ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Brownian Coagulation at High Concentrations

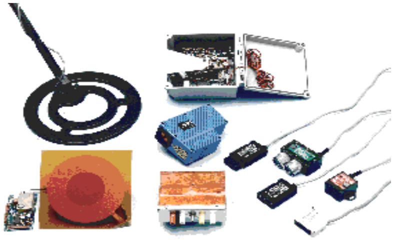
M.C. Heine* and S.E. Pratsinis

Particle Technology Laboratory, Institute of Process Engineering
Department of Mechanical and Process Engineering
ETH Zurich, Switzerland

*currently at Bühler AG, Uzwil, Switzerland

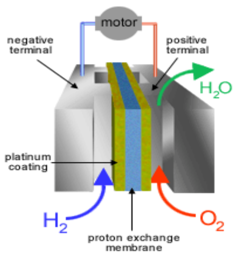
PTL: from Fundamental Understanding to Final Performance

Sensors



Advanced Pigments

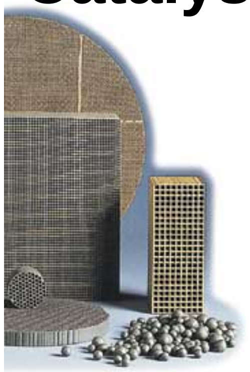
Fuel Cells



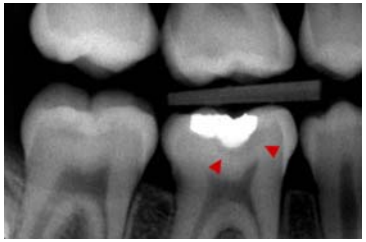
Particle Synthesis, Characterization & Modeling for scale-up

Nutrition

Catalysts

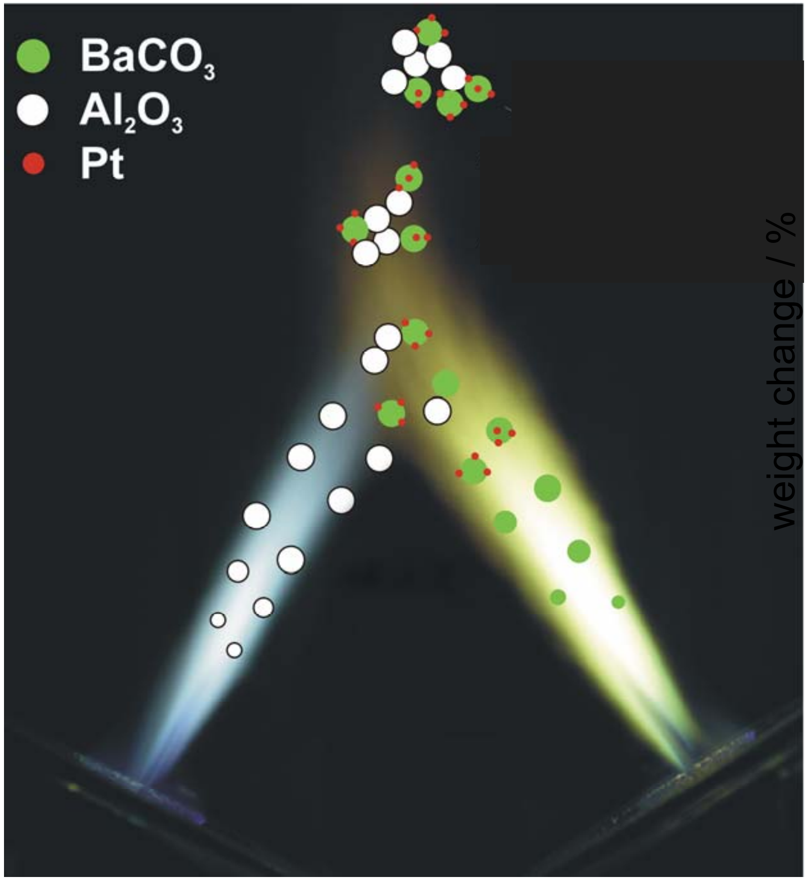


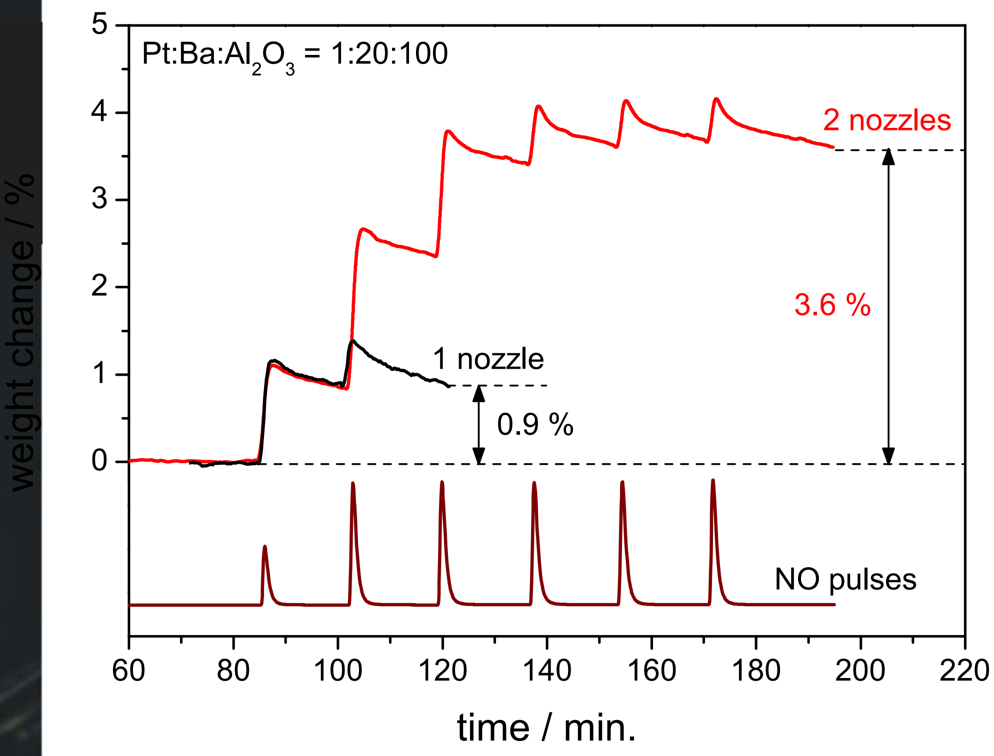
Batteries



Biomaterials

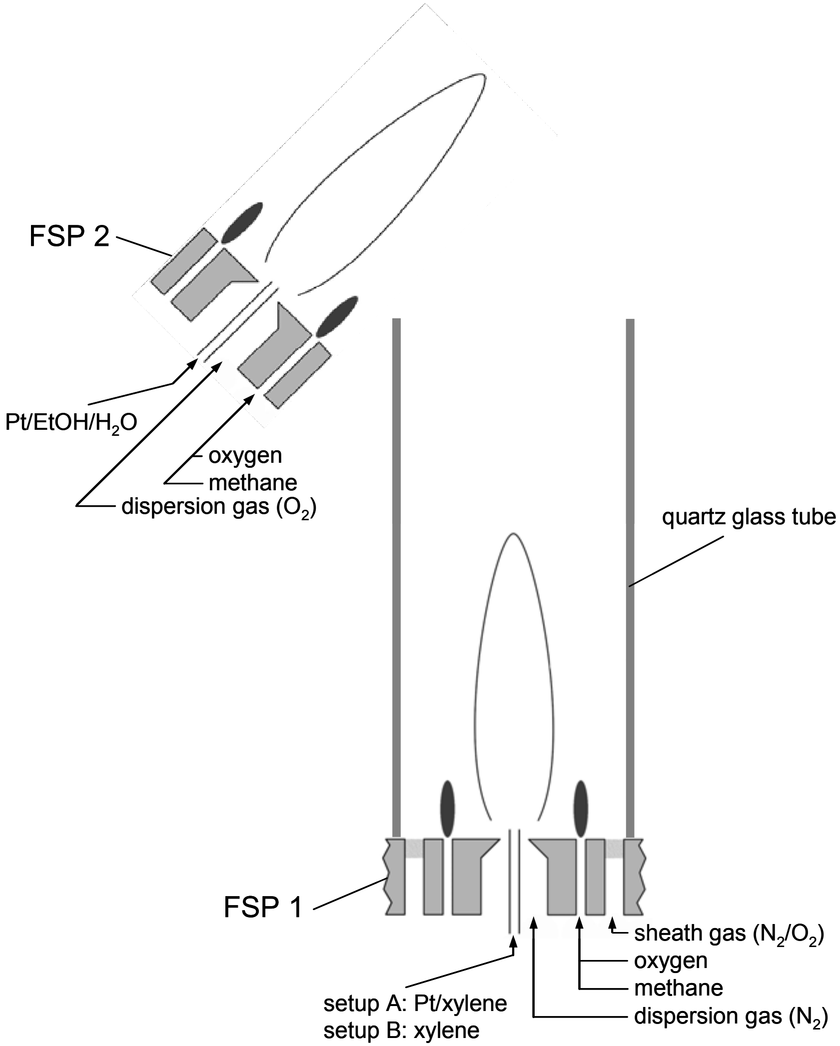
2-flame synthesis of Pt/Ba/Al_2O_3 for NO_x storage reduction



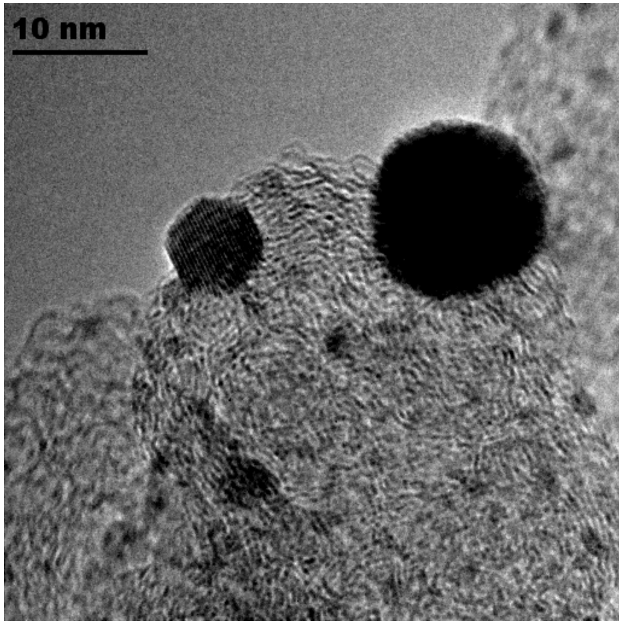


R. Strobel, M. Piacentini, L. Mädler, M. Maciejewski, A. Baiker, SEP, *Chem. Mater.*, **18, 2532** (2006).

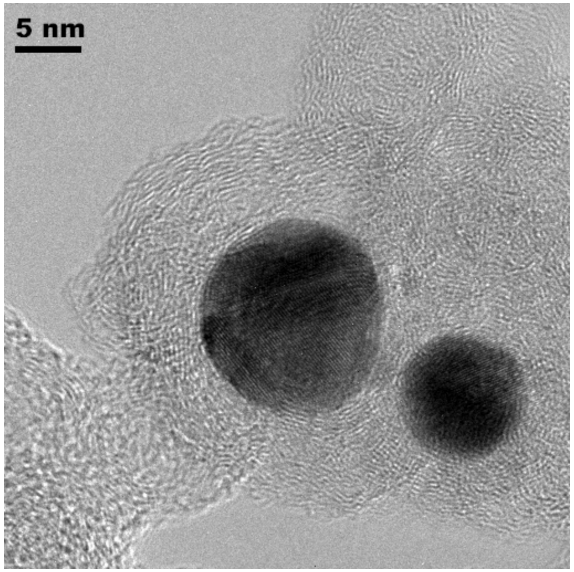
FSP-made Pt/Carbon particles



2-FSP



1-FSP

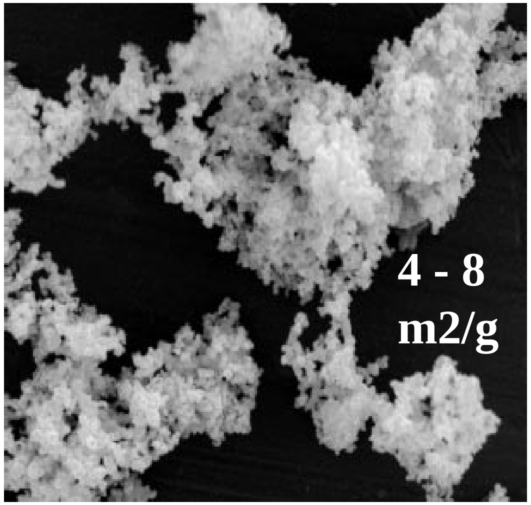


TiO_2

Paints

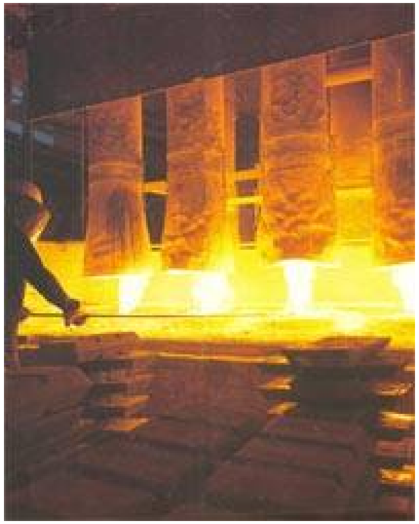
Tires, inks

Ni for batteries



Carbon Black

materials-made in aerosol flow reactors today

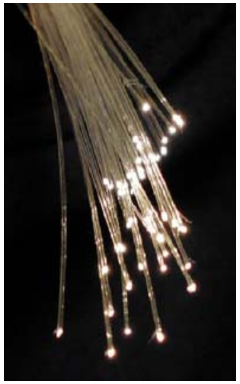


Vulcanizing ZnO by Zn vapor – air oxidation

SiO_2

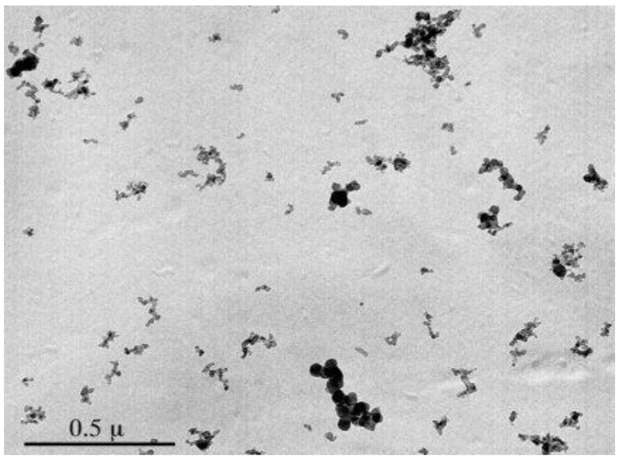
Flowing aid

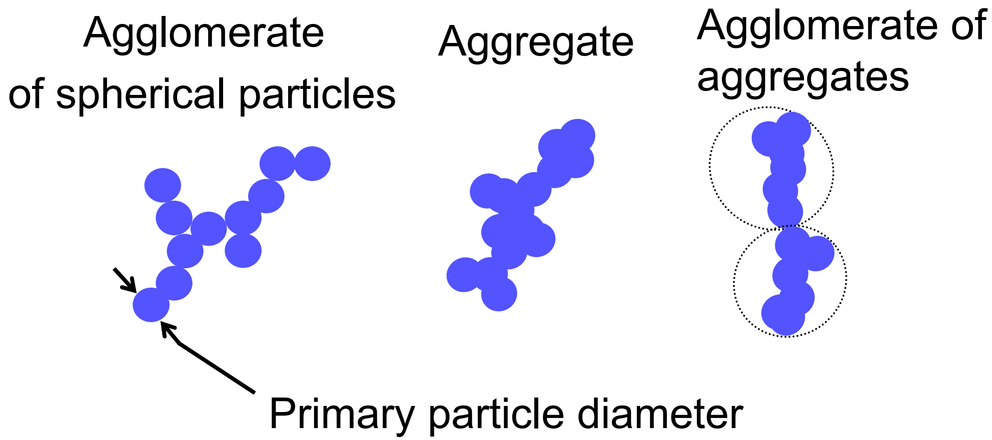
Optical fibers



Motivation

Typical exhaust soot are *not* spherical but agglomerates:

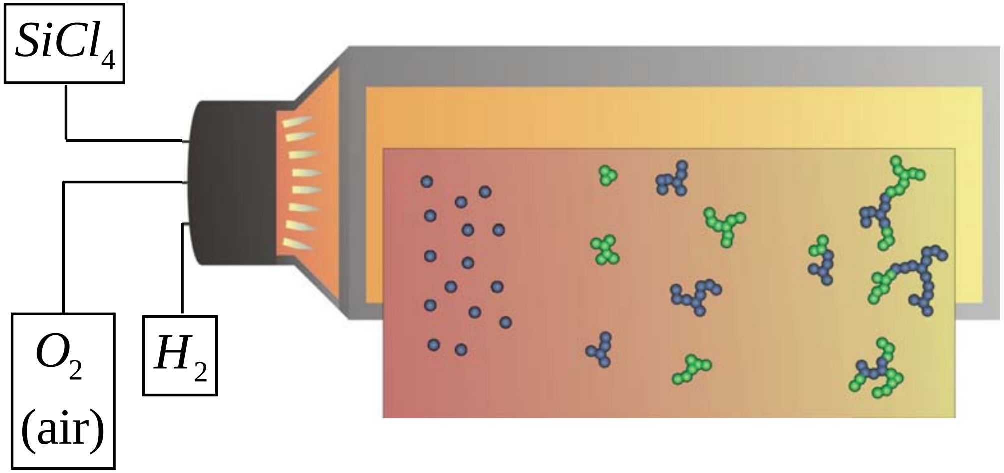




Diesel soot (Miller, 2007)
(Link: http://www2a.cdc.gov/niosh-nil/report.asp?ID=111&go=moreinfo&go2=)

High concentrations of exhaust soot gas concentration in the range of 10^5-10^8 #/cm^3

Synthesis of Fumed Silica by $SiCl_4$ Hydrolysis



Initial concentration:
$y(SiCl_4)$ ~ 12 mol%
$\phi_s(SiO_2)$ ~ 0.01% @ 300 K

- Chemical Reaction
- Particle Formation
- Coagulation and coalescence

Hannebauer, B.; Menzel, F. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1485-1490.

Monodisperse Silica Aerosol Dynamics for $SiCl_4$ Oxidation, Coagulation and Sintering

Total Number Concentration

$$\frac{dN}{dt} = -\frac{1}{2}\beta N^2 \rho_g - \frac{d[SiCl_4]}{dt}$$

Total Surface Area Concentration

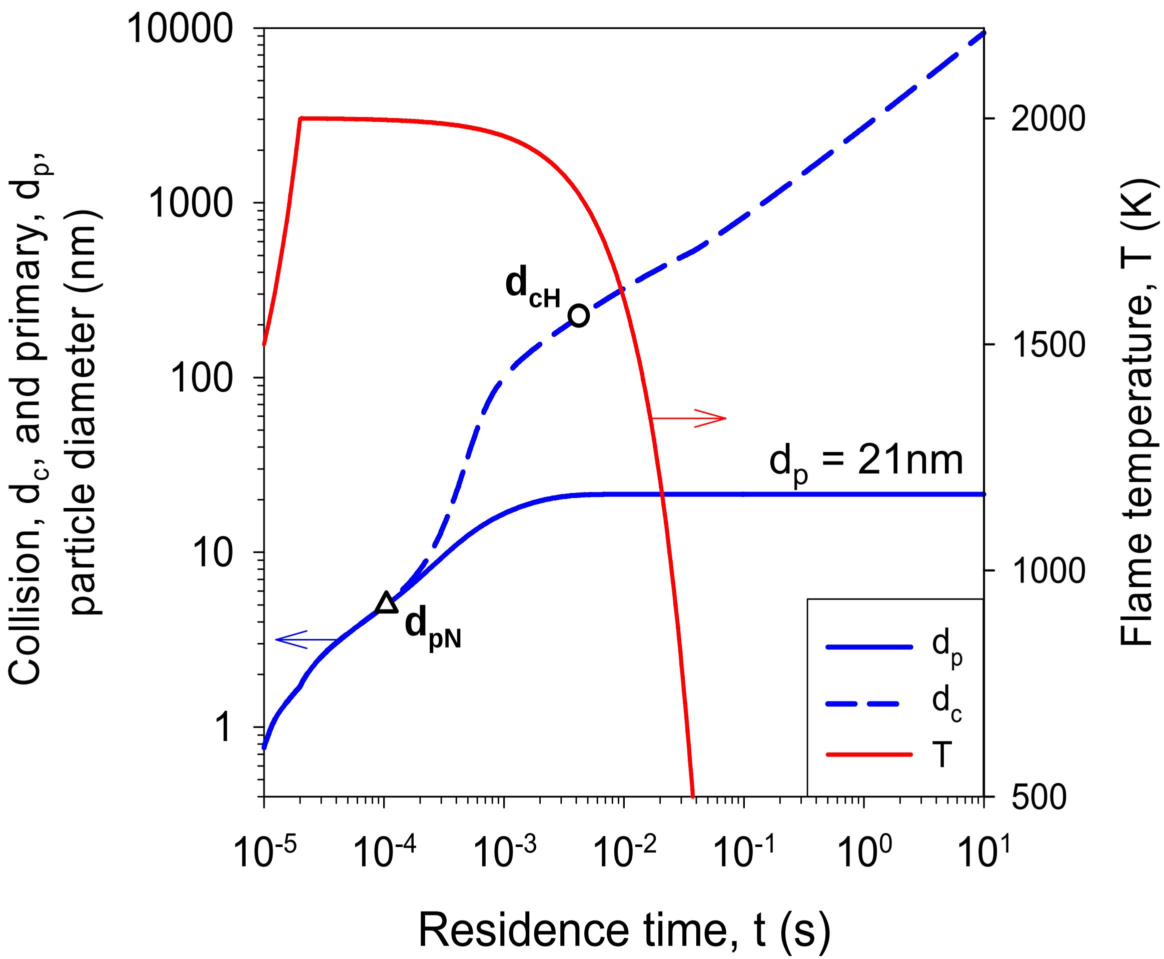
$$\frac{dA}{dt} = -\frac{d[SiCl_4]}{dt}\alpha_m - \frac{1}{\tau_s}(A - N\cdot\alpha_s)$$

Total Volume Concentration

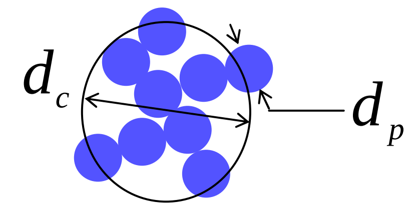
$$\frac{dV}{dt} = -\frac{d[SiCl_4]}{dt}v_m$$

F.E. Kruis, K. Kusters, SEP, B. Scarlett, *Aerosol Sci. Technol*. **19**, 514-526 (1993)

Particle Size Evolution during SiO_2 Synthesis

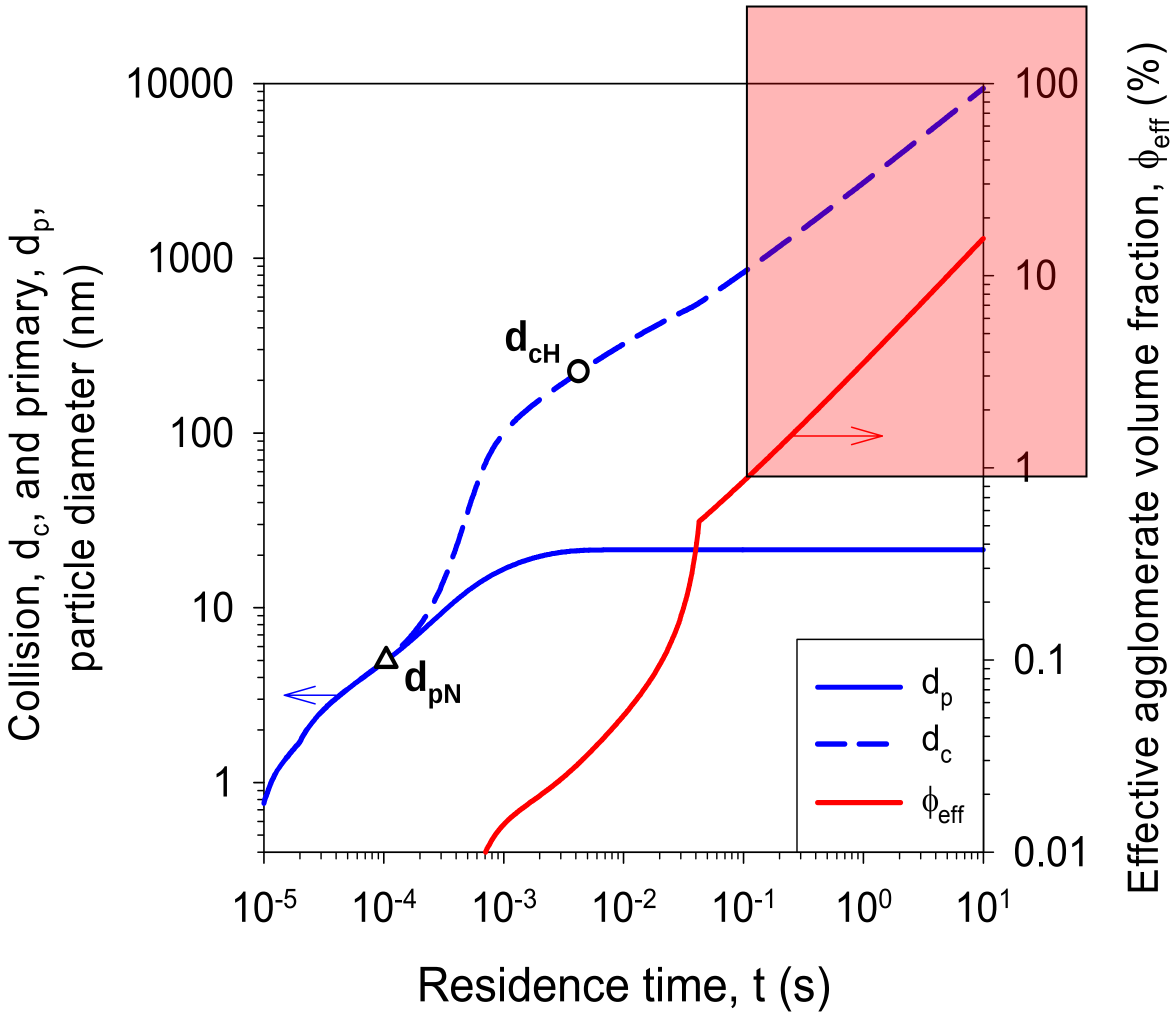


$D_f = 1.8$

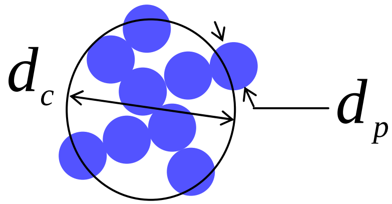


M.C. Heine, SEP, *Langmuir*, **22**, 10238-10245 (2006).

High Effective Agglomerate Volume Fraction



$$D_f = 1.8$$



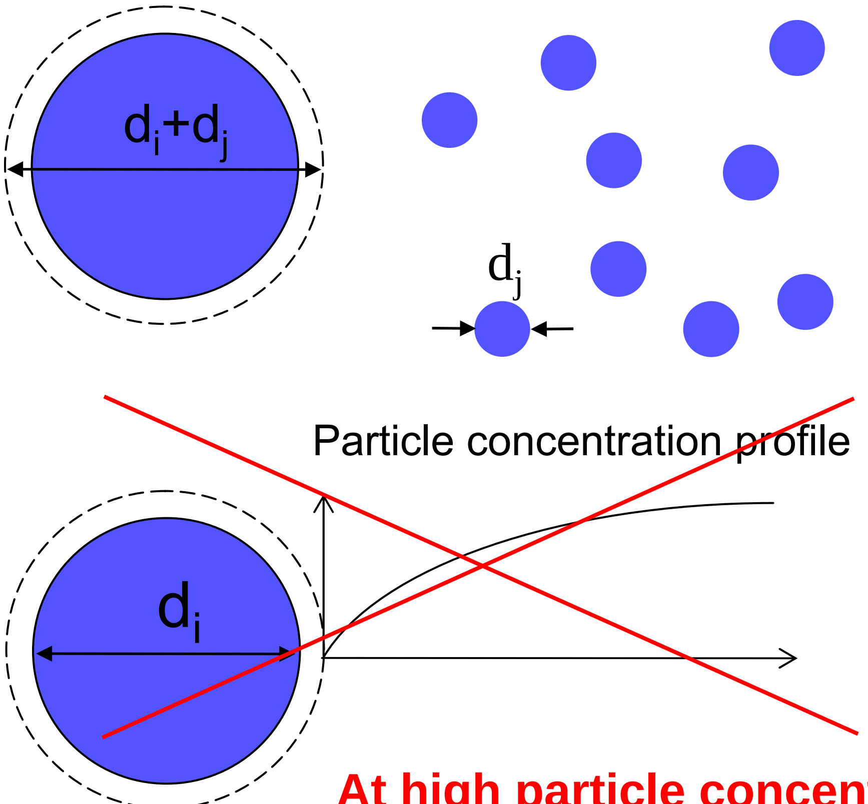
$$\phi_{eff} = N\frac{\pi}{6}d_c^3 \geq \phi_s$$

$$\phi_s < 0.01\%$$

M.C. Heine, SEP, *Langmuir*, **22**, 10238-10245 (2006).

Derivation of the Collision Frequency Function

(Brownian Continuum Regime)



Model assumptions:

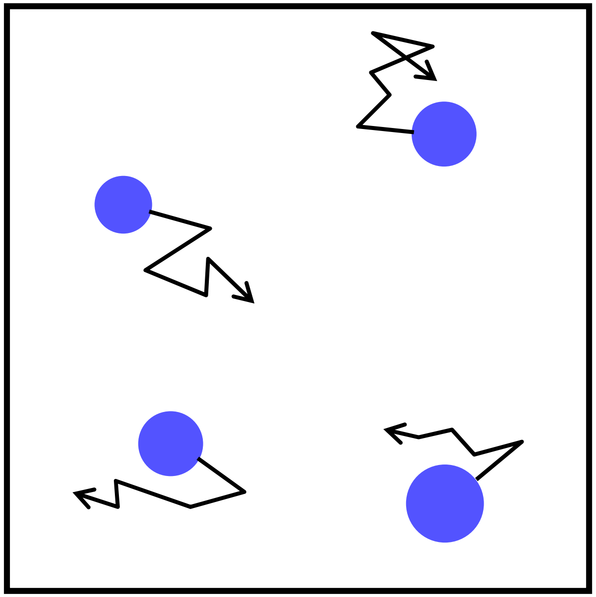
- Equilibrium particle concentration profile
- Sufficiently dilute concentrations

$$\beta_{i,j} = 2\pi\left(d_i + d_j\right)\left(D_i + D_j\right)$$

At high particle concentrations the key model assumptions are no longer valid

M. Smoluchowski (1917)

Langevin Dynamics (LD) Simulations



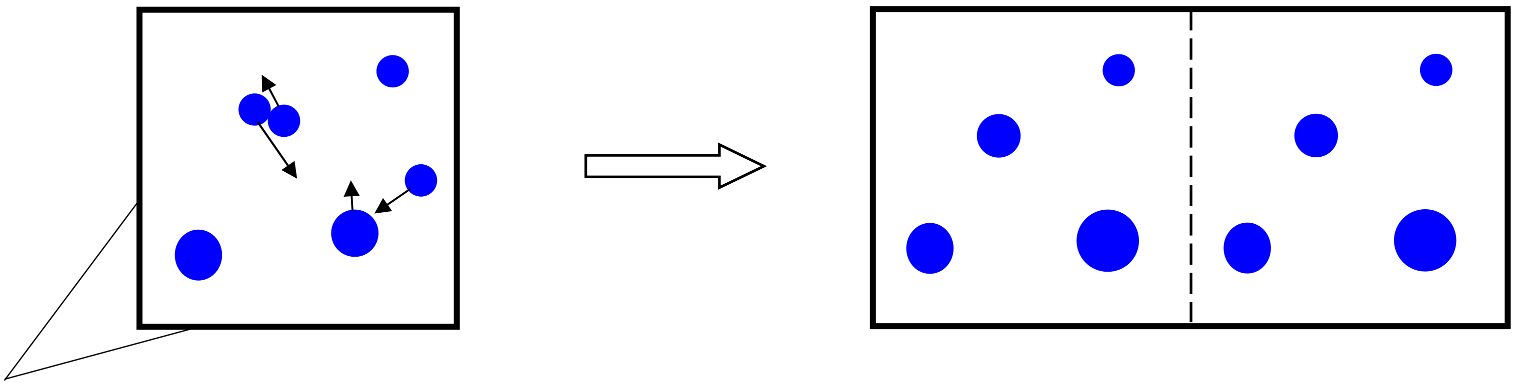
Equation of particle motion:

$$m_i \dot{\mathbf{v}} + \frac{3\pi\eta d_i}{C_i}\mathbf{v} + \mathbf{F}_{\mathbf{Brownian}} = 0$$

Numerical solution procedure:

D.L. Ermak, H. Buckholz, *J. Comput. Phys.* **1980**, *35*, 169-182.
A. Gutsch, SEP, F. Loffler, *J. Aerosol. Sci.* **1995**, *26*, 187-199.

Polydisperse Particle Growth (Full Coalescence)



Periodic boundaries

Particle collisions

New diameter, position
and velocity
(Mass and inertia balance)

n □

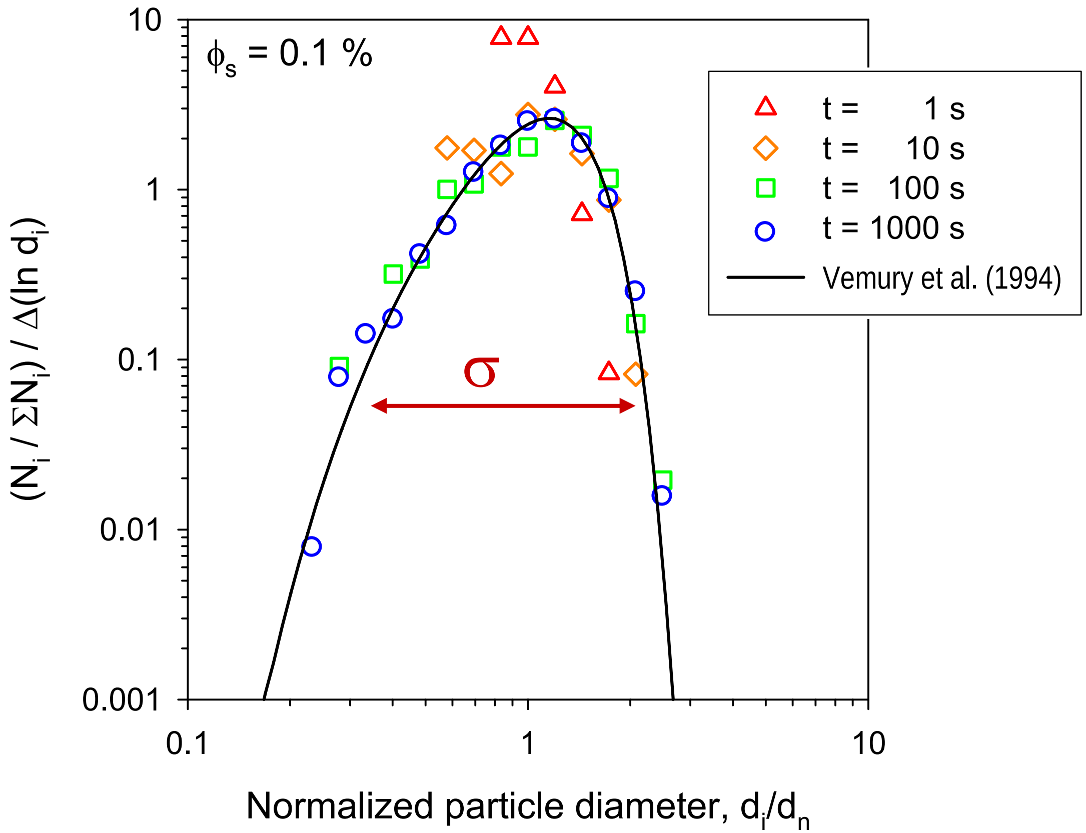
$\phi_s = const$

Initially n_0 = 2000 particles

If n ≤ 1000 the domain size is duplicated in turns in x, y and z-direction

2000 ≥ n ≥ 1000 at all times

Self-preserving Size Distribution



Air properties:

$T = 293$ K

$p = 1$ bar

2000 monodisperse particles

$D_f = 3$

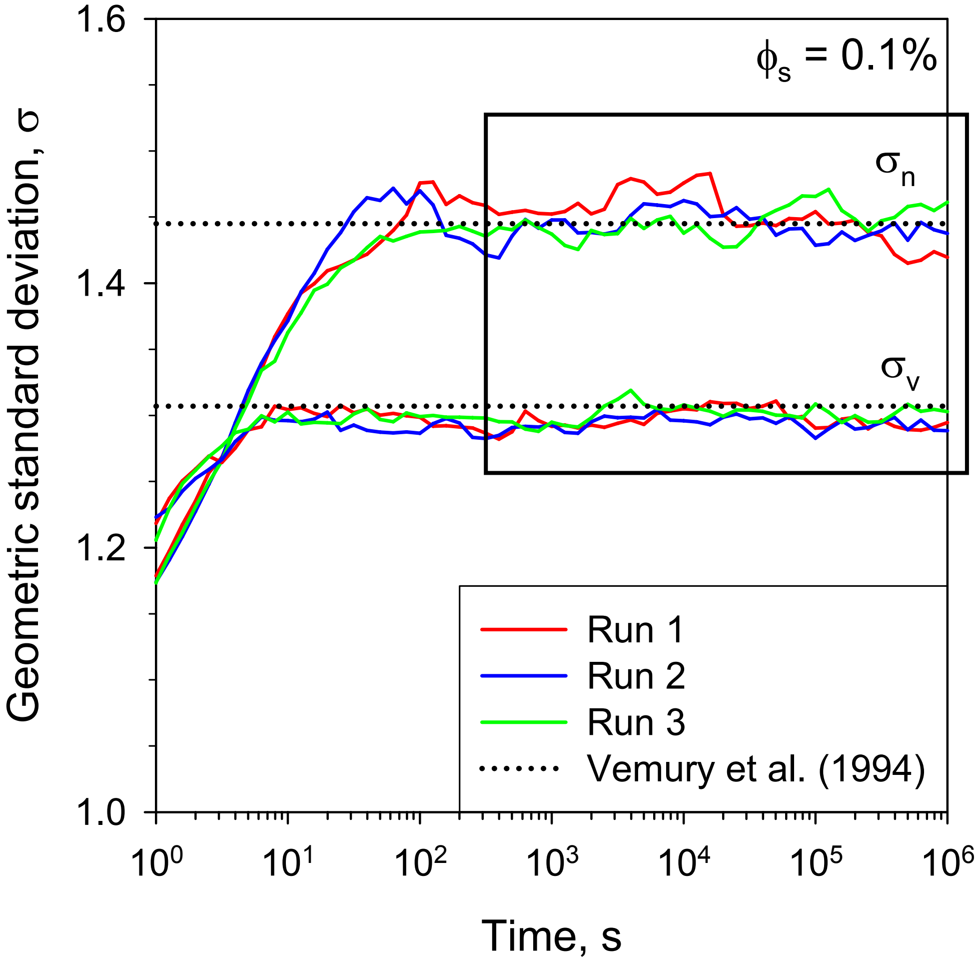
$d_0 = 1\ \mu m$

$\rho_p = 1\ g/cm^3$

$N_0 = 2 \times 10^9\ \#/cm^3$

Brownian Continuum Regime

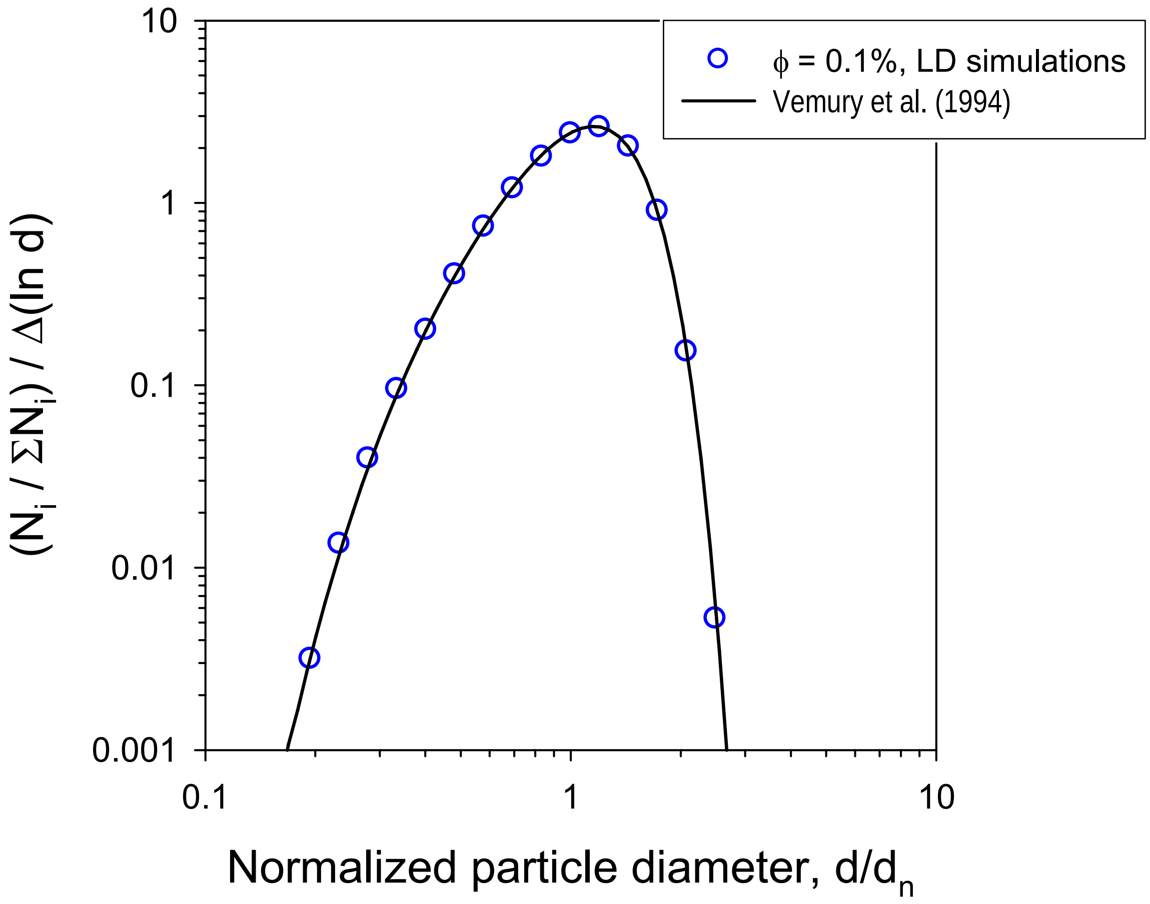
Polydispersity for Dilute Concentrations



	LD simulation	Vemury et al. (1994)
Number:	$\sigma_n \approx 1.45$	$\sigma_n = 1.445$
Volume:	$\sigma_v \approx 1.30$	$\sigma_v = 1.307$

M.C. Heine, SEP, *Langmuir*, **23**, in press (2007).

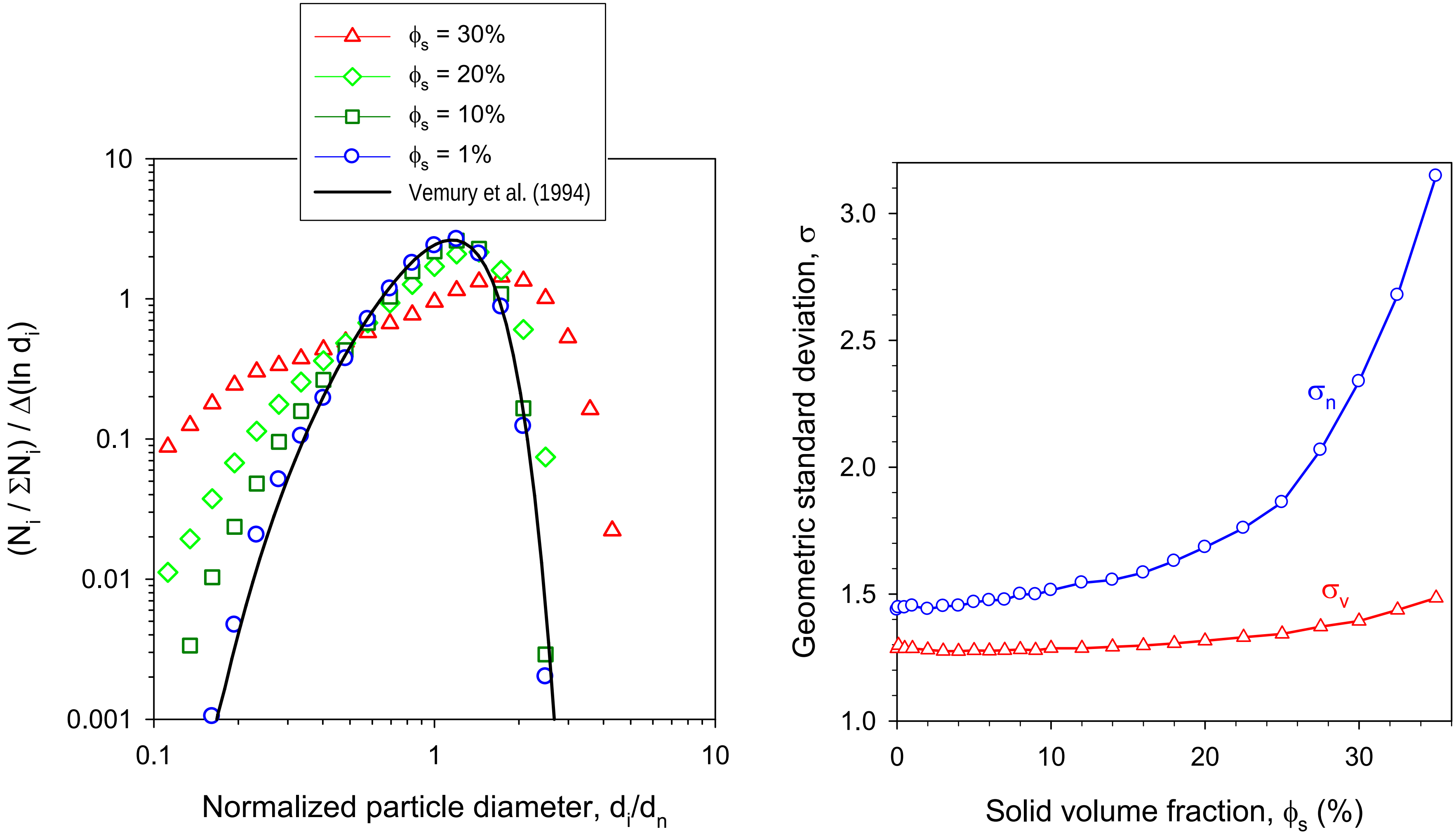
Averaged Self-preserving Size Distribution



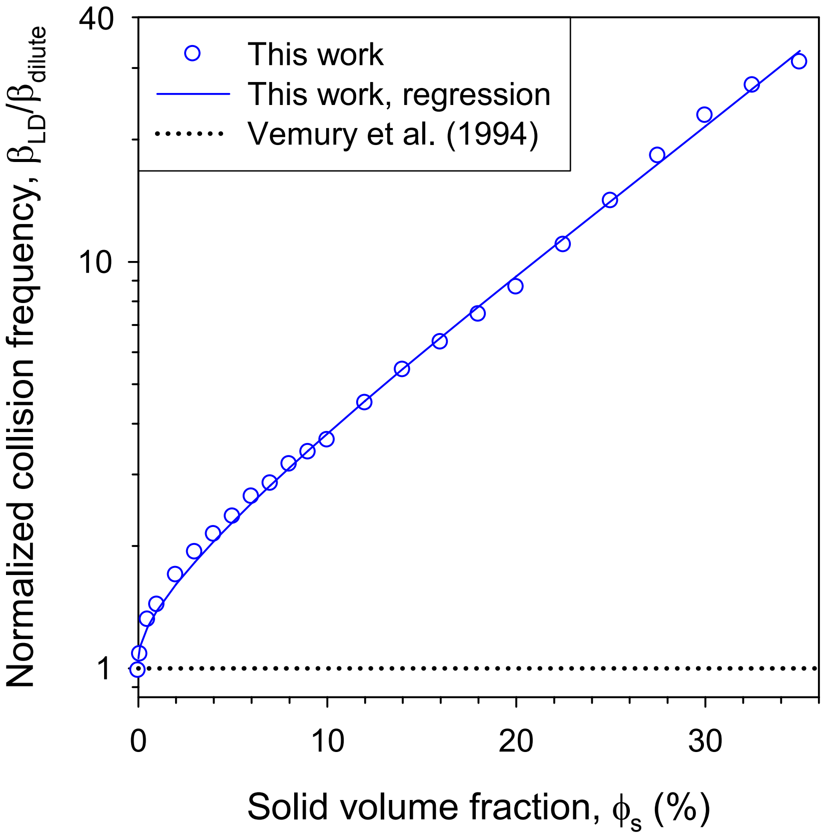
Average of 90 distributions after self-preservation is attained

Validation of the LD simulations

Self-preserving Size Distribution depends on ϕ_s



Coagulation Accelerates with Increasing ϕ_s

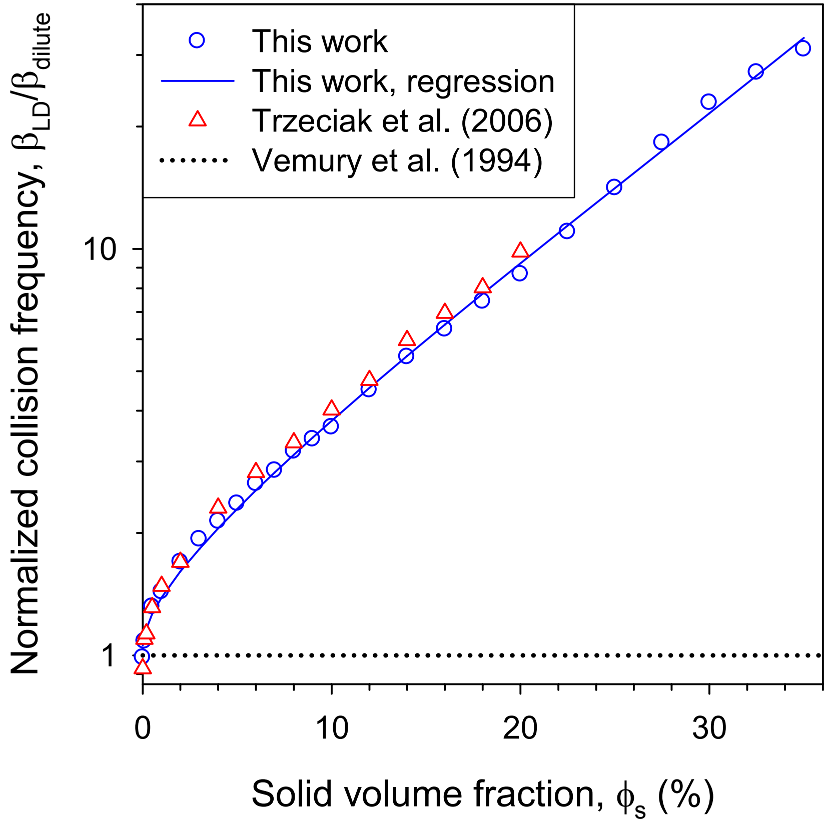


ϕ_s	$\beta_{LD}/\beta_{dilute}$
0.01%	± 0%
0.1%	+ 8%

$$\beta_{dilute} = 1.0734 \frac{8k_bT}{3\mu}$$

$$\frac{\beta_{LD}}{\beta_{dilute}} \approx 1 + \frac{2.5}{1-\phi}(-\log\phi)^{-2.7}$$

Coagulation Accelerates with Increasing ϕ_s

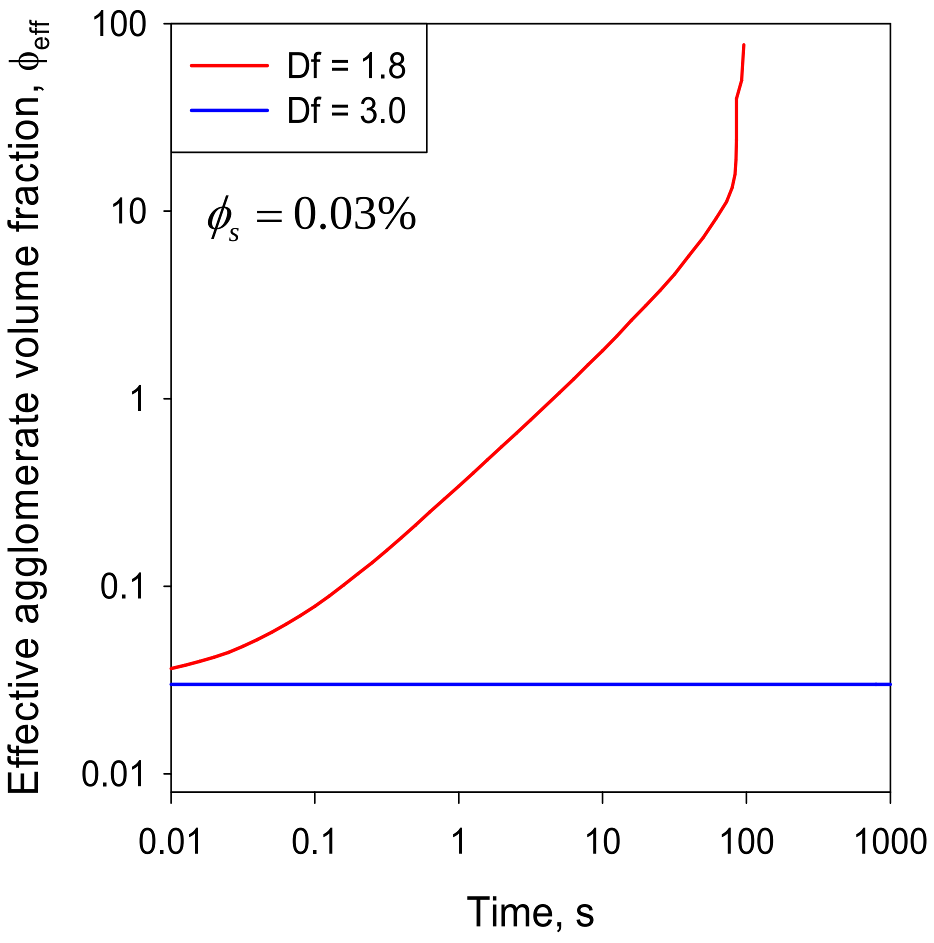


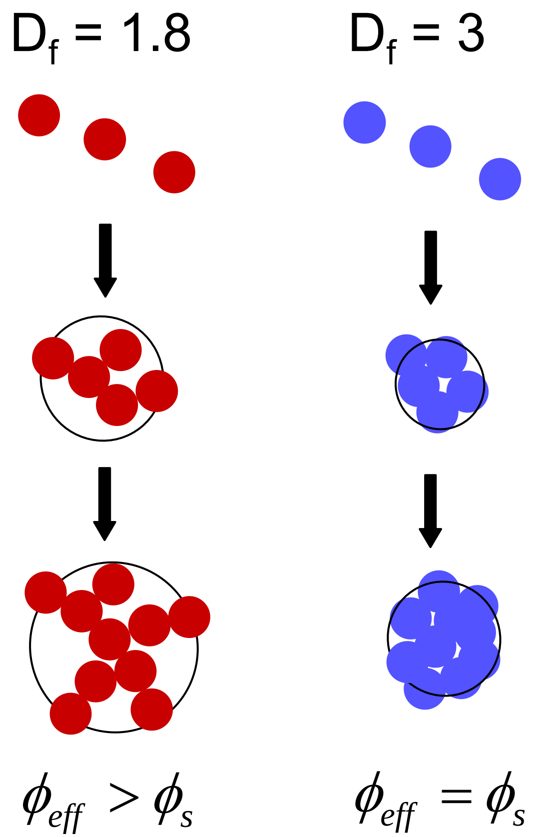
LD simulations by Trzeciak et al. (2006)
Counting particle collisions

Assumptions:

- Constant particle diameter
- Monodisperse particles
- After collision one particle is redistributed

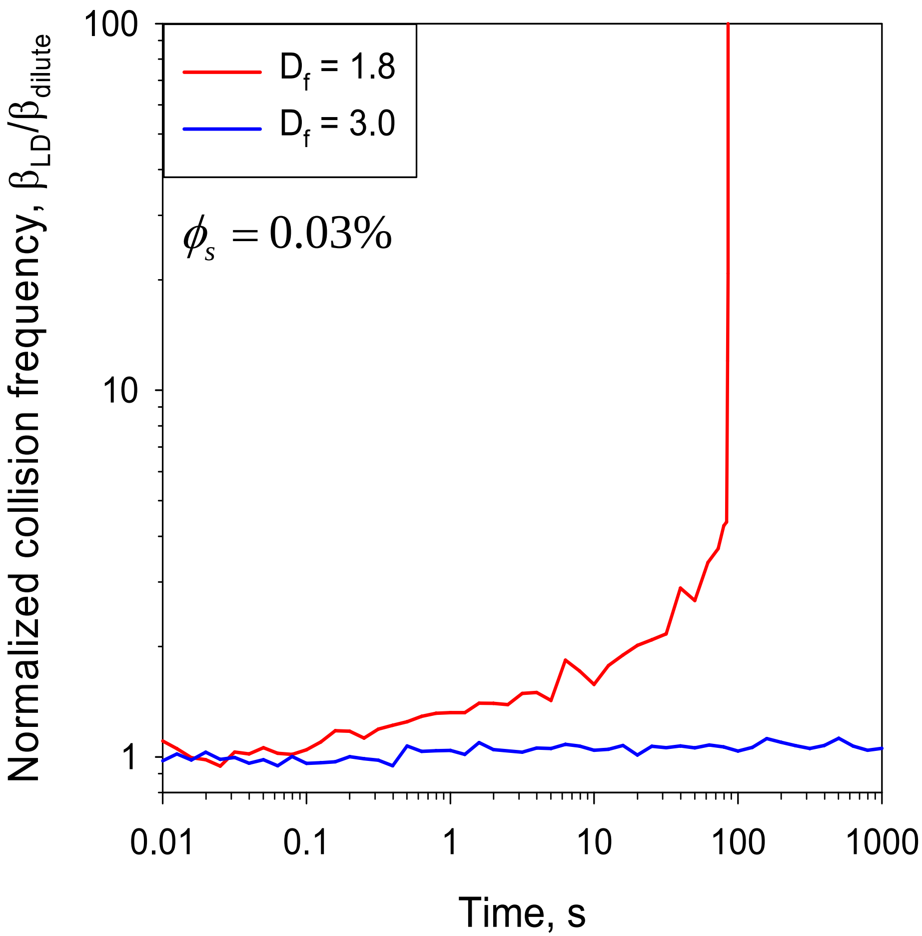
ϕ_{eff} Increases during Fractal Particle Growth

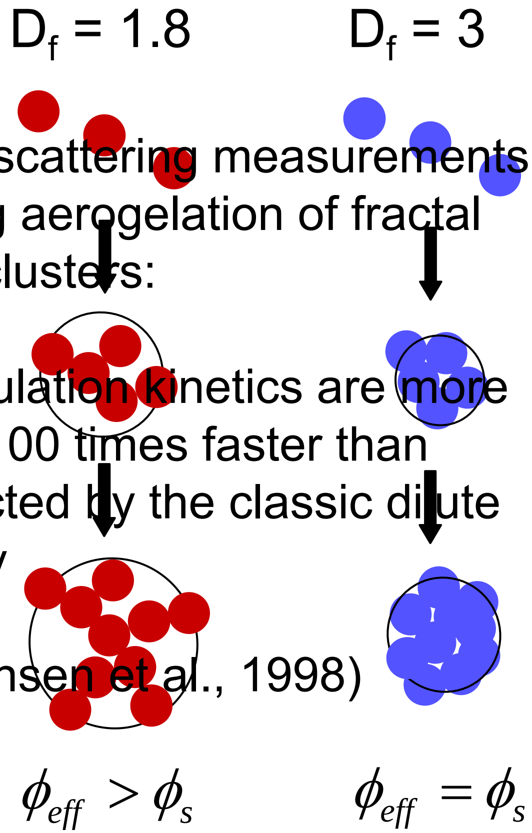




d_0 = 220 nm
$N_0 = 5.4 \times 10^{10}$ #/cm^3

Coagulation Kinetics Accelerate for $D_f < 3$



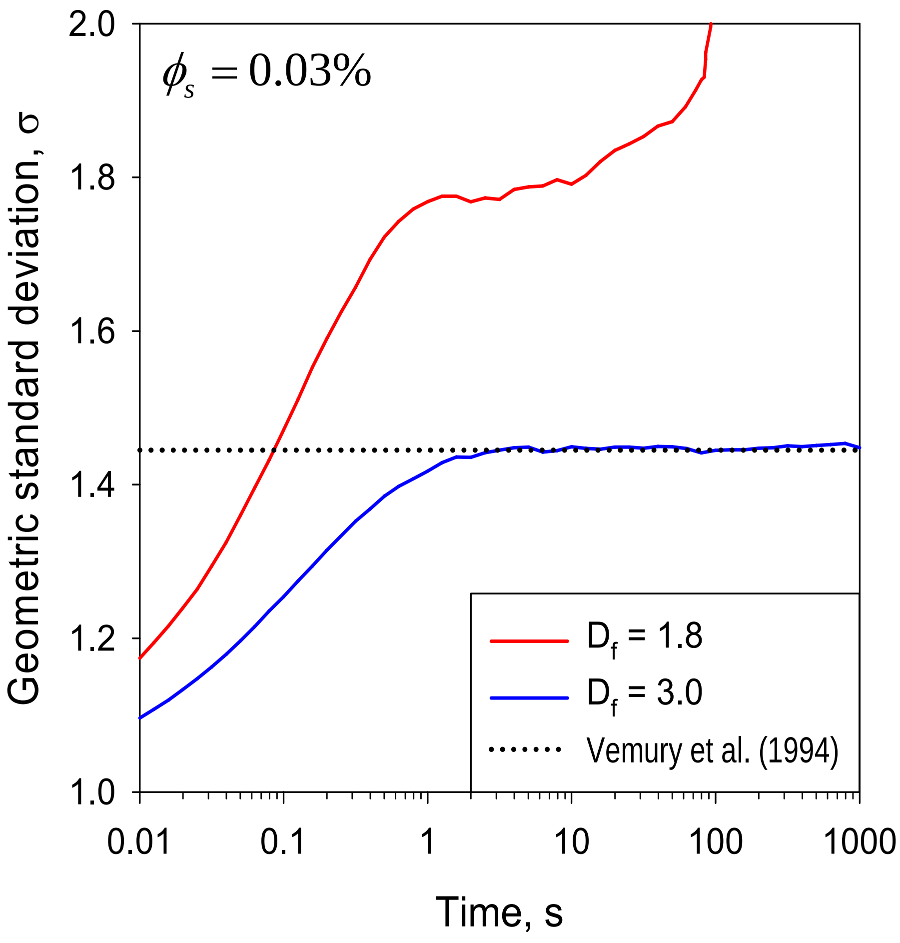


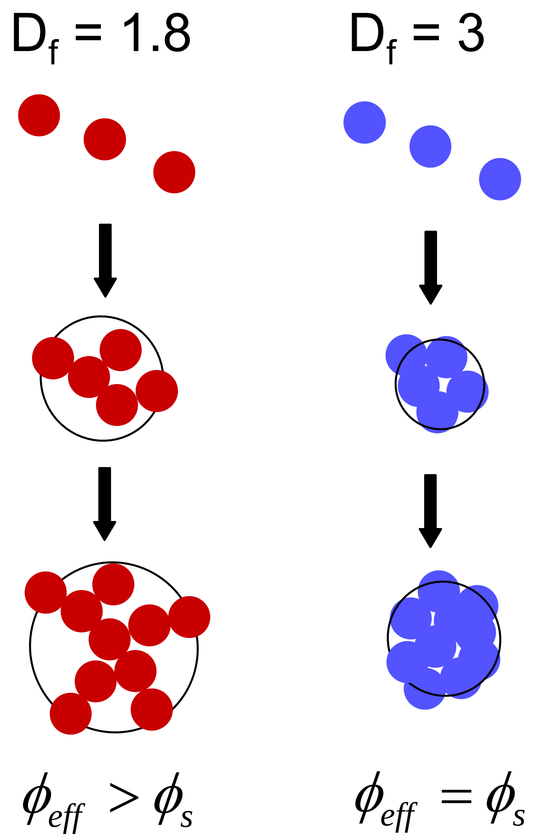
Light scattering measurements during aerogelation of fractal soot clusters:

Coagulation kinetics are more than 100 times faster than predicted by the classic dilute theory

(Sorensen et al., 1998)

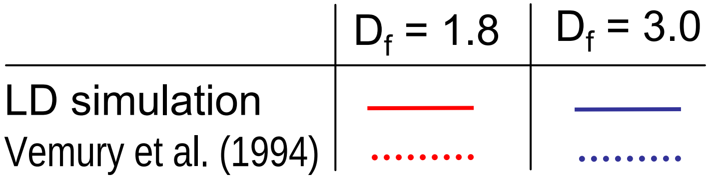
No Self-preserving Distribution Exists for $D_f < 3$



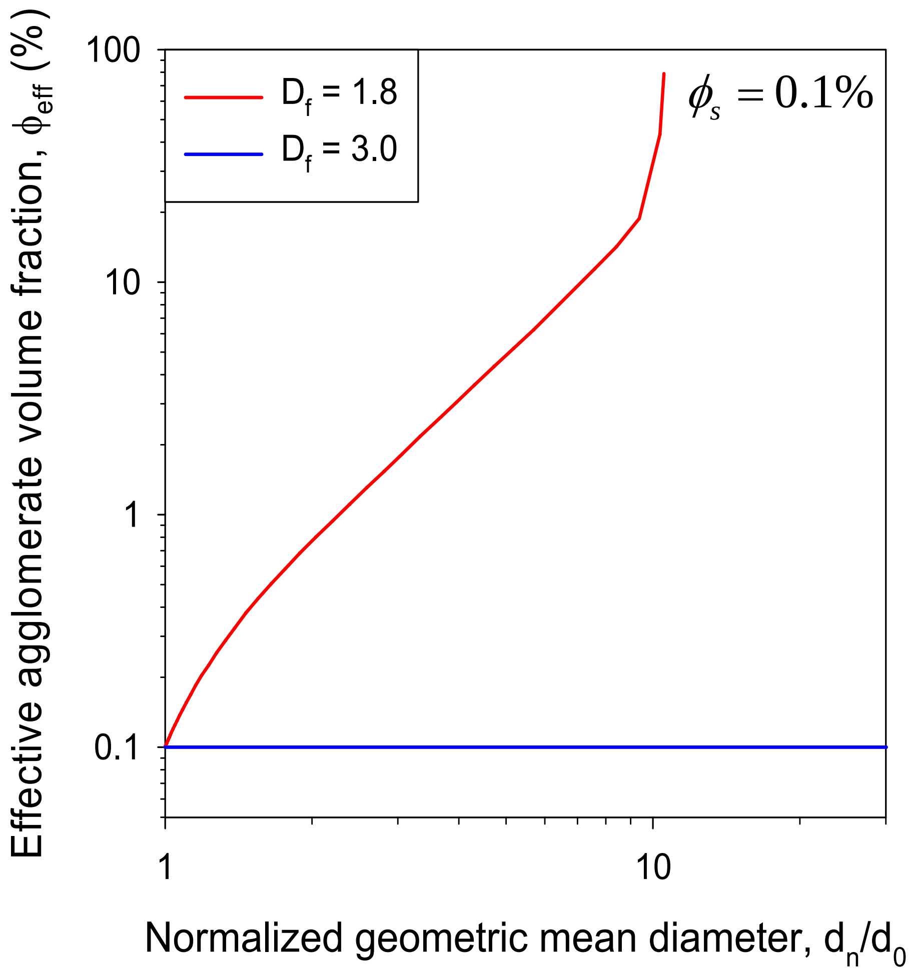


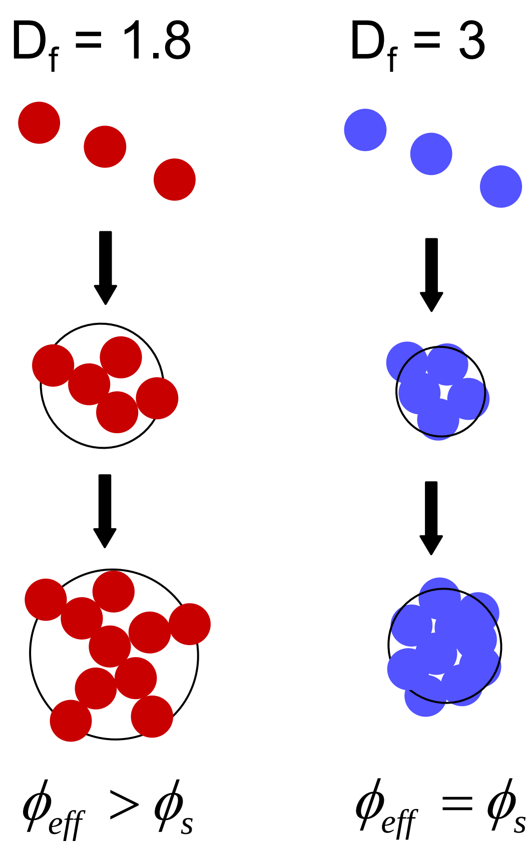
Conclusions

- Langevin dynamics have been used to determine the coagulation frequency (Brownian continuum) from first principles reproducing classic results at dilute conditions
- Particle growth accelerates at high concentrations (about 10 times at 20 vol%)
- Self-preservation was found up to 35 vol% for $D_f = 3$ but self-preserving size distributions broaden for increasing ϕ_s
- For coagulation with $D_f < 3$ no self-preserving size distribution exists

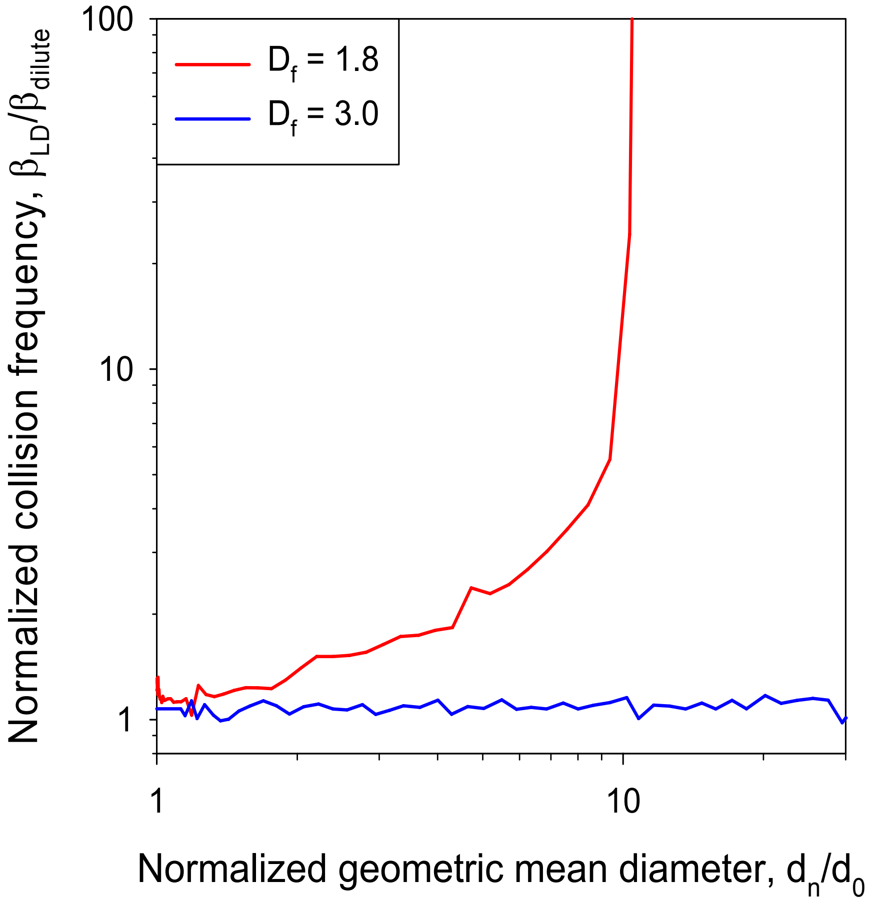

D_f = 1.8
D_f = 3.0
LD simulation
Vemury et al. (1994)

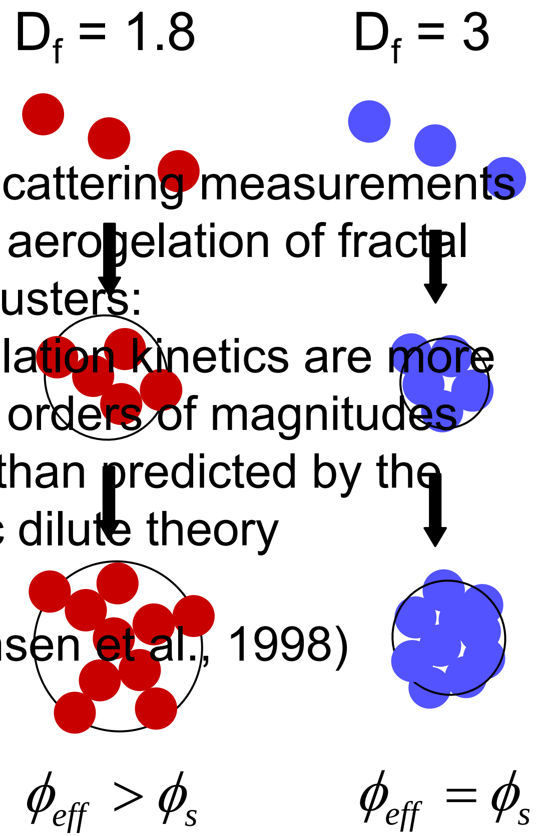
ϕ_{eff} Increases during Fractal Particle Growth





Coagulation Kinetics Accelerate for $D_f < 3$

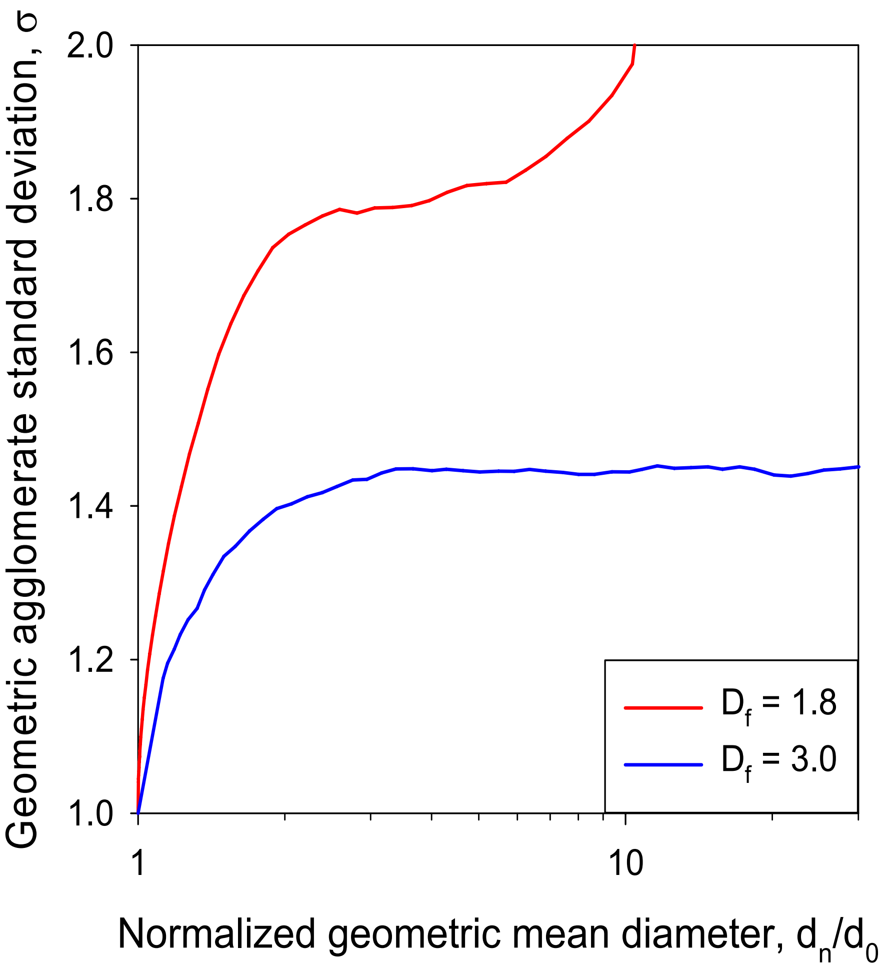


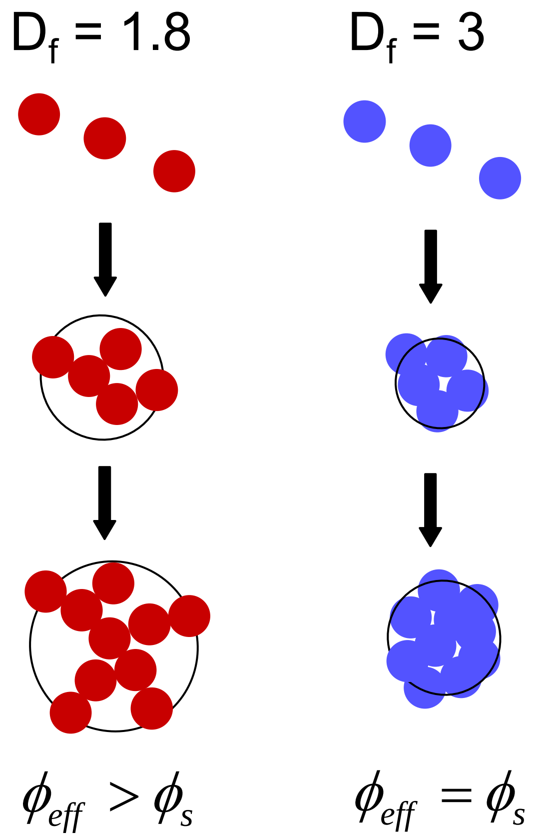


Light scattering measurements during aerogelation of fractal soot clusters:
Coagulation kinetics are more than 2 orders of magnitudes faster than predicted by the classic dilute theory

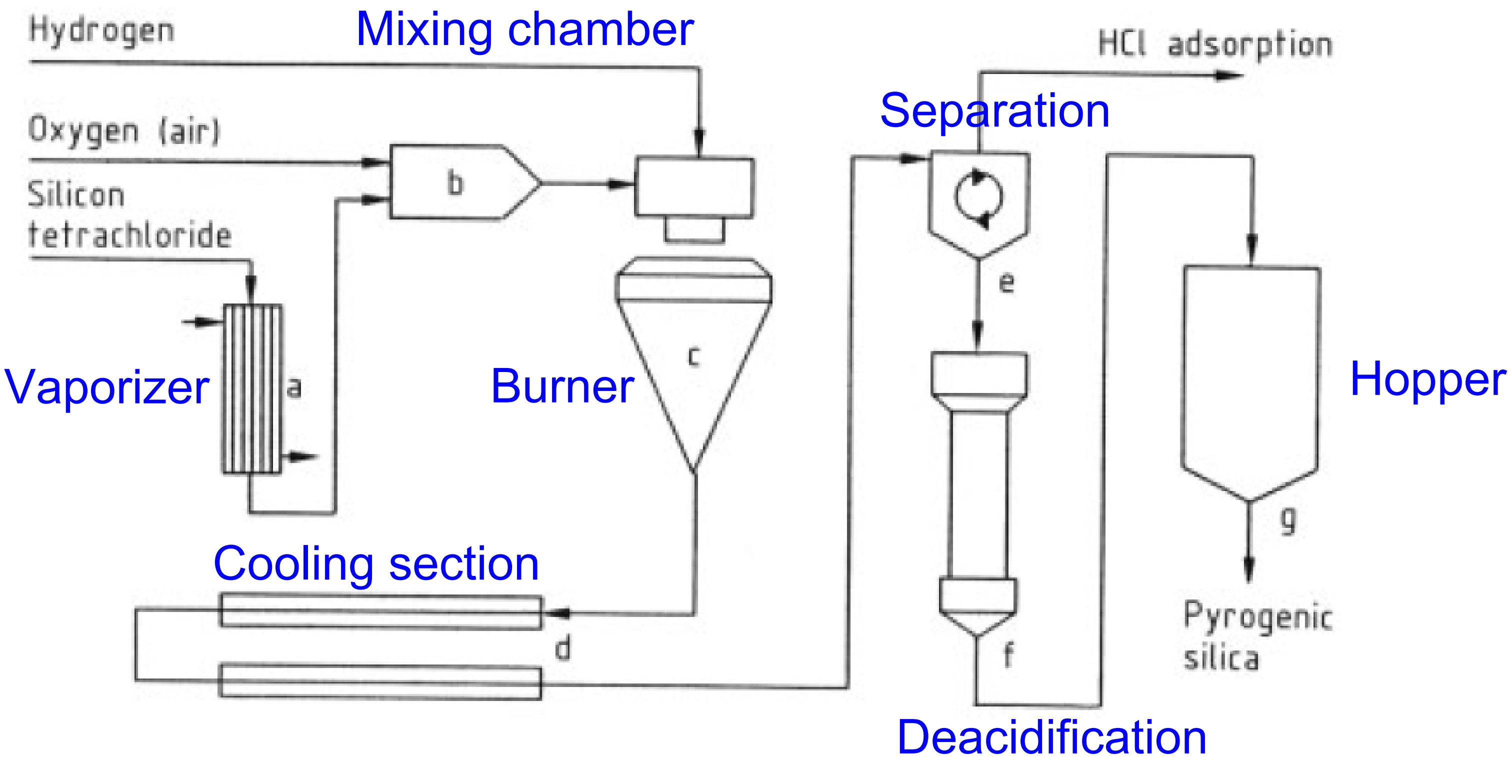
(Sorensen et al., 1998)

No Self-preserving Distribution Exists for $D_f < 3$





Production of Pyrogenic Silica



High precursor concentration:

($SiCl_4$ / H_2 / O_2 / N_2) = 1.0 / 2.1 / 1.1 / 4.3

Initial $SiCl_4$ mole fraction: $\phi_{SiCl4,0}$ = 12%

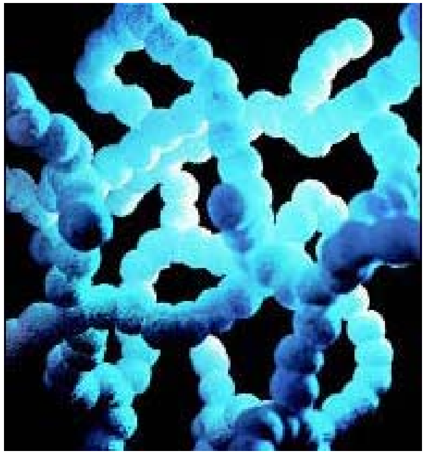
SiO_2 solid volume fraction: 0.002% at 1500 K

(Hannebauer and Menzel, 2003)

Ullmann's Encyclopedia of Industrial Chemistry, *WILEY-VCH*, (2005)

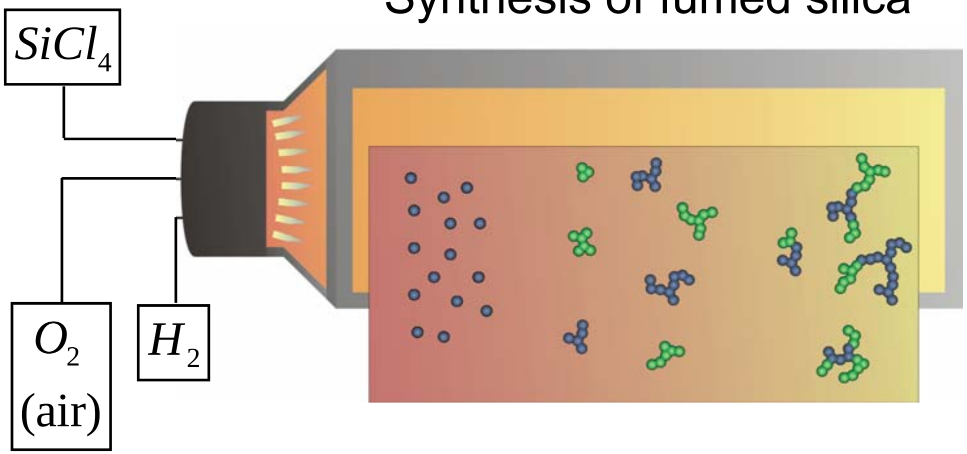
Pyrogenic Silica

Company	Degussa	Cabot	Wacker
Product name	Aerosil	CAB-O-SIL	HDK
Surface area (m^2/g)	90 - 380	130 - 380	110 - 440
Primary particle diameter (nm)	7.2 - 30.3	7.2 - 21.0	6.2 - 24.8
Hard agglomerate diameter (nm)		200 - 300	



Particle Growth by Coagulation

Synthesis of fumed silica

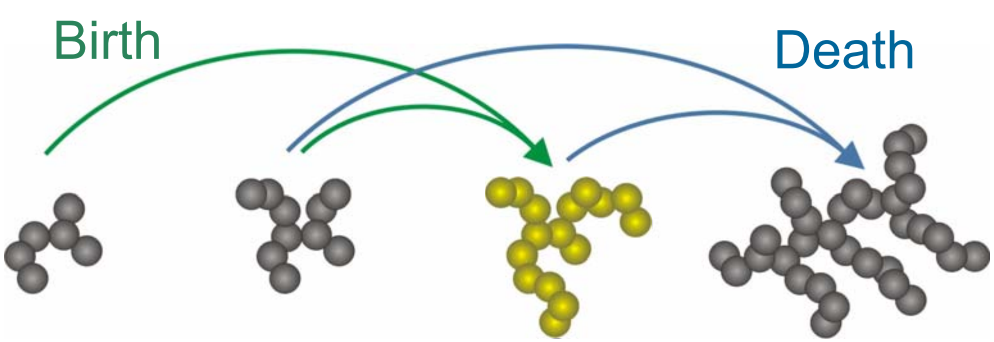


Initial concentration:
$y(SiCl_4) \sim 12$ mol%

$\phi_s(SiO_2) \sim 0.01\%$ @ 300 K

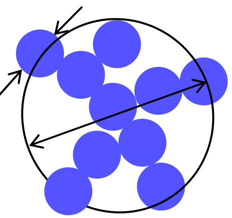
(Hannebauer and Menzel, 2003)

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v \beta(\tilde{v}, v-\tilde{v})\, n(\tilde{v},t)\, n(v-\tilde{v},t)\, d\tilde{v} - \int_0^\infty \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\, d\tilde{v}$$



Agglomerate and Primary Particle Size Definitions

Primary particle diameter



Agglomerate collision diameter

$$d_p = \frac{6V}{A}$$

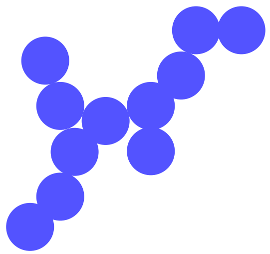
$$\phi_{sol} = N_{aggl} n_p \frac{\pi}{6} d_p^3$$

$$d_c = d_p n_p^{1/D_f}$$

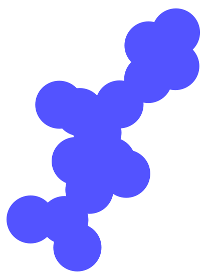
$$\phi_{eff} = N_{aggl} \frac{\pi}{6} d_c^3$$

$$D_f \sim 1.8$$

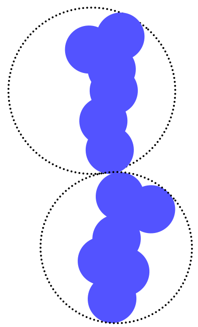
Soft agglomerate
of spherical particles



Hard agglomerate



Soft agglomerate



Nucleation, Coagulation and Sintering of Particles

Monodisperse Population Balance Model

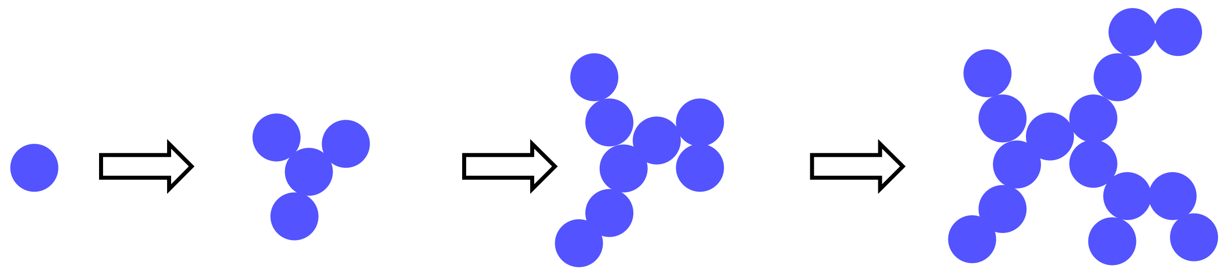
Kruis et al. (1993)

- Balance of particle number, surface area and volume
- Neglecting particle size distribution

Reaction/ Nucleation

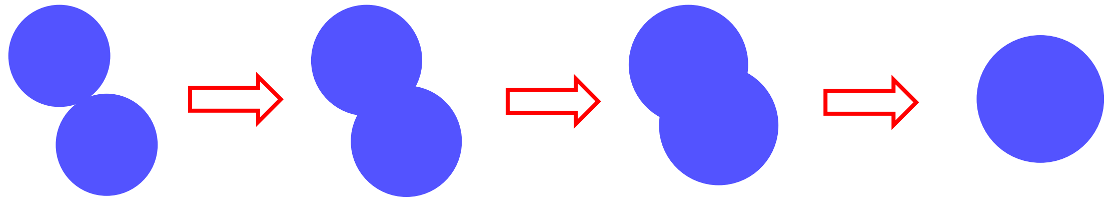
$SiCl_4$ (gas) $\longrightarrow$ SiO_2 (solid)

Coagulation



Sintering

(Koch & Friedlander, 1990)



Monodisperse Model for Chemical Reaction, Coagulation and Sintering

Total Number Concentration

$$\frac{dN}{dt} = -\frac{1}{2}\beta N^2 \rho_g - \frac{d[SiCl_4]}{dt}$$

Total Surface Area Concentration

$$\frac{dA}{dt} = -\frac{d[SiCl_4]}{dt}\alpha_m - \frac{1}{\tau_s}(A - N \cdot \alpha_s)$$

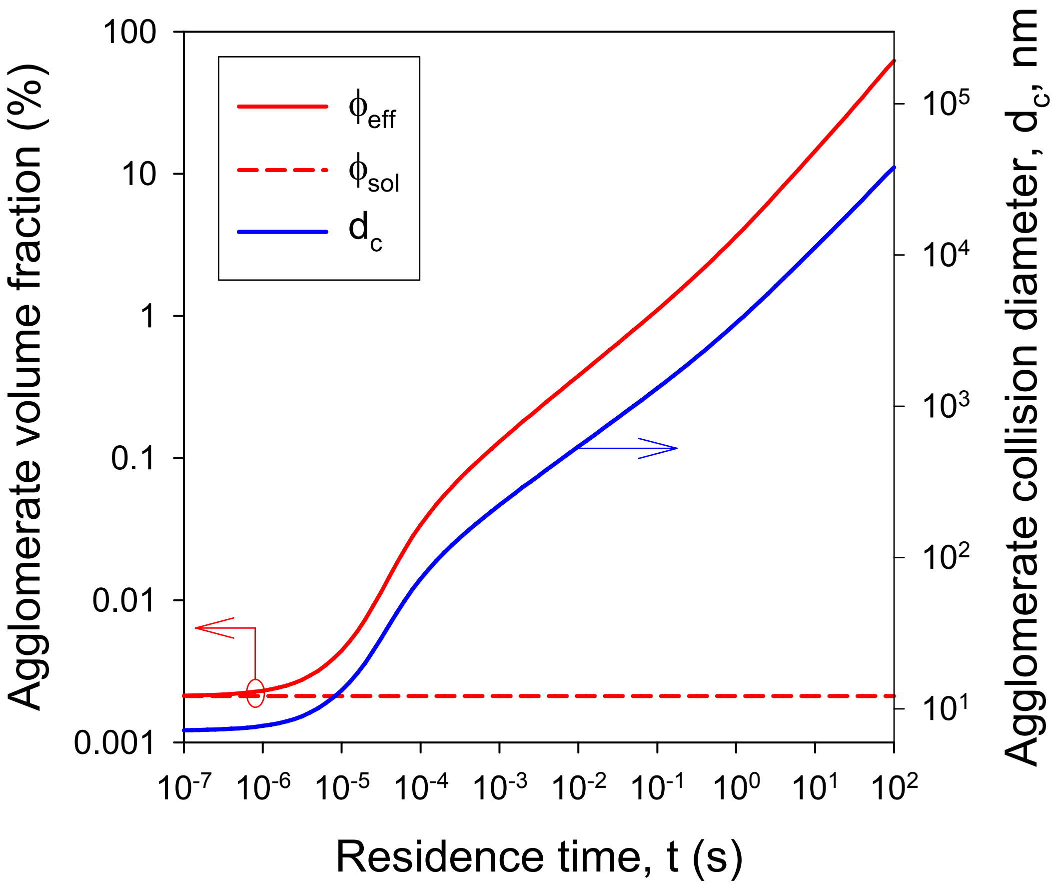
Total Volume Concentration

$$\frac{dV}{dt} = -\frac{d[SiCl_4]}{dt} v_m$$

$$\tau_s = 6.5 \times 10^{-15} d_p \exp\left(\frac{8.3 \times 10^4}{T}\left(1 - \frac{d_{p,\min}}{d_p}\right)\right)$$

(Kruis et al., 1993)

Φ_{eff} Increases during Coagulation



$$\phi_{SiCl_4,0} = 12\%$$

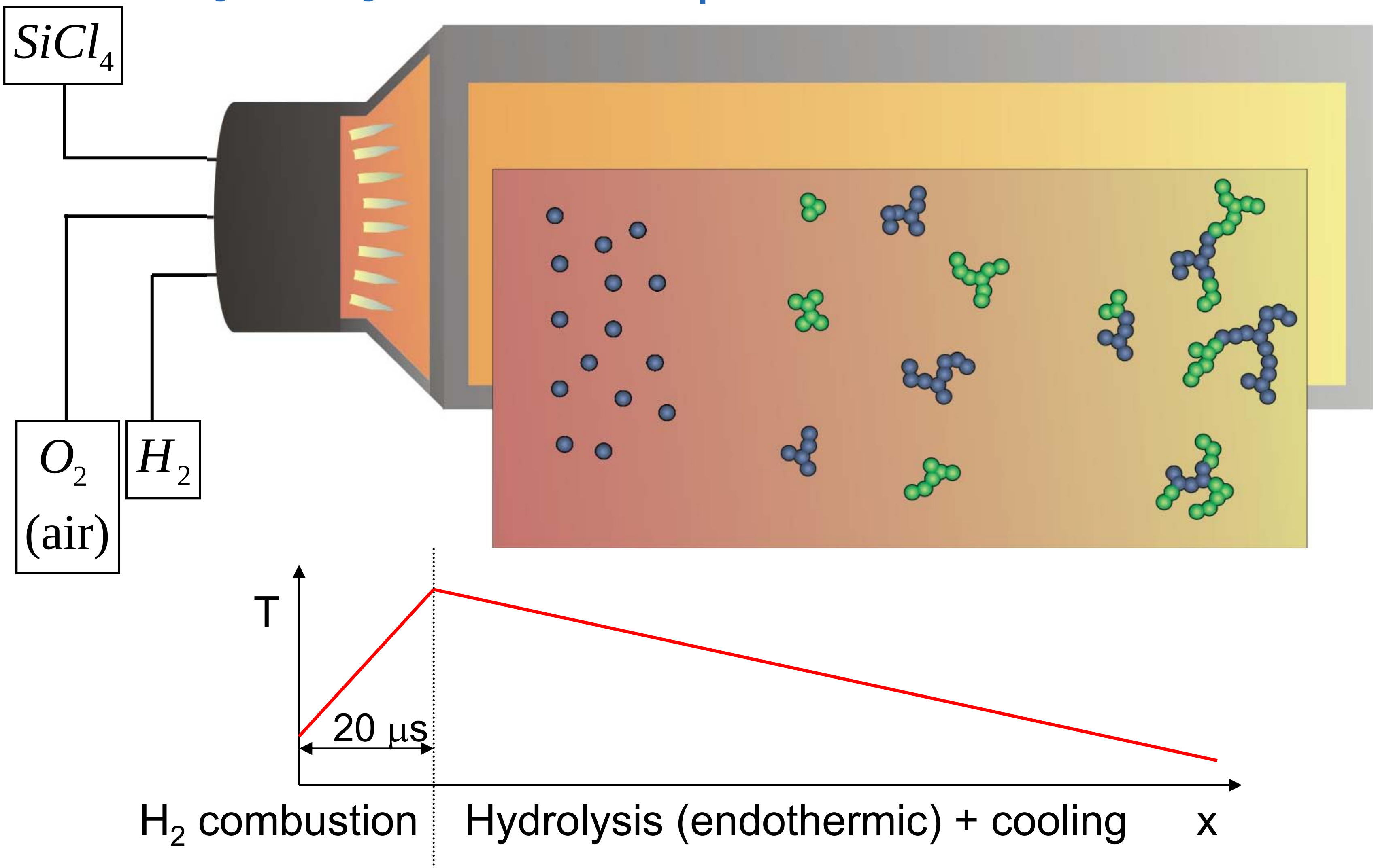
T = 1500 K

Density SiO_2 particle: 2.2 g/cm³
Density combustion gas: 0.26 g/l

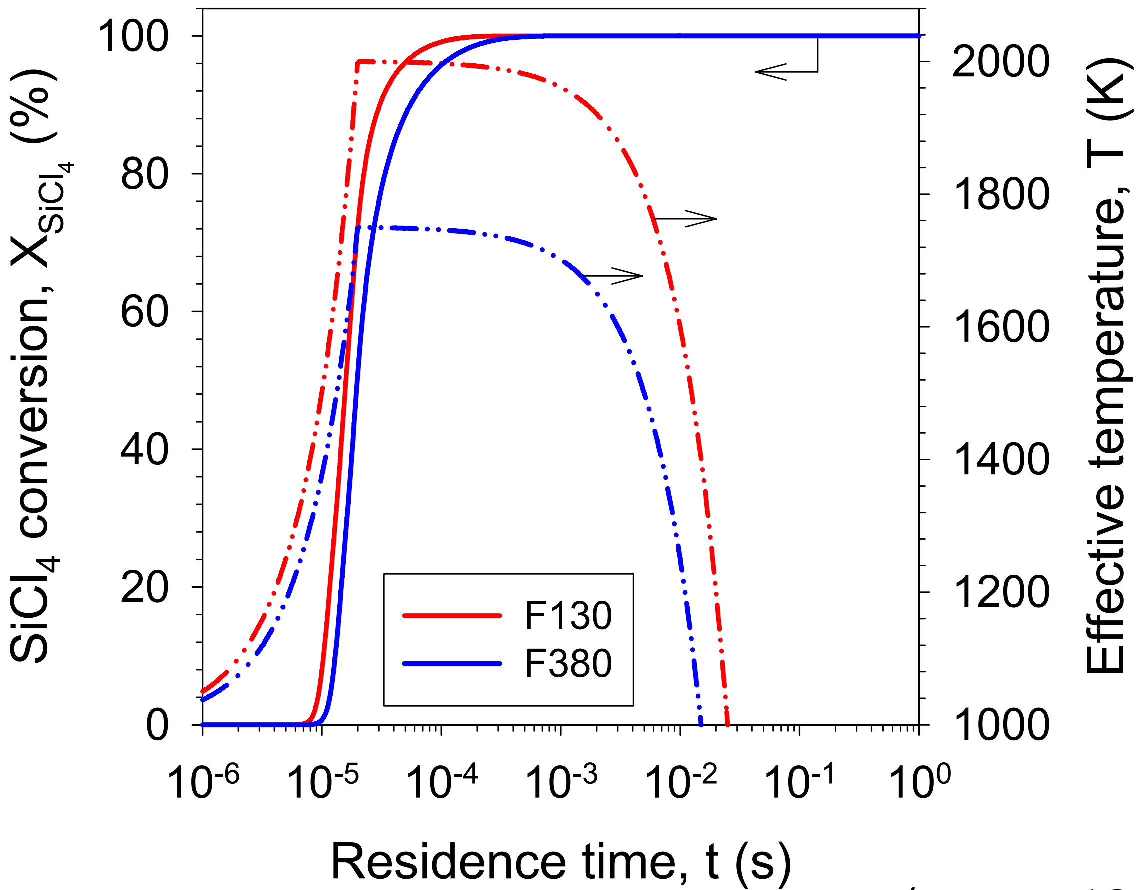
$$\phi_{solid} = 0.002\%$$

Coagulation of initially non-agglomerated particles (d_p = 7.1 nm, SSA = 380 m²/g)

Flame Hydrolysis of $SiCl_4$



Flame Temperature and Precursor Conversion



$$\phi_{SiCl_4,0} = 12\%$$

	F130	F380
SSA (m^2/g)	**130**	**380**
T_{init} (K)	**1000**	**1000**
T_{max} (K)	**2000**	**1750**
Cooling rate (10^3 K/s)	**40**	**50**

Typical flame cooling rates:

Zirconia producing spay flame:

CR ~ 100×10^3 K/s

Heine and Pratsinis (2005)

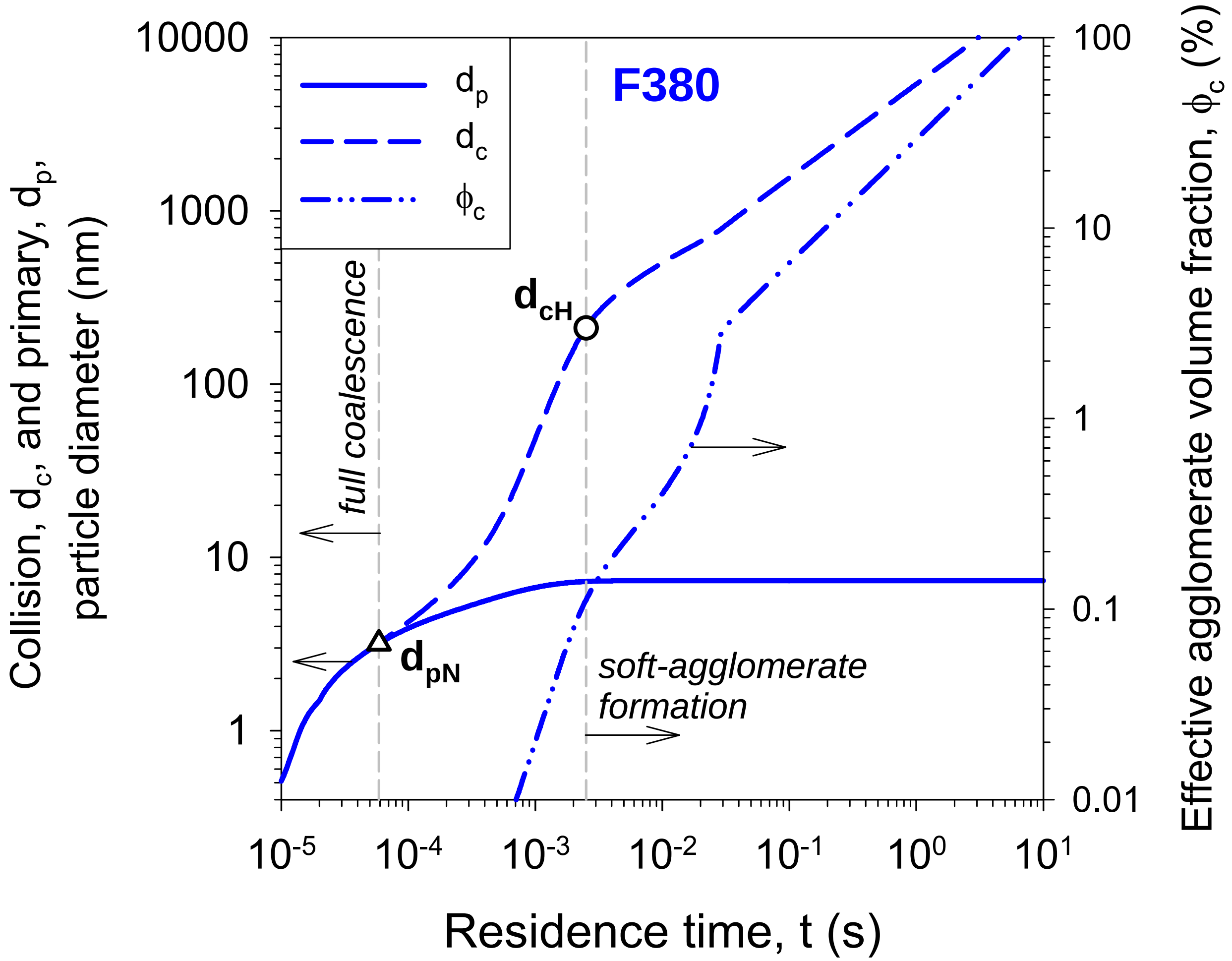
Premixed titania producing flame:

CR ~ 10 to 30×10^3 K/s

Tsantilis et al. (2002)

Kammler et al. (2003)

Particle Size Evolution in Cold Flame

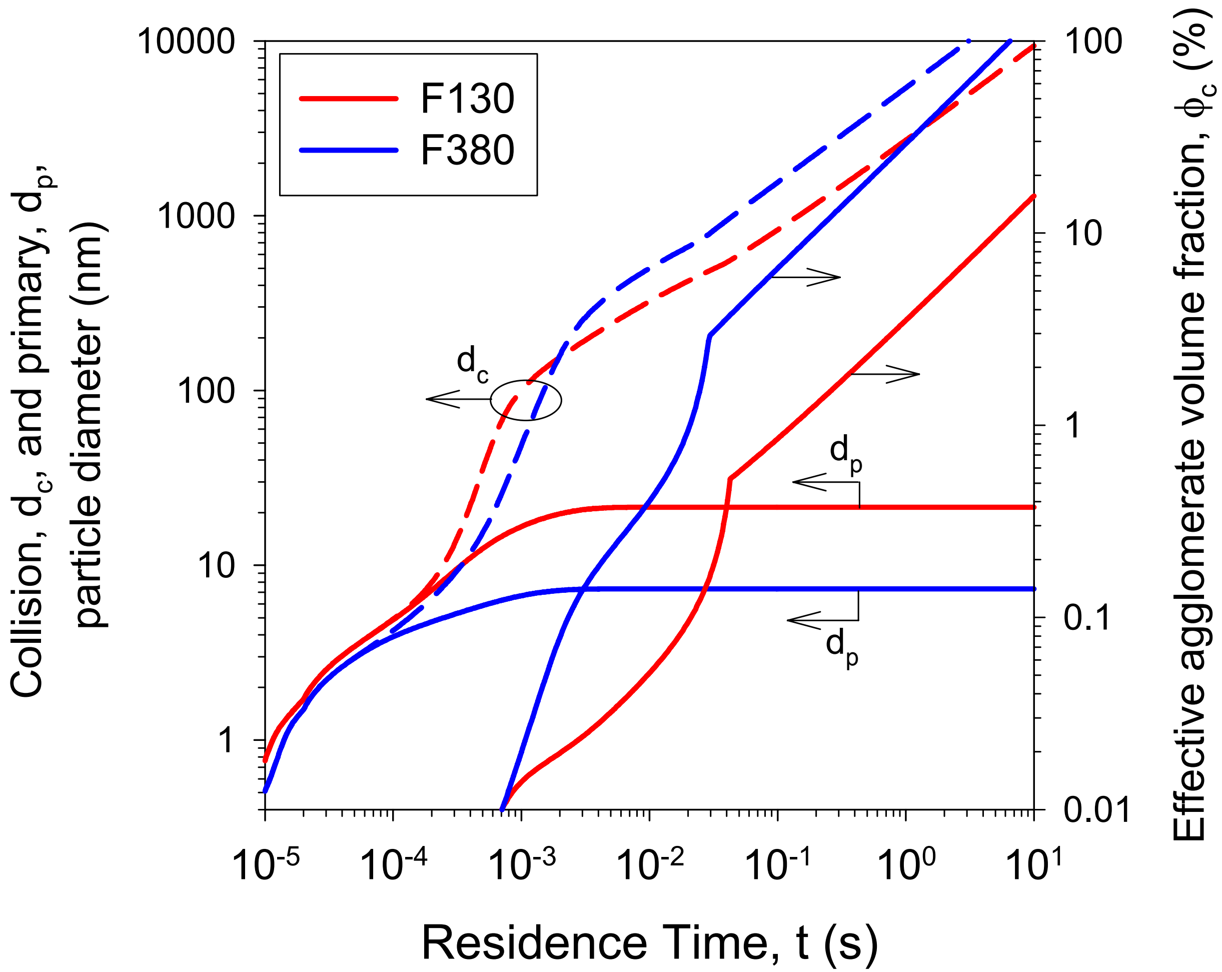


Final particle size:

d_p = *7.1 nm*

$$\phi_{SiCl_4,0} = 12\%$$

Particle Size Evolution



t (ϕ=1%) = 0.13 s

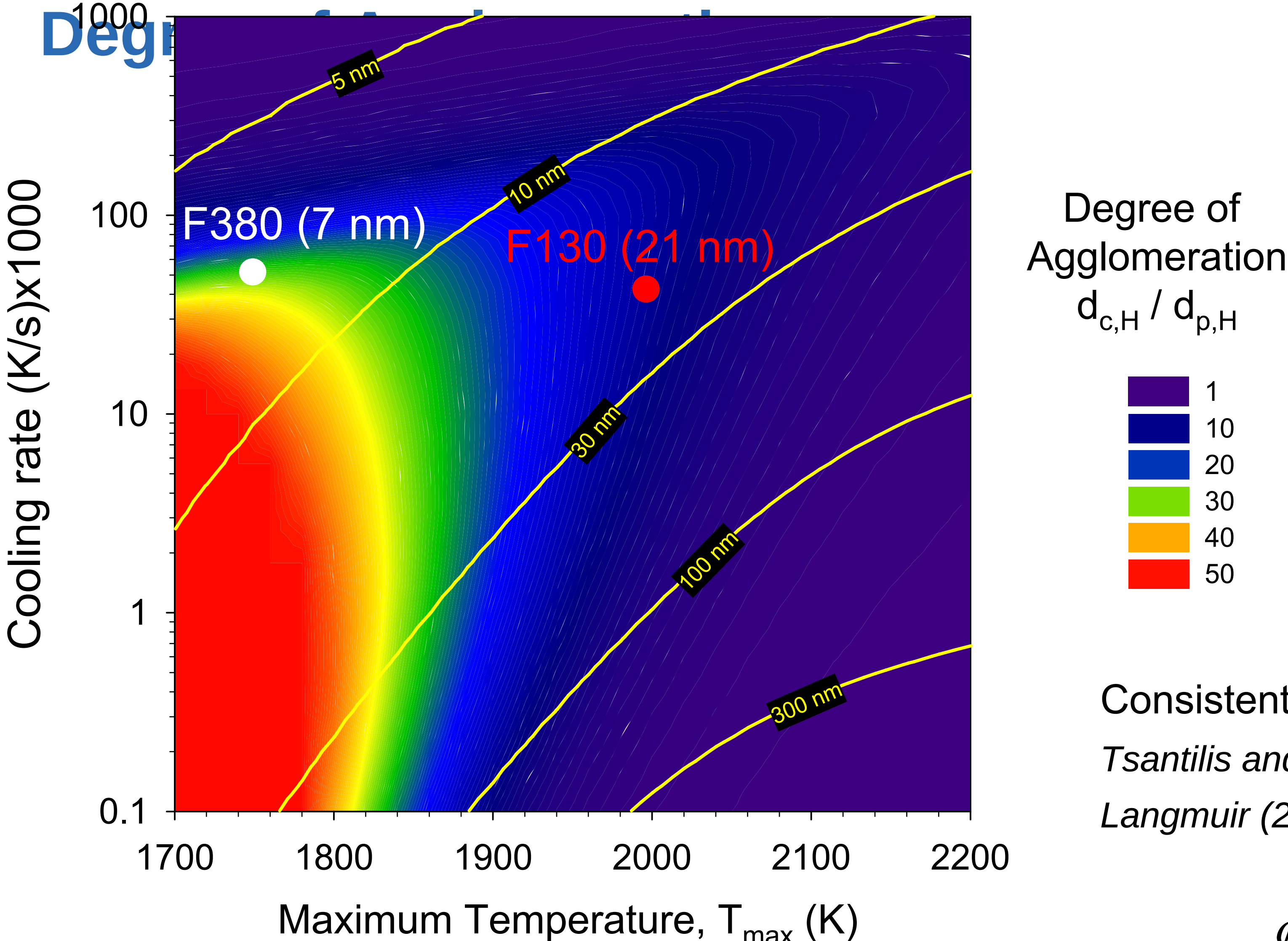
t (ϕ=10%) = 5.1 s

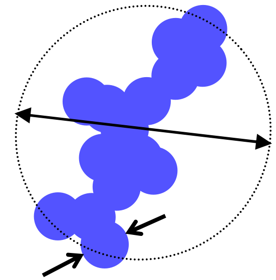
t (ϕ=1%) = 0.02 s

t (ϕ=10%) = 0.19 s

$\phi_{SiCl_4,0} = 12\%$

Degr



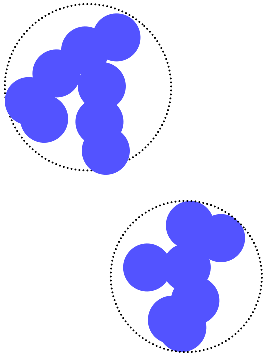


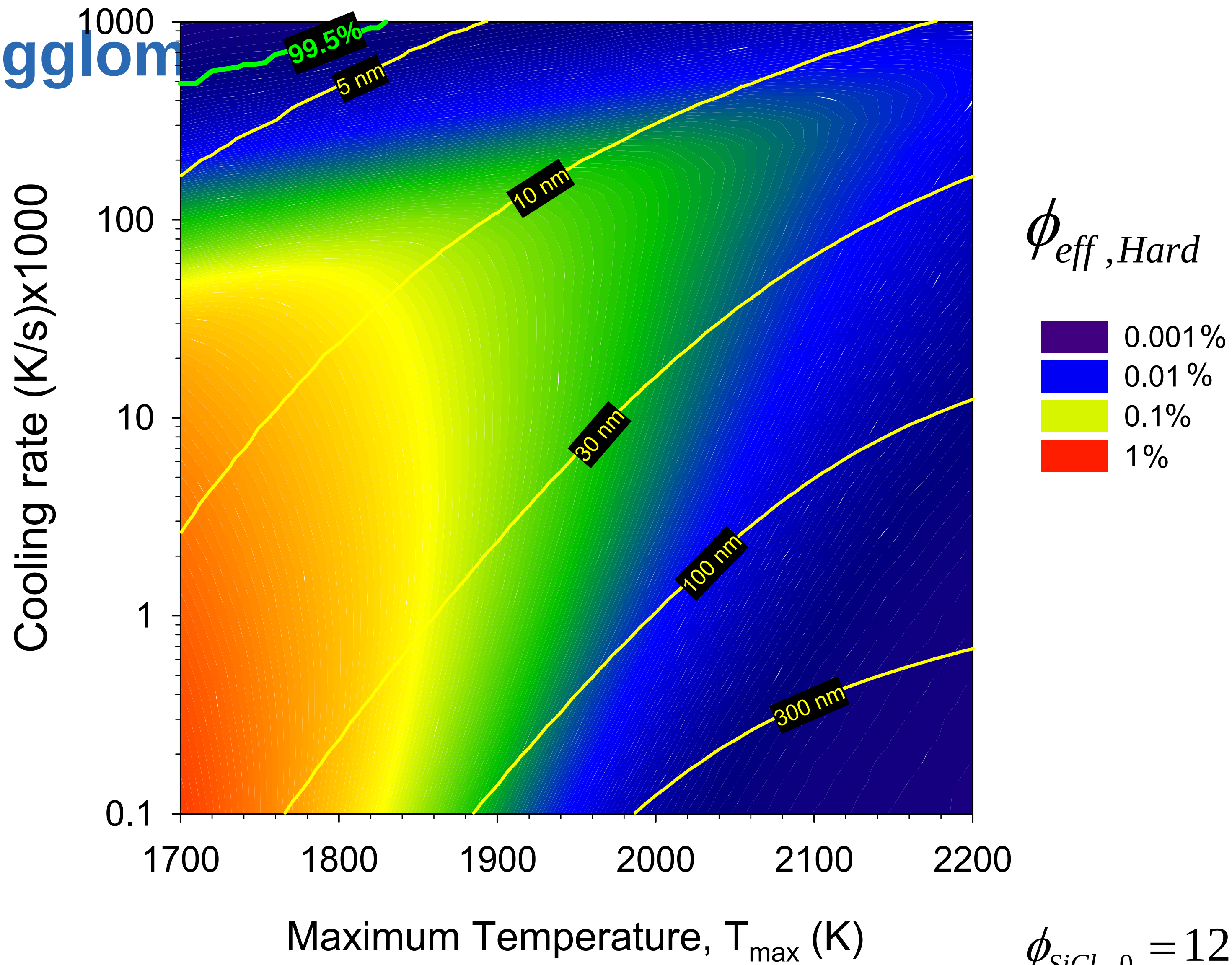
Consistent with

Tsantilis and Pratsinis, Langmuir (2004)

$$\phi_{SiCl_4,0} = 12\%$$

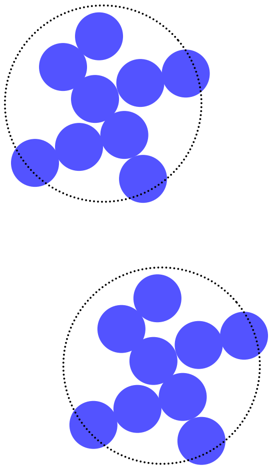
Hard Agglom

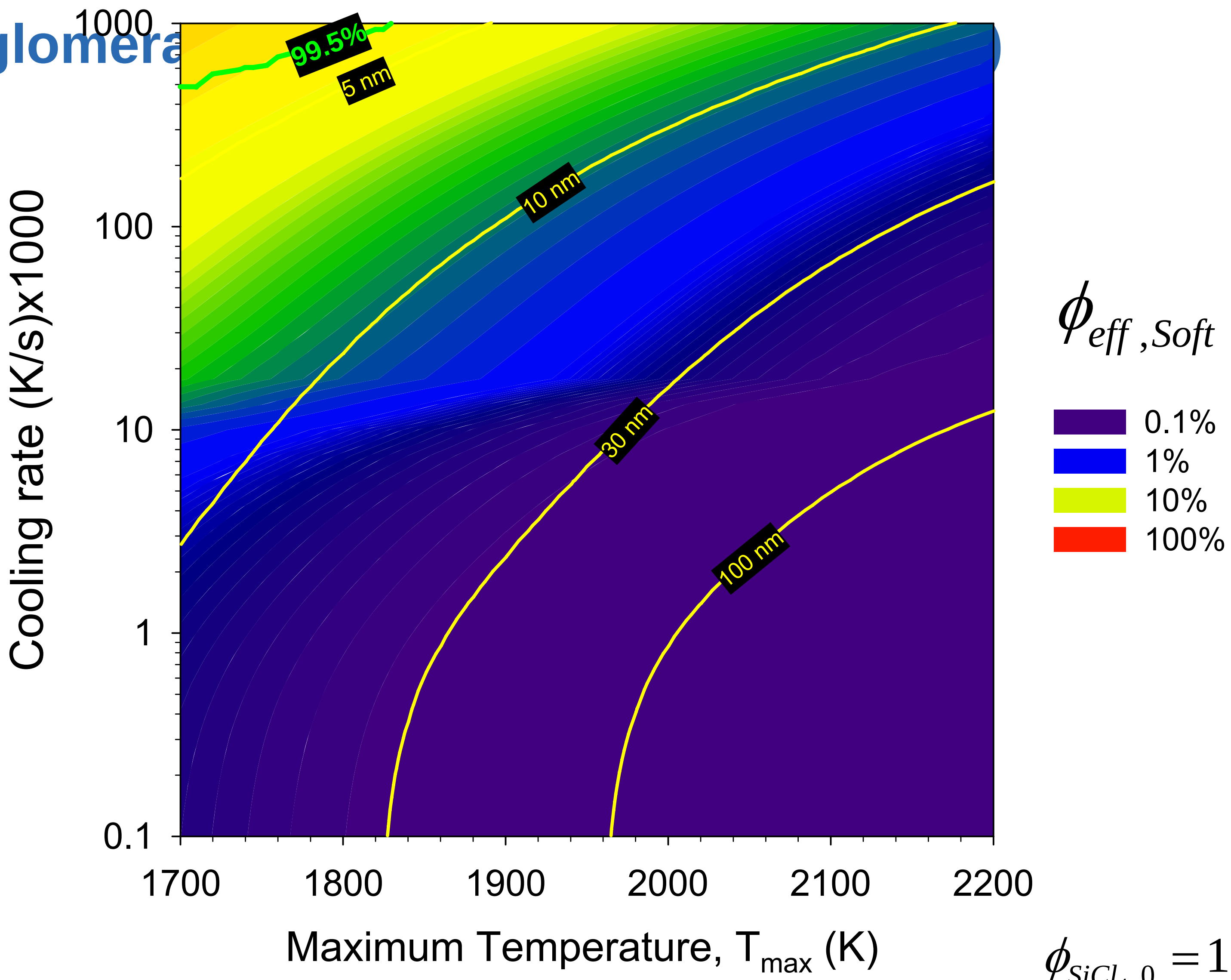




$\phi_{SiCl_4,0} = 12\%$

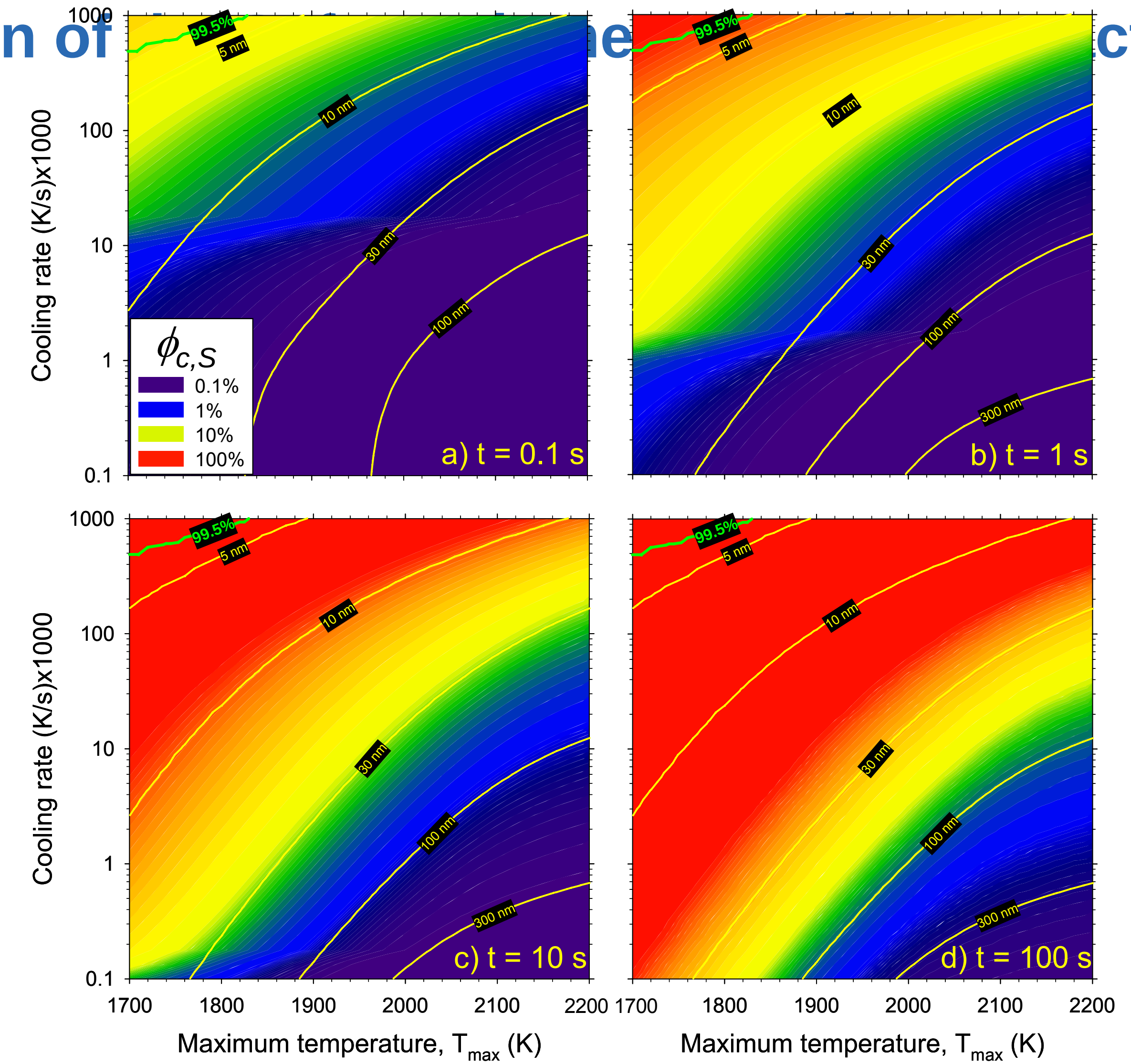
Soft Agglomera



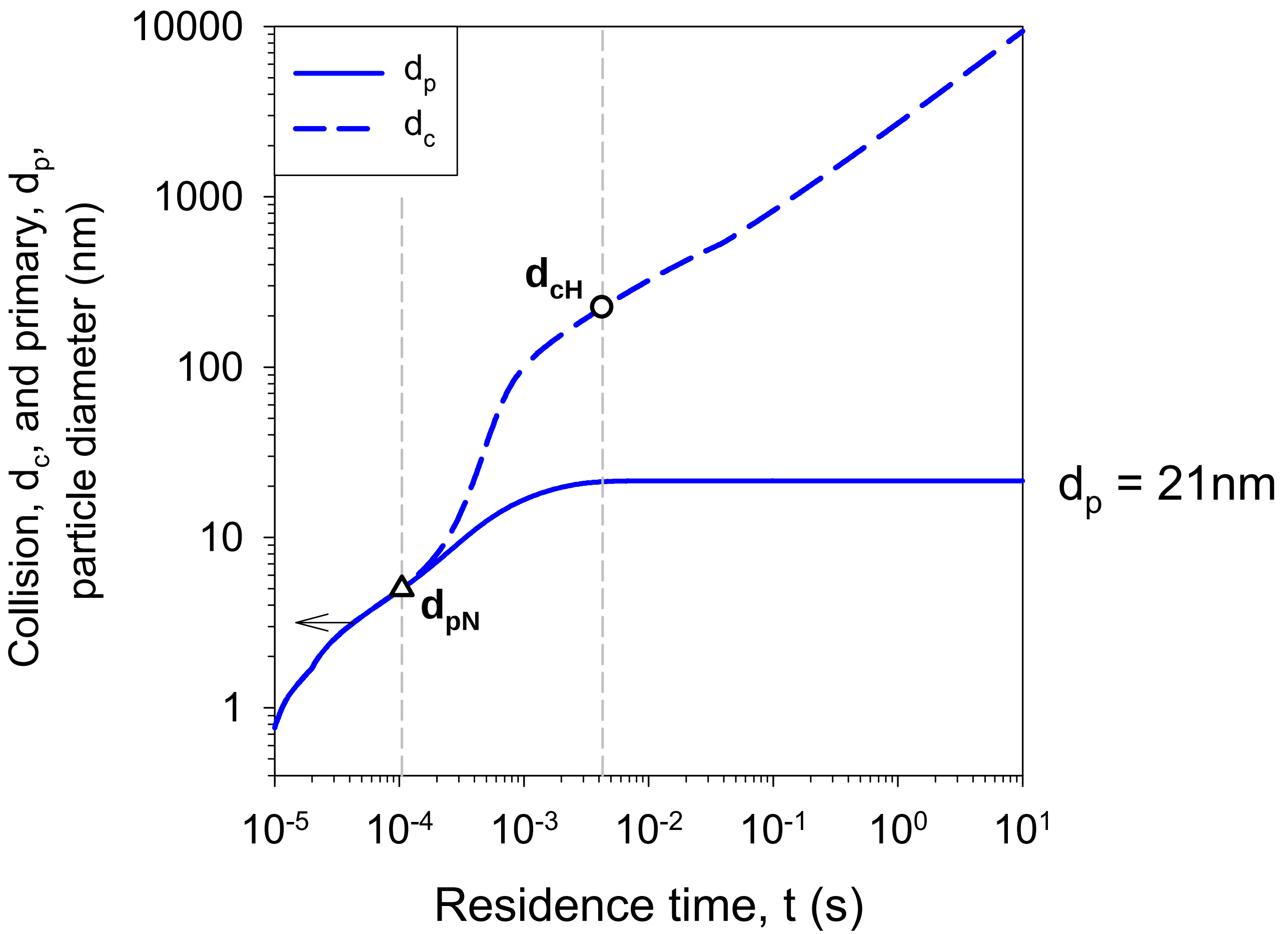


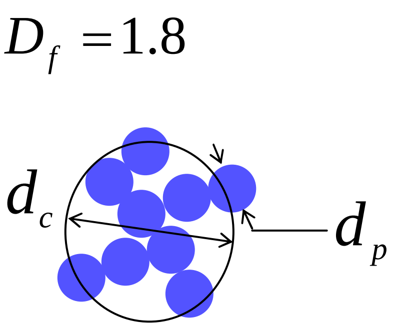
$\phi_{SiCl_4,0} = 12\%$

Evolution of … e… ction



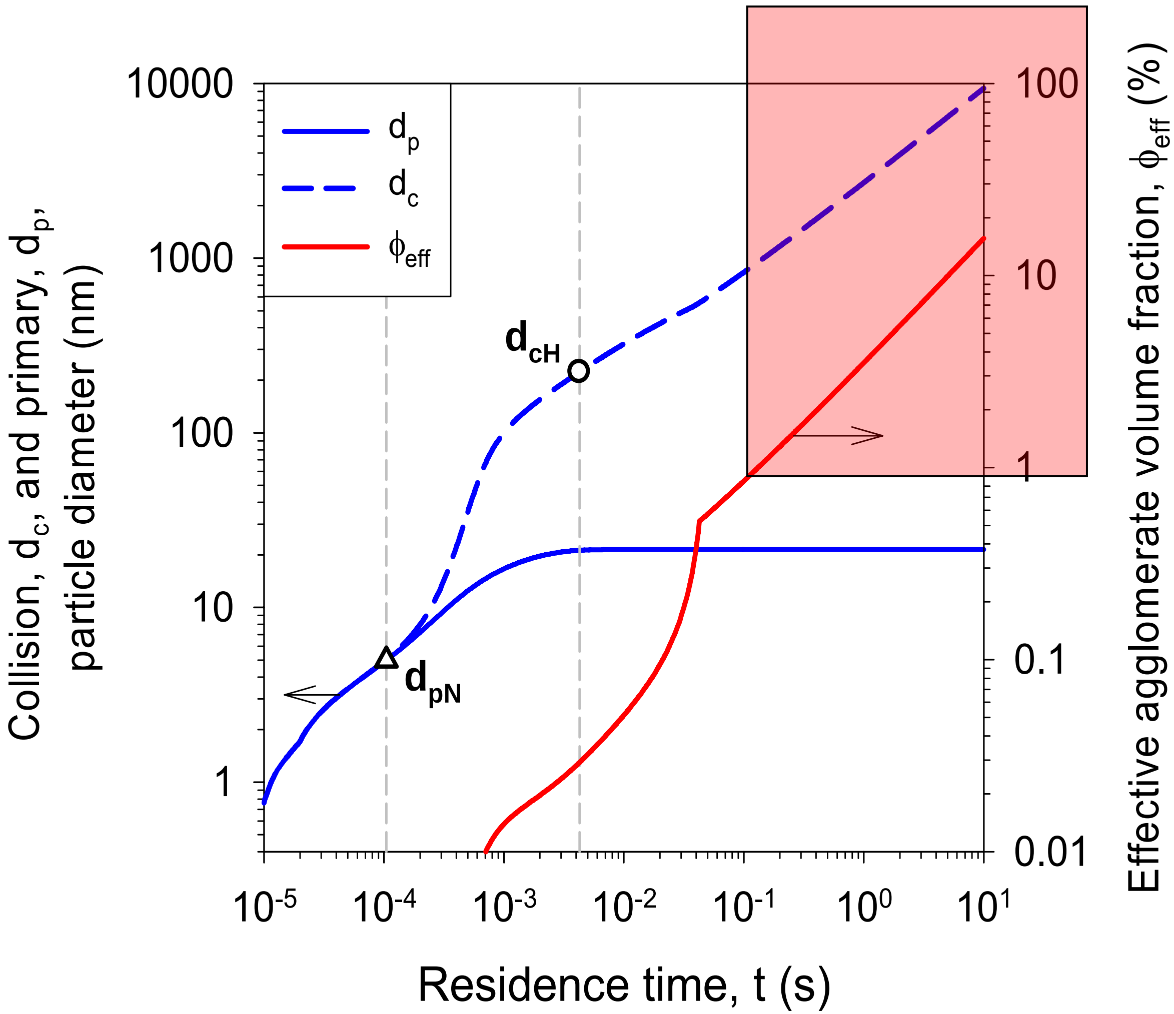
Particle Size Evolution during SiO_2 Synthesis



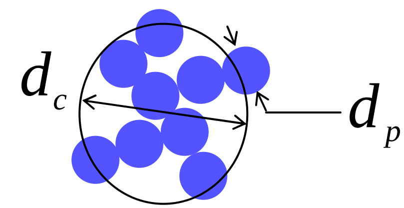


Heine & Pratsinis (2006)

High Effective Agglomerate Volume Fraction



$$D_f = 1.8$$

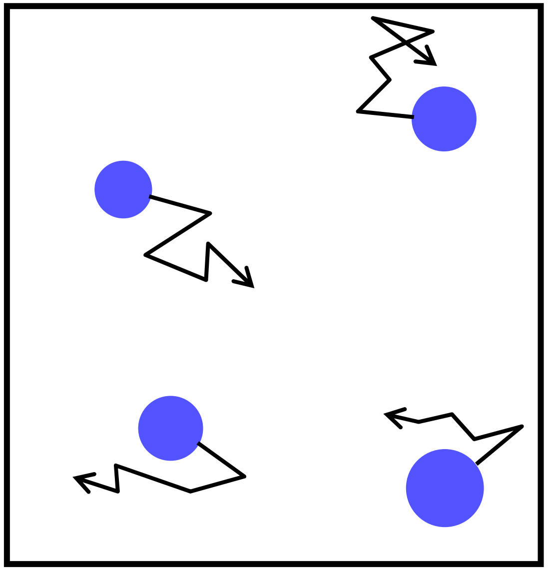


$$\phi_{eff} = N \frac{\pi}{6} d_c^3 \geq \phi_s$$

$$\phi_s < 0.01\%$$

Heine & Pratsinis (2006)

Langevin Dynamics (LD) Simulations



Equation of particle motion:

$$m_i \dot{\mathbf{v}} + \frac{3\pi\eta d_i}{C_i}\mathbf{v} + \boxed{\mathbf{F}_{\mathbf{Brownian}}} = 0$$

Numerical solution procedure:

Ermak and Buckholz (1980)
Gutsch et al. (1995)

Validation of particle trajectories:

3 dimensional particle trajectories allow calculation of the diffusion coefficient D

$$3D = \frac{\langle \mathbf{x}^2 \rangle}{2t}$$

D is identical to theoretical value (±0.01%)

Kinetics of Brownian Coagulation

Theory was derived for coagulation in colloidal suspensions is absence of a electrical double layer ("rasche Koagulation")

Collision frequency:
(Brownian Continuum)

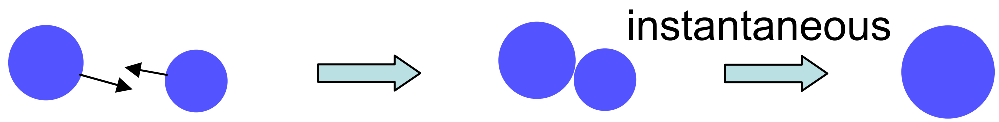
$$\beta_{i,j} = 2\pi\left(d_i + d_j\right)\left(D_i + D_j\right)$$

with $$D_i = \frac{k_b T}{3\pi\mu_{fluid} d_i}$$

M. Smoluchowski (1917)

Full coalescence: $D_f = 3$

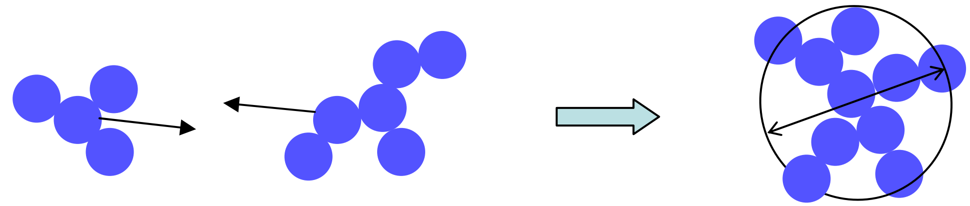
$$\phi_s = \phi_{eff} = N\frac{\pi}{6}d^3 = const \quad \forall\ t$$



No coalescence: $D_f < 3$

$$\phi_{eff} = N_{aggl}\frac{\pi}{6}d_c^3$$

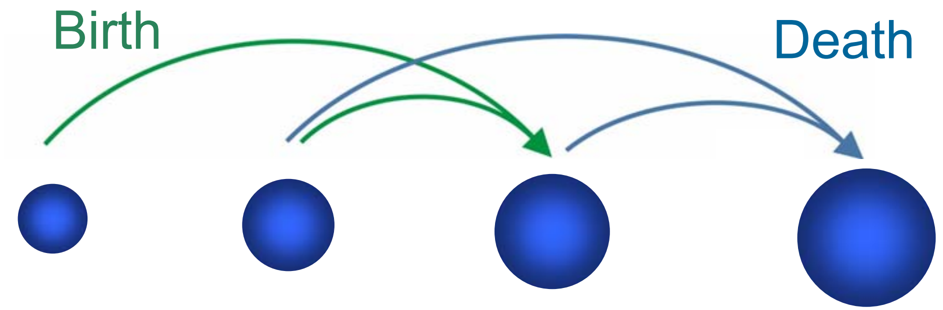
ϕ_{eff} □ for N □



$$d_c = d_p n_p^{1/D_f}$$

Particle Growth by Coagulation

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v \beta(\tilde{v}, v-\tilde{v})\, n(\tilde{v},t)\, n(v-\tilde{v},t)\, d\tilde{v} - \int_0^\infty \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\, d\tilde{v}$$



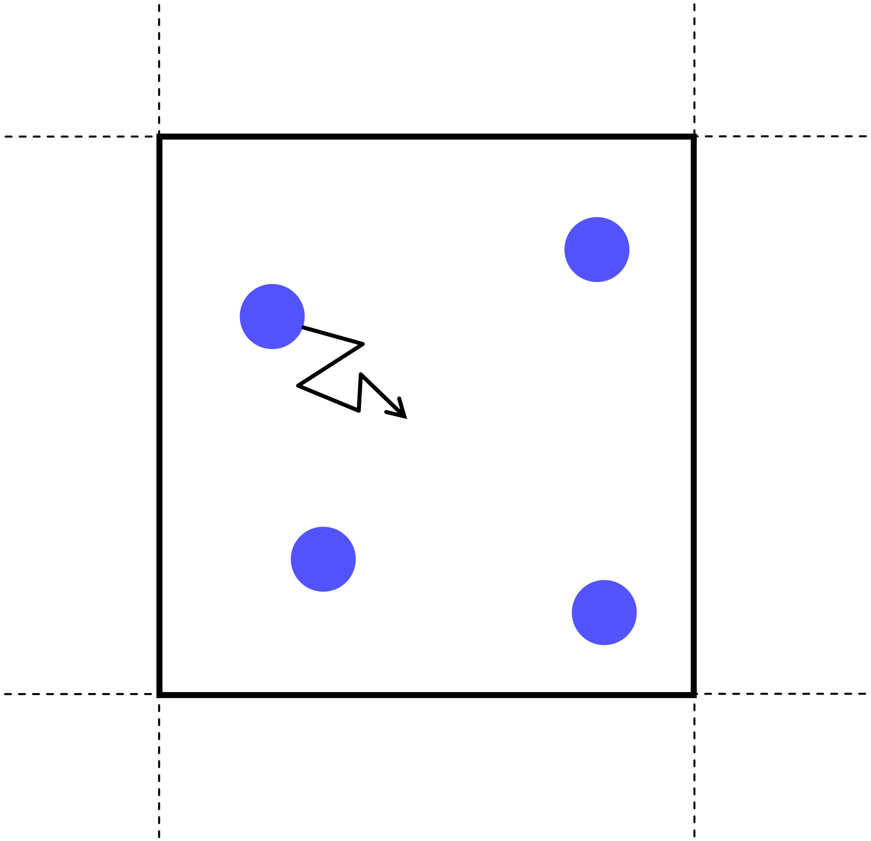
Starting point of all particle population balances in suspensions and aerosols

Solution techniques:

- Analytical
- Moment methods
- Sectional discretization
- Monte-Carlo
- …

M. Smoluchowski (1916)

Langevin Dynamics Simulations



Equation of particle motion

$$m_i \dot{\mathbf{v}} + \frac{3\pi\eta d_i}{C_i}(\mathbf{v} - \mathbf{w}) + \mathbf{F}_{\mathbf{Brownian}} = 0$$

Partial integration of particle motion

$$\mathbf{v}(t+\Delta t) = \mathbf{V} + \mathbf{v}(t)e^{-\alpha\Delta t}$$

$$\mathbf{r}(t+\Delta t) = \mathbf{R} + \mathbf{r}(t) + \frac{\mathbf{v}(t)}{\alpha}(1 - e^{-\alpha\Delta t})$$

with $\alpha = \frac{f}{m_p} = \frac{18\eta}{\rho_p d^2 C}$

V and **R** are stochastic components for particle velocity and displacement

Ermak and Buckholz (1980)
Gutsch et al. (1995)

Correction of Monodisperse Coagulation

Monodisperse coagulation:
(Brownian Continuum)

$$\frac{dN}{dt} = -\frac{\gamma}{2}\beta_{mono}N^2$$

$$\beta_{mono} = 8\pi dD = \frac{8k_B T}{3\mu_g}$$

$$\gamma = 1$$

Corrected
coagulation kinetics:

Friedlander (2000)

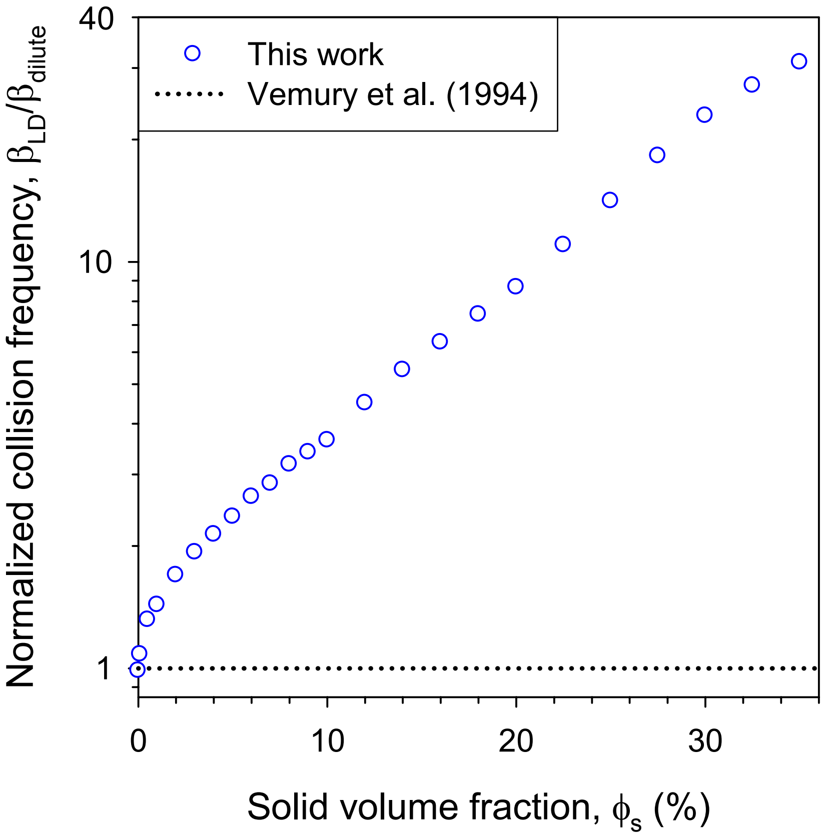
$$\gamma_{theory} = 1.073$$

Polydispersity
accelerates coagulation

Kinetics form
Langevin dynamics:
(from 1 calculation)

$$\gamma = \frac{2}{\beta_{mono}} \frac{\frac{1}{N} - \frac{1}{N_0}}{t - t_0}$$

Coagulation Accelerates with Increasing ϕ_s



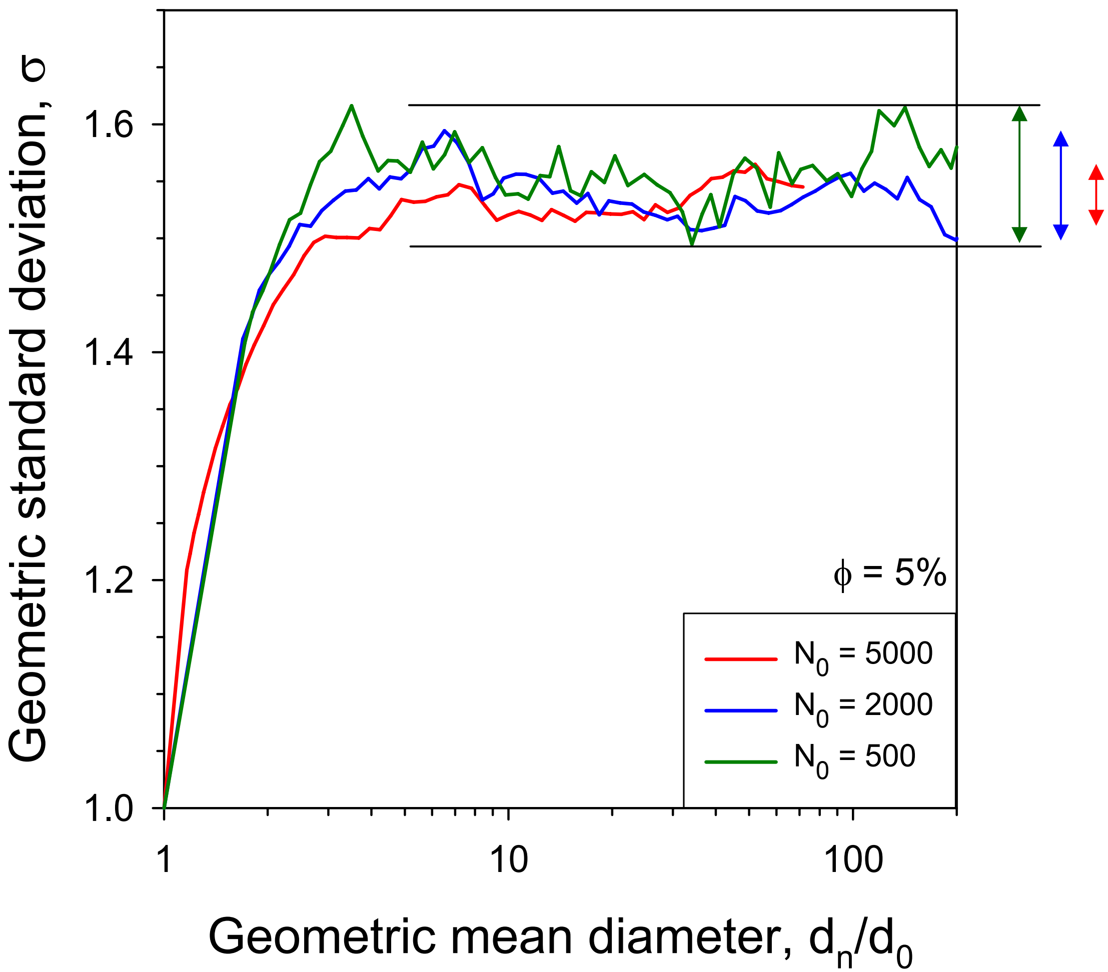
$$\beta_{LD} = 2\frac{\frac{1}{N_2}-\frac{1}{N_1}}{t_2-t_1}$$

$$\frac{\beta_{LD}}{\beta_{dilute}} \approx 1+\frac{2.5}{1-\phi}(-\log\phi)^{-2.7}$$

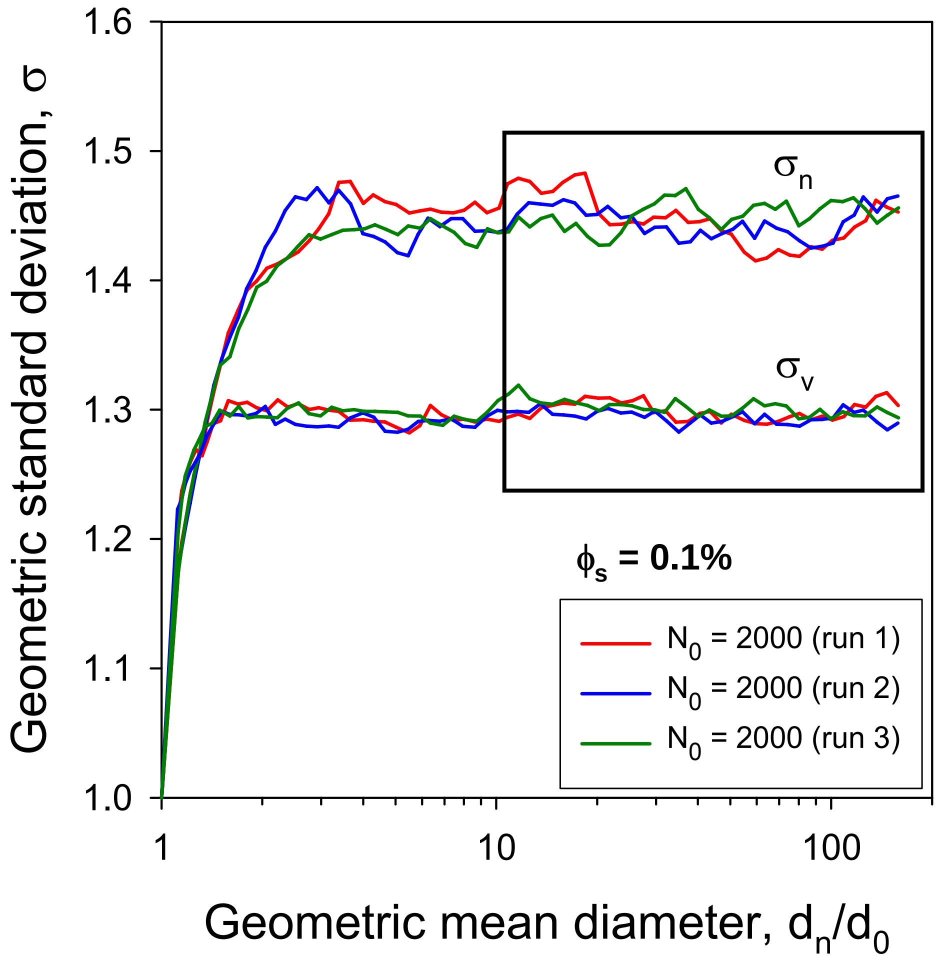
$$\beta_{dilute} = 1.0734\frac{8k_bT}{3\mu}$$

ϕ_s	$\beta_{LD}/\beta_{dilute}$
0.01%	$\pm$ 0%
0.1%	+ 8%

Accuracy increases with Number of Particles



Polydispersity for “dilute” conditions



Averaged:

$\sigma_n \approx 1.45$

$\sigma_v \approx 1.30$

Friedlander and Wang (1966)

$\sigma_n = 1.44$

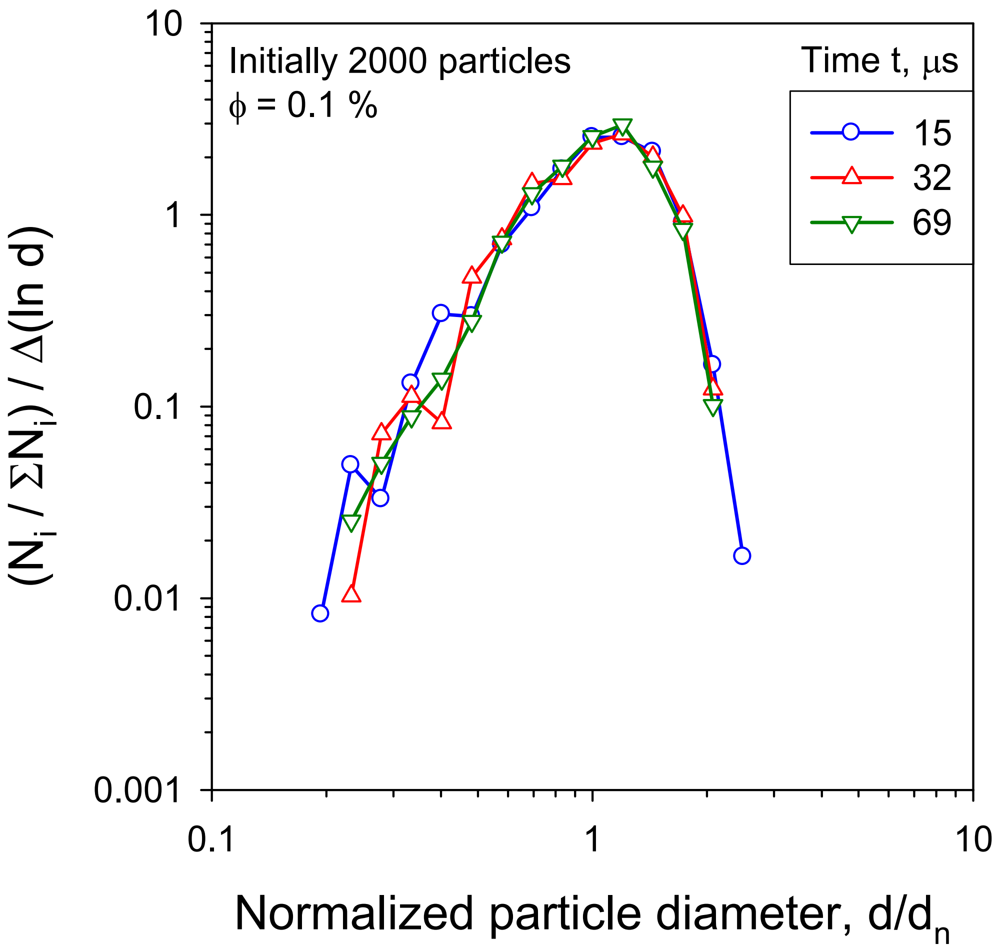
$\sigma_v = 1.28$

Sectional: $v_{i+1}/v_i = 2^{1/4}$

$\sigma_n = 1.448$

$\sigma_v = 1.307$

Self-preserving particle size distributions



Air properties:

T = 293 K

p = 1 bar

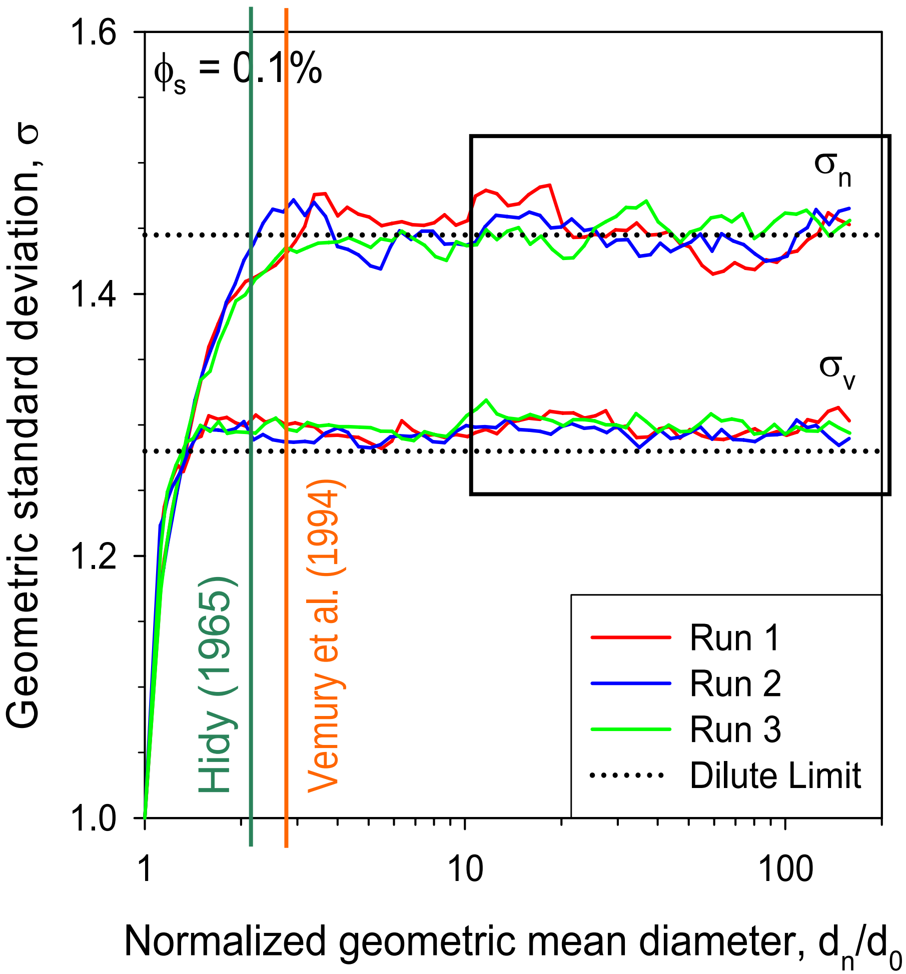
Particles:

d_0 = 1 µm

ρ_p = 1 g/cm³

$$\beta_{dilute} = 6.4\times10^{-16}\ \mathrm{m^3/s}$$

Polydispersity for Dilute Concentrations



Langevin dynamics simulations:

$$\sigma_n \approx 1.45$$

$$\sigma_v \approx 1.30$$

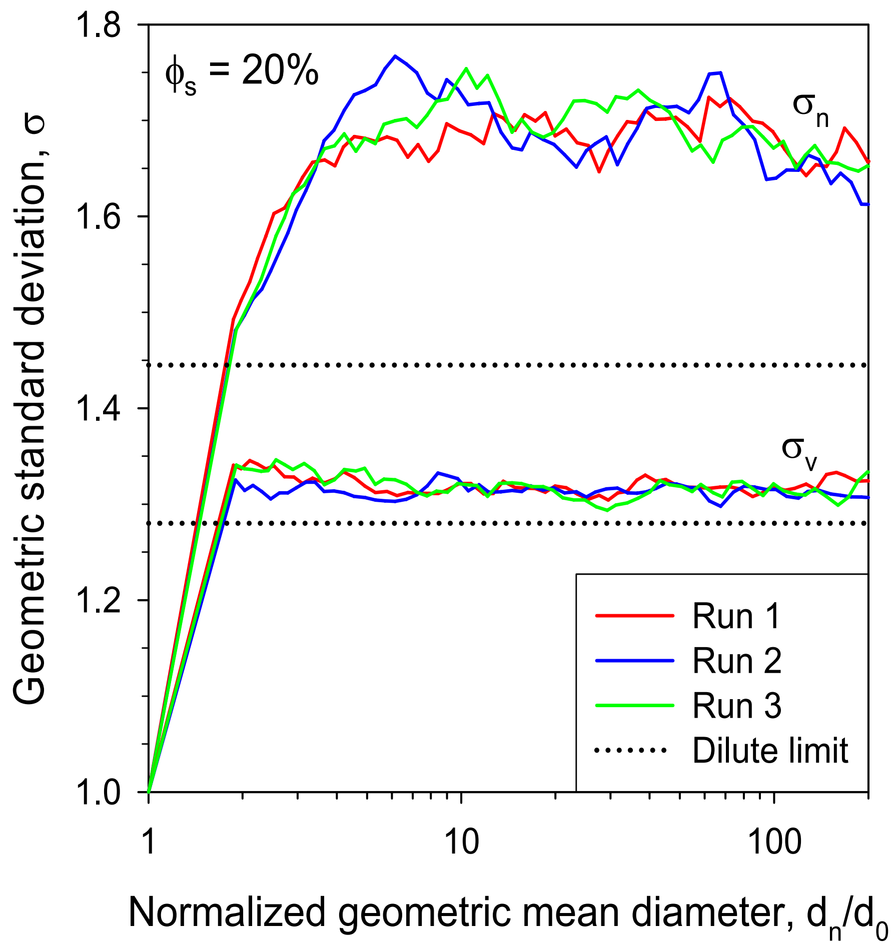
Vemury et al. (1994)

$$\sigma_n = 1.445$$

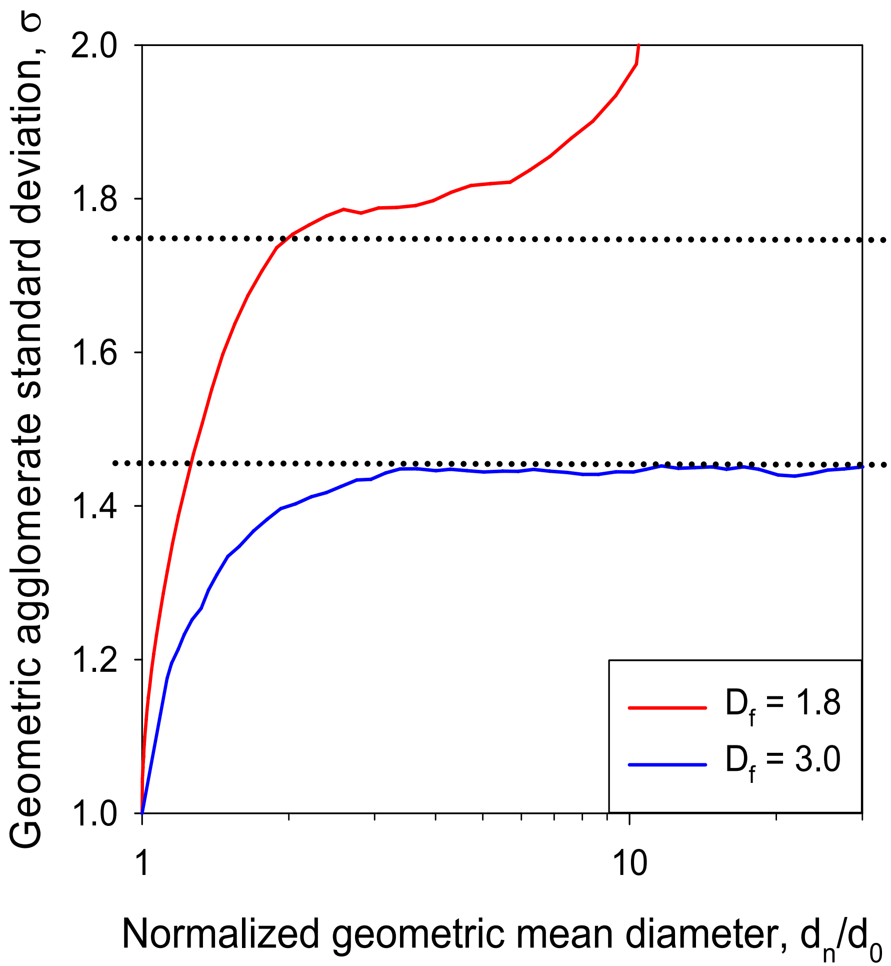
Xiong & Pratsinis (1991)

$$\sigma_v = 1.28$$

Self-preservation at high ϕ_s



No Self-preserving Distribution Exists for $D_f < 3$

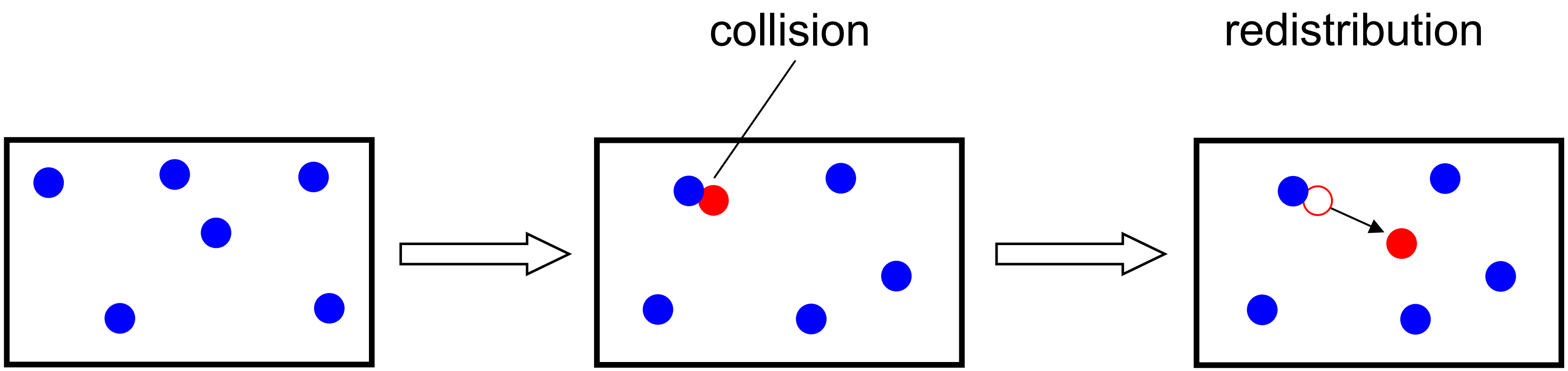


Vemury et al. (1994)

Vemury et al. (1994)

Monodisperse Coagulation (Trzeciak et al., 2004)

Goal: determine $\beta_{mono}(d)$ at constant diameter and volume fraction



Monodisperse particles are randomly dispersed and move by Brownian motion

Collision is counted

Particle size remains constant

Particle volume fraction remains constant

One collision particle is redistributed either randomly or by preserving the average particle pair distribution function

Validation by averaged Particle Diffusivity

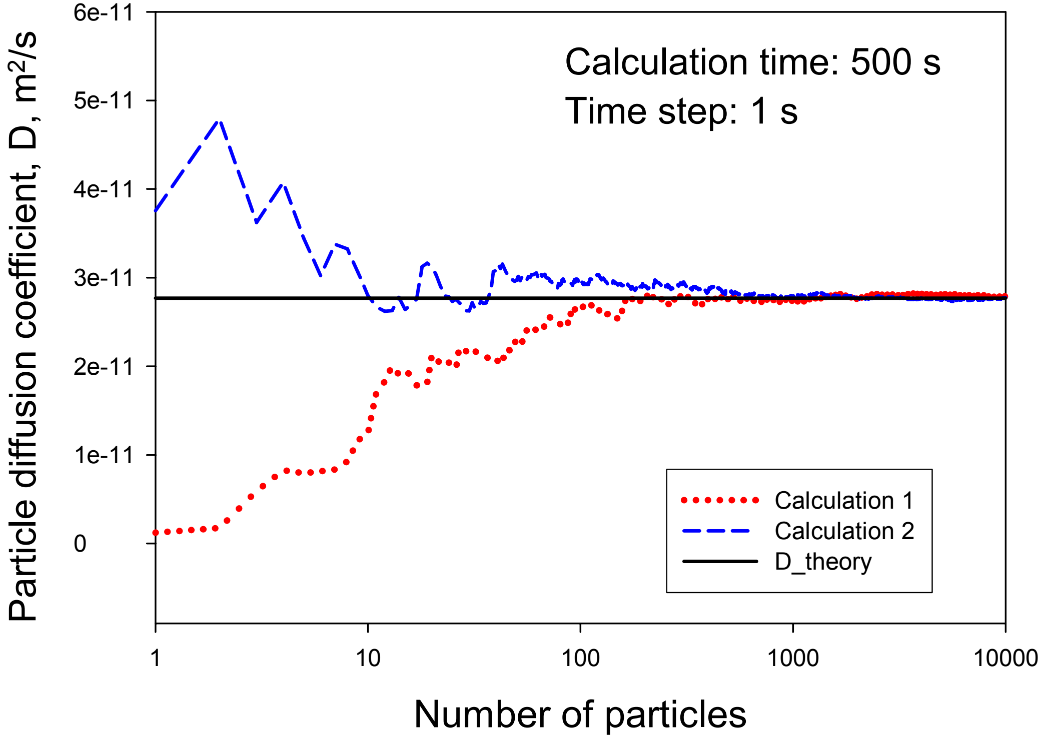
- Particle trajectories are calculated by integration of the equation of particle motion using the theoretical friction coefficient

- Diffusivity is calculated from average particle displacement

$$D = \frac{\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle}{6t}$$

- Calculated diffusivity is compared to the theoretical diffusivity

Validation of Particle Diffusion



3 dimensional particle trajectories allow calculation of the diffusion coefficient D

$$3D = \frac{\langle \mathbf{x}^2 \rangle}{2t}$$

D is identical to theoretical value (±0.01%)

- Particle diameter 1000 nm
- Spherical particles in air at 20°C, 1 ATM
- Friedlander (1977)

$$D_{theory} = 2.77 \times 10^{-11} \text{ m}^2/\text{s}$$