The Effect of Primary Particle Polydispersity on the Morphology and Mobility Diameter of the Fractal Agglomerates in Different Flow Regimes

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Outline

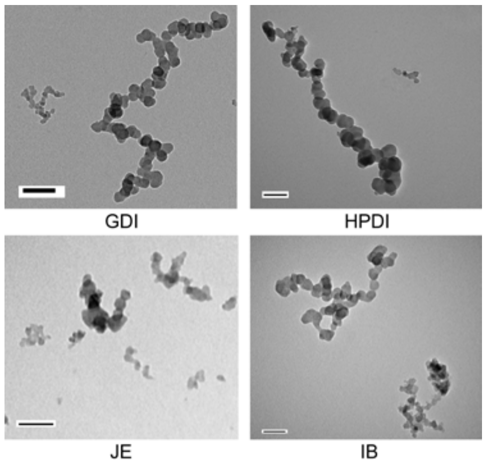
- Motivation
- Method
- Results
  - Morphology
  - Mobility Diameter in the Free Molecular Regime
  - Mobility Diameter in the Stokesian Regime
- Conclusion

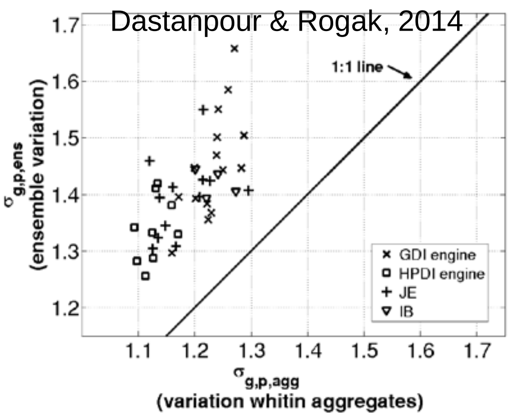
Motivation

- **Aerosol and colloidal agglomerates are formed in industrial and natural environments**
  - Production rate of synthetic particles
  - Aerosol residence time in atmosphere
  - Motion under different flow regimes
  - Size distribution and emission rate
- **Major assumptions:**
  - Spherical structure (Flagan 2008)
  - Fractal clusters BUT composed of monodisperse primary particles (Lall & Friedlander 2006)

Motivation

- **Soot particles are composed of poylispersed primary particles**

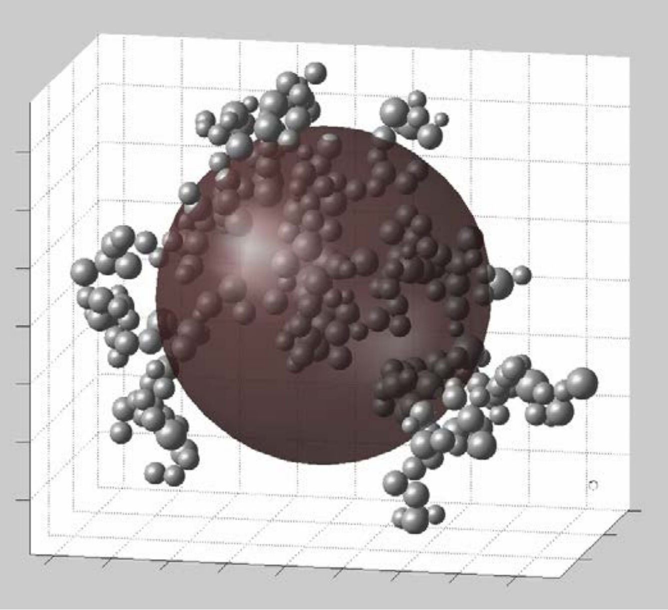




- **Effect of primary particle polydispersity**
  - Light absorption and scattering (RDG-FA) (Farias et al. 1996)
  - Fractal dimension (Eggersdorfer & Pratsinis 2012)
  - Mass, Surface area, Projected area, Gyration radius, Mobility diameter

Method

- **Particle generation (Eggersdorfer & Pratsinis)**
  - Hierarchical cluster-cluster agglomeration
  - Point-touching monomers
  - Number of the primary particles (N_p): 16, 32, 64, 128, 256, 512
  - Log-normal size distribution for primary particles
  - Geometric standard deviation of primary particle size (σ_g): 1.0, 1.2, 1.4, 1.6
  - 100 particles for each N_p and σ_g (2400 in total)



Method

- **Geometric parameters**
  - Gyration radius

$$R_g^2 = \frac{1}{N_p}\sum_{i=1}^{N_p}(a_{i-CM}^2 + R_i^2)$$

  - Mass-fractal dimension

$$N_\mathrm{p} = k_\mathrm{f}\left(\frac{R_\mathrm{g}}{R_\mathrm{pg}}\right)^{D_\mathrm{f}}$$

  - Surface area and mass

- **Free molecular regime**
  - Each particle was projected into 50 random orientations

$$d_\mathrm{m,FM} \cong \overline{d_\mathrm{a}} = 2\sqrt{\frac{\overline{a_\mathrm{a}}}{\pi}}$$

  - Rogak et al. 1993 as confirmed by Monte-Carlo momentum transfer simulations of Chan & Dahneke 1981; Mackowski 2006

Method

- **Continuum regime: Stokesian Dynamics**
  - Grand resistance matrix: Durlofsky et al. 1986 algorithm
  - Exact two-body resistance functions of unequal primary particles Jeffrey & Onishi 1984 and Kim & Karrila 2013

$$\begin{bmatrix} \overline{F_n} \\ \overline{T_n} \\ \overline{\overline{S_n}} \end{bmatrix} = \begin{bmatrix} A & \tilde{B} & \tilde{C} \\ B & C & \tilde{H} \\ G & H & M \end{bmatrix} \begin{bmatrix} \overline{U_n} - \overline{U^\infty} \\ \overline{\Omega_n} - \overline{\Omega^\infty} \\ -\overline{\overline{E^\infty}} \end{bmatrix}$$

$\overline{F_n}$, $\overline{T_n}$, and $\overline{\overline{S_n}}$ are the force, torque, and stresslet
$\overline{U}$, $\overline{\Omega}$, and $\overline{\overline{E}}$ are translational and angular velocities, and rate of strain tensor

$$A_{\alpha\beta} = 3\pi(a_\alpha + a_\beta)\hat{A}_{\alpha\beta}$$
$$B_{\alpha\beta} = \pi(a_\alpha + a_\beta)^2\hat{B}_{\alpha\beta}$$

$$\hat{A}_{ij} = X^A_{\alpha\beta} e_i e_j + Y^A_{\alpha\beta}(\delta_{ij} - e_i e_j)$$
$$\hat{B}_{ij} = Y^B_{\alpha\beta}\epsilon_{ijk} e_k$$

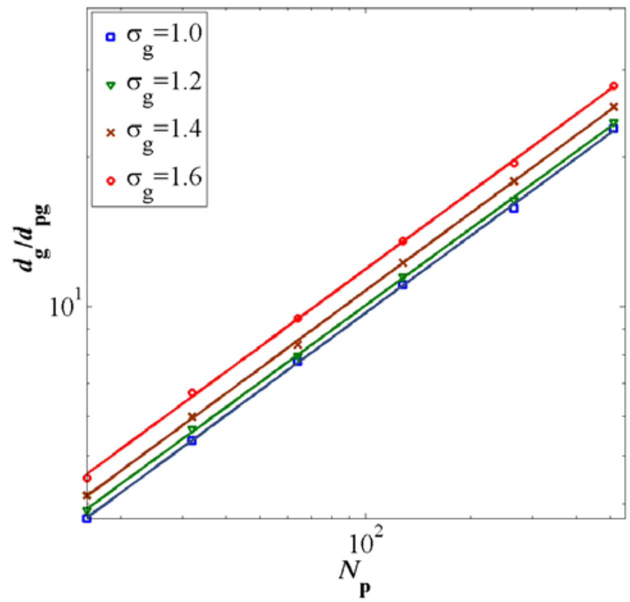
$$X^A_{11} = 6\pi a \sum_{k=0}^{\infty} f_{2k}(\gamma)\left(\frac{a}{2R}\right)^{2k}$$
$$X^A_{12} = -6\pi a \sum_{k=0}^{\infty} f_{2k+1}(\gamma)\left(\frac{a}{2R}\right)^{2k+1}$$
$$Y^B_{11} = 4\pi a^2 \sum_{k=0}^{\infty} f_{2k+1}(\gamma)\left(\frac{a}{2R}\right)^{2k+1}$$
$$Y^B_{12} = -4\pi a^2 \sum_{k=0}^{\infty} f_{2k}(\gamma)\left(\frac{a}{2R}\right)^{2k}$$

$$X^A_{\alpha\beta}(s,\lambda) = X^A_{(3-\alpha)(3-\beta)}(s,\lambda^{-1})$$
$$Y^A_{\alpha\beta}(s,\lambda) = Y^A_{(3-\alpha)(3-\beta)}(s,\lambda^{-1})$$
$$Y^B_{\alpha\beta}(s,\lambda) = -Y^B_{(3-\alpha)(3-\beta)}(s,\lambda^{-1})$$

$$R = |x_2 - x_1|$$
$$d = (x_2 - x_1)/R$$
$$\gamma = b/a$$

Results

- **Mass-Fractal dimension**
  - Fractal dimension decreased from 1.78 to 1.73 as primary particle polydispersity increased (consistent with Eggersdorfer & Pratsinis 2012)
- **Gyration radius**
  - 18% increase in R_{g} at σ_{g}=1.6



  - Fixed median diameter (d_{pg}):

$$\overline{d_{\mathrm{p}}} = d_{\mathrm{pg}} e^{0.5 \ln^2 \sigma_{\mathrm{g}}}$$ (Seinfeld & Pandis 2012)

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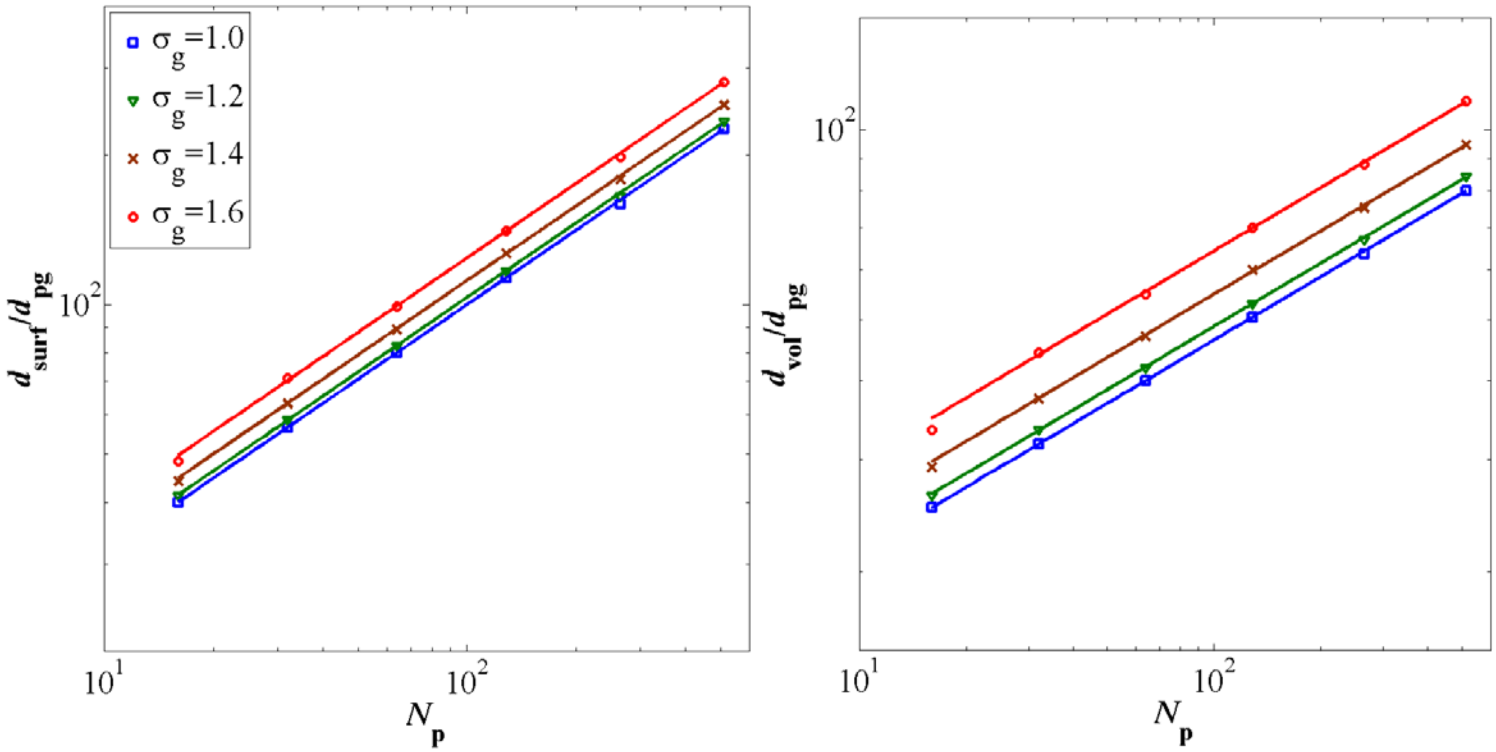
Results

- **Surface area and mass**



Results

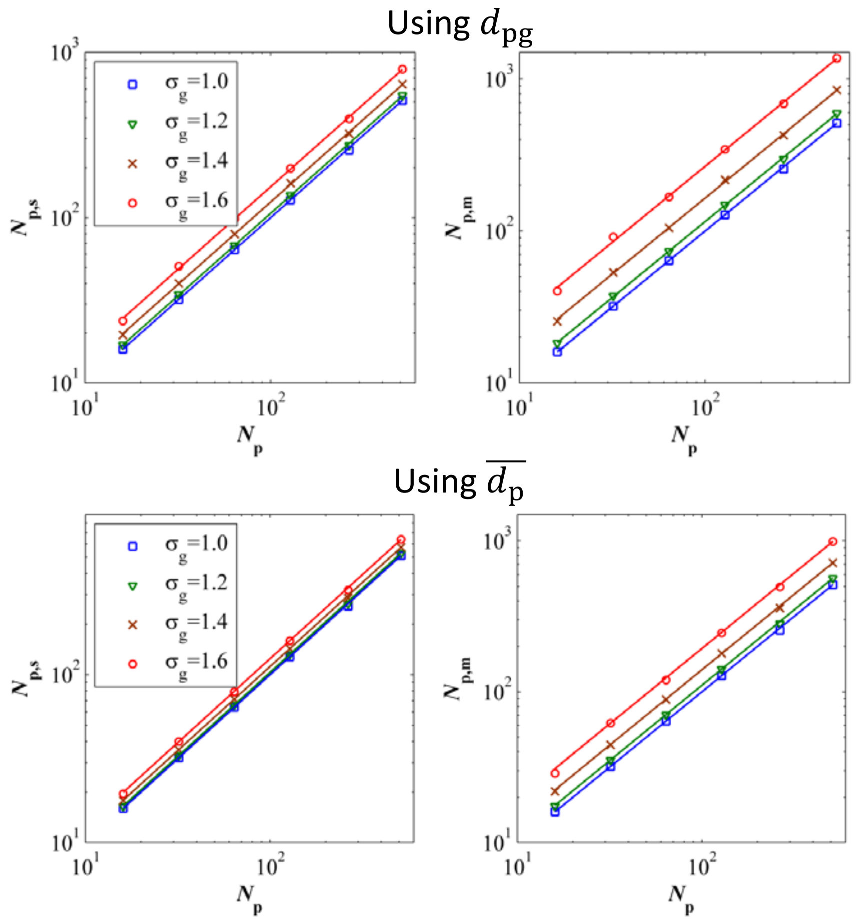
- **Surface area and mass**

$$m_{agg} = \frac{\pi}{6} \rho d_p^3 N_p$$

- Even a slight polydispersity (σ_g=1.2) results in 12-16% overestimation of N_p (compared to $N_{p,s}$)

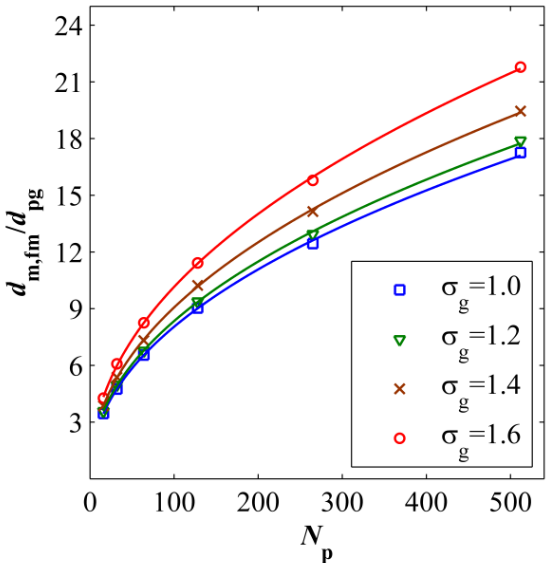
$$N_{p,m} = (0.82 + 0.18\, \sigma_g^{6.28})\, N_p$$

$$N_{p,s} = (1 + 0.06\, \sigma_g^{5.08})\, N_p$$



Results

- **Free molecular regime mobility diameter**
  - 50 random projections
  - Hit-or-miss scanning algorithm



$$d_{\mathrm{m,fm}} = d_A = k_{\mathrm{m,fm}}\, d_{\mathrm{pg}}\, N_{\mathrm{p}}^{D_{\mathrm{m,FM}}}$$

σ_g	$D_{m,fm}$	$k_{m,fm}$
1.0	0.46	0.970 (±0.011)
1.2	0.46	1.006 (±0.010)
1.4	0.46	1.095 (±0.010)
1.6	0.46	1.226 (±0.012)

$k_{\mathrm{m,fm}}$ increases up to **26%** when σ_{g} reaches 1.6

➢ $\boldsymbol{d_{m,fm} = (0.94 + 0.03\,\sigma_g^{4.8})\, d_{pg}\, N_p^{0.46}}$

Sorensen 2011: $d_{\mathrm{m,fm}} = d_{\mathrm{p}}\, N_{\mathrm{p}}^{0.46}$, all N_{p}

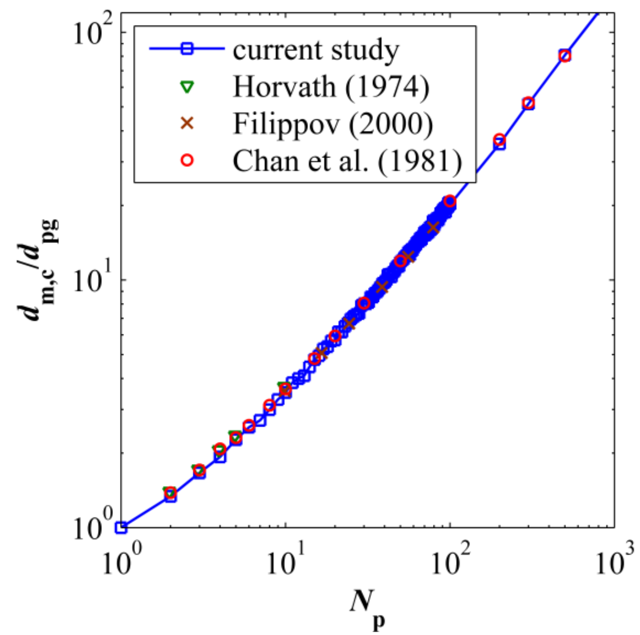
Results

▪ Continuum regime mobility diameter

- Doublets (SD compared to analytical solutions and LBM (Binder et al. 2006)

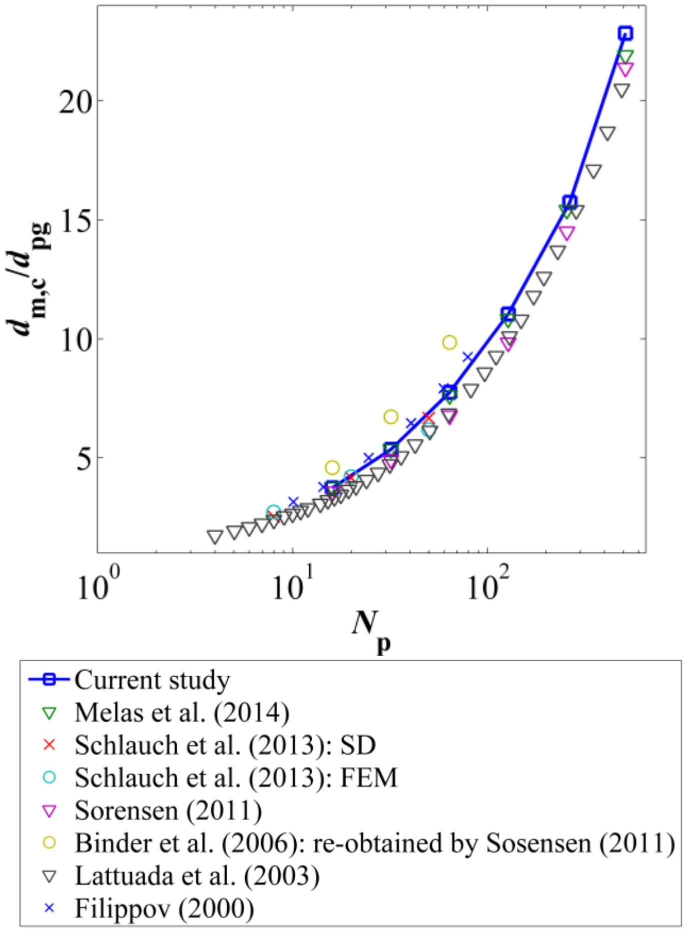
Flow	Normalized F_d	Binder et al. (2006)		Relative Difference (%)	
xyz	SD	Analytical	LBM	SD to Analytical	SD to LBM
001	1.23	1.29	1.27	-4.9	-3.3
101	1.33	1.36	1.36	-2.3	-2.3
100	1.43	1.43	1.4	0.0	2.1
111	1.37	1.36	1.35	0.7	1.5

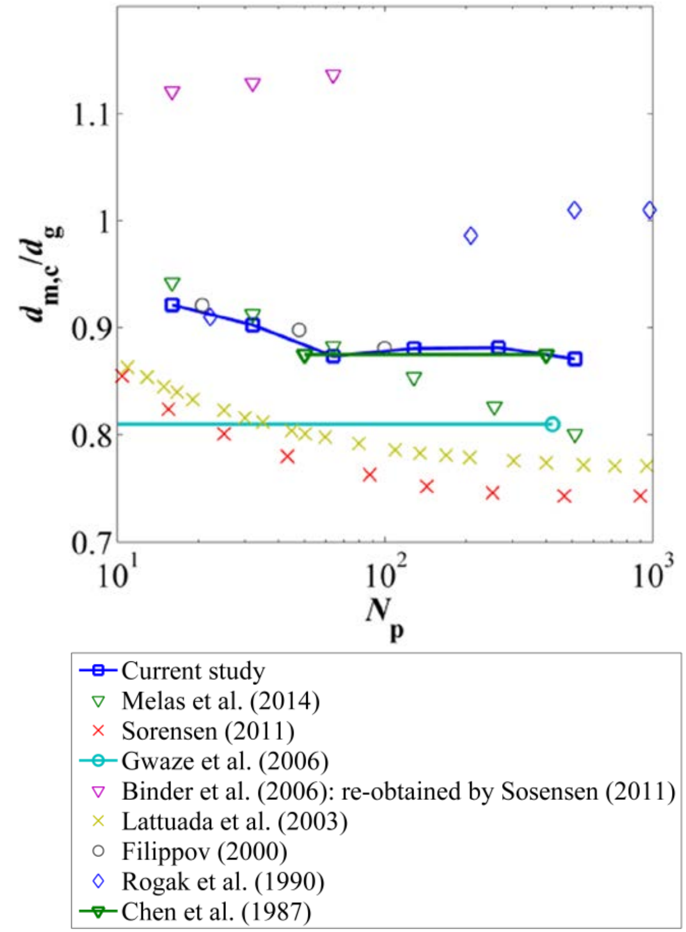
- Straight chains



Results

- <u>Continuum regime mobility diameter</u>





Results

- **Continuum regime mobility diameter**
  - 50 random orientations

$$d_{\mathrm{m,c}} = k_{\mathrm{m,c}}\, d_{\mathrm{pg}}\, N_{\mathrm{p}}^{D_{\mathrm{m,c}}}$$

σ_g	$D_{m,c}$	$k_{m,c}$
1.0	0.52	0.887 (±0.005)
1.2	0.52	0.917 (±0.004)
1.4	0.52	0.987 (±0.010)
1.6	0.52	1.086 (±0.005)

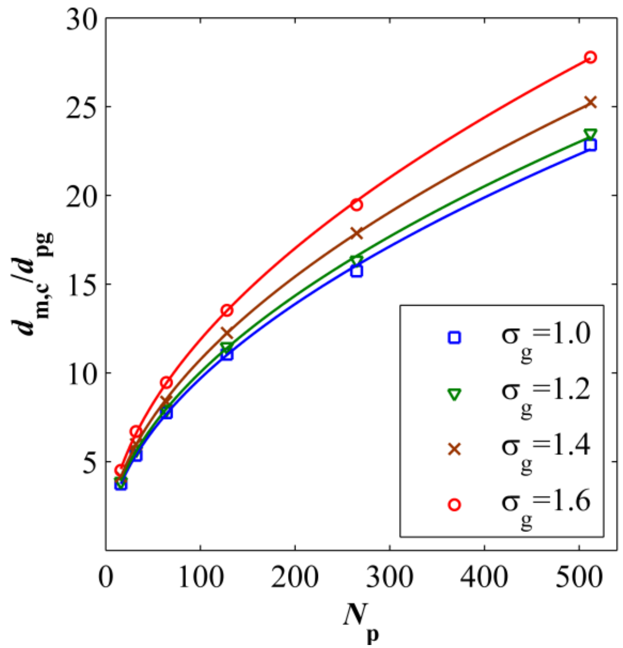
$k_{\mathrm{m,c}}$ increases up to **22%** when σ_g=1.6

➢ $\boldsymbol{d_{\mathrm{m,c}}} = (0.85 + 0.03\, \sigma_g^{4.4})\, d_{\mathrm{pg}}\, N_{\mathrm{p}}^{0.52}$

Sorensen 2011

$$d_{\mathrm{m,c}} = d_{\mathrm{p}}\, N_{\mathrm{p}}^{0.46}, N_{\mathrm{p}} < 100$$

$$d_{\mathrm{m,c}} = 0.65\, d_{\mathrm{p}}\, N_{\mathrm{p}}^{0.52}, N_{\mathrm{p}} > 100$$



- **$\beta = R_{\mathrm{m,c}}/R_g$ is approximately independent of primary particle polydispersity in the continuum regime**

Conclusions

- **For a fixed N_p and d_pg, the physical size of the aggregate increases substantially with σ_g**
  - Arithmetic average primary particle size, surface area, total mass, Gyration radius
- **Mobility diameter of fractal agglomerates increase with σ_g**
  - Free molecular regime: ~26% for σ_g=1.6
  - Continuum regime: ~23% for σ_g=1.6
- **In the continuum regime, the ratio of $d_\mathrm{m,c}/d_\mathrm{g}$ is approximately independent of the primary particle polydispersity**
- **Nearly all of the changes in continuum mobility diameter are due to the change in radius of gyration**
- **Considerable variation of $d_\mathrm{m,c}/d_\mathrm{g}$ in the literature cannot all be ascribed to calculation or measurement error: different cluster aggregation mechanism yield different structures**