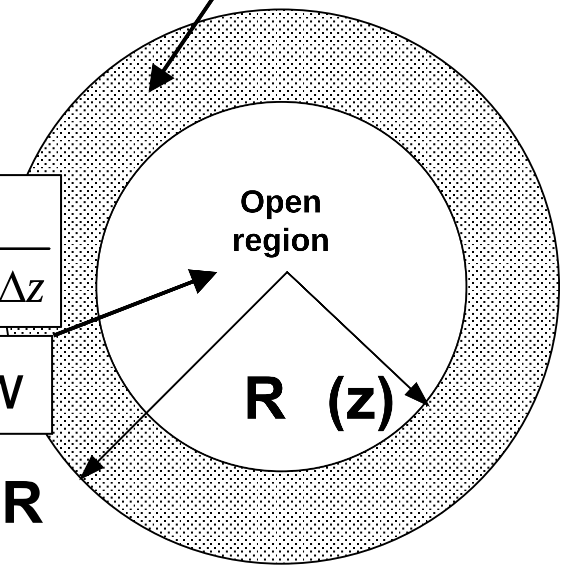


LD model

$$\phi_{sd,clog}(z) = \frac{V_p(z)}{\pi(R_c^2 - R_o^2)\Delta z}$$

Poiseuille's law

Darcy's law



Simplified model

Equi-pressure

dP/dz (dep.) = dP/dz (open)

Two region pressure-drop model 3

Compressible flow

$$\Delta P = P_0 - \sqrt{P_0^2 - \frac{16 Q_0 P_0 \mu}{\pi} \int_0^{\delta(t)} \frac{dz}{8(R_c^2 - R_o(t,z)^2) B_0(t,z) + R_o(t,z)^4}}$$

R_o : Radius of open region

R_c : Initial capillary radius

$\delta(t)$: thickness of deposit

P_0: Inlet pressure (1 bar)

Q_0: Flow at P_0

μ: Viscosity

$B_0(z)$: Darcy permeability

Valid both inside and outside capillary!

$$R_o = R_c \rightarrow \text{Poiseuille's law}$$

However, above the deposit, when $R_o = R_c$ we set $dP/dz = 0$

Two region pressure-drop model 4

Compressible flow (cont.)

At <u>cake growth</u> (t > t_{cl}, clogging) $R_o \rightarrow 0$

$$\Delta P = P_0 - \sqrt{P_0^2 - \frac{2Q_0P_0\mu}{\pi R_c^2}\int_0^{\delta(t)}\frac{dz}{B_0(t,z)}}$$

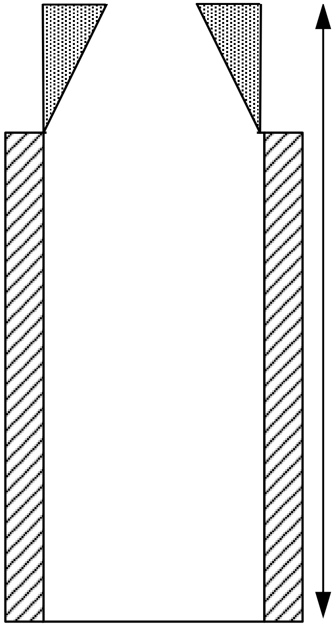
$$= \underbrace{P_0 - \sqrt{P_0^2 - \frac{2Q_0P_0\mu}{\pi R_c^2 B_{0c}}\delta_{cake}(t)}}_{\text{Pressure-drop over cake (const } \phi_{sd,c})} + \underbrace{\Delta P_{clog}}_{\text{Pressure-drop in clog}}$$

Same equation as in article

”Filtration theory”

B_{0c} : Darcy permeability in cake (constant)

Before clogging



Two region pressure-drop model 5

Cake growth (cont.) : $R_o = 0$ and $\eta \to 1$ (all particles filtered)

$$\delta_{cake}(t)\pi R_c^2 \phi_{sd,c} = C_0 v_p Q_0 (t - t_{cl}) \longrightarrow \delta_{cake}(t) = \frac{C_0 v_p Q_0 (t - t_{cl})}{\pi R_c^2 \phi_{sd,c}}$$

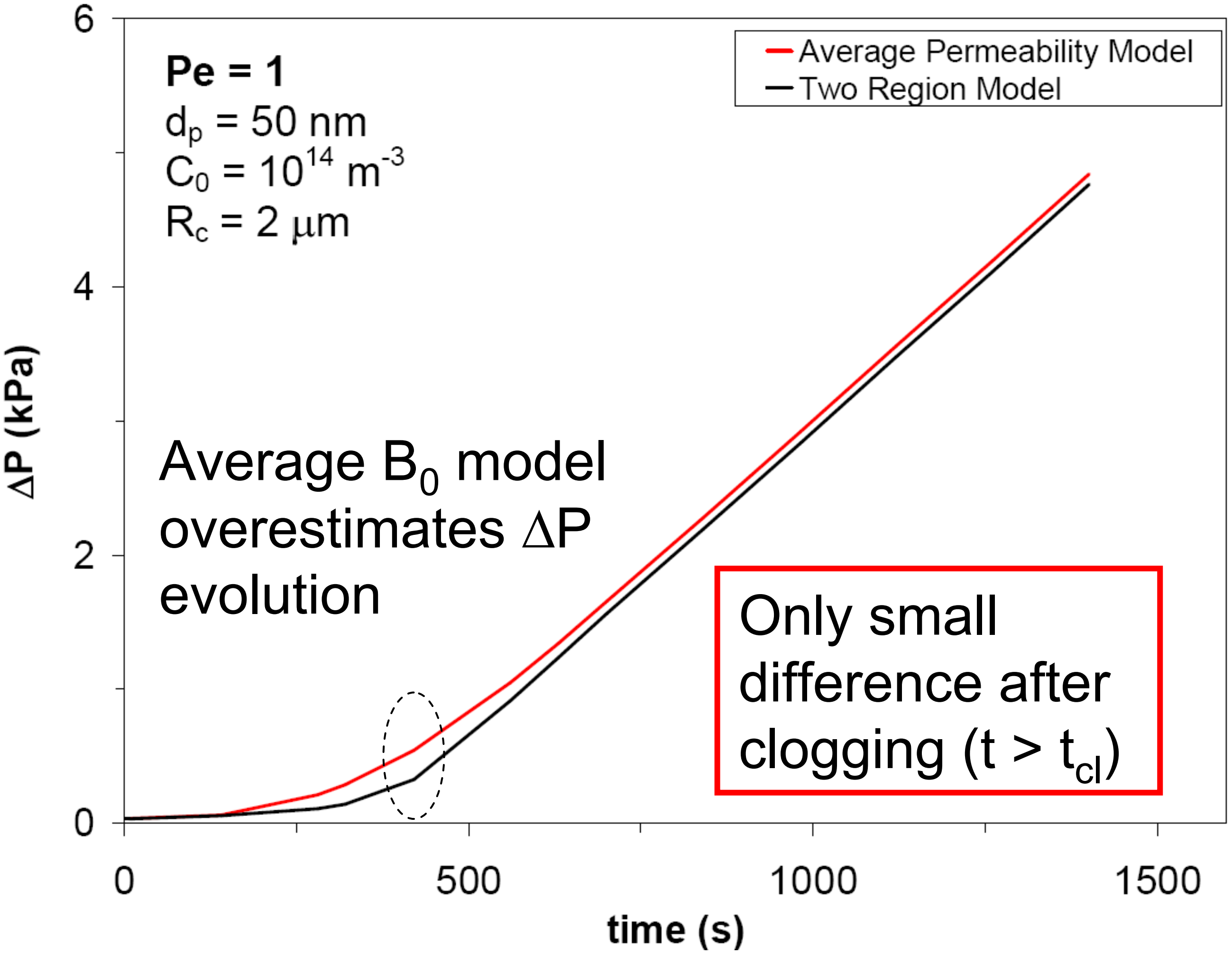
$$\Delta P = \underbrace{P_0 - \sqrt{P_0^2 - \frac{2Q_0^2 P_0 \mu C_0 v_p}{\left(\pi R_c^2\right)^2 B_{0c} \phi_{sd,c}} (t - t_{cl})}}_{\text{Pressure-drop over cake (const } \phi_{sd,c})} + \underbrace{\Delta P_{clog}}_{\text{Pressure-drop in clog}}$$

δ_{cake}	Height of filtercake
C_0	Aerosol concentration
v_p	Volume of 1 particle
t_{cl}	Clogging time

Incompressible flow

$$\Delta P = \frac{8 Q_0 \mu}{\pi} \int_0^{\delta(t)} \frac{dz}{8(R_c^2 - R_o(t,z)^2) B_0(t,z) + R_o(t,z)^4}$$

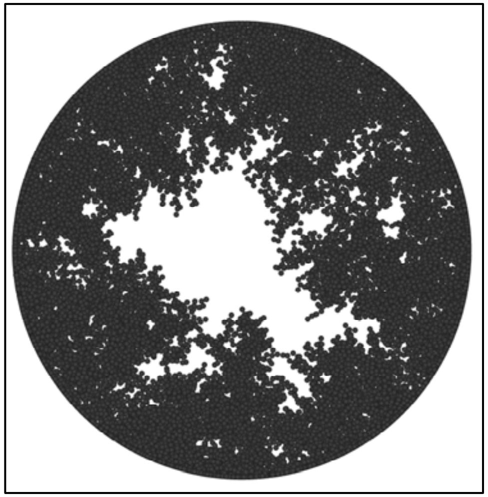
Pressure-drop model comparison 1



Average B_0 model overestimates ΔP evolution

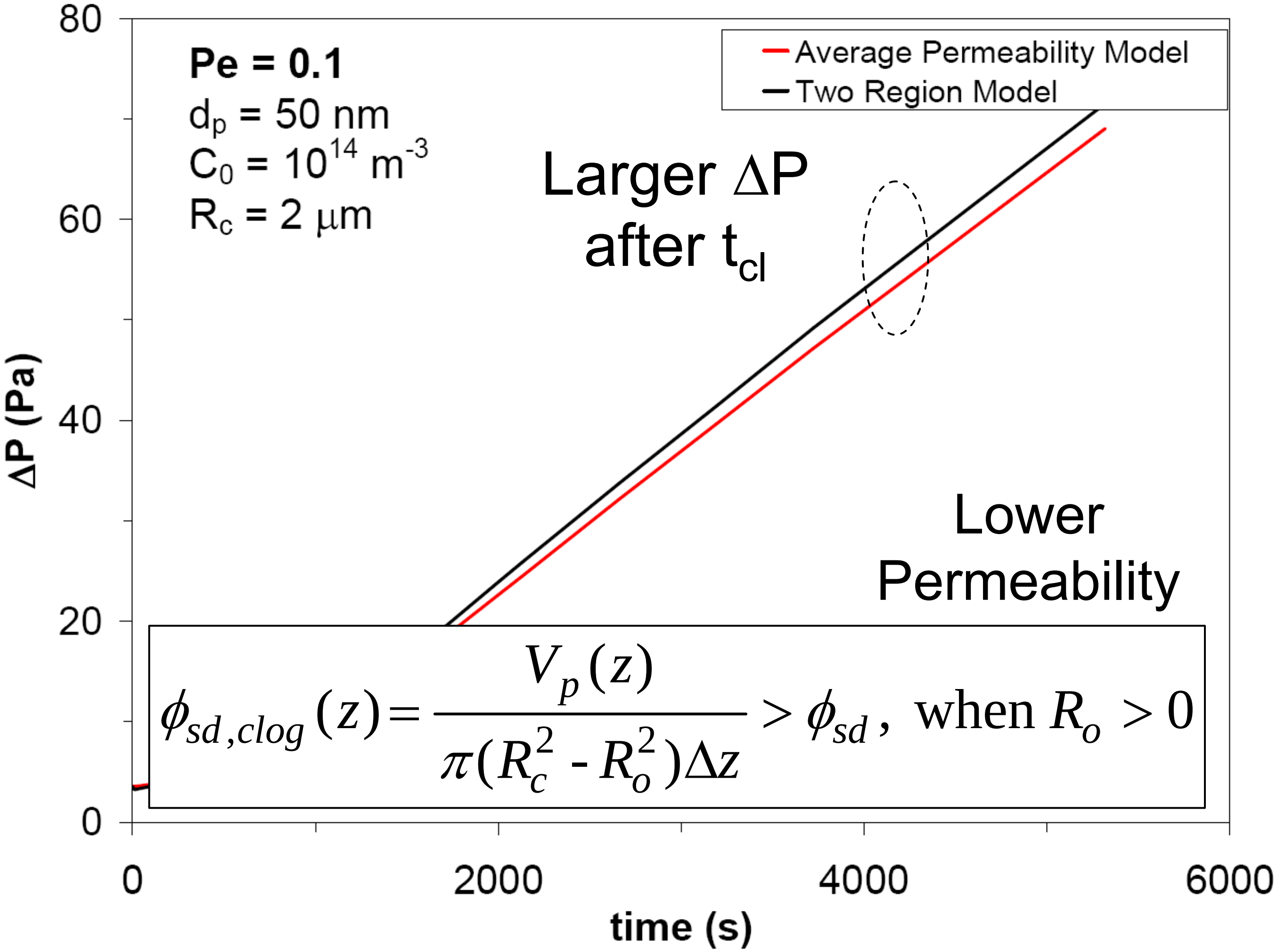
Only small difference after clogging ($t > t_{cl}$)

Pressure-drop model comparison 2



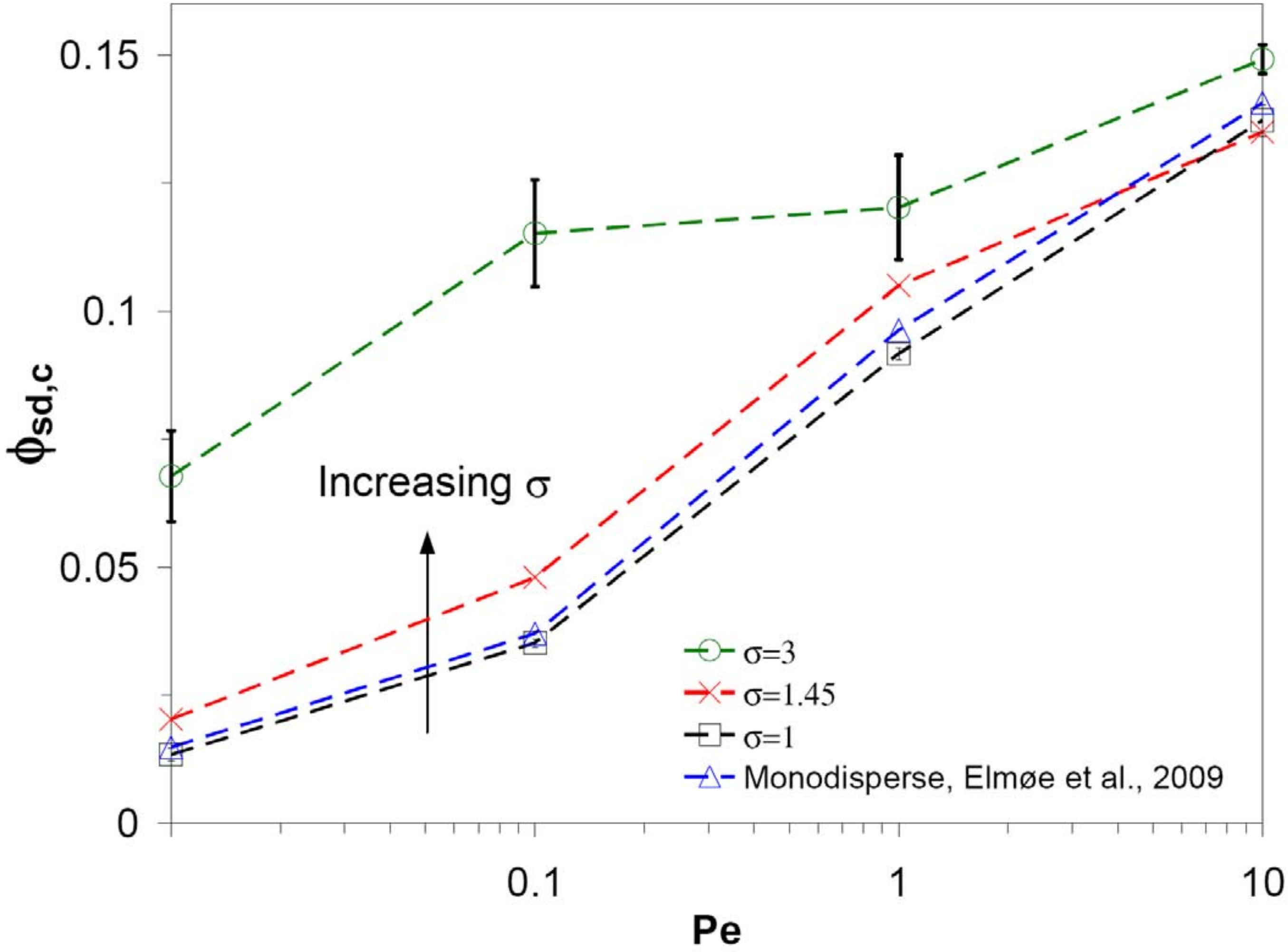
$R_o > 0$

$t = t_{cl}$
(2000 s)

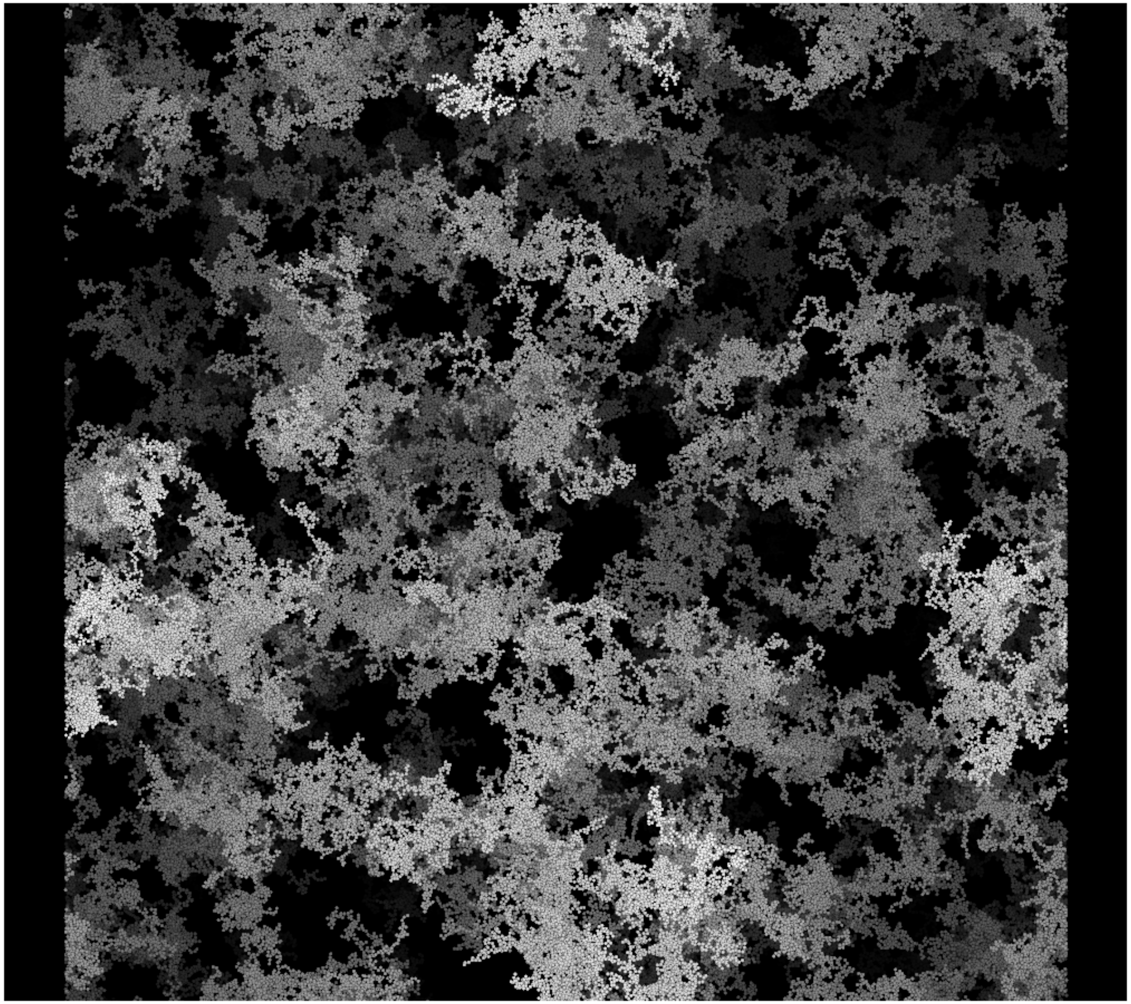


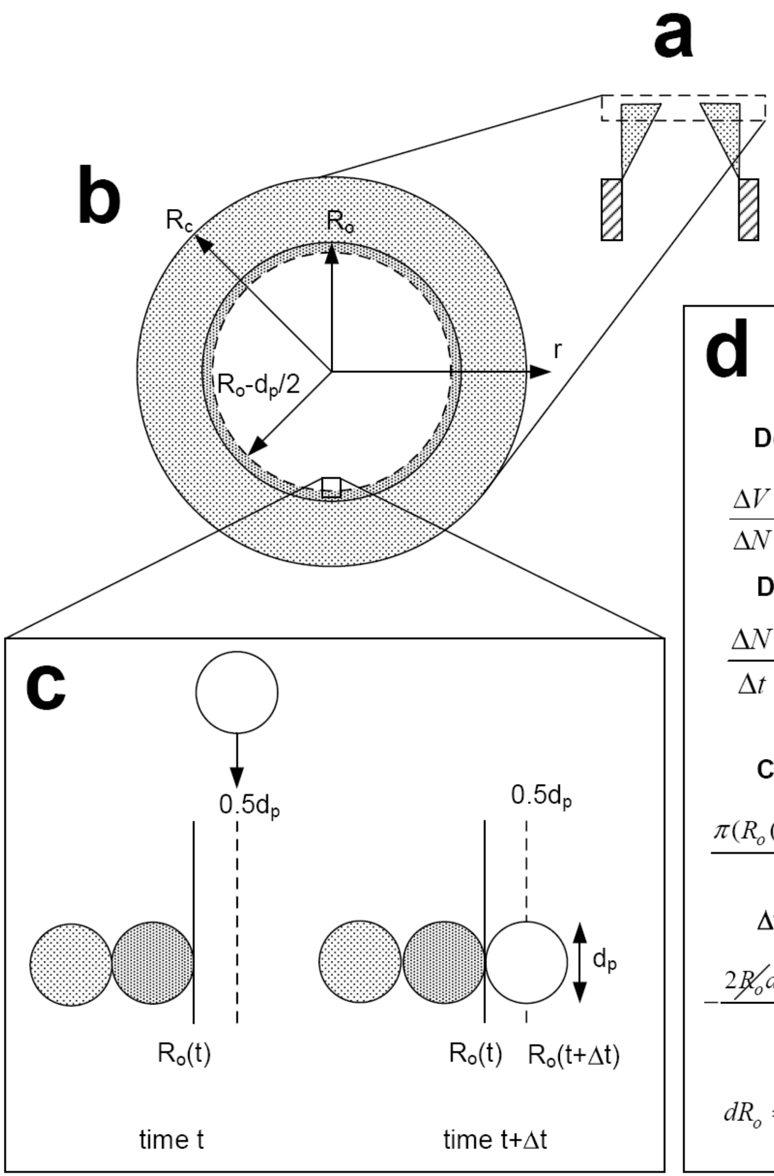
$$\phi_{sd,clog}(z)=\frac{V_p(z)}{\pi(R_c^2-R_o^2)\Delta z}>\phi_{sd}\,,\ \text{when } R_o>0$$

$\phi_{sd,c}$: Influence of polydispersity



Agglomerate deposition





d

Deposited volume per particle:

$$\frac{\Delta V}{\Delta N} = v_p = \frac{\pi(R_o(t)^2 - R_o(t+\Delta t)^2)\cdot d_p \cdot \phi_{sd,c}}{\Delta N}$$

Deposited particles per time:

$$\frac{\Delta N}{\Delta t} = QC_0 \cdot \underbrace{\frac{R_o d_p}{R_c^2}}_{\text{Fraction intercepted}}$$

Combined:

$$\frac{\pi(R_o(t)^2 - R_o(t+\Delta t)^2)\cdot d_p \cdot \phi_{sd,c}}{\Delta t} = QC_0 v_p \frac{R_o(t) d_p}{R_c^2}$$

$\Delta t \rightarrow 0$

$$-\frac{2\cancel{R_o} dR_o \cdot \cancel{d_p} \cdot \phi_{sd,c}}{dt} = \underbrace{\frac{Q}{\pi R_c^2}}_{U} C_0 v_p \cancel{R_o}\cancel{d_p}$$

$$dR_o = -\frac{UC_0 v_p}{2\phi_{sd,c}} dt$$

Langevin dynamics

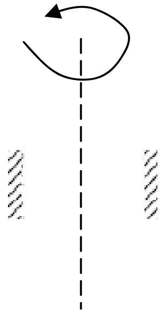
Equation of motion

$$m\dot{\mathbf{v}} = -f(\mathbf{v}-\mathbf{w}) + \mathbf{F} + \mathbf{X}$$

m	Particle mass	$\dot{\mathbf{v}}$	Particle acceleration
$\mathbf{v}$	Particle velocity	$\mathbf{w}$	Fluid velocity
$\mathbf{F}$	External forces	$\mathbf{X}$	Brownian force

Friction coefficient f = $3\pi\mu d_p/C_c(d_p)$

Calculation of pressure-drop



Pressure drop in capillary:

Hagen-Poiseulle equation

Pressure-drop in cake before clogging:

Modified D'Arcy's law

Pressure-drop in cake:

D'Arcy's law

Pressure drop in capillary

Basis: Hagen-Poiseuille

Assumptions - in a slice dz:

- Particle deposition decreases effective capillary size (Spurny et al., 1969; Fan and Gentry, 1978)
- Deposited layer << permeable than open part of capillary

$$P\frac{dP}{dz} = -\frac{8\mu U P_0}{(1-\phi_{sd}(t,z))^2 R_c^2}$$

- P : Pressure (Pa)
- z : Depth (m)
- U : Face velocity (m/s)
- P_0 : Inlet pressure (101325 Pa)
- R_c : Capillary radius (μm)
- μ : Gas viscosity (kg/ms)
- $\phi_{sd}(t,z)$: Solid volume fraction of deposit at pos. ”z” and time ”t”.

Darcy permeability

Basis: Darcy's law

Assumption - in a slice dz:

Application of an effective permeability

Effective pore size →

Effective permeability

(Jackson, 1977)

$$B_0(t,z) = \frac{d_p^2}{72}\frac{(1-\phi_{sd}(t,z))^3}{\phi_{sd}^2(t,z)}$$

Particle size, d_p*, Solid volume fraction,* ϕ_{sd} →

Effective pore size, D_c, (Ergun and Orning, 1949)

$$\frac{D_c(t,z)}{d_p} = \frac{2}{3}\frac{1-\phi_{sd}(t,z)}{\phi_{sd}(t,z)}$$

$$P(t)\frac{dP(t)}{dz} = -\frac{\mu Q_0 P_0}{\pi R_c^2 B_0(t,z)}$$

Simplified clog model 1

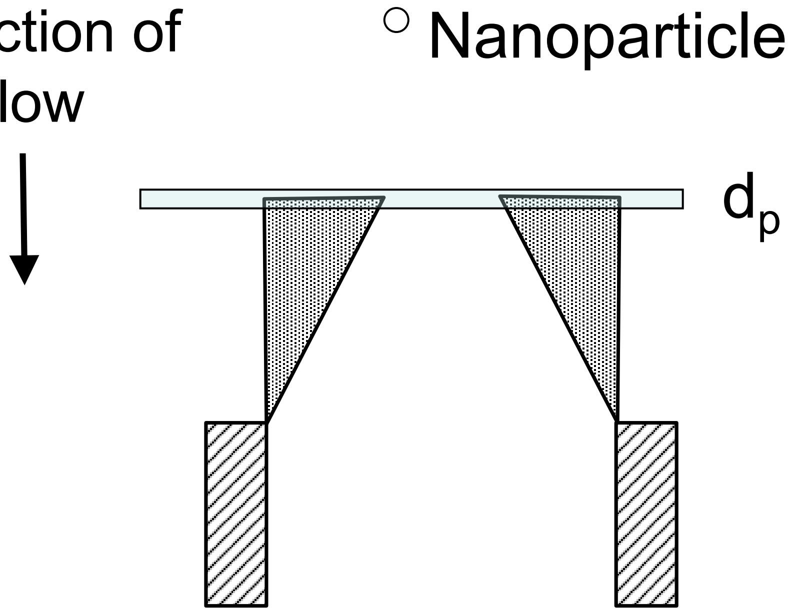
Assumptions:

Particles deposited by interception

Clog $\phi_{sd,clog} = \phi_{sd,c}$

$$\phi_{sd,clog}(z) = \frac{V_p(z)}{\pi(R_c^2 - R_o^2)\Delta z} = \phi_{sd,c}$$

Clogging at $R_o = 0$



LD model

Cross-sectional view

Simplified model

Simplified clog model 2

Interception area

Fraction of particles within

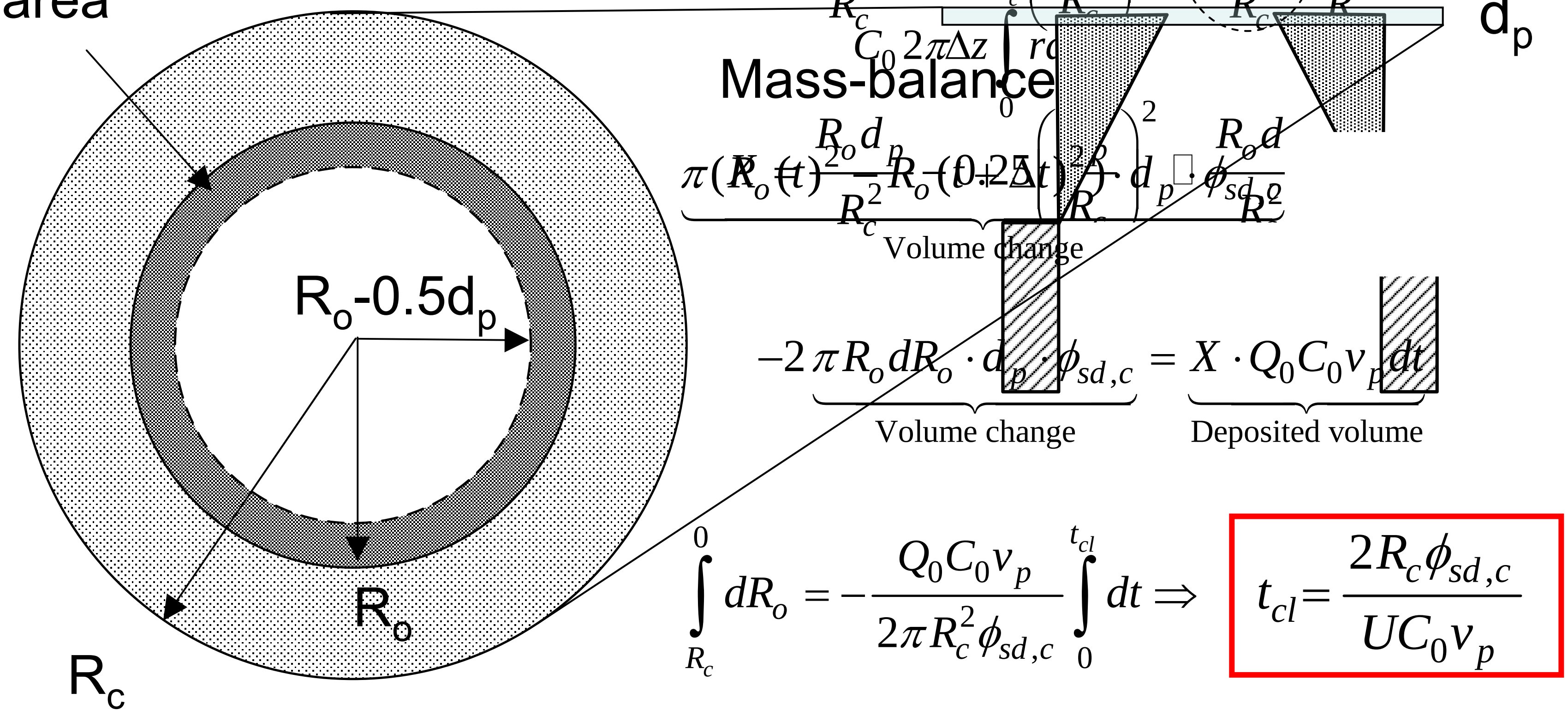
$$X = \frac{C_0 2\pi\Delta z \int_{R_o-0.5d_p}^{R_o} r\,dr}{C_0 2\pi\Delta z \int_0^{R_c} r\,dr} = \frac{R_o^2 - (R_o - 0.5d_p)^2}{R_c^2} \Rightarrow$$

$$X = \frac{R_o d_p}{R_c^2} - 0.25\left(\frac{d_p}{R_c}\right)^2 \square \frac{R_o d_p}{R_c^2}$$

Mass-balance

$$X = \frac{R_o d_p}{R_c^2} - 0.25\left(\frac{d_p}{R_c}\right)^2 \square \frac{R_o d}{R_c^2}$$

$$\underbrace{\pi(R_o(t)^2 - R_o(t+\Delta t)^2)\cdot d_p \square \cdot \phi_{sd,c}}_{\text{Volume change}}$$



$$\underbrace{-2\pi R_o dR_o \cdot d_p \cdot \phi_{sd,c}}_{\text{Volume change}} = \underbrace{X \cdot Q_0 C_0 v_p dt}_{\text{Deposited volume}}$$

$$\int_{R_c}^{0} dR_o = -\frac{Q_0 C_0 v_p}{2\pi R_c^2 \phi_{sd,c}} \int_0^{t_{cl}} dt \Rightarrow \boxed{t_{cl} = \frac{2R_c\phi_{sd,c}}{UC_0 v_p}}$$

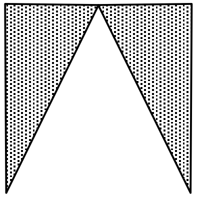
Estimation of clogging time

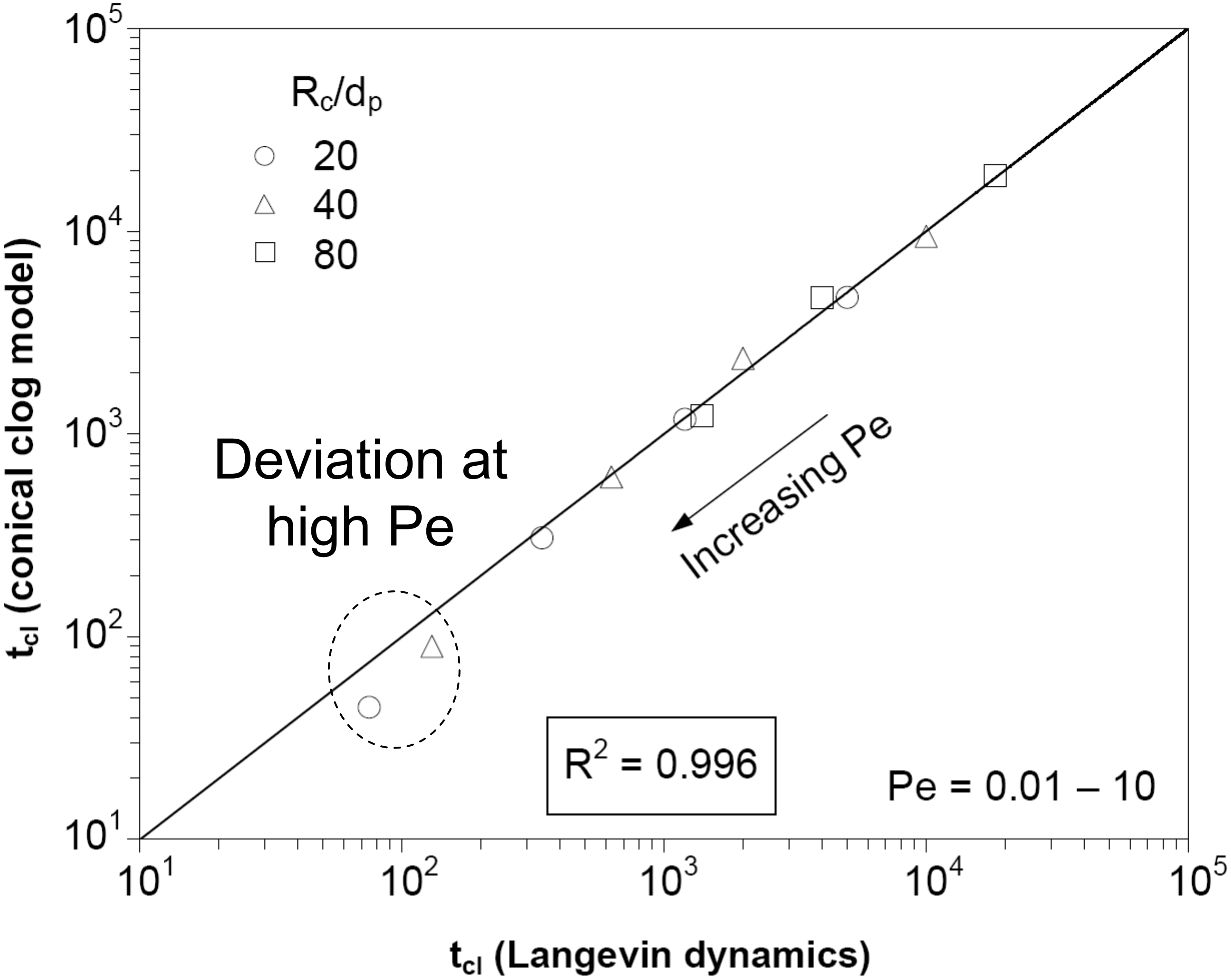
$$t_{cl} = \frac{2R_c\phi_{sd,c}}{UC_0 v_p}$$

R_c: Capillary radius

C_0: Aerosol concentration

v_p: Volume of single particle





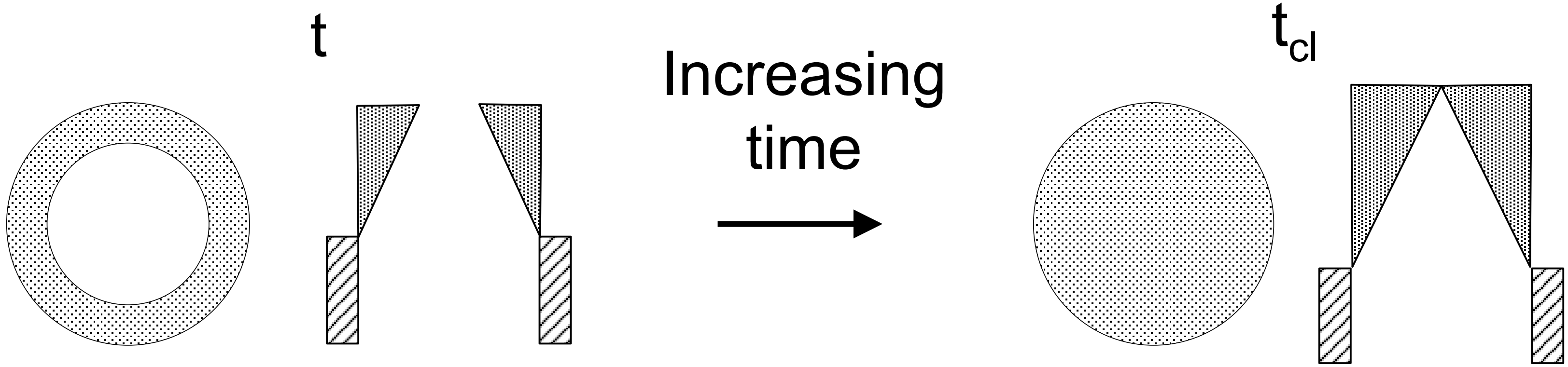
Deviation at high Pe

$R^2 = 0.996$

Pe = 0.01 – 10

Clogging height

Growth of cone



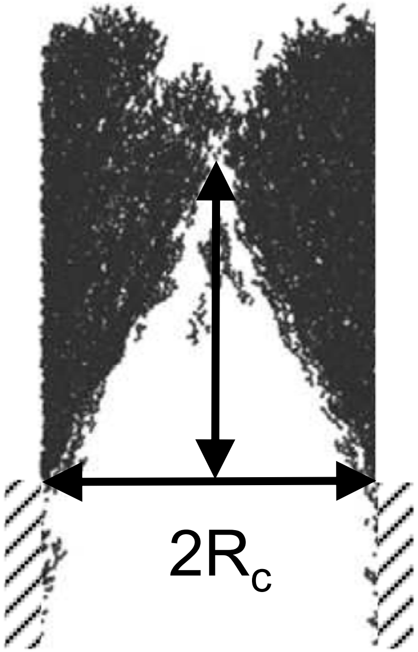
Mass-balance: shaded area

$$\delta_{cl} = \frac{UC_0 v_p}{\phi_{sd,c}} t_{cl} \Rightarrow$$

$$\underbrace{\pi(R_c^2 - R_o^2)\Delta z \cdot \phi_{sd,c}}_{\text{Volume increase of cone}}$$

Height of cone

$$\delta_{cl} = 2R_c \ ?$$

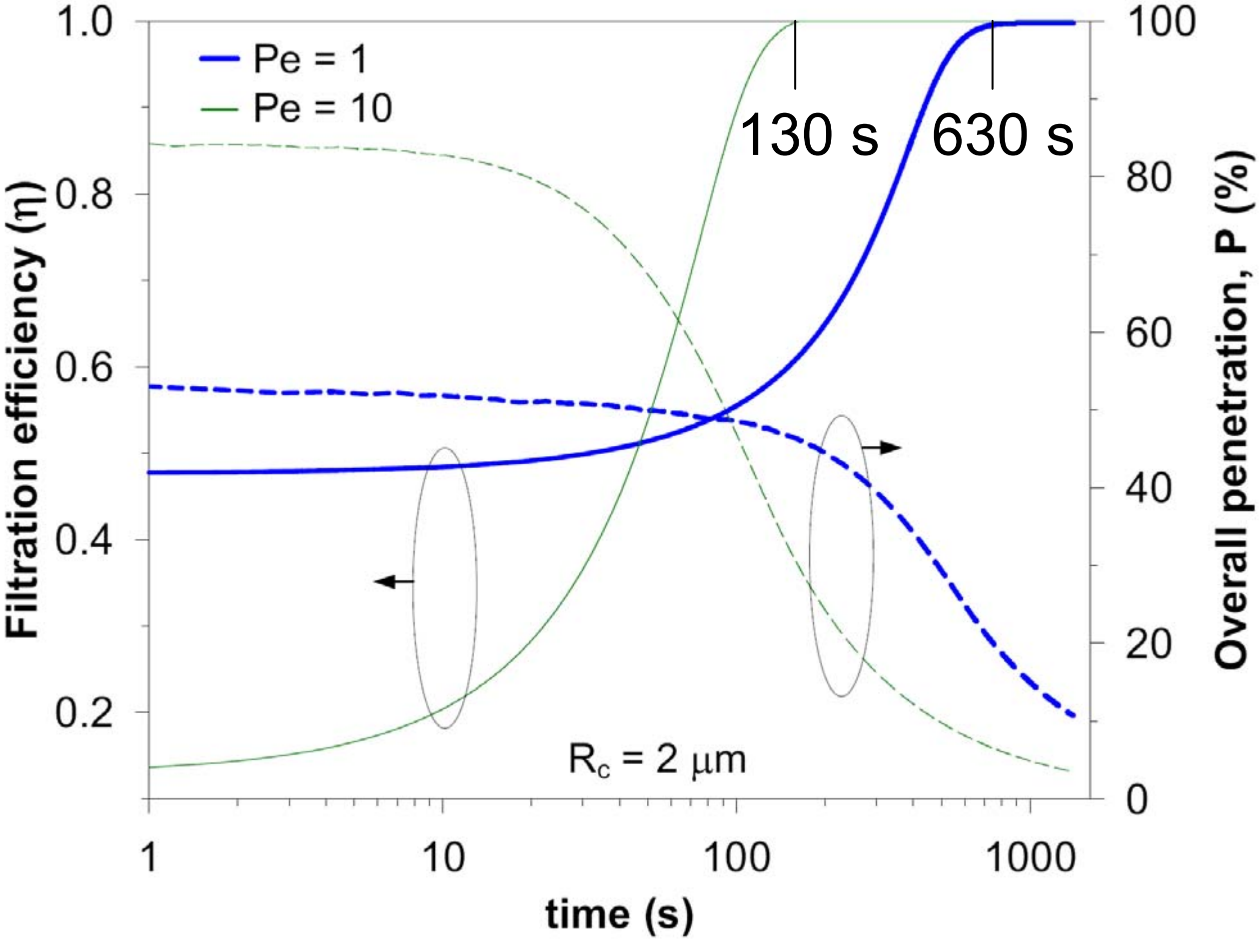


Pe = 10

Evolution of filtration efficiency

$\eta \rightarrow 1$ at $t = t_{cl}$

Initially, more particles penetrate at high Pe



Nanoparticle filtration 2

- Formation of filter cake
  - Effect of varying filtration rate, filter geometry, particle/aggregate morphology on time for formation of filter cake (clogging time, t_{cl}) and cake solid volume fraction ($\phi_{sd,c}$)
- Optimization of filtration efficiency η

Reduction of pressure-drop ΔP

Outline

- Filtration theory
- Our approach
- Evolution of cake structure and pressure drop
- Conclusions