Multiparticle Sintering Dynamics: From Fractal-Like Aggregates to Compact Structures

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Real-time characterization of nanoparticles is necessary for continuous monitoring of aerosol manufacturing and airborne pollutant particles, but is still challenging as these particles restructure [1] and sinter or coalesce [2]. Gas-borne nanoparticles tend to cluster and form irregular structures which influence their transport properties, effective surface and density or scattering behavior, to name a few. In materials synthesis, for example, structure plays a crucial role in final product performance. In paints, TiO_2 non-aggregated particles (agglomerates) are sought that can be easily dispersed on their constituent primary particles. While for catalysts or lightguides, open aggregates are preferred to facilitate gas transport in and out of pellets or preforms. Furthermore, sinter necks are important for the mechanical stability of nanoparticle layers [3], enhanced electron transport and sensitivity of gas sensors [4] especially when made from narrowly-distributed aggregates [5] and electrical conductivity [6]. In design of nanoparticle synthesis by aerosol processes the variation of D_f during particle formation hardly affects the primary particle diameter but is important in determining the collision diameter and in return the aggregate diameter [7].

By now it is reasonably well understood that such aggregates form by gas and surface reaction, particle coagulation and partial coalescence or sintering. As chemical reactions in high temperature aerosol processes are completed much faster than particle dynamics, the detailed structure of these aggregates is largely determined by the interplay of particle collision and coalescence or sintering. In the absence of sintering between the primary particles, agglomerates (rather than aggregates) are formed with well-defined structure and fractal-dimension, D_f, depending only on the particle collision mechanism. For example, agglomerates made by a) diffusion limited agglomeration [DLA, 8] have $D_f = 2.5$, b) ballistic particle-cluster agglomeration $D_f = 3.0$ [BPCA, 9] and c) diffusion limited cluster-cluster agglomeration $D_f = 1.8$ [DLCA, 10]. Aggregates may undergo further coagulation leading to formation of agglomerates (physically-bonded) that may undergo restructuring & break-up [1].

Once coalescence or sintering starts between constituent primary particles, sinter necks are formed between them converting the agglomerates to aggregates. During sintering, the latter progressively densify until complete compact (e.g. $D_f = 3$) structures are formed at sufficiently long process times at high temperatures. This has been experimentally demonstrated during silica formation in hot-wall [11] and laminar diffusion flame reactors by small angle X-ray diffraction [12]. In reality, however, it is rather seldom to have enough process time to complete particle coalescence. As a result, aggregates are formed with D_f in-between those predicted by particle collision alone (as above) and the those for compact particles that underwent full coalescence as has been shown computationally for 2-D structures [13] and experimentally for nanosilica $D_f = 1.5\text{-}2.4$ [14]. Figure 1 shows the temporal evolution of the effective fractal dimension of a DLCA agglomerate with 256 primary particles during viscous sintering. At the beginning of sintering (Fig. 1, at $t/\tau_0 = 0 - 2$) the highly ramified aggregate branches straighten when primary particles approach each other (reduction of center-to-center distance). This internal restructuring practically unfolds the aggregate and D_f is reduced. However the branches continue shrinking while conserving mass. Further downstream D_f increased as aggregates compacted by sintering-coalescence consistent with in-situ measurements by small angle X-ray scattering [SAXS, 12].

Although models exist to characterize agglomerates of spherical particles, up to now, the primary particle size has to be fitted from electron micrographs, which is time consuming and expensive. Apparently there is a need for (online) characterization of fractal-like particles. Here a method is developed to determine the constituent (primary) particle number, n_p, and diameter, d_p, in such structures from their mass and mobility diameter in the free molecular and transition regime. Such data are typically obtained by differential mobility analyzer (DMA) and aerosol particle mass analyzer (APM) measurements of high temperature aerosols encountered in materials processing and engine emissions. Emphasis is placed in determining n_p and d_p in fractal-like agglomerate structures. The method is applied and compared to such measurements, microscopic images, and correlations in the literature. Primary particle size estimations from prior models show a significant overestimation if the agglomerate size is much larger than that of the primary particle. Reasonable agreement between the present method and primary particle diameters from counting electron micrographs is found[3]. The proposed method allows characterizing nanoparticle agglomerates with respect to d_p and n_p without any fitting together with their structure from DMA-APM measurements.

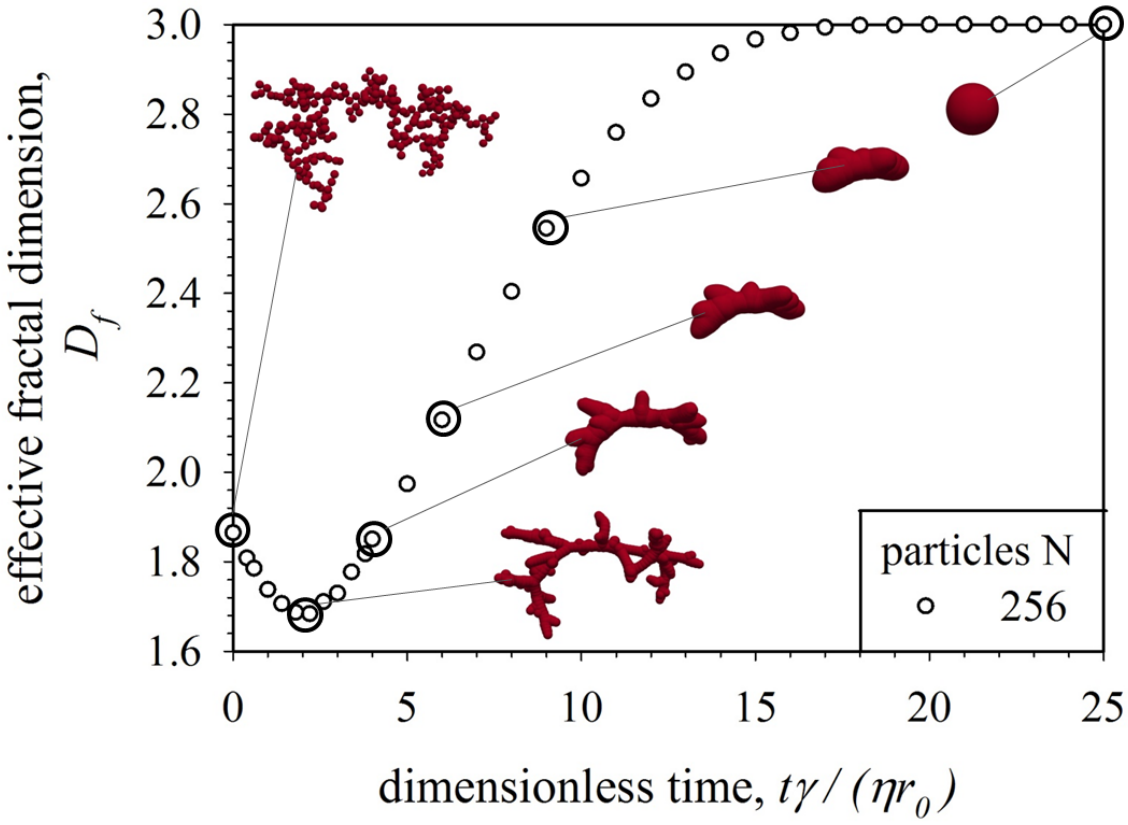

Figure 1: Evolution of the effective fractal dimension D_f during viscous sintering of an agglomerate with 256 primary particles.

[1] M.L. Eggersdorfer, D. Kadau, H.J. Herrmann, S.E. Pratsinis, Journal of Colloid and Interface Science 342 (2010) 261.
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[5] H. Keskinen, A. Tricoli, M. Marjamaki, J.M. Makela, S.E. Pratsinis, Journal of Applied Physics 106 (2009).
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[13] M.K. Akhtar, G.G. Lipscomb, S.E. Pratsinis, Aerosol Sci. Technol. 21 (1994) 83.
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Multi-particle sintering of fractal-like aggregates

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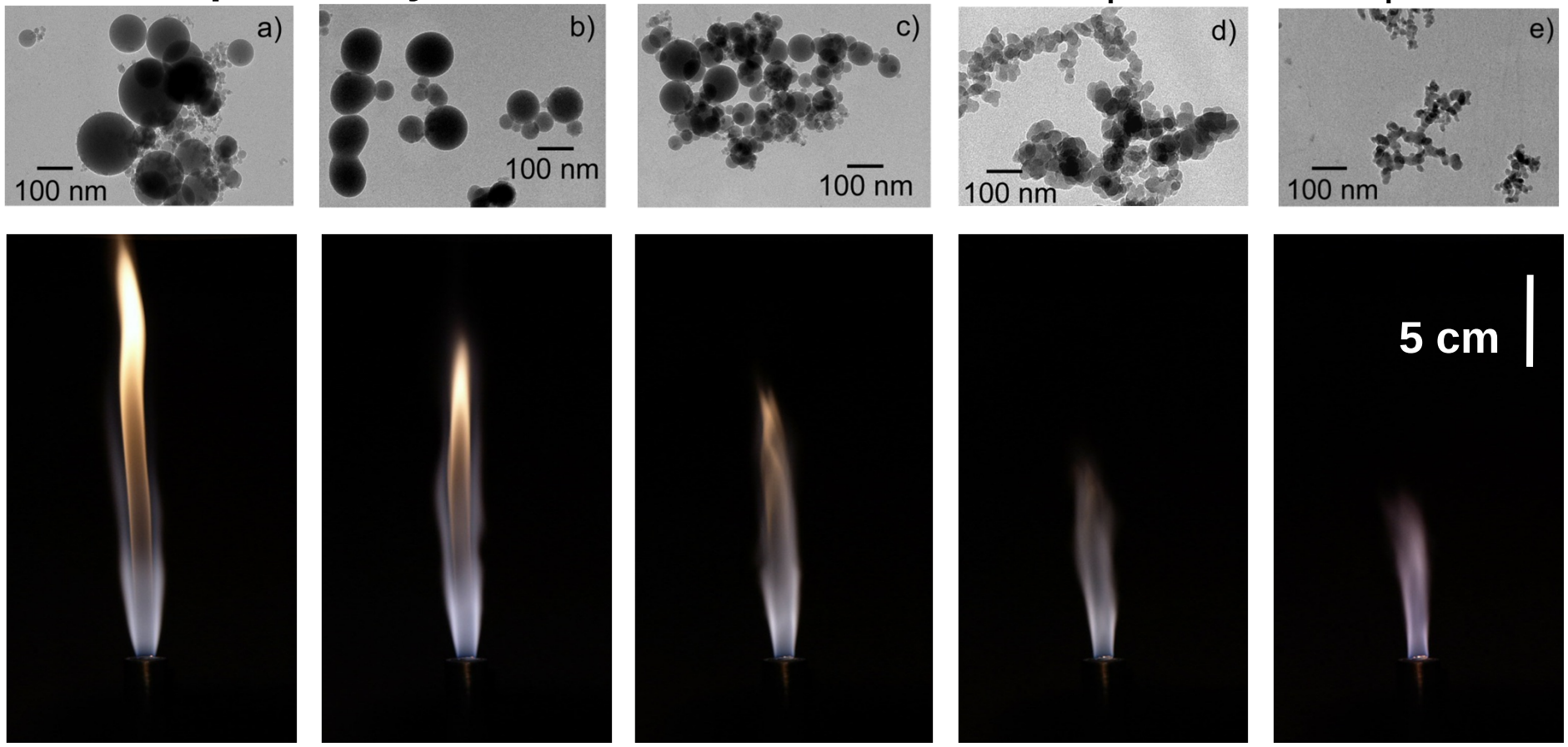
17 g/h SiO_2

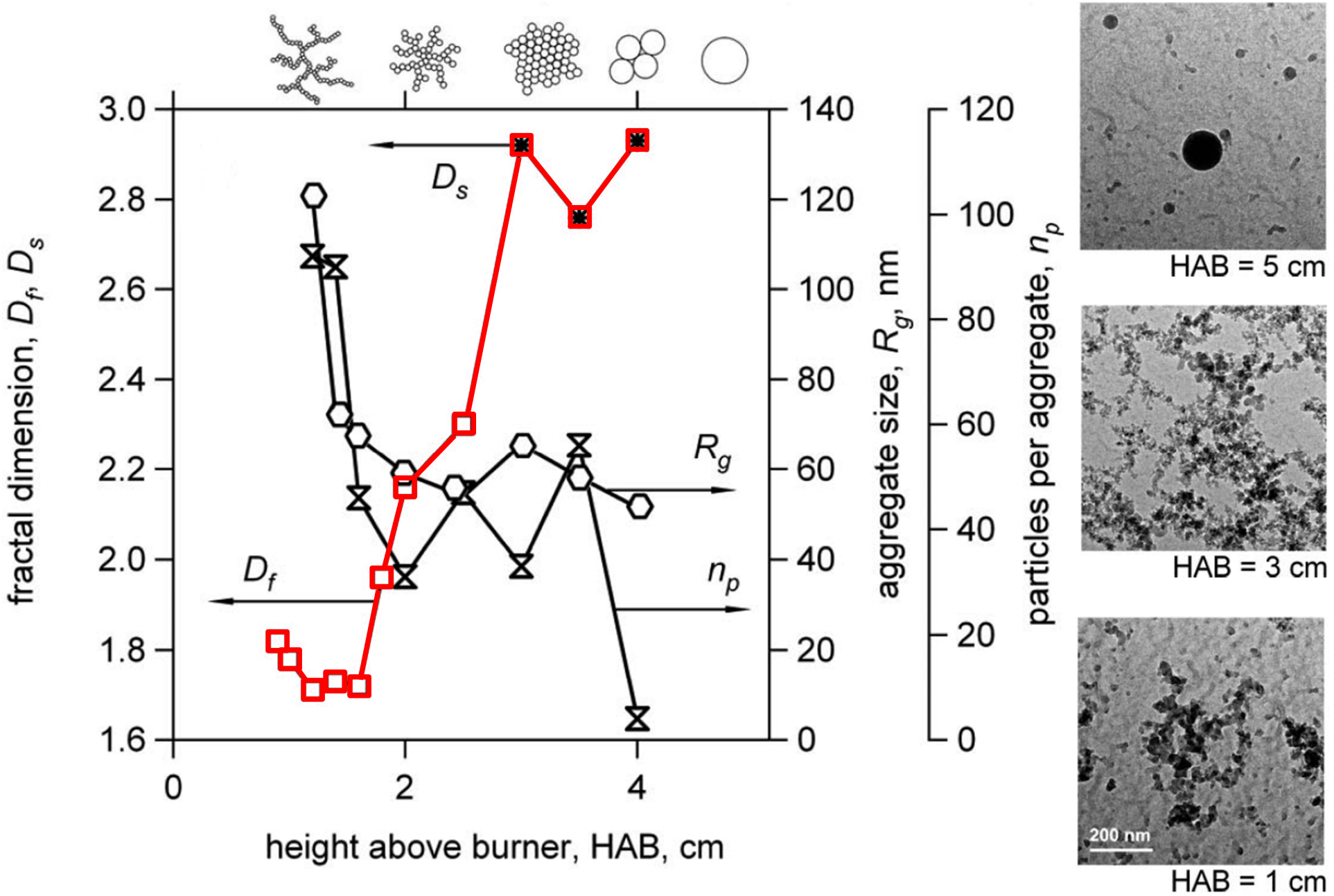
← filter powder by SAXS: non-fractal → D_f=1.6 D_f=1.9



2.5 **4.7** **8.5** **13.3** **24**

Oxygen flow rate, l/min

R. Mueller, H.K. Kammler, S.E. Pratsinis, A. Vital, G. Beaucage, P. Burtscher, *Powder Technol.,* **140** *(*2004) 40-48.



A. Camenzind, H. Schulz, A. Teleki, G. Beaucage, T. Narayanan & S.E. Pratsinis, Eur. J. Inorg. Chem. (2008) 911-918.

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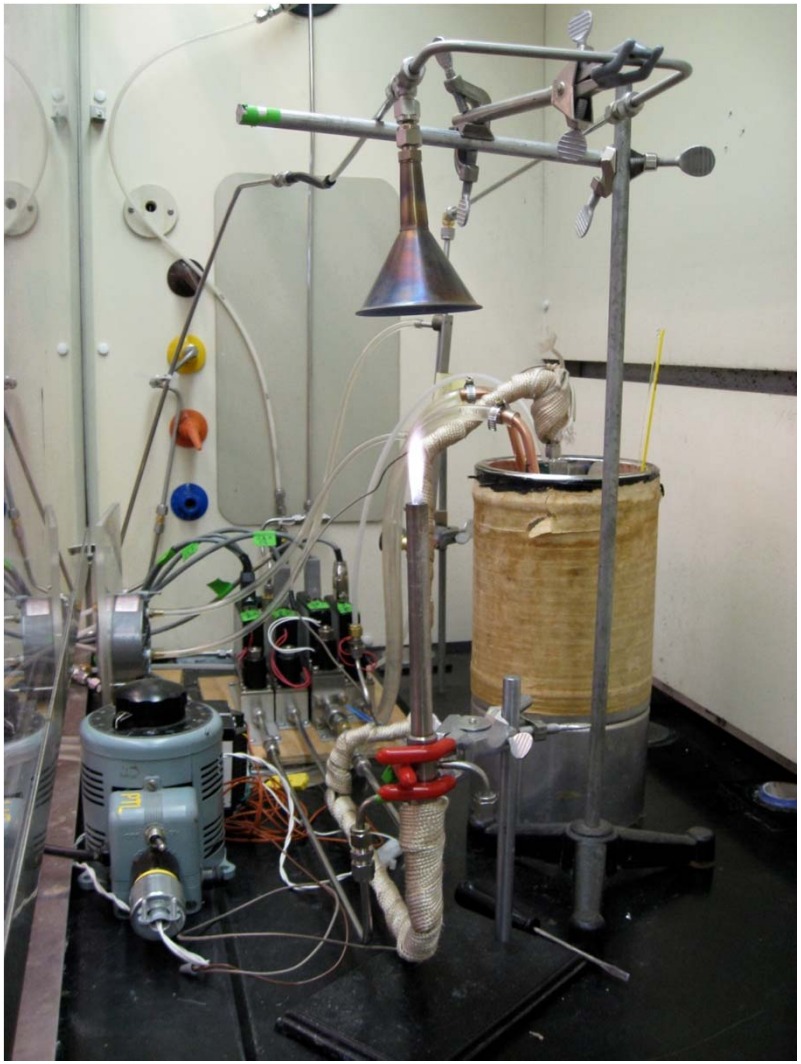
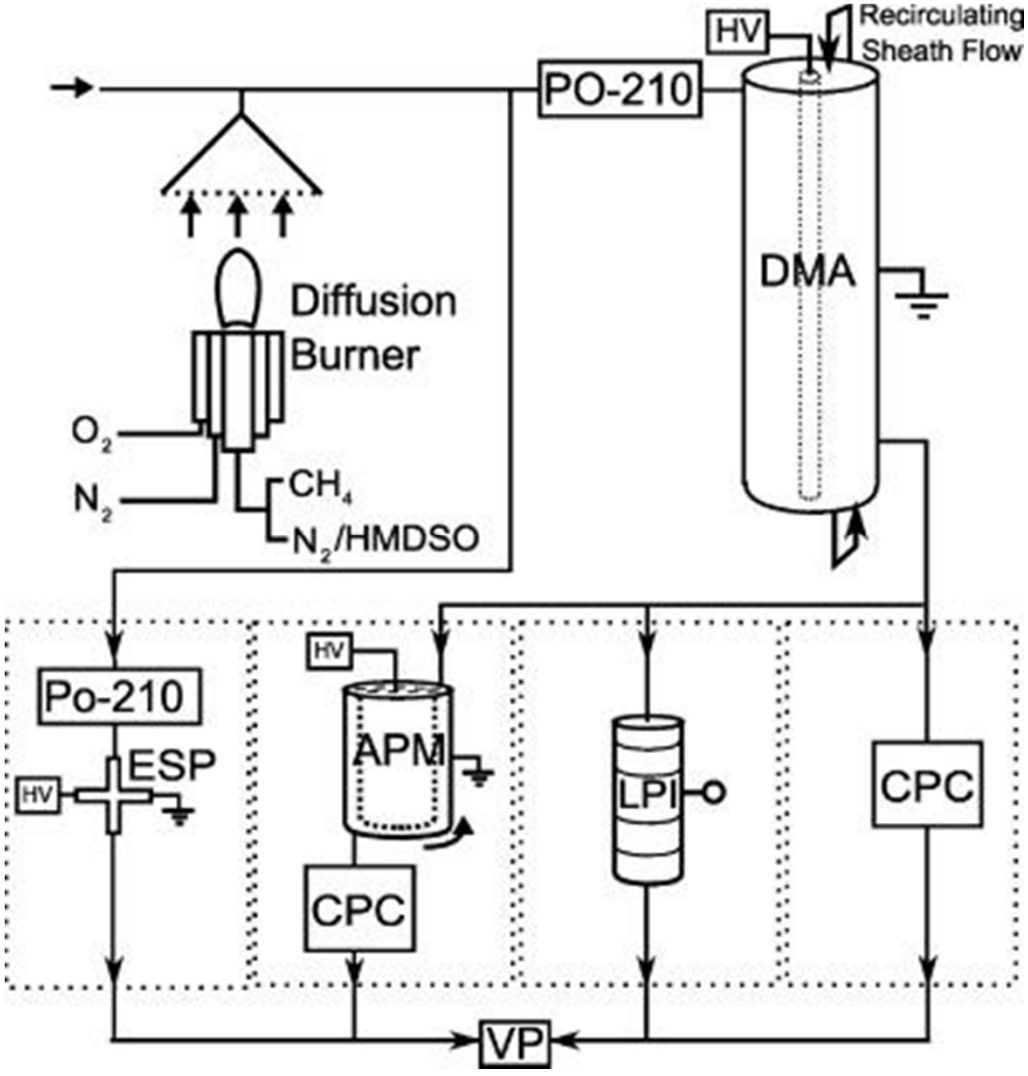
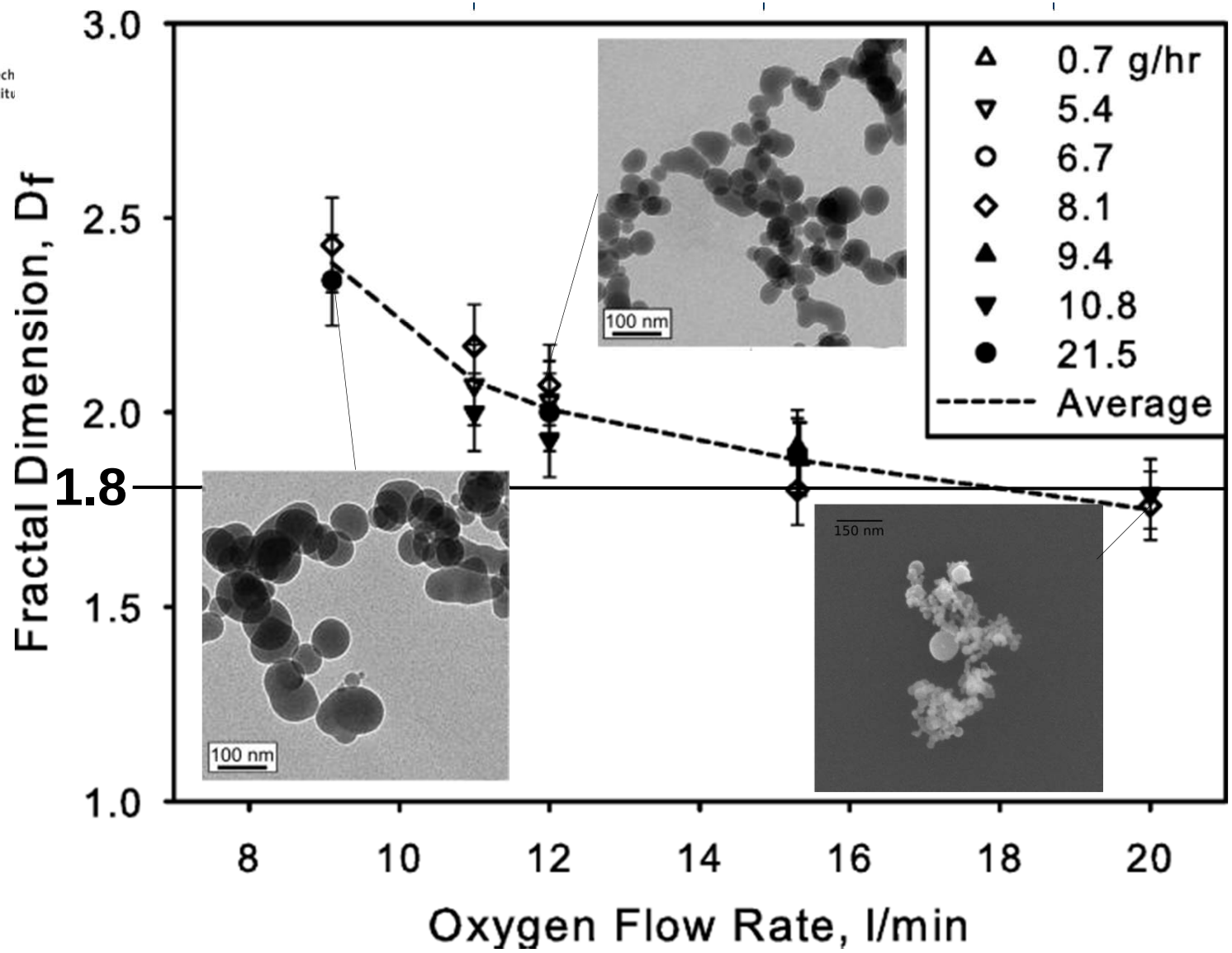
Mass-mobility particle size distributions





J.H. Scheckman, P.H. McMurry and S.E. Pratsinis, *Langmuir* **25** (2009) 8248-8254.



- We develop a model for **multi-particle sintering** and investigate

Evolution of structure

J.H. Scheckman, P.H. McMurry and S.E. Pratsinis, *Langmuir* **25** (2009) 8248-8254.

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Current state of knowledge

- Well - defined asymptotic D_f (1.6 - 2.5) for various collision mechanisms (DLA, DLCA, RLA etc.) of spherical non-aggregated (non-sintered) particles (Meakin, Mandelbrot)

- Empirical expressions exist for the evolution of D_f

  Artelt, C.; Schmid, H. J.; Peukert, W., On the relevance of accounting for the evolution of the fractal dimension in aerosol process simulations. *J. Aerosol. Sci.* **2003,** *34*, 511-534.

Goal:

- Understand the evolution of structure (D_f) for accurate simulation of aggregate and agglomerate sizes

Sintering

1. Geometric model for beginning of viscous sintering for 2 equally sized particles.
2. Phenomenological sinter model for coalesence:

$$\frac{dA}{dt} = -\frac{1}{\tau_f}\left(A - A_f\right)$$

3. Geometric model for full coalescence of viscous sintering for polymers of 2 equllay sized particles.
4. Molecular dynamics (MD) simulations of 2 – 110 primary particles of **SINGLE** chains and irregular structures.
   - Final sinter time: $t = \frac{4\eta r_0}{3\gamma}\left(N-1\right)^{0.68^{D_f}}$
5. Volume of fluid simulations of **SINGLE** chains of 2 – 10 primary particles and regular structures.
   - Best scaling (viscous sintering) with $r_f = N^{1/3} r_0$

J. Frenkel, *J. Phys.* **9** (1945) 385-391.
W. Koch & S.K. Friedlander, *J. Colloid Interface Sci.* **140** (1990) 419-427.
O. Pokluda, C.T. Bellehumeur & J. Vlachopoulos, *AIChE J.* **43** (1997) 3253-3256.
T. Hawa & M.R. Zachariah, *J. Aerosol Sci.* **38** (2007) 793-806.
M.J. Kirchhof, H.J. Schmid & W. Peukert, *Phys. Rev.* E **80** (2009) 026319.

Simulation Method: Two-Particle Sintering

Geometric Model

1. Energy balance[1]

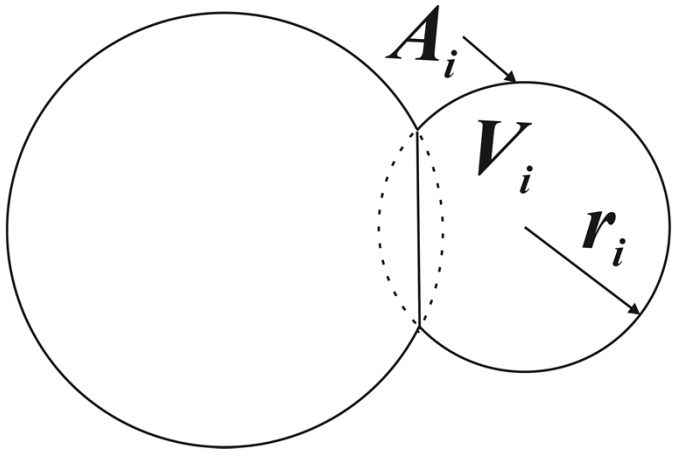
$$\gamma \frac{dA_i}{dt} = \iiint 3\eta\dot{\varepsilon}^2 dV_i = 3\eta\dot{\varepsilon}^2 V_i$$

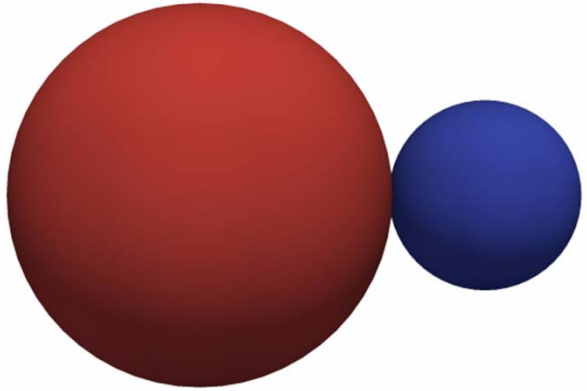
Constant strain rate ε in particle

Change in surface energy = viscous dissipation

2. Mass balance[2]

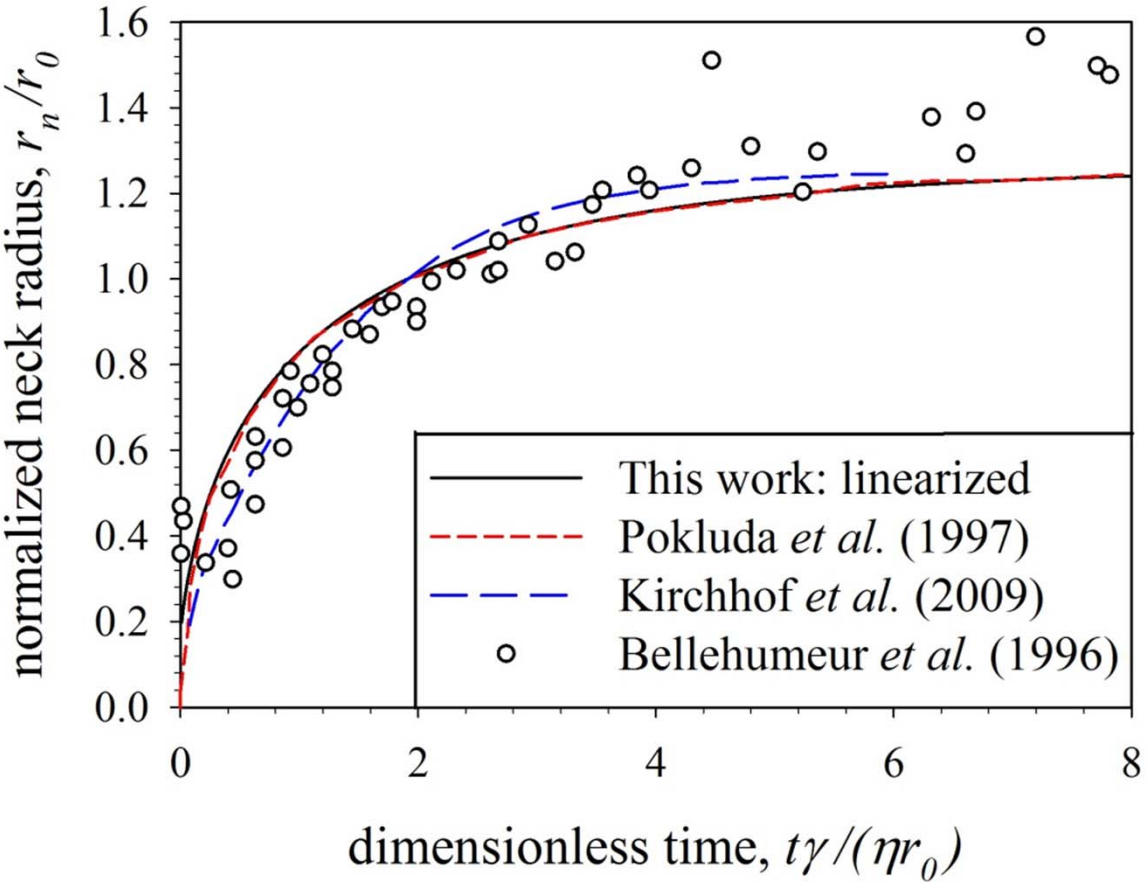
$$\frac{dV_i}{dt} = 0$$





1. J. Frenkel, *J. Phys.* **9** (1945) 385-391.
2. R.M. Kadushnikov, V.V. Skorokhod, I.G. Kamenin, V.M. Alievskii, E.Y. Nurkanov, D.M. Alievskii, *Powder Metall. Met. C+* ***40*** (2001) 154-163.

Two Particle Sintering: equally-sized particles

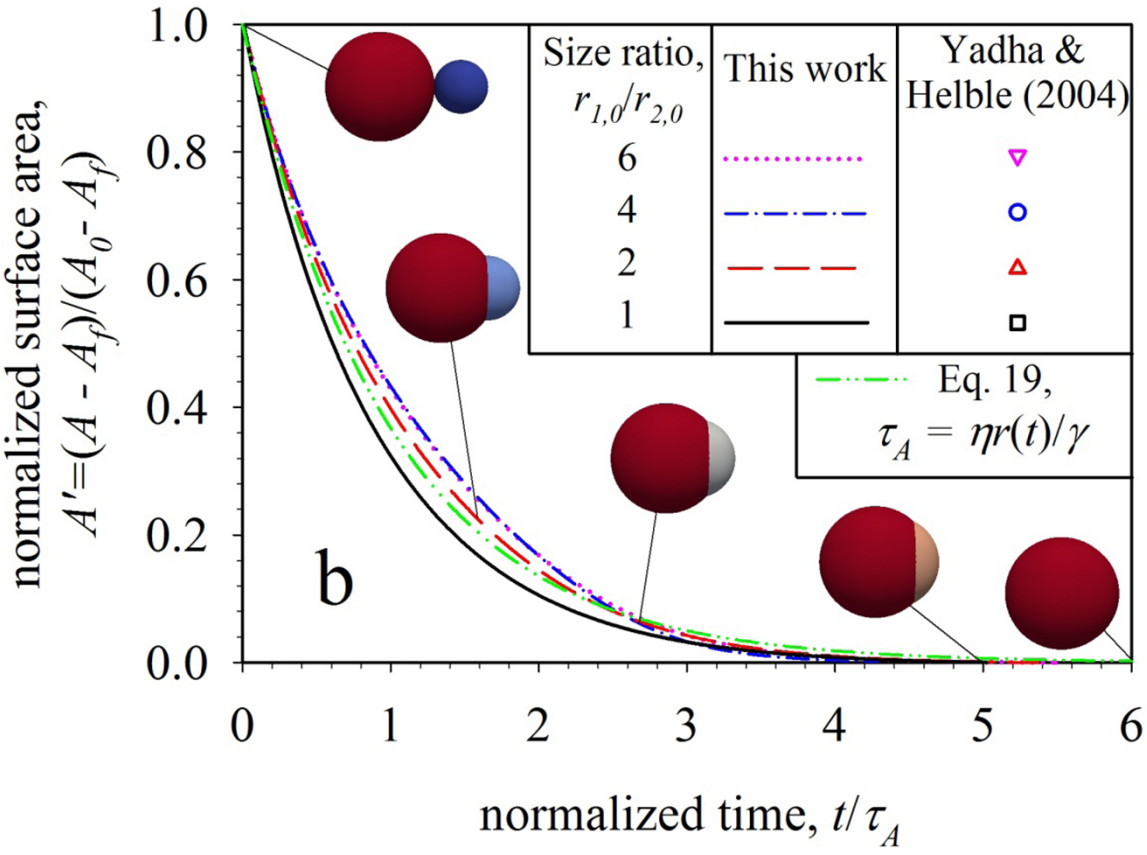


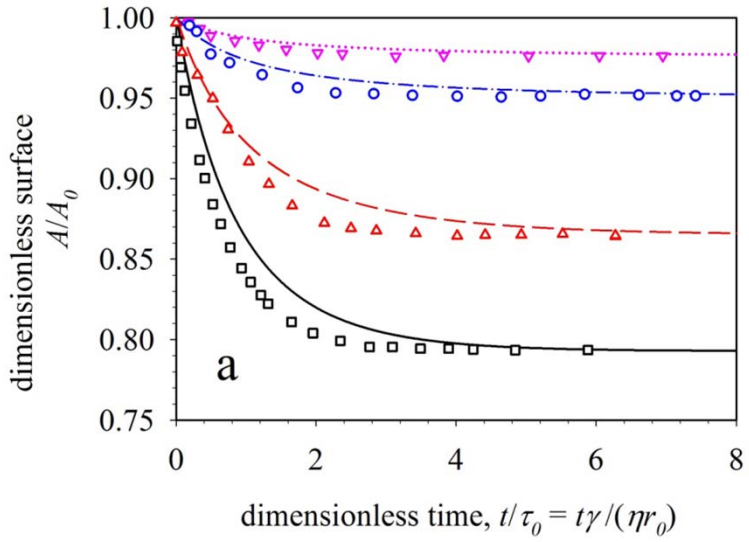
O. Pokluda, C.T. Bellehumeur & J. Vlachopoulos, *AIChE J.* **43** (1997) 3253-3256.

C.T. Bellehumeur, M.K. Bisaria & J. Vlachopoulos, *Polym. Eng. Sci.* **36** (1996), 2198-2207.

M.J. Kirchhof, H.J. Schmid & W. Peukert, *Phys. Rev.* E **80**(2009) 026319.

Two-Particle Sintering: unequal particles

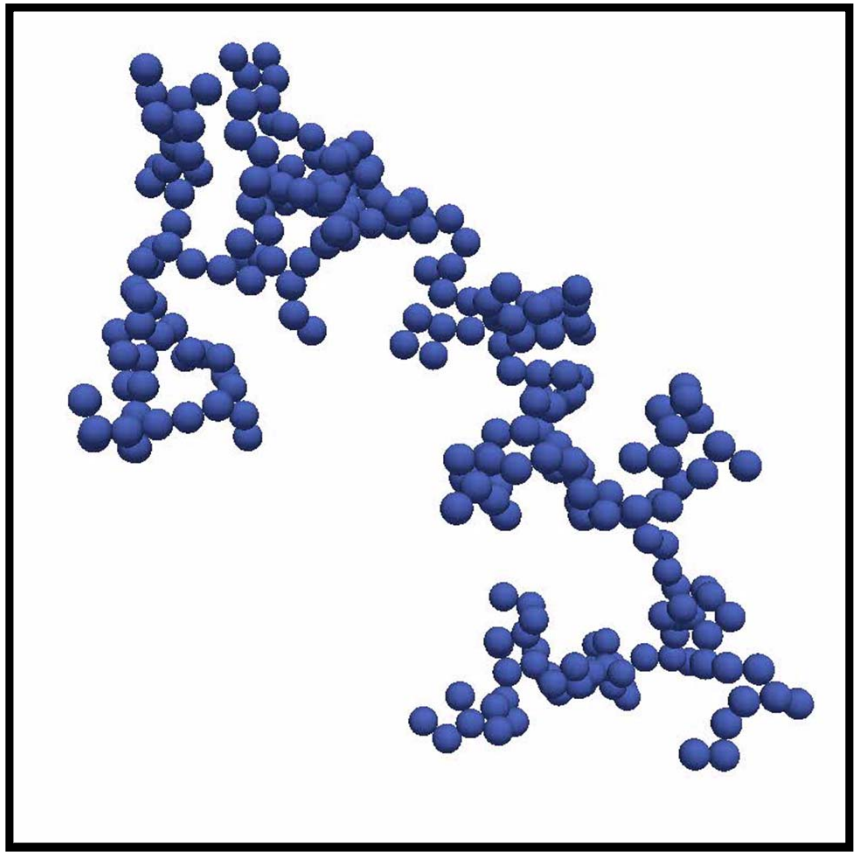




M.L. Eggersdorfer, D. Kadau, H.J. Herrmann, S.E. Pratsinis, *Langmuir*, **27**, 6358-67 (2011).

Simulation Method: Multi-Particle Sintering

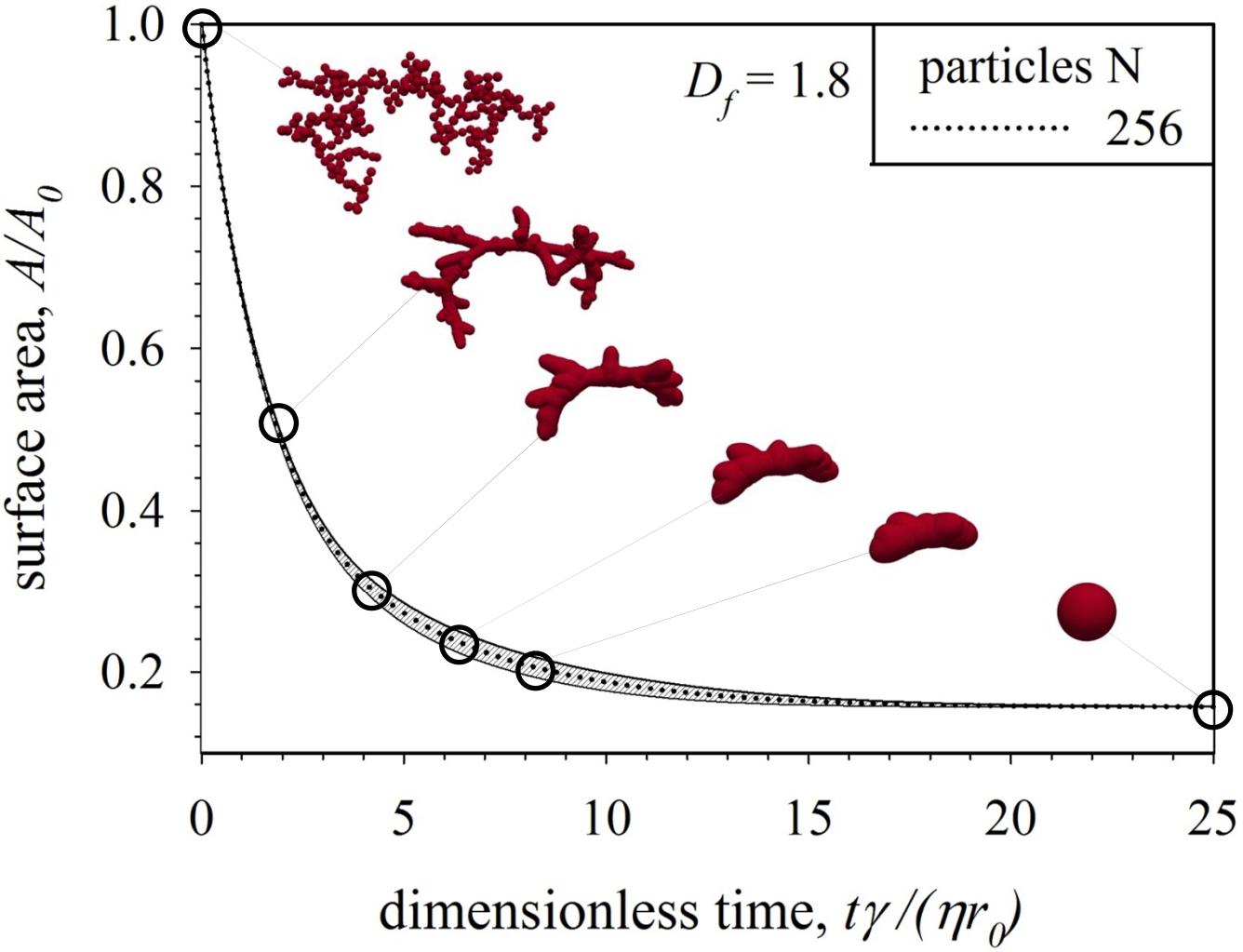
- Color: particle size based on curvature
- Vorlume[1] software to calculate particle volume, surface and neck area.
- SHAKE[2] algorithm to fulfill constraints for particle distances.
- Simulate viscous sintering of aggregates:
  - N = 2 – 512 primary particles
  - Average over 50 aggregates of each size (irregular structures)



1. F. Cazals, H. Kanhere & S. *Loriot, INRIA Tech Report* No. 7013 (2009).
2. J.P. Ryckaert, G. Ciccotti & H.J.C. Berendsen, *J. Comp. Phys.* **23** (1977) 327-341.

Multi-particle Sintering: Aggregates, D_f = 1.8

average over 50 aggregates



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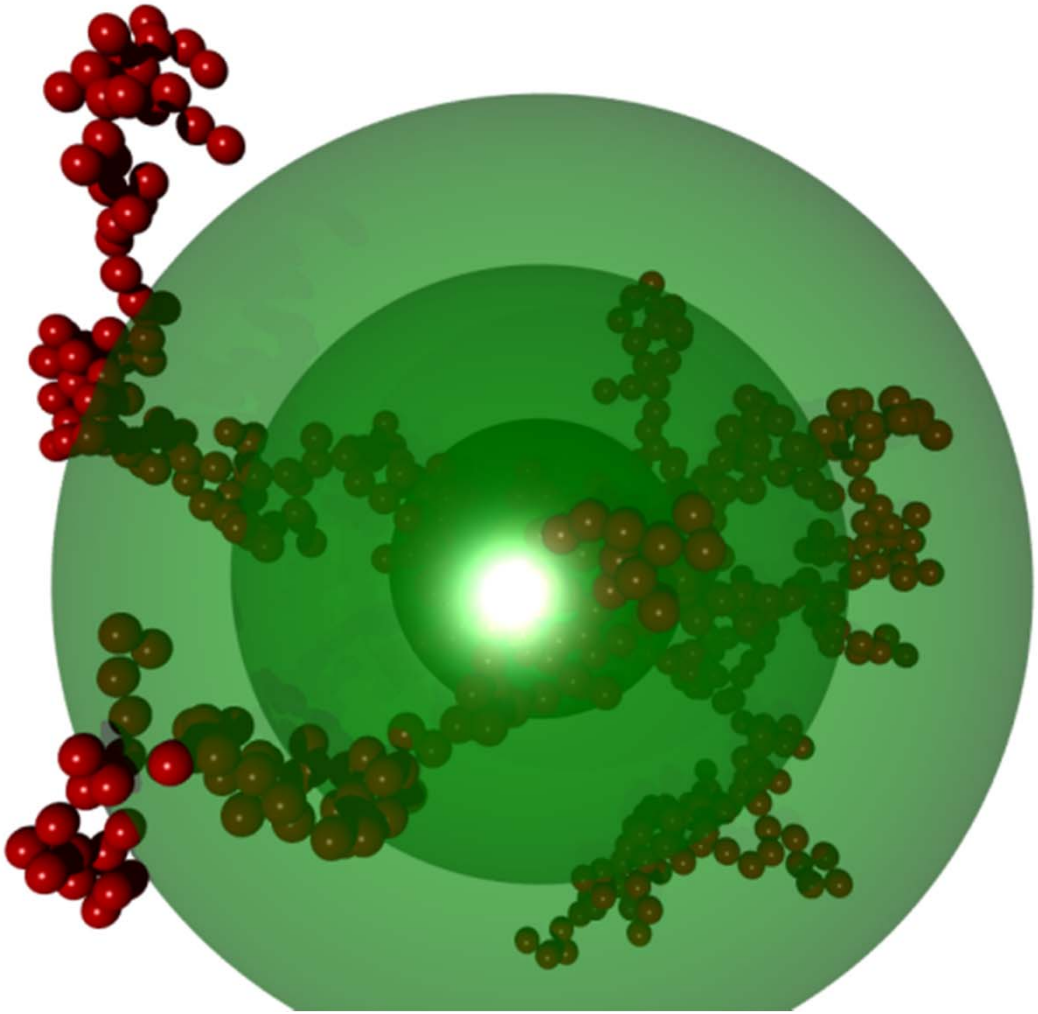
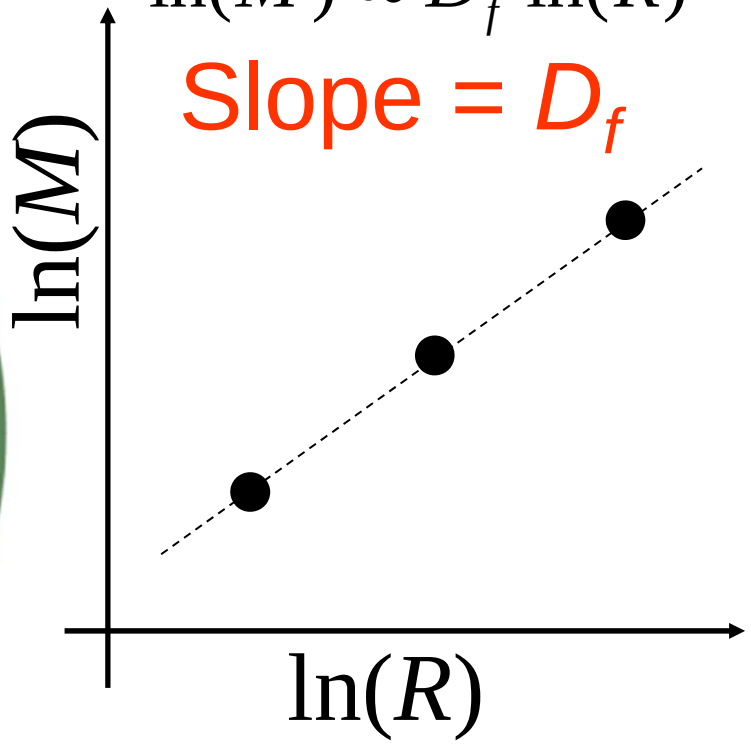
Evolution of D_f a Single Aggregate



$$M \propto R^{D_f}$$

$$\ln(M) \propto D_f \ln(R)$$

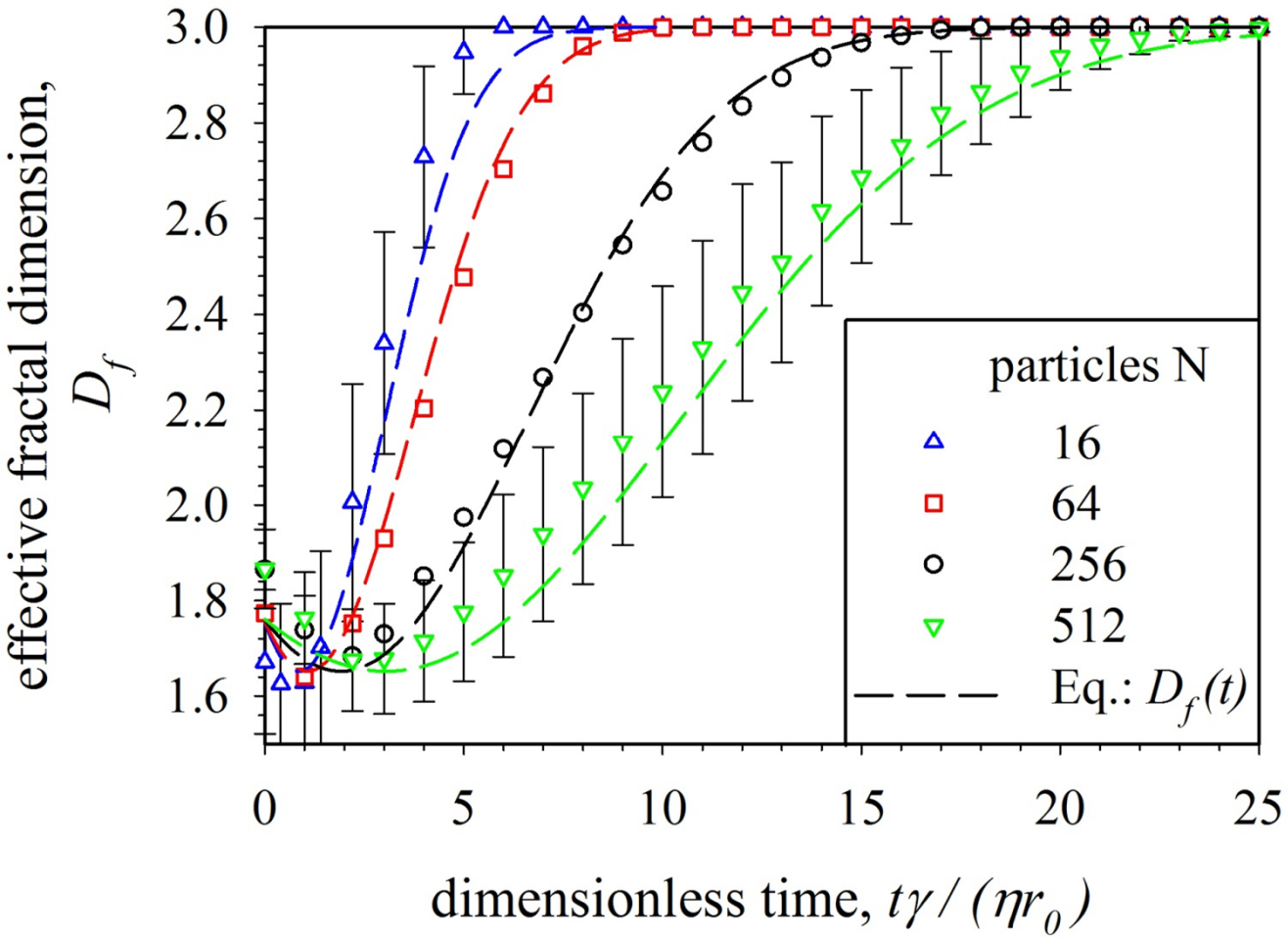
Slope = D_f



Method: Algorithm of Forrest and Witten

S.R. Forrest & T.A. Witten, *J. Phys A.* **12** (1979) L109-L117.

Evolution of fractal dimension, D_f



Aggregates are initially becoming more open.

Equation for the evolution of Df:

$$D_f(t) = 3 - (A)\exp\left(-\left(\frac{t\gamma/\eta r_0 - B}{C}\right)^2\right)$$

$$A = 2.5 - 0.64 \cdot D_{f,0}$$

$$B = -1.1 \cdot D_{f,0} + 0.0044 \cdot N + 2.77$$

$$C = 0.015 \cdot N - 6.3 \cdot D_{f,0} + 14.16$$

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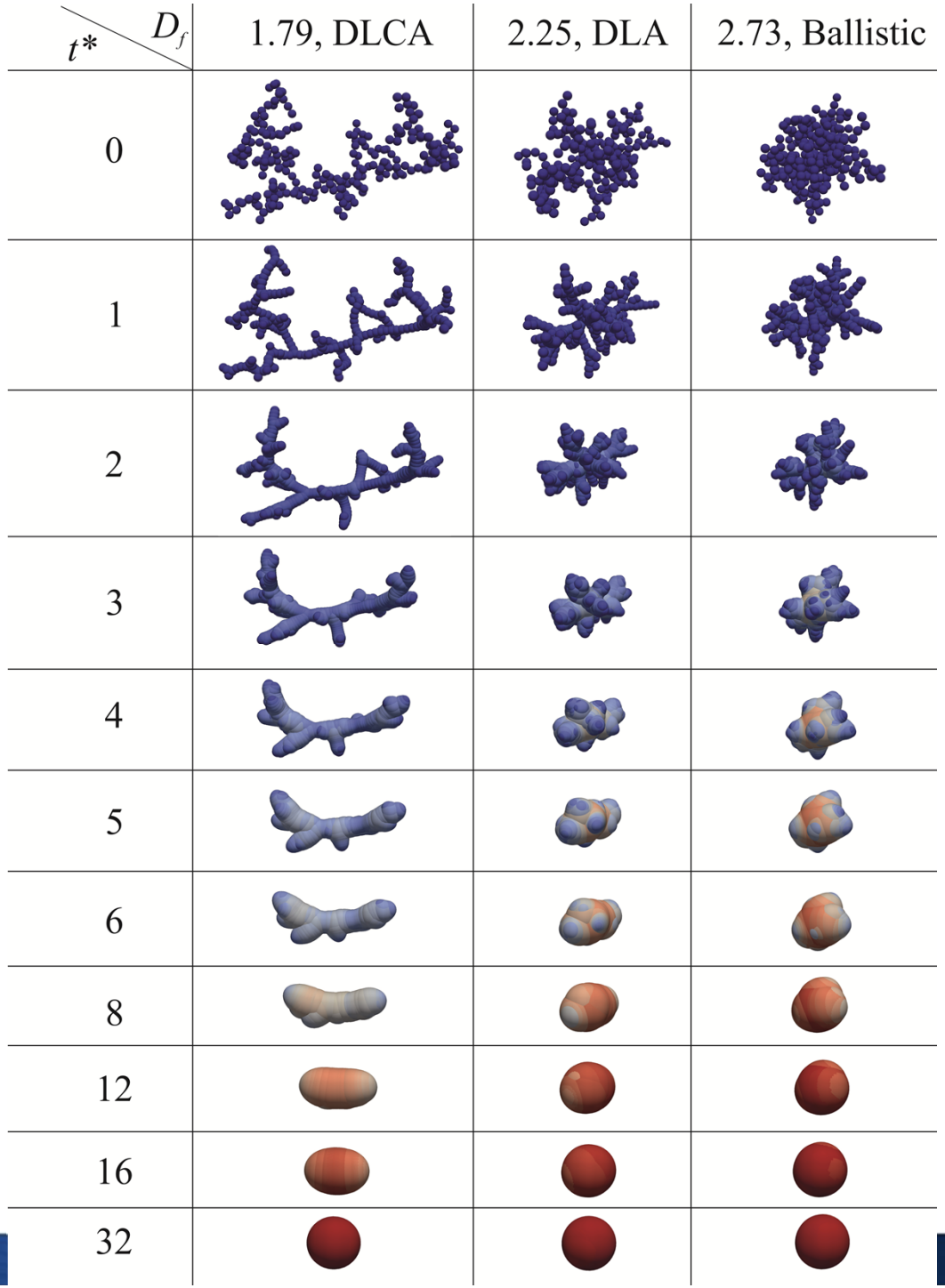
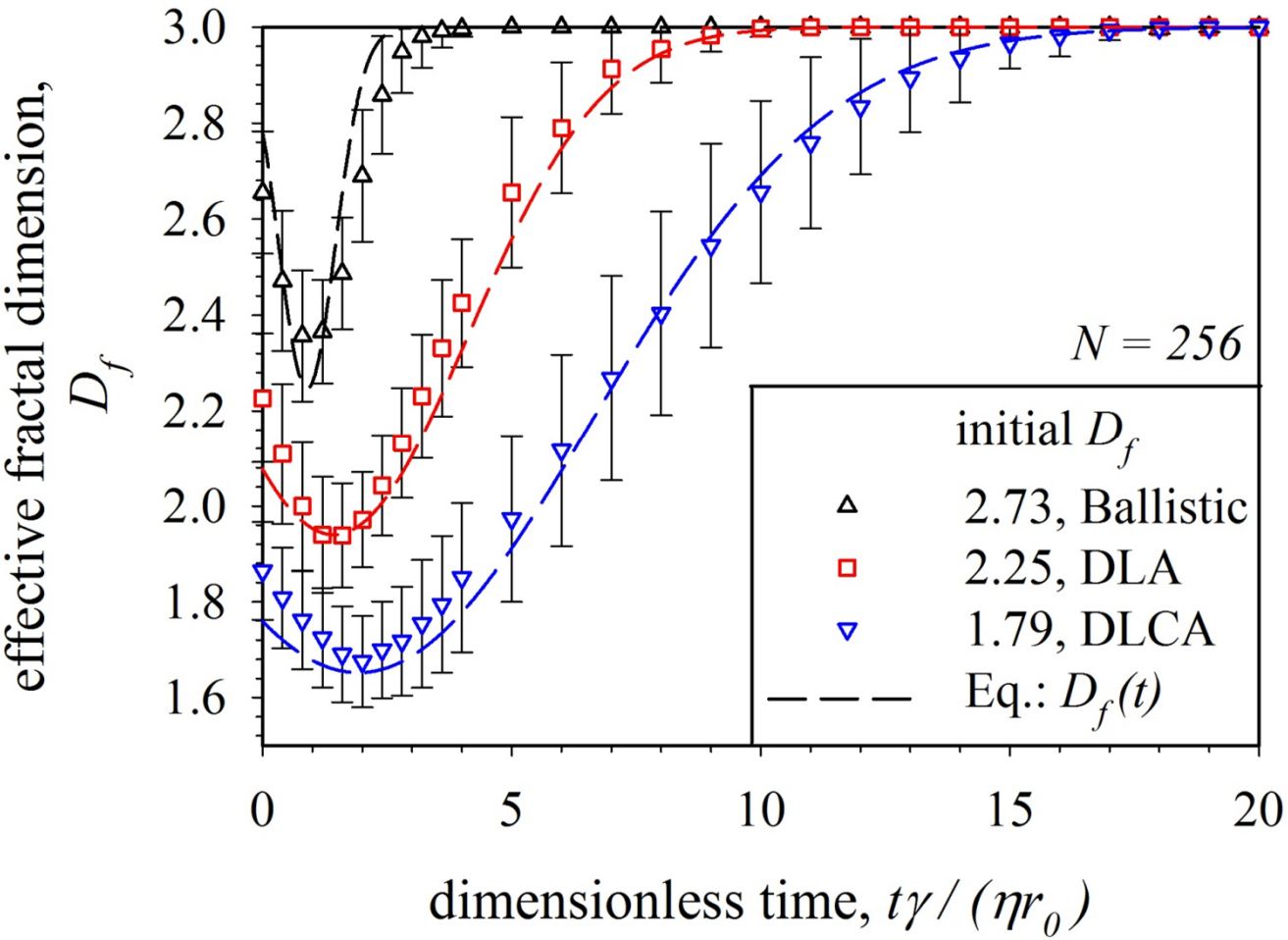
Evolution of aggregate structure for clusters made by DLCA, DLA and Ballistic motion



M.L. Eggersdorfer, D. Kadau, H.J. Herrmann, S.E. Pratsinis, *Langmuir*, **27**, 6358-67 (2011).

Effect of initial D_f



More compact aggregates sinter faster.

$$D_f(t) = 3 - A\exp\left(-\left(\frac{t\gamma}{\eta r_0} + B\Big/C\right)^2\right)$$

$$A = 2.5 - 0.64 \cdot D_{f,0}$$

$$B = -1.1 \cdot D_{f,0} + 0.0044 \cdot N + 2.77$$

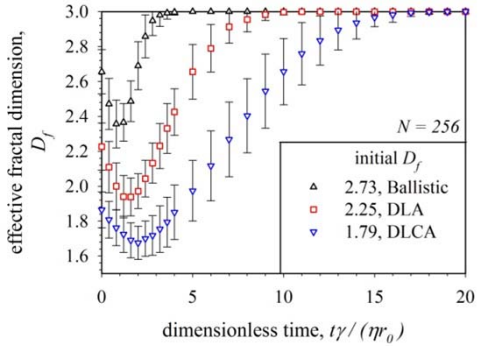
$$C = 0.015 \cdot N - 6.3 \cdot D_{f,0} + 14.16$$

Summary and Conclusions

- **By energy and mass balances → multi-particle sintering.**

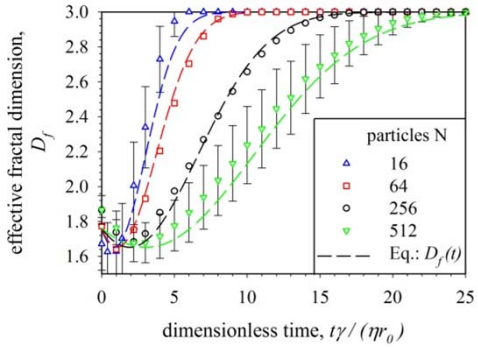
- **During sintering, aggregates become initially more open.**

- **More compact aggregates sinter faster.**



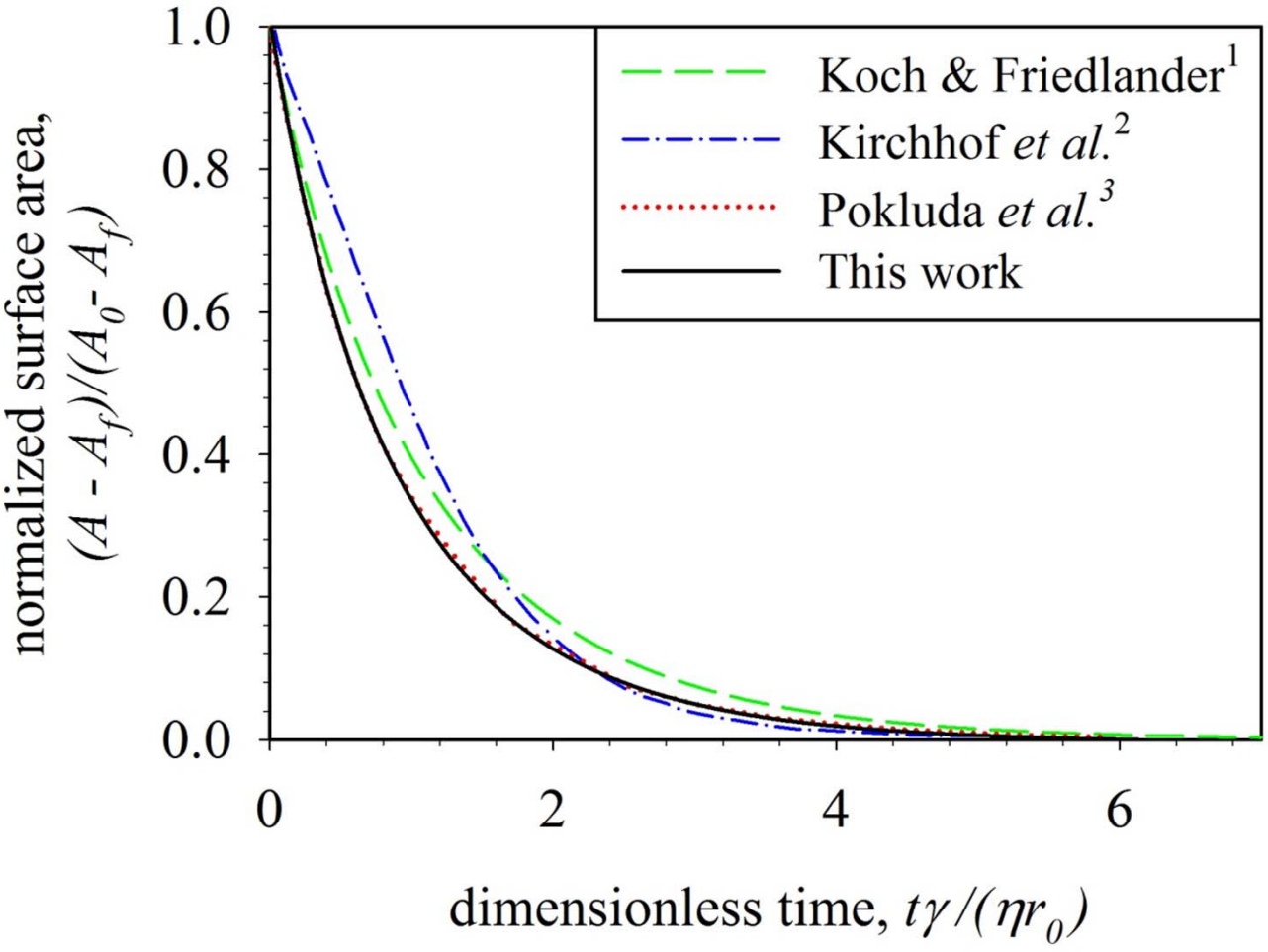
- **Developed an equation for the evolution of D_f.**

$$D_f(t) = 3 - A\exp\left(-\left(\frac{t\gamma}{\eta r_0} + B\Big/C\right)^2\right)$$



Thank you for listening!

2-Particle Sintering: Equal Particle Size



Koch & Friedlander Model[1]:

$$\frac{dA}{dt} = -\frac{1}{\tau_f}\left(A - A_f\right)$$

$$\frac{A - A_f}{A_0 - A_f} = \exp\left(-\frac{t}{\tau_f}\right)$$

Characteristic sintering time:

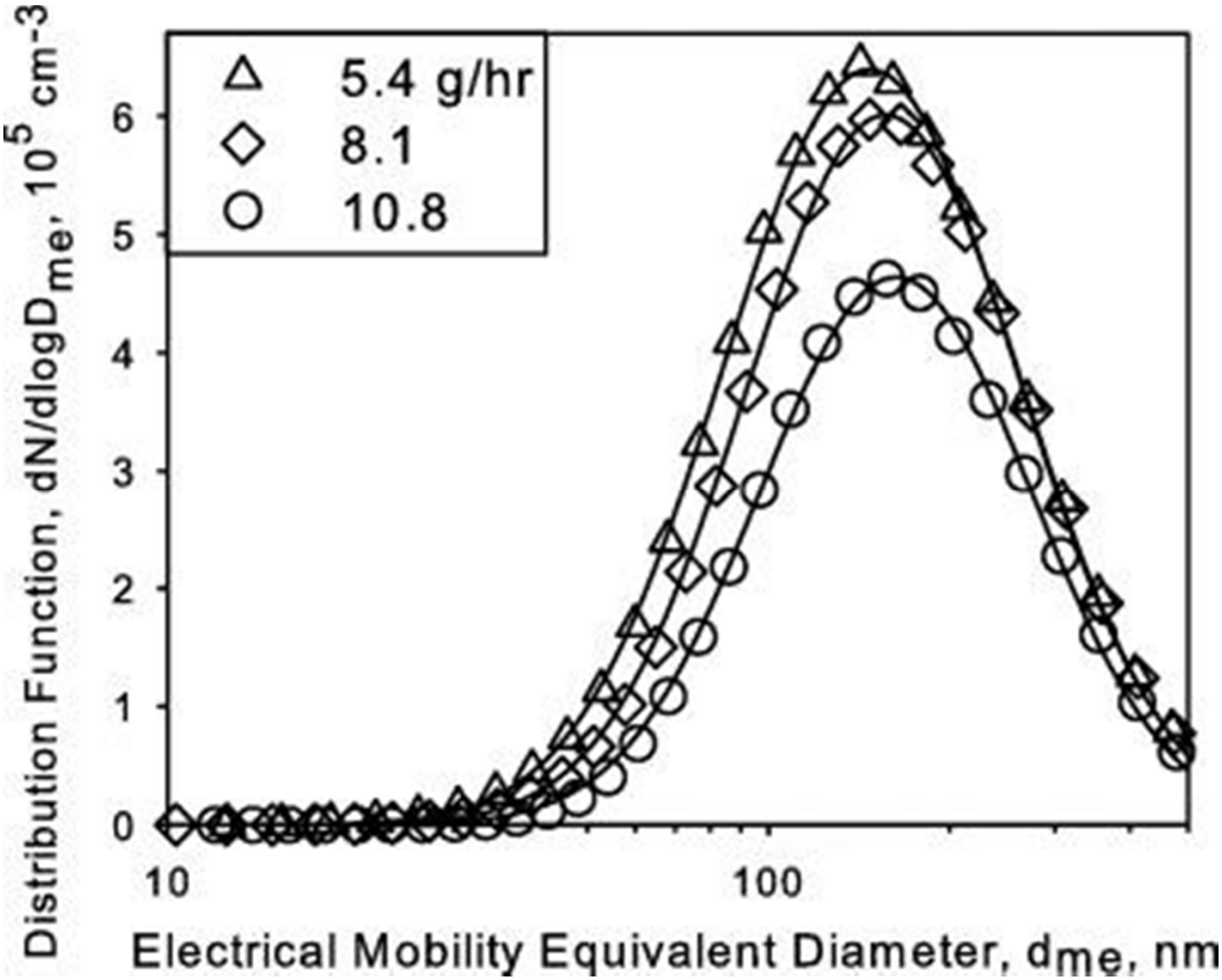
$$\tau_f = \frac{\eta r(t)}{\gamma}$$

1. W. Koch & S.K. Friedlander, *J. Colloid Interface Sci.* **140** (1990) 419-427.
2. M.J. Kirchhof, H.J. Schmid & W. Peukert, *Phys. Rev.* E **80** (2009) 026319.
3. O. Pokluda, C.T. Bellehumeur & J. Vlachopoulos, *AIChE J.* **43** (1997) 3253-3256.

Literature - Viscous Sintering

Who	Model	Sintering stage	# particles	Result
Frenkel (1945)	Geometric model	Initial sintering	2, same size	corrected: $\frac{\Delta d}{d_0} = \frac{3}{8}\frac{\gamma}{\eta r_0} t$
Koch & Friedlander (1990)	Phenomenological	Full coalescence	2, same size	$\frac{dA}{dt} = \frac{1}{\tau_f}\left(A - A_f\right)$
Pokluda et al. (1997)	Geometric model	Full coalescence	2, same size	
Yadha & Helble (2004)	Geometric model+ CFD	Full coalescence	2, differently sized	Small particle dominates sintering
Hawa & Zachariah (2006, 2007a, 2007b)	MD	Full coalescence	2-110, differently sized, irregular structures	Final sinter time, no surface evolution $t = t_{Frenkel}\left(N-1\right)^{0.68\wedge D_f}$
Cho & Biswas (2006)	Geometric model	Used Frenkel expression of initial neck growth for full coalescence	2, same size	
Kirchhof et al. (2009)	Volume of fluid method (CFD)	Full coalescence	2-10 particles, regular structures	$\frac{d\left(A-A_f\right)/\left(A_0-A_f\right)}{dt} = -0.67\frac{\gamma}{\eta r_f}$ Initial sintering

Agglomerate size distribution



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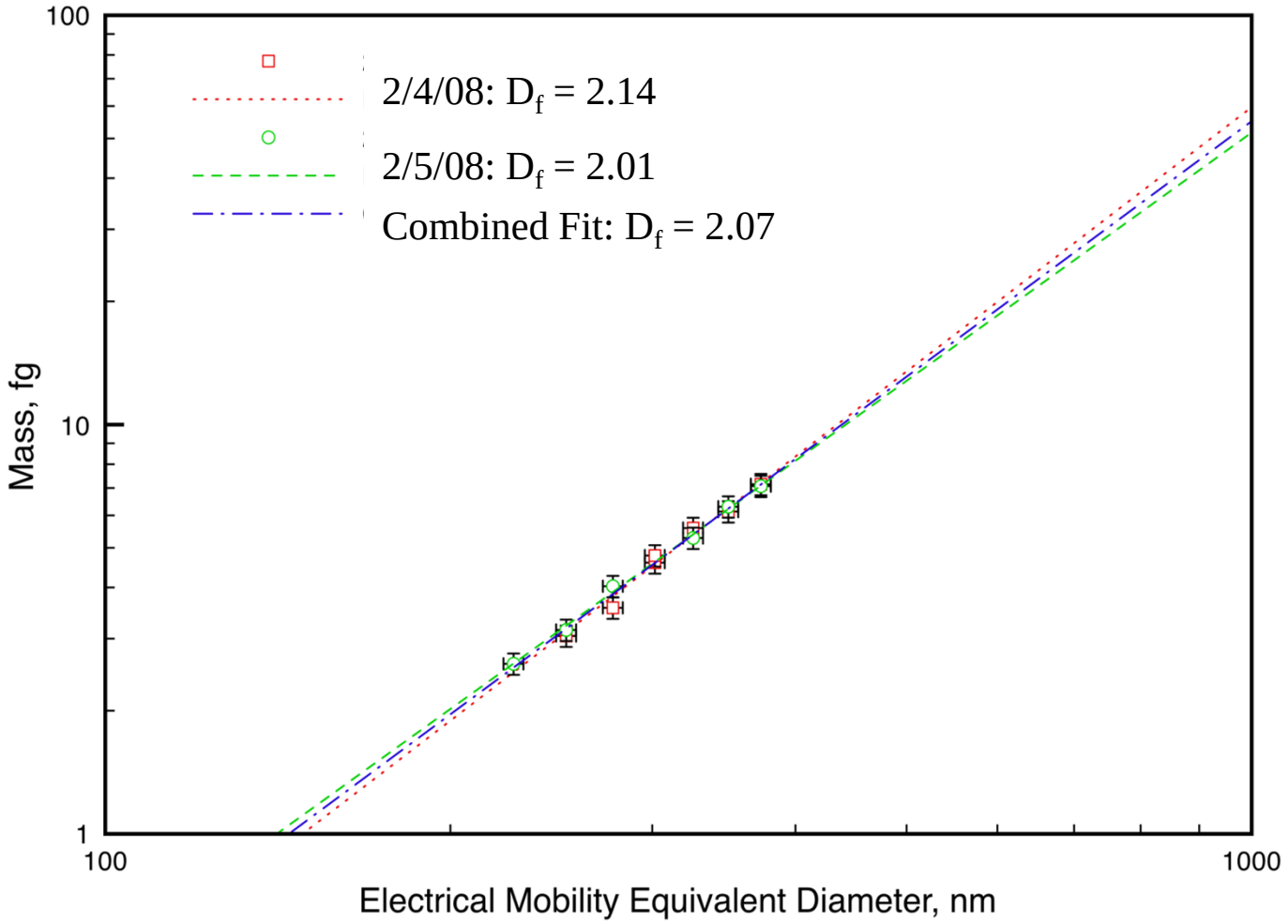
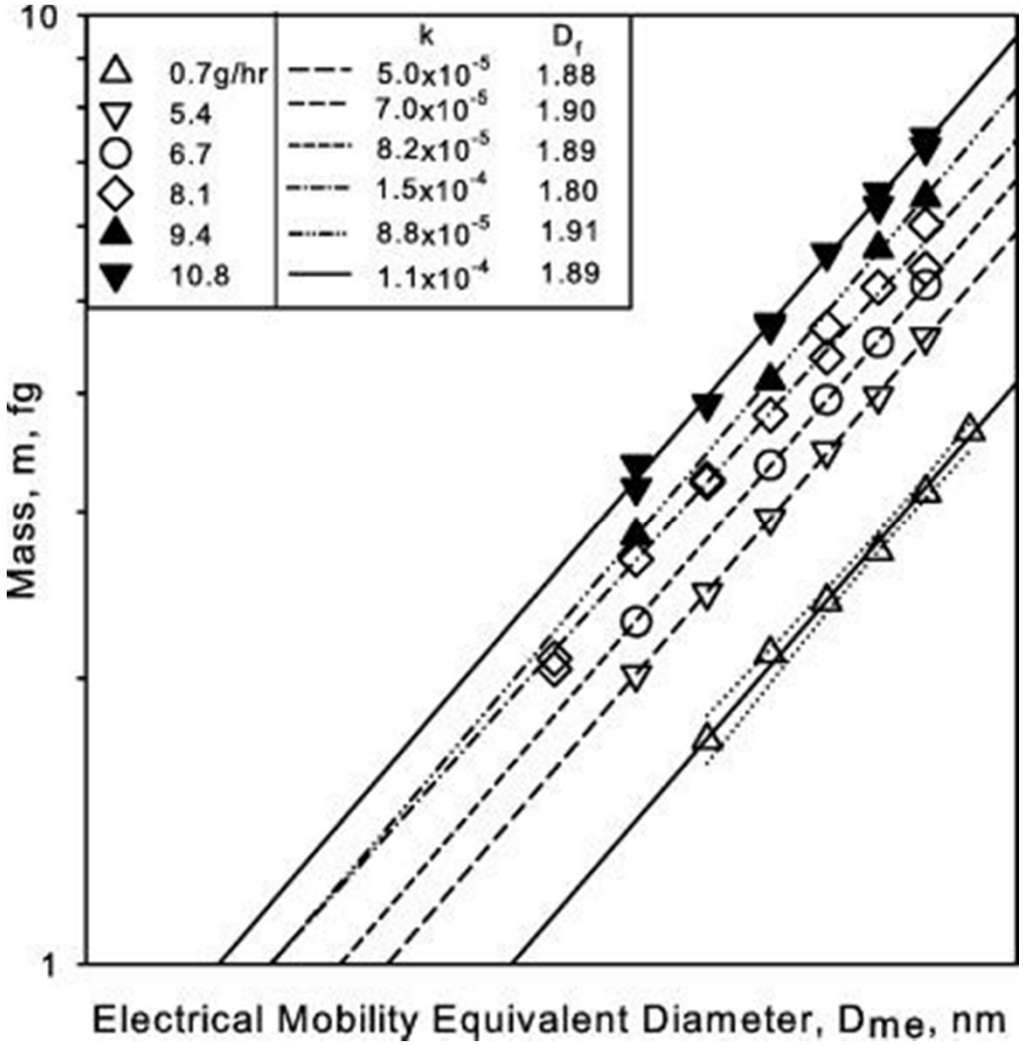
Mass + Mobility → Agglomerate Structure





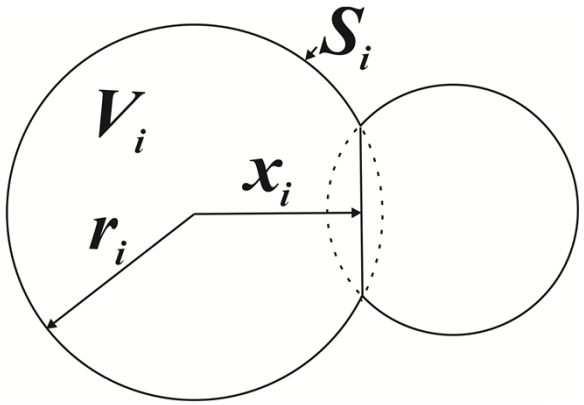
J.H. Scheckman, P.H. McMurry and S.E. Pratsinis, *Langmuir* **25** (2009) 8248-8254.

Simulation Method – Two-particle Sintering

Energy balance[1]

$$\underbrace{\gamma \frac{dS_i}{dt}}_{} = \underbrace{\iiint 3\eta\dot{\varepsilon}^2 dV}_{} = 3\eta\dot{\varepsilon}^2 V$$

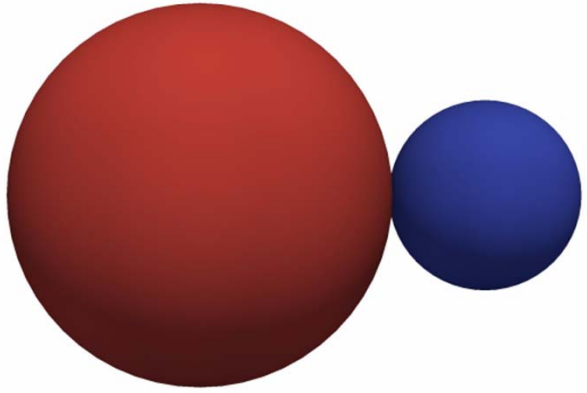
Change in surface energy = viscous dissipation



$$\frac{dS_i}{dt} = \frac{\partial S_i}{\partial r_i} \cdot \frac{dr_i}{dt} - \frac{\partial S_i}{\partial x_i} \cdot \frac{dx_i}{dt}$$

Mass balance[2]

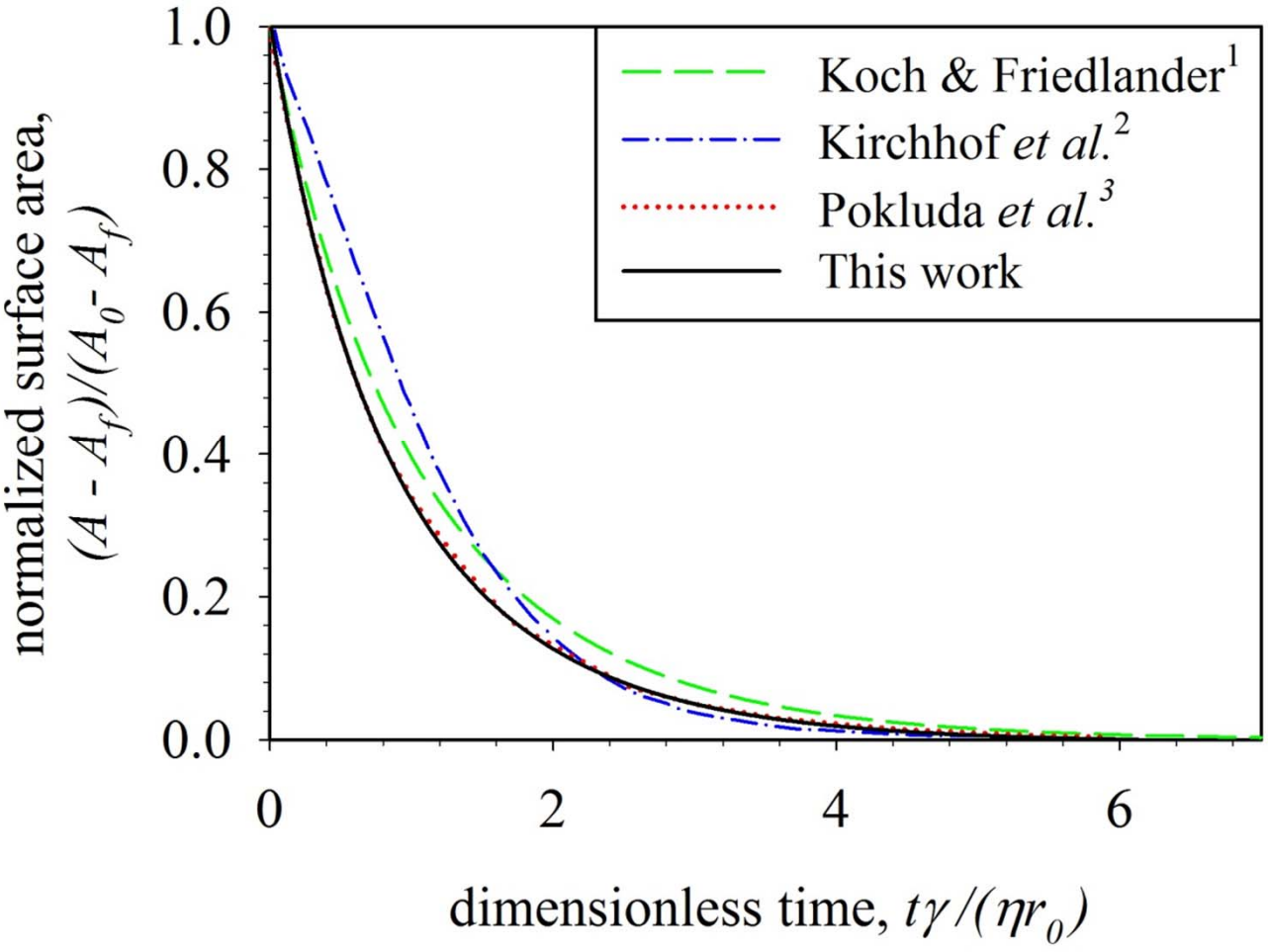
$$\frac{dV_i}{dt} = \frac{\partial V_i}{\partial r_i} \cdot \frac{dr_i}{dt} - \frac{\partial V_i}{\partial x_i} \cdot \frac{dx_i}{dt} = 0$$



1. J. Frenkel, *J. Phys.* **9** (1945) 385-391

2. R.M. Kadushnikov, V.V. Skorokhod, I.G. Kamenin, V.M. Alievskii, E.Y. Nurkanov, D.M. Alievskii, *Powder Metallurgy and Metal Ceramics* ***40*** (2001) 154-163.

2-Particle Sintering: Equal Particle Size



Koch & Friedlander Model[1]:

$$\frac{dA}{dt} = -\frac{1}{\tau_f}\left(A - A_f\right)$$

$$\frac{A - A_f}{A_0 - A_f} = \exp\left(-\frac{t}{\tau_f}\right)$$

Characteristic sintering time:

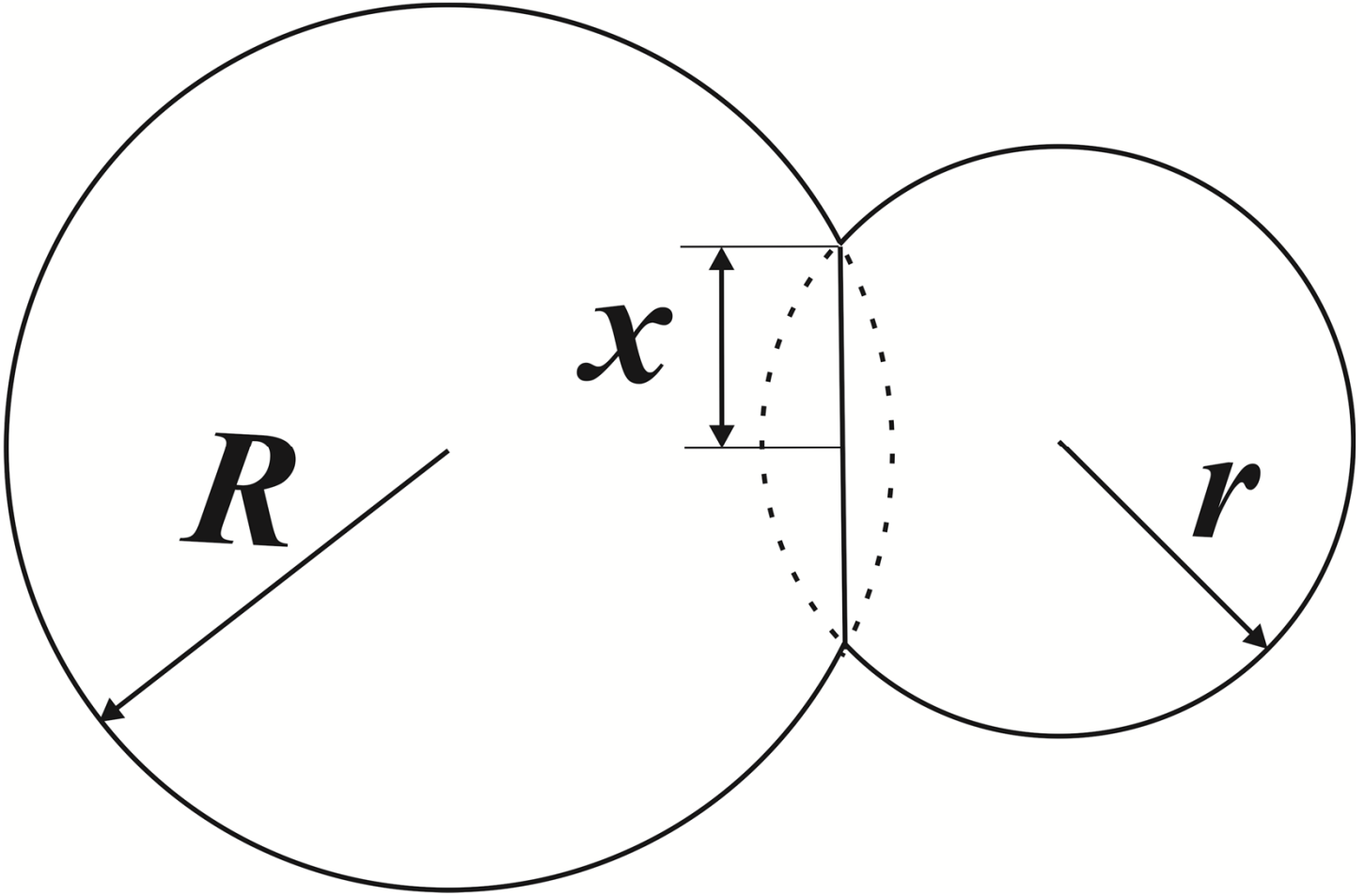
$$\tau_f = \frac{\eta r(t)}{\gamma}$$

1. W. Koch & S.K. Friedlander, *J. Colloid Interface Sci.* **140** (1990) 419-427.
2. M.J. Kirchhof, H.J. Schmid & W. Peukert, *Phys. Rev.* E **80** (2009) 026319.
3. O. Pokluda, C.T. Bellehumeur & J. Vlachopoulos, *AIChE J.* **43** (1997) 3253-3256.

$$\frac{dA}{dt} = -\frac{1}{\tau_f}\left(A - A_f\right) \quad \text{With} \quad \tau_f = \frac{\eta r}{\gamma} = \frac{\eta 3V}{\gamma A}$$

$$A(t) = \frac{A_f}{1 - \left(1 - \left(\frac{A_f}{A_0}\right)\exp\left(-\frac{\gamma A_f}{3\eta V}t\right)\right)}$$

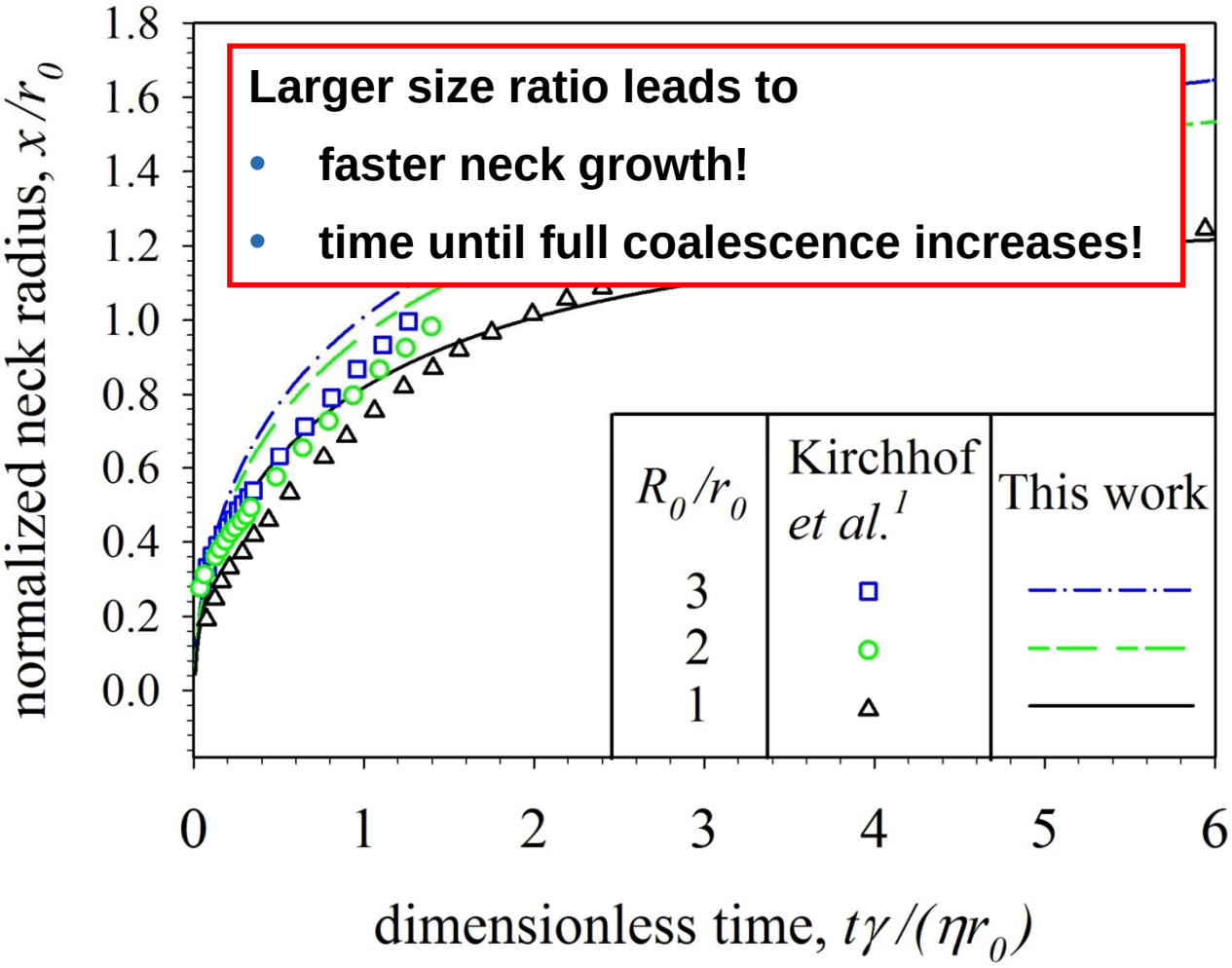
2-Particle Sintering – Arbitrary Size Ratio

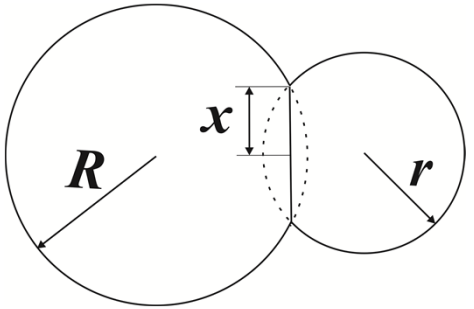


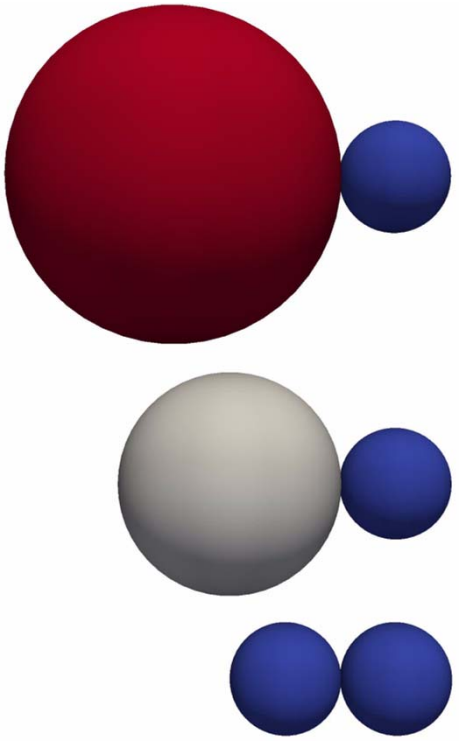
2-Particle Sintering – Arbitrary Size Ratio

Larger size ratio leads to

- **faster neck growth!**
- **time until full coalescence increases!**

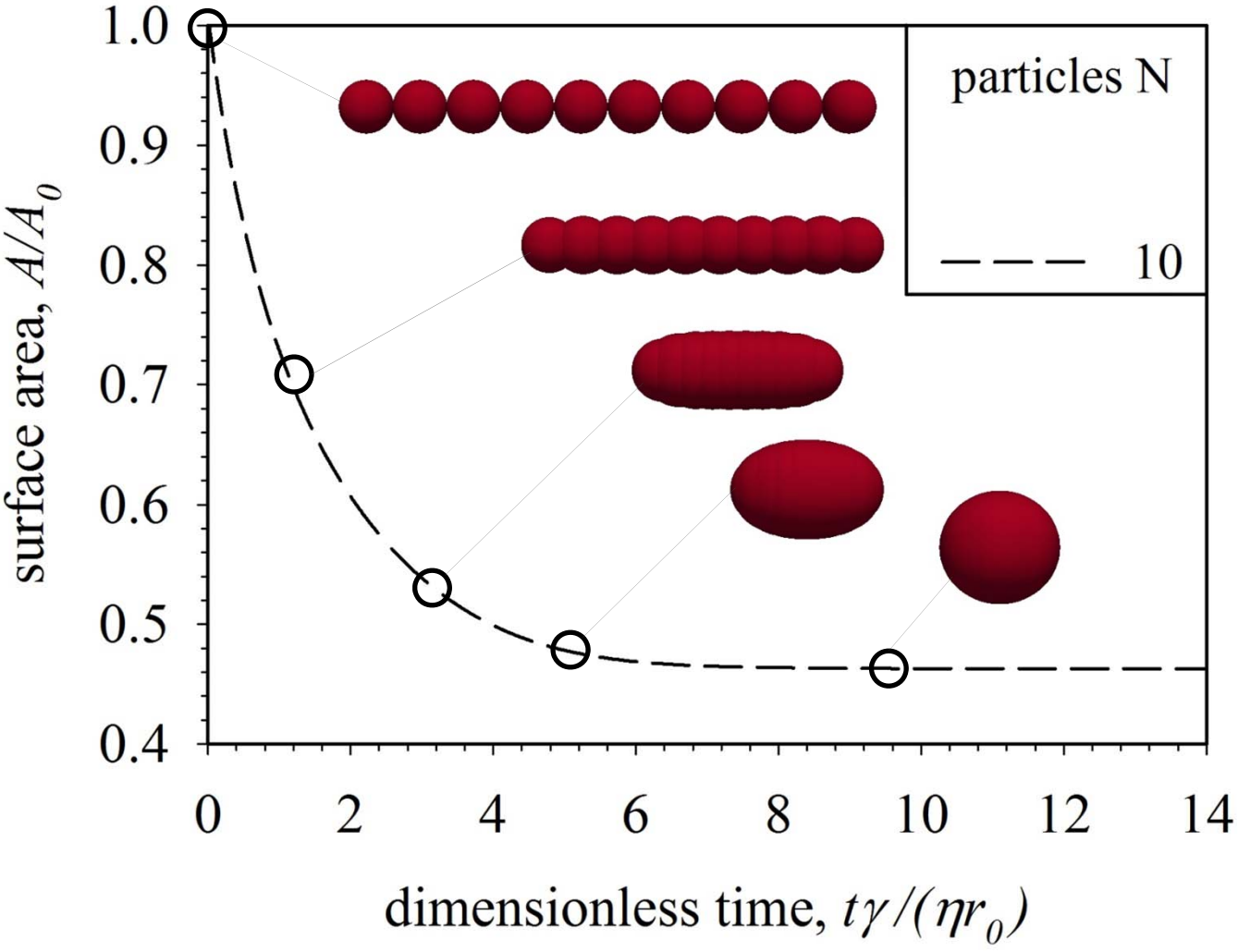




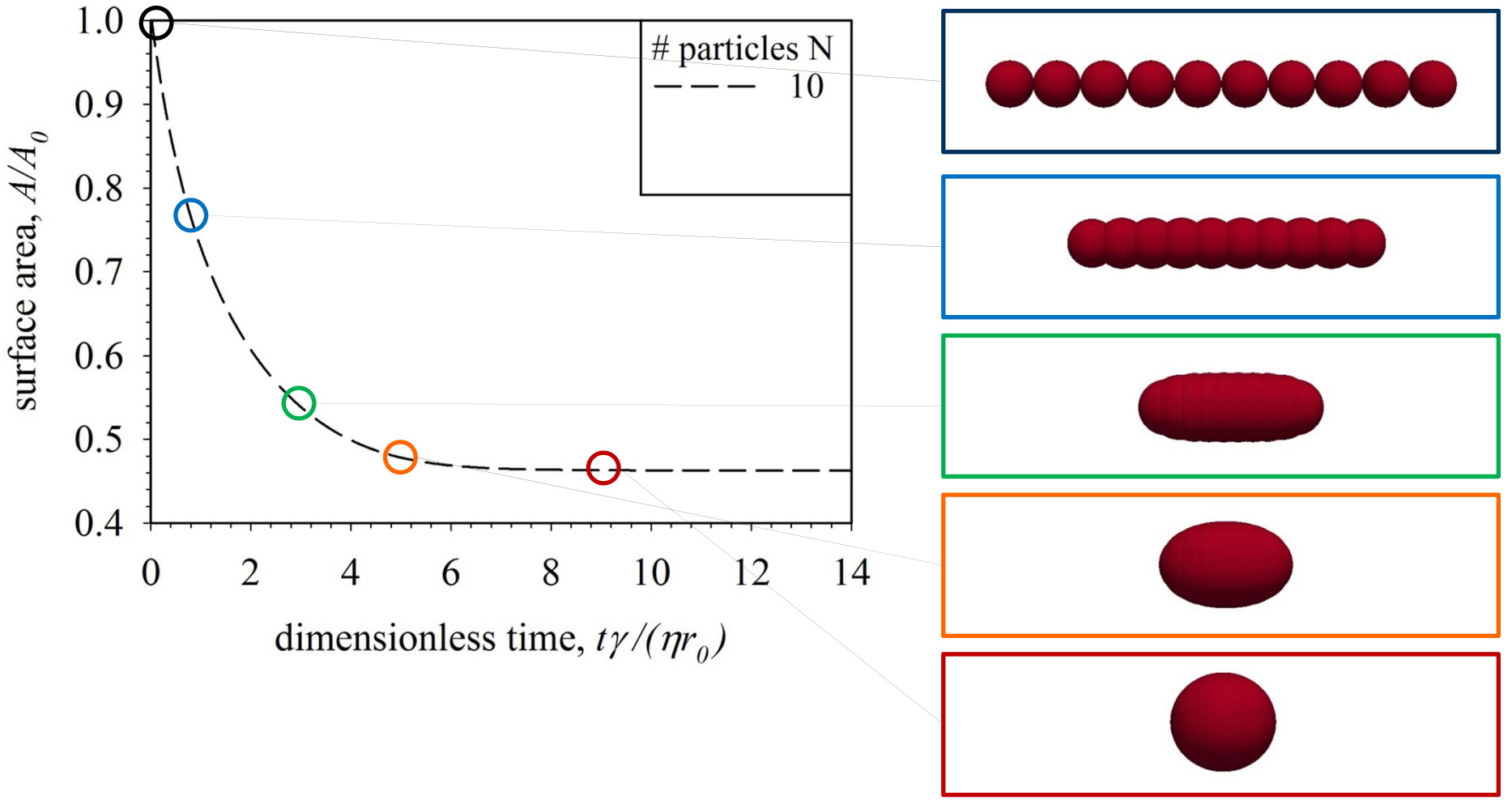


1. M.J. Kirchhof, H.J. Schmid & W. Peukert, *Phys. Rev.* E **80** (2009) 026319.

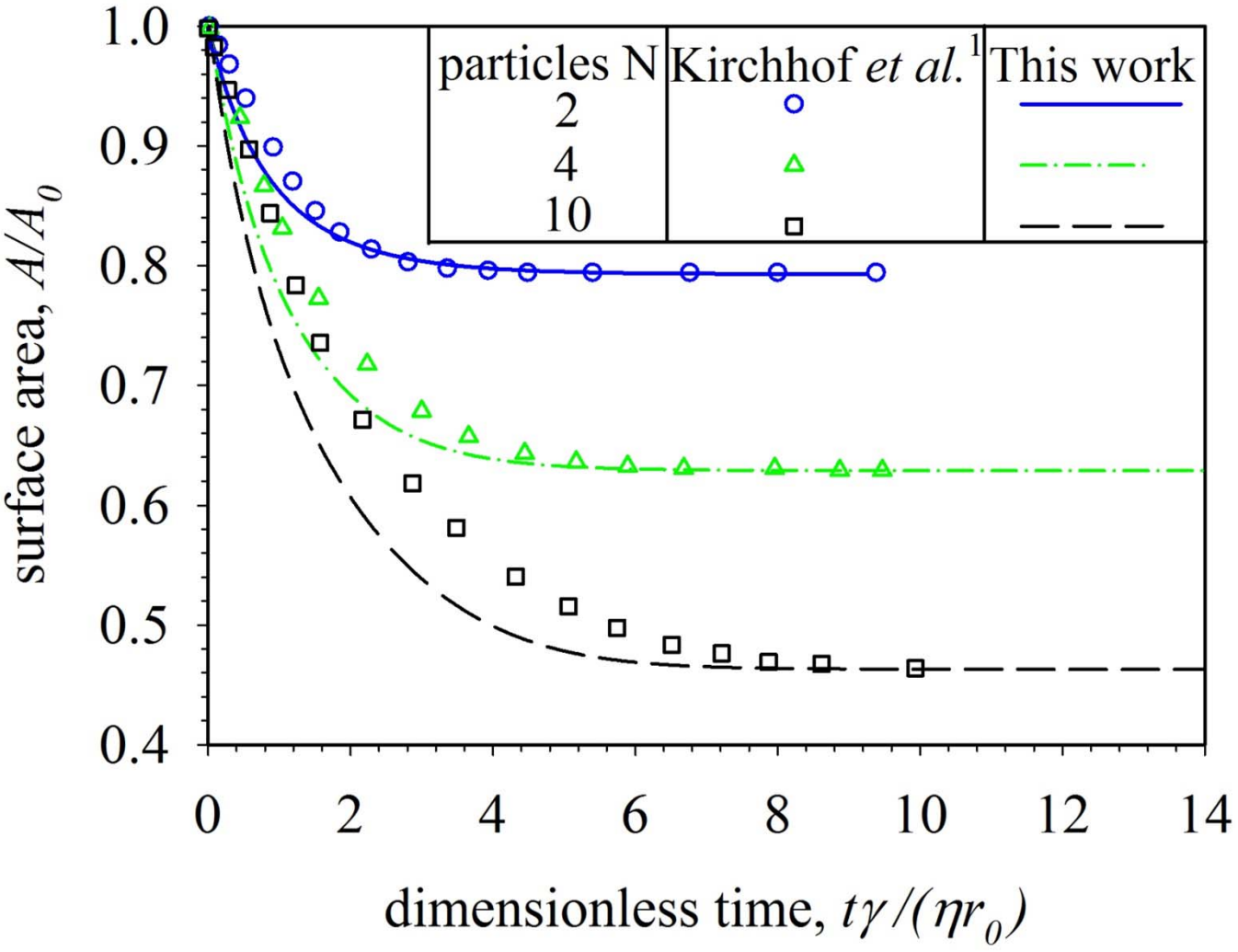
Multi-particle Sintering: Chain Aggregates of Equally Sized Pirmary Particles



Multi-particle Sintering: Chain Aggregates of Equally Sized Pirmary Particles

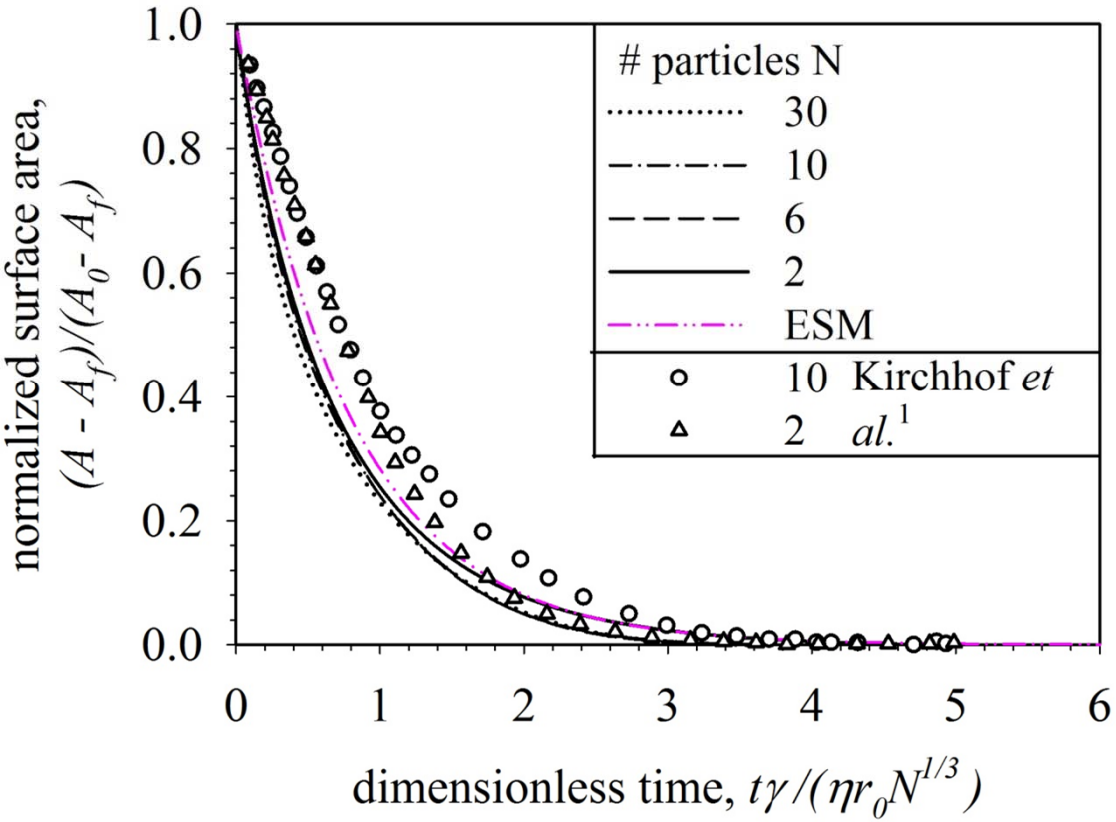


Multi-particle Sintering: Chain Aggregates of Equally Sized Pirmary Particles



1. M.J. Kirchhof, H.J. Schmid & W. Peukert, *Phys. Rev.* E **80**(2009) 026319.

Multi-particle Sintering: Chain Aggregates



- Scaling for chains[1]:

  Radius of coalesced sphere

$$r_f = N^{1/3} r_0$$

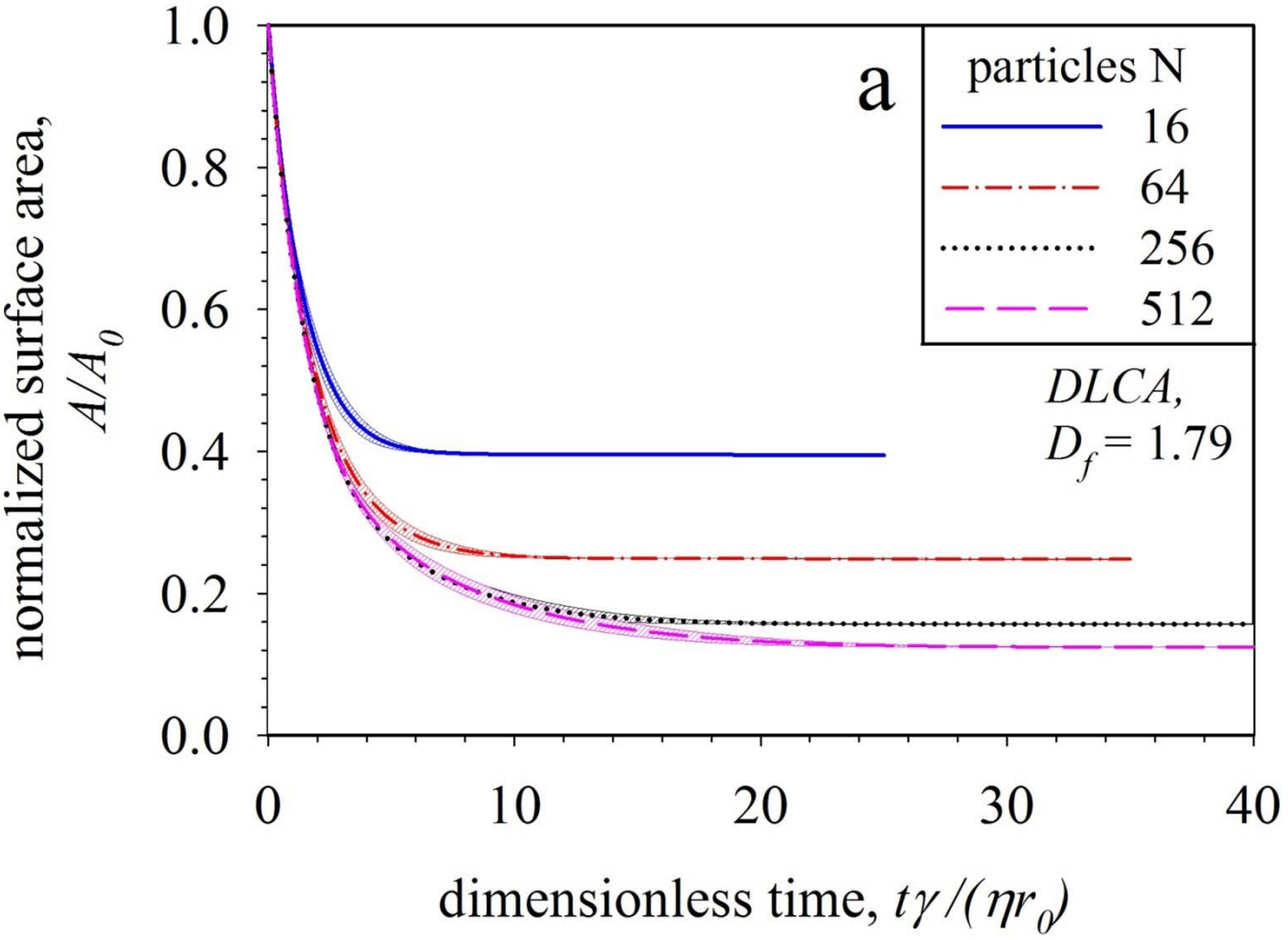
- ESM:

$$\tau_f = \frac{1}{2^{1/3}} \frac{\eta r_0}{\gamma} N^{1/3}$$

1. M.J. Kirchhof, H.J. Schmid & W. Peukert, *Phys. Rev.* E **80**(2009) 026319.

Multi-particle Sintering: Irregular Aggregates, D_f = 1.8

average over 50 aggregates



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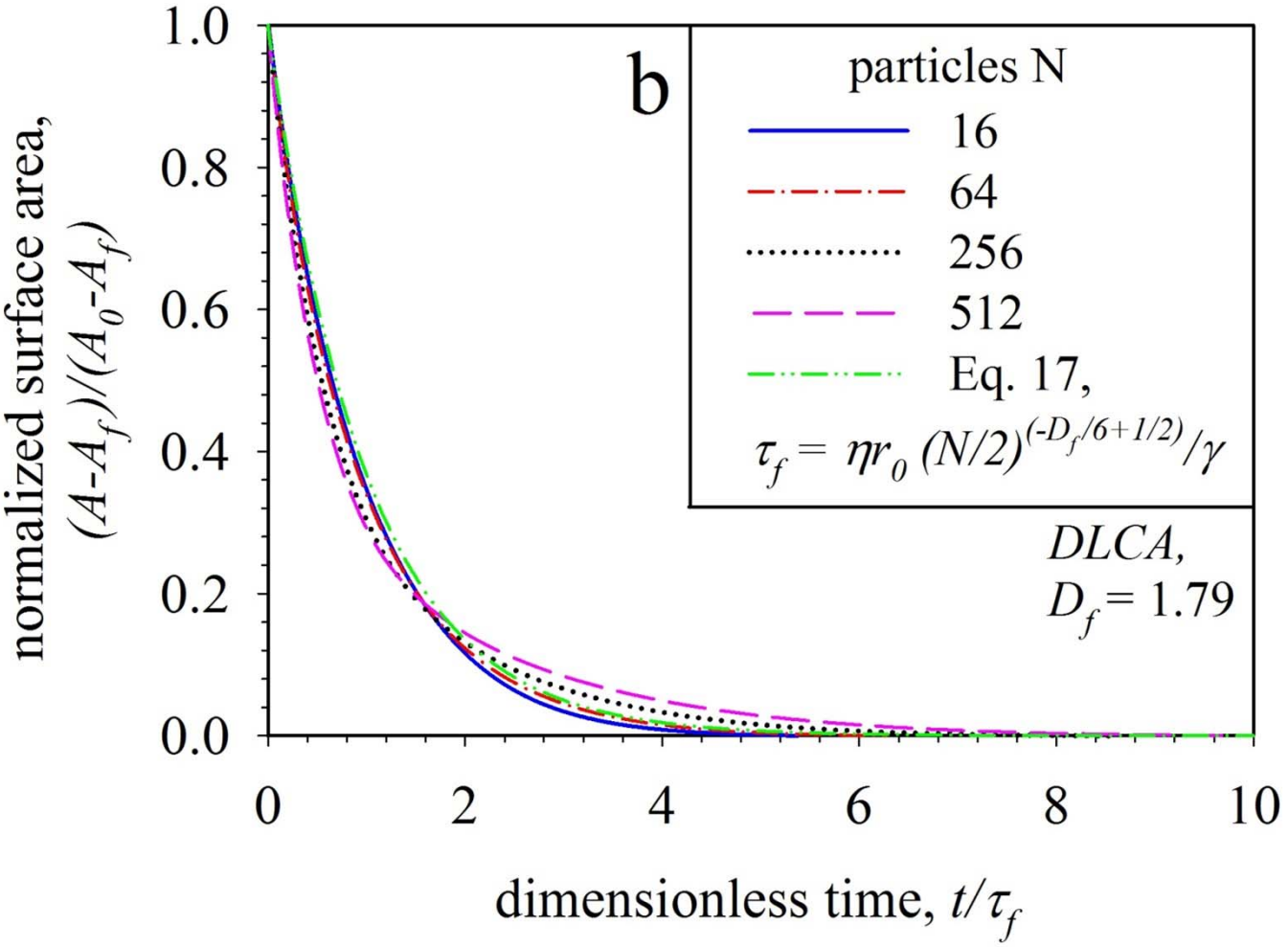

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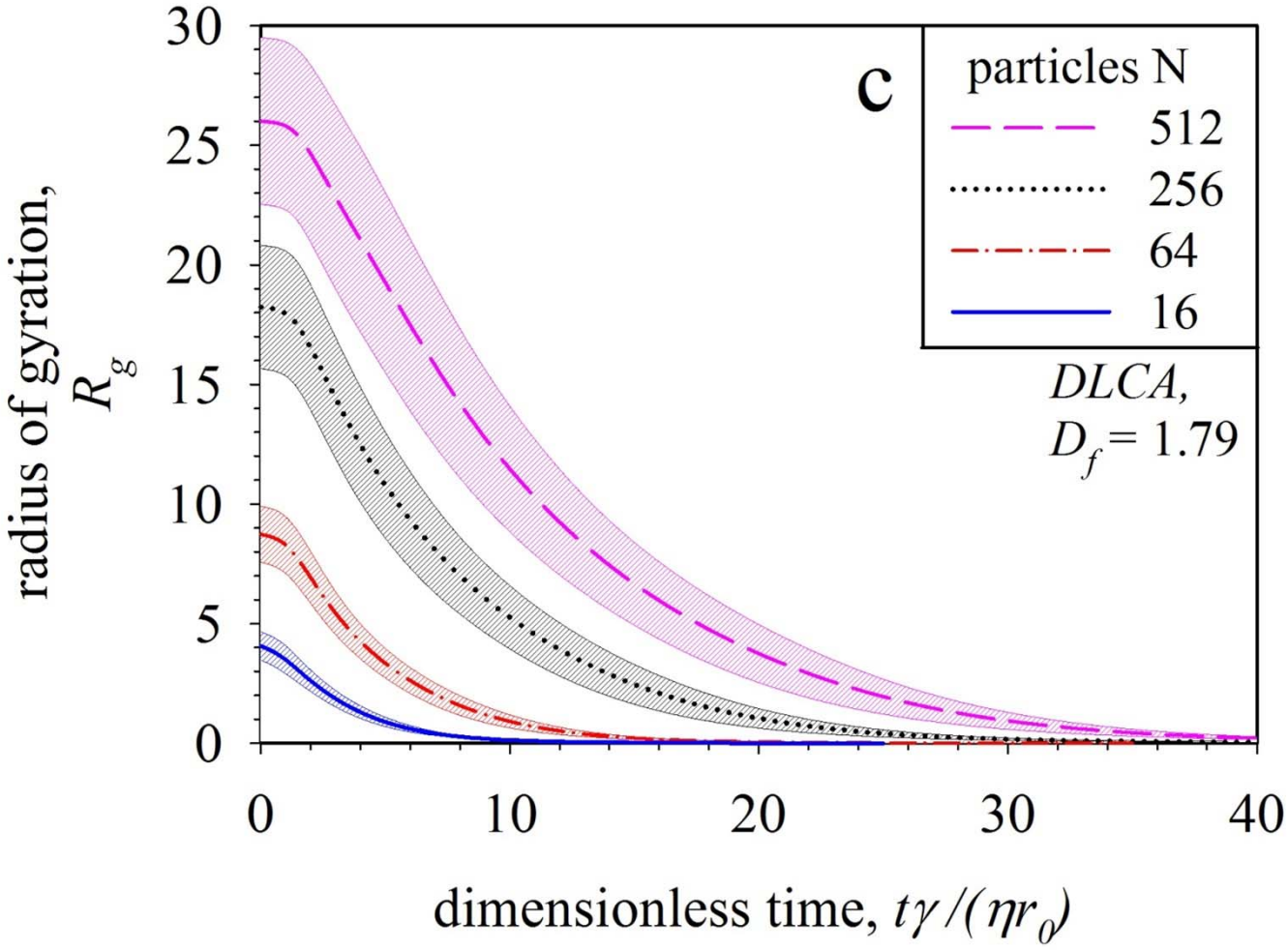
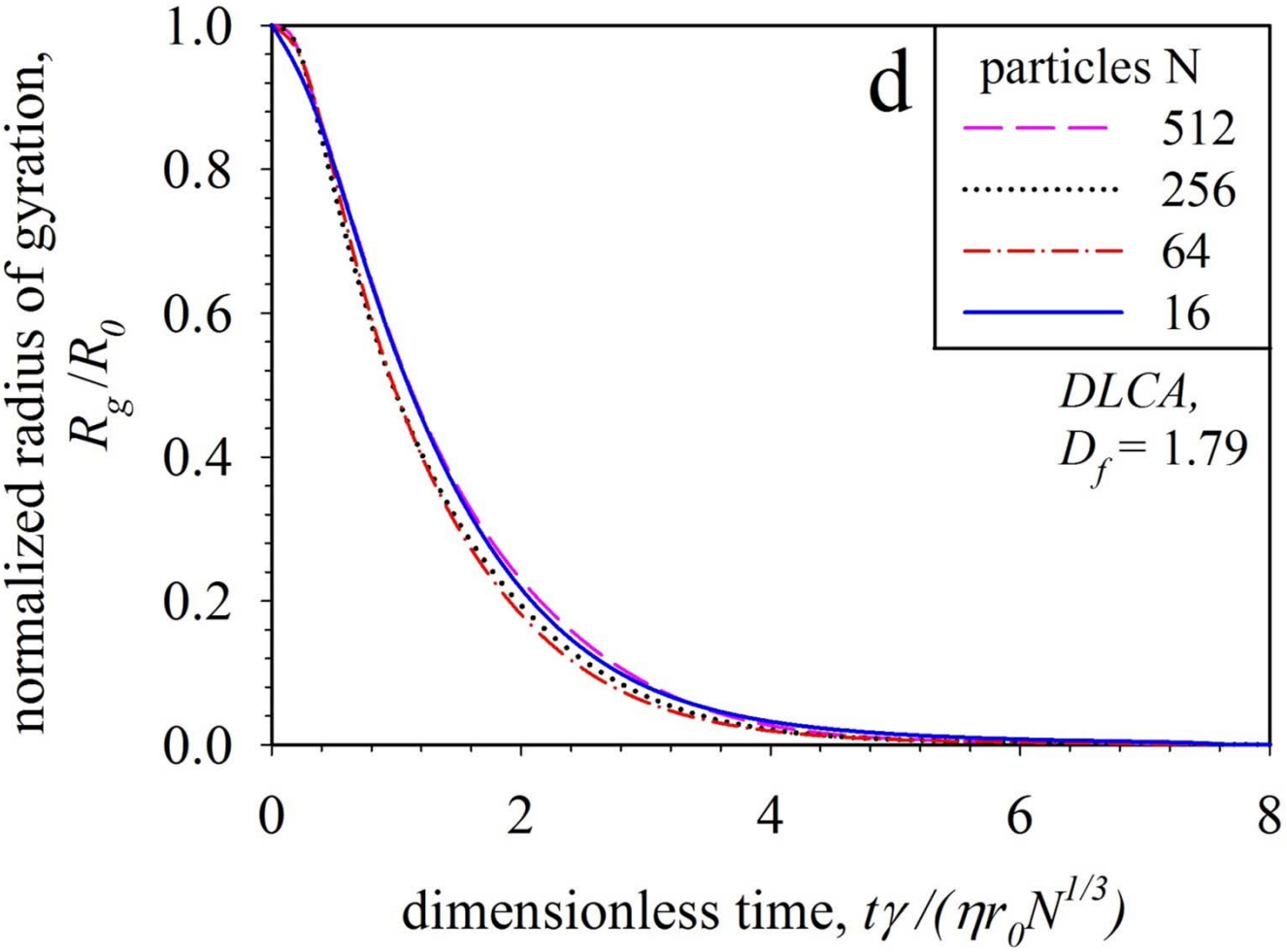


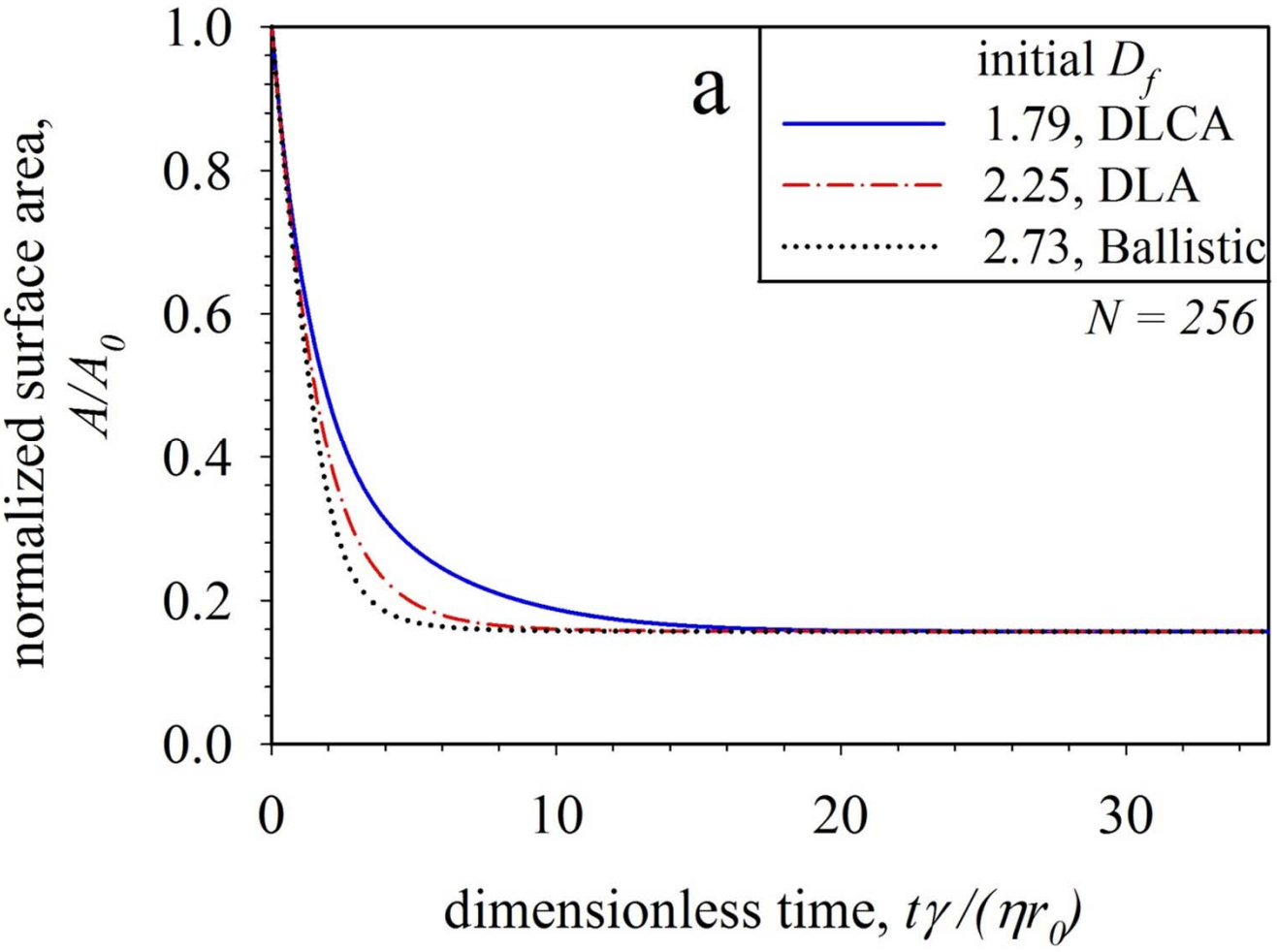
Multi-particle Sintering: Irregular Aggregates, D_f = 1.8

average over 50 aggregates



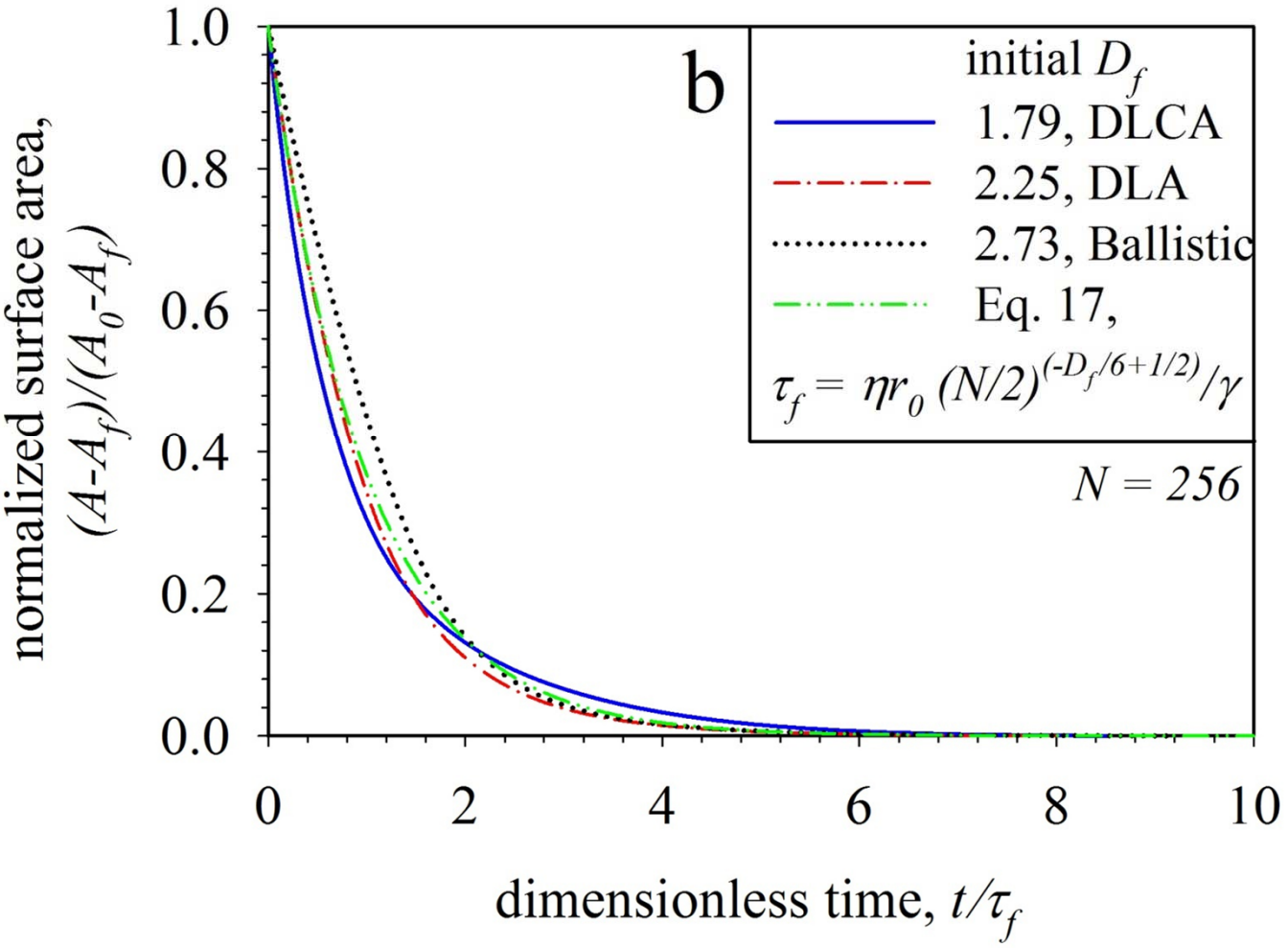
Multi-particle Sintering: Irregular Aggregates

average over 50 aggregates



Multi-particle Sintering: Irregular Aggregates

average over 50 aggregates



Multi-particle Sintering: Irregular Aggregates

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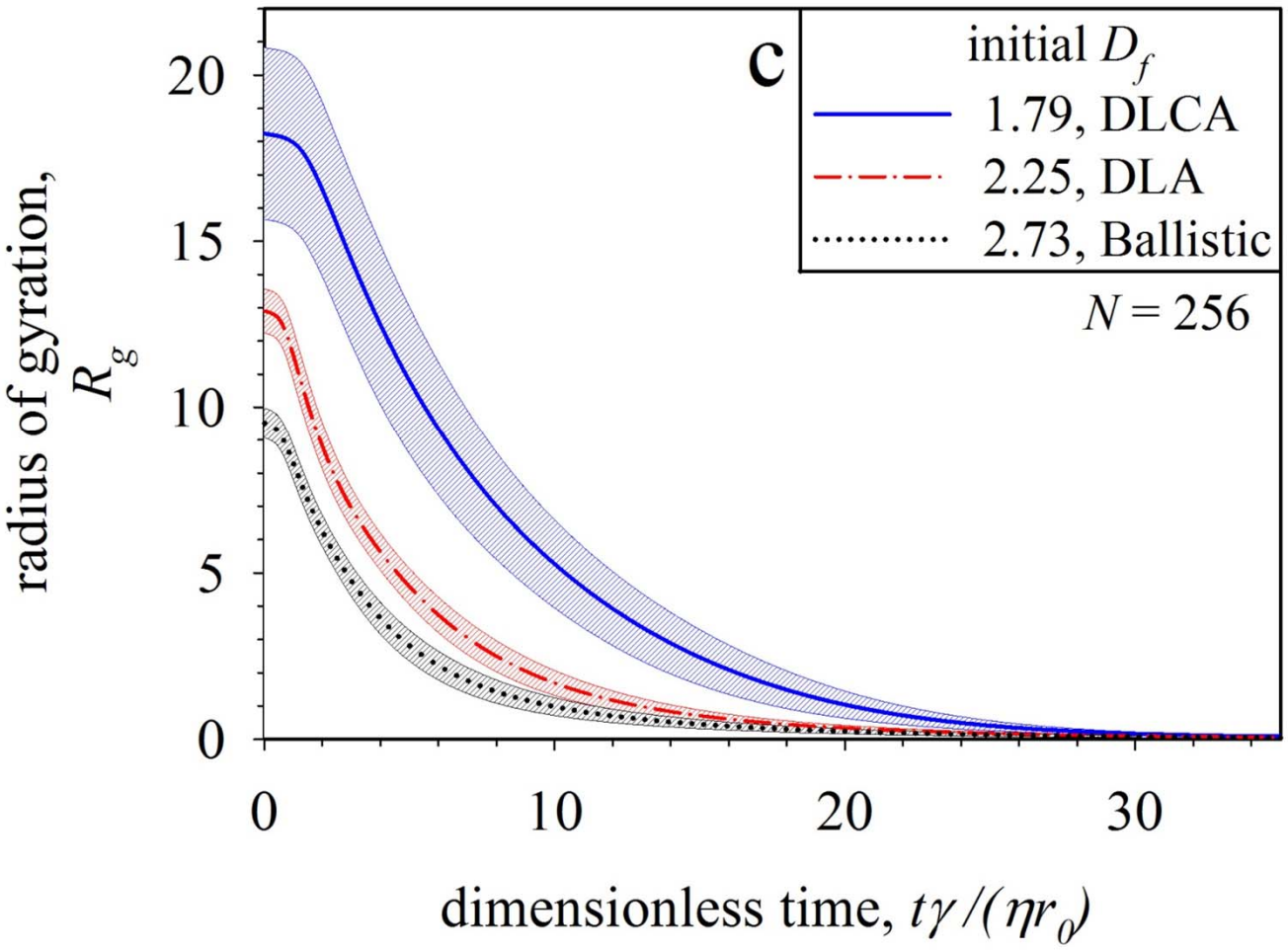
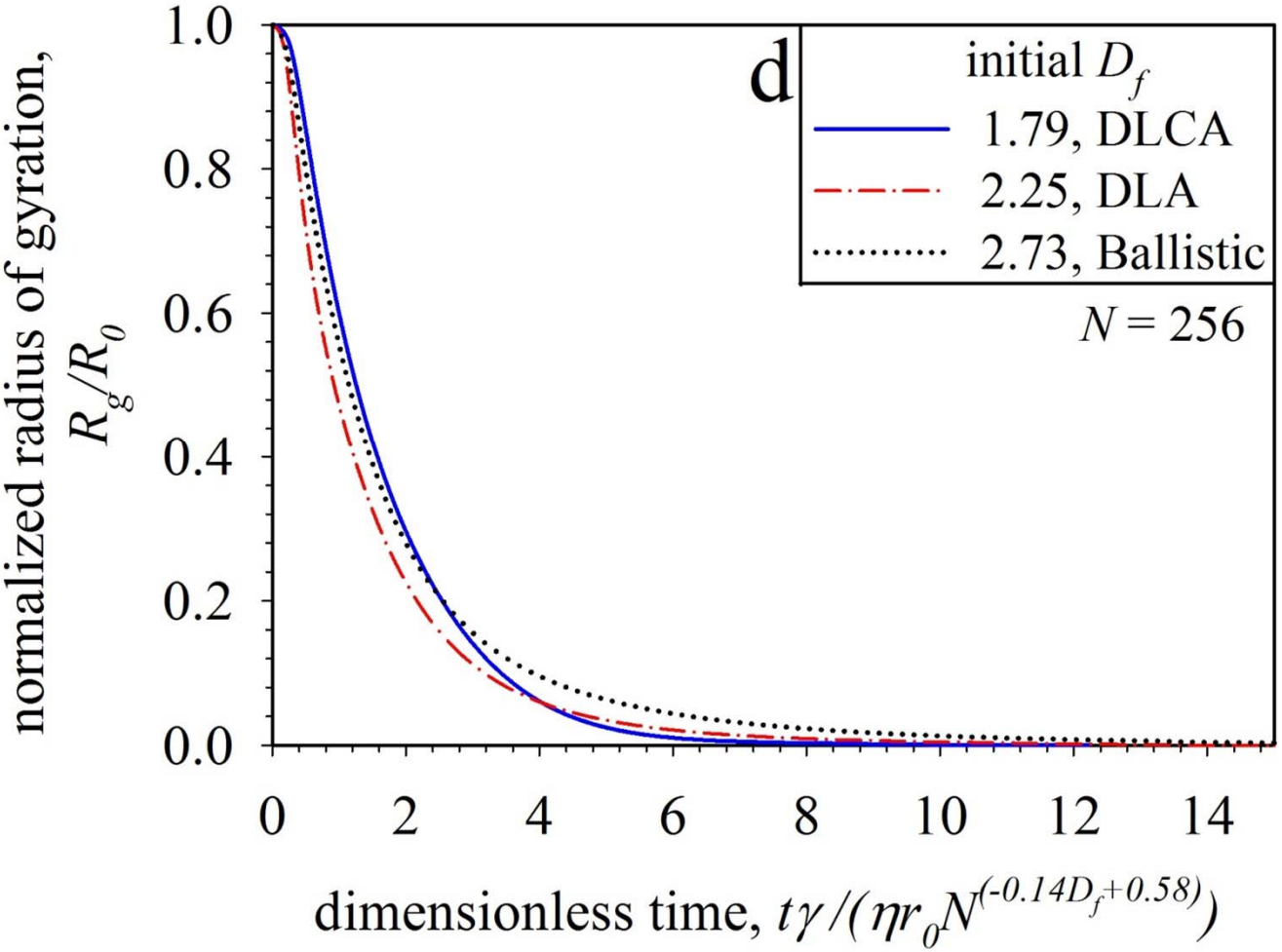


Multi-particle Sintering: Irregular Aggregates

average over 50 aggregates



Derivation for two equally sized particles …

$$\frac{dV}{dt} = \sum_i \frac{dV_i}{dt} = 0$$

$$\frac{dV_i}{dt} = \frac{\partial V_i}{\partial r_i} \cdot \frac{dr_i}{dt} - \frac{\partial V_i}{\partial x_i} \cdot \frac{dx_i}{dt} = 0$$

$$V_i = \frac{2}{3}\pi r_i^3 + \pi r_i^2 x_i - \frac{1}{3}\pi x_i^3$$

$$\frac{\partial V_i}{\partial x_i} = \pi\left(r_i^2 - x_i^2\right) = S_n$$

$$\frac{\partial V_i}{\partial r_i} = 2\pi\left(r_i^2 + r_i x_i\right) = S_i$$

$$\frac{dr_i}{dt} = \left(\frac{\partial V_i}{\partial x_i} \cdot \frac{dx_i}{dt}\right) / \frac{\partial V_i}{\partial r} = \frac{dx_i}{dt} \cdot \frac{S_n}{S_i}$$

$$\gamma \frac{dS_i}{dt} = \iiint 3\eta\dot{\varepsilon}^2 dV = 3\eta V \dot{\varepsilon}^2$$

$$\dot{\varepsilon} = \frac{1}{r_i}\frac{dx_i}{dt}$$

$$\frac{dS_i}{dt} = \frac{\partial S_i}{\partial r_i} \cdot \frac{dr_i}{dt} - \frac{\partial S_i}{\partial x_i} \cdot \frac{dx_i}{dt}$$

$$S_i = 4\pi r_i^2 - 2\pi r_i\left(r_i - x_i\right) = 2\pi r_i^2 + 2\pi r_i x_i$$

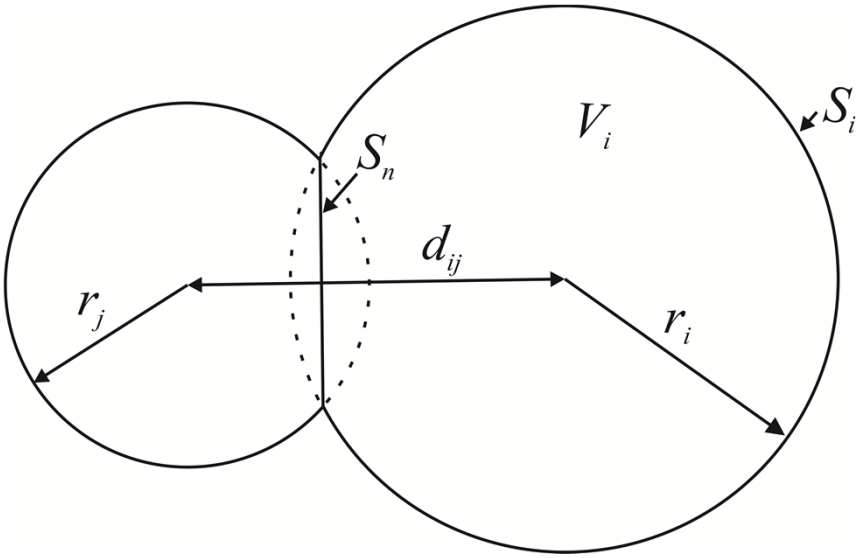
$$\frac{\partial S_i}{\partial x_i} = 2\pi r_i \qquad \text{and} \qquad \frac{\partial S_i}{\partial r_i} = 4\pi r_i + 2\pi x_i$$

$$\frac{dx_i}{dt} = \frac{\left(2\pi r_i - \left(4\pi r_i + 2\pi x_i\right)\frac{S_n}{S_i}\right)\gamma r_i^2}{3\eta V_i}$$

$$\frac{dr_i}{dt} = \frac{dx_i}{dt} \cdot \frac{S_n}{S_i}$$

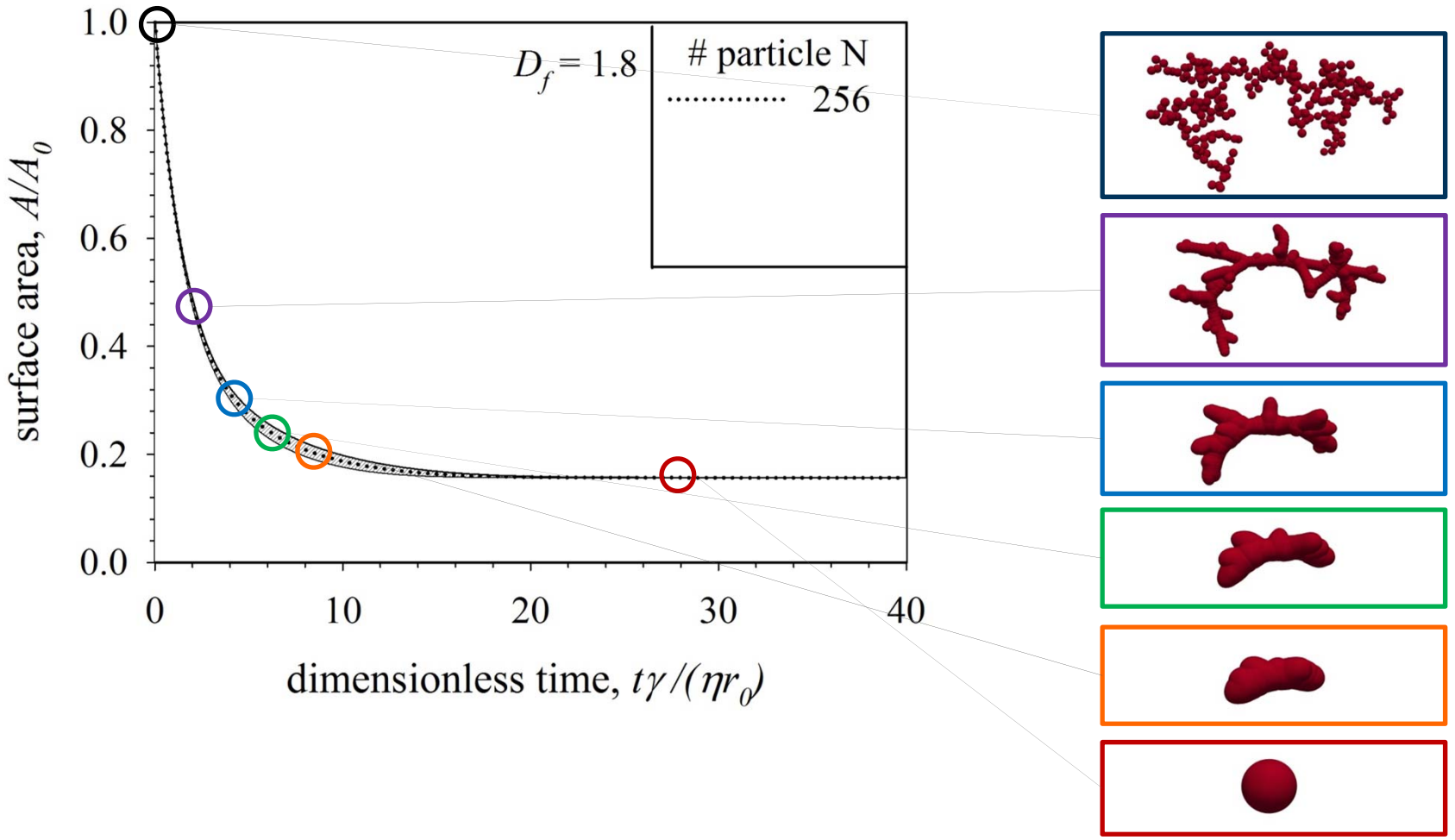
$$\frac{dd_{ij}}{dt} = \frac{2\pi\gamma r_i^2 d_{ij}\left(r_i\left(d_{ij} - x_i\right) - r_i r_j \cdot D_j - \left(2r_i d_{ij} + x_i d_{ij} - r_i^2\right)\cdot D_i\right)}{3\eta V_i\left(r_i \cdot D_i - r_j \cdot D_j + d_{ij} - x_i\right)^2}$$

$$\frac{dr_i}{dt} = D_i \cdot \frac{dd_{ij}}{dt}$$



Multi-particle Sintering: Irregular Aggregates, D_f = 1.8

Hierarchical cluster-cluster aggregation[1] – average over **50 aggregates**



1. R. Botet, R. Jullien, M. Kolb, *J. Phys. A* **17** (1984) L75-L79.

Evolution D_f = 1.8