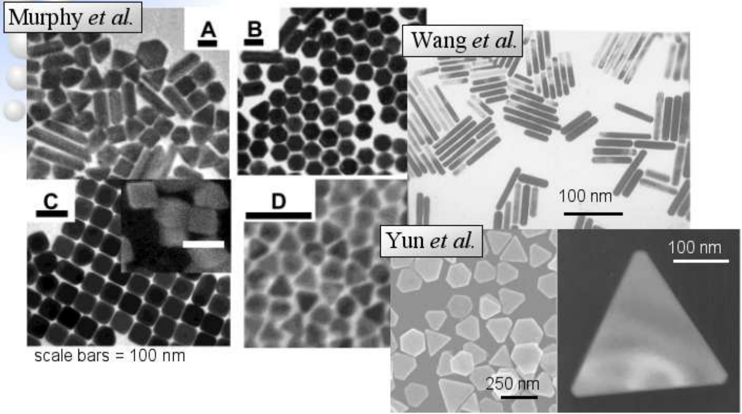
Understanding the UV-visible-NIR scattering of non-spherical metallic nanoparticles

Stuart W. Prescott, Paul Mulvaney

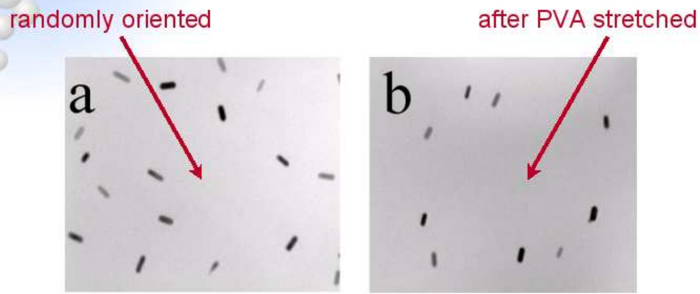
Particulate Fluids Processing Centre
School of Chemistry
University of Melbourne

Recent synthetic achievements



Uses of nanorods

Au nanorods (AR ~2.9) in a PVA film

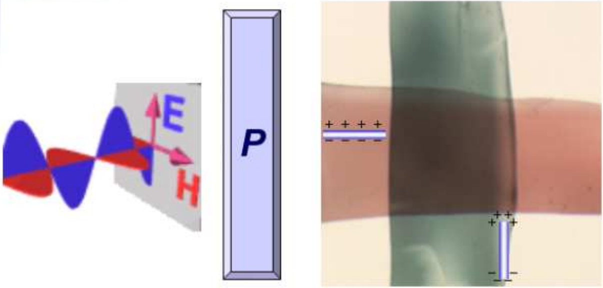


Pérez-Juste *et al. Advanced Functional Materials*, 15, *1065*, **2005**

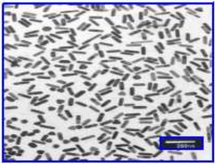
Uses of nanorods

Stretching of PVA aligns rods

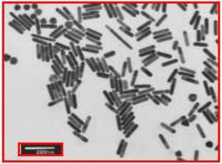
- photograph under polarised light:



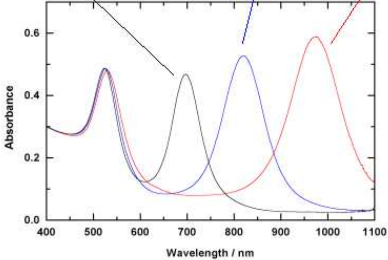
A.R.: 2.25
Width: 20.7 nm
Length: 46 nm



A.R.: 3.35
Width: 22.4 nm
Length: 75 nm

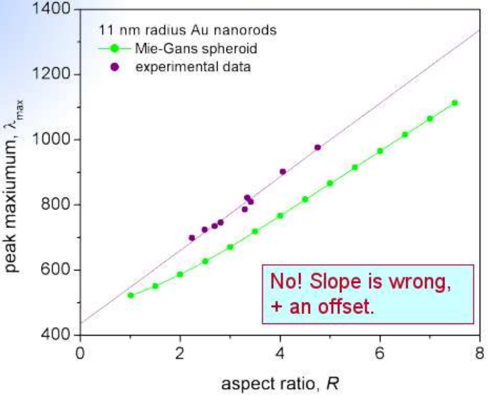


A.R.: 4.75
Width: 22.8 nm
Length: 108 nm



FWHM ~100nm

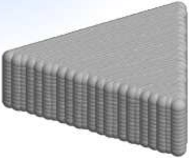
Are these prolate spheroids (ellipsoids)?

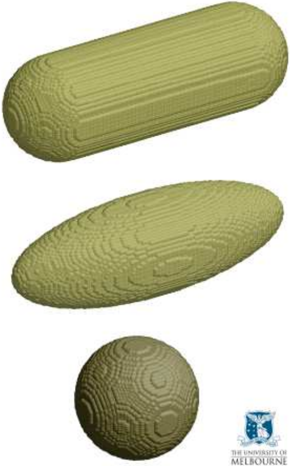


All spectra are for gold nanorods in water

Correctly predicting λ_{max}

Investigating influence of particle shape and size:

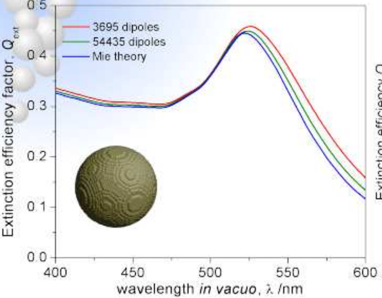


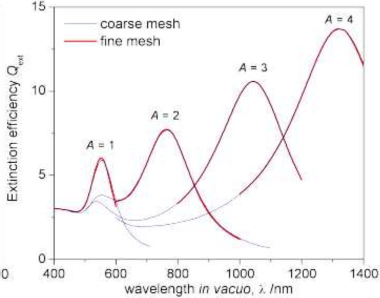


Discrete Dipole Approx. Model

Cubic array of dipoles (Draine & Flatau)

Checking DDA for nanoparticles





DDA captures target and spectrum features

34189 dipoles

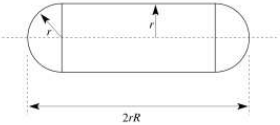
294293 dipoles

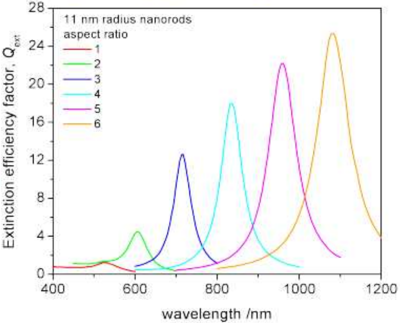
THE UNIVERSITY OF MELBOURNE

DDA for Au spherically capped cylinders

For aspect ratio, *R*

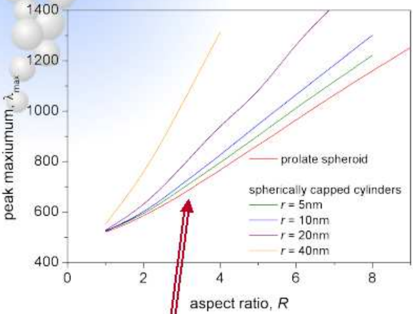
- spherical end cap, radius *r*
- particle length *2rR*
- cylinder length 2*r*(*R*–1)

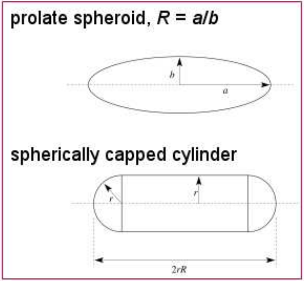




λ_{max} varies with *R*, and becomes more intense

λ_{max} varies with rod width?





λ_{max} independent of rod width for Mie-Gans prolate spheroid

Also recently reported by Brioude, *et al.*, *J. Phys. Chem. B*, 109, *13138*, **2005**.

Spectra & Geometrical Factors

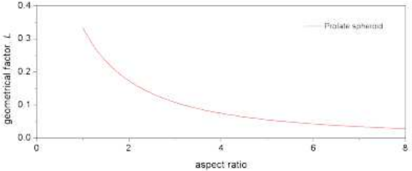
Polarisability, α, gives extinction:

- single parameter expression for $Q_{ext}(\lambda)$
- geometrical factor L (sphere has L=1/3)

$$\alpha = V\frac{\varepsilon - \varepsilon_m}{\varepsilon_m + L\left(\varepsilon - \varepsilon_m\right)}$$

$$Q_{\mathrm{ext}}(\lambda) = \frac{2\pi\sqrt{\varepsilon_m}}{G\lambda}\,\mathrm{Im}\left\{\alpha\right\}$$

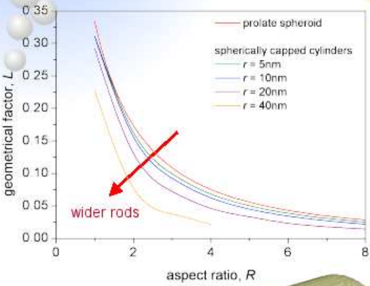
$$Q_{\mathrm{ext}}(\lambda) = \frac{2\pi V \varepsilon_{\mathrm{m}}^{3/2}}{G L^2 \lambda}\frac{\varepsilon''}{\left(\varepsilon' + \frac{1-L}{L}\varepsilon_m\right)^2 + \left(\varepsilon''\right)^2}$$

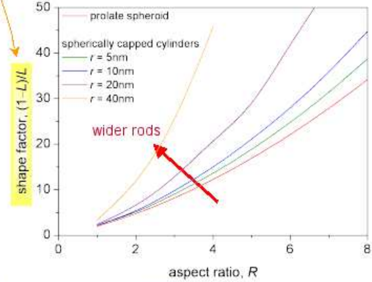


(*L* shown for longitudinal mode only)

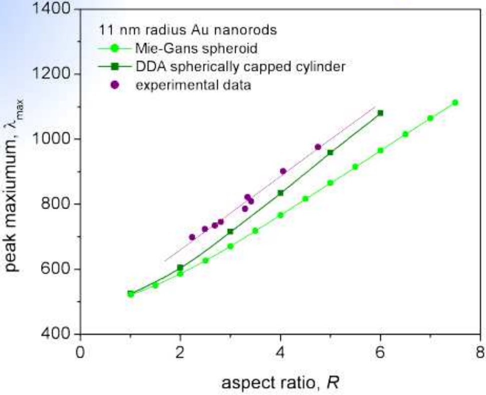
L and rod width

$$Q_{\text{ext}}(\lambda) = \frac{2\pi V \varepsilon_{\text{m}}^{3/2}}{GL^2\lambda} \frac{\varepsilon''}{\left(\varepsilon' + \frac{1-L}{L}\varepsilon_m\right)^2 + (\varepsilon'')^2}$$





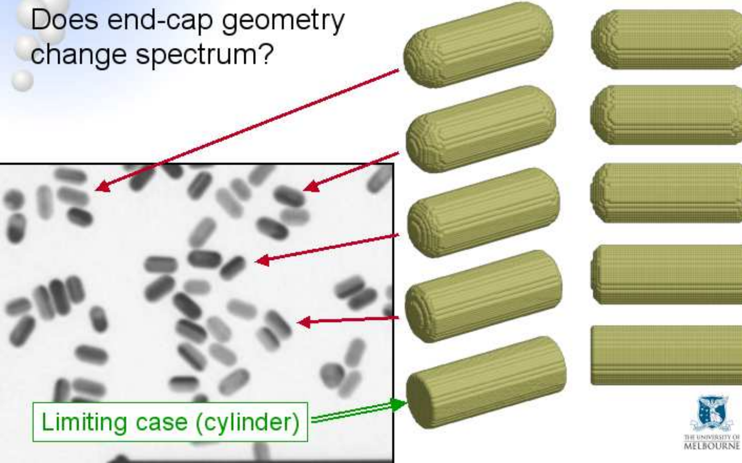
DDA gets closer…



…but there is room for improvement

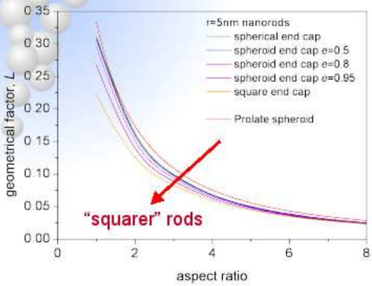
End-cap effects

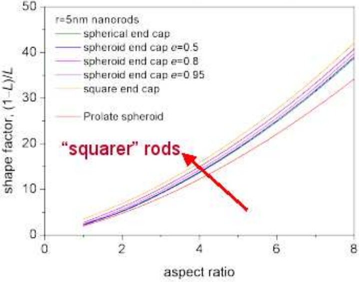
Does end-cap geometry change spectrum?



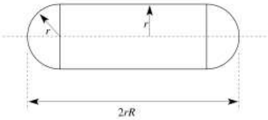
THE UNIVERSITY OF MELBOURNE

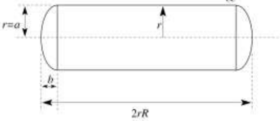
L and end-cap shape





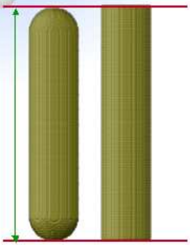
For the spheroid end caps, eccentricity: $e^2 = 1 - \frac{b^2}{a^2}$

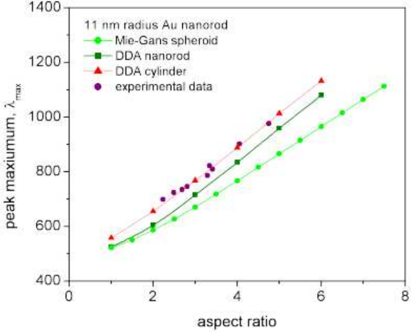




Limits on λ_{max} using DDA

λ_{max} should be between cylinder and rod:



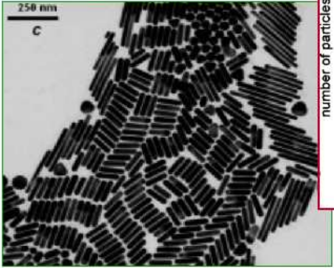


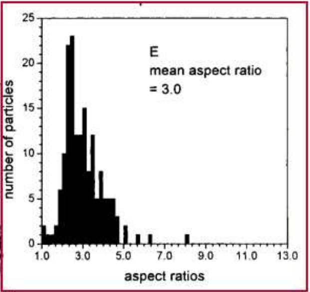
...cylinders seem to be the closest geometry?
something must be wrong...

THE UNIVERSITY OF MELBOURNE

Sample purity

How does a distribution of rods sizes change the spectrum?

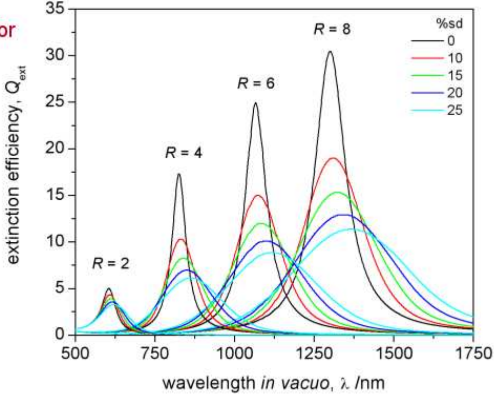




Example data from Yu *et al., J. Phys. Chem. B*, 101**,** *6661*, **1997**.

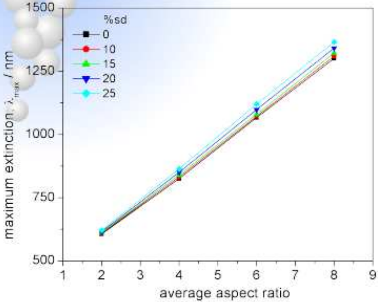
"Synthetic" spectra

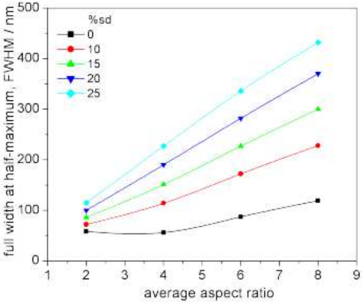
1. Find functional form for geometrical factor, $L(R,r)$
2. Calculate spectra for each bin in discrete particle length distribution
3. Add weighted component spectra



Geometrical factor, L, becomes powerful tool

Limits from "synthetic" spectra



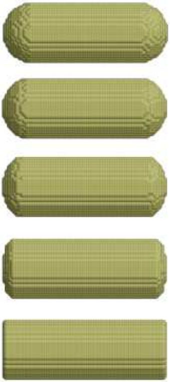


- red-shift of λ_{max} due to broadening of distribution
- FWHM also increases

Conclusions: predicting λ_{max}

Must consider:

- particle shape
  - these are nanorods *not* ellipsoids
  - width is important *not just aspect ratio*
- subtle end effects
  - spheroid end cap?
- particle size distribution
  - control it? reduce it? purify?



Conclusions: characterisation

Spectrometric characterisation of nanorods...

- for a given aspect ratio,
  - ellipsoid model gives uniquely determined λ_{max}
  - DDA: λ_{max} depends on width too
- with an independent measure of width...

  ...and known end-cap geometry...

  ...and a Gaussian distribution

  - (λ_{max}, FWHM) uniquely determines
    - "light-scattering average" aspect ratio
    - standard deviation of distribution

PFPC

THE UNIVERSITY OF MELBOURNE

Acknowledgements

- Support of the Victorian Institute for Chemical Sciences High Performance Computing Facility is gratefully acknowledged.

- The Particulate Fluids Processing Centre is established and supported under the Australian Research Council's Research Centres Programme.

- Prof. Bruce T. Draine (DDSCAT program).

Copies available from nano**nano**nano.net

PFPC

THE UNIVERSITY OF MELBOURNE