The asymptotic Structure and Size Distribution of fractal-like Aerosols made by Agglomeration

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Agglomeration refers to the formation of physically attached primary particles by coagulation. It occurs in environmental and industrial processes, especially in low temperature regions where sintering or coalescence are rather slow. Understanding agglomeration is essential for optimal process design for manufacture of nanomaterials as their fractal structure affects their handling and processing and eventually their performance. The high particle concentrations encountered during nanomaterial manufacturing lead to formation of agglomerates with well-defined asymptotic structure and size distribution given by their fractal-like dimension and self-preserving size distribution, respectively.

The growth and detailed structure of fractal-like aerosol particles undergoing agglomeration is investigated here from the free molecular to the continuum regime by discrete element modeling. Particles in the free molecular regime follow ballistic trajectories described by an event driven method whereas in the near continuum (gas-slip) and continuum regimes Langevin Dynamics describe their diffusive motion. The simulations are validated by the attainment of the collision frequency and self-preserving size distribution (SPSD) of fully coalescing particles in free molecular and continuum regimes as well as the corresponding asymptotic fractal dimensions, D_f, of 1.91 and 1.78 by ballistic and diffusion-limited cluster-cluster agglomeration, respectively.

The evolution of agglomerate structure from perfect spheres ($D_f = 3$) to the above well-known asymptotic fractal-like structures is simulated in detail and a simplified expression is extracted that can be readily used in process design for synthesis of nanomaterials or in environmental models for ambient aerosols (e.g. air pollution and climate forcing). Fractal-like agglomerates exhibit considerably broader SPSD than spherical particles when made by coagulation-agglomeration: the number-based geometric standard deviation of the radius of gyration of agglomerates in the free molecular and continuum regimes is 2.27 and 1.95, respectively, compared to that of spherical particles of 1.45. The quasi-self-preserving geometric standard deviation of the radius of gyration of agglomerates exhibits a characteristic minimum of 1.65 in the transition regime at Knudsen numbers, $Kn \approx 0.2$. In contrast, their D_f linearly shifts from 1.91 in the free molecular to 1.78 in the continuum regime.

Keywords: agglomeration, fractal dimension, self-preserving size distribution, discrete element method.

Coagulation - Agglomeration of Fractal-like Particles: Structure & Self-Preserving Size Distribution

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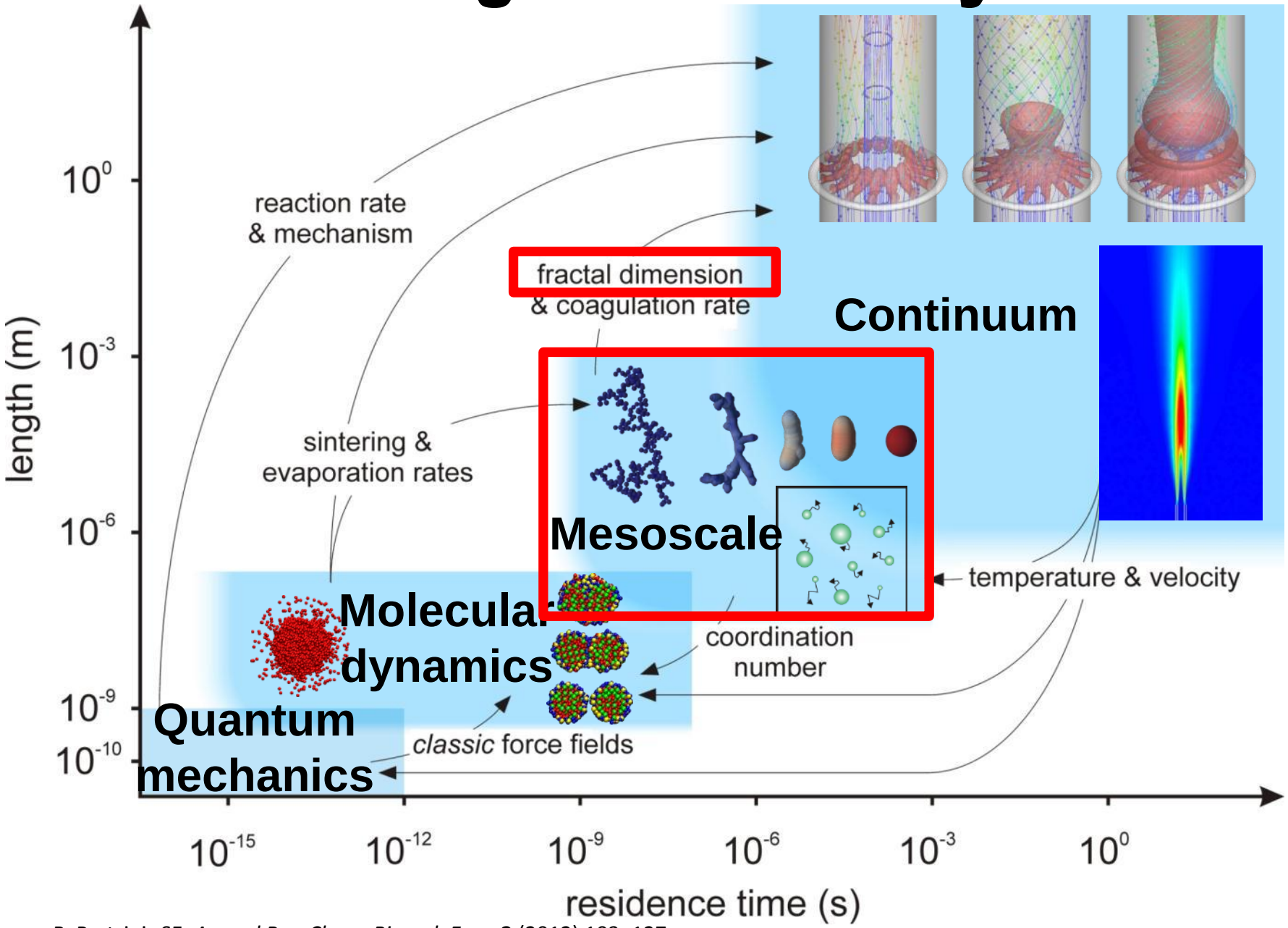
FNSNF
Fonds national suisse
Schweizerischer Nationalfonds
Fondo nazionale svizzero
Swiss National Science Foundation

erc
European Research Council
Established by the European Commission

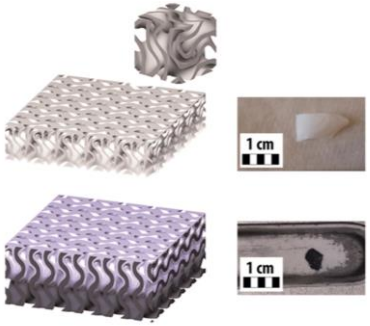
Multiscale Design of Aerosol Synthesis



Buesser B, Pratsinis SE, *Annual Rev. Chem. Biomol. Eng.*, **3** (2012) 103–127.

Introduction

Structure: affects product characteristics (e.g. rheological properties[1]) & performance, radiative forcing[2], visibility[3]

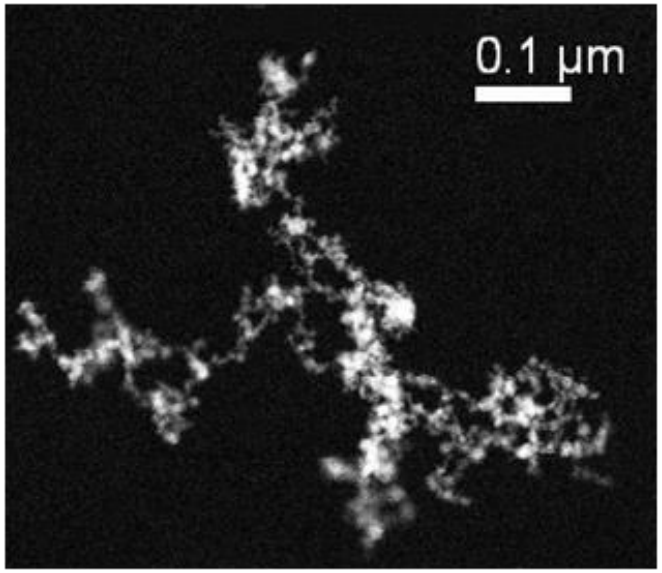


Hard agglomerates:
catalysis, lightguide preforms, electroceramic devices

Soft agglomerates:

Reinforcing rubbers

Suspensions (e.g. pigments)



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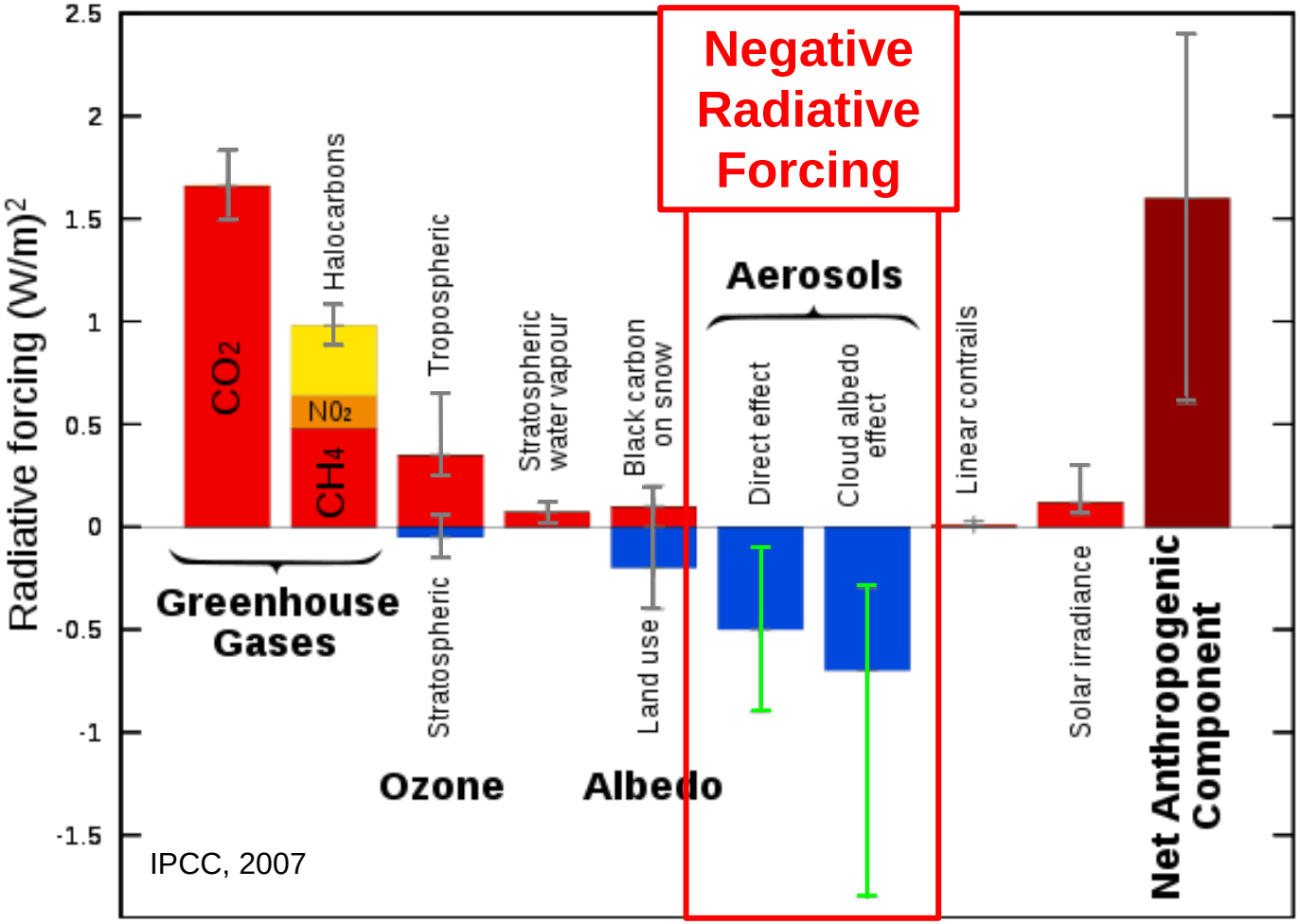
3. Berry MV, Percival IC. (1986). *Opt. Acta,* **33**, 577-591.

Introduction



Connect emissions to aerosol size measurements

Monitoring combustion emissions & atmospheric aerosols

Motivation

Optimal aerosol reactor & process design

Close control of **<u>particle size</u>** & **<u>structure</u>** →
catalytic activity and selectivity[1]

Open aggregates facilitate gas transport in and out of pellets

- Introduction of detailed structure (D_f) in collision rates, β

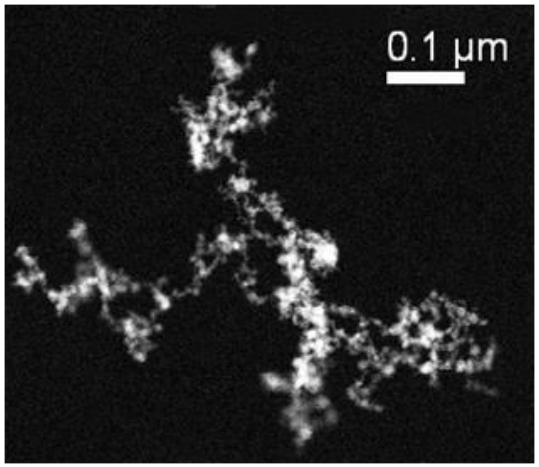
$$\beta = \beta\left(D_f, d_c\right)$$

Need a reliable D_f descriptor

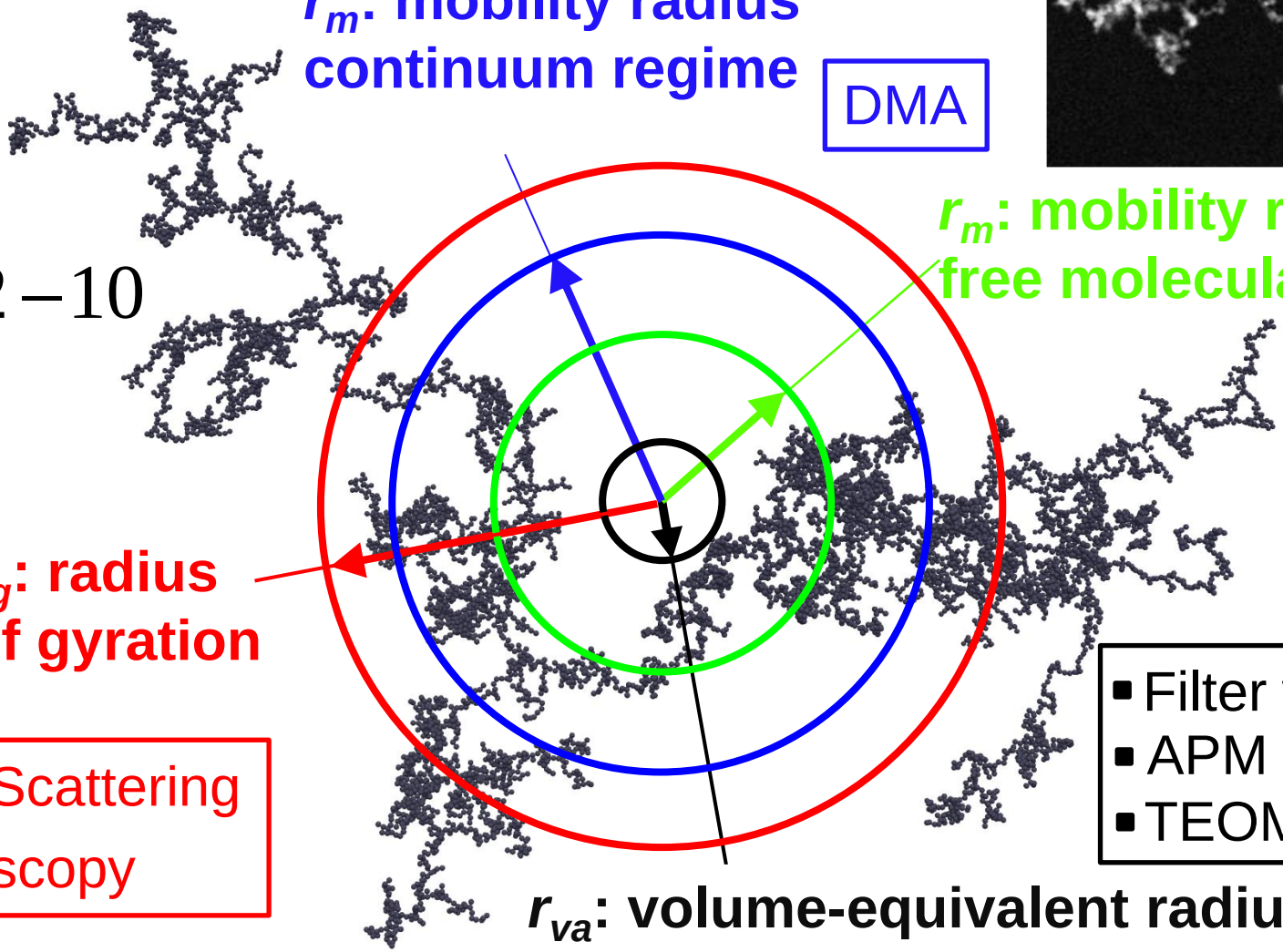
Controlled agglomeration can minimize costly separation techniques

1. Christopher P, Linic S. (2010) *Chem. Cat. Chem.*, **2**, 78-83.

Agglomerate Characterization



$$\frac{r_g}{r_{va}} = 2 - 10$$



***r_m*: mobility radius continuum regime**

DMA

***r_m*: mobility radius free molecular regime**

***r_g*: radius of gyration**

- Light Scattering
- Microscopy

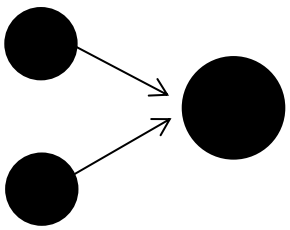
- Filter weighing
- APM
- TEOM

***r_{va}*: volume-equivalent radius**

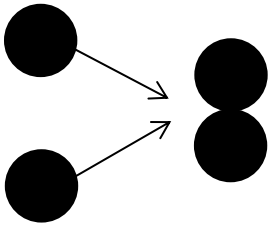
1. Eggersdorfer ML, Pratsinis SE. (2014) Adv. Powder Technol., **24**, 71-90.

Previous Work

- Brownian coagulation of *spheres*[1,2]



- *Non-spherical* particles



collisional growth and dynamics[3]

determination of evolving structure[4,5,6,7]

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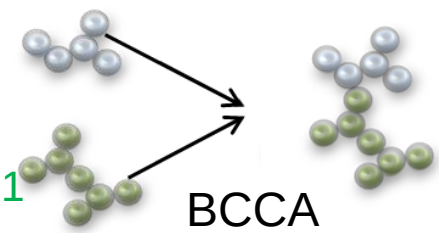
Simulation Method

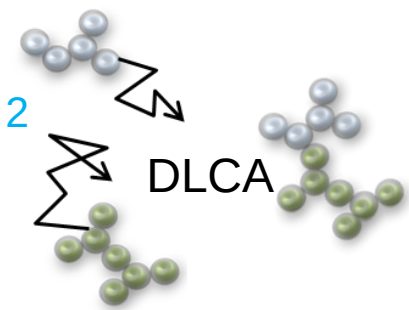
SiO_2 particles (like fumed silica), T = 27 ^oC

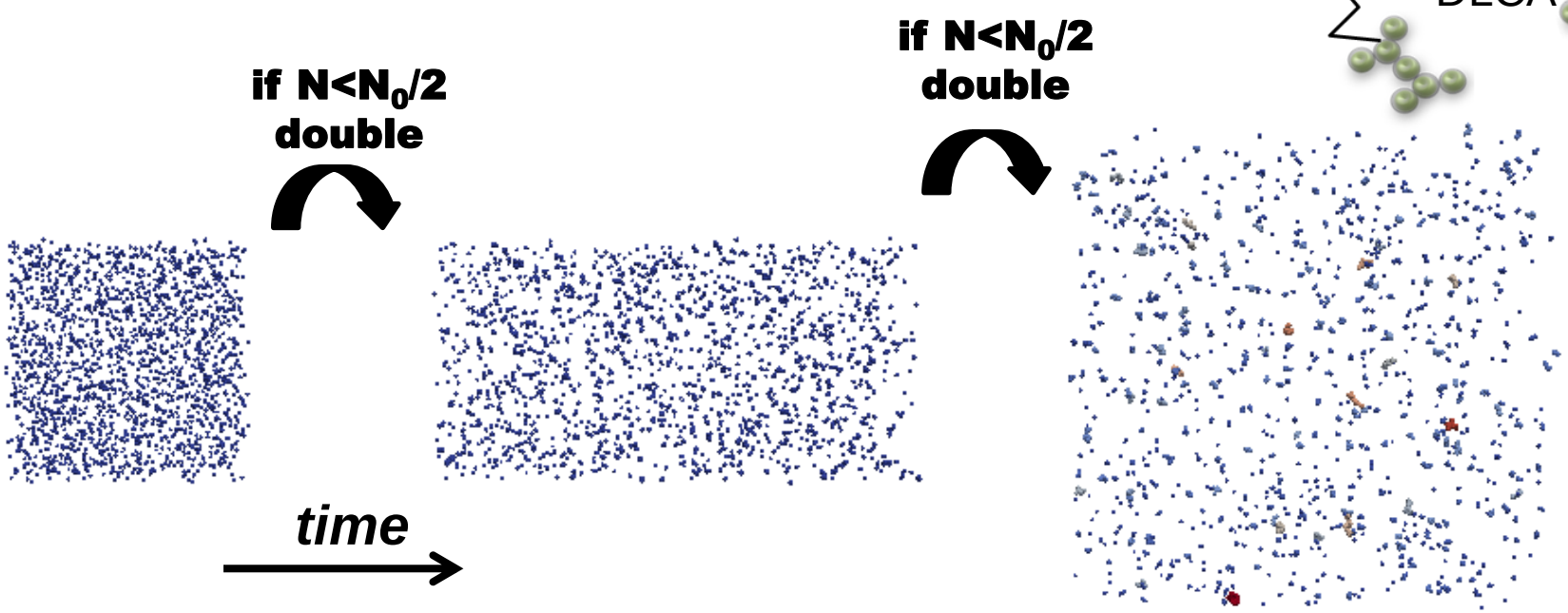
Free molecular regime →

Event-driven method [1]



Continuum regime → Langevin Dynamics [2]





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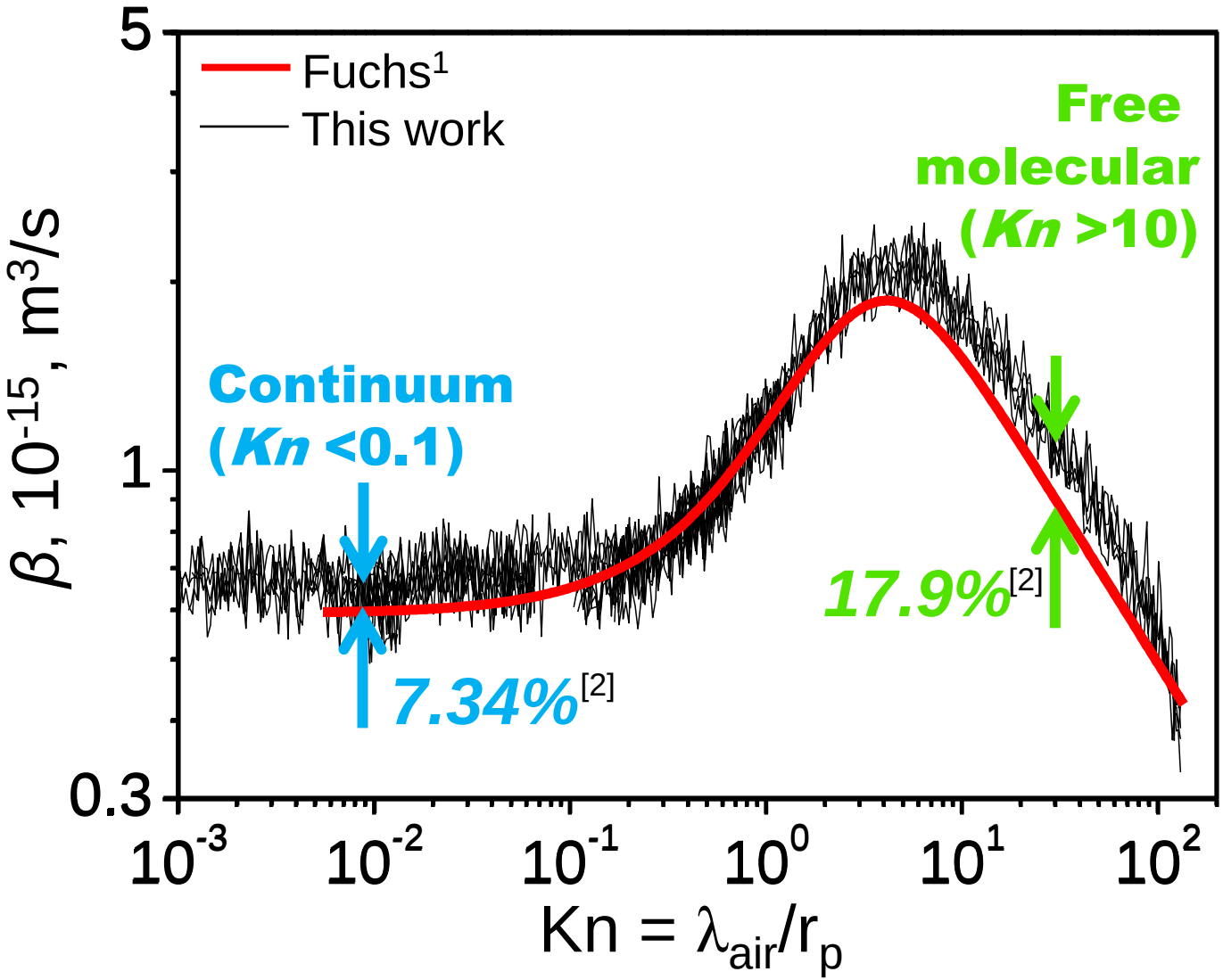
Validation – Full Coalescence

Collision Frequency Function, β



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

Enhancement due to *polydispersity from the rapid attainment of SPSD*

1. Fuchs NA. (1964). Mechanics of Aerosols. Macmillan, New York.
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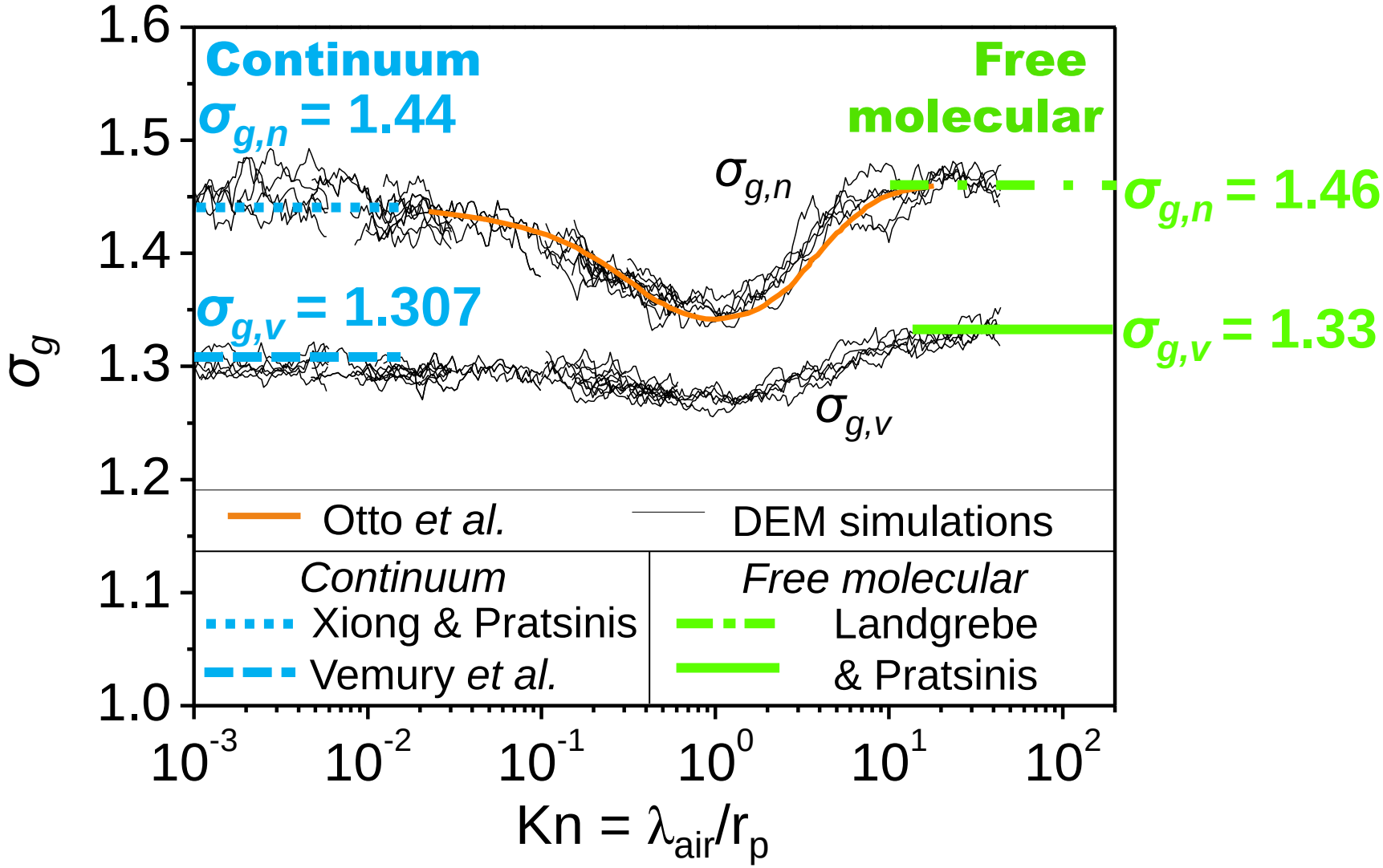
Validation – Full Coalescence

Geometric Standard Deviation



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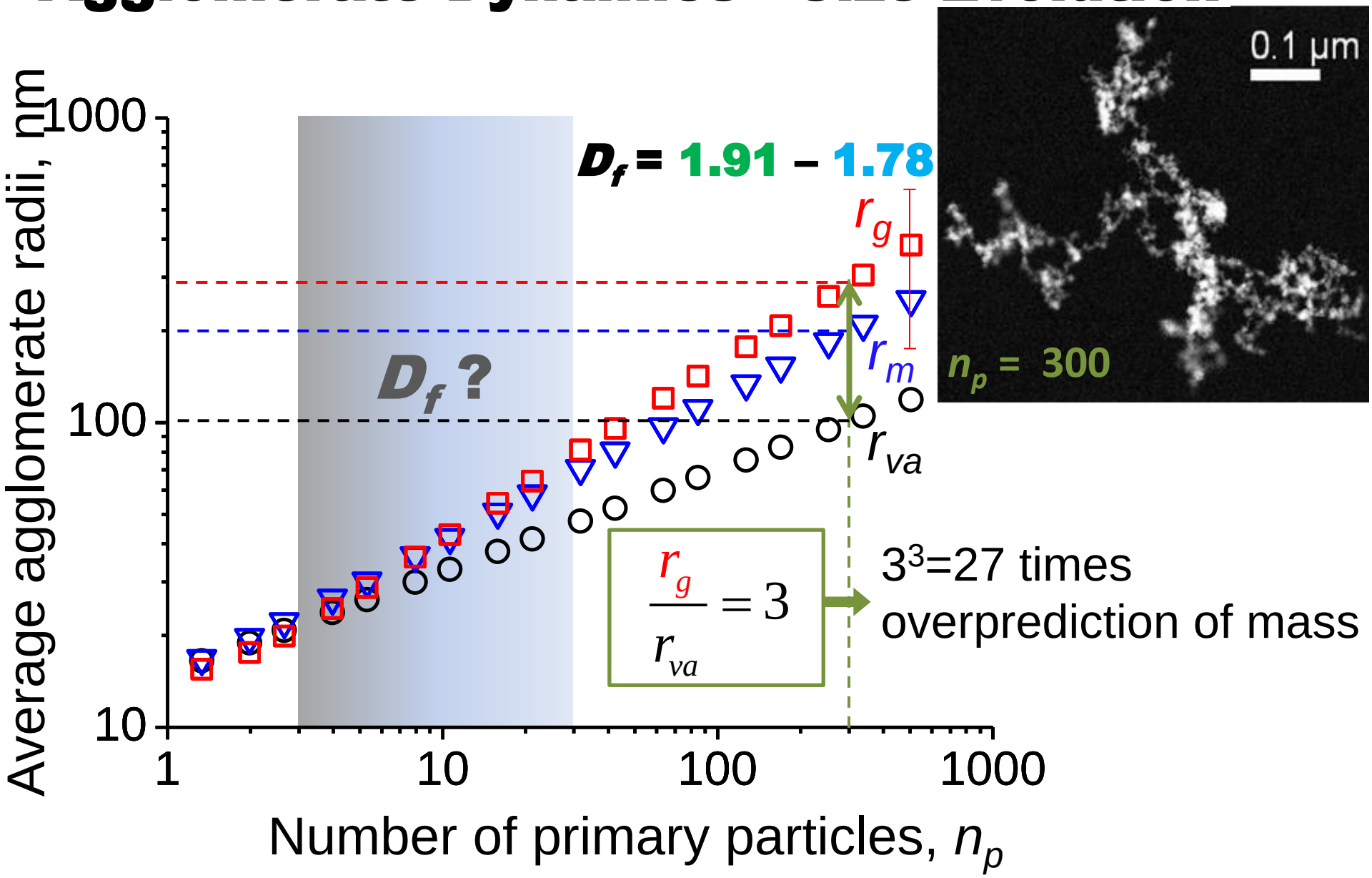
Agglomerate Dynamics - Size Evolution



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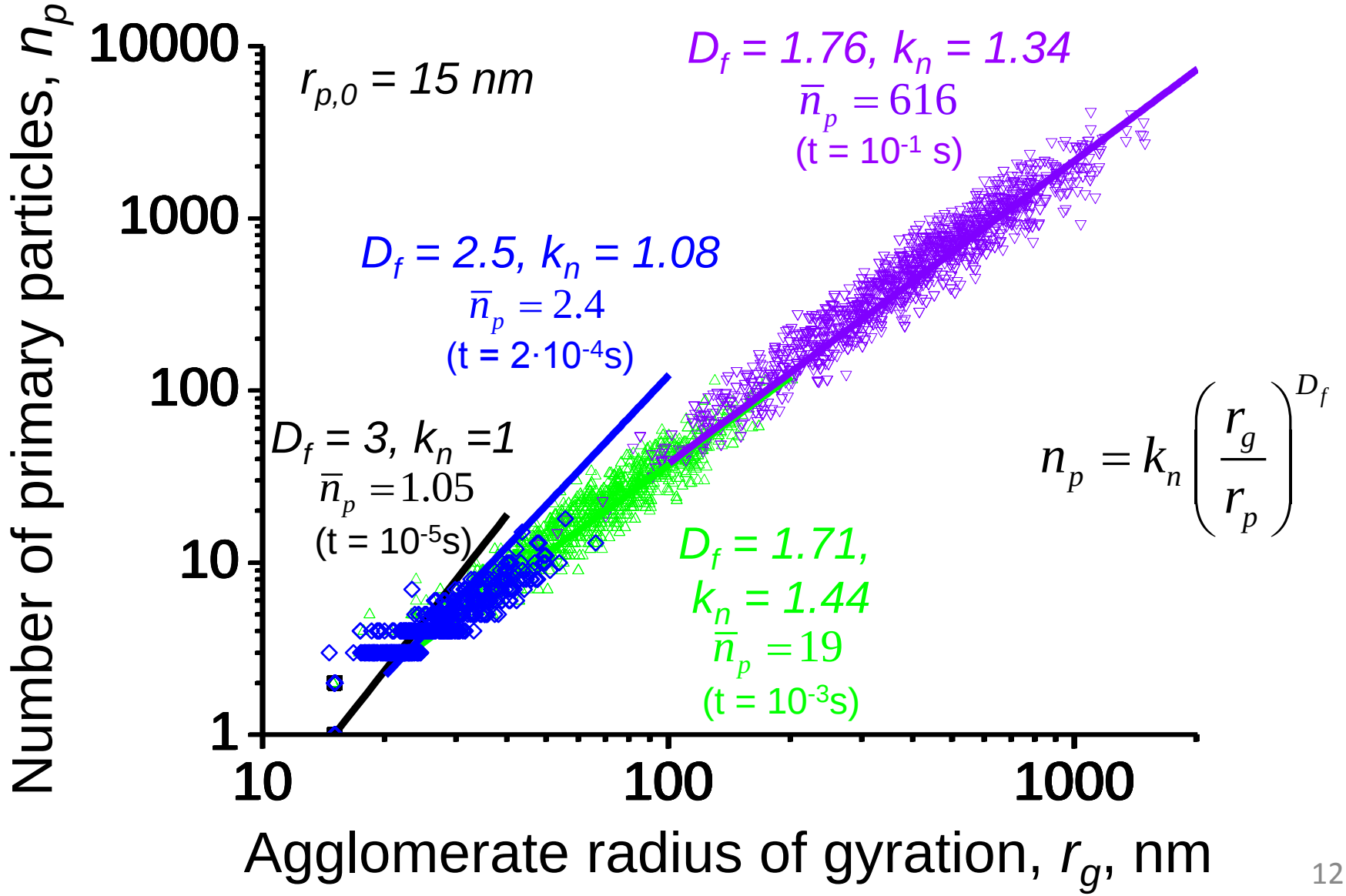
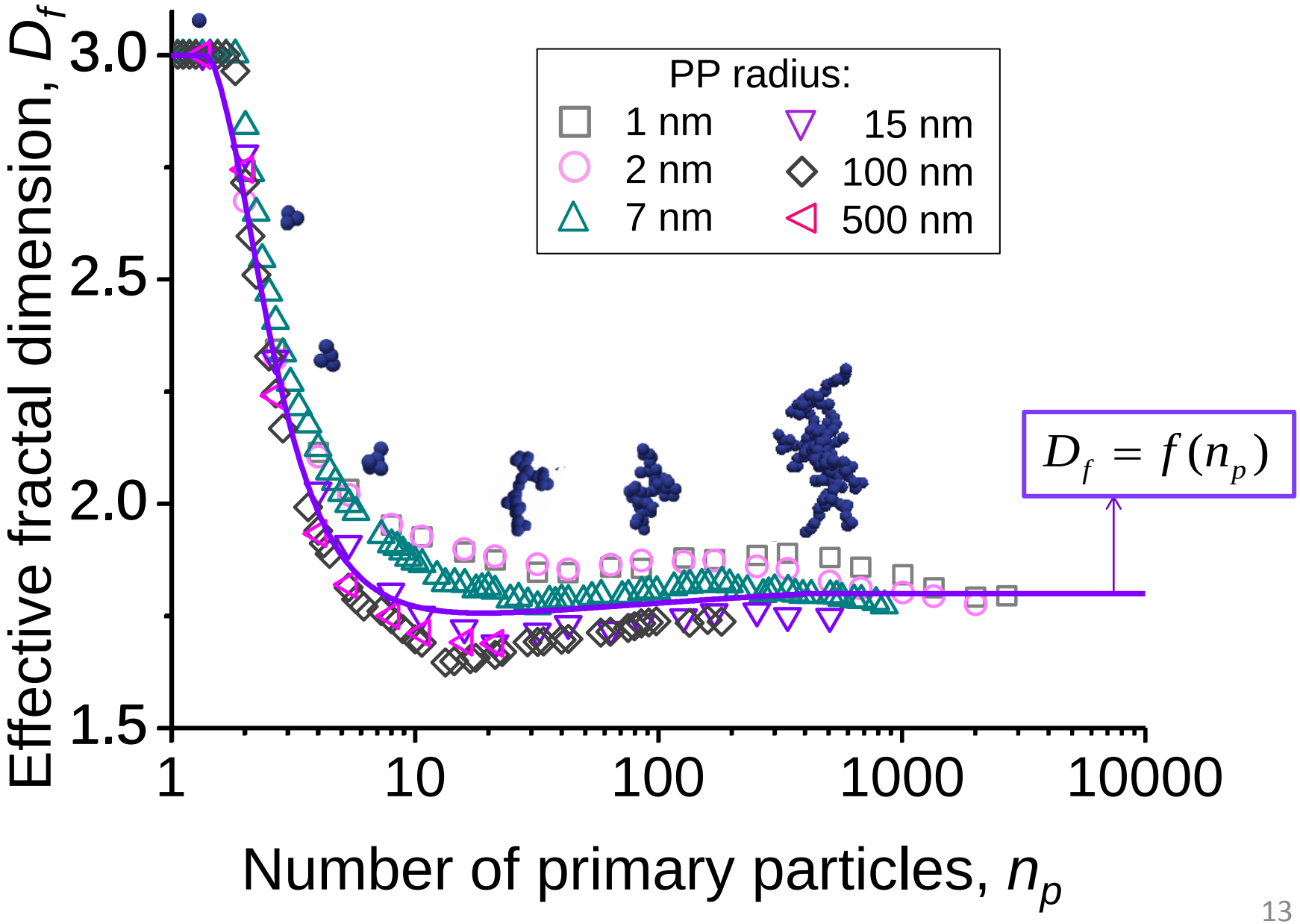
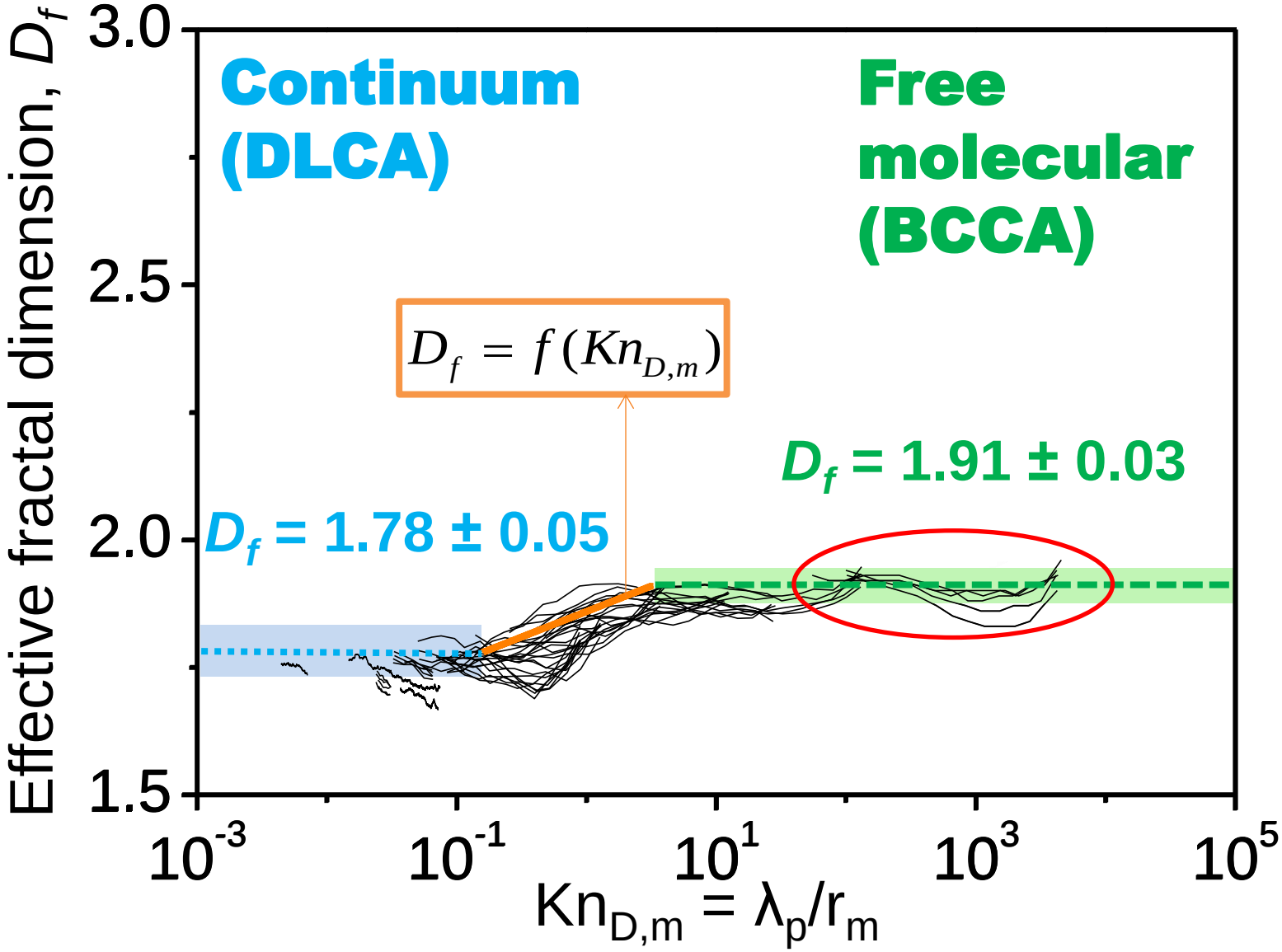
Evolution of Agglomerate Structure by Coagulation



Evolution of Average Agglomerate Structure



Agglomerate Structure Evolution



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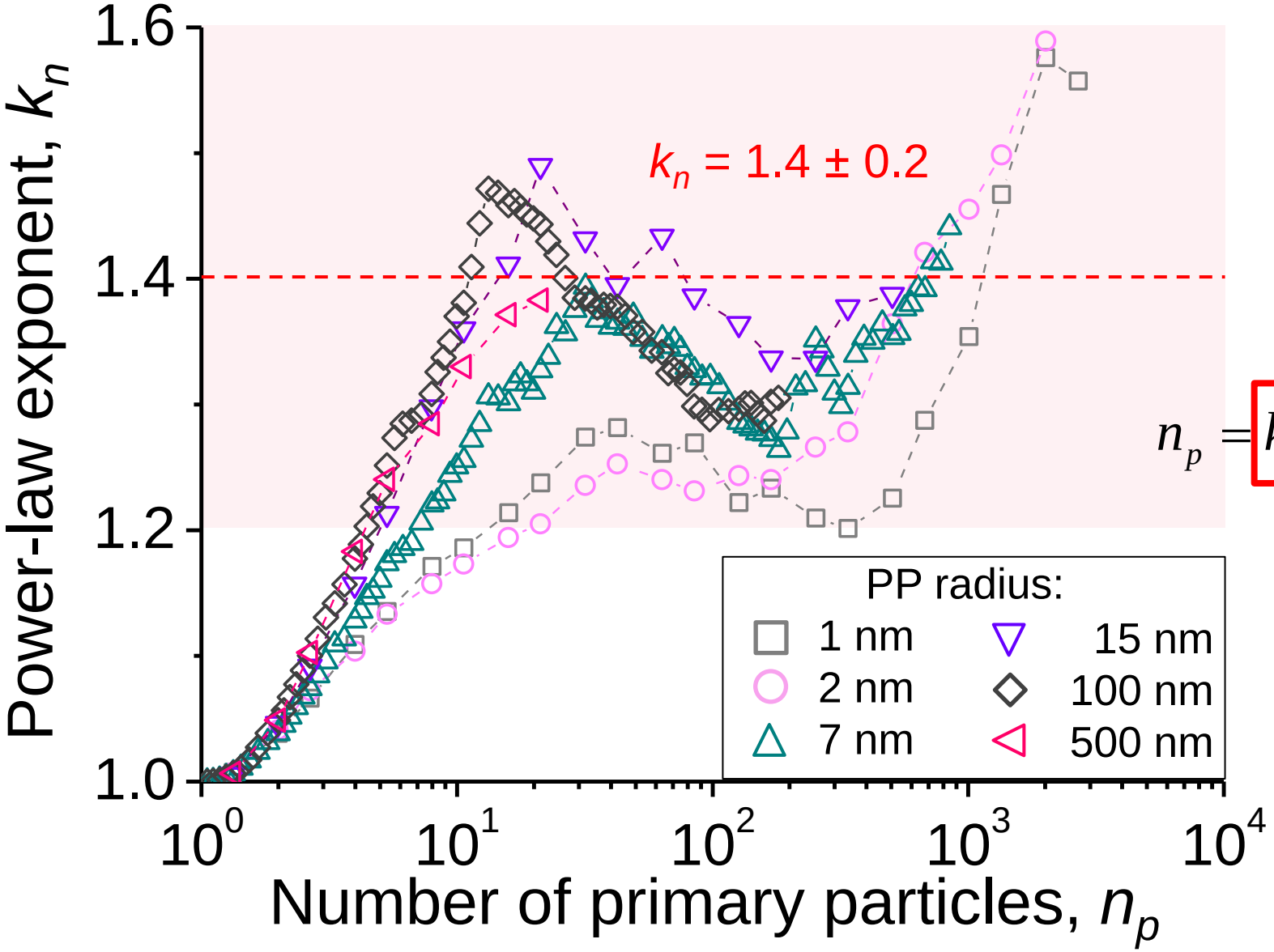
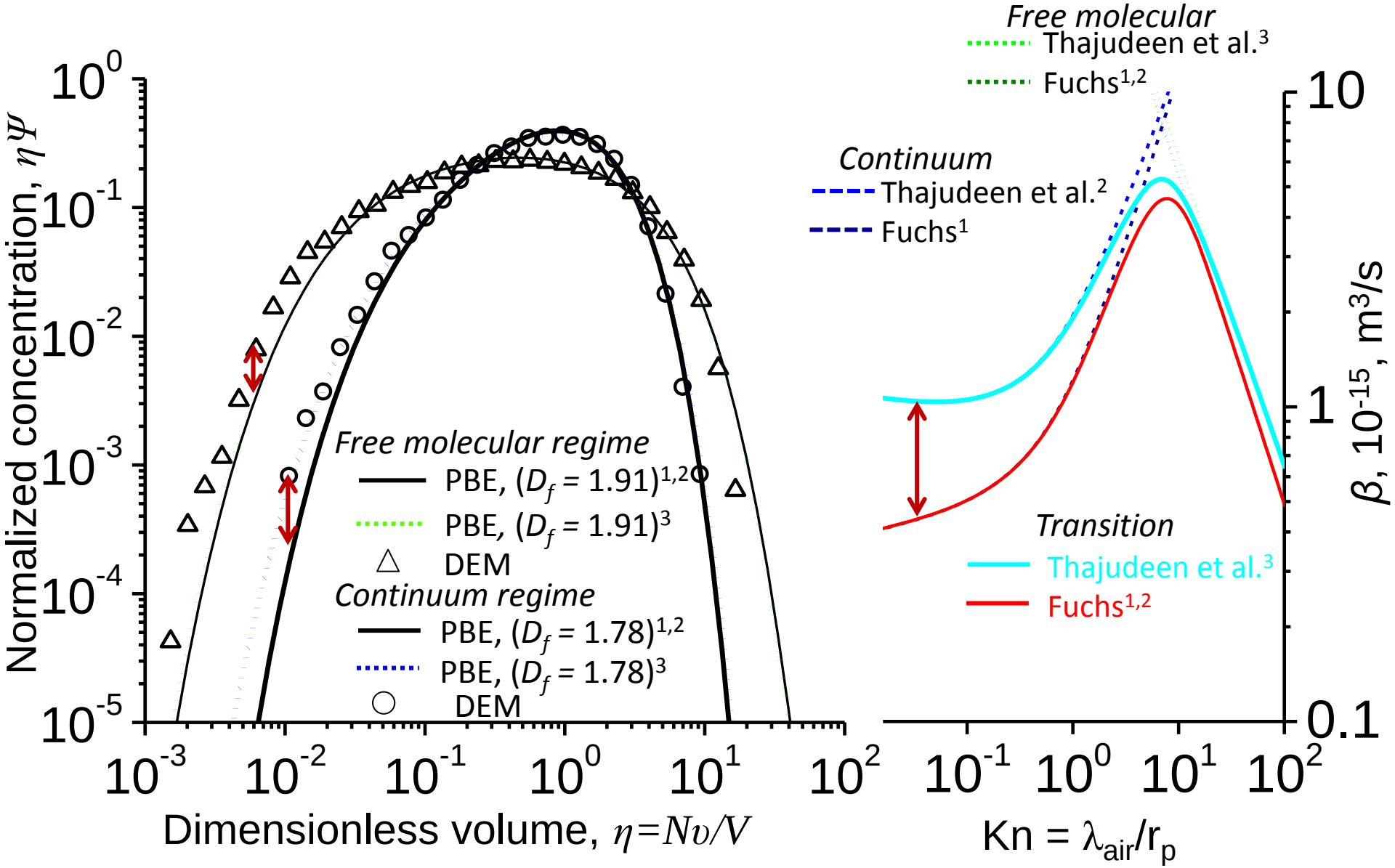
Evolution of Average Agglomerate Structure



$$n_p = \boxed{k_n}\left(\frac{r_g}{r_p}\right)^{D_f}$$

Agglomerate Self-Preserving Size Distribution



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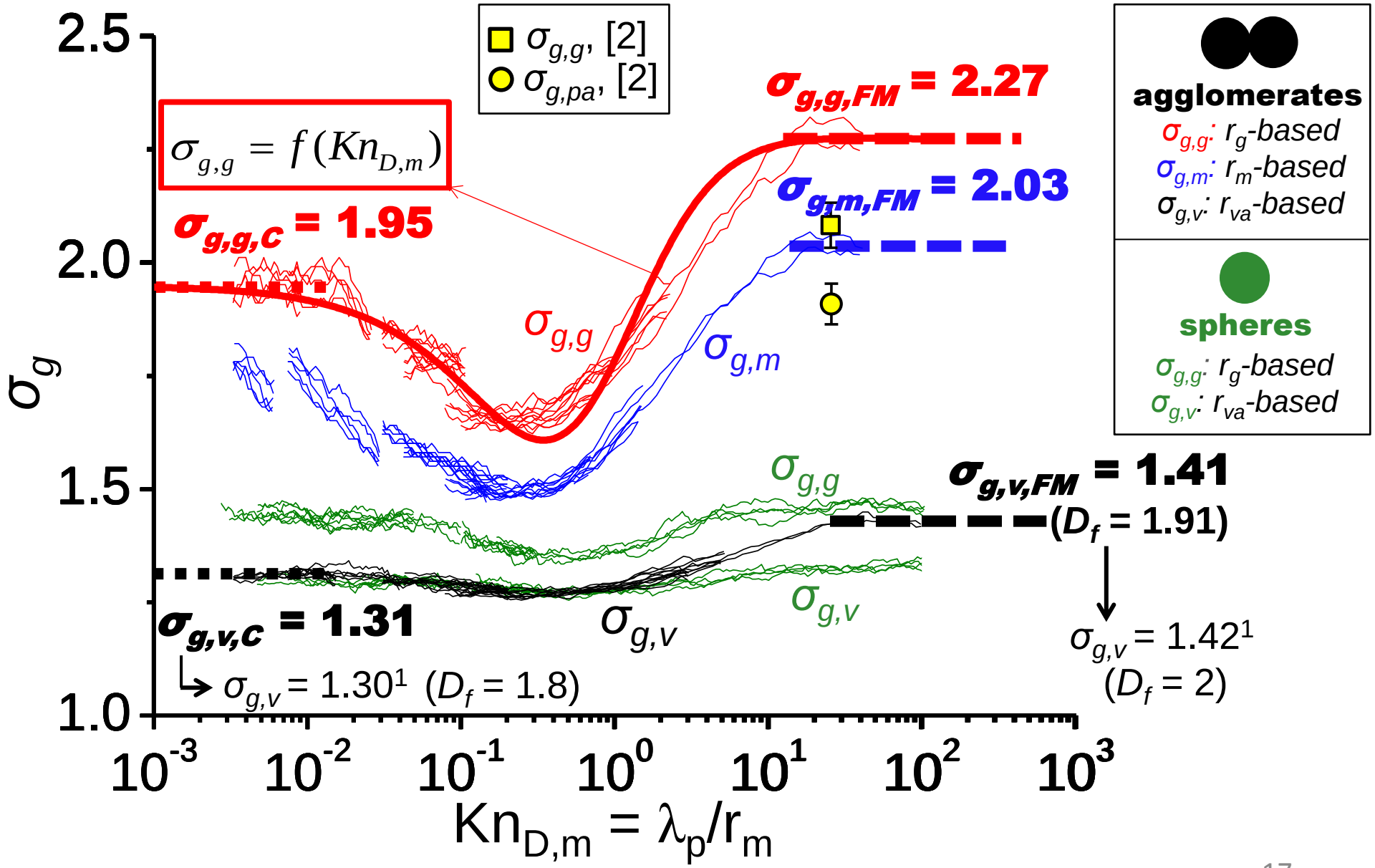
3. Thajudeen et al. (2012). Aerosol Sci. Technol., 46, 1174–1186.

Geometric Standard Deviation



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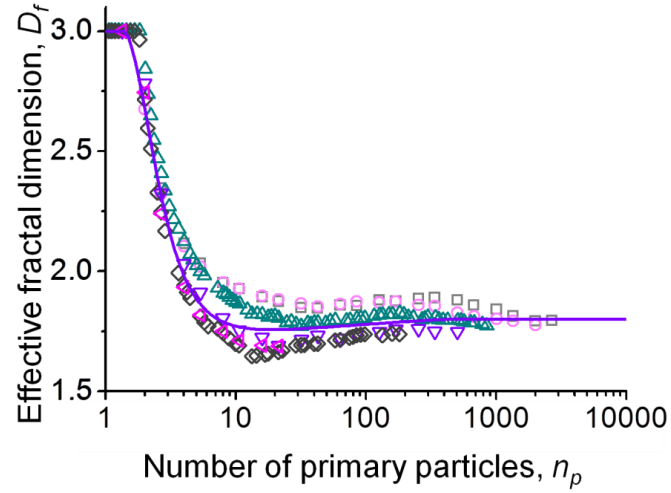
Conclusions

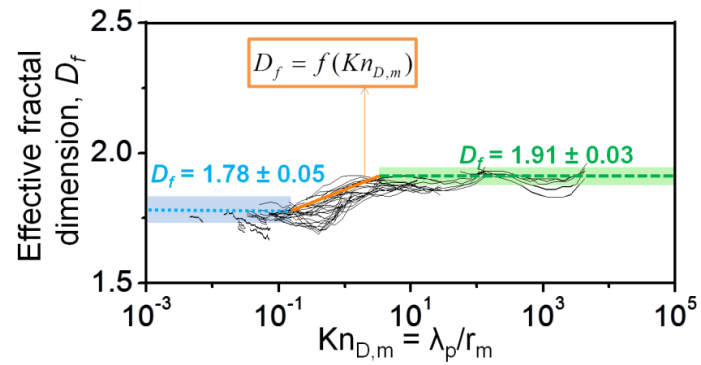
- D_f evolution from spherical to fractal-like particles: $D_f = f(n_p)$



Transition regime:

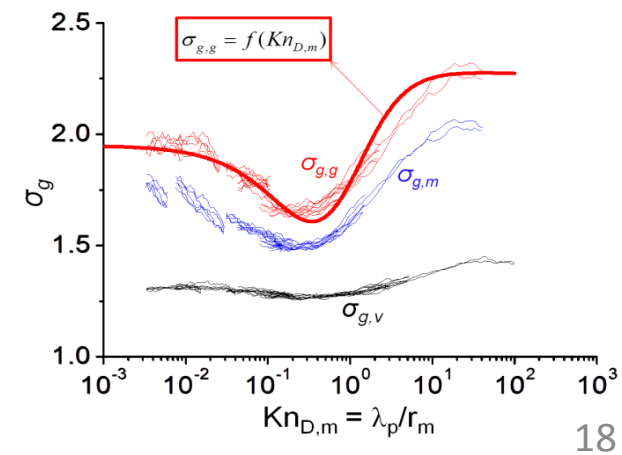
- *Structure*: $D_f = f(Kn_{D,m})$

  linear function



- *Geometric Standard Deviation*:

$$\sigma_{g,g} = f(Kn_{D,m})$$



THANK YOU FOR YOUR ATTENTION!