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Uncertainties in the Traditional 2D-TEM Characterisation of Carbon Nanoparticles

20th ETH-Conference on Combustion Generated Nanoparticles

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Outline

- Background
- Methodology
- Results
  - 2D TEM sensitivity to angle of projection
  - Comparison between 3D-TEM and standard 2D-TEM
- Conclusions

Why characterise soot nanoparticles?

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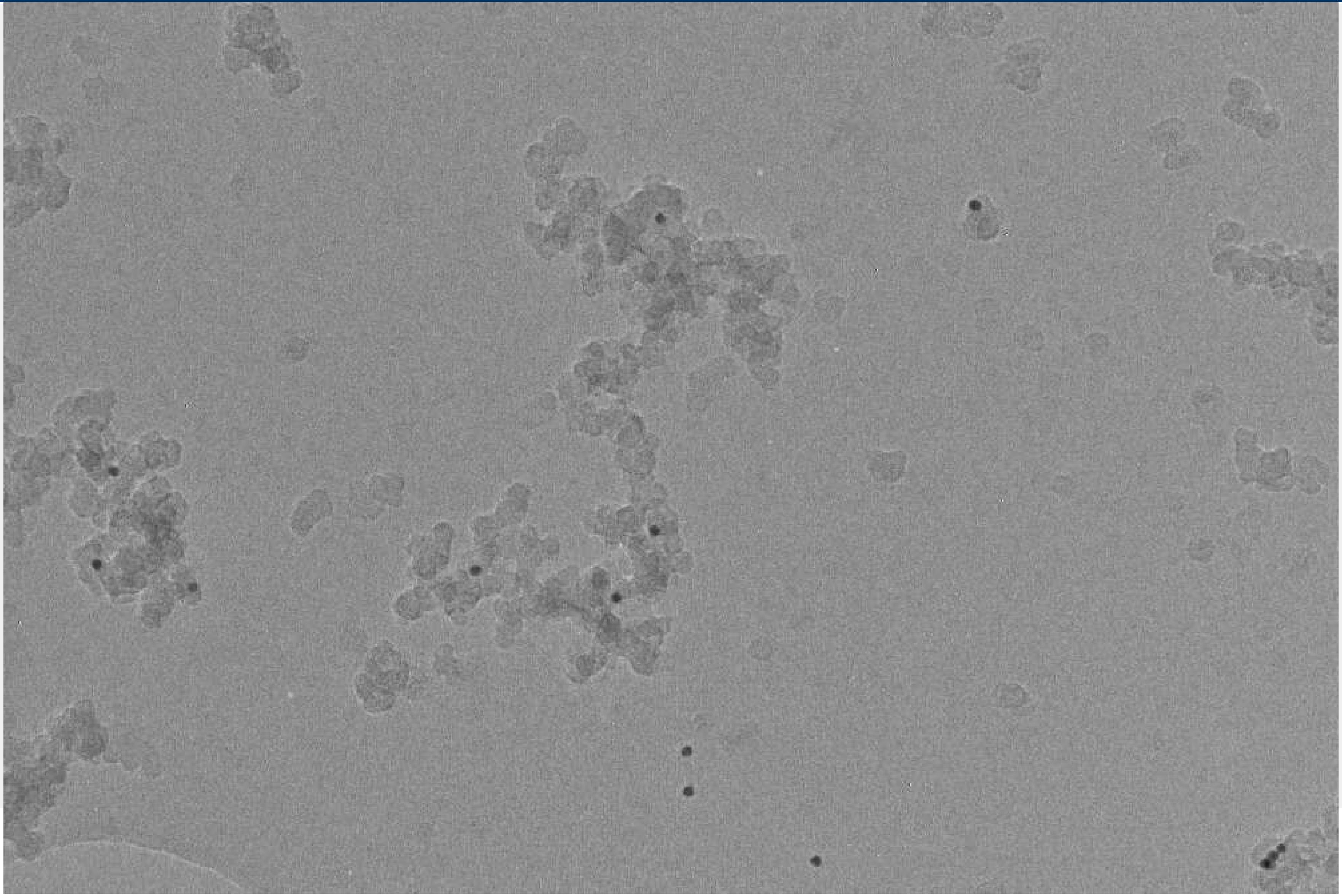
Automotive engines produce soot particles

- Harmful to human health
- Contribution to greenhouse effect
- Lubricant oil thickening (↓ efficiency, ↑ fuel consumption)
- Engine wear

Detailed characterisation needed

- Improved modelling/CFD study
  - Greater knowledge of soot formation and oxidation
- Minimising soot formation (engine & fuel design)
- Manage soot once formed (lubricants, particulate filters, etc.)

Traditional route: Characterising Parameters using TEM



Traditional route: Characterising Parameters using TEM

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Projected Area (A_{eff})

- Region of interest (ROI) selection
- Subjective due to low contrast
- Directly determines all other parameters

Mean Primary Particle Diameter (d_p)

- ROI selection
- Average of those clearly visible
- **Assumption**: All PP spherical with constant diameter

Number of Primary Particles (N_p)

- $N_p = k_a \left(\frac{A_{eff}}{A_p}\right)^{\alpha}$
- A_p = primary particle cross section
- k_a = 1.15; α = 1.09
- Derived from simulation of flame-generated soot (variety of fuels and flame types)

Volume (V)

- $V = \frac{\pi {d_p}^3}{6} N_p$
- Simple multiple of primary particle volume

Surface Area (S_a)

- $S_a \approx N_p \pi {d_p}^2$
- Gross overestimation (internal surface area)
- Not often used

Radius of Gyration (R_g)

- Pixel based measurements
- $R_g = \sqrt{\frac{\sum_{i=1}^{n_{px}} {r_i}^2}{n_{px}}}$

Fractal Dimension (D_f)

- Box-counting method
- $D_f = \lim_{\varepsilon \to 0} \frac{log N(\varepsilon)}{log(^1/_\varepsilon)}$
- Obtained from plot of log(-ε) vs log(N)

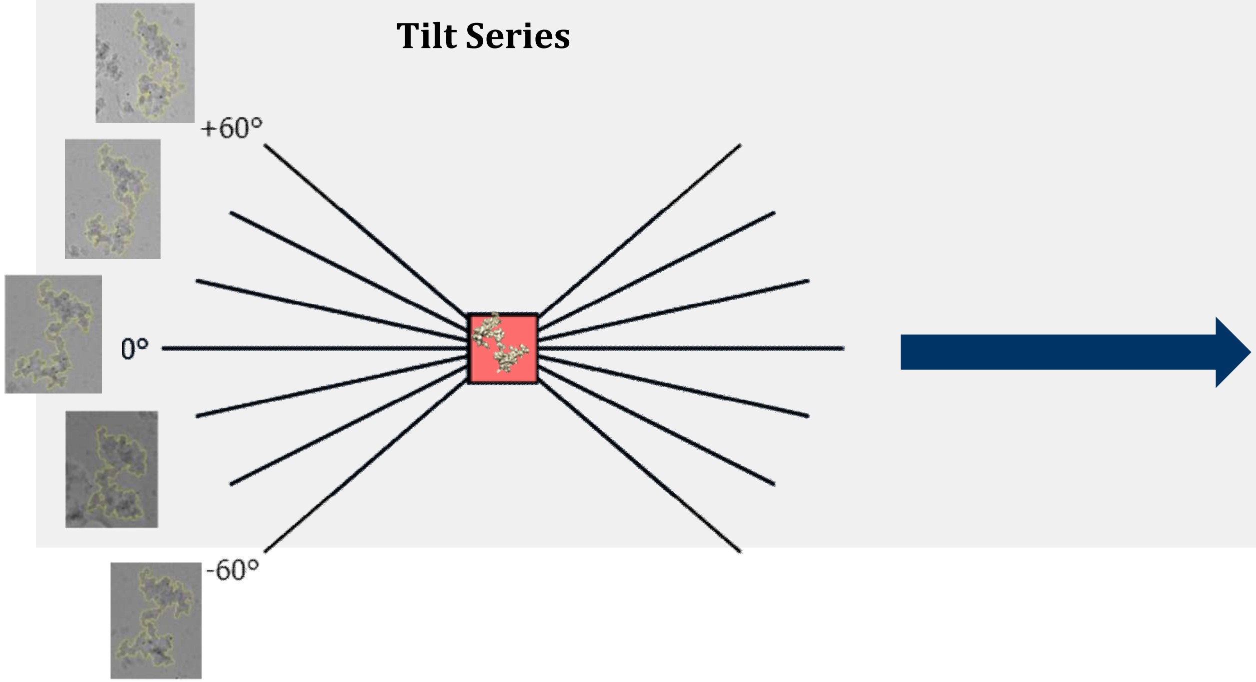
My PhD:
Is 3D Reconstruction an option?

Pros: Accurate reconstructions removes uncertainty associated with 2DTEM: corrections factors, 2D parameters

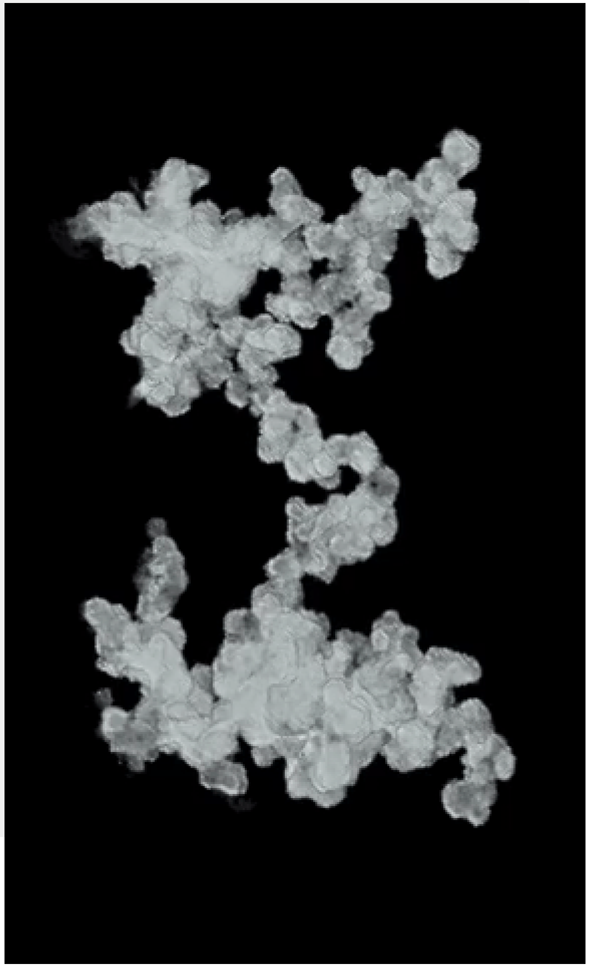
Cons: Time consuming & subjective segmentation. Models are known to be elongated – measured values have ill defined level of uncertainty

Fourier Slice Theorem: FT of full set of 2D projections contained information required to recreate particle in 3D

Tilt Series



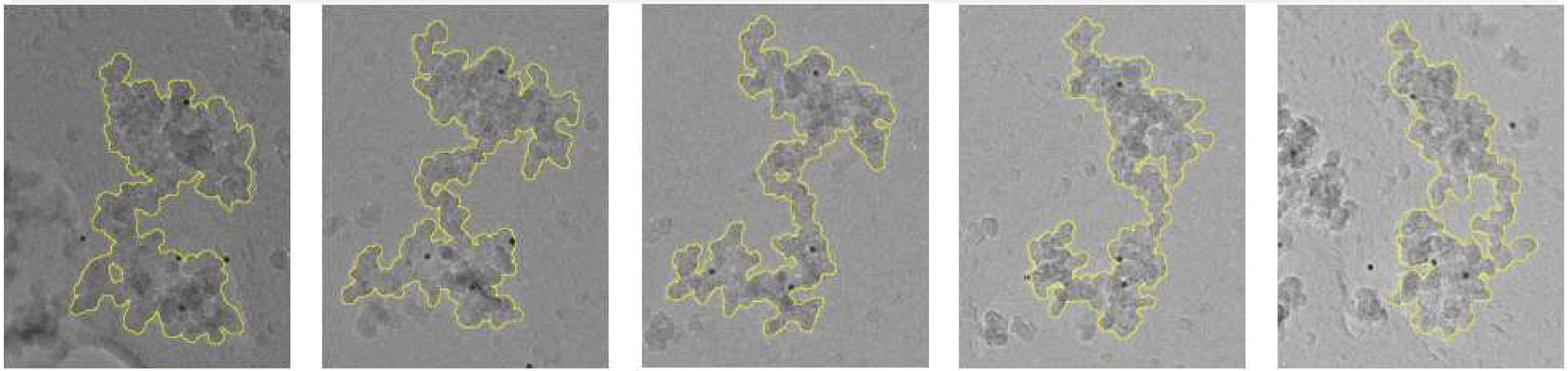
Reconstructed Particle



3D analysis indicates 2D-TEM is sensitive to angle of projection:

- Tilt-series provides us with >100 projections of the same particle
- Traditionally we only characterise particles from a single projection
- Particle showed significant differences in apparent morphology
- How much can parameters vary with angle of projection?

- An introductory investigation into uncertainty associated with single projection calculations



-60° **-28°** **0°** **+28°** **+60°**

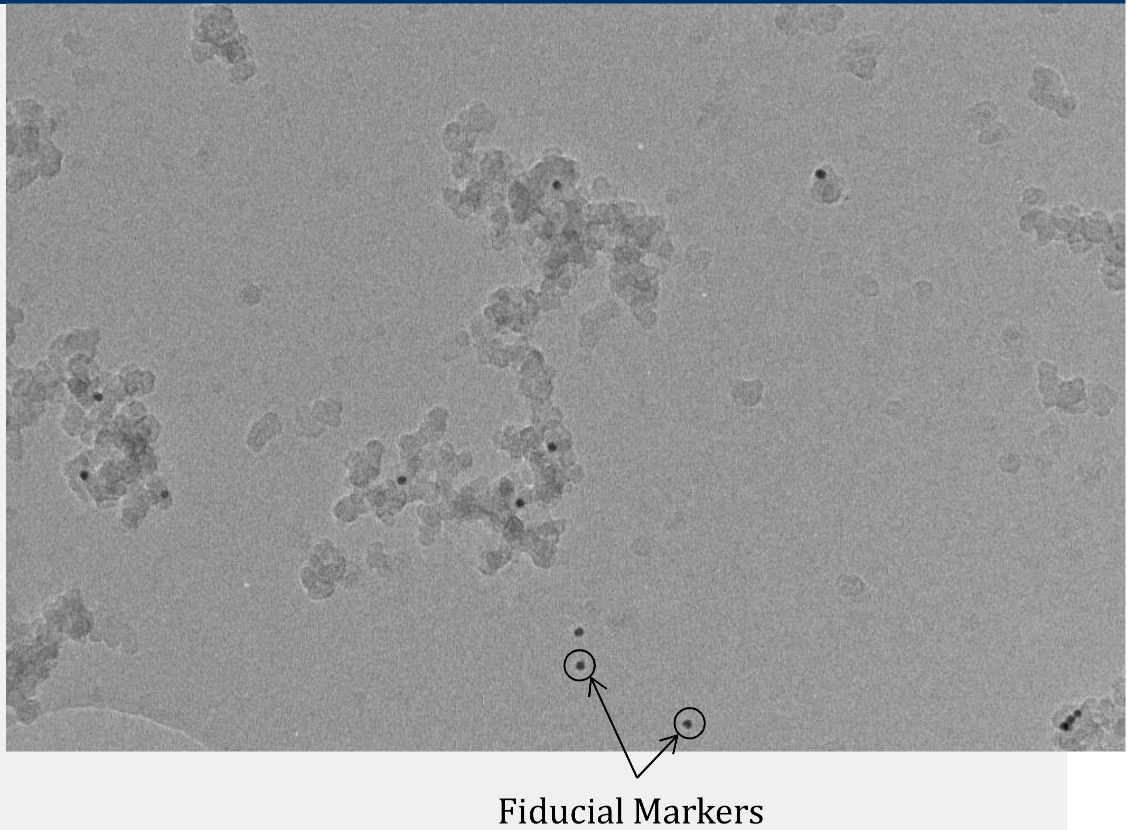
2D-TEM & Uncertainties: Literature

- Correlating 2D with 3D results using semi-empirical simulations (number of primary particles, fractal dimension, surface area)[1-3]
  - 3D-D_f on average 10-20% > 2D-derived D_f [3]
- Effect of operator experience [4]
- Number of particles needed for convergence of means [4]
- References to orientation of particles
  - "variations of up to 20% for the D_f when analyzing in different orientations" [5]
  - Adachi's 3D study of soot considered orientation of 3D model

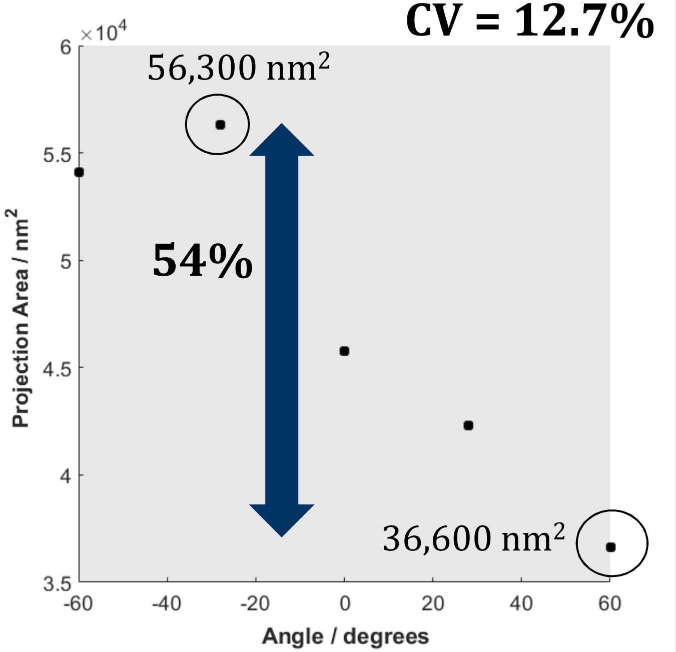
[1] U.O. Koylu, G.M. Faeth, Combust. Flame 89 (1992) 140–156.
[2] B. Hu, B. Yang, U.O. Koylu, Combust. Flame 134 (2003) 93–106.
[3] S.N. Rogak, R.C. Flagan, Part. Part. Syst. Charact. 9 (1992) 19-27
[4] K. Kondo, T. Aizawa, SAE Technical Paper 2013-01-0908, 2013
[5] M. Wentzel, H. Gorzawski, K.H. Naumann, H. Saathoff, S. Weinbruch, Aerosol Sci. 34 (2003) 1347-1370
[6] K. Adachi, S.H. Chung, H. Friedrich, P.R. Buseck, J. Geophys. Res. 112 (2007)

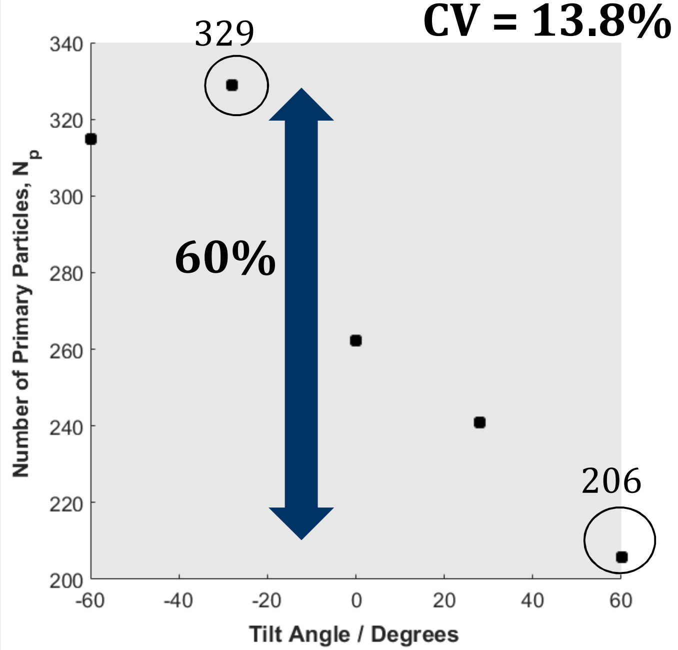
Methodology

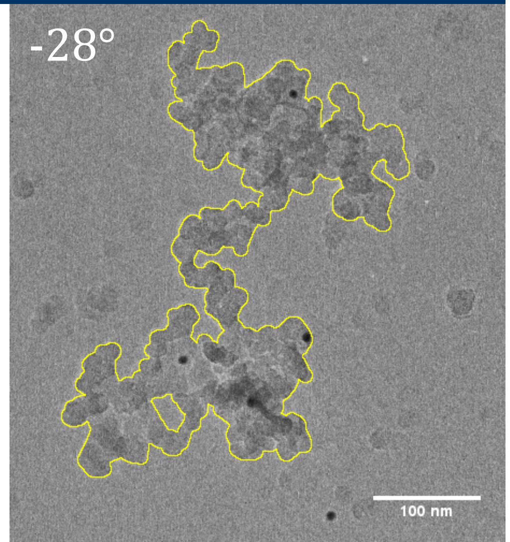
- Images captured using JEOL 2100F TEM equipped with a Gatan Orius CCD camera operating at 200 kV
- Flame-generated soot deposited onto a graphene oxide support film
- High contrast gold nanoparticles added for alignment of images (spherical with diameter = 10 nm)
- TEM images were captured every 1° over a ±60° range (121 images in total)

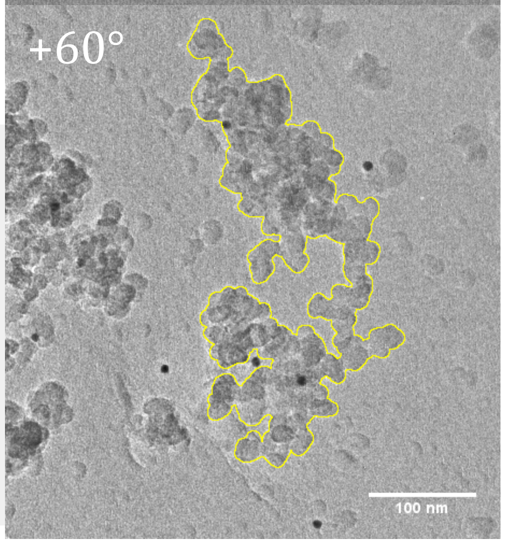


Sensitivity of A_{eff} & Np to angle of projection









Projected Area

- Results over significant range
- Maximum 54% > minimum
- CV = (SD/mean) x 100
- Projected area particularly sensitive to angle of projection

Np, Volume, Surface Area

- Identical variation (V & S_a both derived from N_p)
- Similarly sensitive to angle of projection

Sensitivity of Radius of Gyration to angle of projection

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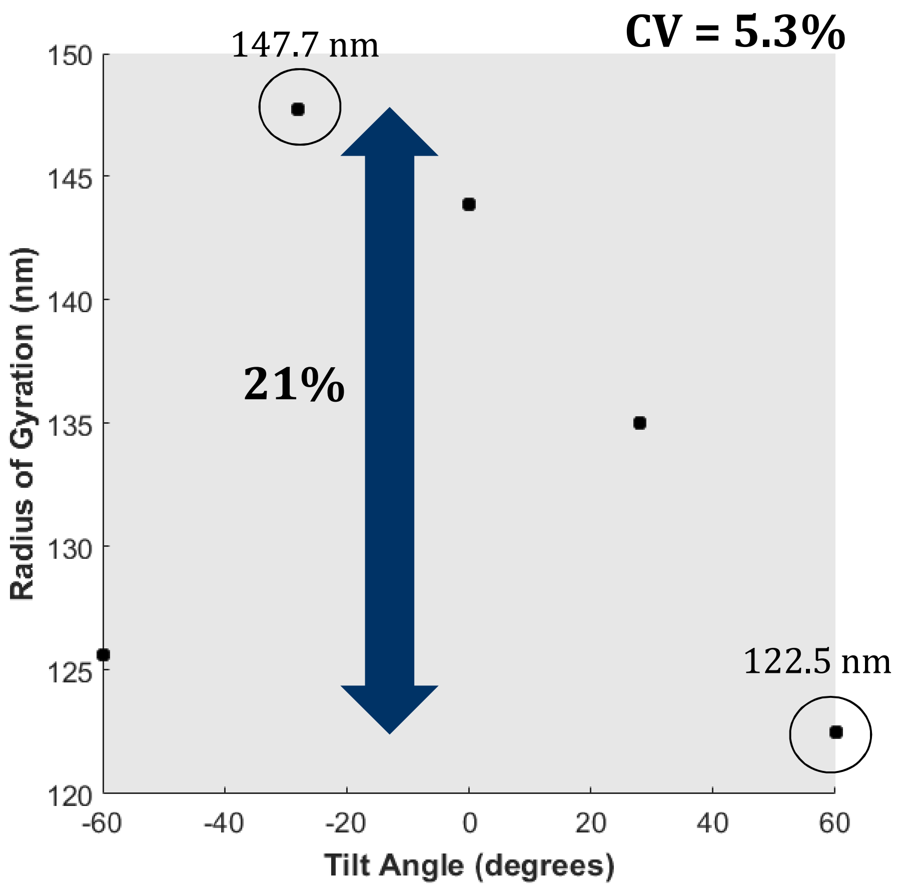
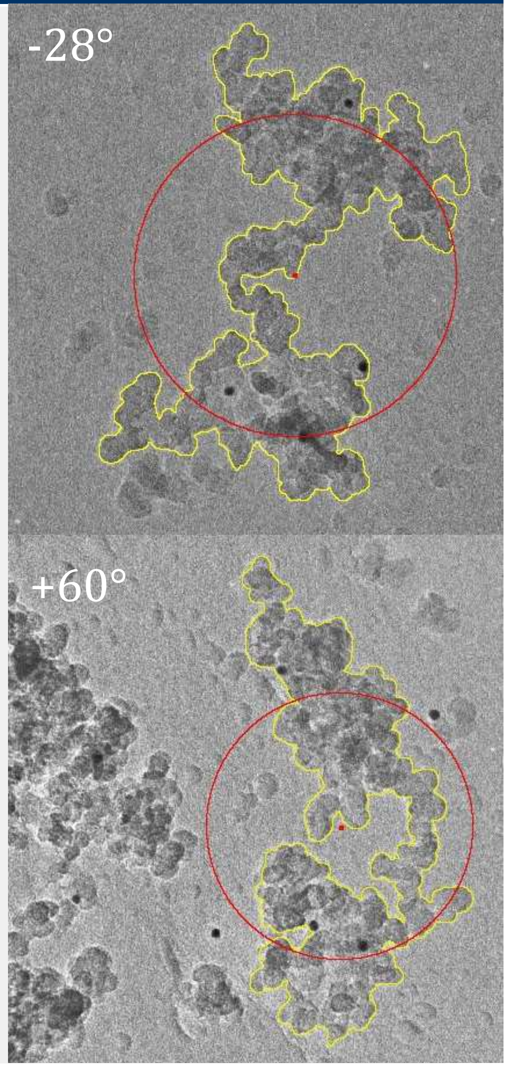


- Variation not directly linked to projected area
- Significant range of results (although < A_{eff})
- Accuracy of 2D-derived R_g depends on depth of particle; more accurate for ‘thinner’ particle



Sensitivity of Fractal Dimension to angle of projection

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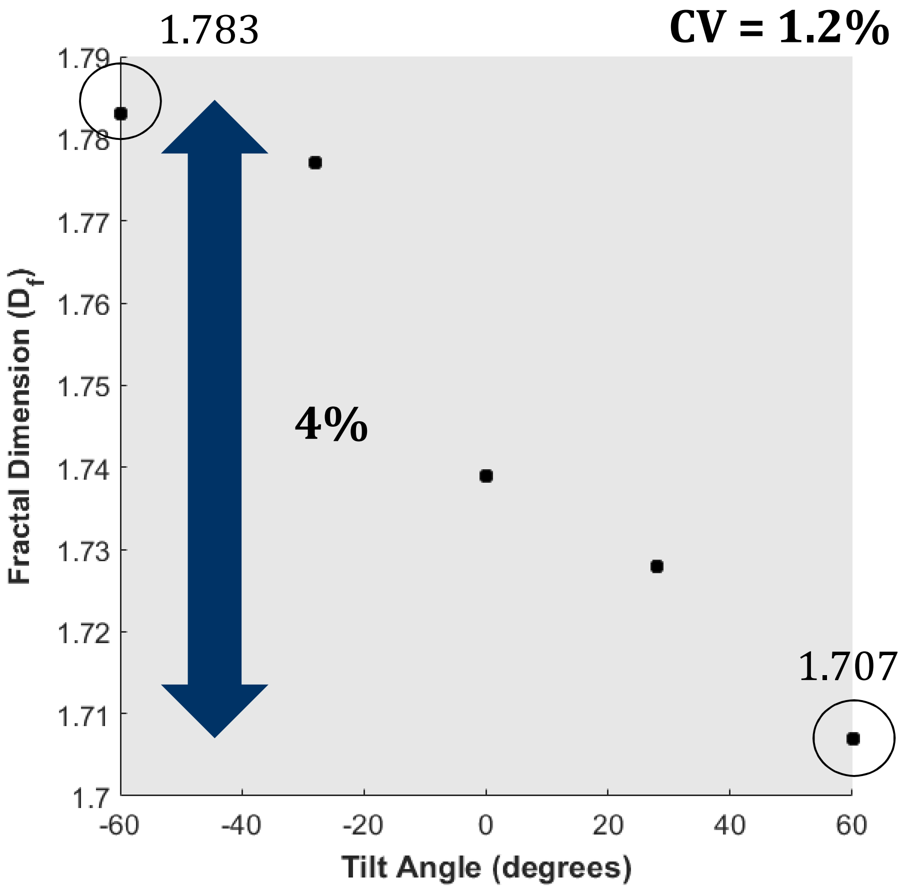
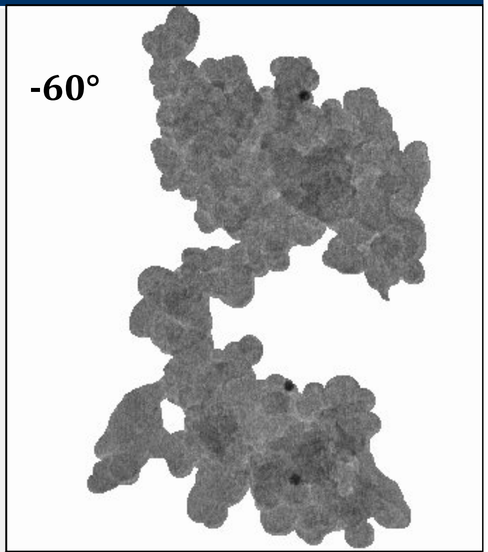
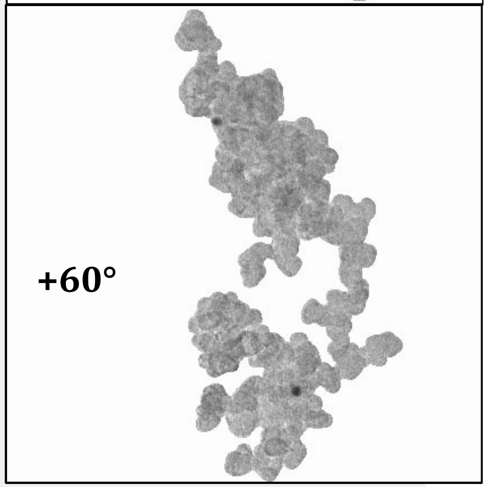


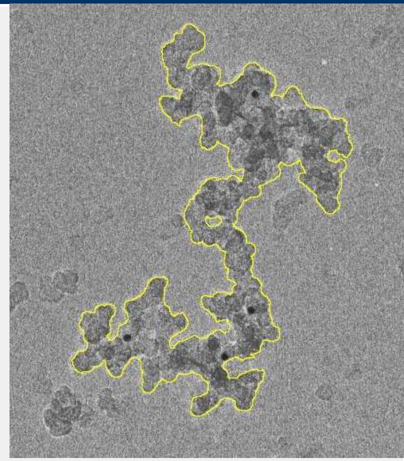
- Narrow range
  - Single image good representation of all 2D projections
- Box-counting is a technique for 2D fractals, value can never be > 2
- Accuracy depends on 2D representation of 3D complexity

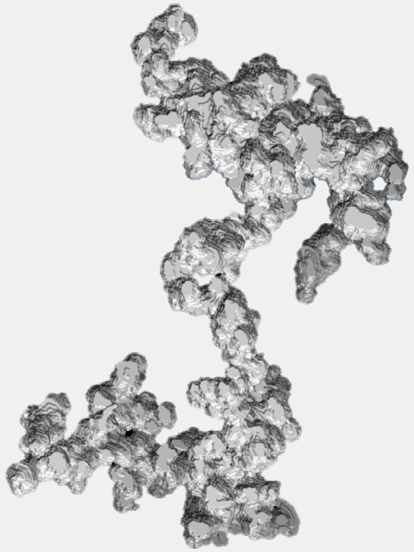




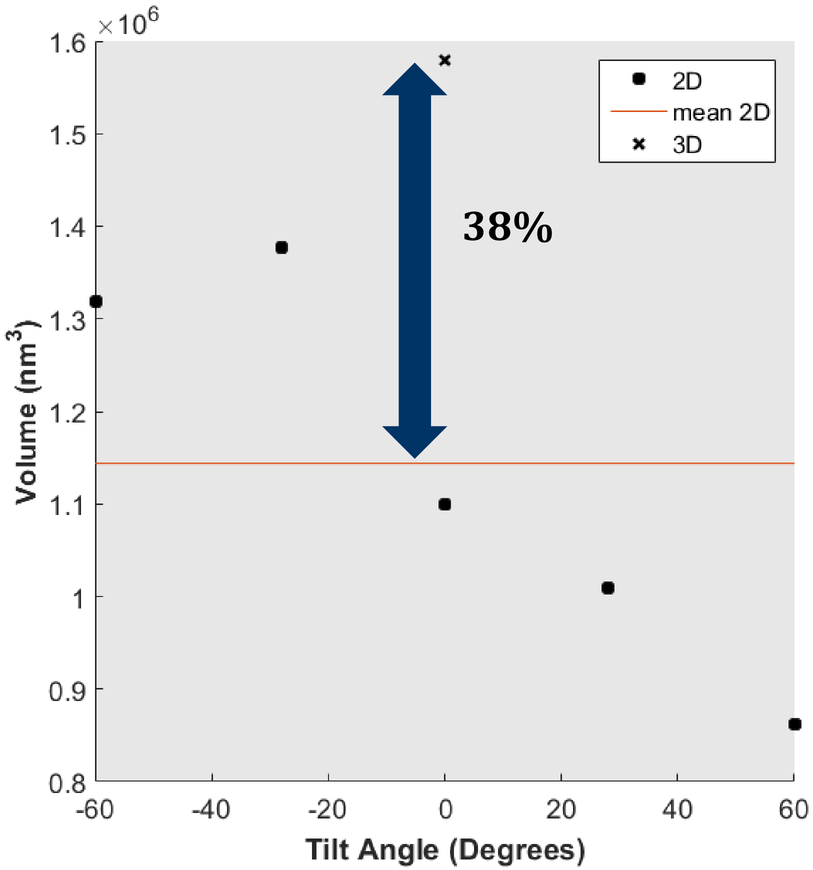
3D measurements

- Volume and surface area measured using UCSF Chimera software
- Radius of gyration measured using ImageJ macro (voxel based calculation)
- Fractal Dimension measured using BoneJ plugin for ImageJ (cube-counting)
- $N_p = {}^{V}/_{V_p}$



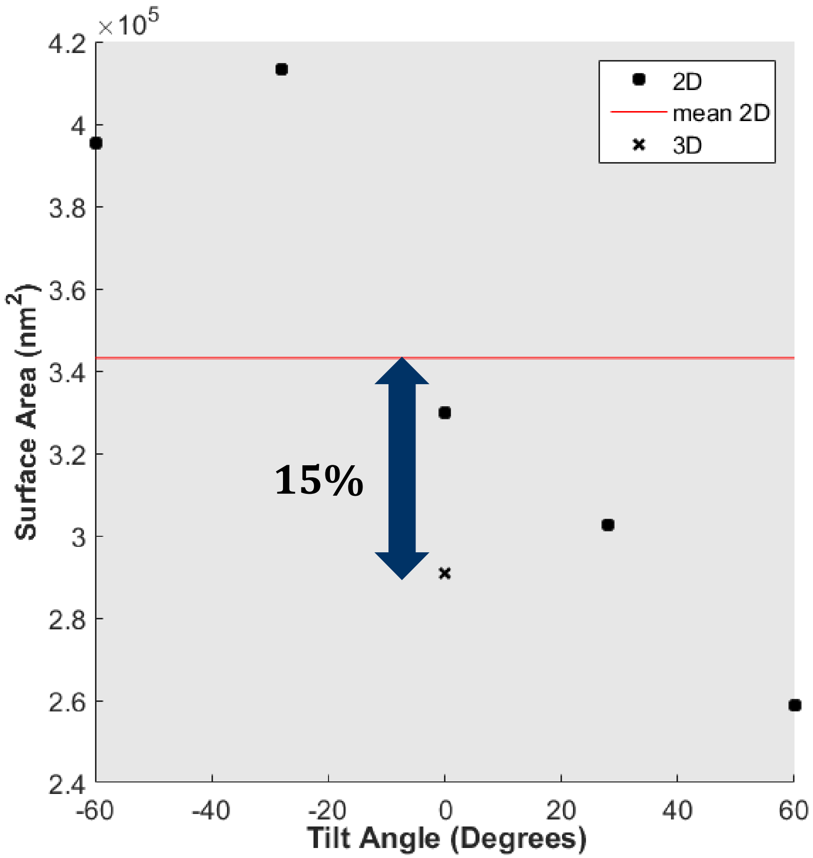


3D vs 2D: Volume & N_p



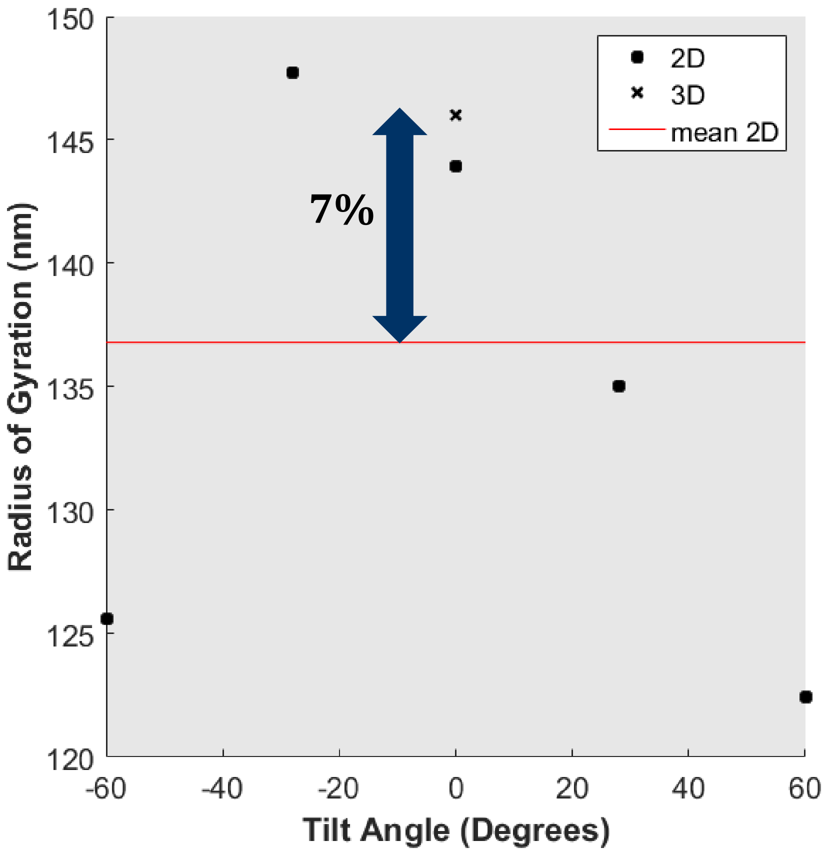
- Volume & N_p show identical relationship to 2D results
- Volume of 3D model significantly under estimated by 2D methods
- Underestimation is in addition to uncertainty within 2D measurements

3D vs 2D: Surface Area



- 2D method an overestimation (not widely used)
- 2D measurements in **excess** of 3D values

3D vs 2D: Radius of Gyration



- For R_g, 2D methods provide closer representation of 3D result
- 'Thicker' particle likely to increase disparity between 2D & 3D results & *vice versa*
- BUT additional level of uncertainty within 2D results

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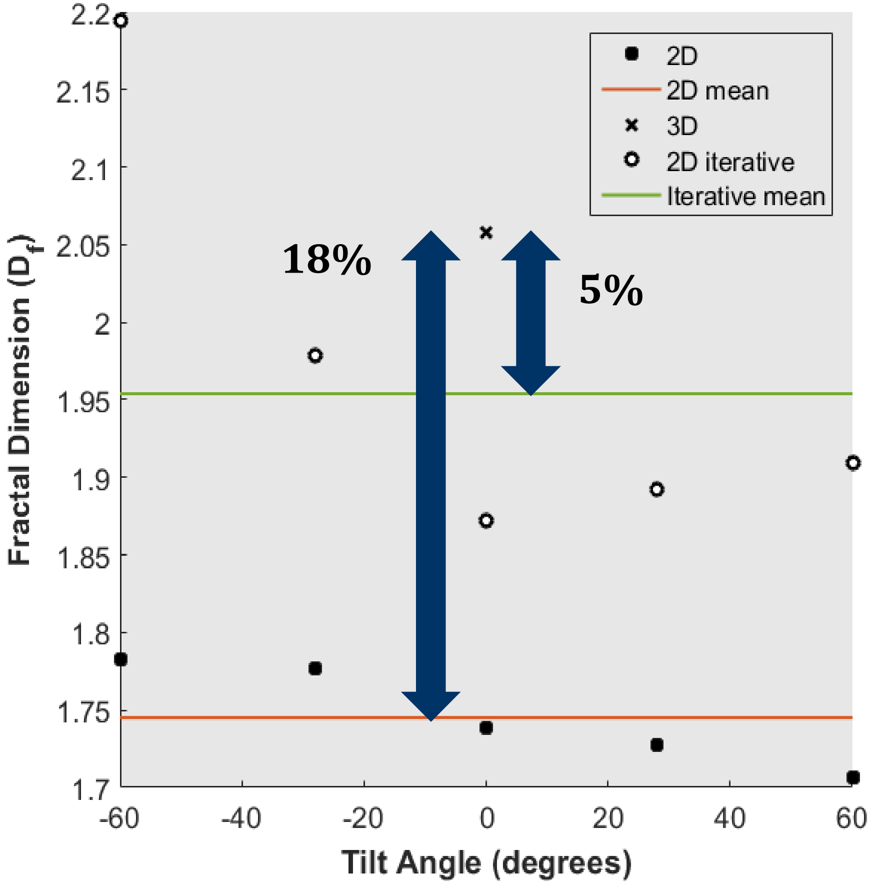
3D vs 2D: Fractal Dimension



- Significant difference compared to 3D results despite narrow range in 2D
- 2D-3D difference similar to that observed by Rogak [1]
- 2D methods limited to $D_f \leq 2$
- Iterative method [2] estimates **3D** fractal dimension ($D_f \leq 3$)
- Iterative method provides more representative results from 2D projections

[1] S.N. Rogak, R.C. Flagan, Part. Part. Syst. Charact. 9 (1992) 19-27
[2] M. Lapuerta, R. Ballesteros, F.J. Martos, J. Colloid Interface Sci. 303 (2006) 149-158

Conclusions

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Our introductory study of **single particle** has allowed us to quantify how values of typical characterising parameters can vary as a function of particle orientation. We have also been able to compare 2D- & 3D-derived results for a **real** particle

2D Sensitivity

- Characterising parameters can vary strongly as particle orientation changes
- A_{eff}, N_p, V, S_a most sensitive parameters
  - **CV = 12.7-13.8%**
- Radius of gyration measured over significant range (**CV = 5.3%**)
- Narrow range for fractal dimension (**CV = 1.2%**)

2D vs 3D

- Volume and number of primary particles underestimate 3D value by **38%** on average
- 2D surface area on average **15% greater** than 3D value (no inclusion of primary particle overlap)
- 2D methods account well for 3D radius of gyration; on average within **7%** of 3D value
- Although box-counting methods provide poor account of 3D value, iterative methods accurately account for 3D morphology

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The authors would like to thank Dr C.D.J. Parmenter for his valuable *insights* and *discussion*.

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