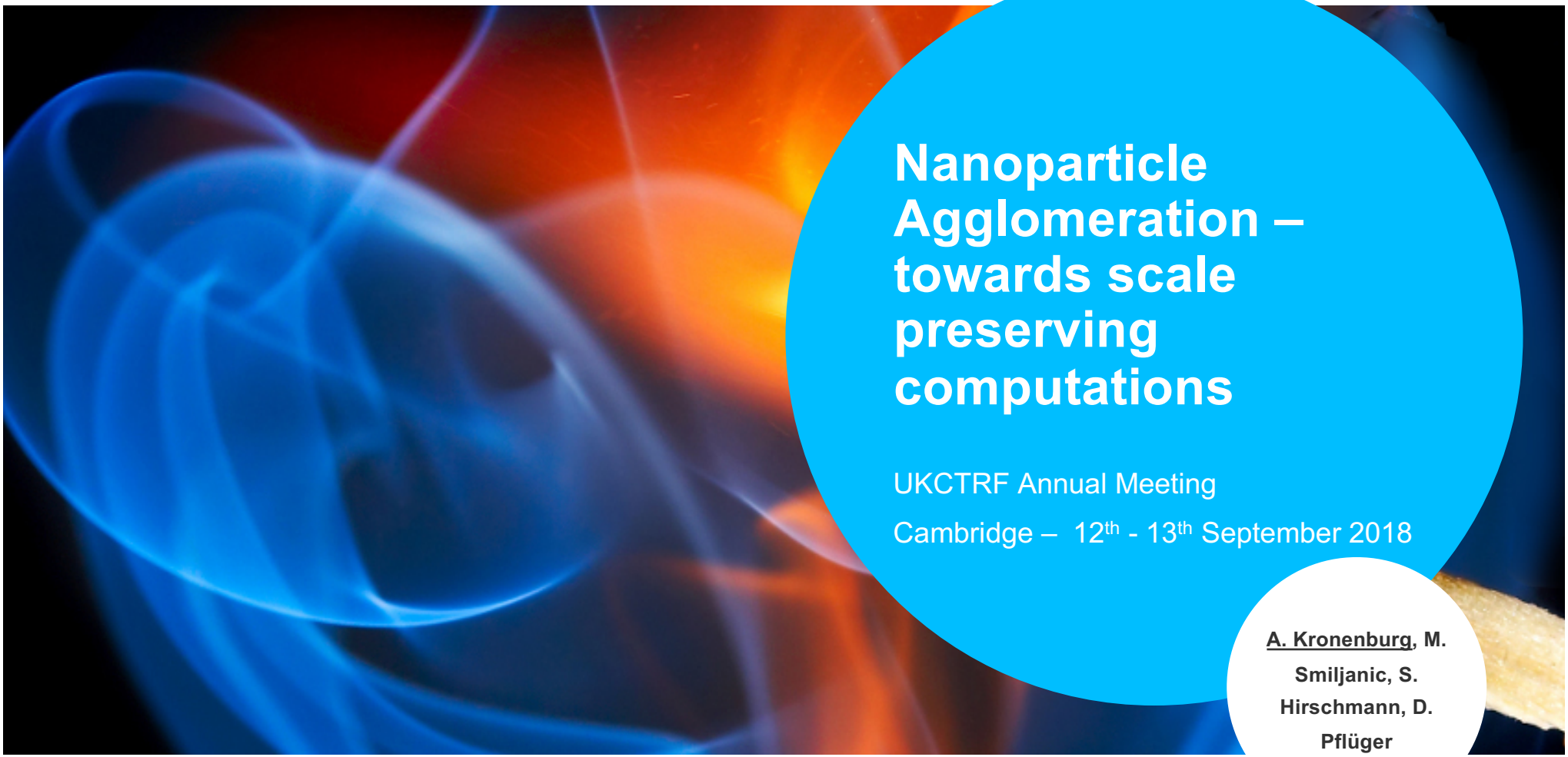
University of Stuttgart
Institut für Technische Verbrennung (ITV)



Nanoparticle Agglomeration – towards scale preserving computations

UKCTRF Annual Meeting

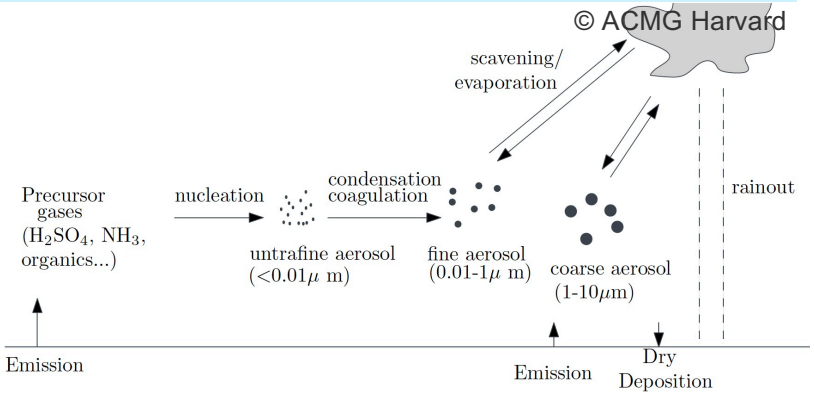
Cambridge – 12th - 13th September 2018

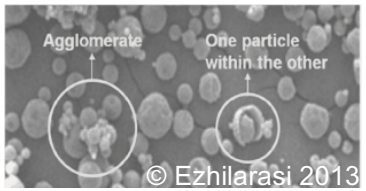
A. Kronenburg, M. Smiljanic, S. Hirschmann, D. Pflüger

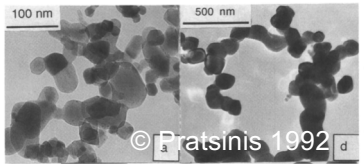
Motivation & Outline

Agglomeration

- Importance
  - Environment – aerosol formation
    - Water purification
    - Exhaust treatment
  - Spray drying
  - Particle flame synthesis

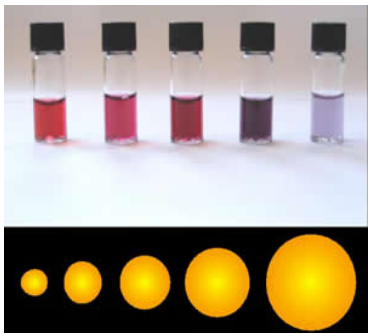






- Agglomeration determines size and size determines properties

  optical/magnetic/electrical/mechanical

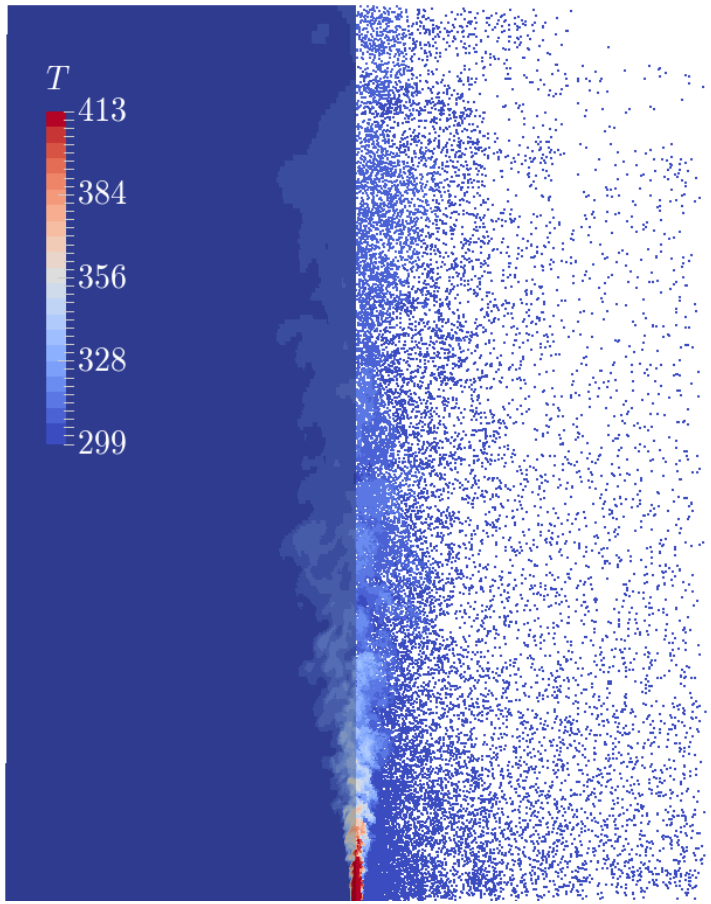


Solution with gold nano-particles (©wikipedia)

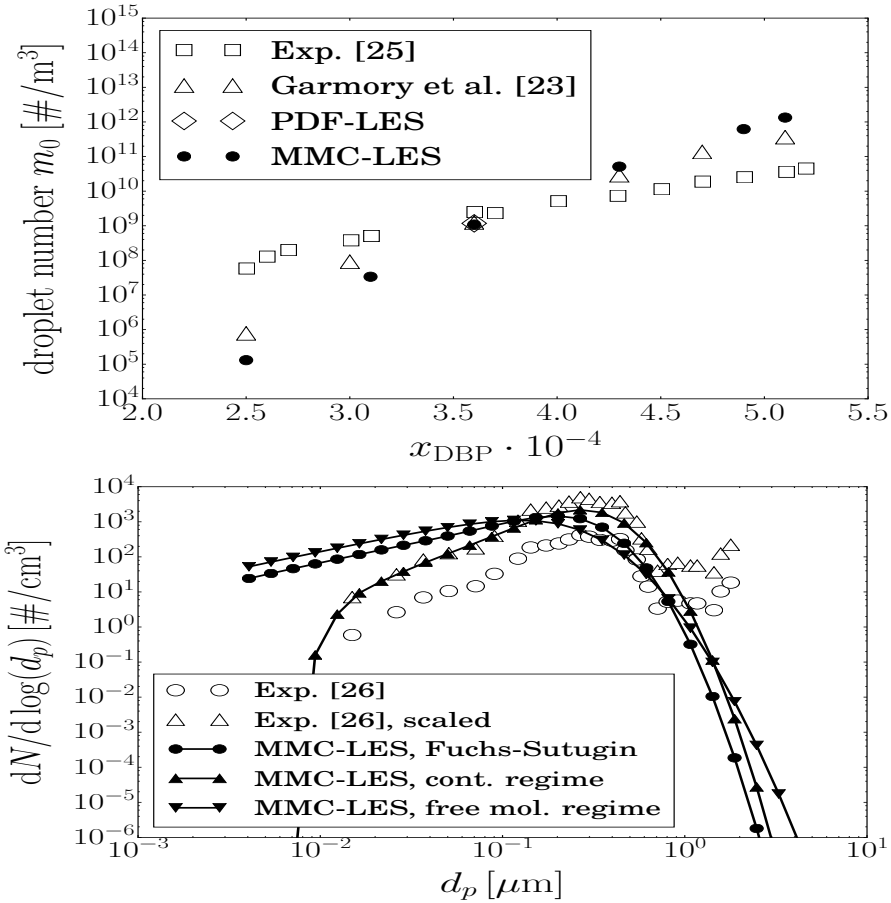
Motivator: Particle Synthesis

Existing PDF-MMC simulations of UCLA experiment (Friedlander)

HOT DBP-LADEN JET IN COLD CO-FLOW



PREDICTED M_0 UND PSD

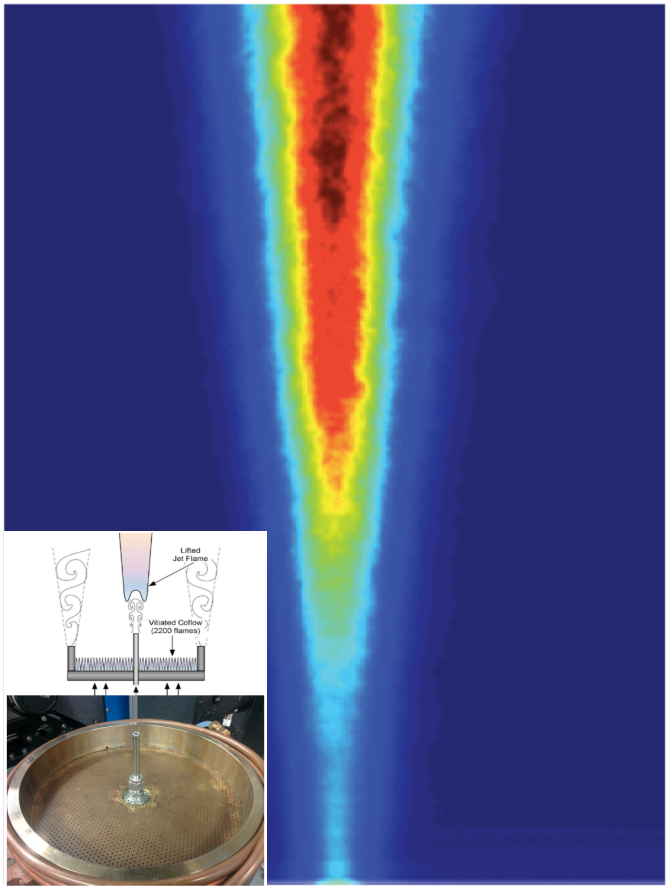


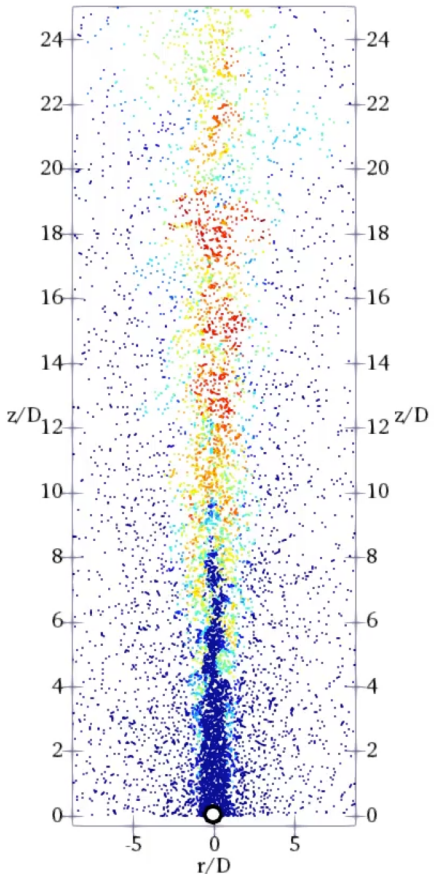
but very dilute and no agglomeration

Motivator: Particle Synthesis

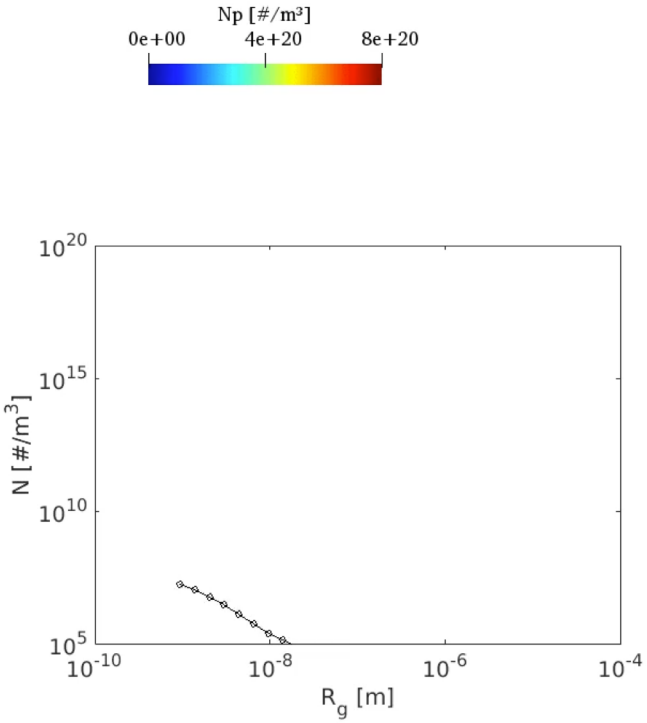
Existing PDF-MMC simulations of silica formation

ELASTIC LIGHT SCATTERING SIGNAL





PREDICTED PSD



G. Neuber et al., Proc. Combust. Inst, in press (2019)

Motivation & Outline

Agglomeration models

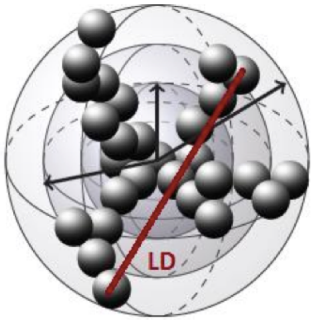
- Motivation
  - Turbulence-chemistry interactions ☑
  - Turbulence-particle interactions ☑
  - Particle-particle interactions ☒
    - Existing models do not usually account for
      - Varying morphology of agglomerate during agglomeration process
      - Effects of flow field other than shear
      - Collision frequencies for fractals in turbulence
- Outline of talk
  - Some hypotheses about morphology
  - Parameterization of D_f
  - Supercomputing or coarse-graining approach?
  - Comparison between coarse-graining and detailed Langevin dynamics

Agglomeration

Collision kernel

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

- Collision frequency, β, dependent on aggregate‘s shape
- Use fractal dimension D_f to characterize shape



$$N = k_f \left(\frac{R_g}{\sigma / 2} \right)^{D_f}$$

⟶ Free molecule regime

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

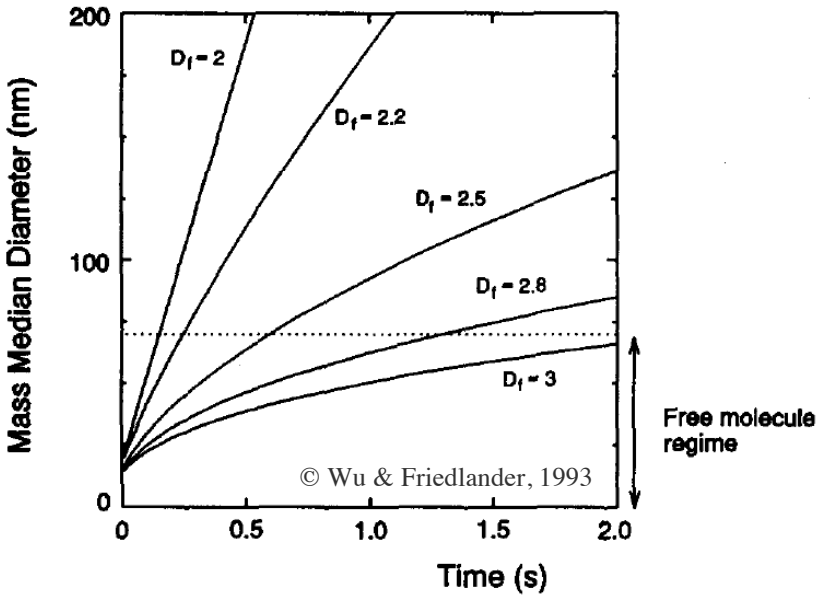
⟶ Continuum regime

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

Agglomeration

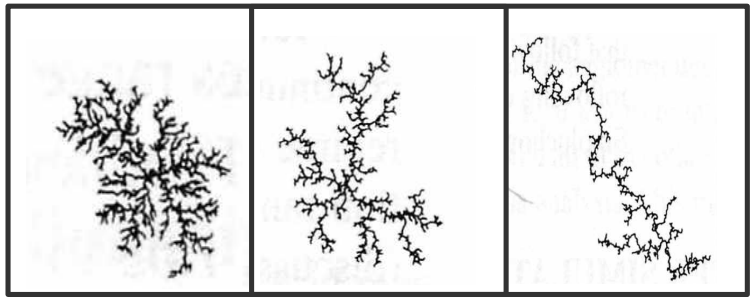
The fractal dimension D_f

IS D_F IMPORTANT?



WHAT IS D_F?

- Hypothesis 1: D_f affected by turbulence.



- Hypothesis 2: D_f is no function of time.

Agglomeration

How to determine D_f?

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

$$m_P \ddot{\mathbf{x}}_\mathbf{i} = F_D + F_{ext} + BdW$$
$$\dot{\mathbf{x}} = \mathbf{v}(t, x)$$

- Use ESPreSo 

  - Molecular dynamics package
  - Attractive-repulsive L-J force

$$U_{LJ}^{attractive}(r) = -\frac{A}{6}\left[\ln\left(\frac{r^2-\sigma^2}{r^2}\right) + \frac{\sigma^2}{2\left(r^2-\sigma^2\right)} + \frac{\sigma^2}{2r^2}\right]$$

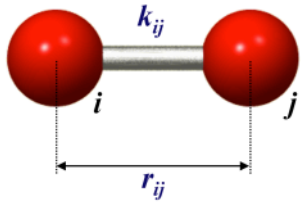
$$U_{LJ}^{repulsive}(r) = -\frac{A\sigma_{LJ}^6}{2520r}\left[\sigma^2\left(\frac{1}{2(r-\sigma)^7} + \frac{1}{2(r+\sigma)^7} + \frac{1}{r^7}\right) - \frac{\sigma}{3}\left(\frac{1}{(r-\sigma)^6} + \frac{1}{(r+\sigma)^6}\right) - \frac{1}{15}\left(\frac{2}{r^5} - \frac{1}{(r-\sigma)^5} + \frac{1}{(r+\sigma)^5}\right)\right]$$

$$U(r) = U_{LJ}^{attractive}(r) + U_{LJ}^{repulsive}(r)$$

Agglomeration

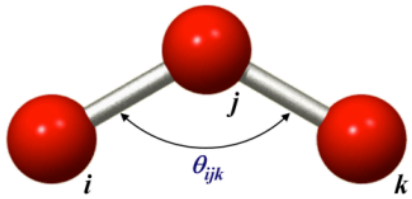
How to determine D_f?

- connect colliding particles to each other with a single bond



$$U_{\text{harmonic-bond}} = \frac{1}{2} k_h \left(r_{ij} - r_0\right)^2 ; k_h = 2\,E_{adh}^{JKR} \Big/ a^2 ; E_{adh}^{JKR} = \psi \pi a^2$$

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

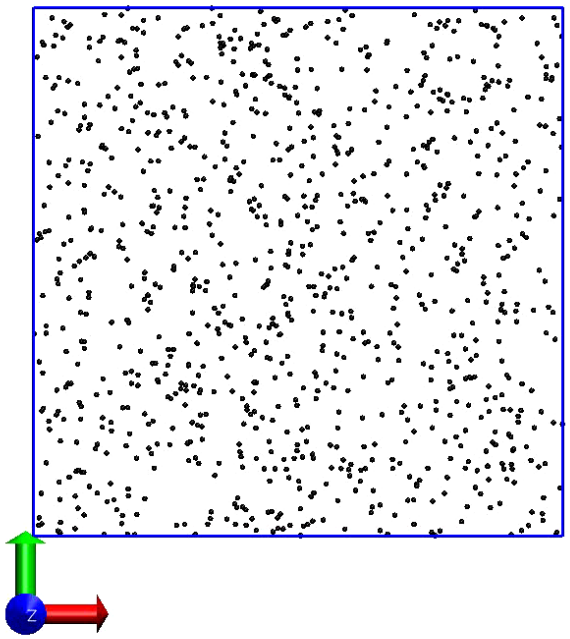


$$U_{\text{angular-bond}} = k_a \left(\theta - \theta_0\right)^2 ; k_a = \frac{k_0}{192} ; k_0 = \frac{3\pi a^4 E_Y}{4\left(\sigma/2\right)^3}$$

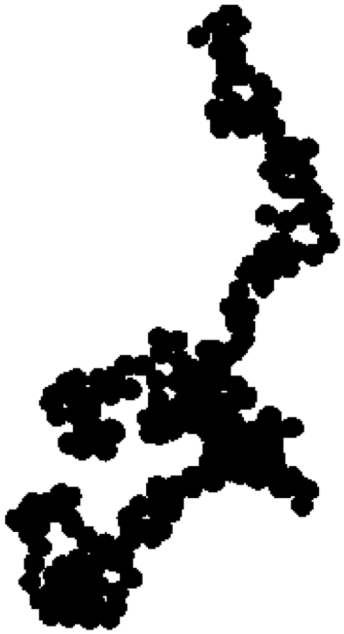
Agglomeration

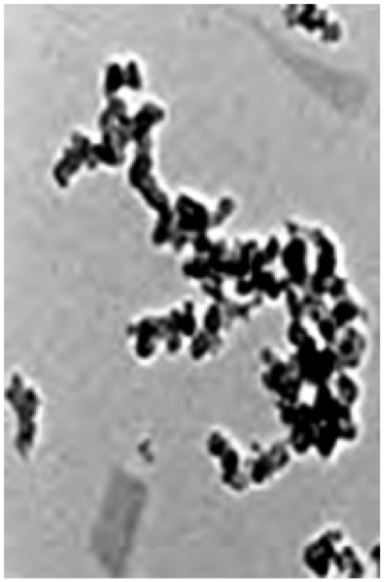
Brownian Motion

LANGEVIN DYNAMICS



COMPARISON SIMULATION - EXP



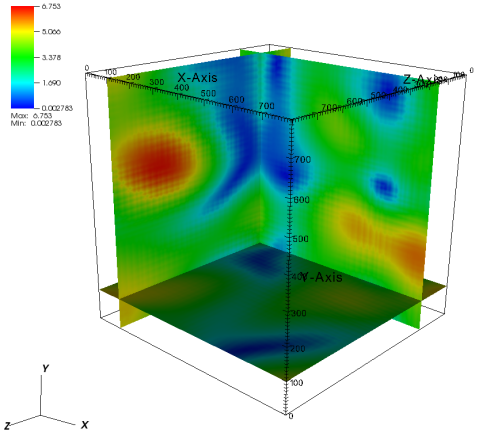


© Tumolva et al., 2010

Langevin Dynamics

Computations setup

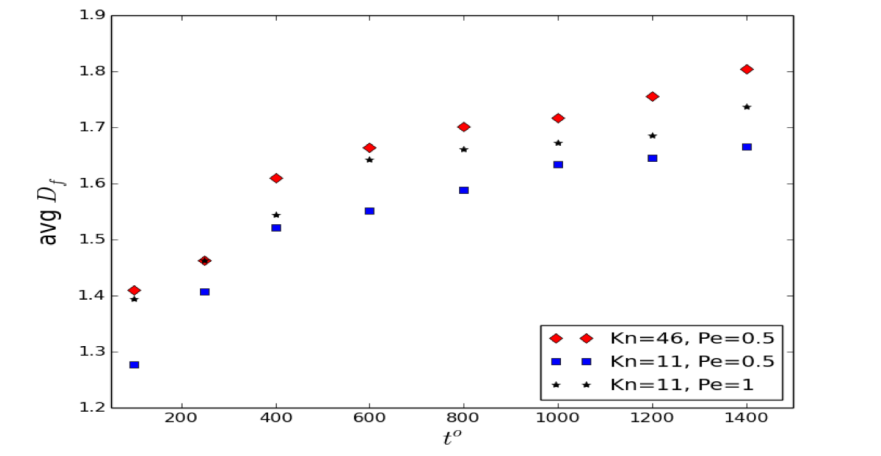
- Different primary particle sizes: σ=5nm, 20nm, 100nm
- Domain size: 800σ
- Number of particles: N_p=3.2·10^6
- Volume fraction: f_v=0.00625
- Superposed flow field
- Number of simulations per case: N_s=5
- Run times: 20,000 – 43,000 CPUh per run to reach t^0=1500.



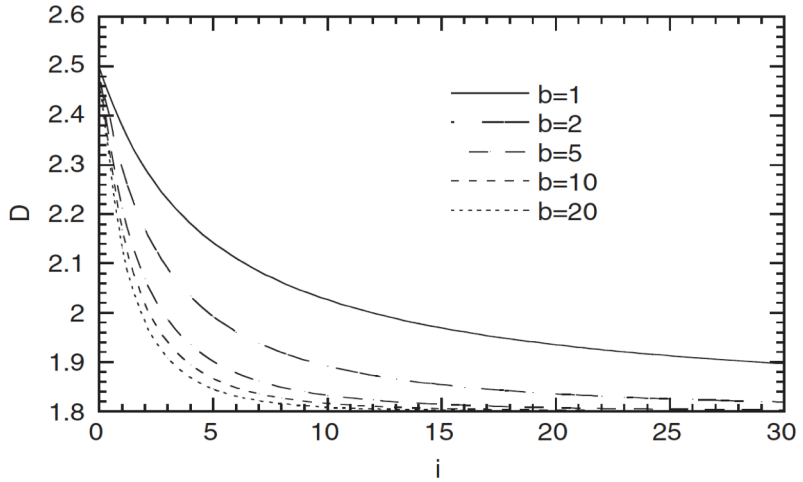
	C1	C2	C3	C4	C5	C6	C7	C8	C9
σ [nm]	5			20			100		
ϵ $[m^2/s^3]$	$4.5 * 10^9$	$1.1 * 10^{11}$	$4.5 * 10^{11}$	$1.1 * 10^8$	$2.7 * 10^9$	$1.1 * 10^{10}$	$6.9 * 10^3$	$1.7 * 10^5$	$6.9 * 10^5$
τ_{BM} [s]	$1.1 * 10^{-9}$	$1.1 * 10^{-9}$	$1.1 * 10^{-9}$	$6.8 * 10^{-8}$	$6.8 * 10^{-8}$	$6.8 * 10^{-8}$	$8.6 * 10^{-6}$	$8.6 * 10^{-6}$	$8.6 * 10^{-6}$
τ_{kol} [s]	$1.1 * 10^{-7}$	$2.1 * 10^{-8}$	$1.1 * 10^{-8}$	$6.8 * 10^{-7}$	$1.4 * 10^{-7}$	$6.8 * 10^{-8}$	$8.6 * 10^{-5}$	$1.7 * 10^{-5}$	$8.6 * 10^{-6}$
Kn [-]	46	46	46	11	11	11	2	2	2
Pe [-]	0.1	0.5	1	0.1	0.5	1	0.1	0.5	1

Results: Langevin Dynamics

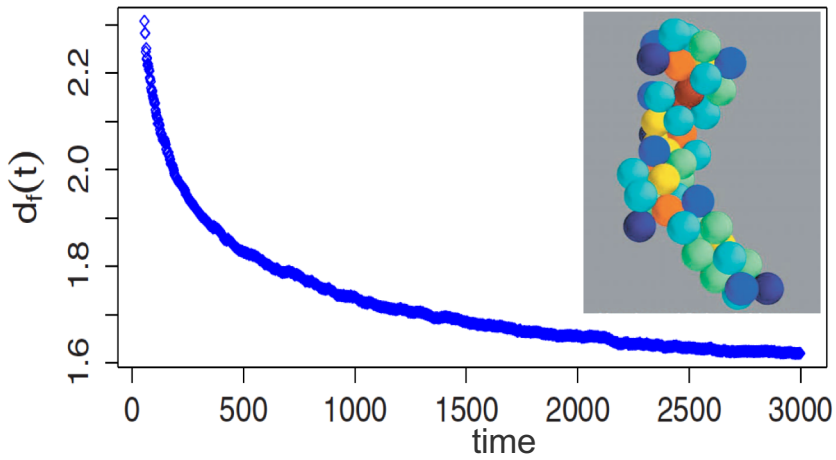
Temporal evolution of average D_f



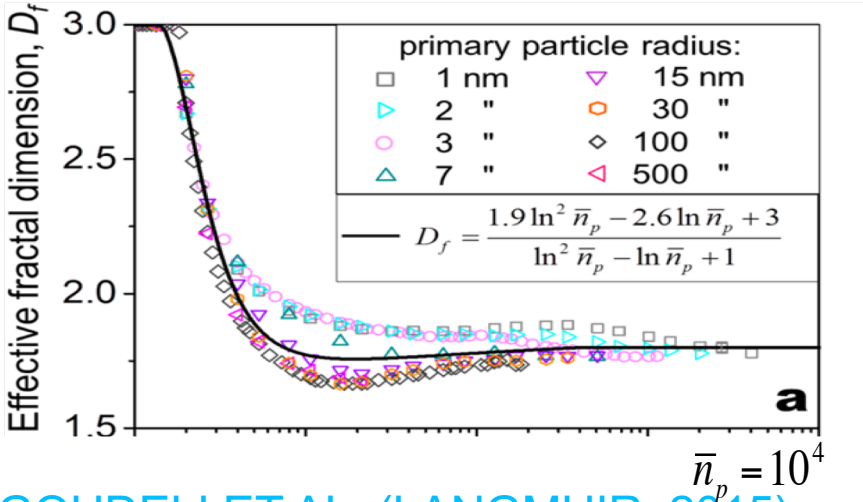
OUR WORK



KOSTOGLOU ET AL. (AS, 2006)



ISELLA & DROSSINOS (PRE, 2010)

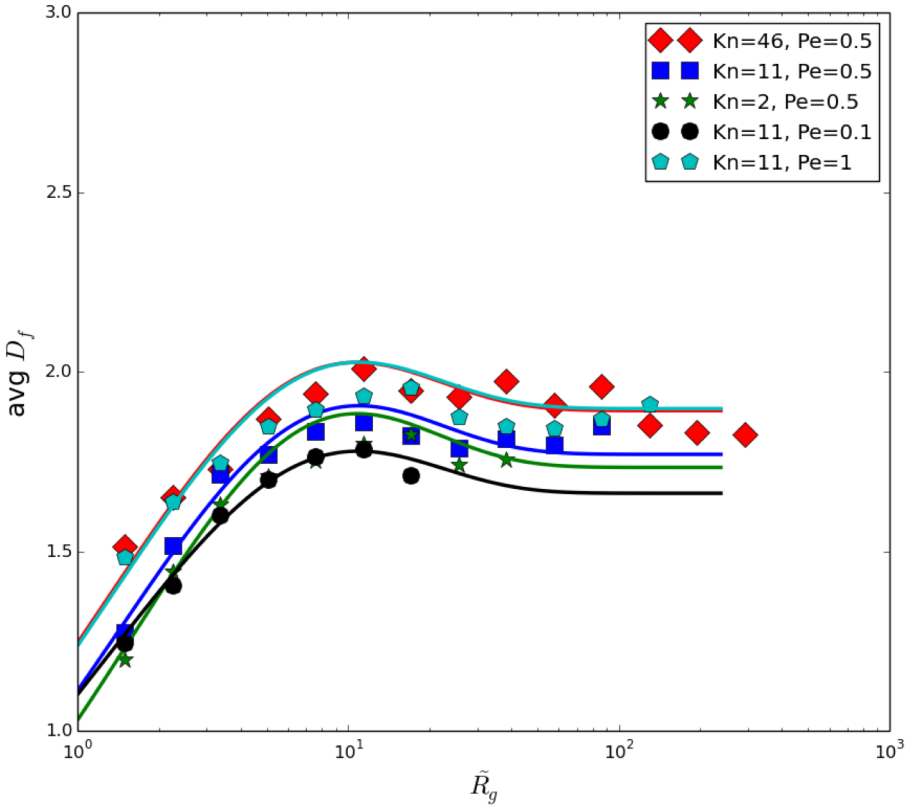


GOUDELI ET AL. (LANGMUIR, 2015)

Results: Langevin Dynamics

Attempt modelling

DEPENDENCE OF D_F=D_F(R_G)
(NO REAL TIME DEPENDENCE)



MODELLING

- Functional dependence

$$D_f(\tilde{R}_g) = f_1 + f_2 = c_1(1 - e^{-c_2\tilde{R}_g^{c_3}}) - c_4(1 - e^{-0.08\tilde{R}_g}).$$

- Modelling constants

constant	modelling assumption	value of coefficients
two-function model		
c_1	DLA limit (cluster - particle)	2.5
c_2	$f_1 + f_2 \stackrel{!}{=} D_f(1)$	-
c_3	$\frac{\partial D_f}{\partial \tilde{R}_g} \mid_{\tilde{R}_g=11} = 0$	-
c_4	DLA limit (cluster-cluster)	0.62
$D_f(1)$	$a - \frac{b}{1+(cPe)^d+(eKn)^f}$	a=1.25, b=0.25, c=1.5, d=7, e=0.08, f=3

- Does not yet help us with assessment of β

Langevin Dynamics

Issues

- Moderately expensive
- Scale separation – we cannot fully bridge the gap between turbulence scales and particle size
- Statistics poor, especially for large clusters
- Very limited info on collision frequencies

- Need scale preservation and need to get “bigger”

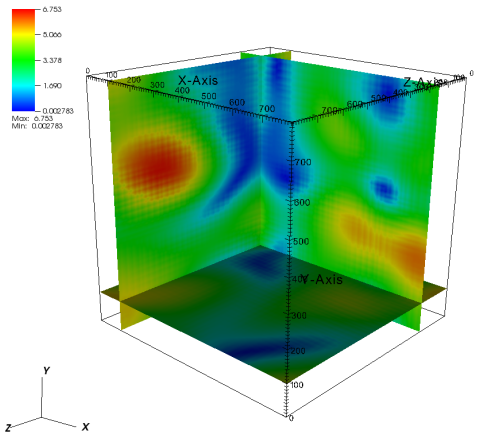
→ 1) use brute force or
2) use coarse graining approach

Langevin Dynamics

Scale Preserving Simulations

- What do I mean with scale preserving?
  - Typical particle size: σ = 20 nm
  - Typical Kolmogorov size: η_{Kol}= 2 μm
  - Turbulent length scale: l_t > 20 μm
  - Domain size: L > 40 μm

(and this is small, C6)



  - Solution above (as L/σ=800 < 2000):
  - rescale DNS turbulence field
    - Cannot keep ratio of η_{Kol}/σ
    - Scaling of gradients (preserve small scale shear)
    - Preserve dissipation

$$\frac{l_0}{t_0} = \text{const}$$

$$\varepsilon = \hat{\varepsilon}\frac{l_0^2}{t_0^3} = \hat{\varepsilon}\frac{u_0^3}{l_0}$$

Langevin Dynamics

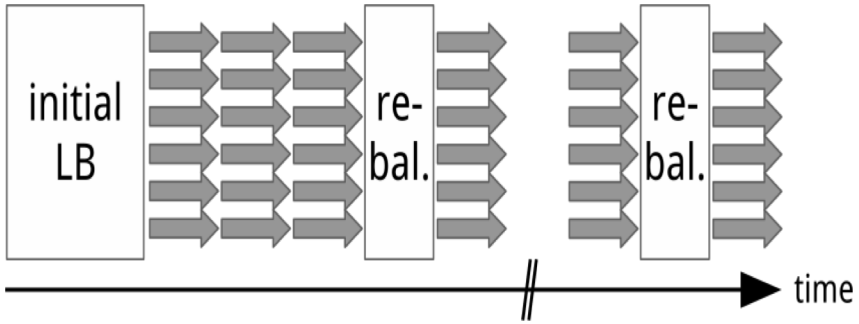
Large Scale Computations

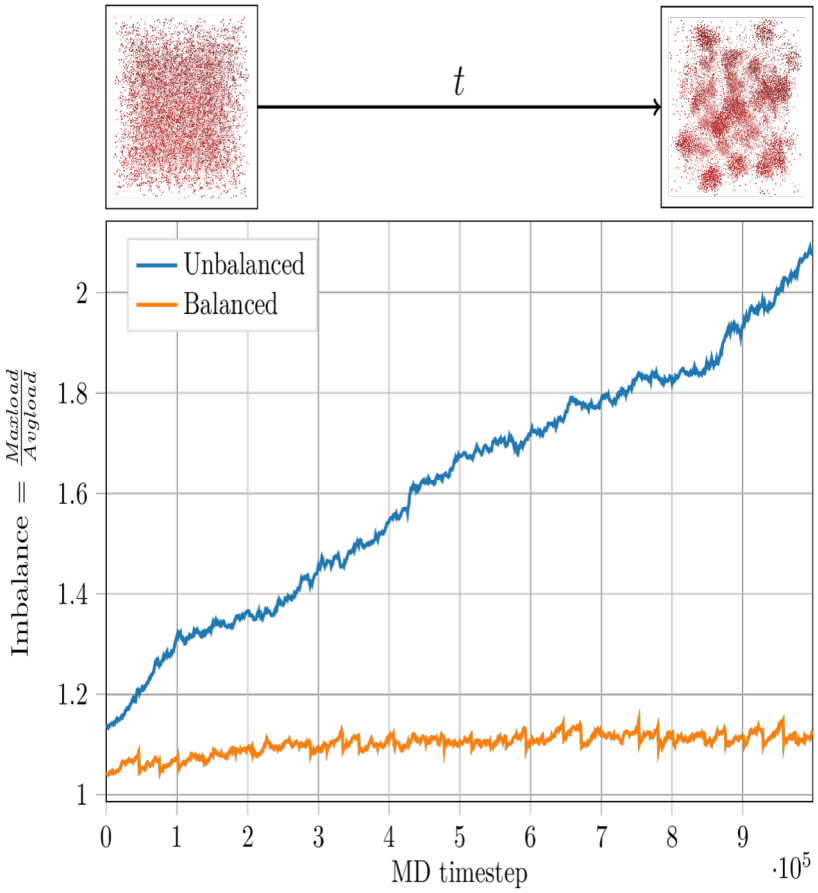
- 1st strategy – make the computations bigger
  - What is do-able?
    - L = 2600 σ
    - N_p = 110·10^6
    - t_{end} = 1200 t^0_{LD}
    - Computational time ~ 2 million core hours – if computations scale
  - But: computational efficiency is the issue

Large Scale Computations

Load Balancing

- MD simulations on multiple processes:
  - Slowest process determines overall runtime
  - Degrading parallel performance for inhomogeneous particle distributions
  - Indicator: imbalance amongst processes
- Remedy:
  - Change subdomains to balance load





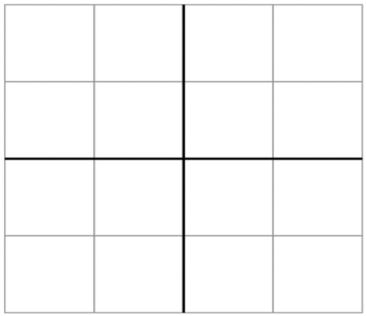
10,000 initially homogeneously distributed Lennard-Jones particles on 8 processors.
Graph shows imbalance amongst subdomains.

Large Scale Computations

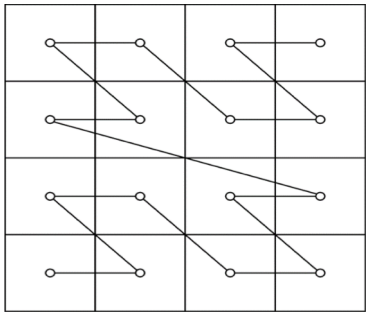
Load Balancing

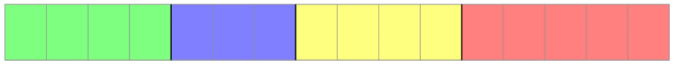
- Methodology of partitioning

  Default: equally sized boxes on grid

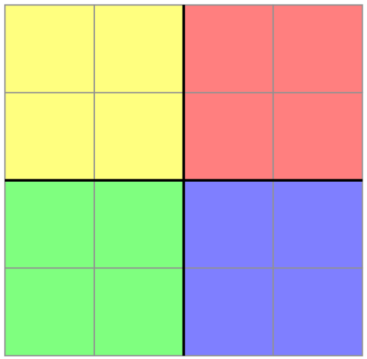


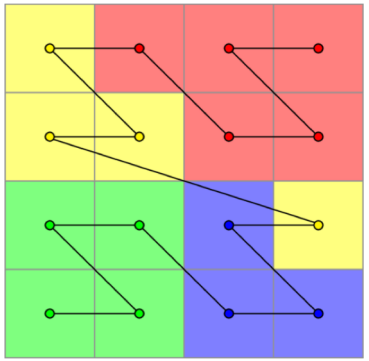
SFC-based partitioning: subdomains defined via linearization of the domain





„chain-on-chain partitioning“

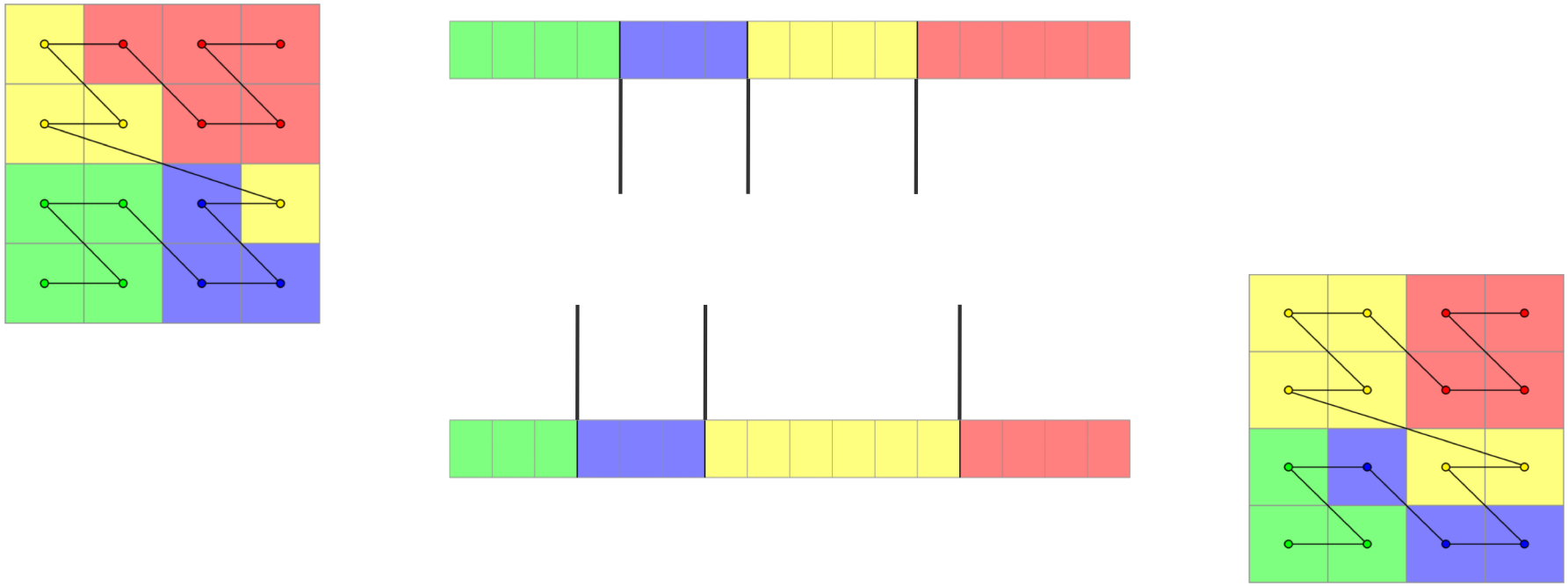




Large Scale Computations

Load Balancing

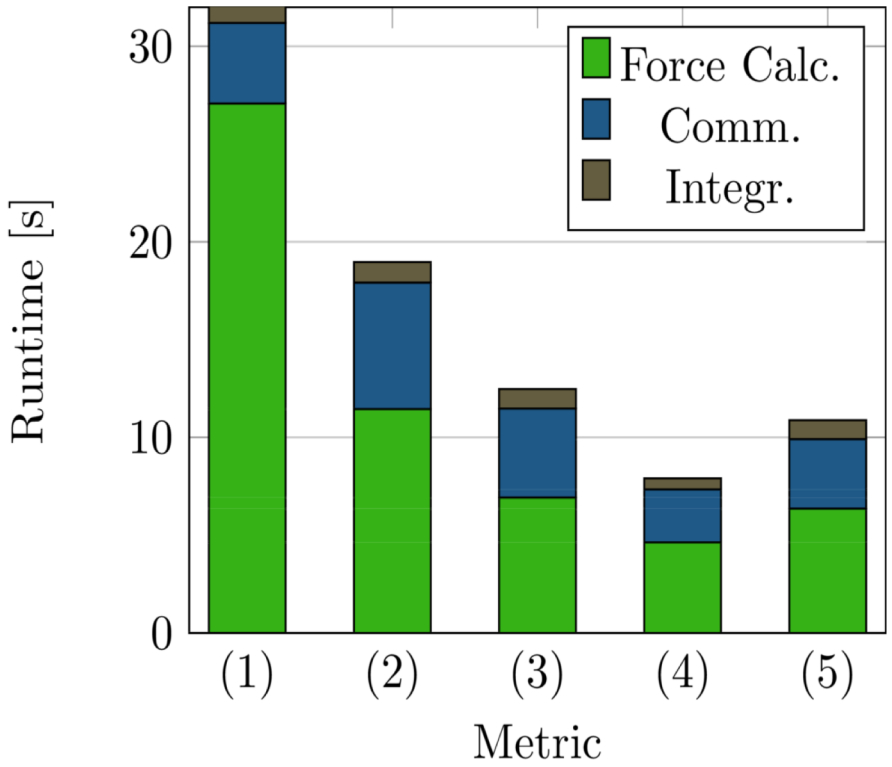
- Repartitioning:
  - Associate a weight w_i with each cell
  - Determine new partition boundaries in 1d -> load of each process is approximate average process load $1/P \sum_i w_i$ for P processes



Large Scale Computations

Load Balancing

- Results
  - Evaluation of end state of particle agglomeration with 3.2 million particles
  - Runtime of 1,000 MD time steps on 2,400 cores on HazelHen



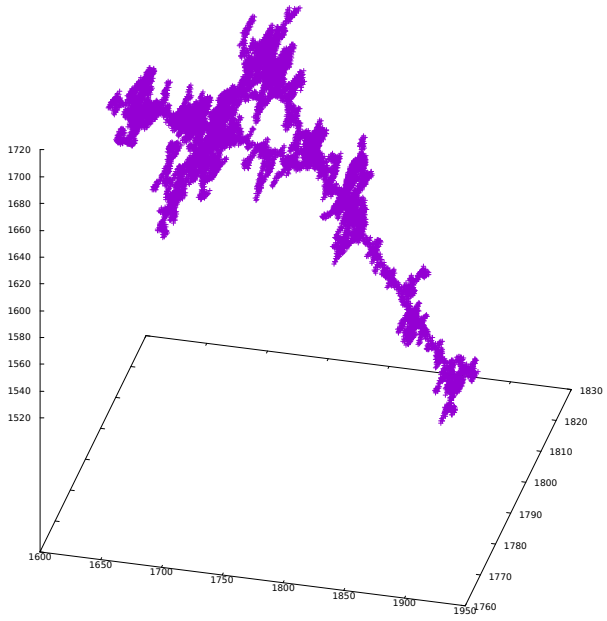
Weights from left to right:

(1) Without repartitioning,
(2) # LJ distance calculations,
(3) # LJ force pairs
(4) # particles,
(5) # bonded interactions.

Large Scale Computations

Issues

- Works on ~ 10,000 cores pretty well
- L=2600σ and 110M particles → larger scales give larger velocities/forces



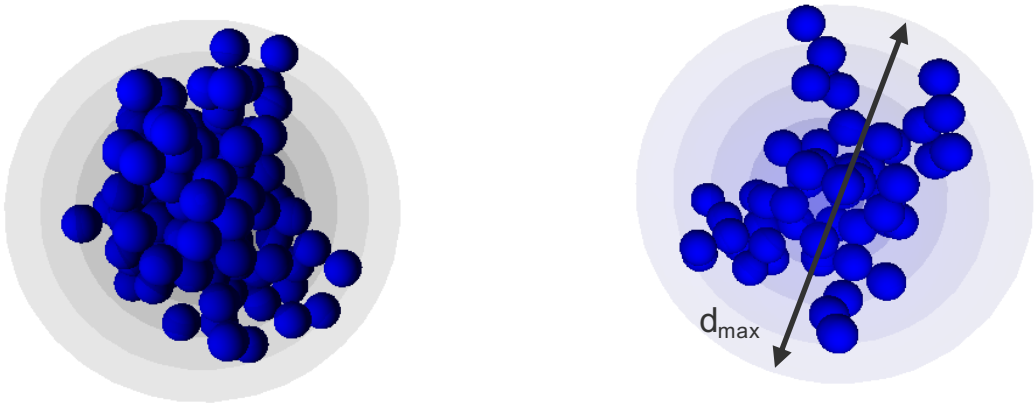
→ need to introduce breakage

hope to show results on next conference

Coarse-Graining (CG)

Benefits/Drawbacks

- 2nd strategy – coarse graining: Replace agglomerate by single coarse-grained particle



- Benefits
  - Increase number of particles, increase size of aggregates, increase domain size, increase width of turbulence spectrum
- Drawbacks
  - loss of detail, introduce additional characteristics for CG particle, quantification of characteristics requires large number of simulation

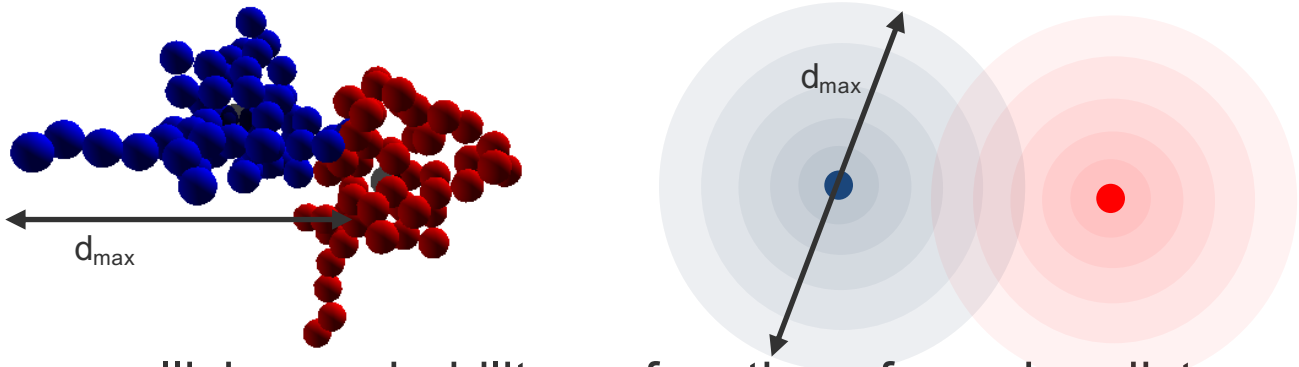
Coarse-Graining

Collision probability

- Characteristics of CG particle
  - Mass
  - Drag coefficient
  - Representative size
  - Morphology
  - Collision frequency

$$\rightarrow \quad m_{CG} = i \cdot m_p$$
$$\gamma_{CG} = 3\pi\mu_f i\sigma_p$$
$$\sigma_{CG} = d_{\max}$$
$$D_f = \text{const}$$
$$\mathrm{P}_{coll} \text{ is modelled}$$

- CG particle with d_{max} - not every overlap leads to a collision

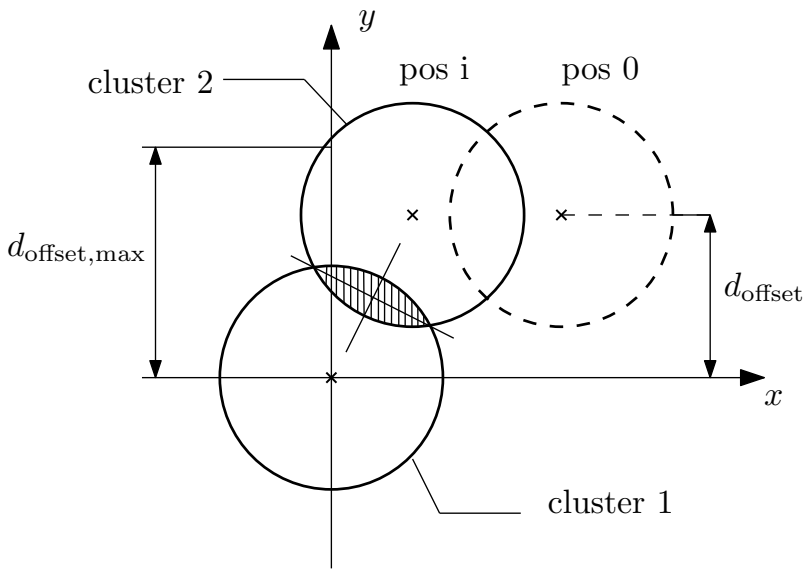


  - Introduce collision probability as function of passing distance

Coarse-Graining

Collision probability

- Collision probability as function of passing distance
  - place 1st agglomerate at (0,0) and rotate randomly
  - place 2nd agglomerate at (d_{max},d_{offset}) and rotate randomly
  - move 2nd cluster parallel to x-axis
  - record probability of collision

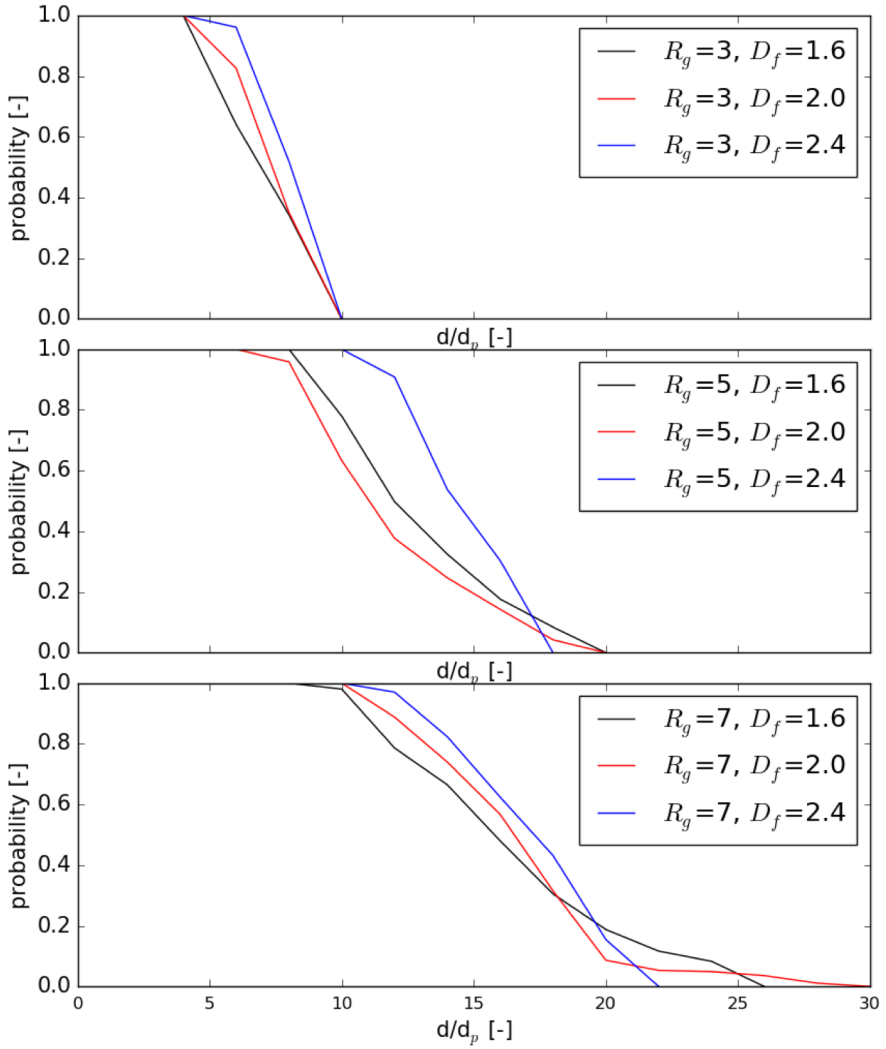


Coarse-Graining

Collision probability

- 9 cases

Represent. agglomerate	N	R_g	D_f
	39	~3	~1.6
	55	~3	~2.0
	100	~3	~2.4
	106	~5	~1.6
	128	~5	~2.0
	205	~5	~2.4
	145	~7	~1.6
	207	~7	~2.0
	309	~7	~2.4



Coarse-Graining

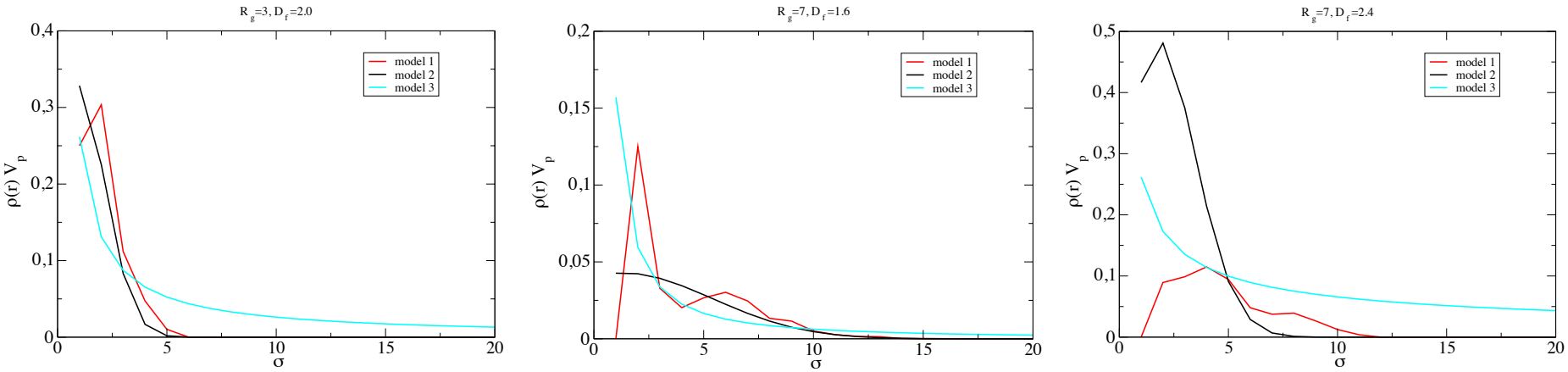
Modelling

- Represent agglomerate by radial density function ρ(r)
  - Model 1 – real radial density function
  - Model 2 – Lattuada et al. (2004)

$$\rho(r) = Ar^{\beta} \exp\left[-\left(\frac{r}{R_c}\right)^{z}\right] \text{ with } R_c = pR_p i^{1/D_f}$$

  - Model 3 – Rogak & Flagan (1990)

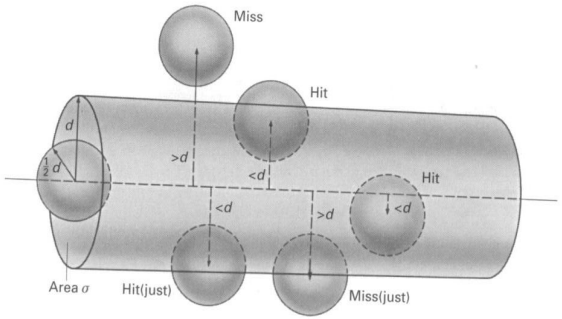
$$\rho(r) = Cr^{D_f - 3}$$



Coarse-Graining

Modelling

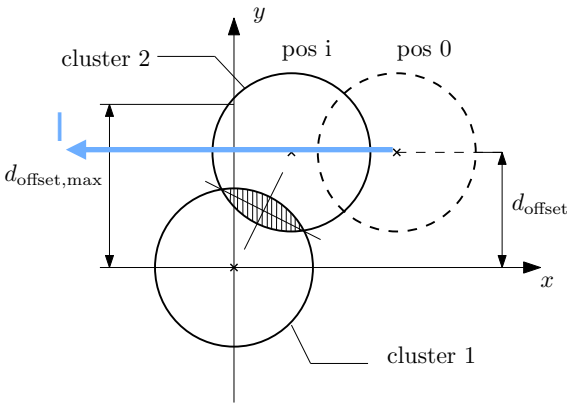
- Use ideas of kinetic gas theory to compute number of collisions



- Solve

$$P_{coll} = \int_{-\infty}^{\infty} \iiint_V \rho_1(r_1)\rho_2(r_2)\pi\sigma_p^2 dx dy dz dl$$

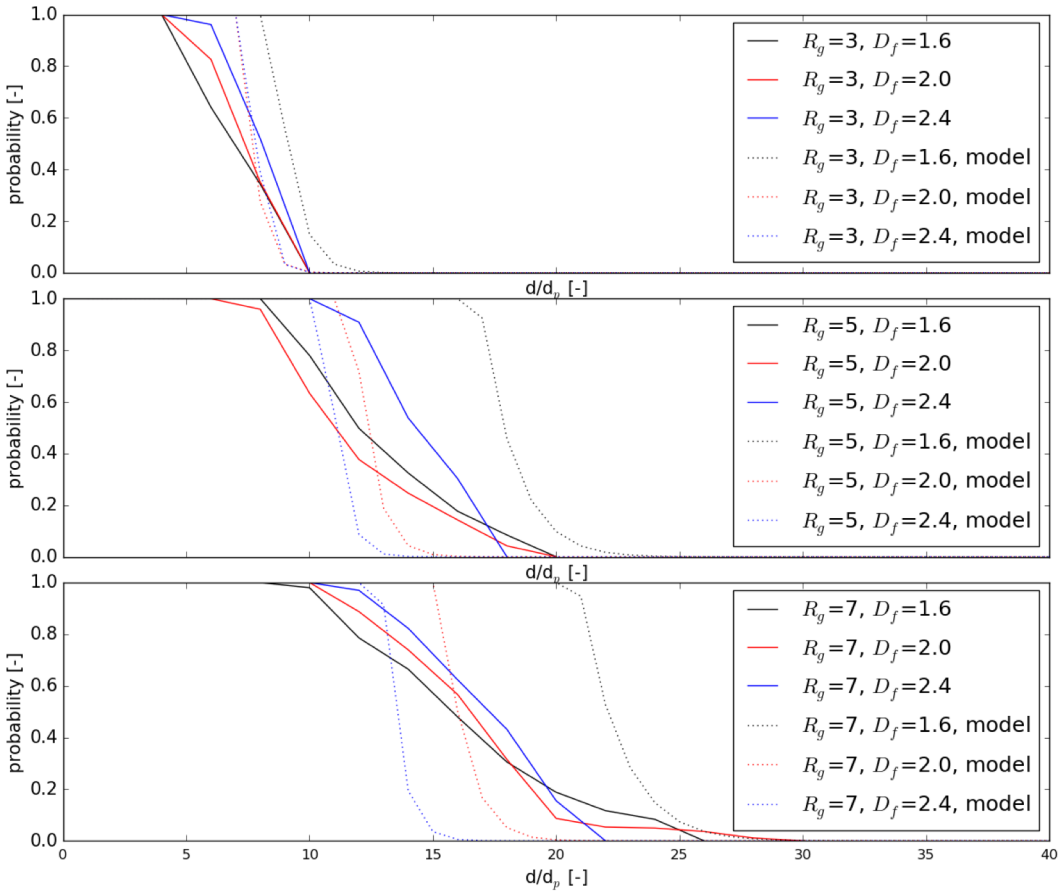
with $r_1^2 = x^2 + y^2 + z^2$ and $r_2^2 = (x-l)^2 + (y-d_{offset})^2 + z^2$



Coarse-Graining

Collision Probabilities

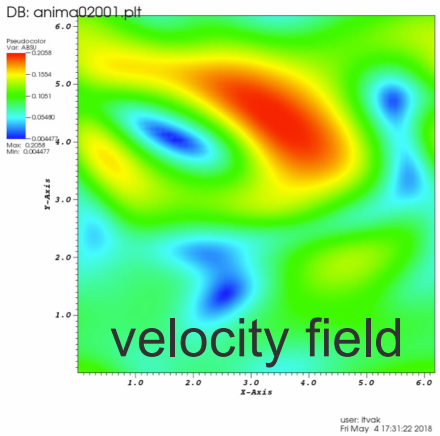
- Direct simulations vs. model 2



Coarse-Graining

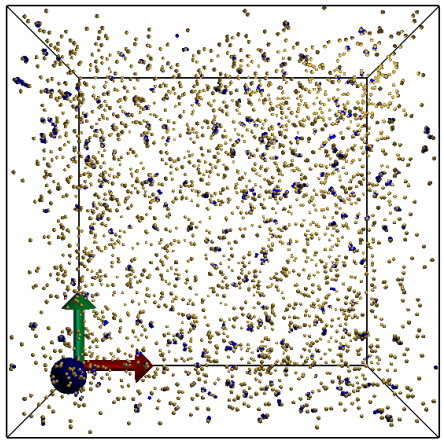
The setups

- Simulations for R_g=3, D_f=1.6, case C8 (σ=100nm)

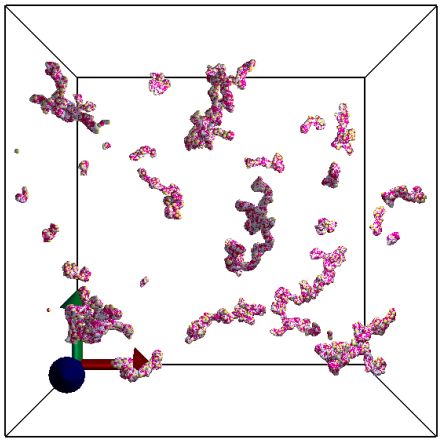


Detailed LD

early time

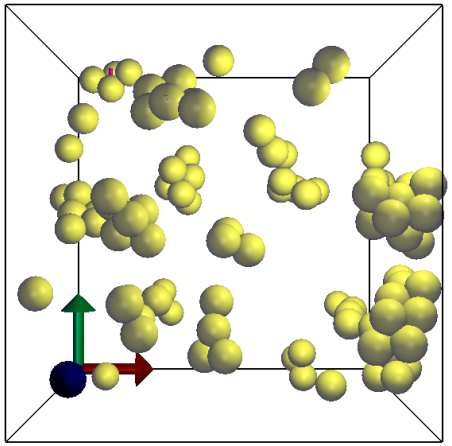


late time



coarse grained

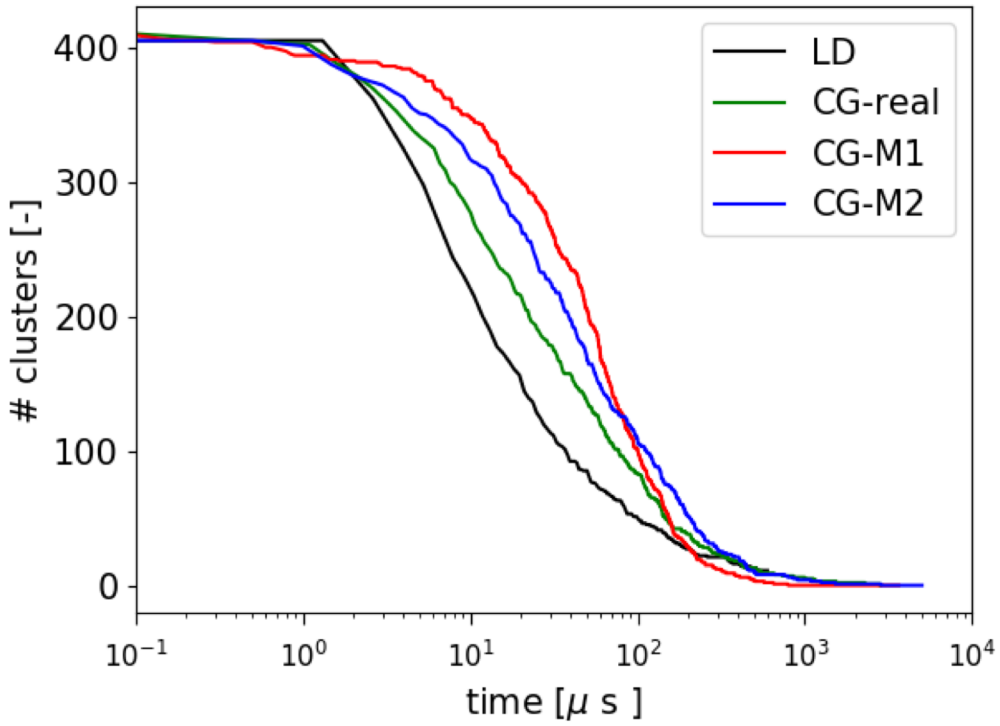
late time



Coarse-Graining

Results

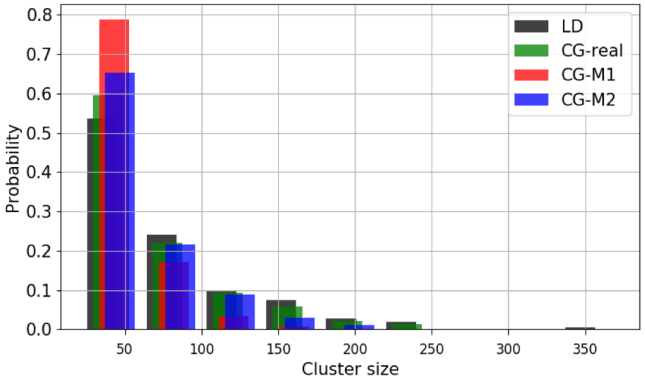
- Number of clusters for R_g=3, D_f=1.6



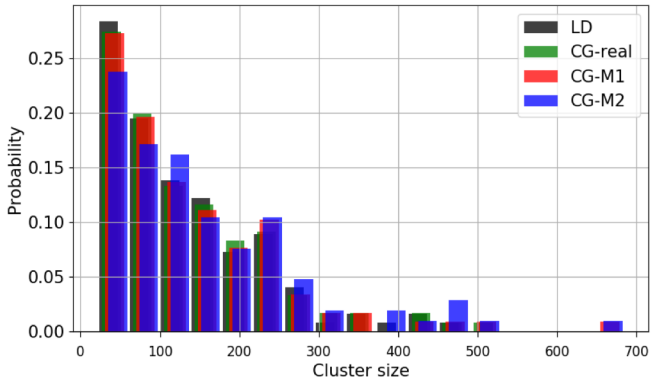
Coarse-Graining

Results

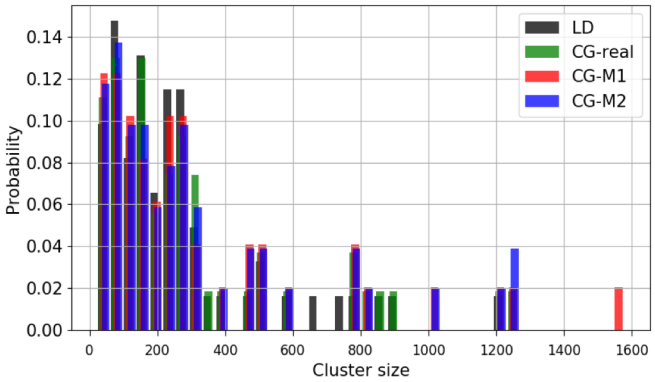
- PSD at different times (R_g=3, D_f=1.6)



t=1 μs



t=10 μs

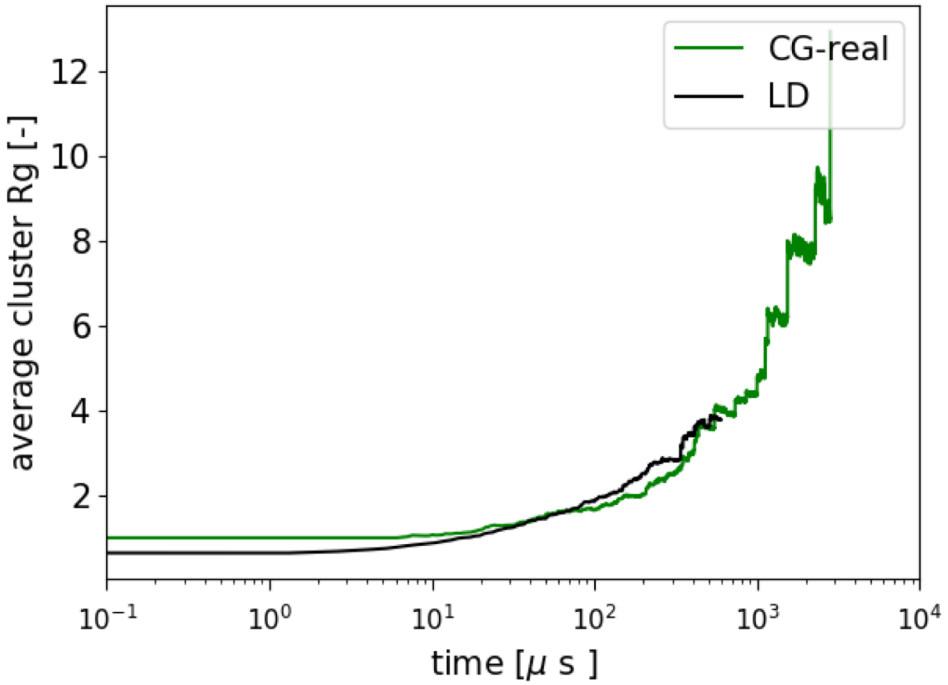


t=200 μs

Coarse-Graining

Results

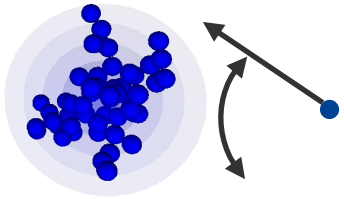
- Average cluster size (R_g=3, D_f=1.6)

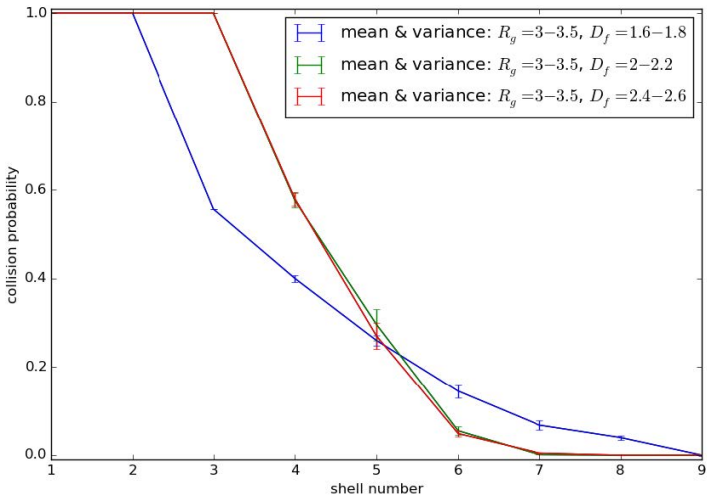


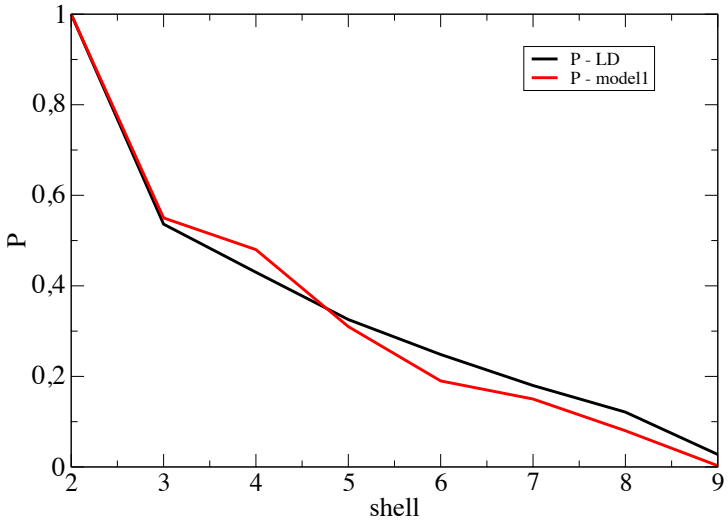
Coarse-Graining

Further steps

- Results semi-successful for modelled radial densities – why?
- Results good if correct collision probability used, but what about …
  - Large uncertainty when basing the analysis on individual clusters
  - Find appropriate characteristics for an average agglomerate of R_g and D_f
  - For collision statistics between single particle and cluster:







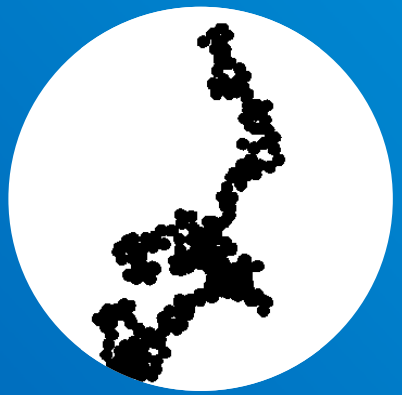
Summary

... and future work

- Achievements
  - Modified MD code to account for particle agglomeration
  - Parameterization of D_f as function of R_g (and turbulent advective field)
  - Lack of sufficient statistics leads to coarse-graining
  - Major issue: collision probability for CG particle
    - Functional dependency computed
    - Functional dependency modelled
  - Large scale computations set up and appropriate CG model proposed
- Issues to be solved in future work
  - Large scale computations for CG validation
  - Varying CG particles
  - Non-sphericity of CG particle
  - Compare new expression with standard expressions for collision kernels

University of Stuttgart
Germany

Thank you!



Literature

G. Inci, A. Arnold, A. Kronenburg, and R. Weeber, "Modelling nano-particle agglomeration using local interactions". Aerosol Sci. Technol., 48:8, 842-852 (2014), DOI: 10.1080/02786826.2014.932942.

G. Inci, A. Kronenburg, R. Weeber and D. Pflueger, “Langevin Dynamics simulation of transport and aggregation of soot nano-particles in turbulent flows”, Flow Turbul. Combust. (2017). DOI: 10.1007/s10494-016-9797-3

Acknowledgements:

G. Inci, R. Weeber, A. Arnold, C. Holm
Funded by DFG under grant number SFB-716/A8