Brownian Coagulation at High Concentrations

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PTL: from Fundamental Understanding to Final Performance

Fuel Cells

Sensors

Advanced Pigments

Nutrition

Catalysts

Particle Synthesis, Characterization & Modeling for scale-up

Batteries

Biomaterials
2-flame synthesis of Pt/Ba/Al₂O₃ for NOₓ storage reduction

FSP-made Pt/Carbon particles

setup A: Pt/xylene
setup B: xylene

FSP 1
FSP 2

Pt/EtOH/H_2O
oxygen
methane
dispersion gas (O_2)

quartz glass tube

sheath gas (N_2/O_2)

1-FSP
2-FSP

10 nm
5 nm
Materials made in aerosol flow reactors today:

- TiO₂: Paints
- Carbon Black: Tires, inks
- Ni for batteries
- Optical fibers: 4 - 8 m²/g
- SiO₂: Flowing aid

Vulcanizing ZnO by Zn vapor – air oxidation, SSA = 1.5 - 2.5 m²/g
**Motivation**

Typical exhaust soot are *not* spherical but agglomerates:

![Image of agglomerates and aggregates](image)

Diesel soot (Miller, 2007)  
([Link](http://www2a.cdc.gov/niosh-nil/report.asp?ID=111&go=moresinfo&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$_4$) $\sim$ 12 mol%
$\phi_s$(SiO$_2$) $\sim$ 0.01% @ 300 K


- Chemical Reaction
- Particle Formation
- Coagulation and coalescence
Monodisperse Silica Aerosol Dynamics for SiCl$_4$ Oxidation, Coagulation and Sintering

Total Number Concentration
\[
\frac{dN}{dt} = -\frac{1}{2} \beta N^2 \rho_g - \frac{d[\text{SiCl}_4]}{dt}
\]

Total Surface Area Concentration
\[
\frac{dA}{dt} = -\frac{d[\text{SiCl}_4]}{dt} \alpha_m - \frac{1}{\tau_s} (A - N \cdot \alpha_s)
\]

Total Volume Concentration
\[
\frac{dV}{dt} = -\frac{d[\text{SiCl}_4]}{dt} v_m
\]

Particle Size Evolution during SiO$_2$ Synthesis


\[ D_f = 1.8 \]

\[ d_c, d_p \]
High Effective Agglomerate Volume Fraction

\[ D_f = 1.8 \]

\[ \phi_{\text{eff}} = N \frac{\pi}{6} d_c^3 \geq \phi_s \]

\[ \phi_s < 0.01\% \]

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At high particle concentrations the key model assumptions are no longer valid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

\[ m_i \ddot{v} + \frac{3\pi \eta d_i}{C_i} v + F_{\text{Brownian}} = 0 \]

Numerical solution procedure:

Polydisperse Particle Growth (Full Coalescence)

Initially $n_0 = 2000$ particles

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

$2000 \geq n \geq 1000$ at all times

Particle collisions

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

$n = \frac{n_0}{2^k}$

$\phi_v = \text{const}$
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

\[ \sigma_n \approx 1.45 \]
\[ \sigma_v \approx 1.30 \]

<table>
<thead>
<tr>
<th>LD simulation</th>
<th>Vemury et al. (1994)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number:</td>
<td>( \sigma_n \approx 1.45 )</td>
</tr>
<tr>
<td>Volume:</td>
<td>( \sigma_v \approx 1.30 )</td>
</tr>
</tbody>
</table>

Averaged Self-preserving Size Distribution

Average of 90 distributions after self-preservation is attained

Validation of the LD simulations

\[ \frac{N_i}{\sum N_i} / \Delta (\ln d) \]

\[ \phi = 0.1\%, \text{LD simulations} \]

Vemury et al. (1994)
Self-preserving Size Distribution depends on $\phi_s$

1. Normalized particle diameter, $d_i/d_n$
2. Solid volume fraction, $\phi_s (%)$
3. Geometric standard deviation, $\sigma$

Vemury et al. (1994)
Coagulation Accelerates with Increasing $\phi_S$

<table>
<thead>
<tr>
<th>$\phi_s$ (%)</th>
<th>$\beta_{LD}/\beta_{dilute}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01%</td>
<td>± 0%</td>
</tr>
<tr>
<td>0.1%</td>
<td>+ 8%</td>
</tr>
</tbody>
</table>

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

$$\frac{\beta_{LD}}{\beta_{dilute}} \approx 1 + \frac{2.5}{1 - \phi} \left(-\log \phi\right)^{-2.7}$$
Coagulation Accelerates with Increasing $\phi_s$

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

Assumptions:
- Constant particle diameter
- Monodisperse particles
- After collision one particle is redistributed
$\phi_{\text{eff}}$ Increases during Fractal Particle Growth

- $D_f = 1.8$
- $D_f = 3$

$\phi_s = 0.03\%$

$\phi_{\text{eff}} > \phi_s$  \hspace{1cm} $\phi_{\text{eff}} = \phi_s$

$d_0 = 220 \text{ nm}$

$N_0 = 5.4 \times 10^{10} \text{ #/cm}^3$
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)

$\phi_{eff} > \phi_s$

$\phi_{eff} = \phi_s$
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 $\phi_s$.

- For coagulation with $D_f < 3$ no self-preserving size distribution exists.
<table>
<thead>
<tr>
<th>LD simulation</th>
<th>$D_f = 1.8$</th>
<th>$D_f = 3.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vemury et al. (1994)</td>
<td>[Red Marker]</td>
<td>[Red Marker]</td>
</tr>
</tbody>
</table>
Decreases during Fractal Particle Growth

- $D_f = 1.8$
- $D_f = 3$

**Effective agglomerate volume fraction, $\phi_{eff}$**

$\phi_{eff}$ increases as $D_f$ decreases.

- $\phi_{eff} > \phi_s$ for $D_f = 1.8$
- $\phi_{eff} = \phi_s$ for $D_f = 3$

**Graph:**

- X-axis: Normalized geometric mean diameter, $d_n/d_0$
- Y-axis: Effective agglomerate volume fraction, $\phi_{eff}$ (%)

**Legend:**

- $D_f = 1.8$ (red)
- $D_f = 3.0$ (blue)
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)

$\phi_{eff} > \phi_s$

$\phi_{eff} = \phi_s$
No Self-preserving Distribution Exists for $D_f < 3$

Geometric agglomerate standard deviation, $\sigma$

Normalized geometric mean diameter, $d_n/d_0$

$D_f = 1.8$

$\phi_{eff} > \phi_s$

$D_f = 3$

$\phi_{eff} = \phi_s$
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: $\phi_{\text{SiCl}_4,0} = 12\%$
SiO$_2$ solid volume fraction: 0.002% at 1500 K

(Hannebauer and Menzel, 2003)

# Pyrogenic Silica

<table>
<thead>
<tr>
<th>Company</th>
<th>Degussa</th>
<th>Cabot</th>
<th>Wacker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product name</td>
<td>Aerosil</td>
<td>CAB-O-SIL</td>
<td>HDK</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>90 - 380</td>
<td>130 - 380</td>
<td>110 - 440</td>
</tr>
<tr>
<td>Primary particle diameter (nm)</td>
<td>7.2 - 30.3</td>
<td>7.2 - 21.0</td>
<td>6.2 - 24.8</td>
</tr>
<tr>
<td>Hard agglomerate diameter (nm)</td>
<td>200 - 300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Particle Growth by Coagulation

Synthesis of fumed silica

\[
\frac{\partial n(\nu,t)}{\partial t} = \frac{1}{2} \int_{0}^{\nu} \beta(\tilde{\nu}, \nu - \tilde{\nu}) n(\tilde{\nu},t) n(\nu - \tilde{\nu},t) d\tilde{\nu} - \int_{0}^{\infty} \beta(\nu, \tilde{\nu}) n(\nu,t) n(\tilde{\nu},t) d\tilde{\nu}
\]

Initial concentration:
\[y(\text{SiCl}_4) \sim 12 \text{ mol}\%\]
\[\phi_s(\text{SiO}_2) \sim 0.01\% @ 300 \text{ K}\]

(Hannebauer and Menzel, 2003)
Agglomerate and Primary Particle Size Definitions

Primary particle diameter

\[ d_p = \frac{6V}{A} \]

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

Agglomerate collision diameter

\[ d_c = d_p n_p^{1/D_f} \]

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

\[ D_f \sim 1.8 \]

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

SiCl₄ (gas) → SiO₂ (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
\[
\frac{dV}{dt} = - \frac{d[SiCl_4]}{dt} v_m
\]

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

(Kruis et al., 1993)
**Φ_{eff} Increases during Coagulation**

\[ \phi_{SiCl_4,0} = 12\% \]
\[ T = 1500 \text{ K} \]

Density SiO_2 particle: 2.2 g/cm^3  
Density combustion gas: 0.26 g/l

\[ \phi_{solid} = 0.002\% \]

Coagulation of initially non-agglomerated particles  
(d_p = 7.1 nm, SSA = 380 m^2/g)
Flame Hydrolysis of SiCl₄

SiCl₄

O₂

H₂

(air)

H₂ combustion

20 μs

T

Hydrolysis (endothermic) + cooling

x
Flame Temperature and Precursor Conversion

<table>
<thead>
<tr>
<th></th>
<th>F130</th>
<th>F380</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA (m²/g)</td>
<td>130</td>
<td>380</td>
</tr>
<tr>
<td>T&lt;sub&gt;init&lt;/sub&gt; (K)</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>T&lt;sub&gt;max&lt;/sub&gt; (K)</td>
<td>2000</td>
<td>1750</td>
</tr>
<tr>
<td>Cooling rate (10³ K/s)</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

**Typical flame cooling rates:**

- Zirconia producing spay flame:
  
  CR ~ 100x10³ K/s

  *Heine and Pratsinis (2005)*

- Premixed titania producing flame:
  
  CR ~ 10 to 30x10³ K/s

  *Tsantilis et al. (2002)*

  *Kammler et al. (2003)*
Particle Size Evolution in Cold Flame

Final particle size: 
\[ d_p = 7.1 \text{ nm} \]

Effective agglomerate volume fraction, \( \phi_c (\%) \):

\[ \phi_{SiCl_4,0} = 12\% \]
Particle Size Evolution

Effective agglomerate volume fraction, $\phi_c$ (%)

- $t (\phi=1\%) = 0.13 \text{ s}$
- $t (\phi=10\%) = 5.1 \text{ s}$
- $t (\phi=1\%) = 0.02 \text{ s}$
- $t (\phi=10\%) = 0.19 \text{ s}$

$\phi_{SiCl_4,0} = 12\%$
Degree of Agglomeration

\[ \text{dc,H} / \text{dp,H} \]

Temperature, K

Cooling rate (K/s)x1000

Maximum Temperature, \( T_{\text{max}} \) (K)

Consistent with

*Tsantilis and Pratsinis*,


\[ \phi_{\text{SiCl}_4,0} = 12\% \]
Hard Agglomerates – Volume Fraction

\[ \phi_{\text{eff}, \text{Hard}} \]

- 0.001\%  
- 0.01\%  
- 0.1\%  
- 1\%

\[ \phi_{\text{SiCl}_4,0} = 12\% \]

Maximum Temperature, \( T_{\text{max}} \) (K)

Cooling rate (K/s) \times 1000

- 99.5%
- 5 nm
- 10 nm
- 30 nm
- 100 nm
- 300 nm

Temperature, K

1700 1800 1900 2000 2100 2200
Soft Agglomerates – Volume Fraction ($t = 0.1\text{s}$)

$\phi_{eff,Soft}$

Temperature, K

Cooling rate (K/s) x 1000

Maximum Temperature, $T_{max}$ (K)

$\phi_{SiCl_4,0} = 12\%$
Evolution of the Soft Agglomerate Volume Fraction
Particle Size Evolution during SiO$_2$ Synthesis

$D_f = 1.8$

$d_c$  

$d_p = 21$nm

Heine & Pratsinis (2006)
High Effective Agglomerate Volume Fraction

Heine & Pratsinis (2006)

\[ D_f = 1.8 \]

\[ d_c \leq d_p \]

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

\[ \phi_s < 0.01\% \]
Langevin Dynamics (LD) Simulations

Equation of particle motion:
\[ m_i \ddot{v} + \frac{3\pi \eta d_i}{C_i} v + F_{\text{Brownian}} = 0 \]

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 \( D \)
\[ 3D = \frac{\langle x^2 \rangle}{2t} \]
\( D \) 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 \( D_i = \frac{k_B T}{3\pi \mu_{\text{fluid}} d_i} \)

M. Smoluchowski (1917)

Full coalescence: \( D_f = 3 \)

\( \phi_s = \phi_{\text{eff}} = N \frac{\pi}{6} d^3 = \text{const} \ \forall \ t \)

No coalescence: \( D_f < 3 \)

\( \phi_{\text{eff}} = N_{\text{aggl}} \frac{\pi}{6} d_c^3 \)

\( \phi_{\text{eff}} \not= \text{for} \ N \not= \)

\( d_c = d_p n_p^{1/D_f} \)
Particle Growth by Coagulation

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

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

\[ m_i \ddot{v} + \frac{3\pi \eta d_i}{C_i} (v - w) + F_{\text{Brownian}} = 0 \]

Partial integration of particle motion

\[ v(t + \Delta t) = V + v(t)e^{-\alpha \Delta t} \]
\[ r(t + \Delta t) = R + r(t) + \frac{v(t)}{\alpha} (1 - e^{-\alpha \Delta t}) \]

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)

\[
\frac{dN}{dt} = -\frac{\gamma}{2} \beta_{\text{mono}} N^2
\]

\[
\beta_{\text{mono}} = 8\pi dD = \frac{8k_B T}{3\mu_g}
\]

\[
\gamma = 1
\]

Corrected coagulation kinetics:

Friedlander (2000)

\[
\gamma_{\text{theory}} = 1.073
\]

Polydispersity accelerates coagulation

Kinetics form

Langevin dynamics:
(from 1 calculation)

\[
\gamma = \frac{2}{\beta_{\text{mono}}} \left( \frac{1}{N} - \frac{1}{N_0} \right)
\]

\[
\gamma = \frac{2}{t - t_0}
\]
Coagulation Accelerates with Increasing $\phi_s$

\[ \beta_{LD} = 2 \left( \frac{1}{N_2} - \frac{1}{N_1} \right) \left( \frac{t_2 - t_1}{t_2} \right) \]

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

\[ \beta_{dilute} = 1.0734 \frac{8k_b T}{3\mu} \]

<table>
<thead>
<tr>
<th>$\phi_s$</th>
<th>$\beta_{LD}/\beta_{dilute}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01%</td>
<td>$\pm 0%$</td>
</tr>
<tr>
<td>0.1%</td>
<td>$+ 8%$</td>
</tr>
</tbody>
</table>
Accuracy increases with Number of Particles

Geometric mean diameter, $d_n/d_0$

Geometric standard deviation, $\sigma$

$N_0 = 5000$
$N_0 = 2000$
$N_0 = 500$

$\phi = 5\%$
Polydispersity for “dilute” conditions

Friedlander and Wang (1966)

\[ \sigma_n \approx 1.45 \quad \sigma_n = 1.44 \]

\[ \sigma_v \approx 1.30 \quad \sigma_v = 1.28 \]

Sectional: \( v_{i+1}/v_i = 2^{1/4} \)

\[ \sigma_n = 1.448 \]

\[ \sigma_v = 1.307 \]
Self-preserving particle size distributions

Initially 2000 particles

\( \phi = 0.1 \% \)

<table>
<thead>
<tr>
<th>Time ( t, \mu s )</th>
<th>15</th>
<th>32</th>
<th>69</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (N_i / \sum N_i) / \Delta (\ln d) )</td>
<td><img src="graph.png" alt="Graph" /></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Air properties:

- \( T = 293 \) K
- \( p = 1 \) bar

Particles:

- \( d_0 = 1 \) \( \mu m \)
- \( \rho_p = 1 \) g/cm\(^3\)

\[ \beta_{dilute} = 6.4 \times 10^{-16} \text{ m}^3/\text{s} \]
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 $\phi_s$

- $\phi_s = 20\%$
- $\sigma_n$
- $\sigma_v$
- Dilute limit

Normalized geometric mean diameter, $d_n/d_0$
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 $\beta_{\text{mono}}(d)$ 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 $D$

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

$D$ is identical to theoretical value (±0.01%)

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

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