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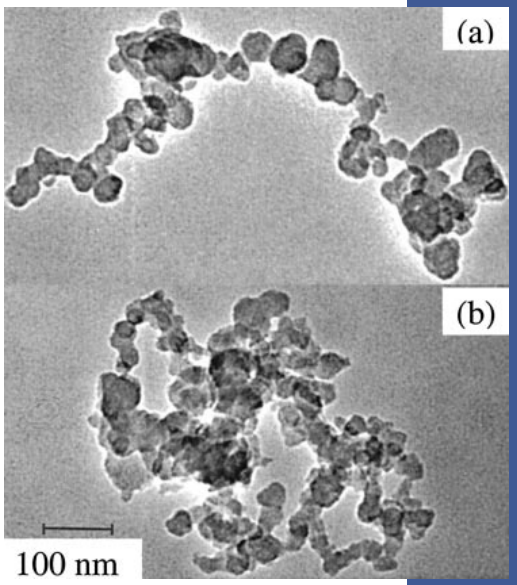
Agglomeration of nano- and micron-sized particles



Prof. Andreas Kronenburg

Acknowledgements: G. Inci (ITV), R. Weeber (ICP), A. Arnold (ICP)

Institut für Technische Verbrennung

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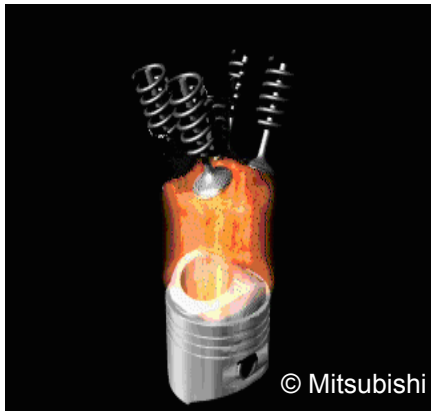
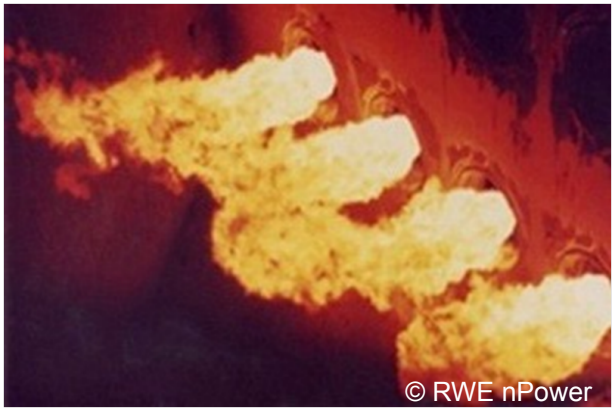
Combustion Technology

- **Importance**
  - **Combustion is everywhere**



Vehicle Propulsion



Energy Engg / Renewable Energies

Aerospace Engineering

- **Vision**
  - **Efficient**
  - **clean**
  - **safe**
- **Motivation - legislation**
  - **Euro VI**
  - **“VISION 2020”**

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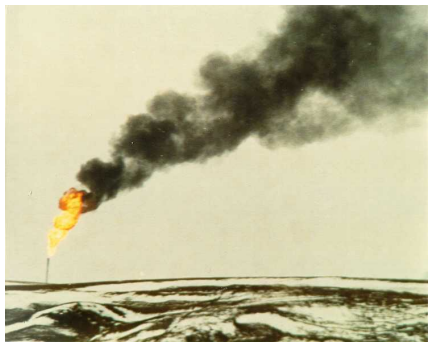
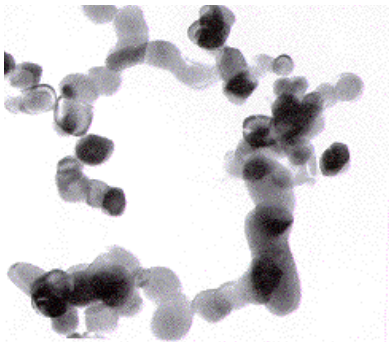
Moving away from energy conversion …

Materials science, environmental engineering

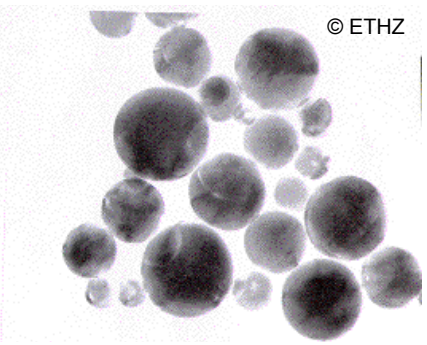
1. example: particle synthesis

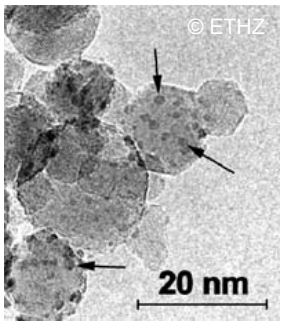


soot



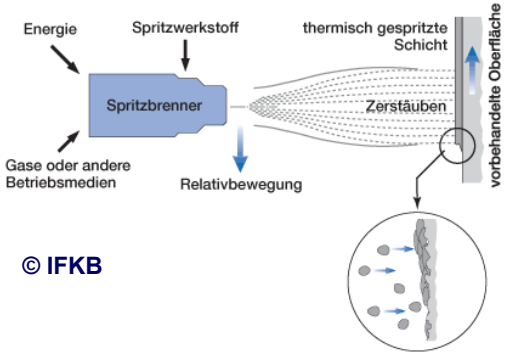
Titania

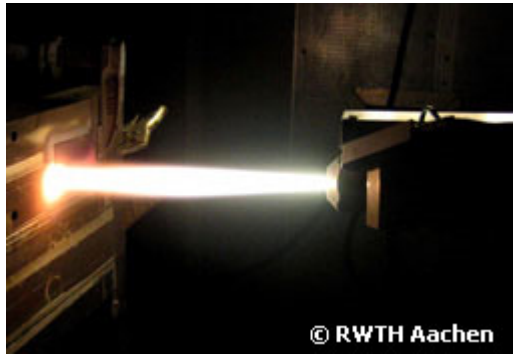




PT/TiO_2

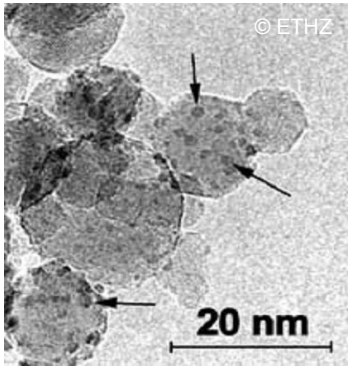
2. example: thermal coating





Particles

- **High temperature (flame) synthesis of nanoparticles constitutes 90% of particle production by mass and value**



Pt/TiO_2 - particle

titanium dioxide

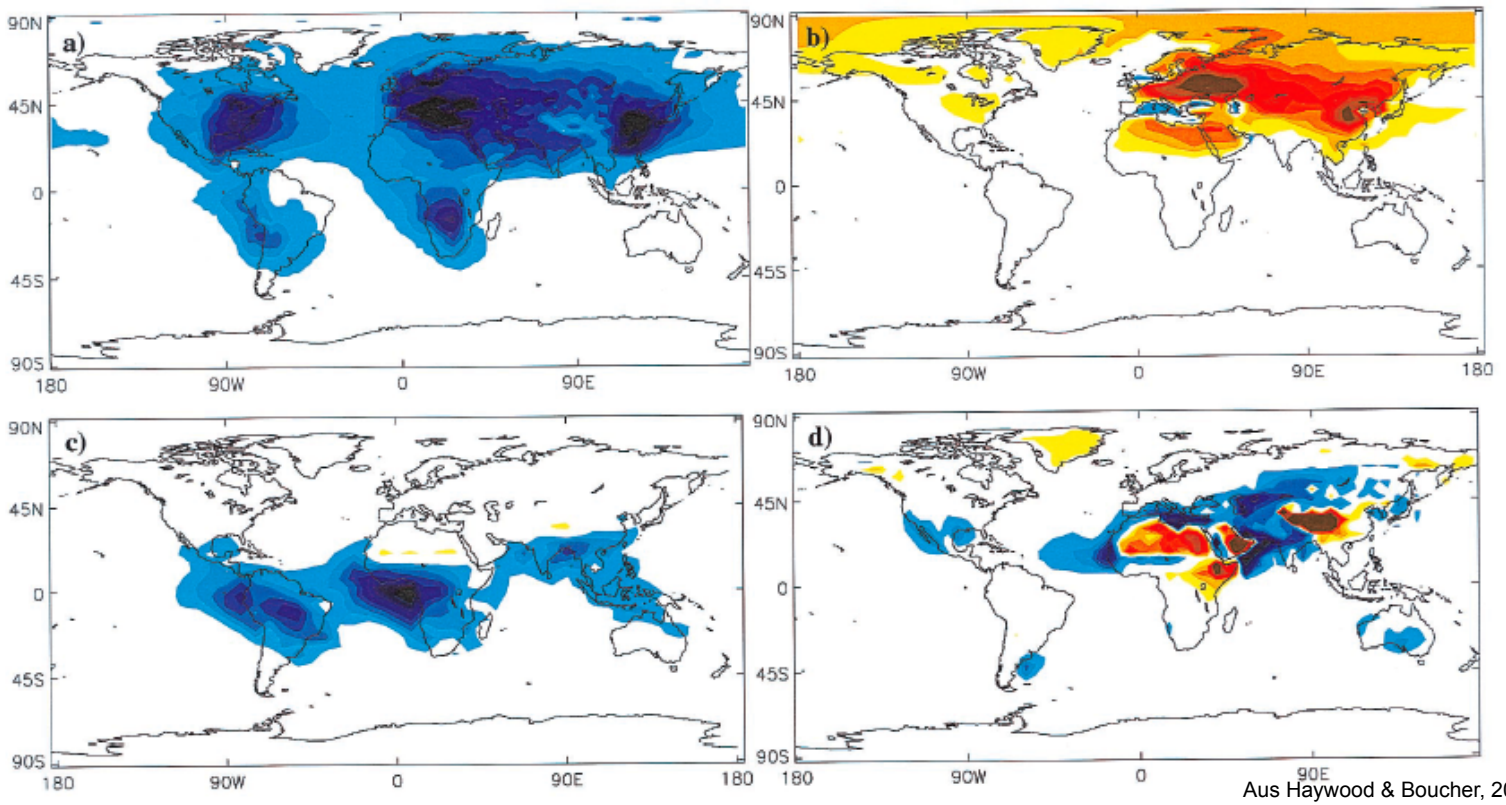
- **BUT: reactor design largely empirical, no models exist**

- **WHY? Estimated computational time is 10^7 years on Earth Simulator due to scale separation, nanometer vs. meters.**

Effects on climate

Most important direct radiative forcing effect through sulfur

- Sulfataerosole: -0.8 W/m^2 to -0.20 W/m^2
- Black Carbon (fossil fuels): +0.03 W/m^2 to +0.30 W/m^2
- biomass: - 0.6 W/m^2 to -0.07 W/m^2



Aus Haywood & Boucher, 2000

SO_3 or sulfates are condensation kernels

⟶ secondary effects (change of microphysical (radiative) properties and of life cycle of clouds

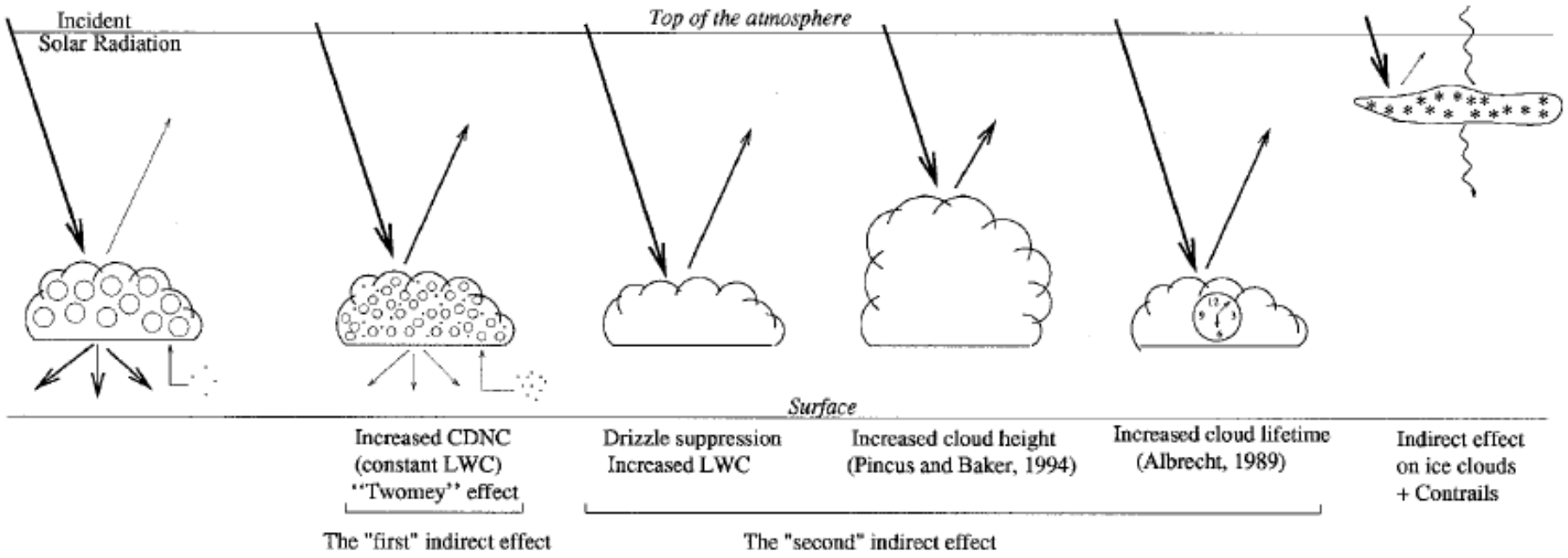
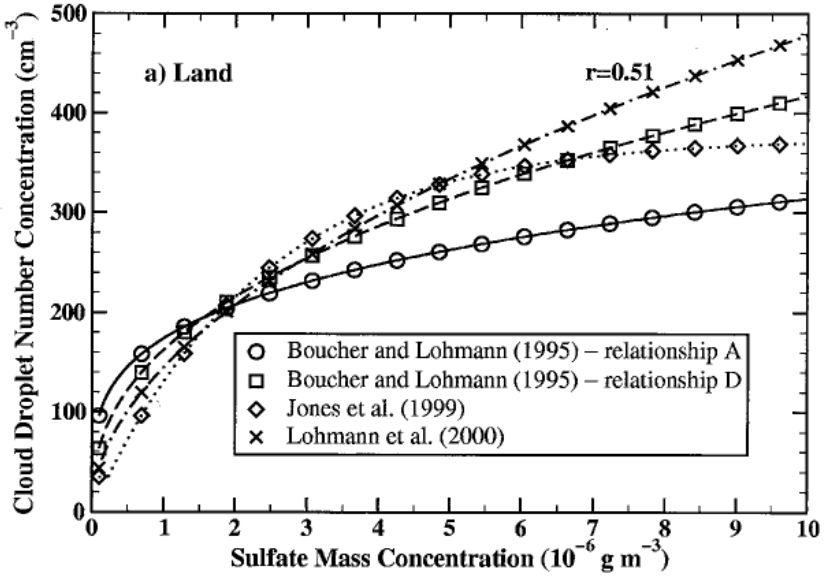
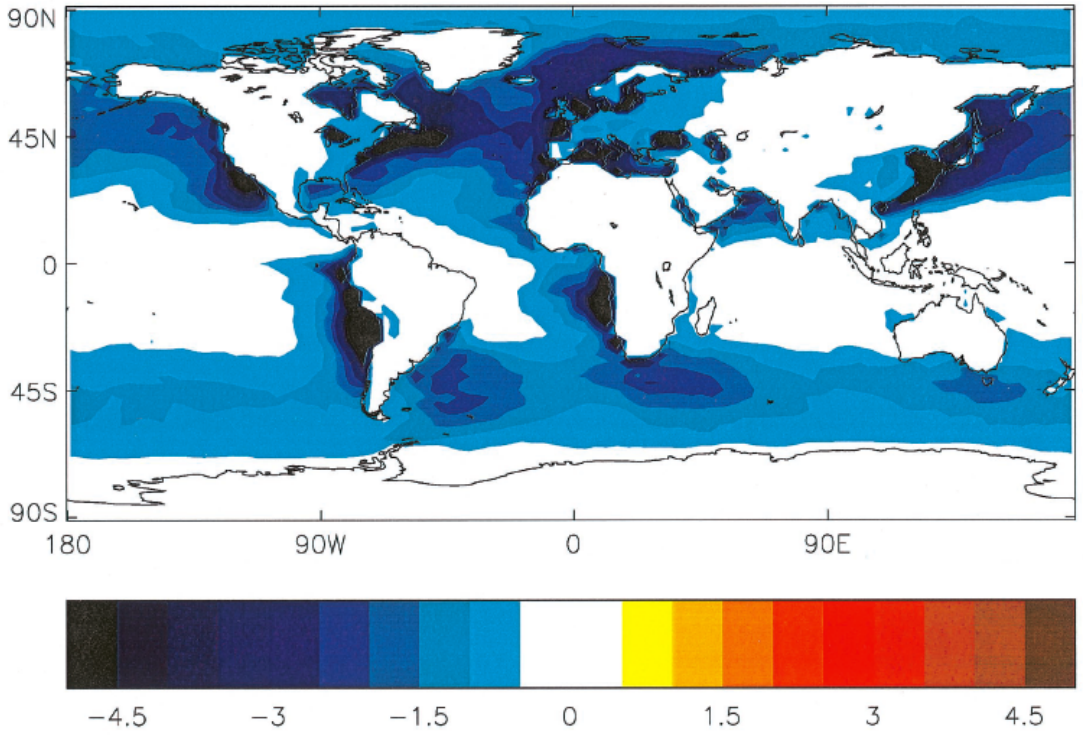


Figure 1. Schematic of the aerosol indirect effects. CDNC means cloud droplet number concentration, and LWC means liquid water content**(aus Haywood & Boucher, 2000).**

Particles

- **indirect radiative forcing**
  - Albedo effect betwee -0.3 W/m^2 to -1.8 W/m^2

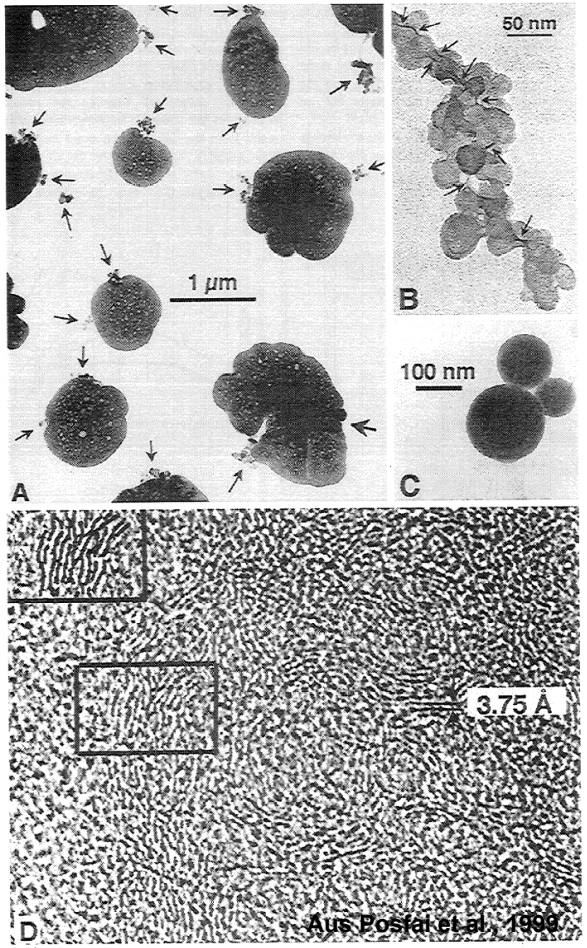


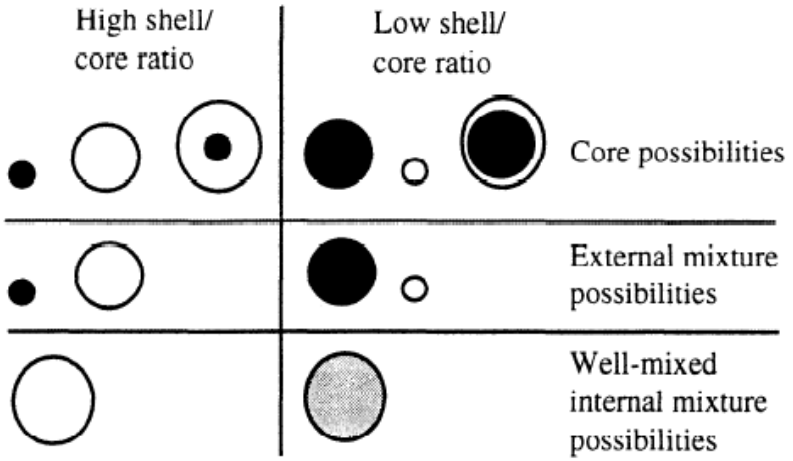


Aus Haywood & Boucher, 2000

Based on computations – predictions extremely difficult

Eample mixing: Sulfates and soot





(aus Jacobson, 2000)

Model: external 50% higher than „core“-model
well-mixed 40% lower than „core“

Radiative forcing:

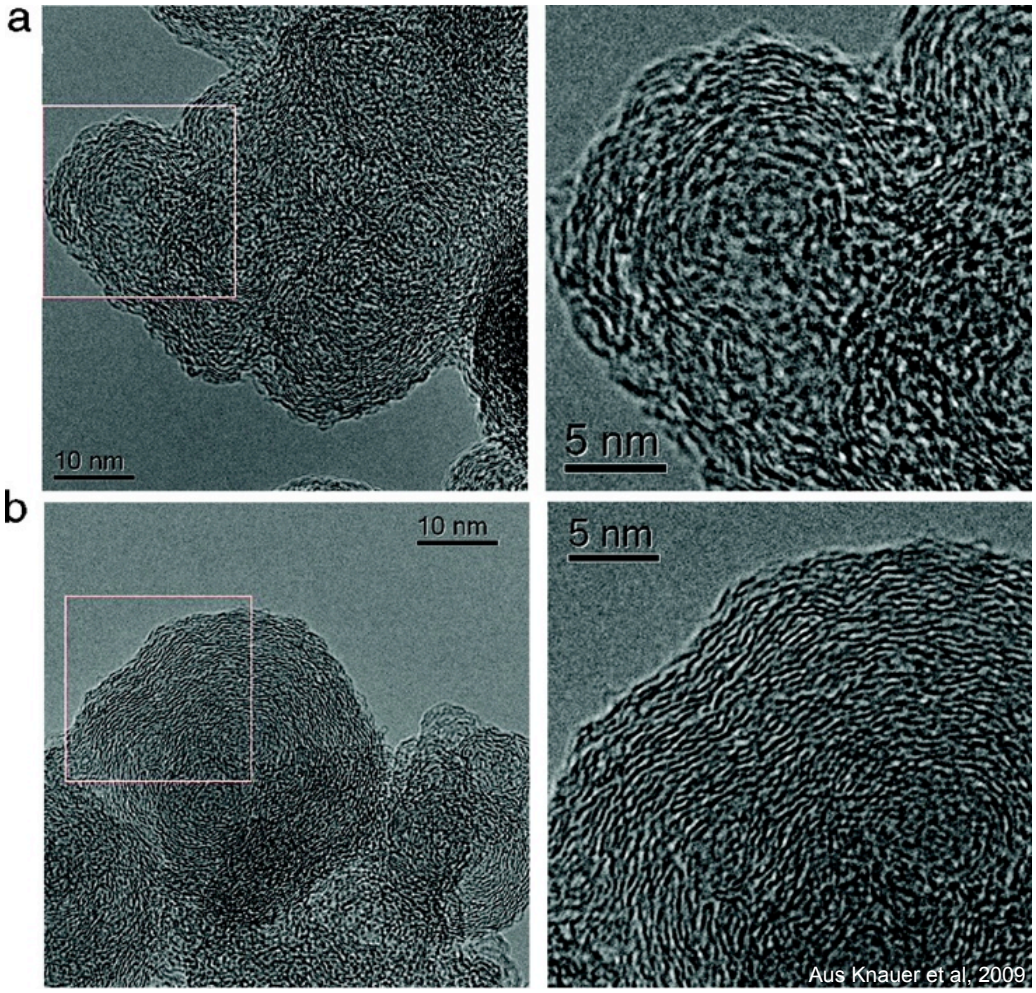
Sulfate -0.8 W/m^2 to -0.2 W/m^2

Carbon +0.2(well mixed) to
+0.36 (internally mixed)

Internal mixing soot/sulfate: every percent of soot
⟶ radiative forcing +0.034 W/m^2

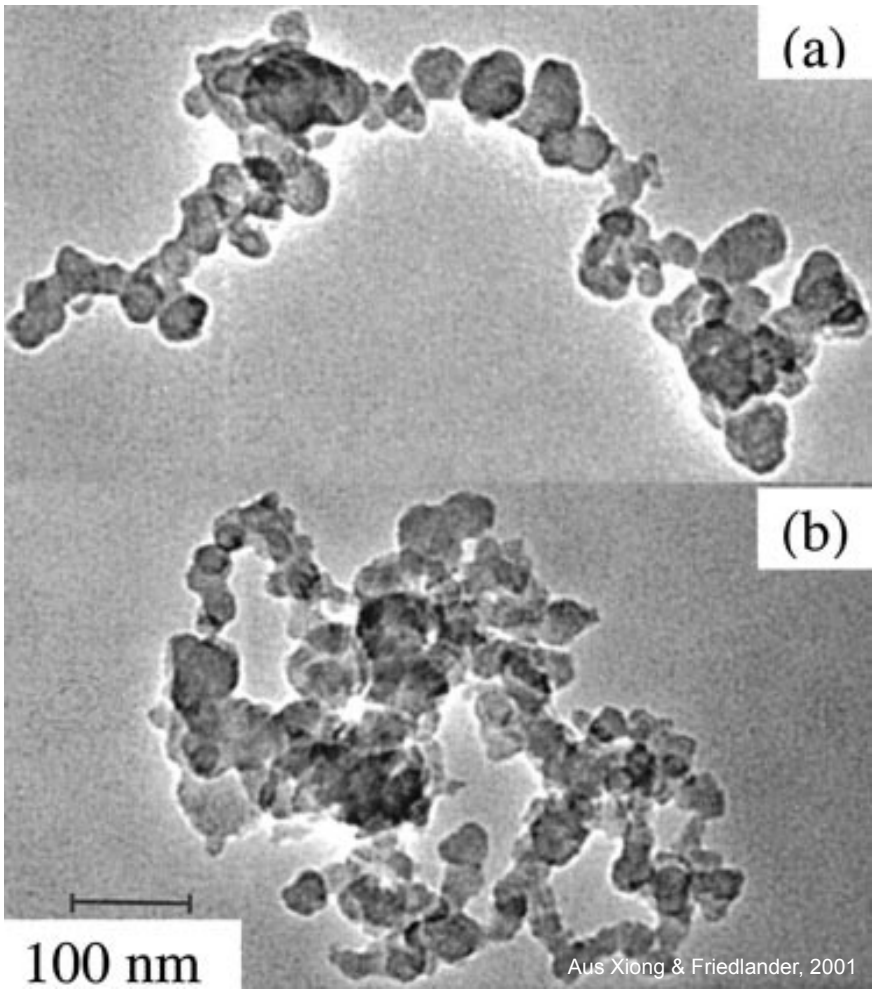
Soot

structure:



Aus Knauer et al, 2009

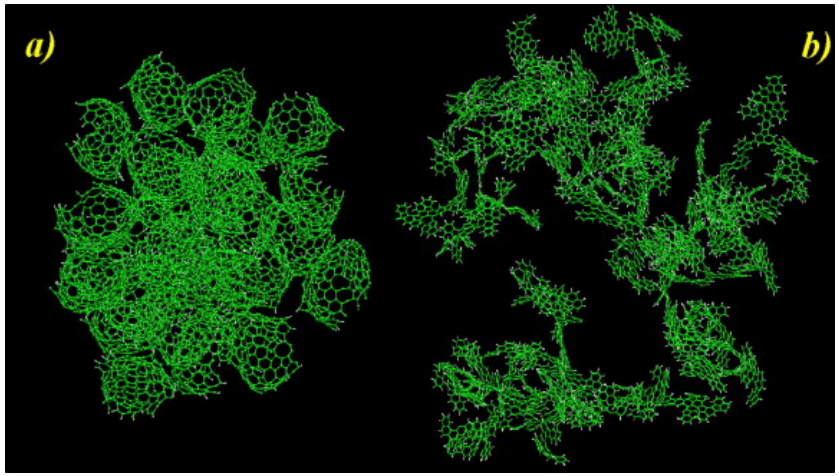
Agglomeration:

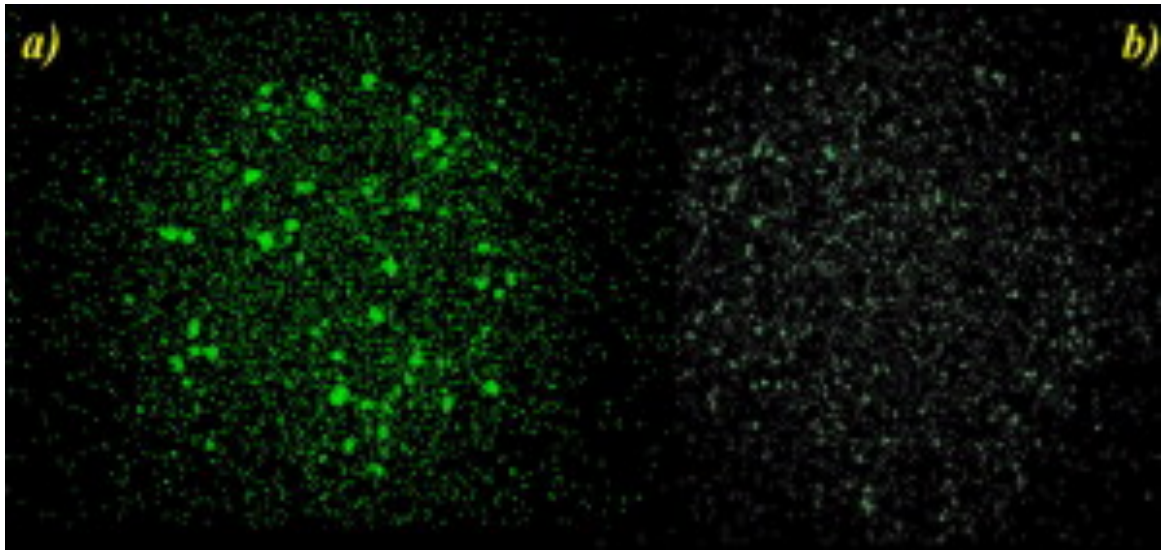


Aus Xiong & Friedlander, 2001

Soot structure

How can the structure be modelled?





Agglomeration of flat ($C_{202}H_{90}$) and spherical ($C_{188}H_{53}$) partikles with “coarse grained” simulationen (© A. Violi & S. Izvekov, 2007)

→ we do not want to go into that much detail

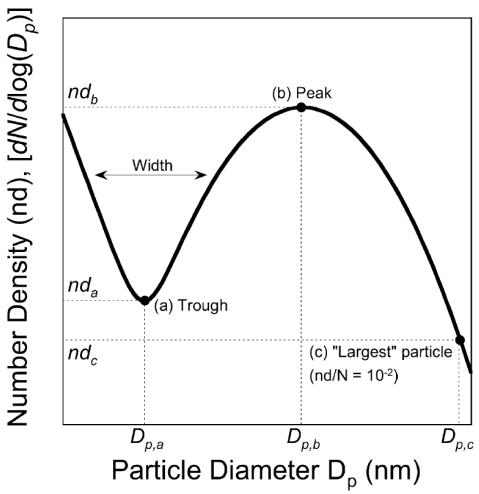
assume “microscopic” soot particles (~ 10-100 nm)

Modelling of agglomeration in turbulent flow:

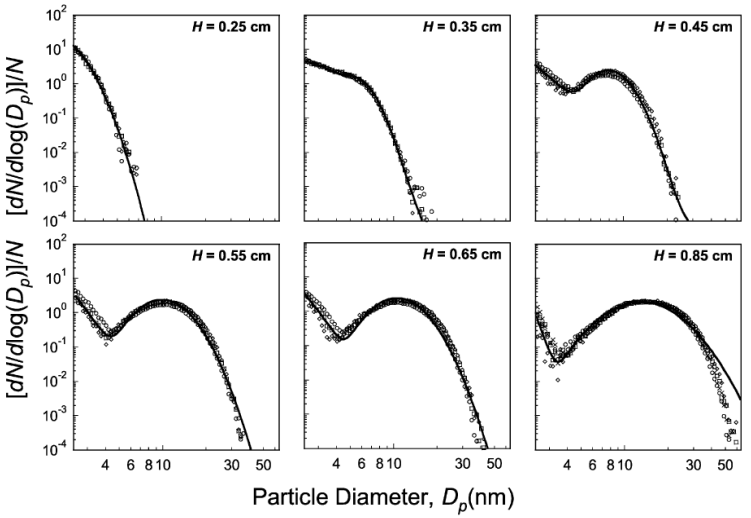
Evolution of particle number density n (PBE or GDE):

$$\frac{\partial n}{\partial t}+\nabla\cdot n\mathbf{u}-\nabla\cdot D\nabla n+\frac{\partial G(v,\mathbf{Y})n(v)}{\partial v}=S(v,\mathbf{Y})+\frac{1}{2}\int_0^v\beta\left(\tilde{v},v-\tilde{v}\right)n\left(\tilde{v}\right)n\left(v-\tilde{v}\right)d\tilde{v}-\int_0^v\beta\left(v,\tilde{v}\right)n\left(v\right)n\left(\tilde{v}\right)d\tilde{v}$$

The particle number density is a function of (v, x, t) – v: particle volume



Typical PSD (Singh et al, 2006) for soot



PSD evolution (A.D. Abid, 2008) for soot

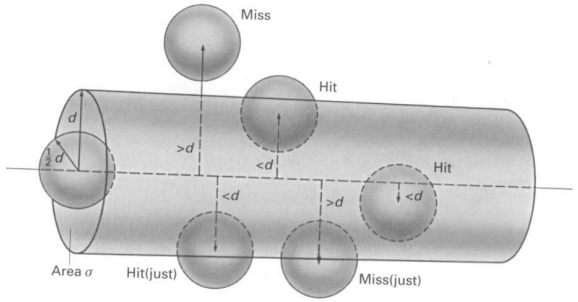
Collision Kernel

Focus on aggregation

What is $\beta(v_i,v_j)$? **collision kernel or collision frequency**

How can it be modelled?

Free molecule range:



$$\beta(v_i,v_j) = \pi(d_{pi}+d_{pj})^2 \left[k_B T/(\pi m_R)\right]^{1/2}$$

Continuum regime:

$$\beta(v_i,v_j) = 4\pi(d_{pi}+d_{pj}) \left[D_i+D_j\right]$$ -D = diffusion coefficient

Collision kernel

Laminar shear and turbulence:

Laminar shear:

$$\beta(v_i, v_j) = \frac{4}{3}\left(v_i^{1/3} + v_j^{1/3}\right)^3 \frac{du}{dx}$$

Turbulence: **shear**

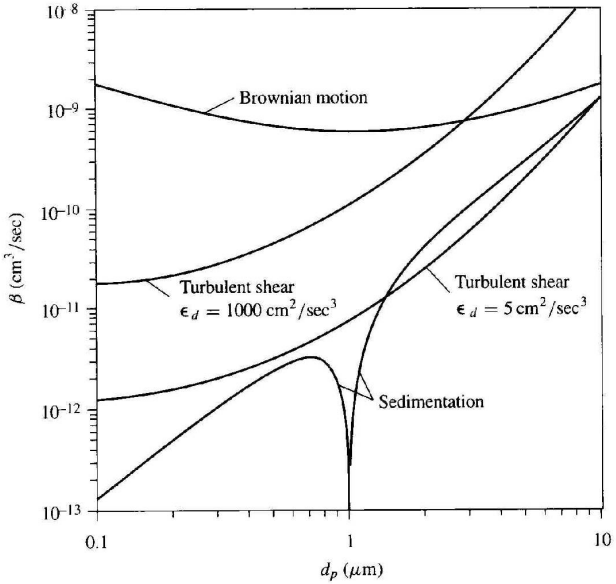
$$\beta(v_i, v_j) = 1.3\left(\frac{\varepsilon_d}{\nu}\right)^{1/2}\left(v_i^{1/3} + v_j^{1/3}\right)^3$$

Saffman Turner limit

inertial coag

$$\beta(v_i, v_j) = 5.7\left(v_i^{1/3} + v_j^{1/3}\right)^2 \left|\frac{1}{\beta_i} - \frac{1}{\beta_j}\right| \frac{\varepsilon_d^{3/4}}{\nu^{1/4}}$$

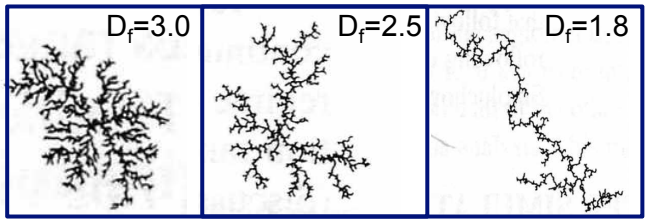
Comparison:



Collision Kernel

Are the particles always spherical?

agglomeration due to turbulence vs. Brownian motion

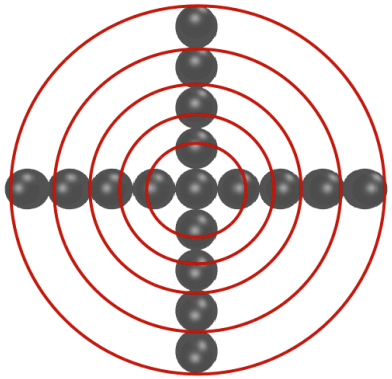


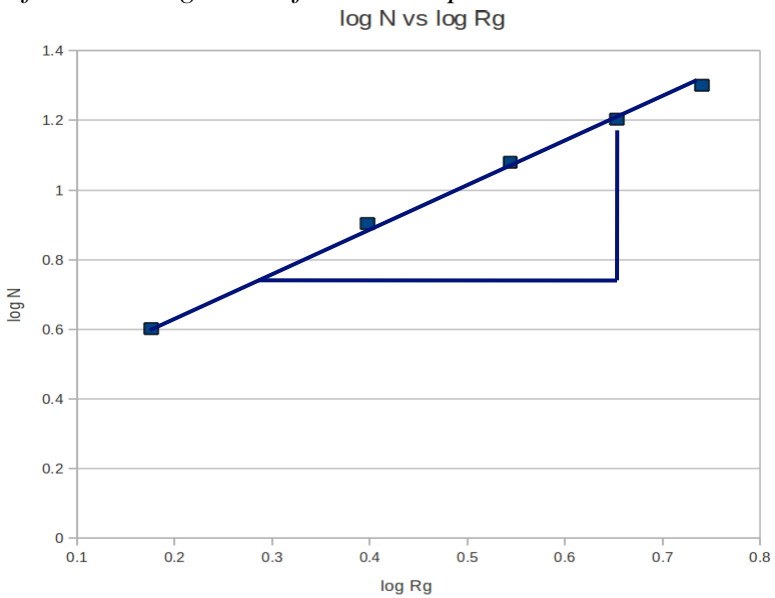
Fractal dimensions during particle agglomeration: agglomeration of primary particles due to convection (e.g. turbulence) (a), and agglomeration of primary particles (b) and of clusters (c) due to Brownian motion (adapted from DW Schaefer, 1988).

Collision Kernel

Fractal Dimension

$$\log\ n_p = \log\ a + D_f \log\ R_g - D_f \log\ d_p$$





Free molecule range:

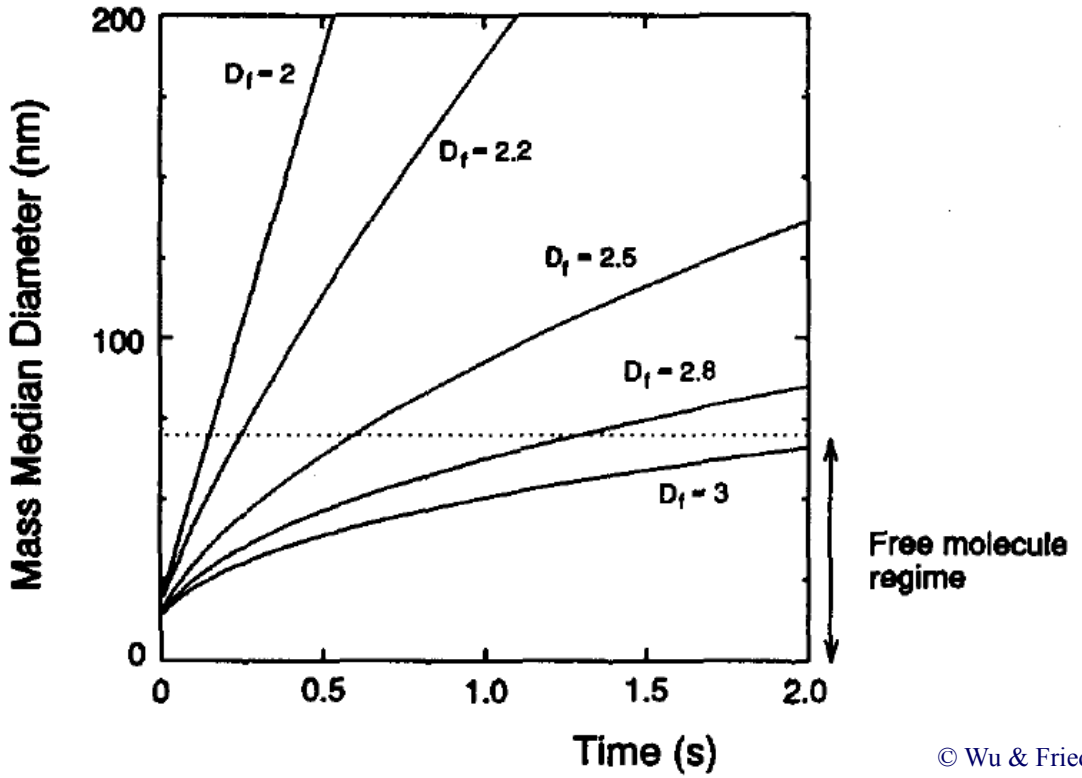
$$\beta\left(v_i, v_j\right) = \left(\frac{6k_bT}{\rho}\right)^{1/2} \left(\frac{3}{4\pi}\right)^{2/D_f - 1/2} d_{p0}^{2-6/D_f} \left(\frac{1}{v_i} + \frac{1}{v_j}\right)^{1/2} \left(v_i^{1/D_f} + v_j^{1/D_f}\right)^2$$

Continuum regime:

$$\beta\left(v_i, v_j\right) = \frac{2k_bT}{3\mu} \left(\frac{1}{v_i^{1/D_f}} + \frac{1}{v_j^{1/D_f}}\right) \left(v_i^{1/D_f} + v_j^{1/D_f}\right)^2$$

Collision kernel

Influence of fractal dimension on diameter:



HOW TO GET D_f?

ESPResSo

The motion and dynamics of the Brownian particles are modelled by solving the Langevin Equations of motion

$$m_P \ddot{\mathbf{x}}_\mathbf{i} = F_D + F_{ext} + BdW \quad \text{(M du/dt + γ u = F(t))}$$
$$\dot{\mathbf{x}} = \mathbf{v}(t, x)$$

How to model particle collision and sticking?

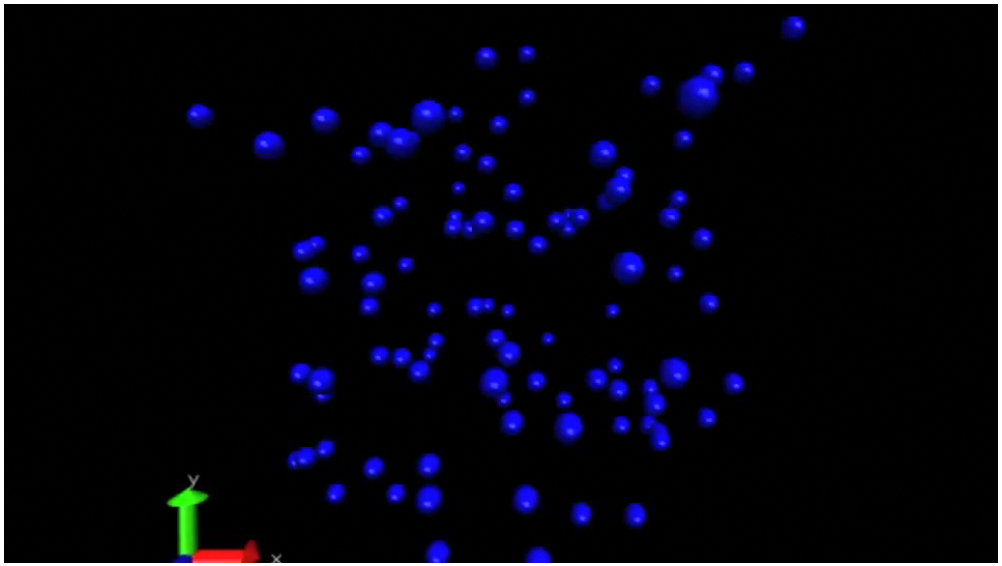
1. highly attractive LJ force

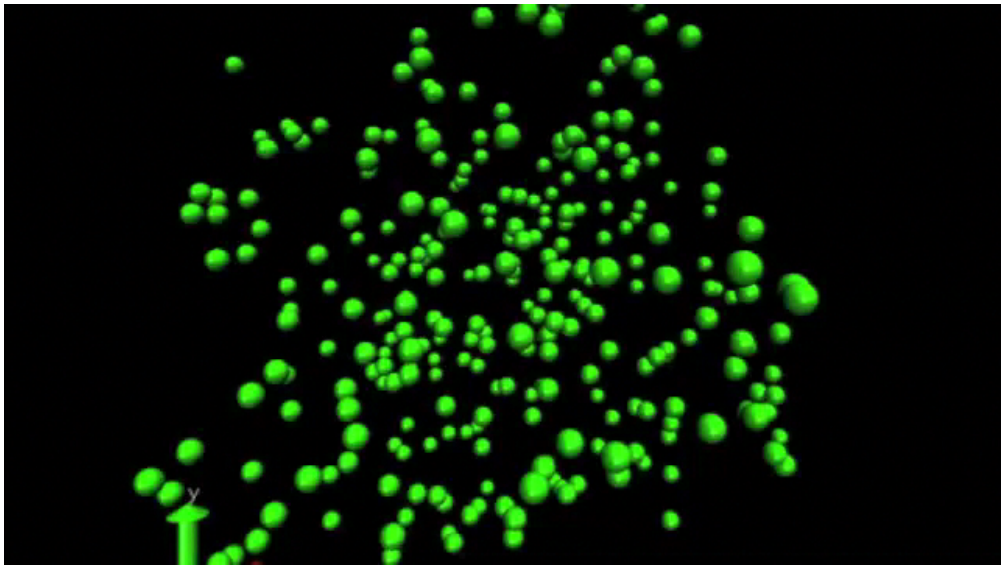
2. connect colliding particles to each other with a single bond

3. connection of 2 contacting particles with a single bond, 3rd particle with angle potential and 4th particle with dihedral potential

Conventional models

Agglomeration of primary particles





LJ potential only

Single bond + angle + dihedral potentials

MD Simulations

1. Highly attractive LJ force

- Due to attractive forces aggregates get compact

2. Connect colliding particles to each other with a single bond

- Due to the spherically symmetric property and elastic property of bonds the connected particles have relative motion to each other

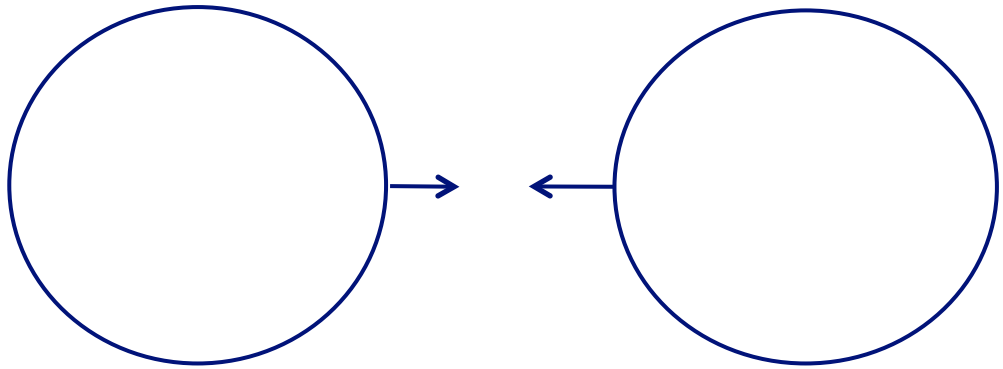
3. Single bond + angle potential + dihedral potential

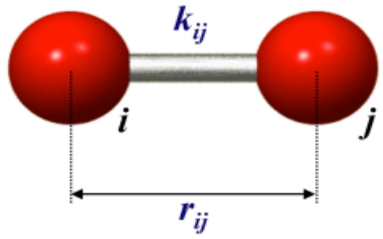
- Cause a rapid energy increase in the system and result in bond broken problem

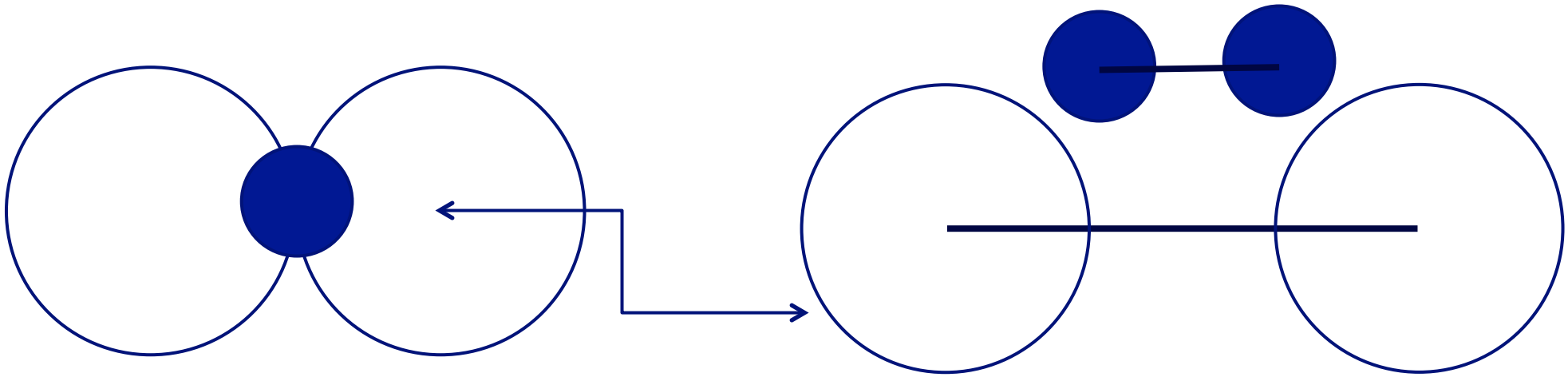
⟶ **We need something else**

Single Bonded Virtual Particles Model

To avoid sliding motion - introduce virtual particles







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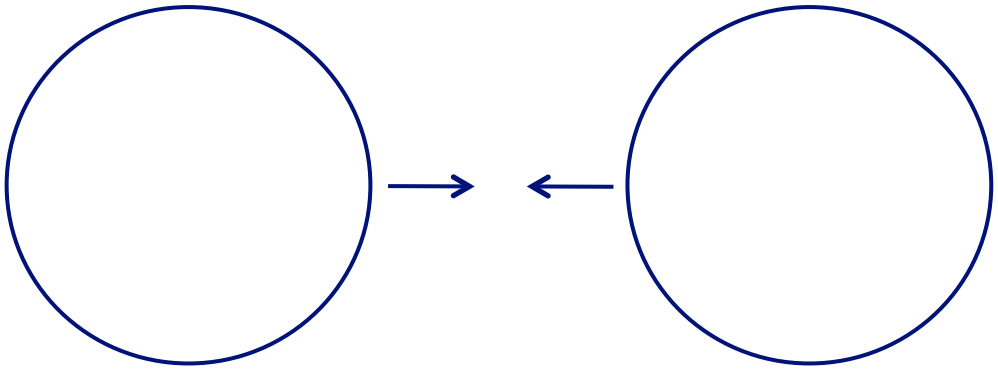
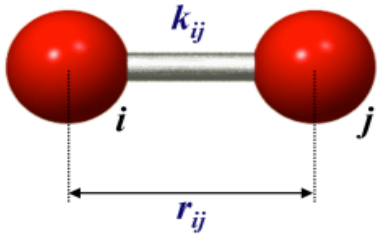
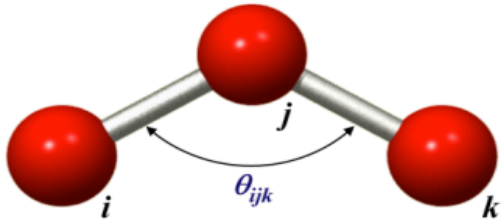
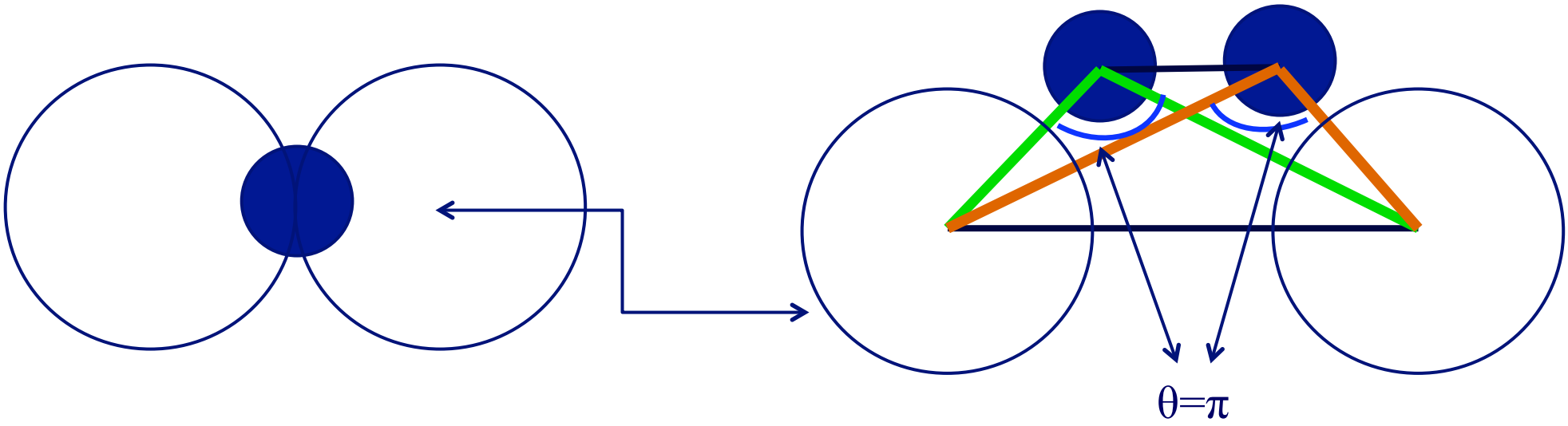
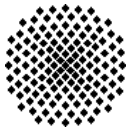
Angle Bonded Virtual Particles Model











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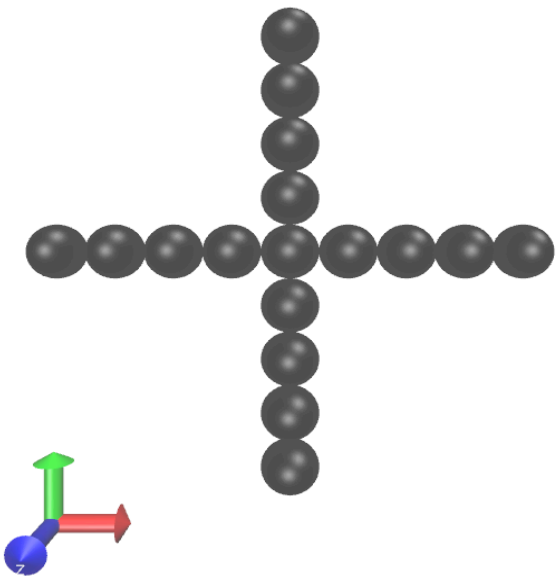
Developed Models

Model Name	*Model Description*	*Acronym*
Model using highly attractive Lennard Jones potential	Collision model with highly attractive Lennard Jones potential	LJ
Single bond model	2-body potential between collided particles	SB
All bonds model	2-body, 3-body and 4-body potential between particles	AB
Single bonded virtual particles model	Collision model with two virtual particles at the collision point and connected by a 2-body potential	SBV
Angle bonded virtual particles model	Collision model with two virtual particles connected through 3-body potential	AnBV

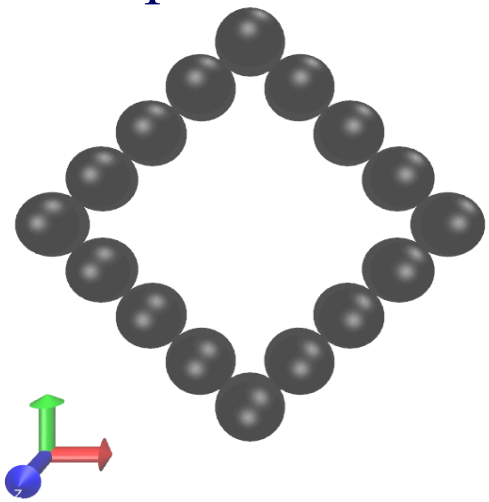
MD Simulations – Test Cases

Pre-defined agglomerates

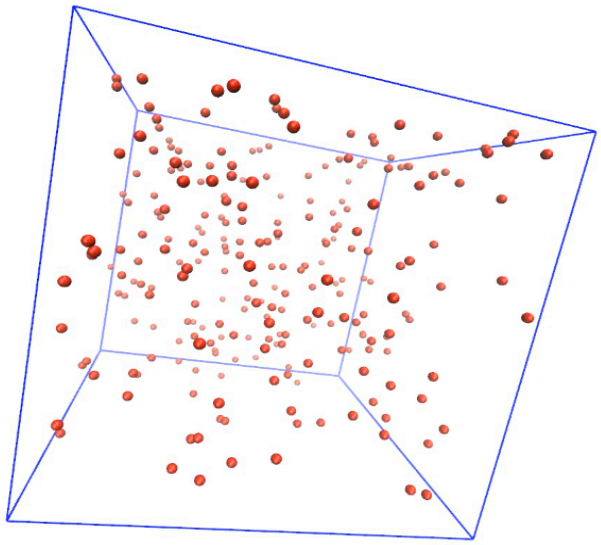
Cross-Shape



Square-Shape



Randomly placed particles



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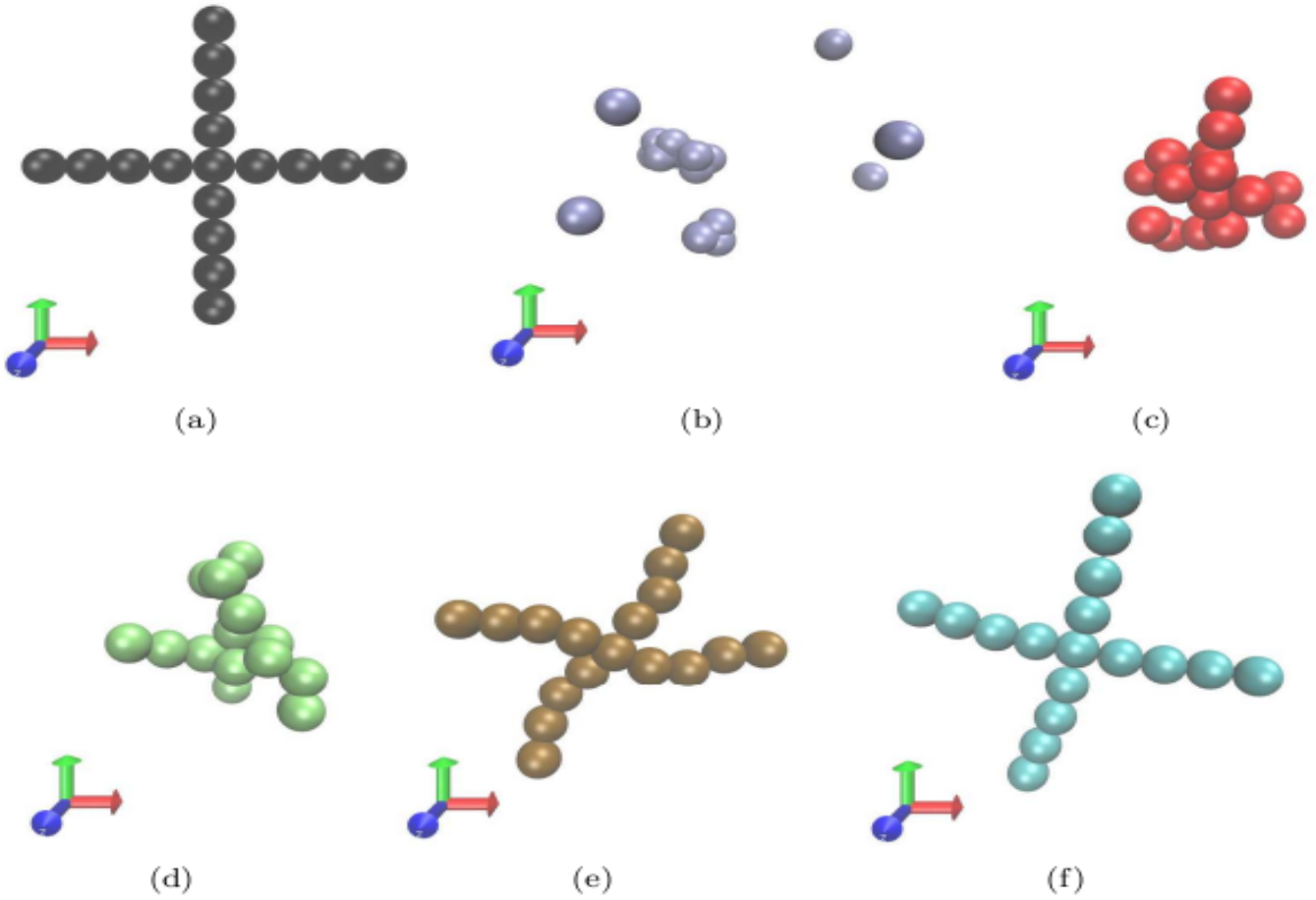
Cross-Shaped Agglomerate



(a) initial structure (Df=1.31)

(b) LJ model

(c) SB model

(d) AB model

(e) SBV model

(f) AnBV model

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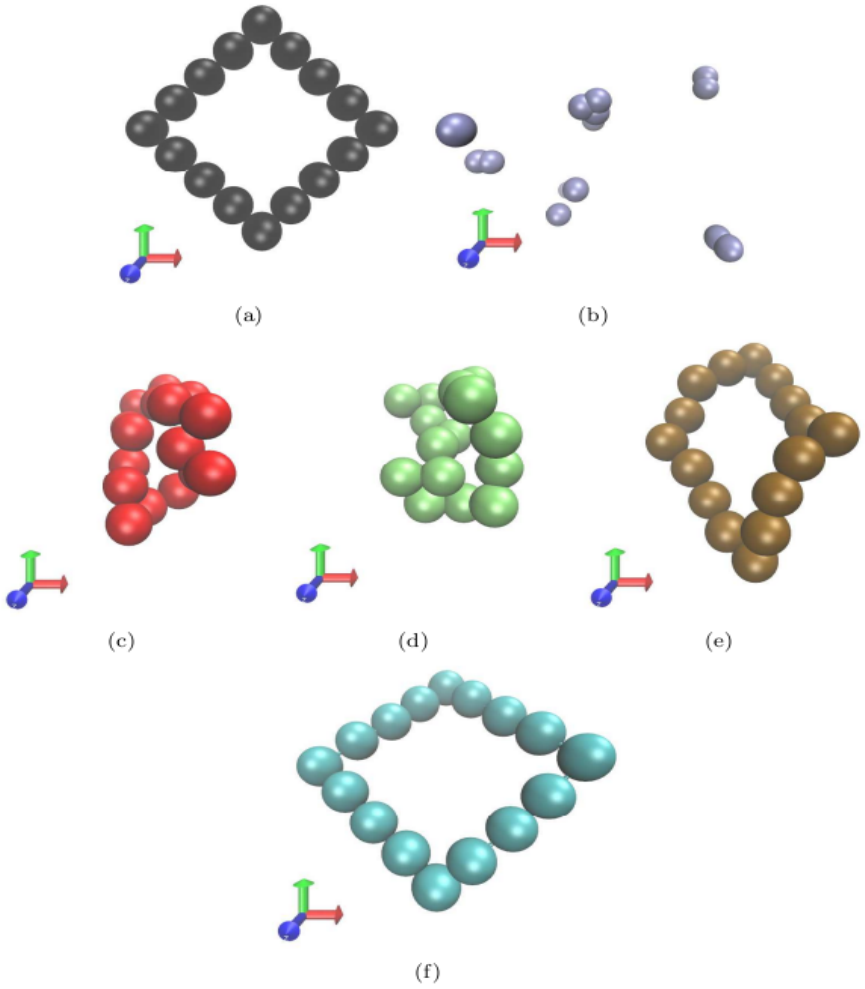
Square-shaped Agglomerate Simulation Results



(a) initial structure

(b) LJ model

(c) SB model

(d) AB model

(e) SBV model

(f) AnBV model

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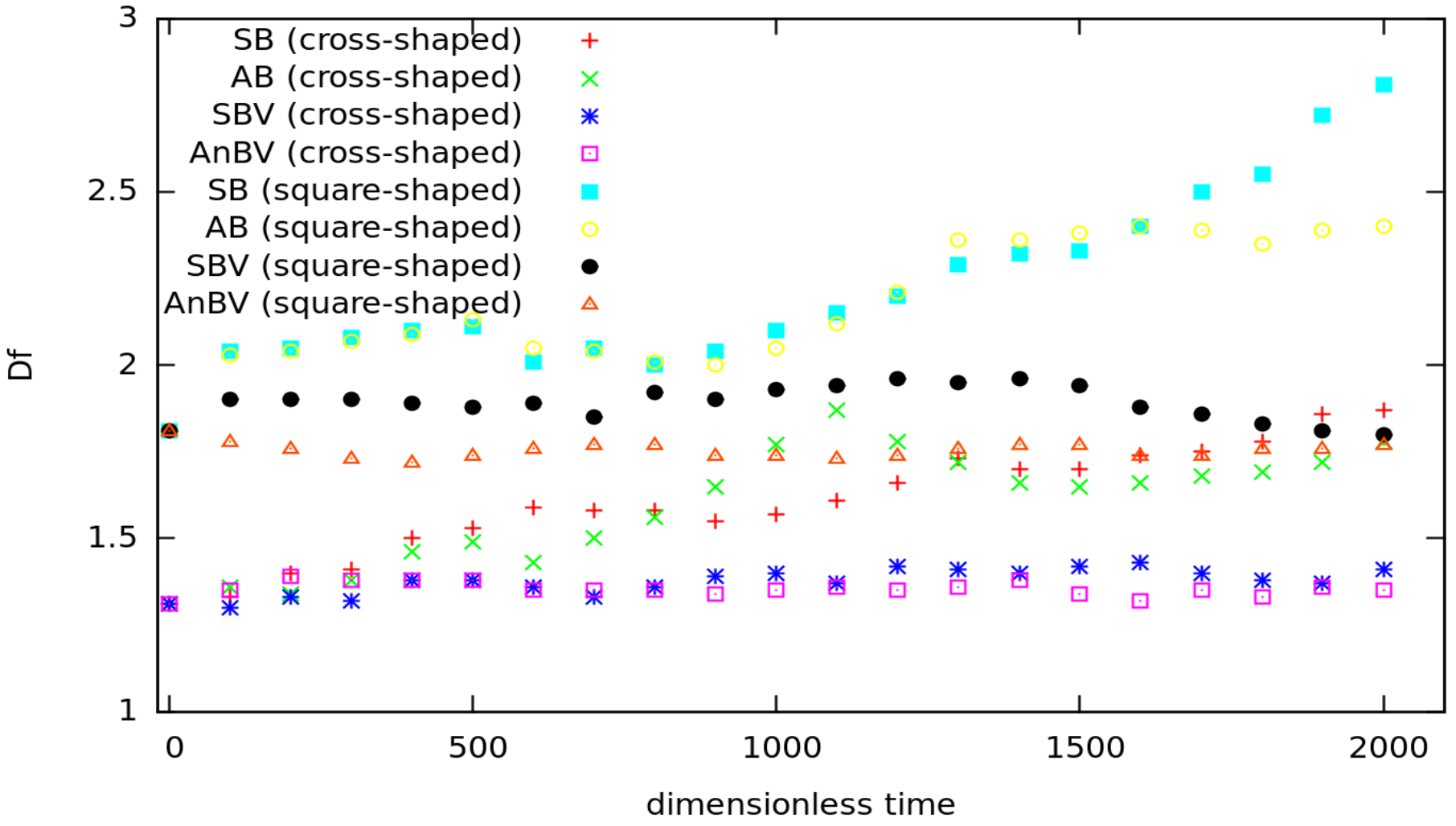
Evolution of fractal dimension



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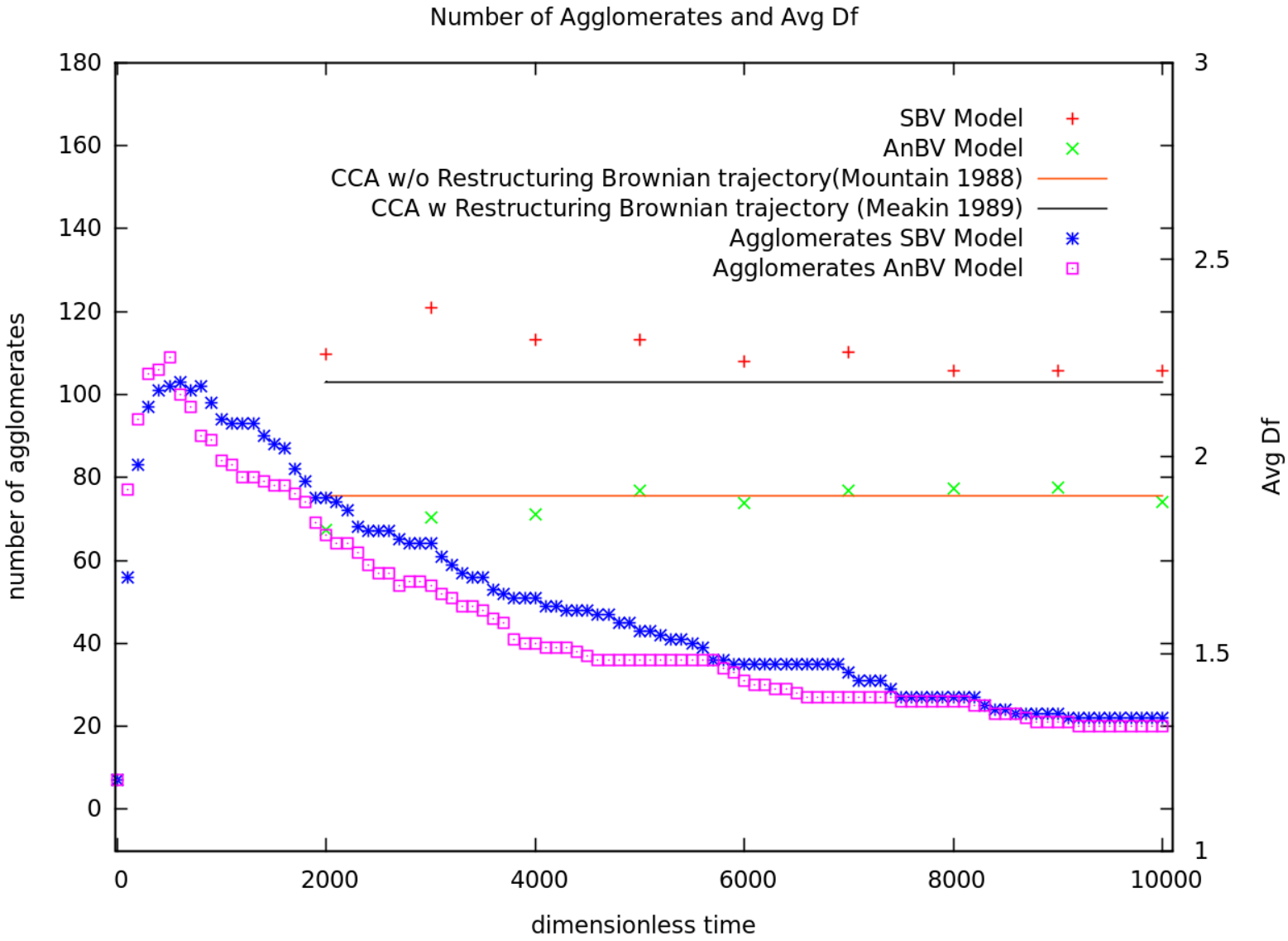
Particle Agglomeration (Case 3a)



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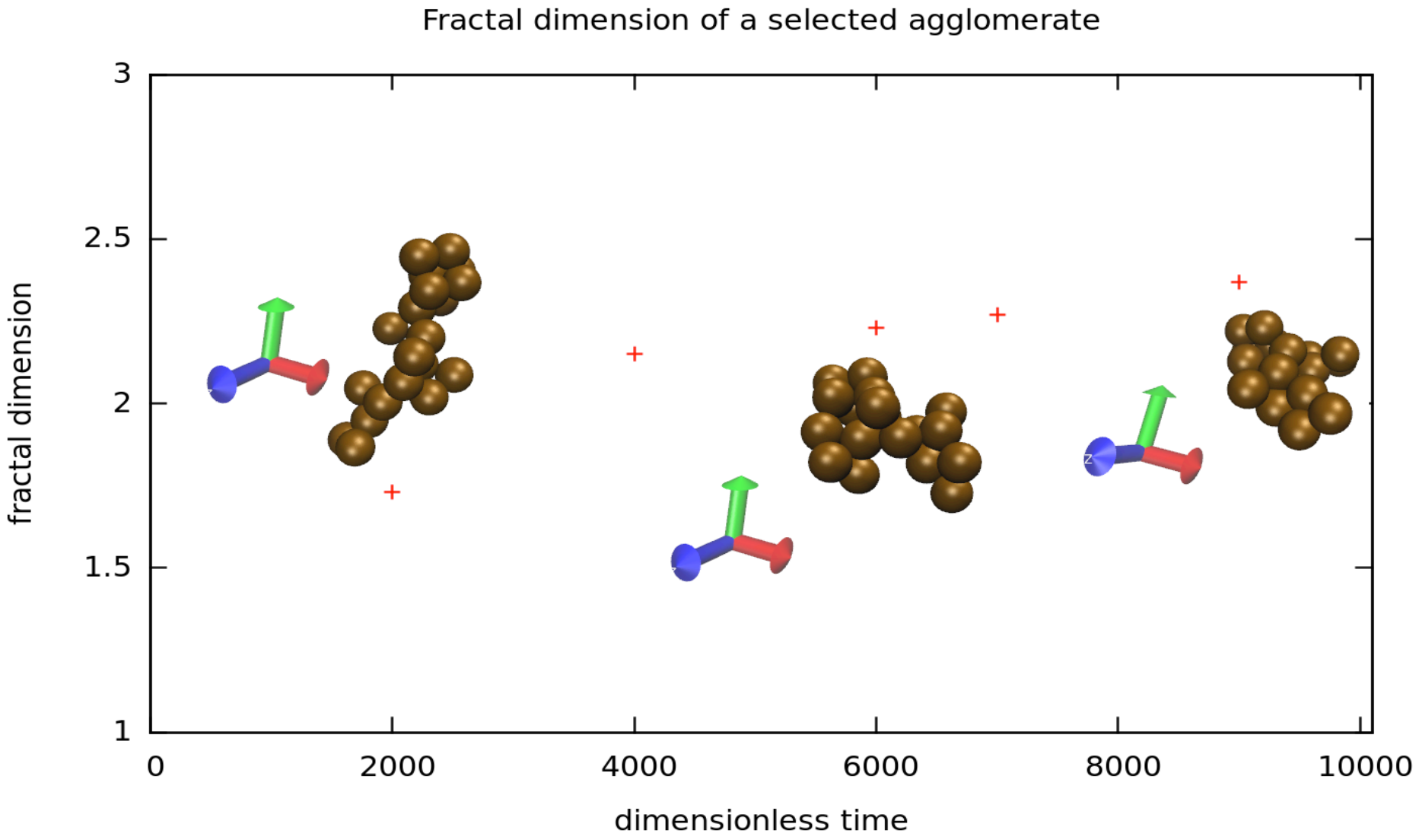
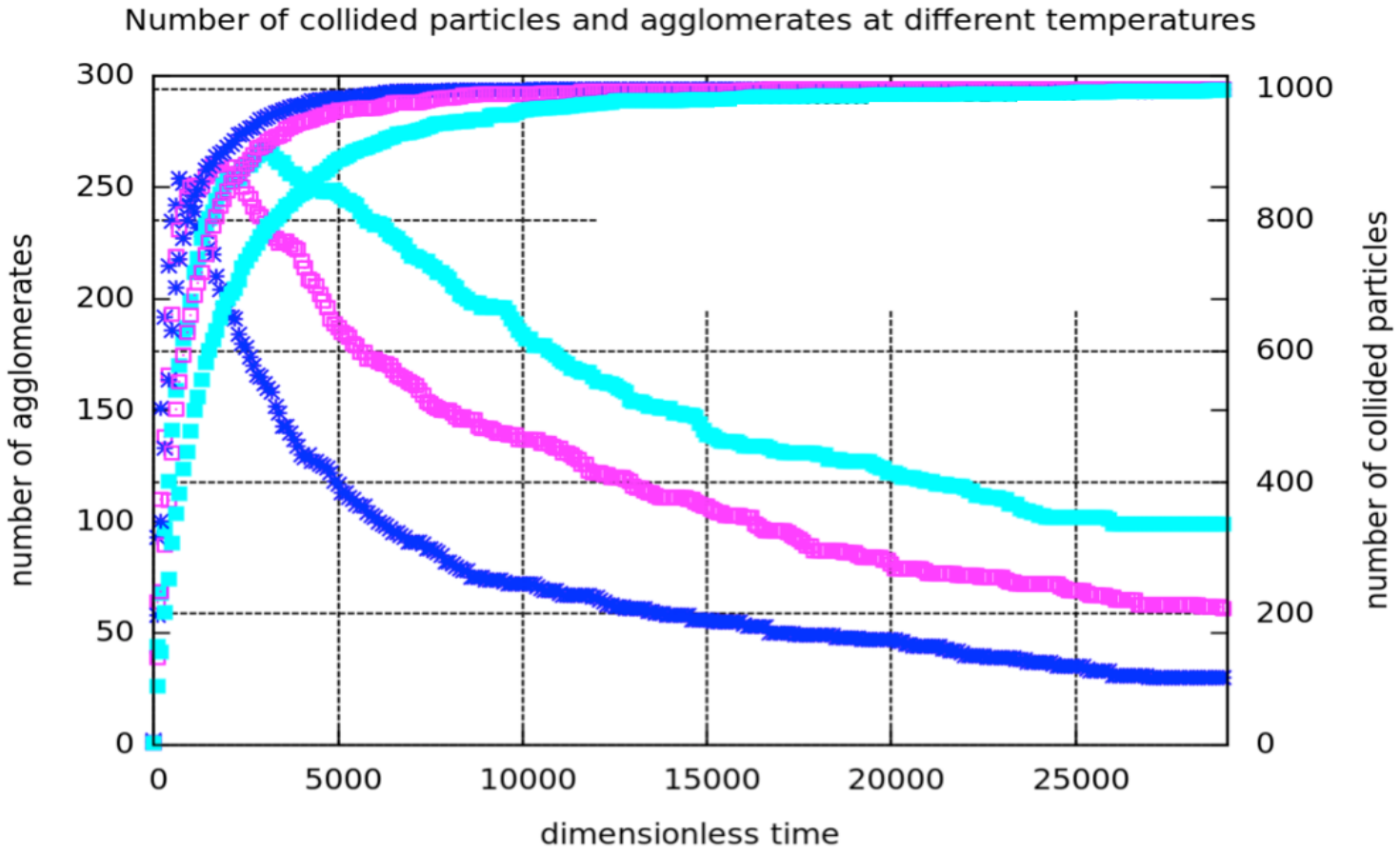
Time evolution using SBV



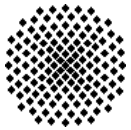
Effect of viscosity



γ/T = 16.4

γ/T = 6.8

γ/T = 3.9



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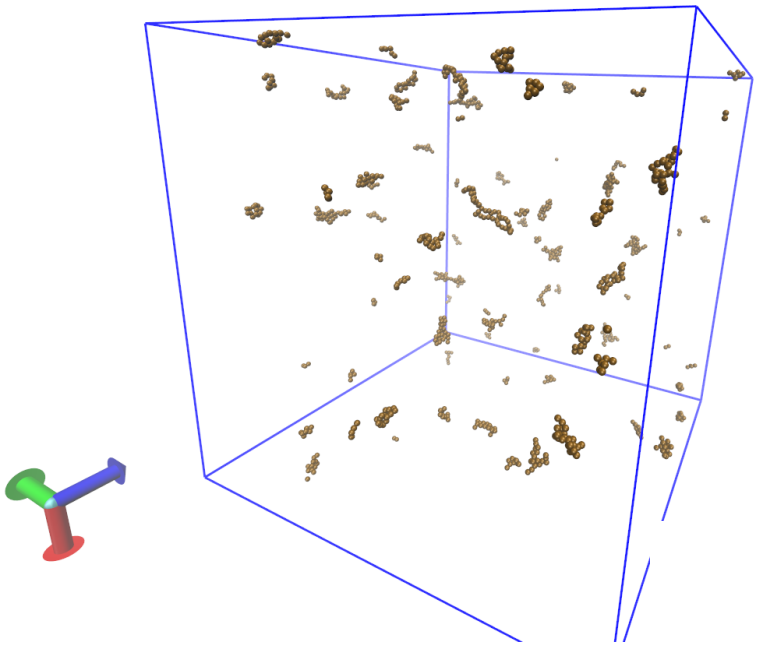
What is this again?

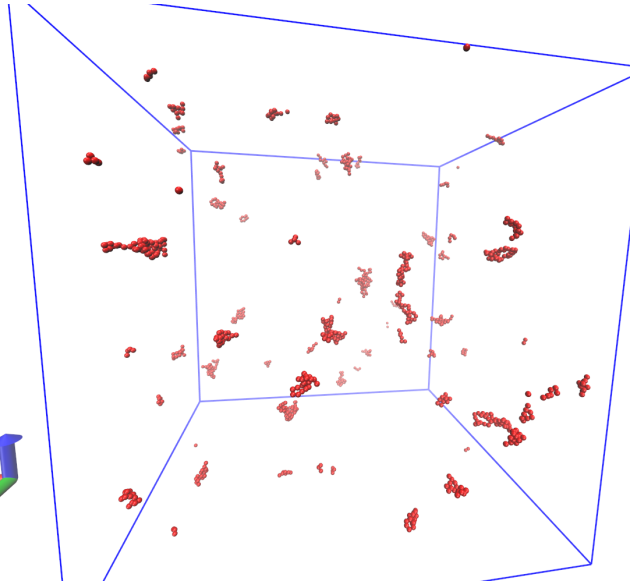
Normilized time/ avg.Df	16.4	6.8	3.9
10000	-	-	1.82
20000	-	1.77	1.77
47000	1.72	-	1.745
52000	-	-	1.73

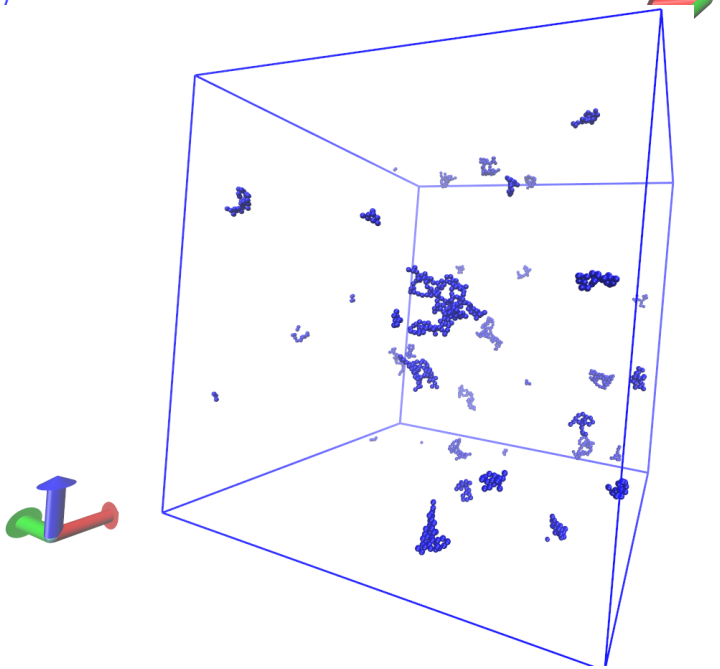
CCA (Brownian Trajectory)
Meakin 1983
Df=1.75 ± 0.05

CCA (Brownian Trajectory) w/o Reconstruction
Kempf 1999
Df=1.8



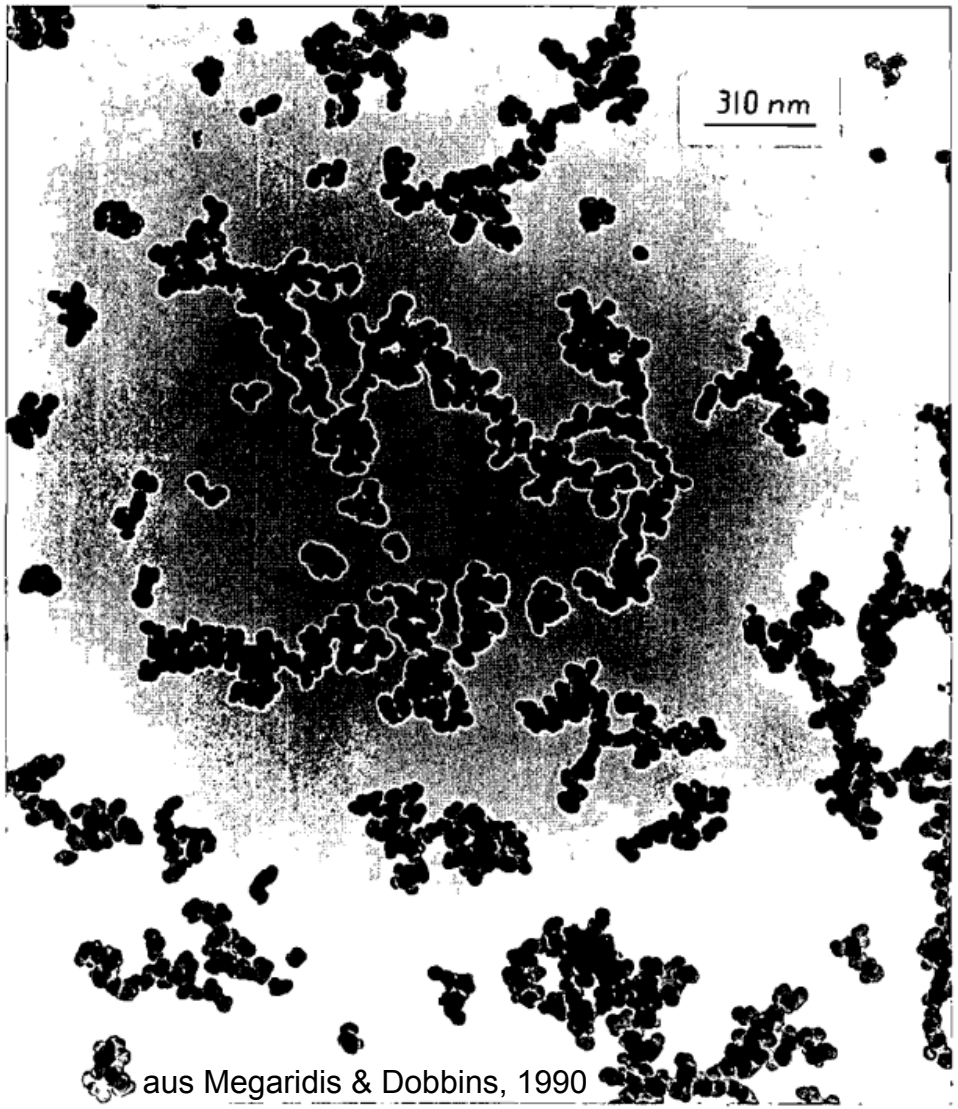
$\gamma/T = 16.4$
$D_f = 1.73$





$\gamma/T = 3.9$
$D_f = 1.74$

$\gamma/T = 6.8$
$D_f = 1.75$



aus Megaridis & Dobbins, 1990

Electron micrograph of soot aggregates extracted from a co-annular ethylene diffusion flame. Position: z = 30mm & r = 2.1mm.

D_f=1.74±0.06 (@ z=15 mm, r=3.7 mm)
D_f=1.62±0.04 (@ z=15 mm, r=3.1 mm)

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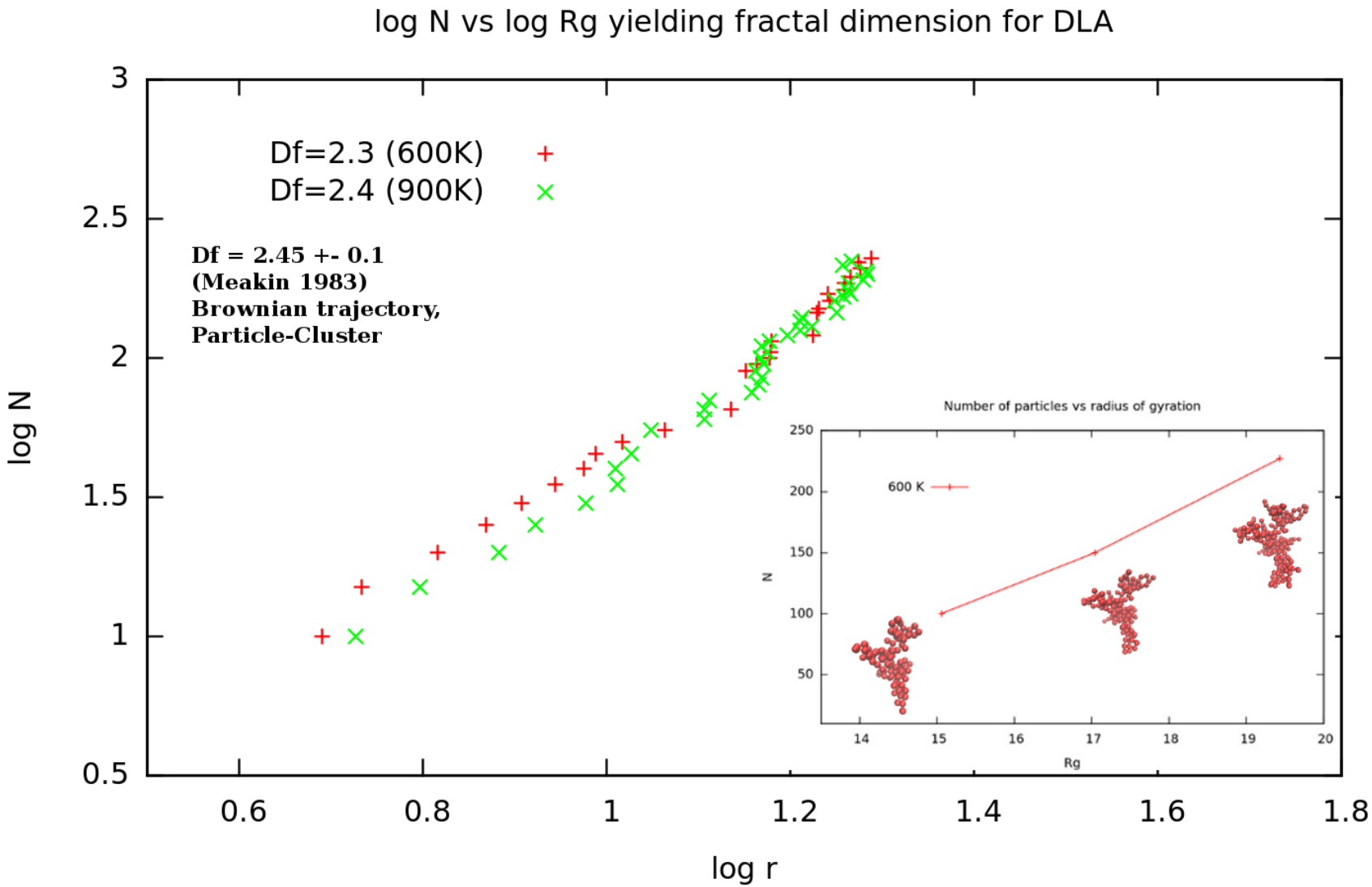
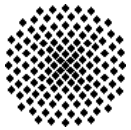
DLA Simulation Results





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Conclusion

Conclusions

- ESPResSo can be used for studies beyond molecular dynamics
- New contact models needed to be implemented
- “Rigid body motion” realized by virtual particles
- Aggregates resemble “real life” soot clusters

Future Work

- Statistics for modelling of D_f and β
- Interaction with flow field