



Particle Shape Determination, Description and Exploitation

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Research area: colloids and interface science

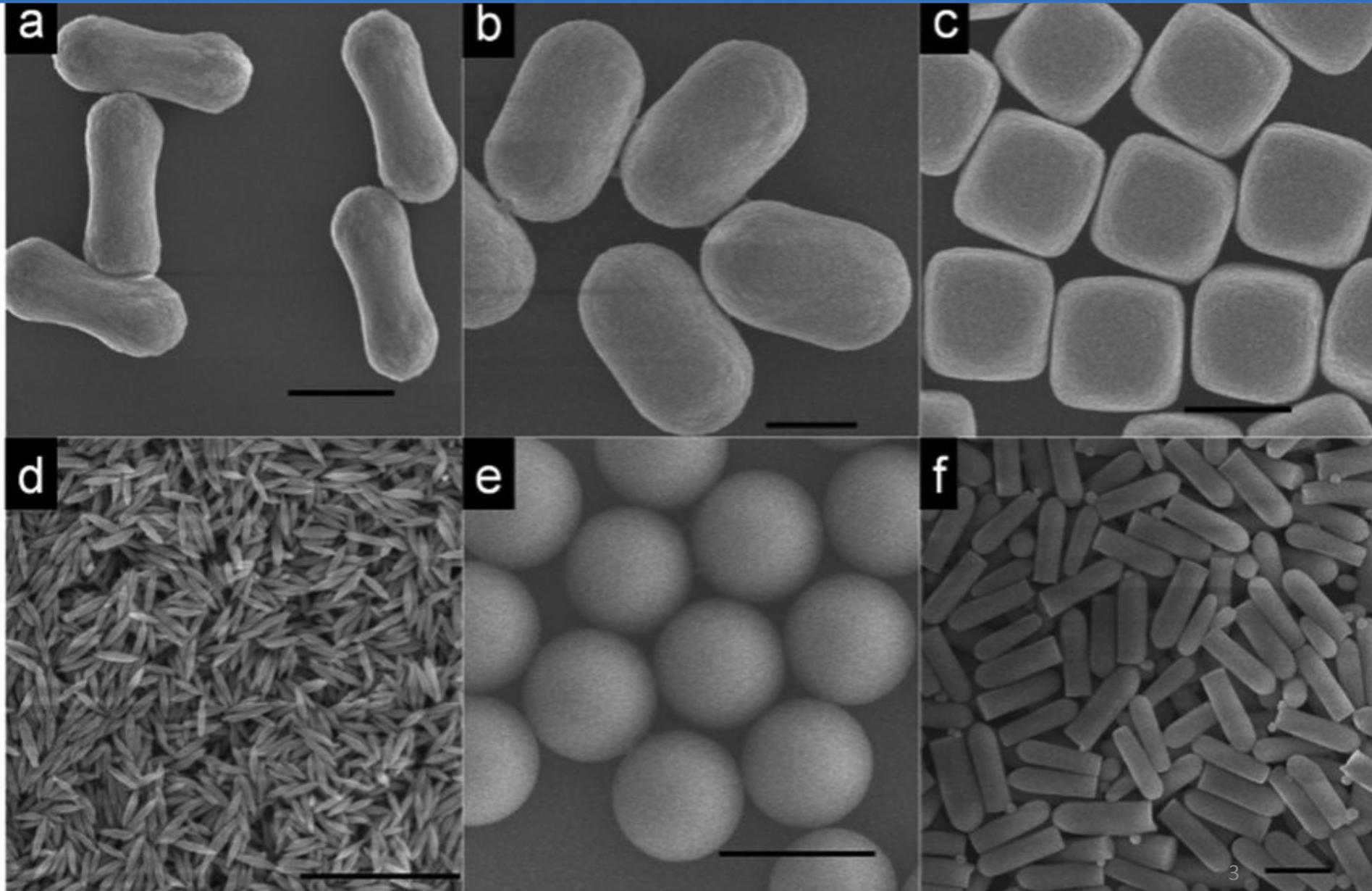
Expertise

- Experiments
- Synthesis of colloids
- Microscopy, Scattering (DLS, SLS, SANS), Rheology, Interfacial tensions/Contact angle, Image analysis

Research Areas

- Colloids at interfaces, Emulsions
- Self-assembly
- Dessication cracks
- Hetero-aggregation in colloidal systems
- Interfacial spreading
- Structure and rheology
- New materials and particles

Research Theme – investigation of particle shape effects



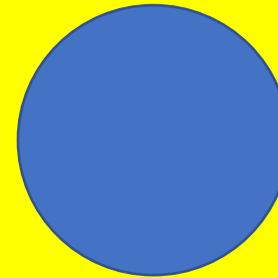
PCCP, 19 (45)
30790-30797 (2017)

Outline

- **Introduction**
- **Classification of anisotropic particles**
- **Particle shape descriptors**
- **Particle shape analysis**
- **Exploiting particle effects - some examples**

Definitions - Isotropic and Anisotropic Particles

- Isotropic particles -- same properties irrespective of the direction of observation



Spherical Particle

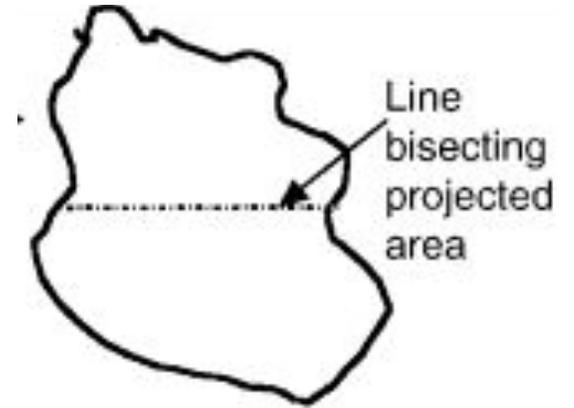
- Anisotropy refers to the extent to which a particle deviates from symmetrical nature.
- Anisotropic particles -- display different properties (physical/chemical) along different axes or orientations.

Characterization of particle shape – Text Book Stuff

Particles of irregular shapes:

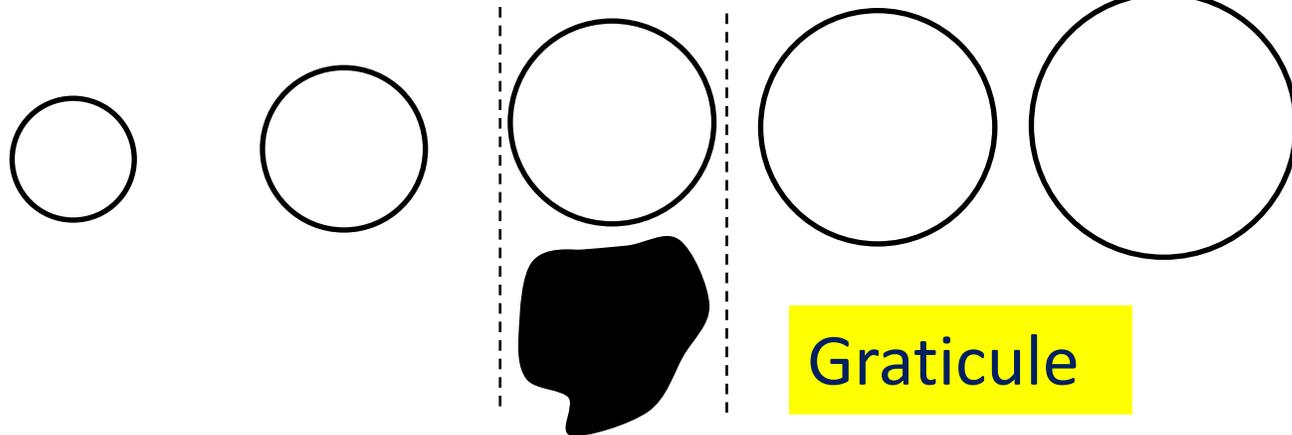
- Sphericity
- Martin's diameter
- Feret's diameter
- Graticule
- Diameter of equivalent circle

$$\Phi = \frac{6}{\frac{D_p}{S_p} v_p}$$

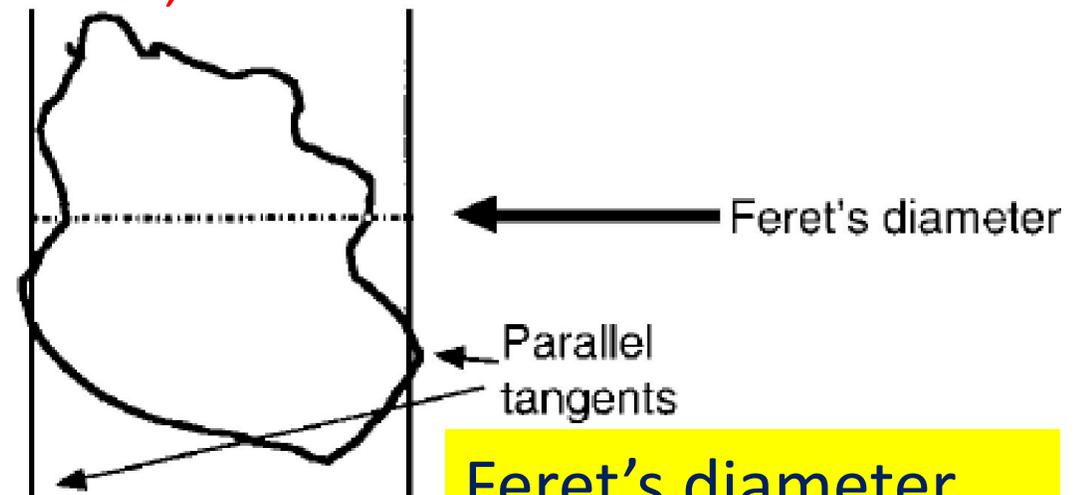


Martin's diameter

Introduction to Particle Technology, Editor(s): Martin Rhodes,
Copyright © 2008 John Wiley & Sons, Ltd



Graticule



Feret's diameter

What's in earlier reviews?

The Shape of Powder Particles and its Influence on Powder Handling

Fridrun Podczeck 2003

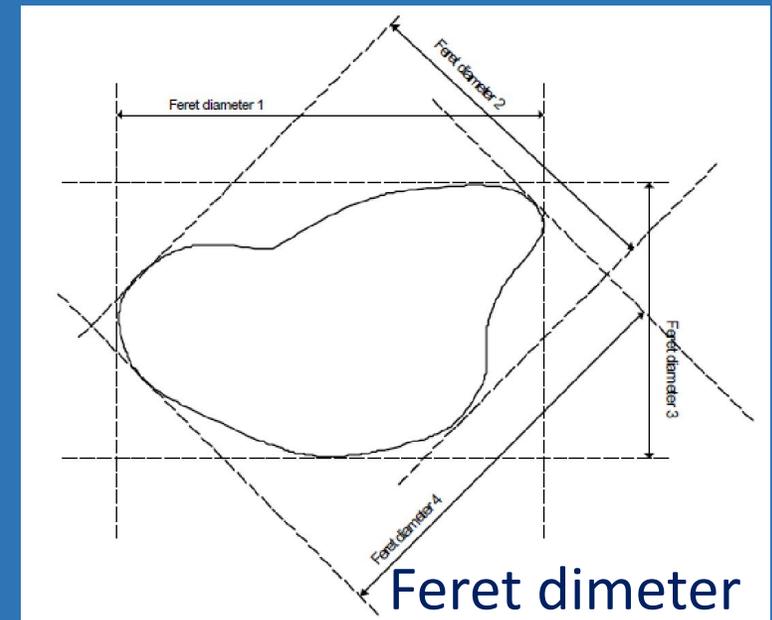
*Department of Pharmaceutics, The School of Pharmacy, University of London, 29/39
Brunswick Square, London WC1N 1AX, UK.*

Description of geometry of particles using four characteristic features i.e. size, shape, roundness and roughness.

Powder handling

- friction and powder flows
- mixing and segregation

Role of particle shape on drug delivery



What's in earlier reviews?

3D PARTICLE CHARACTERISATION : *a review*

University of Liege

Faculty of Applied Sciences

GeomaC « Georesources, Geotechnologies & Building Materials » Dpt

Mineral Resources & Geo-Imaging Lab

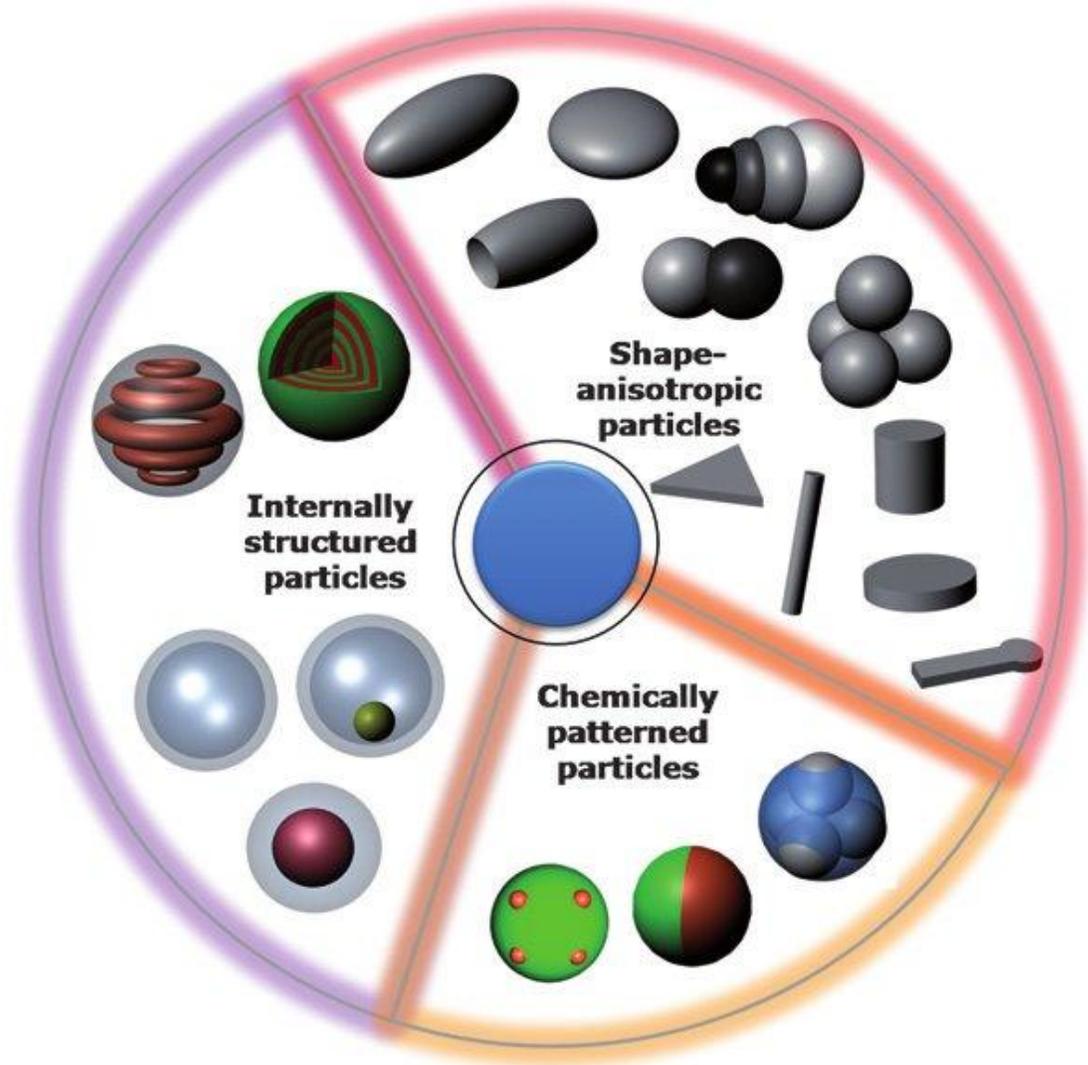
Prof. Eric PIRARD

Overview of Image acquisition techniques

Image analysis

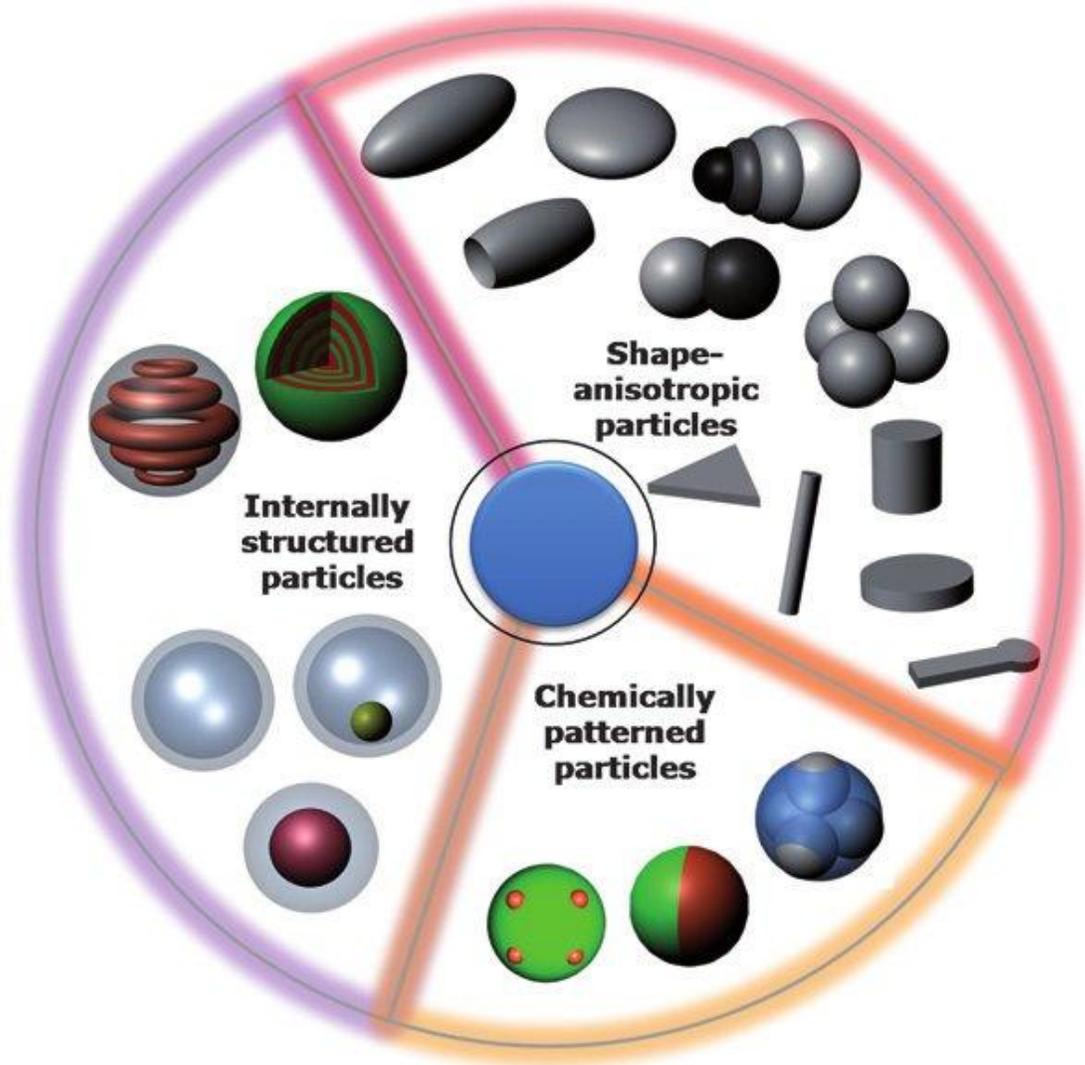
Representation of particles for DEM modeling

Anisotropic particles and their classification

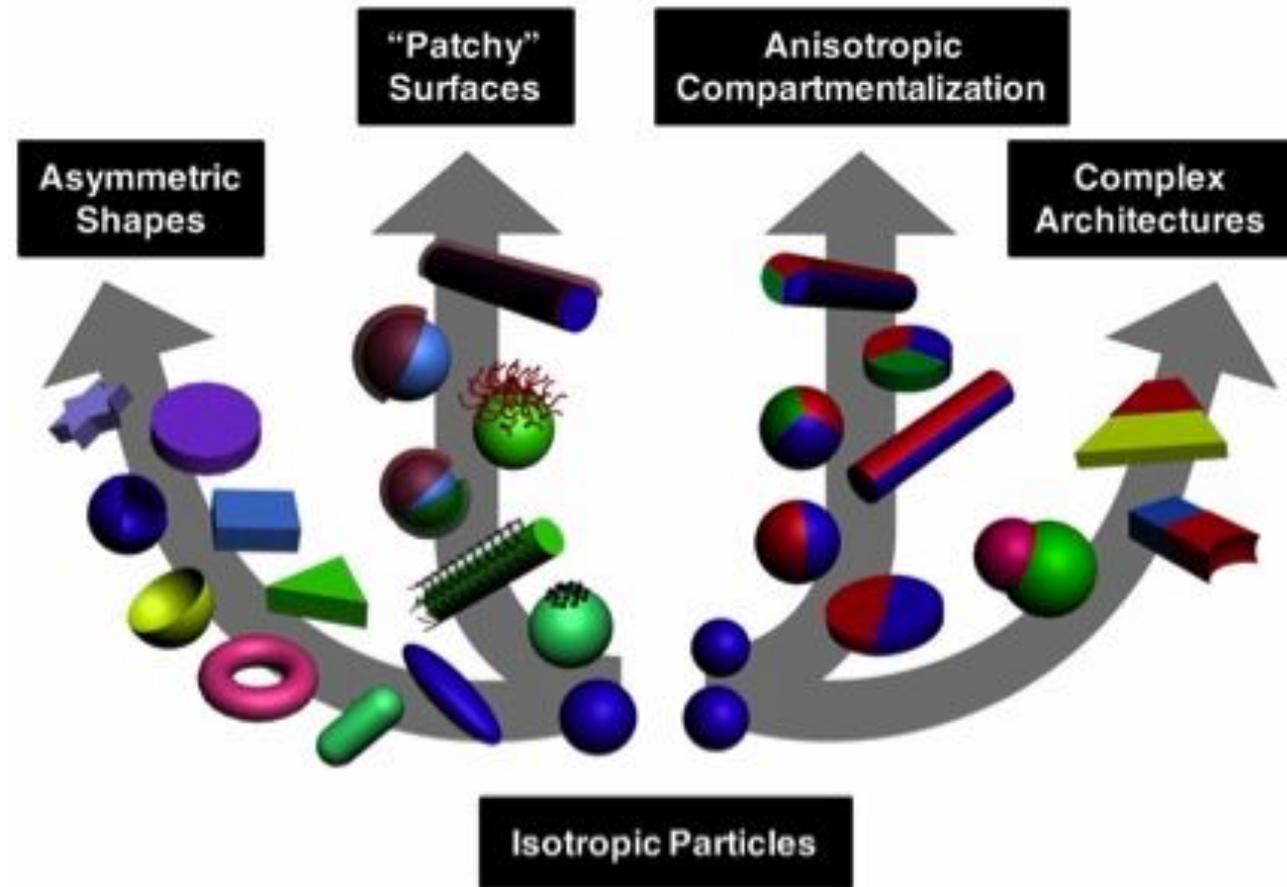


Seung-Man Yang et, al.,
J. Mater. Chem., 2008,18, 2177-2190

Anisotropic particles and their classification



Seung-Man Yang et, al.,
J. Mater. Chem., 2008,18, 2177-2190

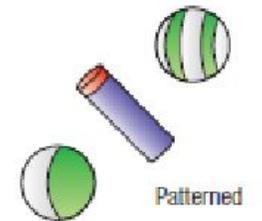
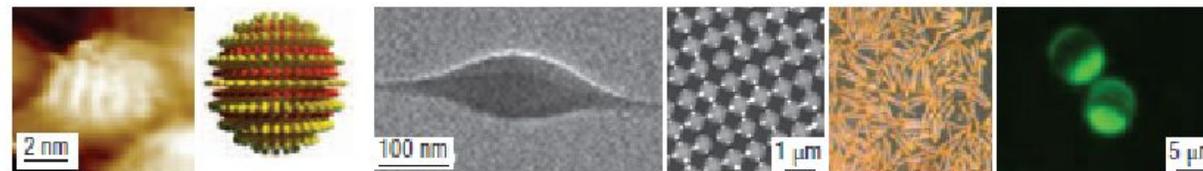
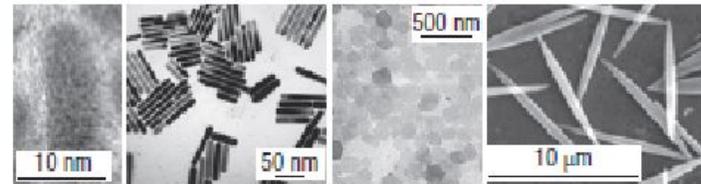
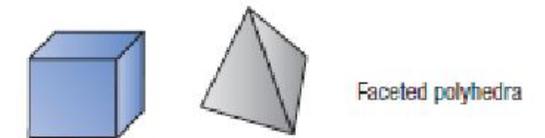
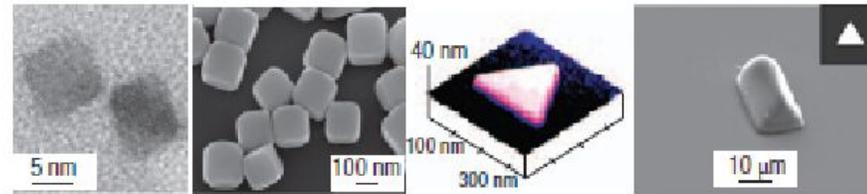
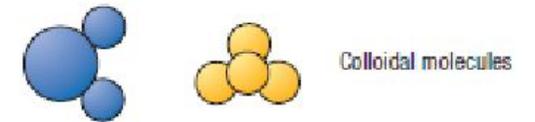
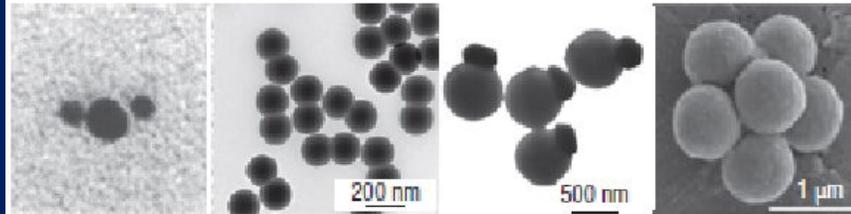
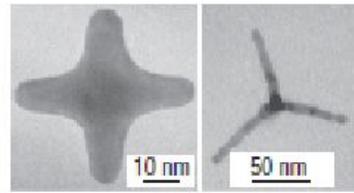


K. J. Lee et. al., Current Opinion in Colloid &
Interface Science (2011) 16, 195-202.

Examples of anisotropic particles

Anisotropic particles

- Mechanical stretching
- Forced hydrolysis
- Seeded growth
- Glancing angle deposition
- Emulsion polymerization
- Modified stober's method
- Biological origin (Bacteria, Virus)
- ...



SC Glotzer, MJ Solomon

Nature materials 6 (8), 557-562 (2007)



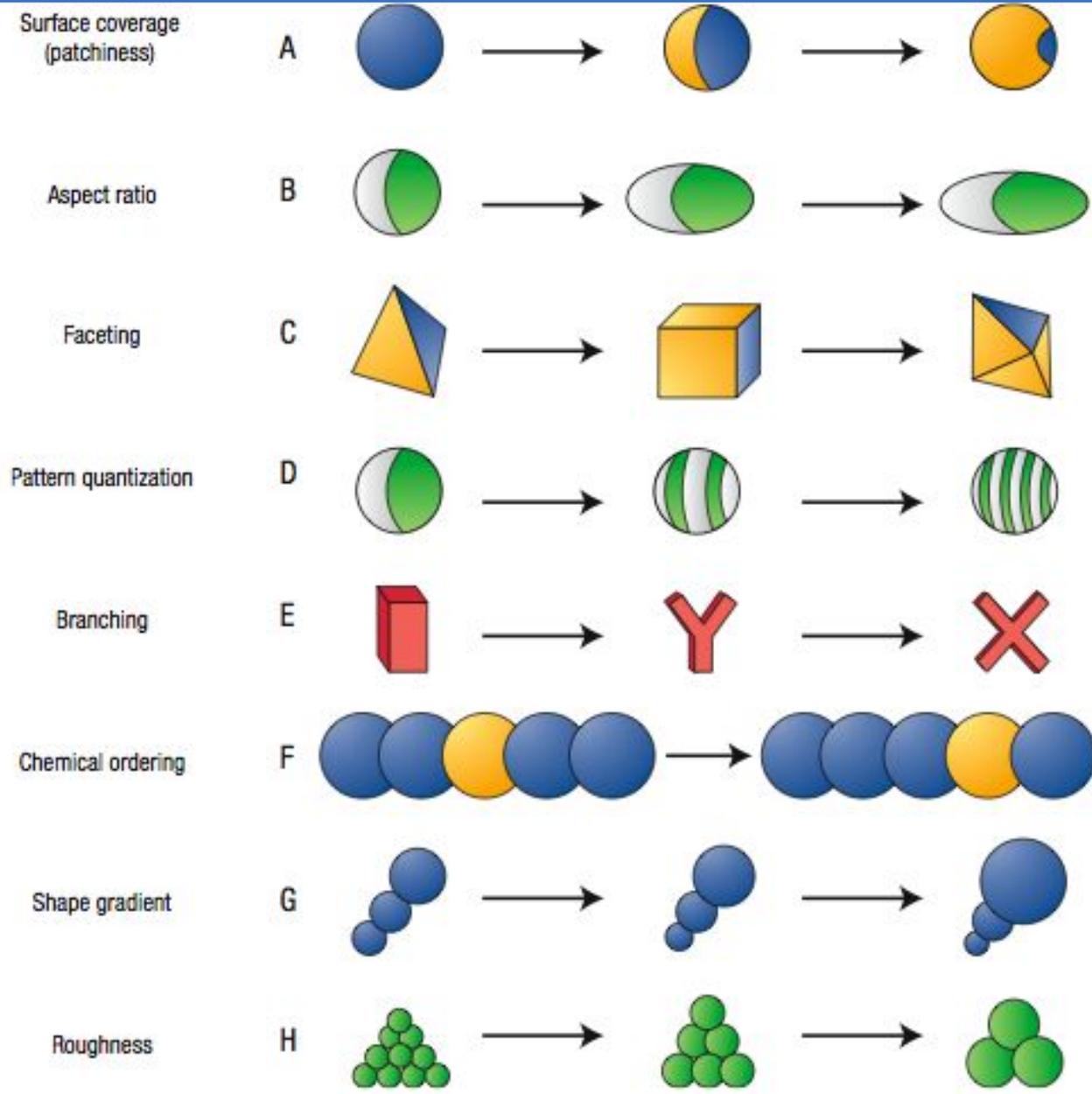
Description of key attributes of anisotropic particles

Extent of anisotropy varies from left to right.

- A: Interaction patchiness via surface coverage,
- B: aspect ratio,
- C: faceting,
- D: interaction patchiness via surface pattern quantization,
- E: branching,
- F: chemical ordering,
- G: shape gradient,
- H: roughness

SC Glotzer, MJ Solomon

Nature materials 6 (8), 557-562 (2007)



Outline

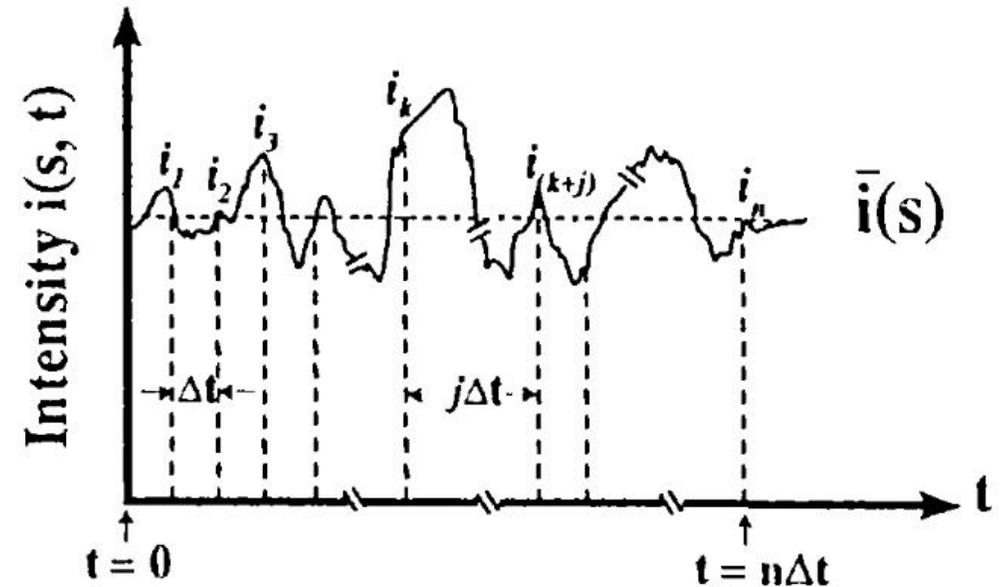
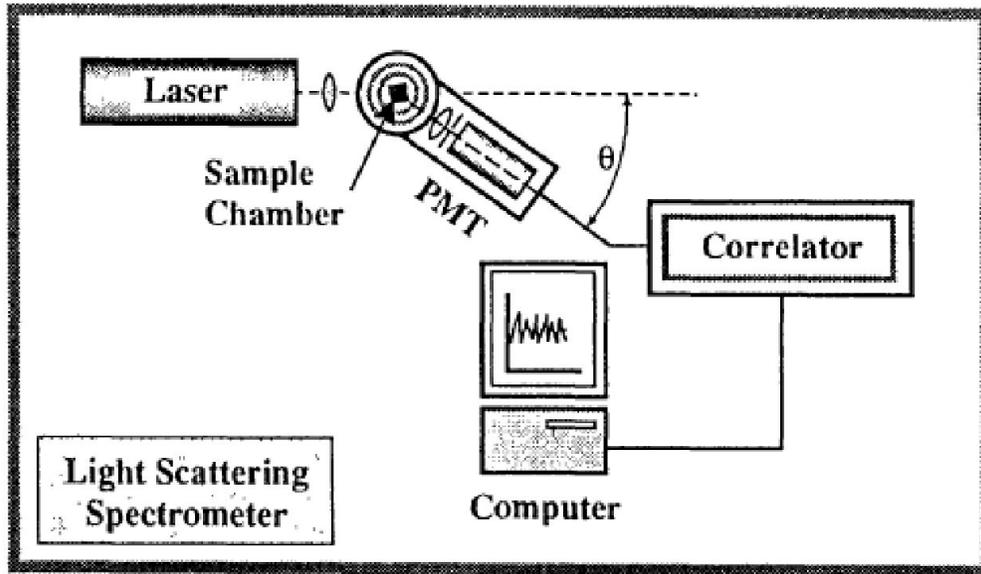
- **Introduction**
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Particle characterization using light scattering

Particle characterization using light scattering

Dynamic light scattering: The fluctuations in light intensity as a function of time is measured at a fixed scattering vector (or scattering angle)

Principles of Colloid and Surface Chemistry, (Paul C. Hiemenz, Raj Rajagopalan) 1997



$$g^2(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} = 1 + \xi |g^1(\tau)|^2$$

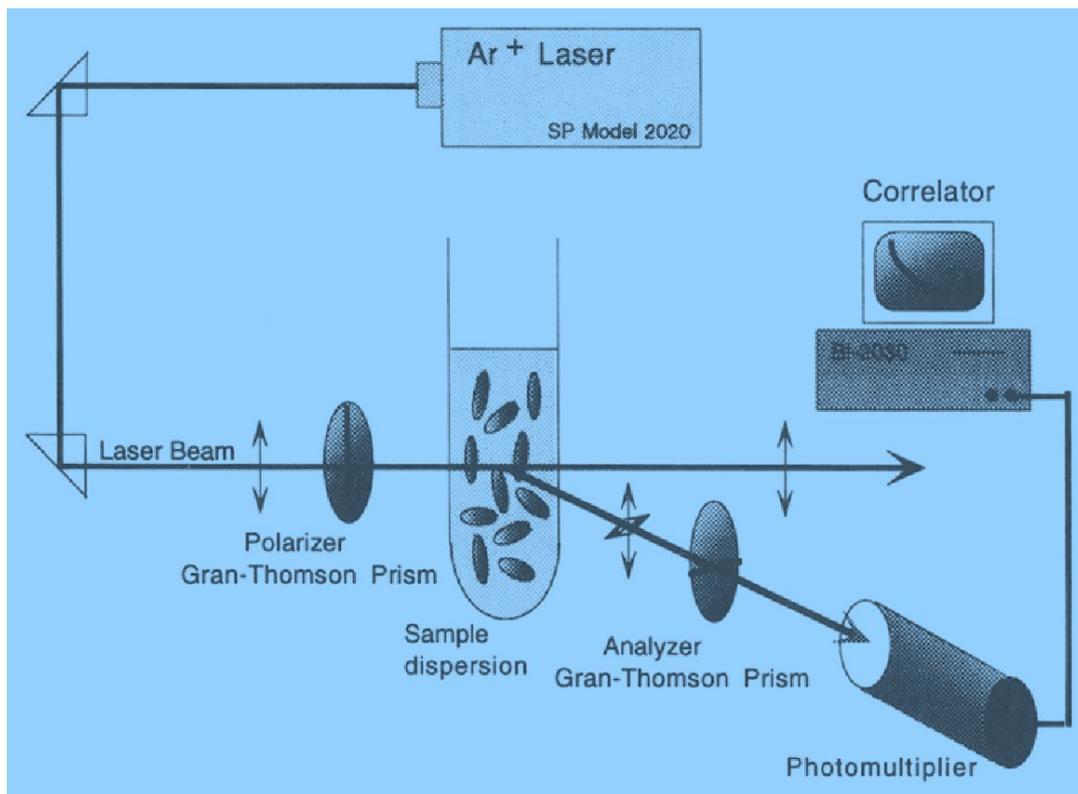
$$g^1(\tau) = Ae^{-Dq^2\tau} + B$$



$$R_h = \frac{kT}{6\pi\eta D}$$

De-polarized DLS

Colloids and Surfaces A: 109,
1996, Pages 137-145



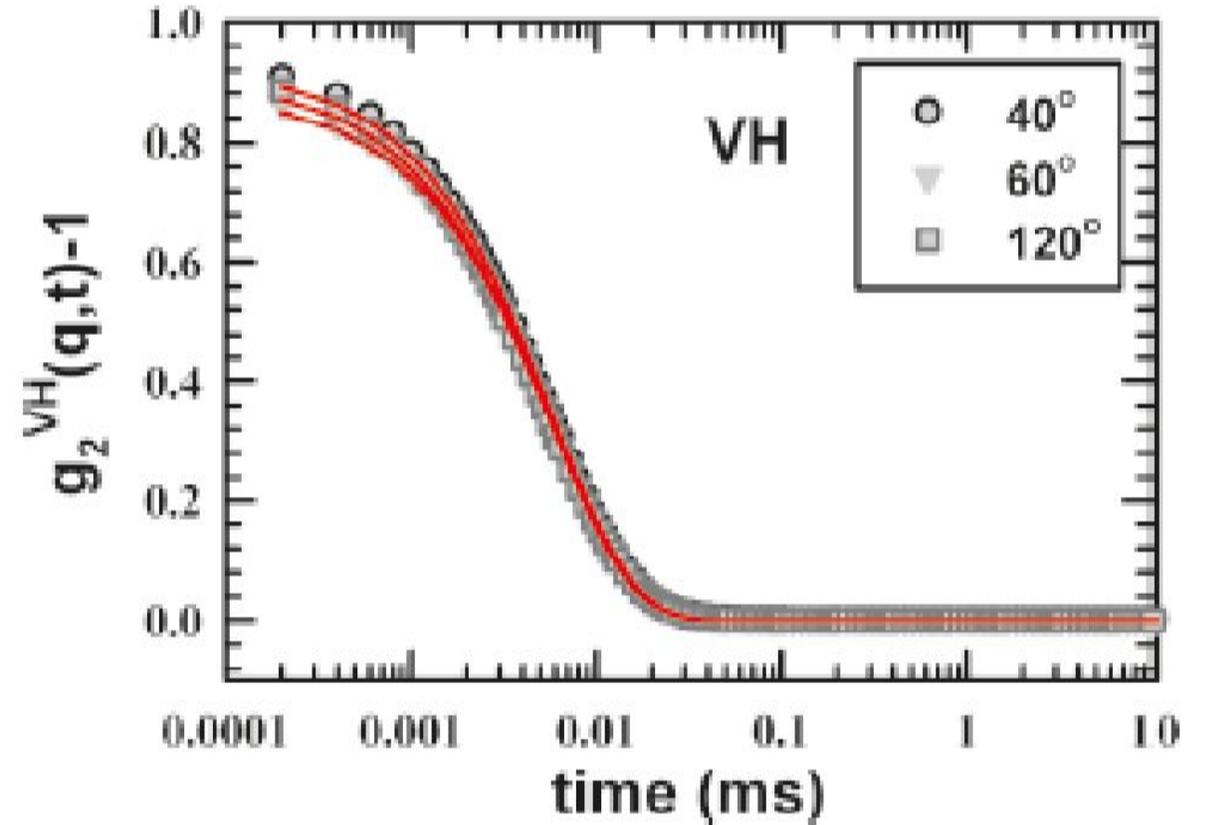
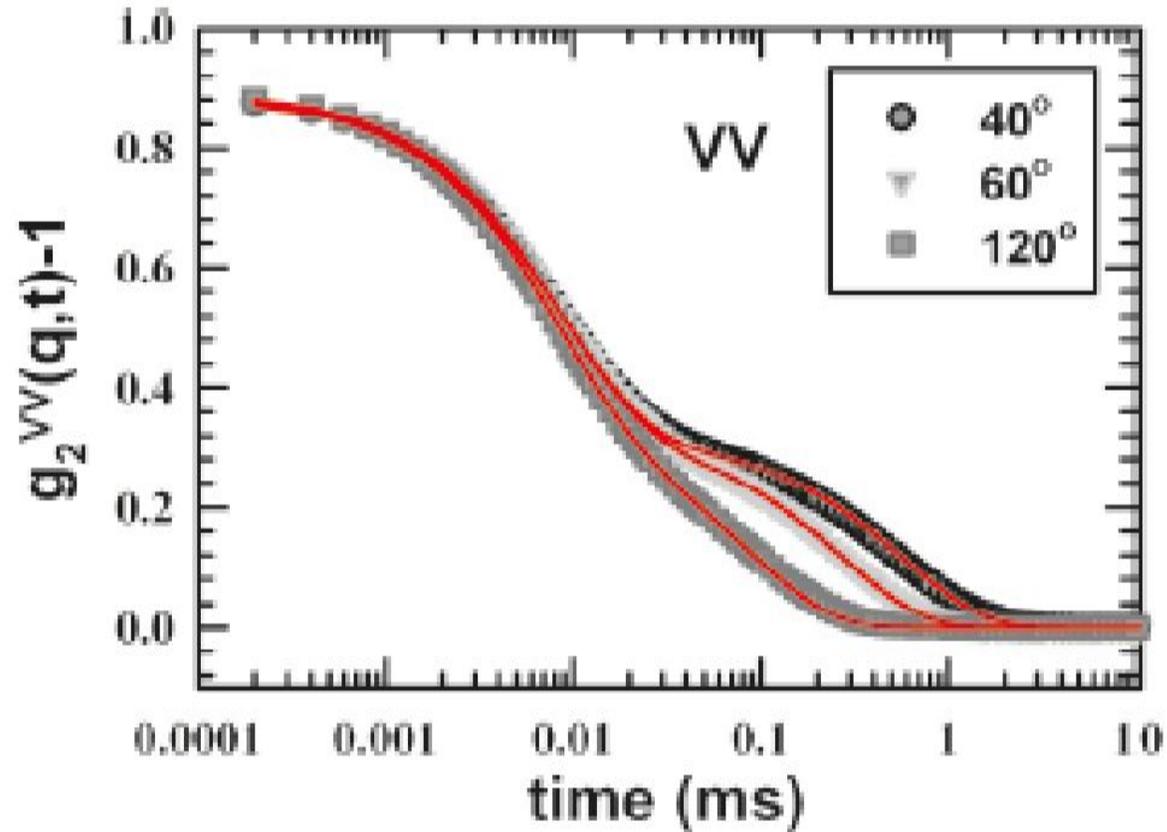
The intensity autocorrelation functions obtained from dynamic light scattering in the vertical–vertical (VV) and vertical–horizontal (VH) modes are analyzed.

$$g_2^{VV}(q, t) - 1 = \beta[A^2 \exp\{-\Gamma_2 t\} + 2AB \exp\{- (\Gamma_2 + \Delta/2)t\} + B^2 \exp\{- (\Gamma_2 + \Delta)t\}]$$

$$g_2^{VH}(q, t) - 1 = \beta' \exp\{- (\Gamma_2 + \Delta)t\}$$

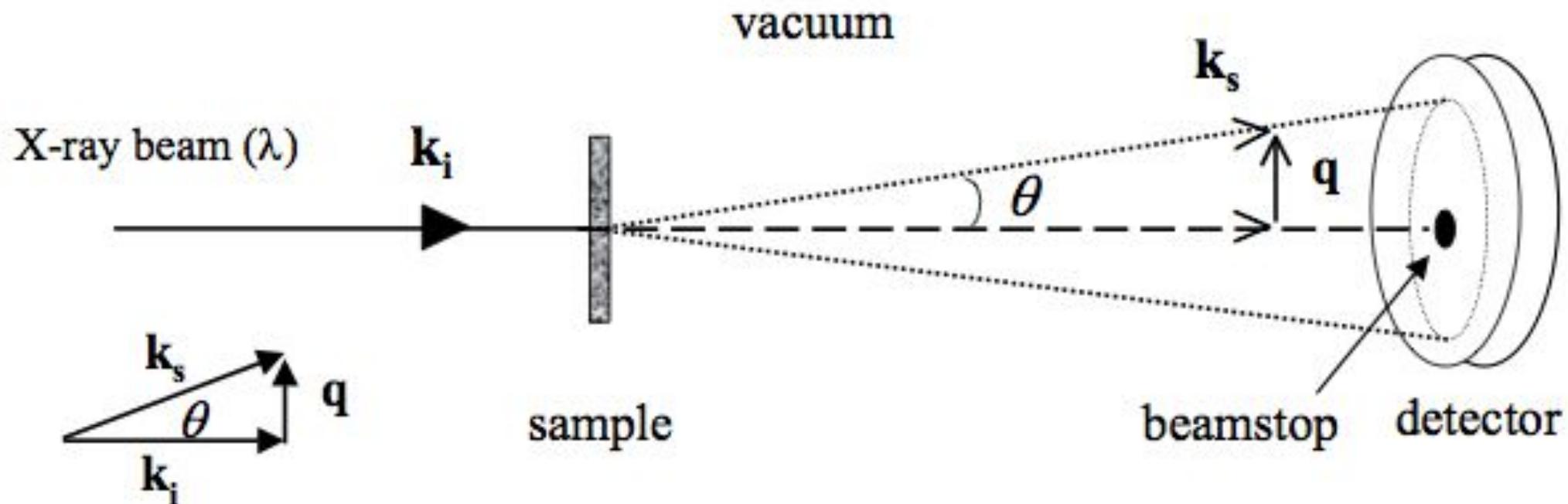
ACS Nano 2011, 5, 6, 4935-4944

Correlation functions measured in VV and VH mode



Particle characterization using light scattering

Static light scattering: The time-average intensity of scattered light is measured as a function of scattering vector (or scattering angle)



Narayanan, T. (2008). Synchrotron Small-Angle X-Ray Scattering. In: Borsali, R., Pecora, R. (eds) Soft Matter Characterization. Springer.

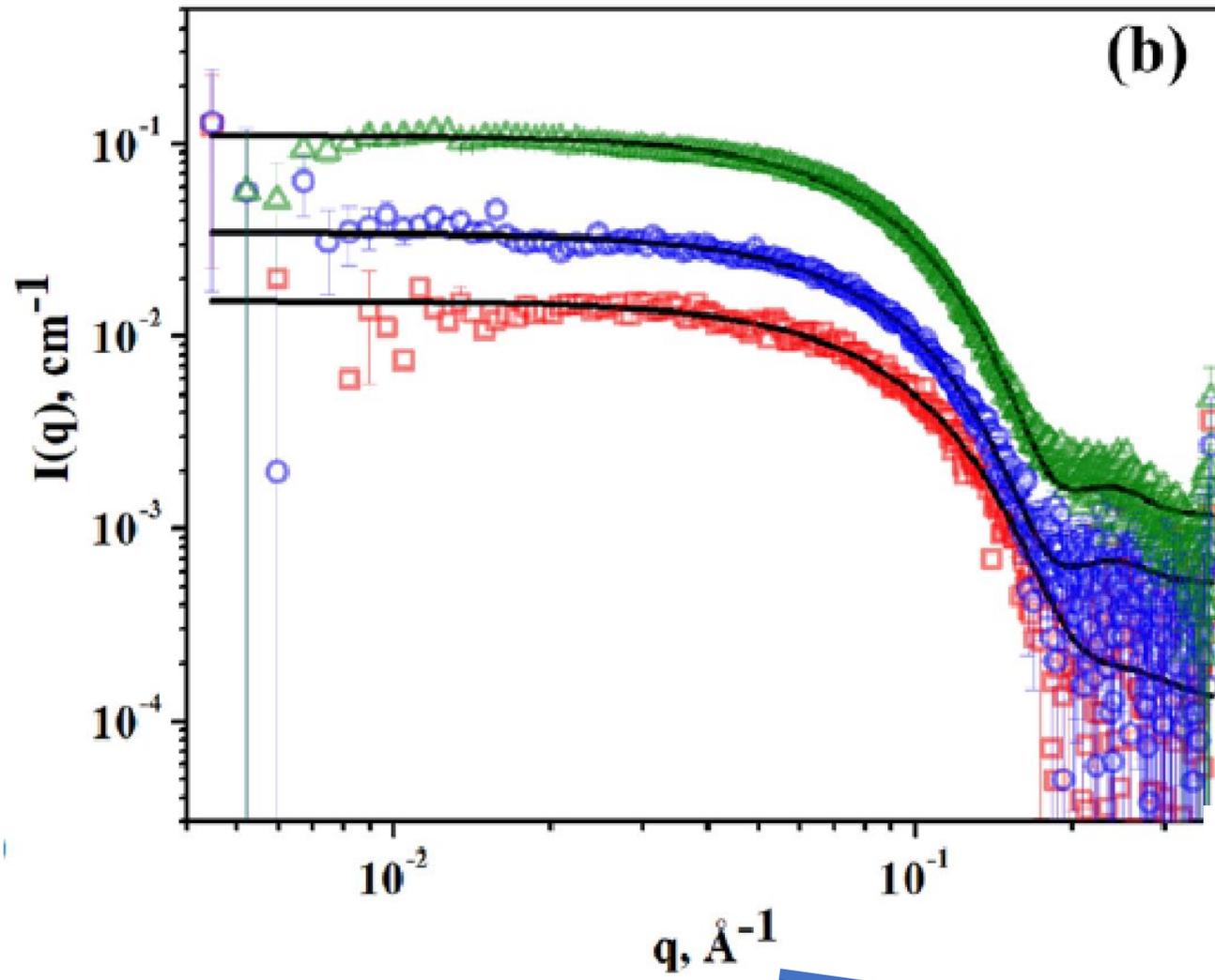
Particle characterization using light scattering

TABLE 5.5 Comparison of the Range Covered by Various Radiation Scattering Methods

Method	Typical wavelength (nm)	Range of s (nm^{-1})
Laser light scattering	500	$1 \cdot 10^{-3}$ – $4 \cdot 10^{-2}$
Small-angle x-ray scattering	0.15	$2 \cdot 10^{-2}$ – $4 \cdot 10^{-1}$
Small-angle neutron scattering	0.4	$7 \cdot 10^{-3}$ – $9 \cdot 10^{-1}$
Wide-angle neutron scattering	0.4	$1 \cdot 10^1$ – $5 \cdot 10^1$

X-rays and Neutrons can help us probe structure at much shorter length scales than what is possible with Laser.

Typical data from static light scattering



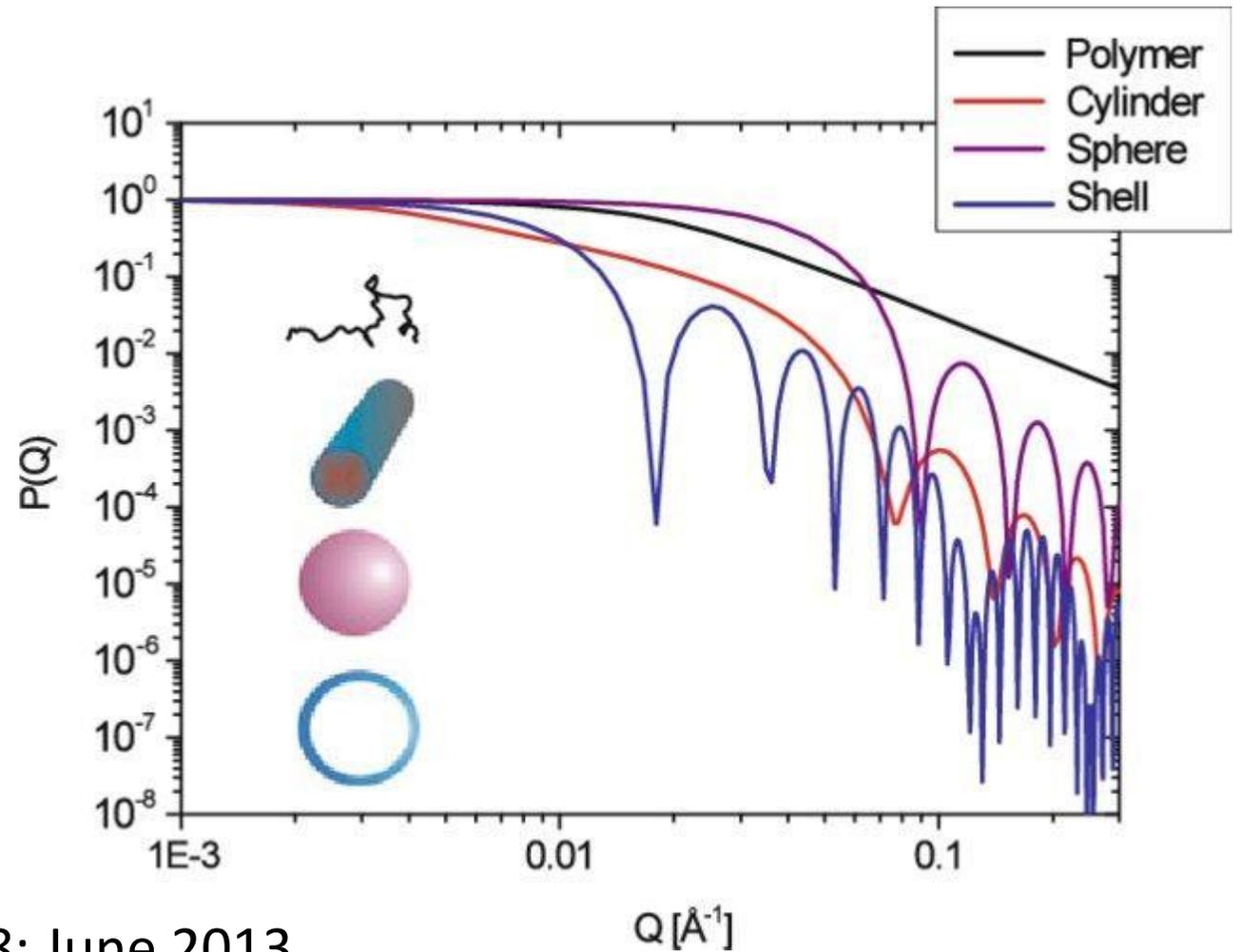
Rastogi, Preetika, et al.. " Langmuir 39.13 (2023): 4701-4711.

$$\frac{4\pi n}{\lambda} \sin \frac{\theta}{2}$$

Shape analysis by form factor analysis

$$I(q) = N_D V_D^2 \Delta\rho^2 P(q, R) S(q, R) + B$$

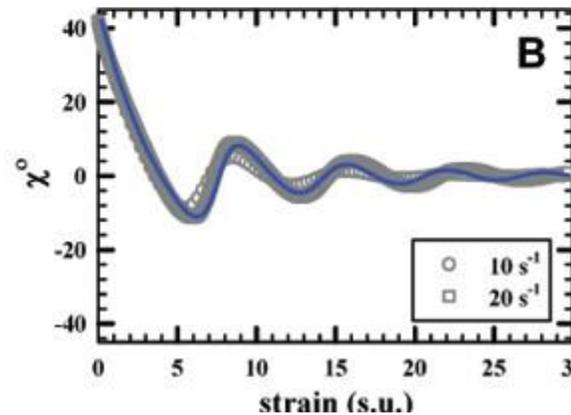
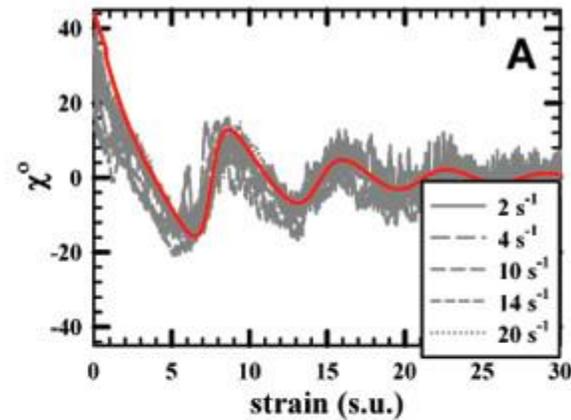
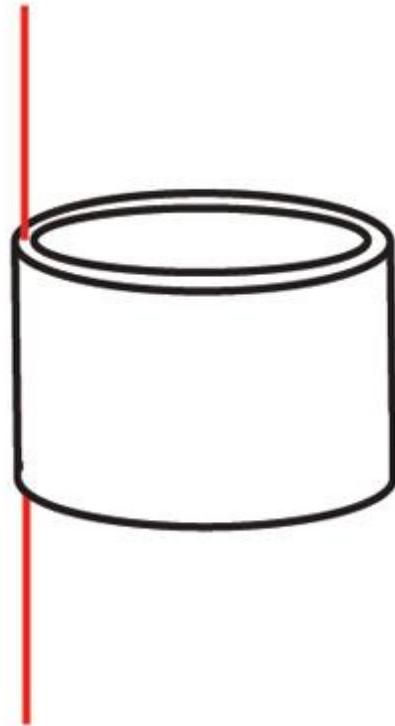
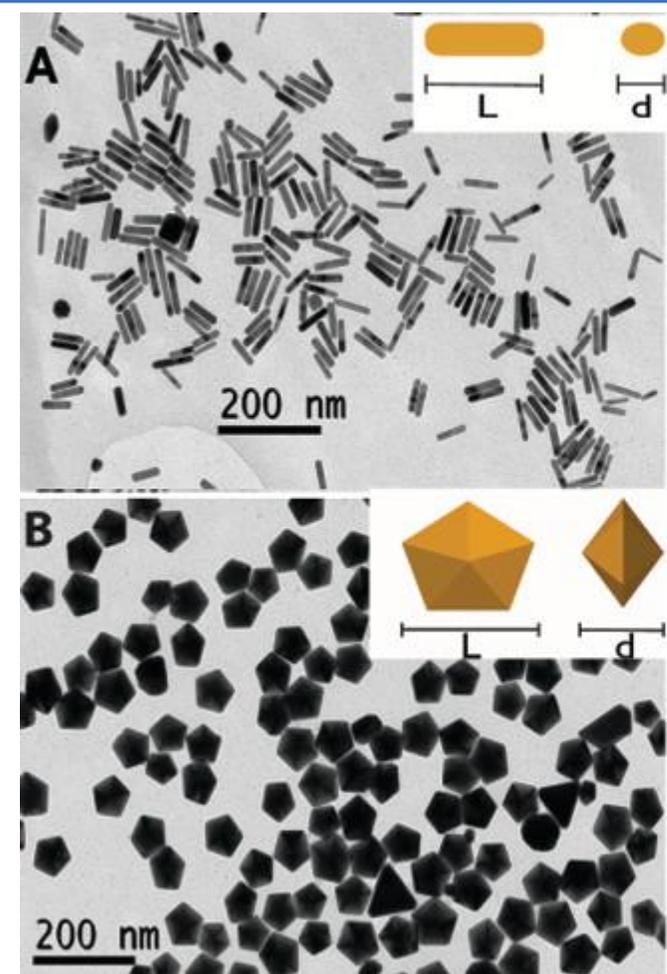
$$P(q, R) = \left(\frac{3(\sin qR - qR \cos qR)}{(qR)^3} \right)^2$$



Advances in Polymer Science 259:51-158; June 2013

Rastogi, Preetika, et al.. " Langmuir 39.13 (2023): 4701-4711.

Rheo-optical tools - flow dichroism



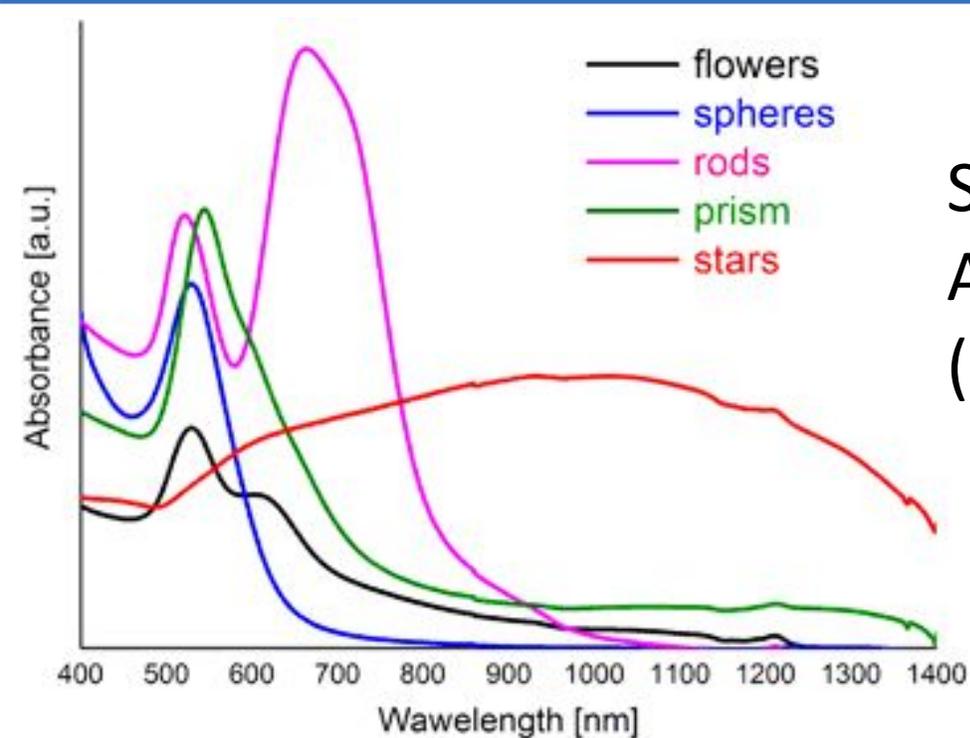
$$\Delta n'' = \frac{\delta'' \lambda}{2\pi l}$$

$$T = \frac{2\pi}{\dot{\gamma}} \left\{ P_D + \frac{1}{P_D} \right\}$$

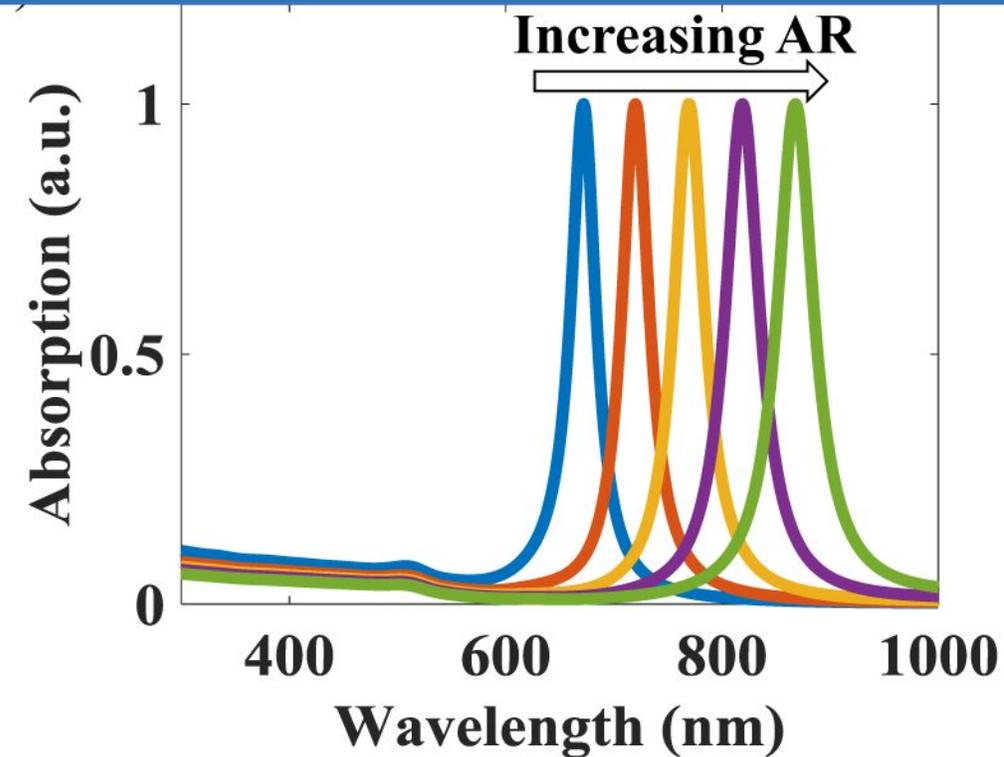
ACS Nano 2011, 5, 6, 4935-4944

$$\tan 2\chi = \frac{2 \int_0^{\infty} (P_D - P_D^{-1}) \sin \frac{4\pi t}{T} g(P_D) dP_D}{\int_0^{\infty} \left\{ P_D^2 - P_D^{-2} - (P_D^2 - P_D^{-2}) \cos \frac{4\pi t}{T} \right\} g(P_D) dP_D}$$

UV-visible absorption spectroscopy



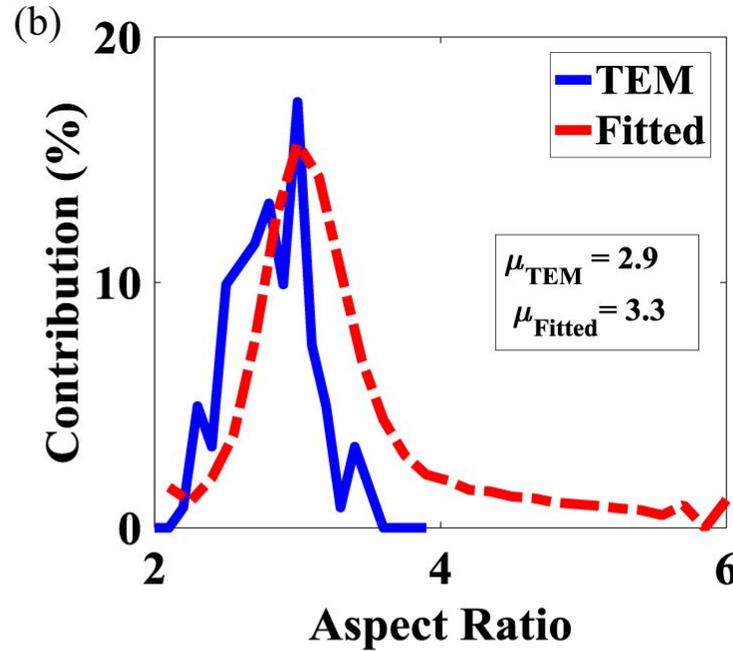
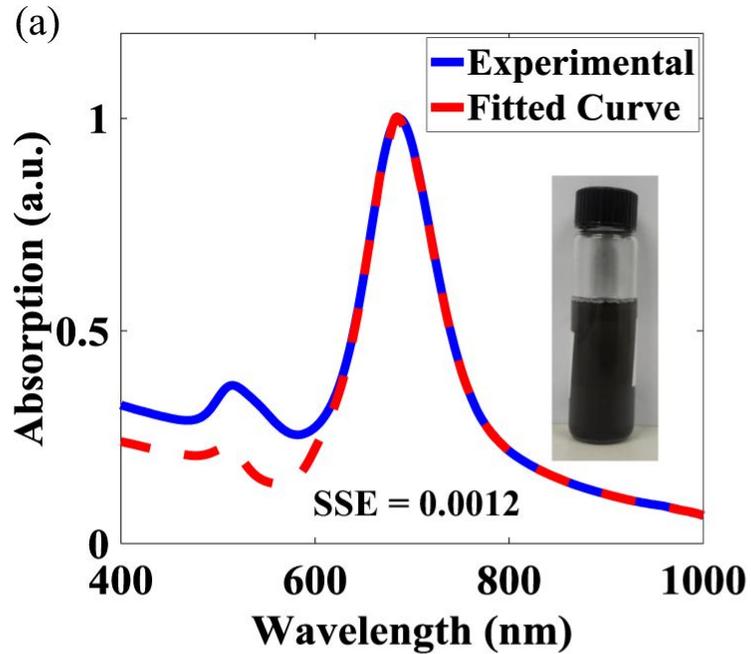
Sci. Reports 9,
Article No: 17469
(2019)



- The interaction of AuNPs with electromagnetic field produces surface plasmon resonance due to the collective oscillation of free conduction electrons
- The position and intensity of the band measured by UV-viz depends on the size, surface morphology and aspect ratio of nanostructures.

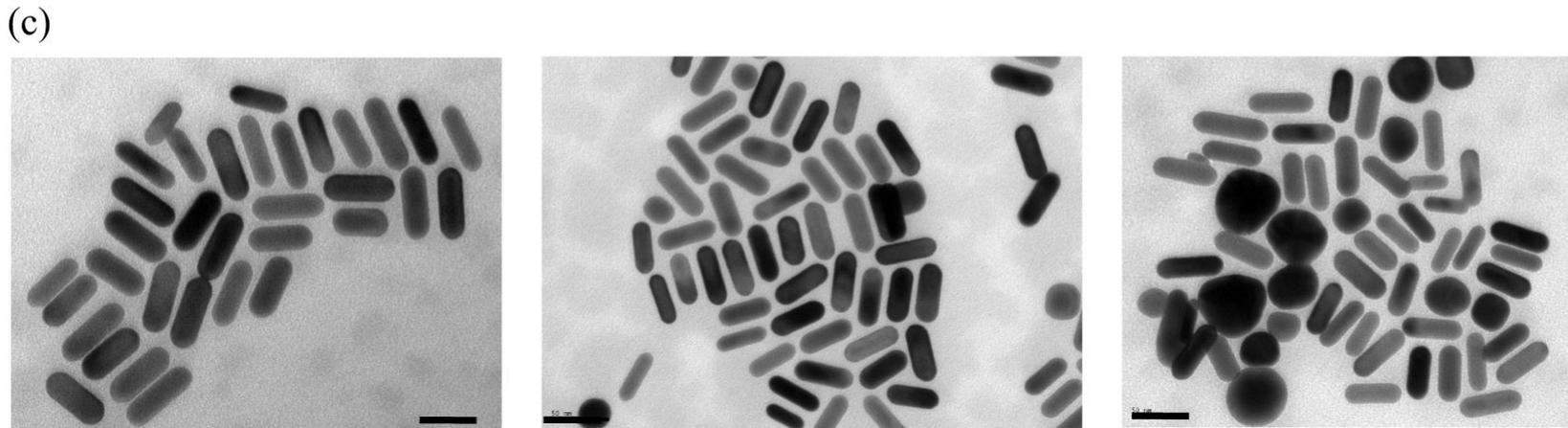
Journal of Materials Science: Materials in Medicine, 28, Article number: 92 (2017)

UV-visible absorption spectroscopy



The absorption coefficient for the AuNPs (A, B, C...) is given by:

$$\gamma = \frac{2\pi NV \epsilon_m^{\frac{3}{2}}}{3\lambda} \sum_{J=A,B,C} \frac{(1/P_J^2)\epsilon_2}{\left(\epsilon_1 + \left[\frac{1-P_J}{P_J}\right]\epsilon_m\right)^2 + \epsilon_2^2}$$



$$P_A = \frac{1 - e^2}{e^2} \left[\frac{1}{2e} \ln \left(\frac{1+e}{1-e} \right) - 1 \right],$$

$$P_B = P_C = \frac{1 - P_A}{2},$$

$$e = \sqrt{1 - \left(\frac{W}{L}\right)^2}.$$

Outline

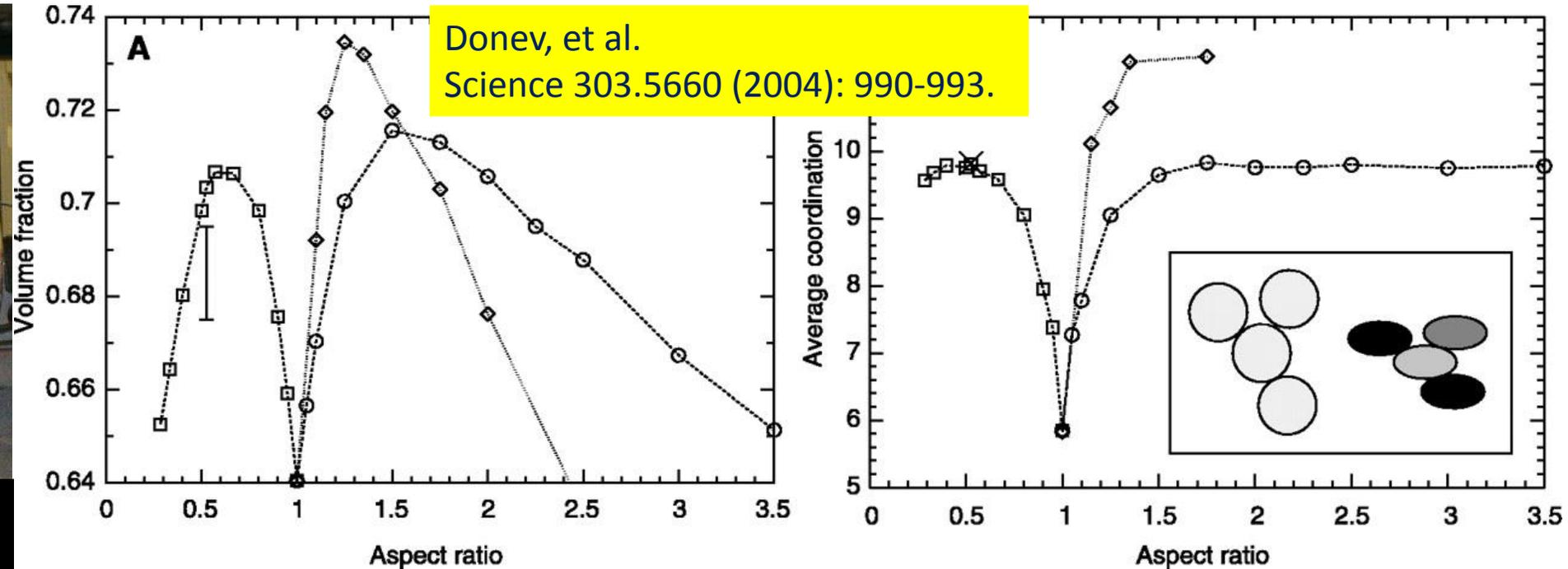
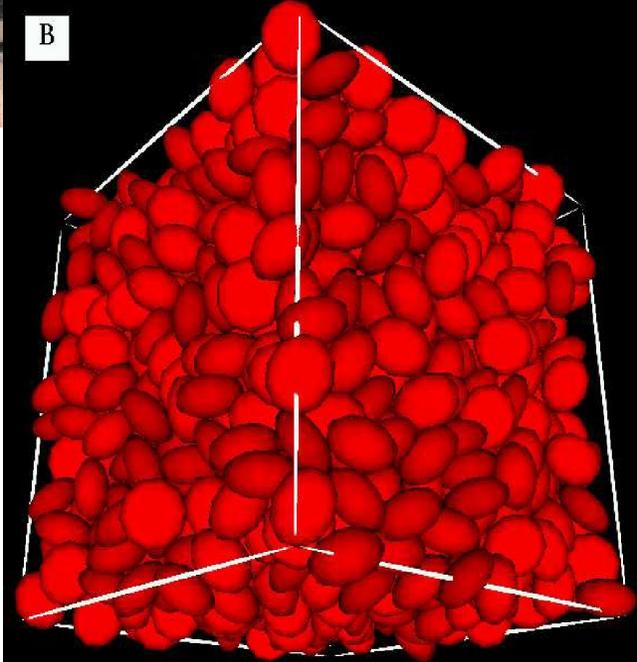
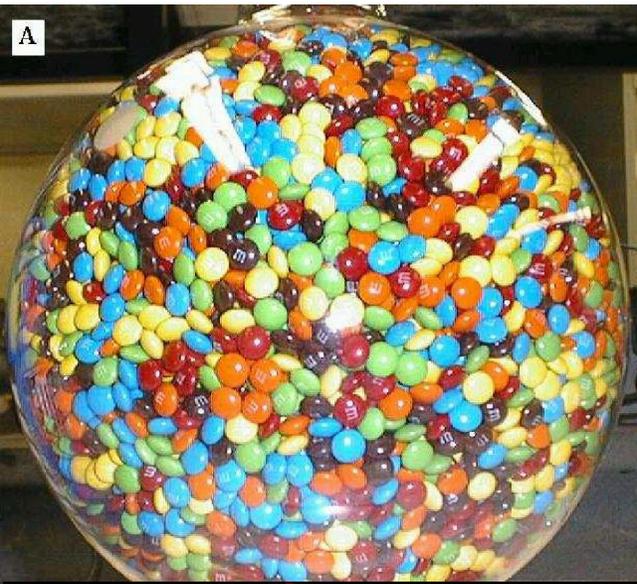
- **Introduction**
- **Classification of anisotropic particles**
- **Particle shape analysis – scattering**
- **Particle shape descriptors**
- **Exploiting particle effects - some examples**

Exploiting particle effects - some examples

- **Packing in 2D/3D and rheology**

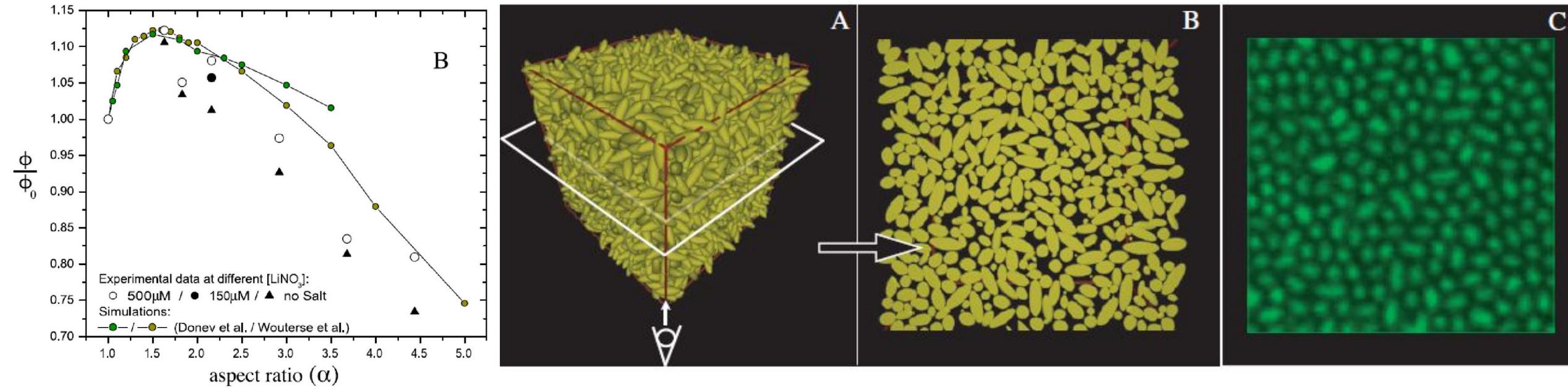
Implications in the design of granular media, development of ceramics, glass formation, fabrication of catalytic supports and novel materials, and discrete geometry.

Packing – granular system



1. The ellipsoids are shown to pack with randomly packing density up to $\phi = 0.68$ to 0.74
2. The higher density is shown to be directly related to the higher number of degrees of freedom per particle and larger number of particle contacts required to mechanically stabilize the packing.
3. The number of contacts per particle (Z) ≈ 10 for our spheroids, as compared to ≈ 6 for spheres.

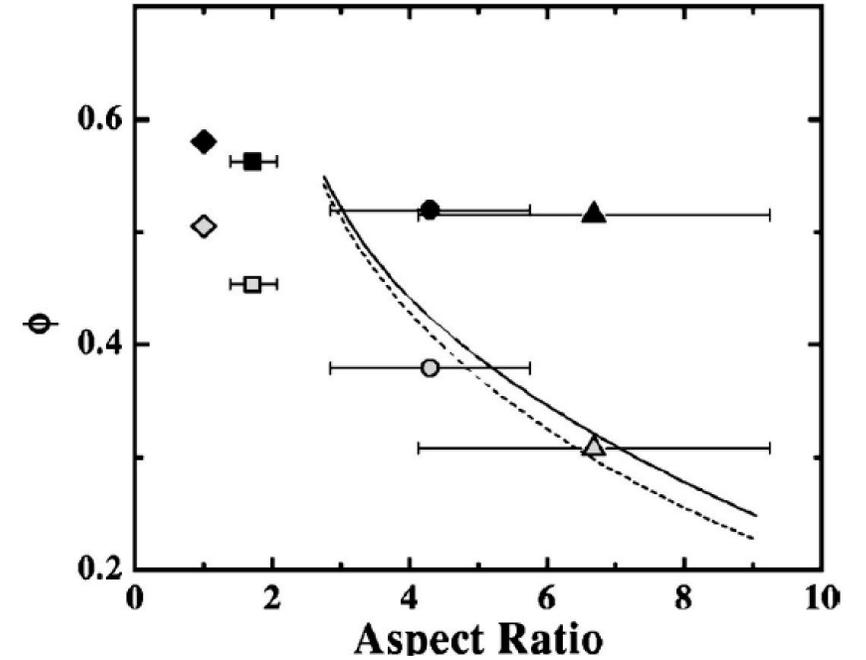
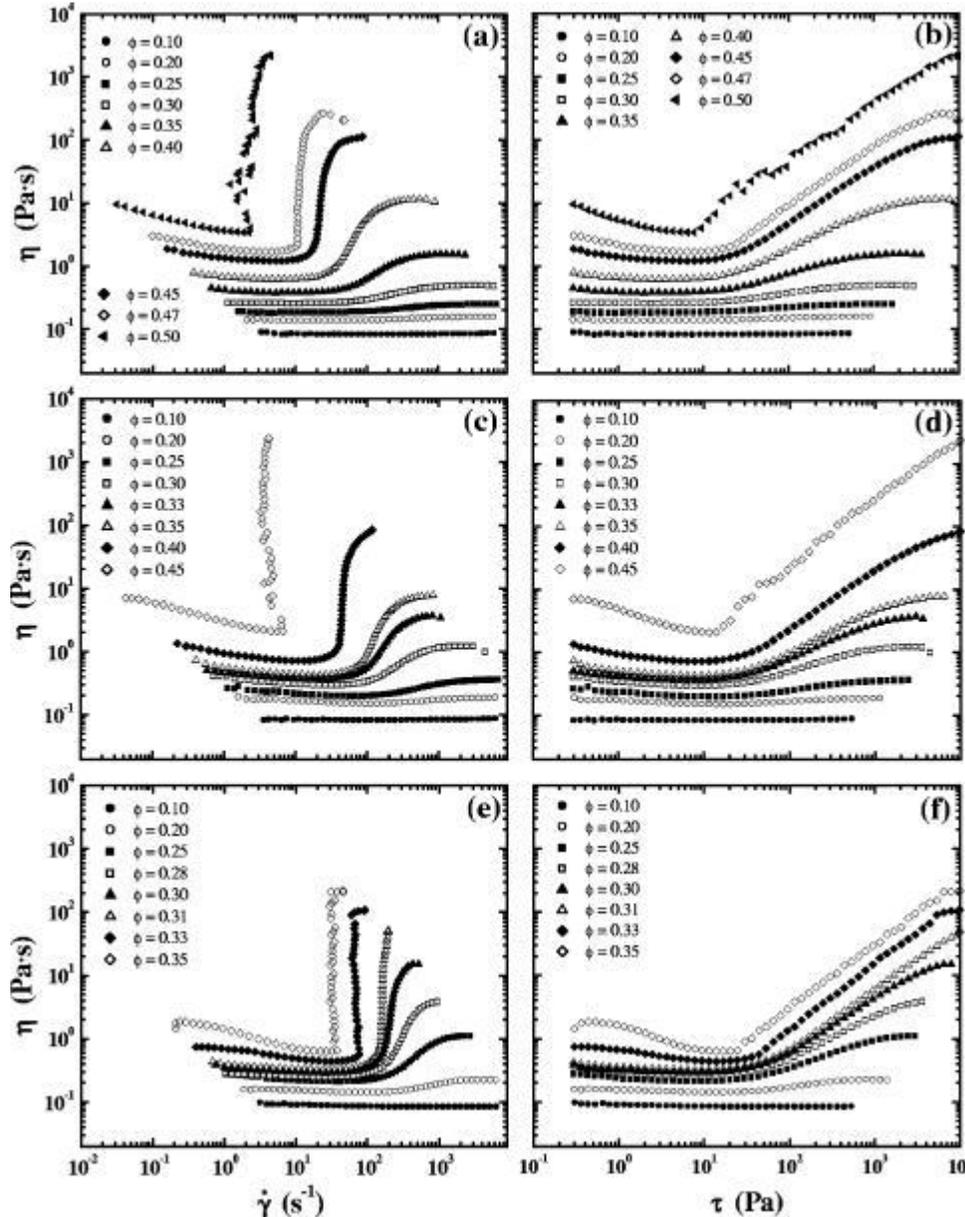
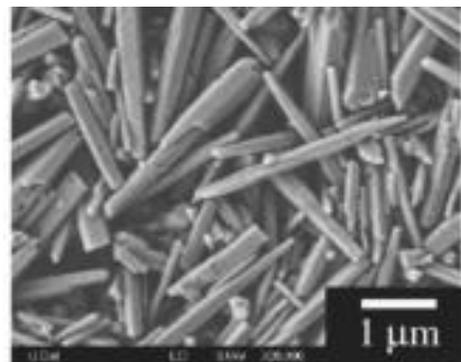
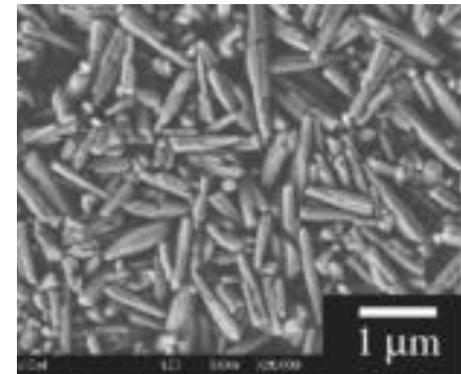
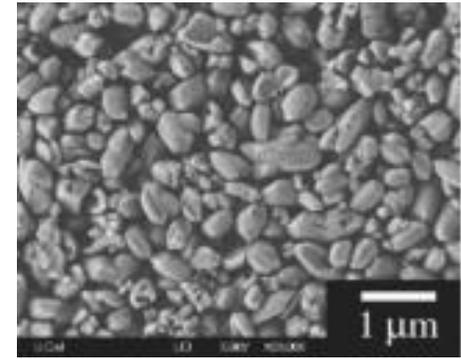
Packing – colloidal system



Sacanna, Stefano, et al. *Journal of Physics: Condensed Matter* 19.37 (2007): 376108.

- ϕ_0 - experimental random sphere packing fraction at 500 μM LiNO_3
- Experiments with colloidal ellipsoids – hematite particles coated with silica
- The density maximum (at an aspect ratio near 1.6) found in computer simulations of granular packings.

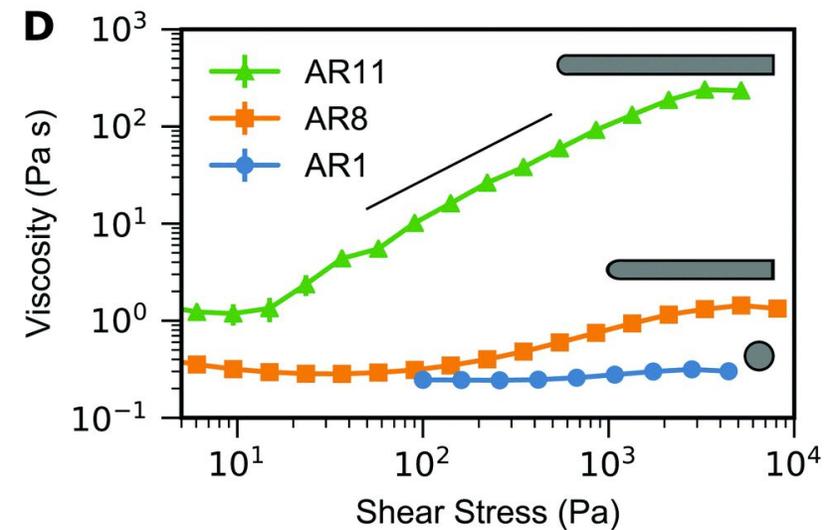
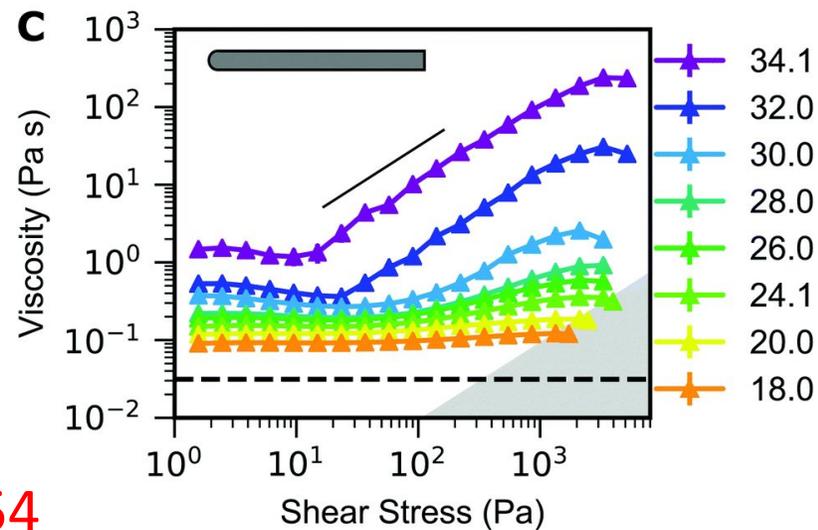
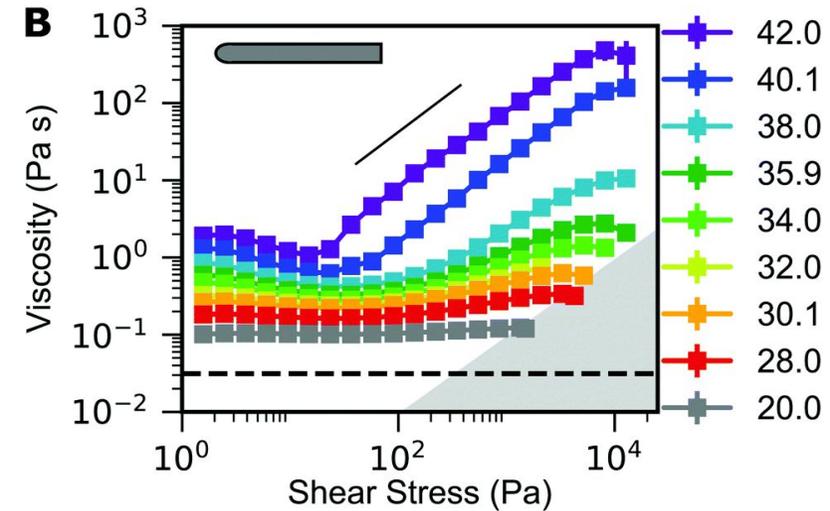
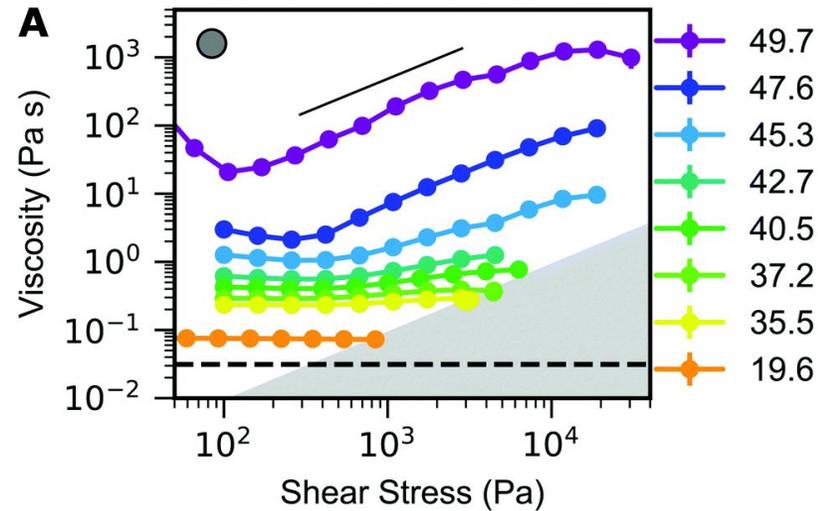
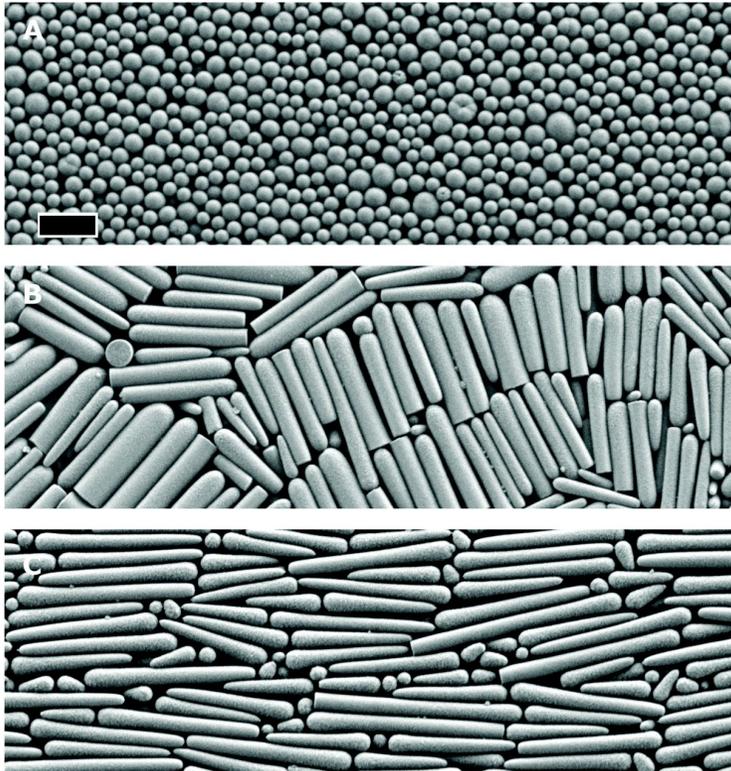
Shear thickening



Critical volume fraction for discontinuous shear thickening (open symbols), maximum packing fraction (filled symbols)

Ronald G. Egres; Norman J. Wagner
Journal of Rheology
49, 719–746 (2005)

Shear thickening



Nicole M. James et. al.,

Soft Matter, 2019,15, 3649-3654

Enhancement of shear thickening is observed with increasing aspect ratio (see figure D)

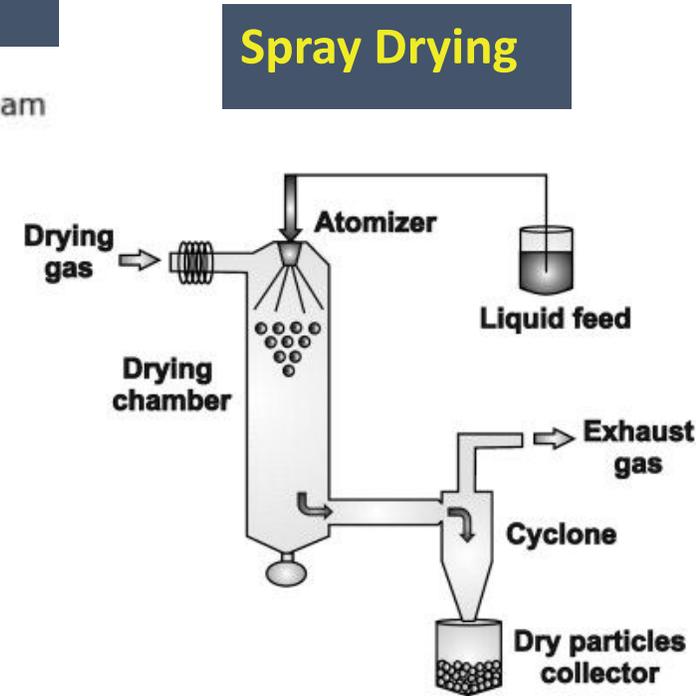
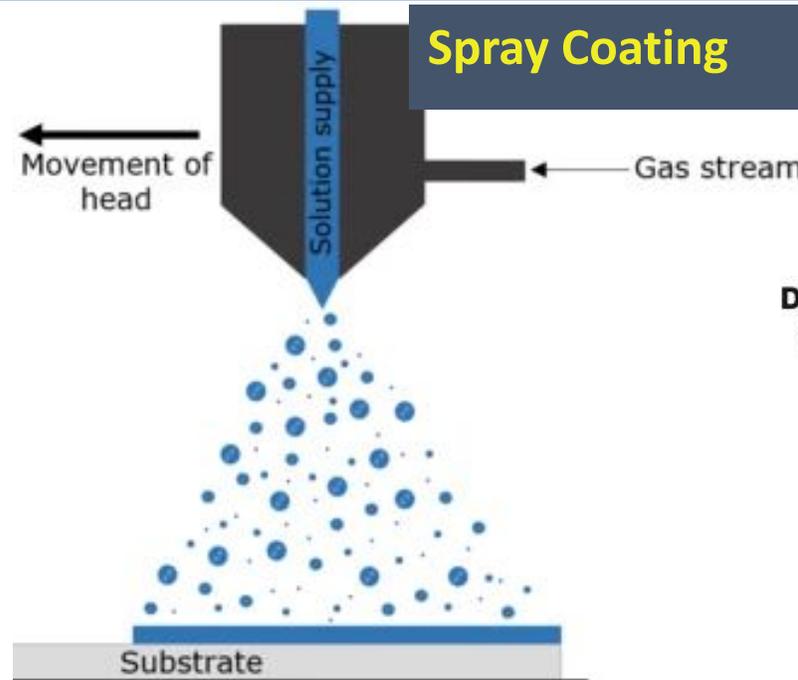
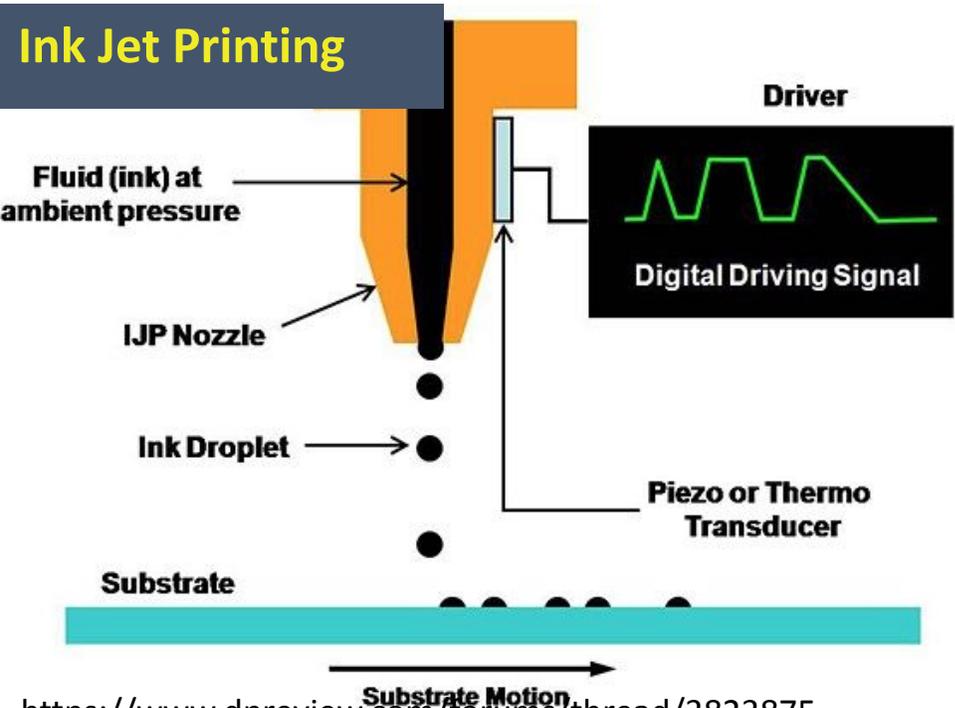
Exploiting particle effects - some examples

- **Drying particle laden drops**

Implications in printing/coating technology,

Drops on Surfaces

- ◆ Spray Coating
- ◆ Spray Drying
- ◆ Ink Jet Printing



<https://www.dpreview.com/forums/thread/3823875>

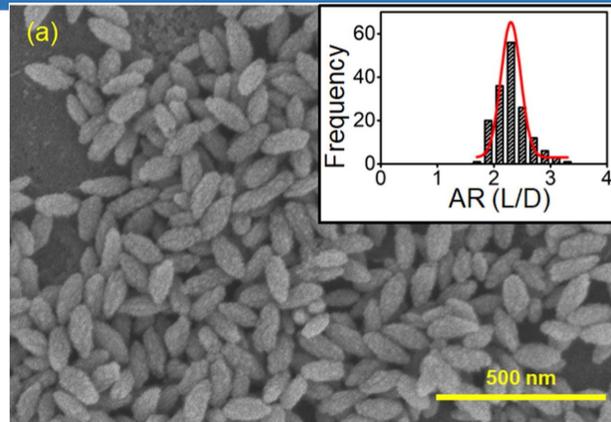
Advances in Colloid and Interface Science, 223, 2015, Pages 40-54

<https://www.123rf.com>

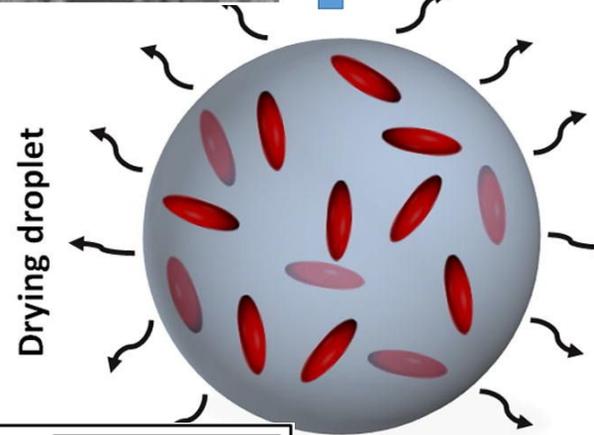
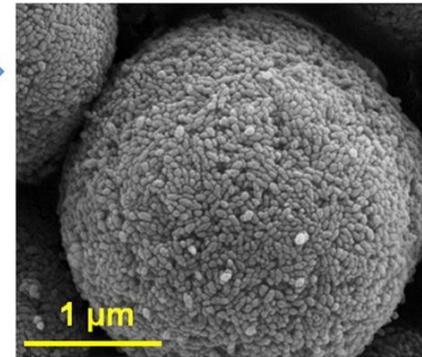
<https://www.ossila.com/pages/opv-large-scale-deposition>

Spray Drying

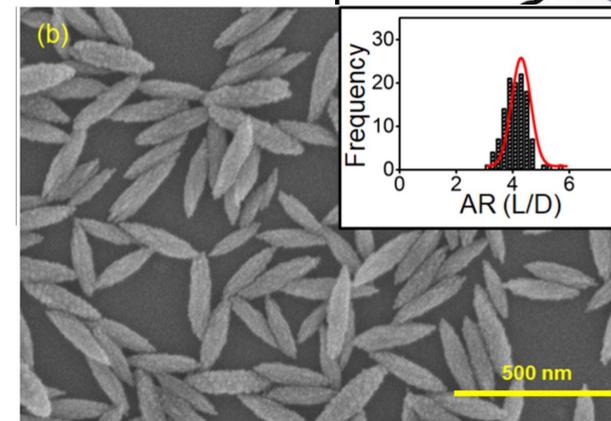
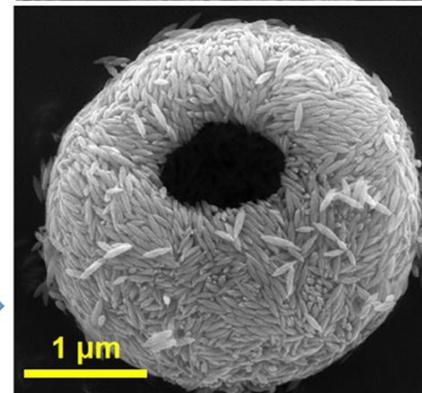
Journal of Colloid and Interface Science
551, 1 September 2019, Pages 242-250



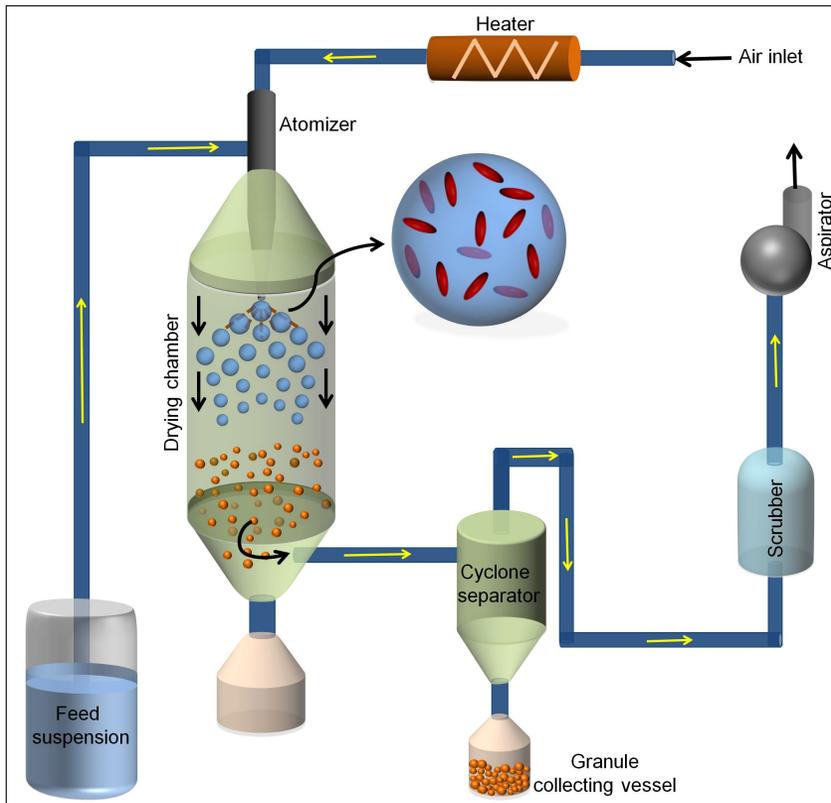
Particle aspect ratio=2.3



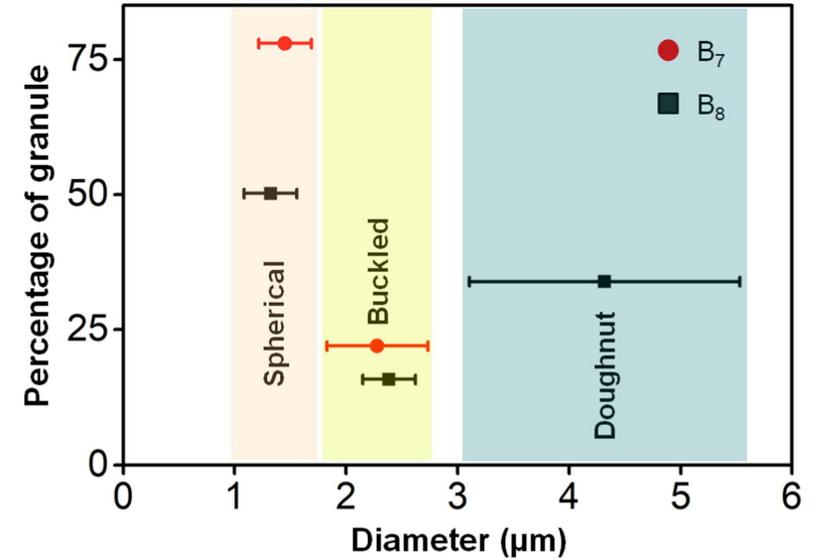
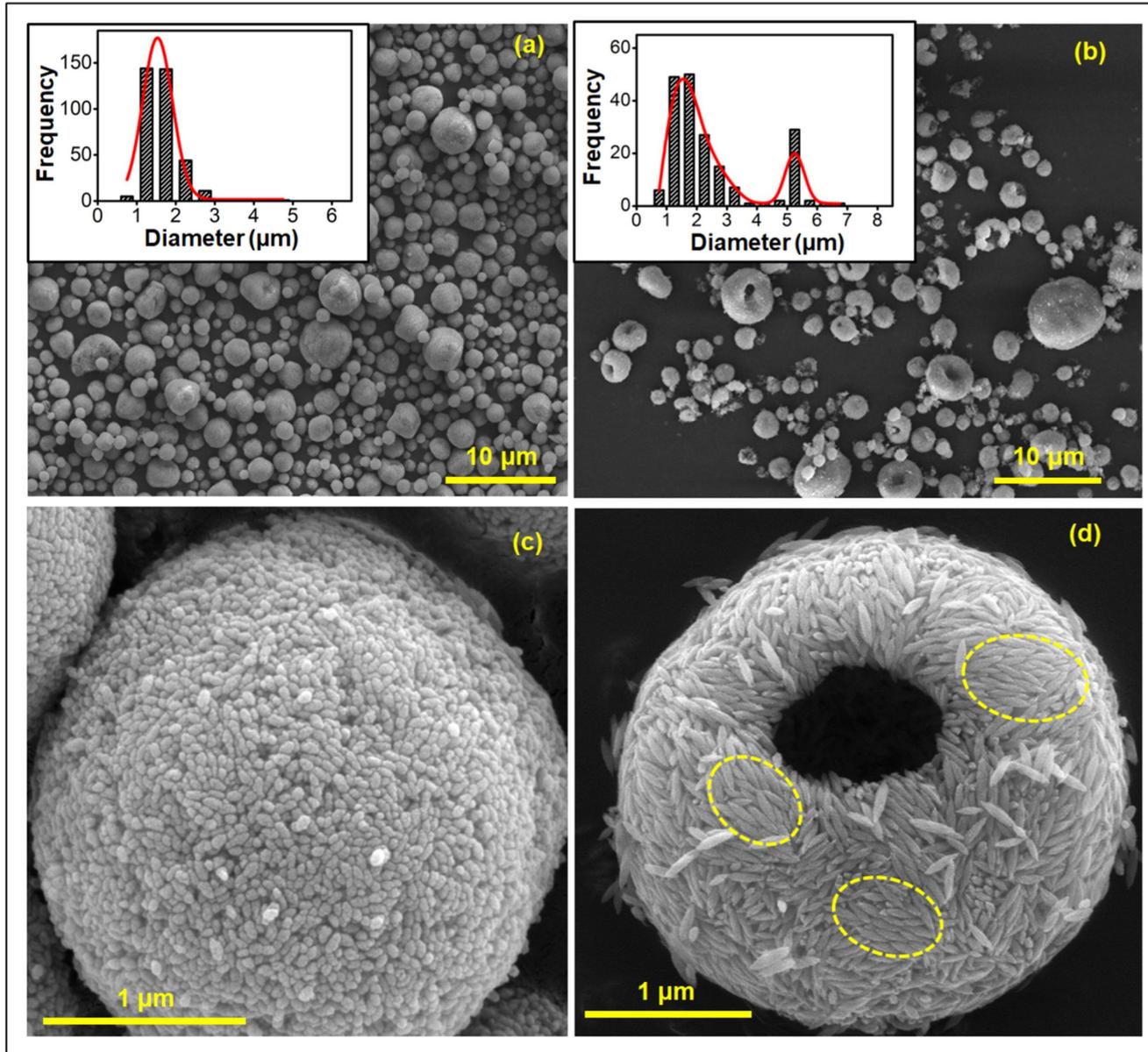
Particle aspect ratio=4.3



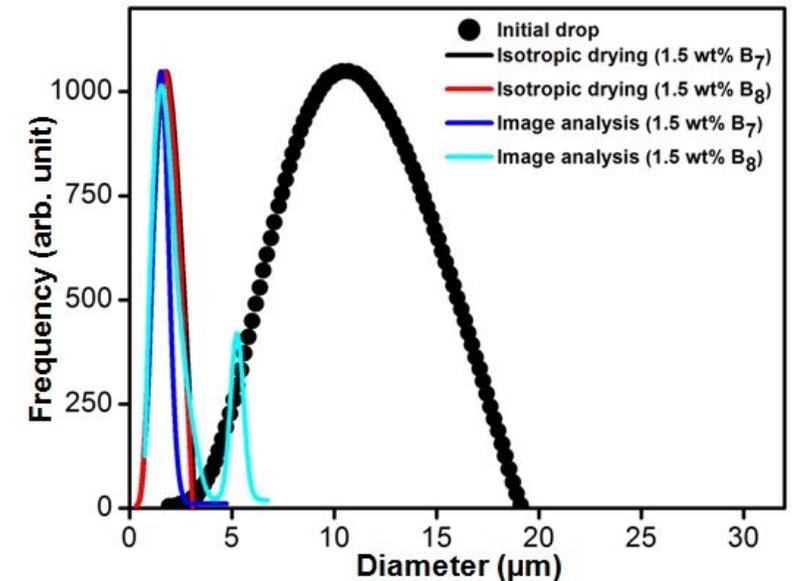
JCIS, 551, 1 September 2019, Pages 242-250



Spray Drying

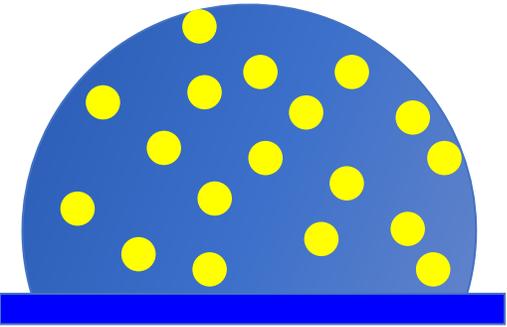


JCIS, 551, 1 September 2019, Pages 242-250



Evaporation of colloidal dispersions

Langmuir 37 (14), 4395–4402, (2021)



Further Insights into Patterns from Drying Particle-Laden Sessile Drops

Dinesh Parthasarathy^{1,2}, Dr. Sumesh P.Thampi², Dr. Parag Ravindran¹, Dr. Madivala G. Basavaraj²

Radial flow

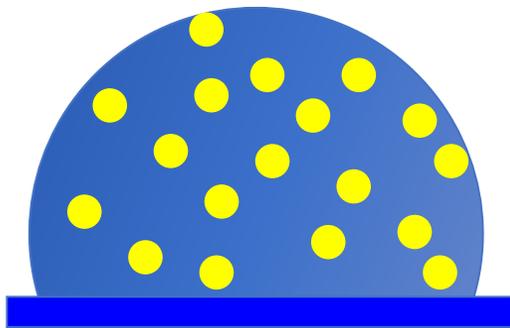
Particle accumulate at the edge

Initial stage – slow

Final stage – fast

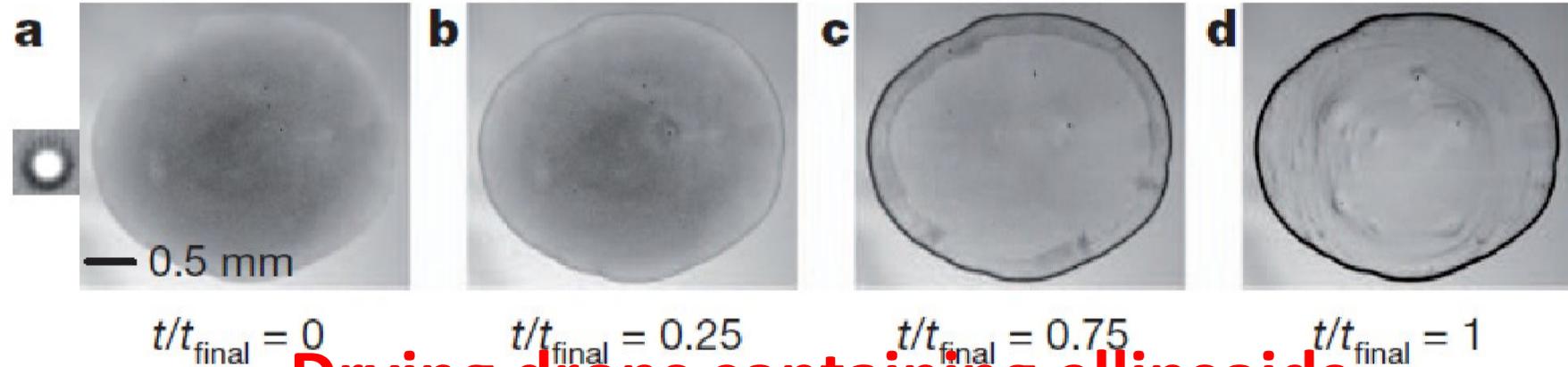
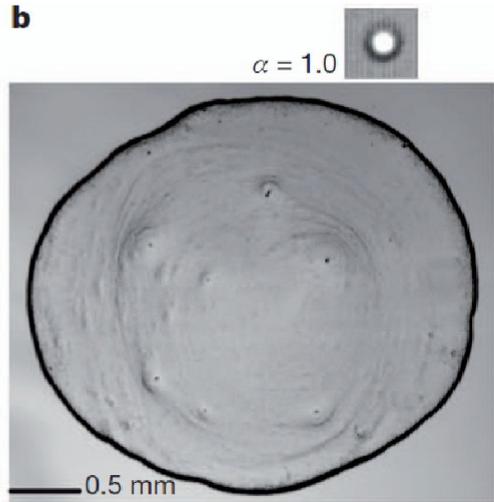
Evaporation of colloidal dispersions

Langmuir 37 (14), 4395–4402, (2021)

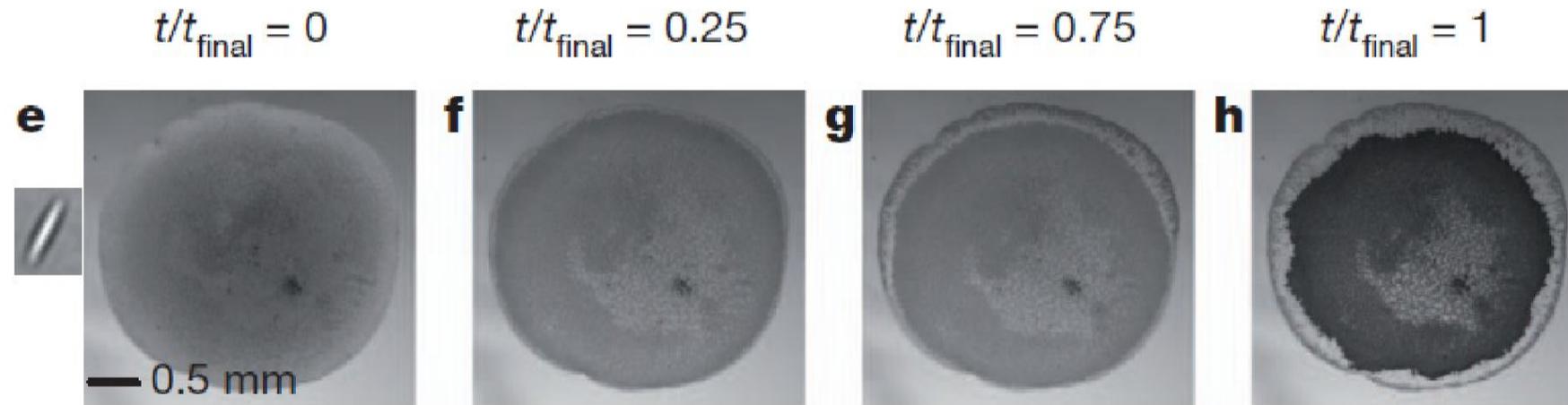
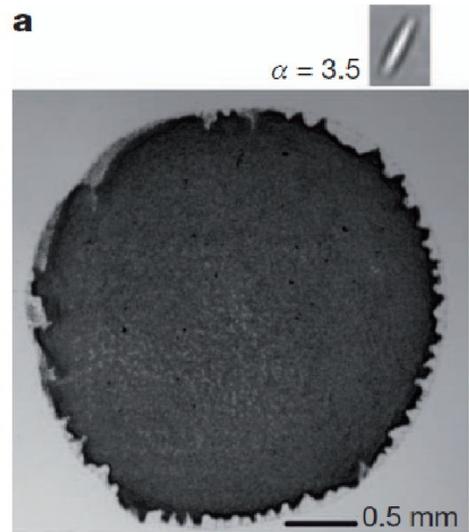


Evaporation of dispersions of non-spherical particles

Drying drops containing spheres



Drying drops containing ellipsoids



Aspect ratio independent

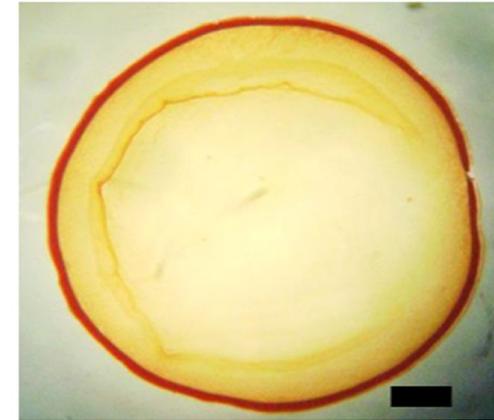
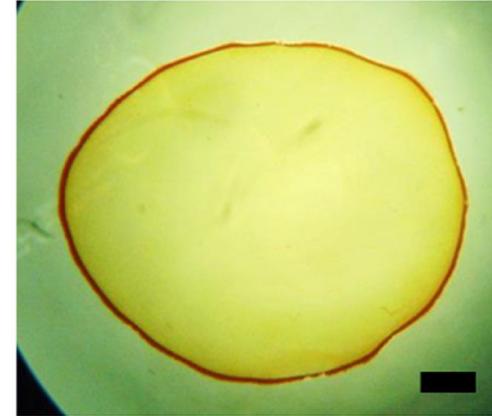
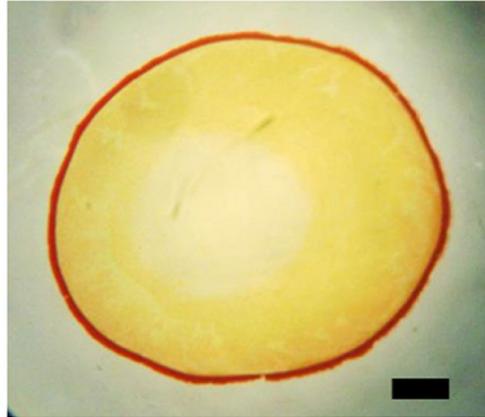


AR 2

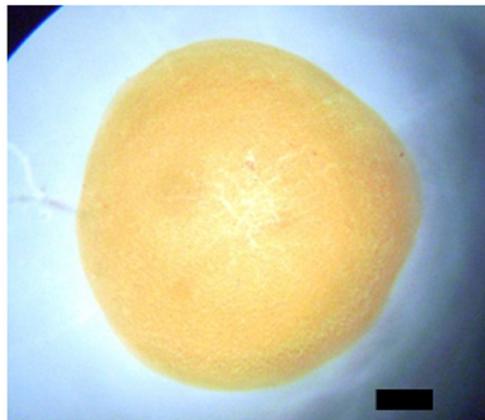
AR 4

AR 6

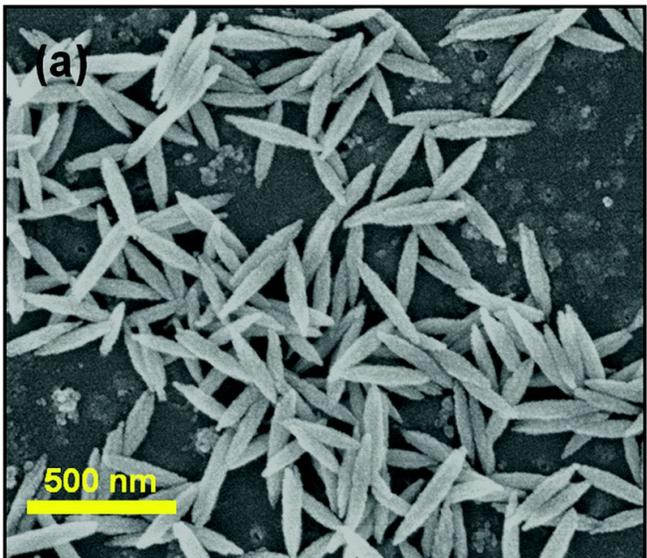
pH 2

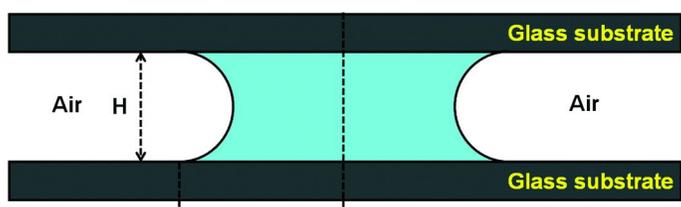


pH 6.5



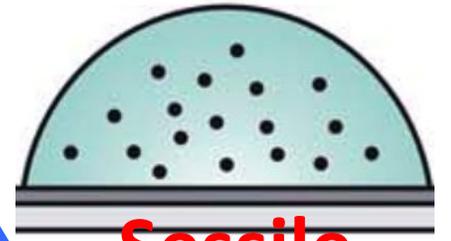
Langmuir 30 (29), 8680-8686 (2014)



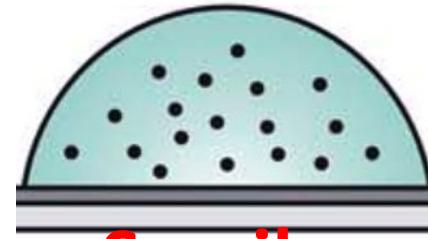


Parallel Plate

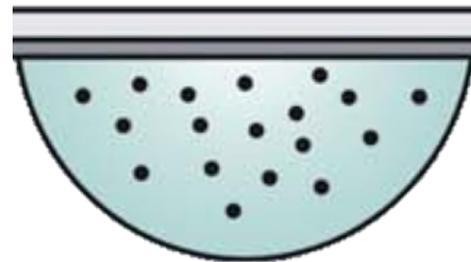
The deposition patterns depend on colloidal interactions and drying configuration, not just on particle shape



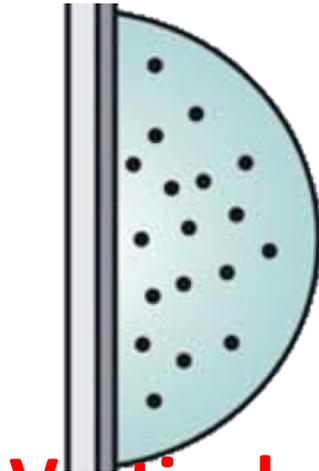
Sessile



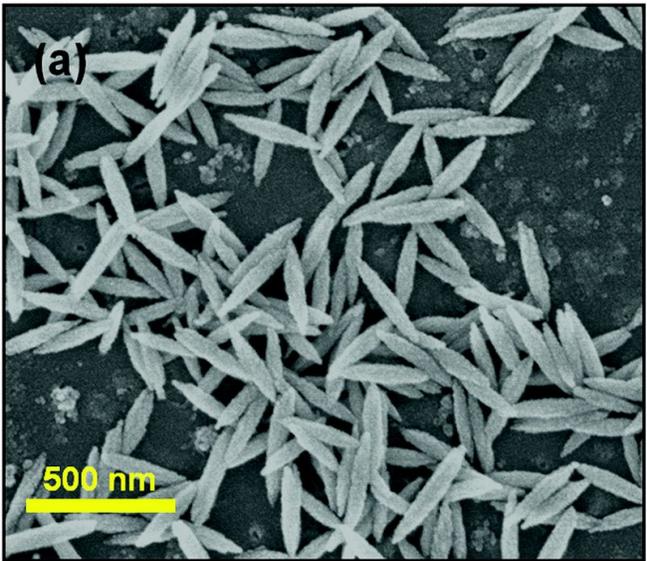
Sessile

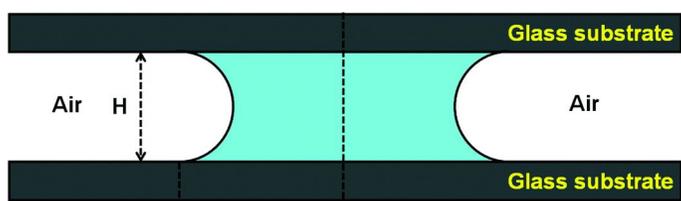


Pendant

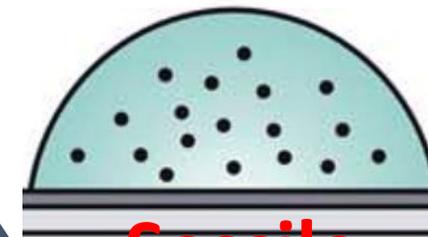
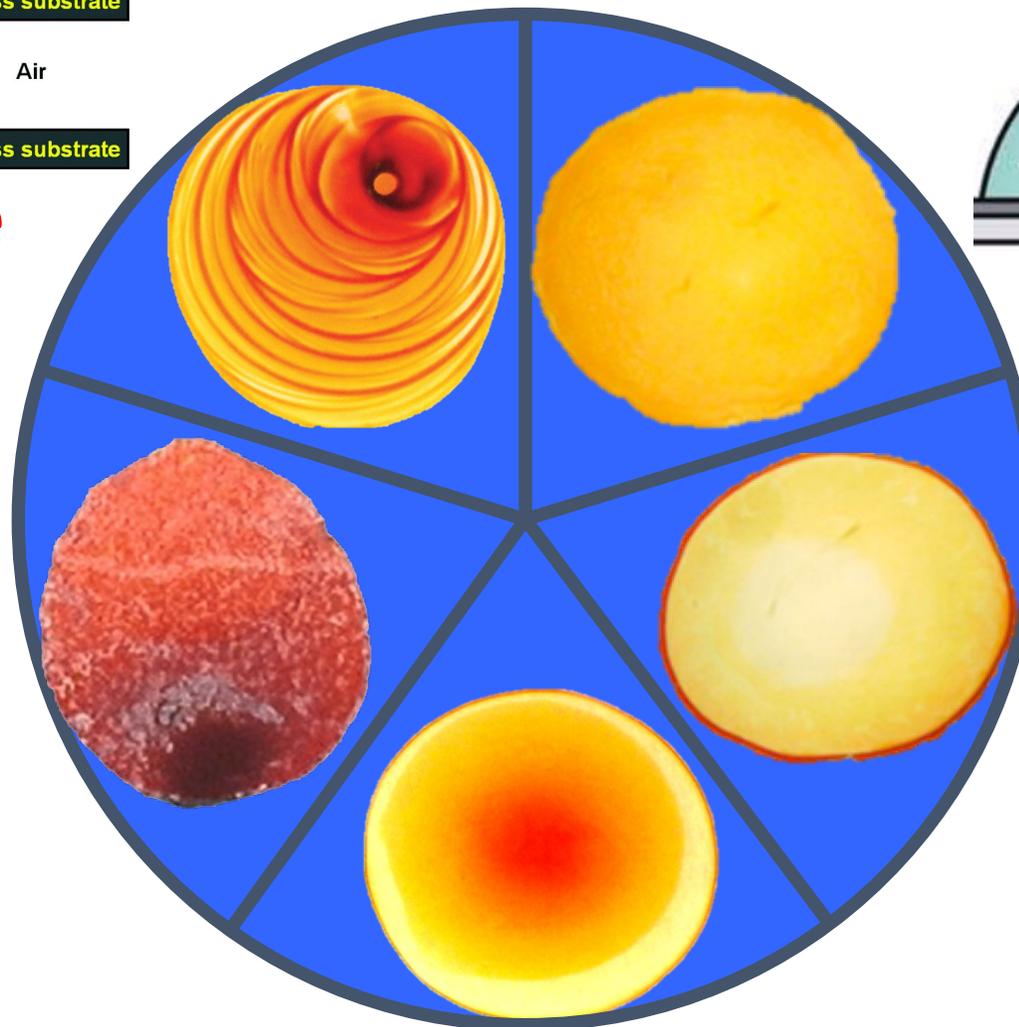


Vertical

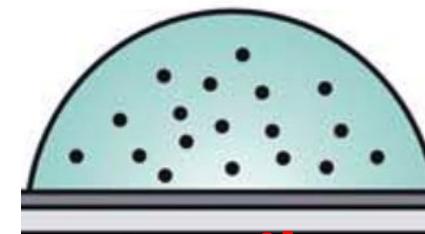




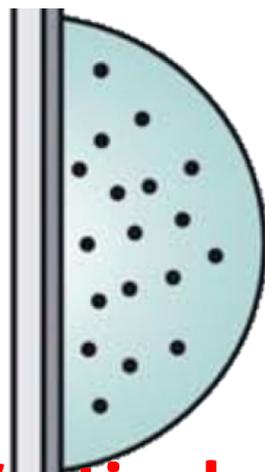
Parallel Plate



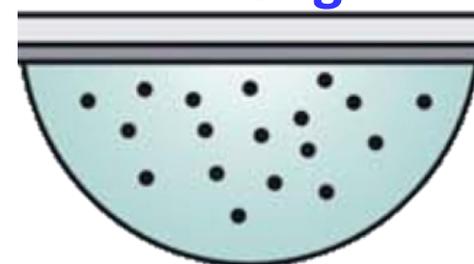
Sessile



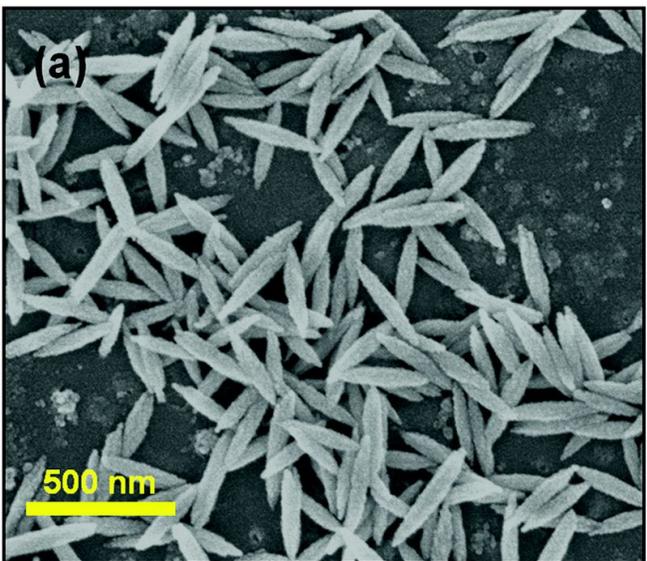
Sessile



Vertical



Pendant



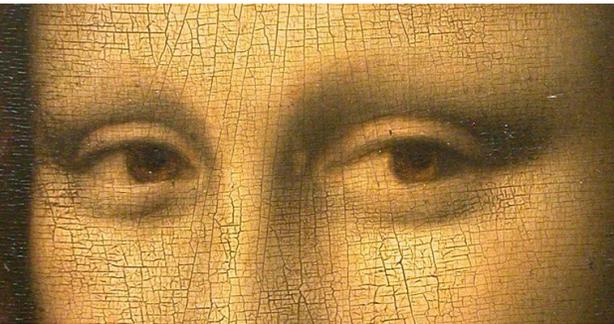
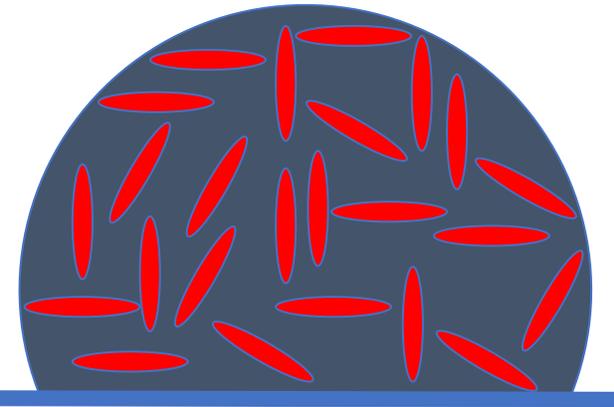
Langmuir 30 (29), 8680-8686 (2014)

Soft Matter, 16 (15), 3753-3761 (2020)

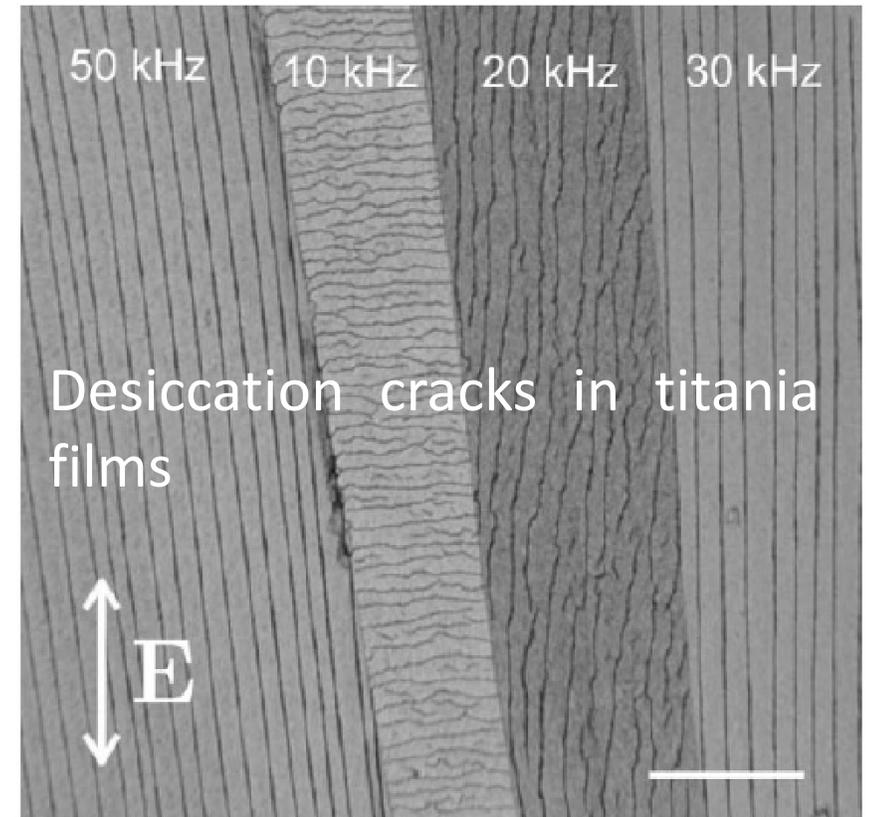
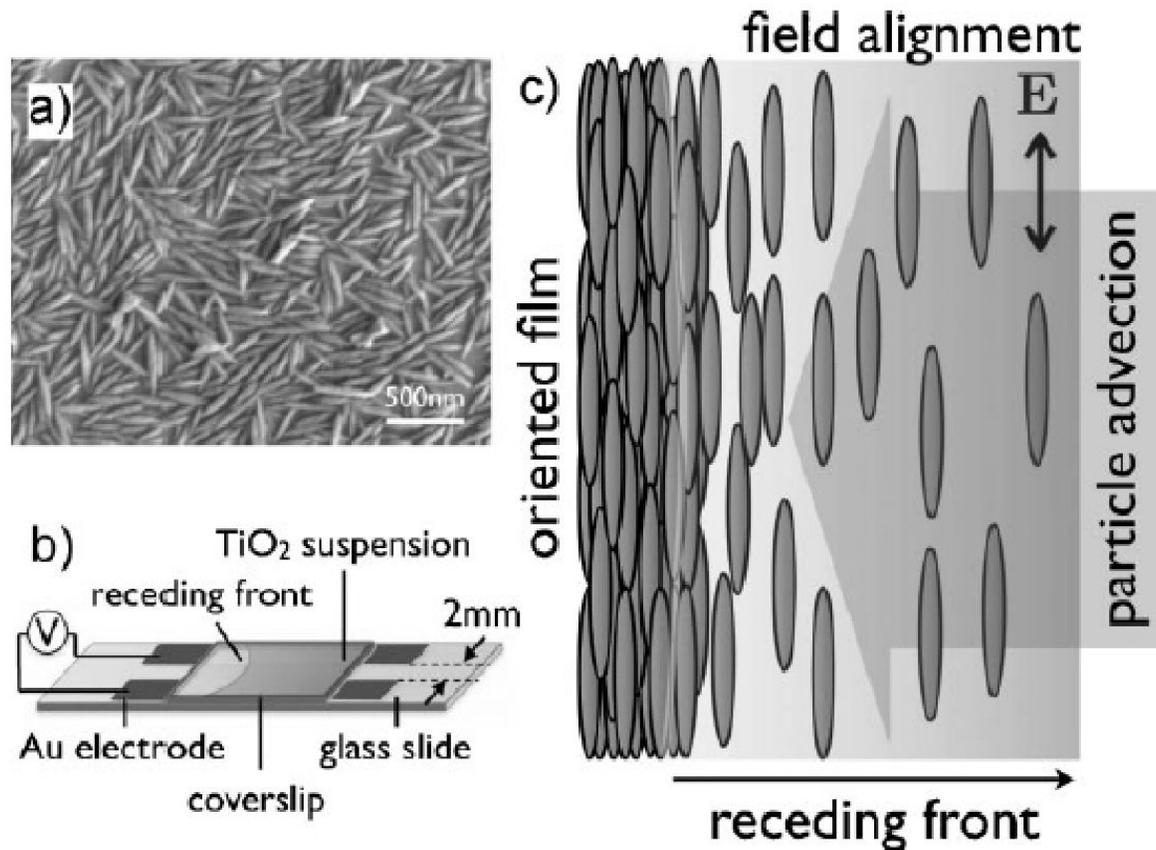
Langmuir, 34, 11473-11483 (2018)

Desiccation cracks

Effect of particle shape, drying geometry, temperature, magnetic field



Desiccation cracks – influence of electric field driven self-assembly

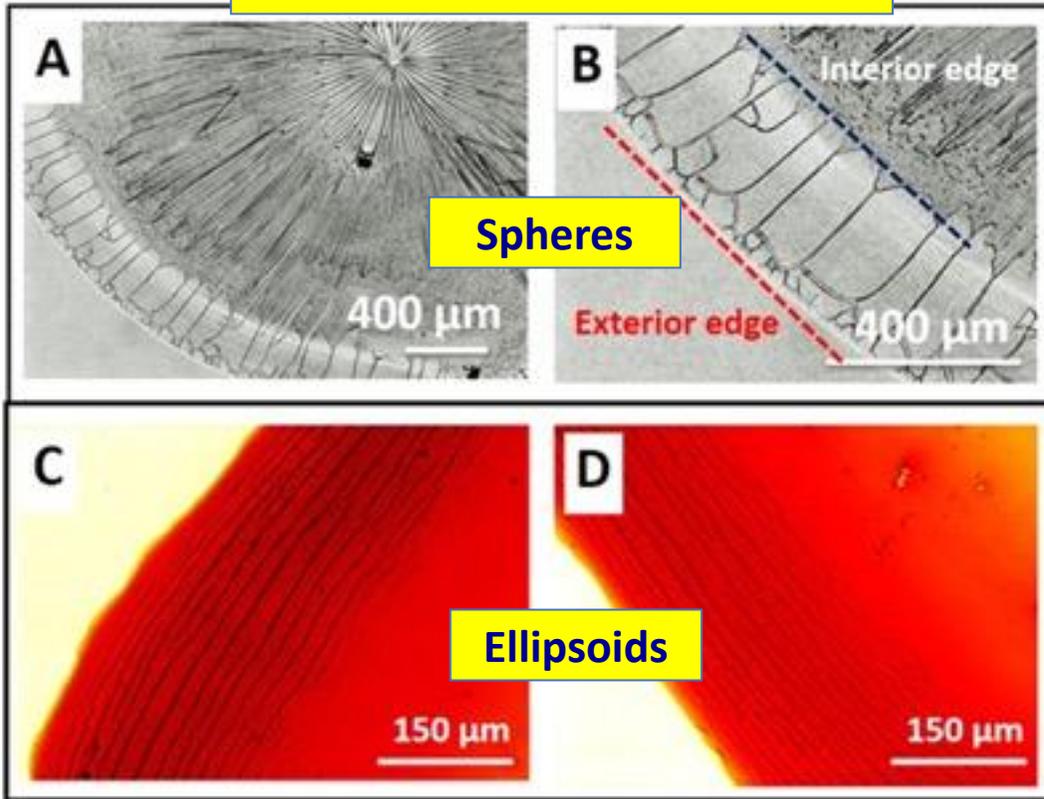


The major axis ~ 260 nm, and the minor axis ~ 62 nm, resulting in an aspect ratio of 4.19. □ field-assisted convective assembly of titania particles □ The particles align as they advect towards the drying front.

M Mittal, EM Furst.
Advanced Functional Materials
19 (20), 3271-3278 (2009)

Desiccation cracks

Particle Shape



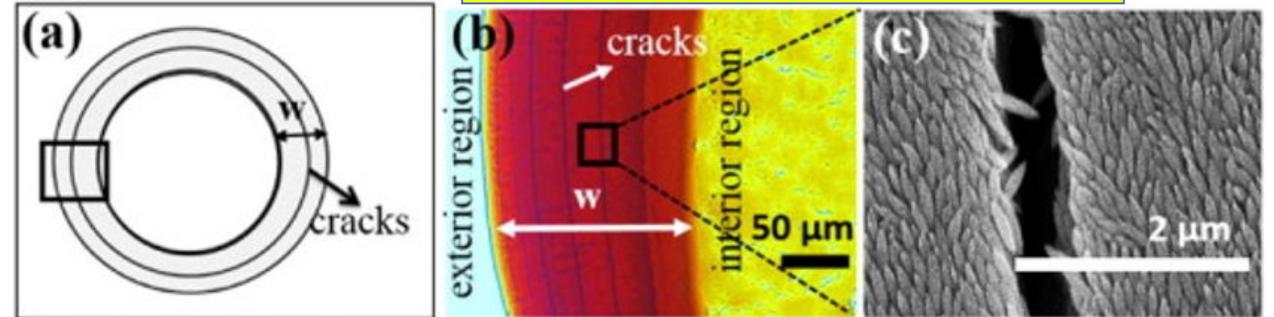
Scientific Reports 6, 30708 (2016)

Phys. Chem. Chem. Phys., 21, 20045-20054 (2019)

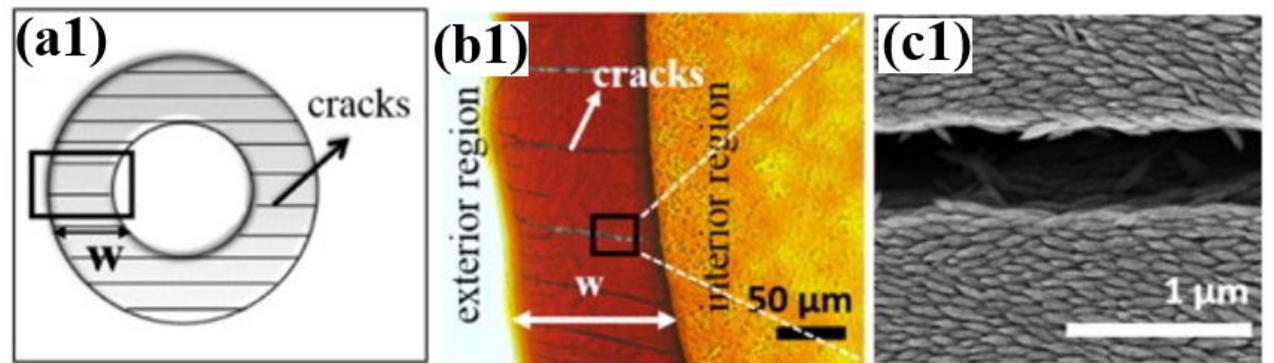
Soft Matter, 13, 5445 - 5452 (2017)

Magnetic Field

$$|\vec{H}| = 0$$



$$|\vec{H}| \neq 0$$



Physical Review E 94 (1), 012618 (2016)

Journal of Colloid and Interface Science, 510, 172–180 (2018).

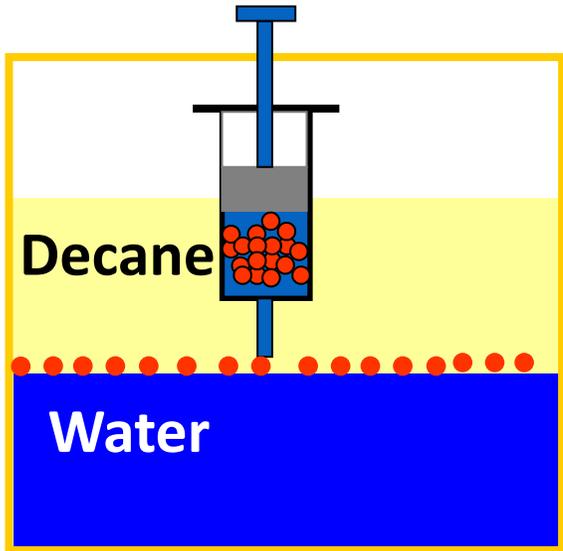
Physical Review Materials 2, 085602 (2018)

Exploiting particle effects - some examples

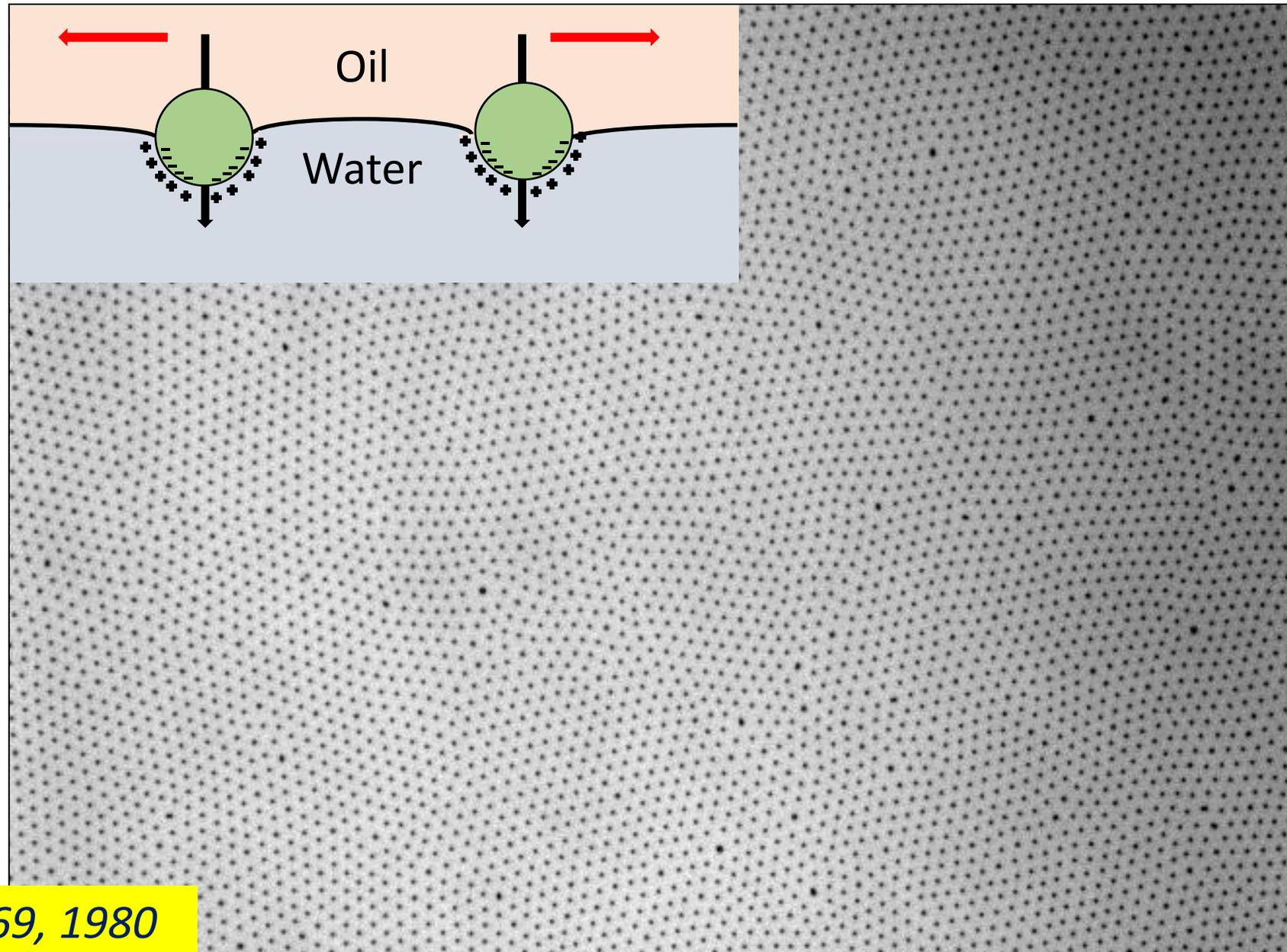
- **Anisotropic particles at interfaces**

Self-assembly, Interfacial rheology and implications in emulsion stabilization

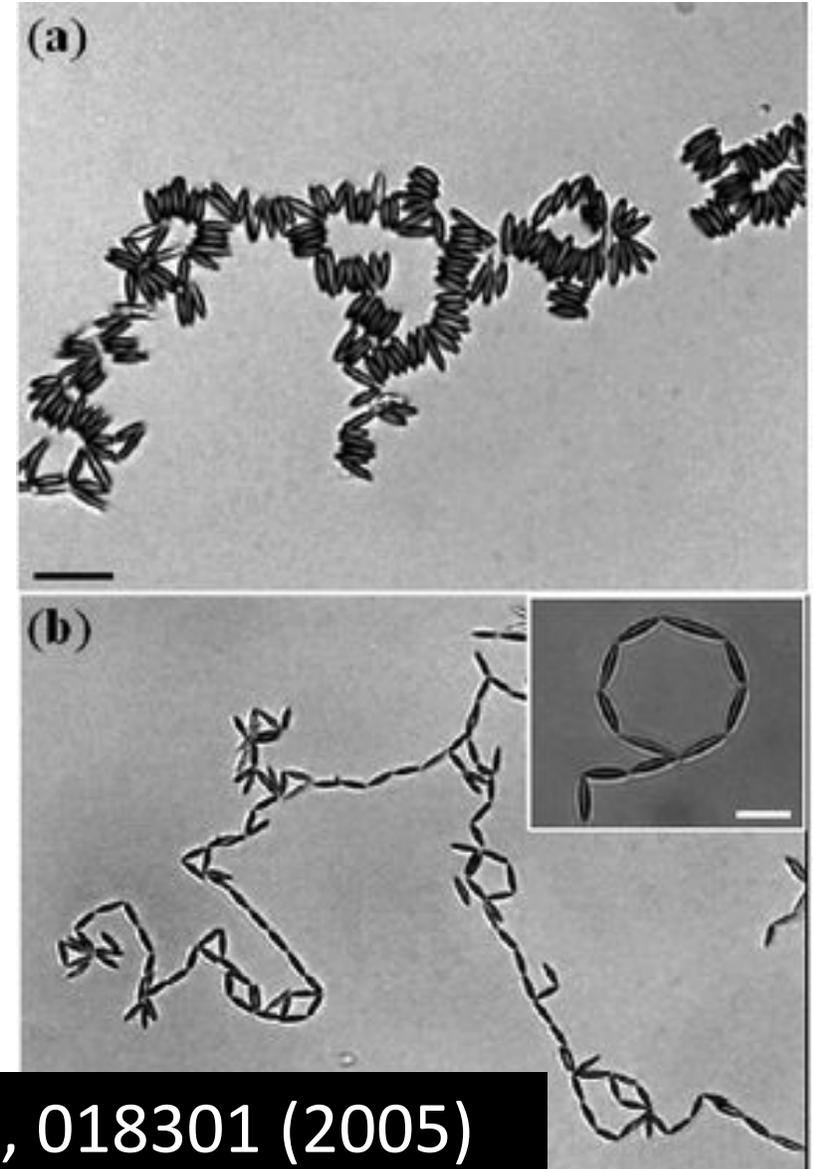
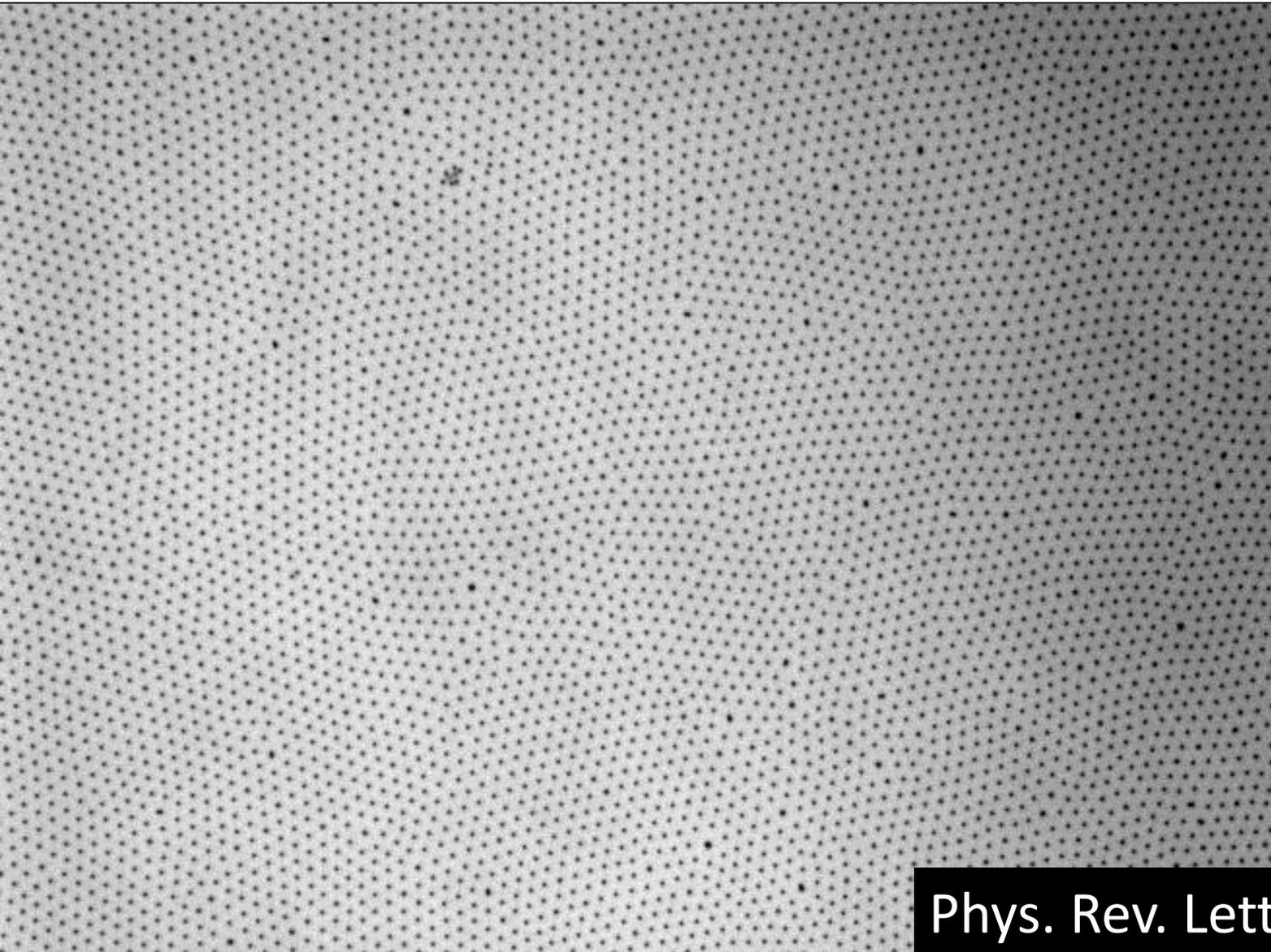
Like-charged spheres at oil-water interface



3 μm PS latex
-85 mV (ζ),
Charge density $-6.7 \mu\text{C}/\text{cm}^2$



Particles at Interfaces: Spheres vs. Ellipsoids



Phys. Rev. Lett. 94, 018301 (2005)

Interface Deformation due to Ellipsoids

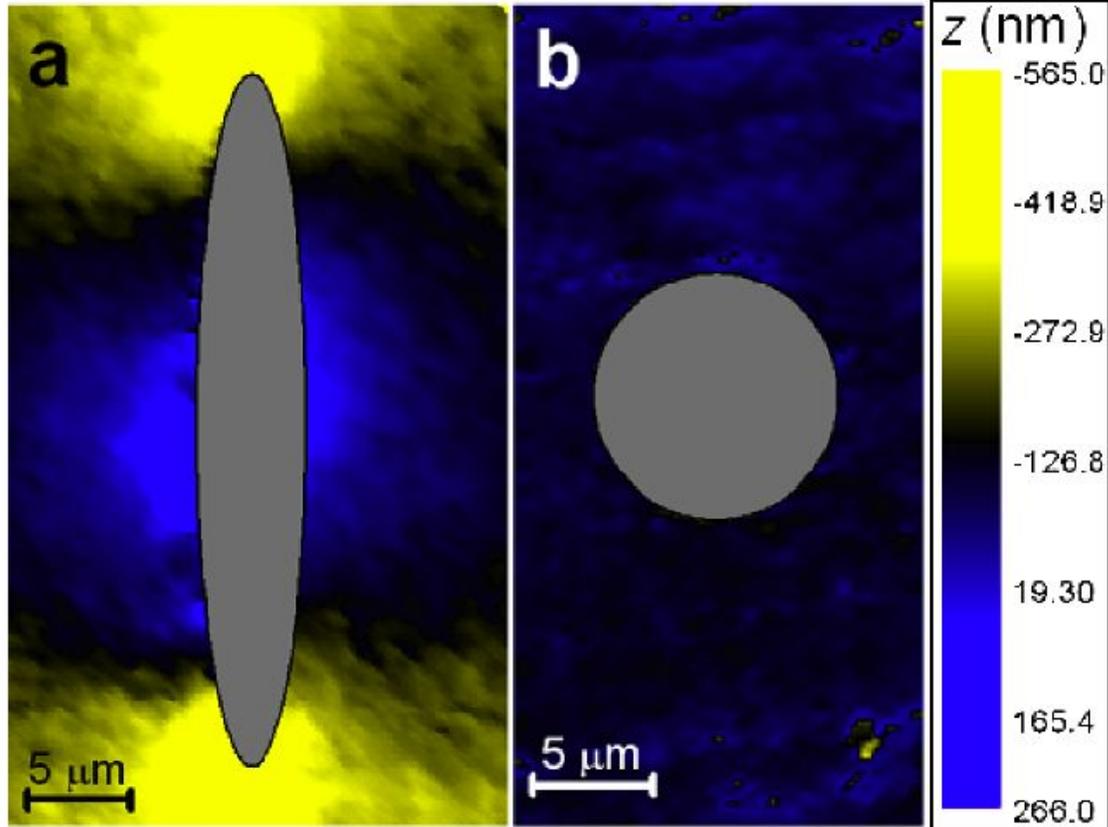
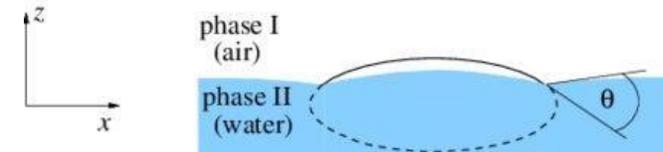
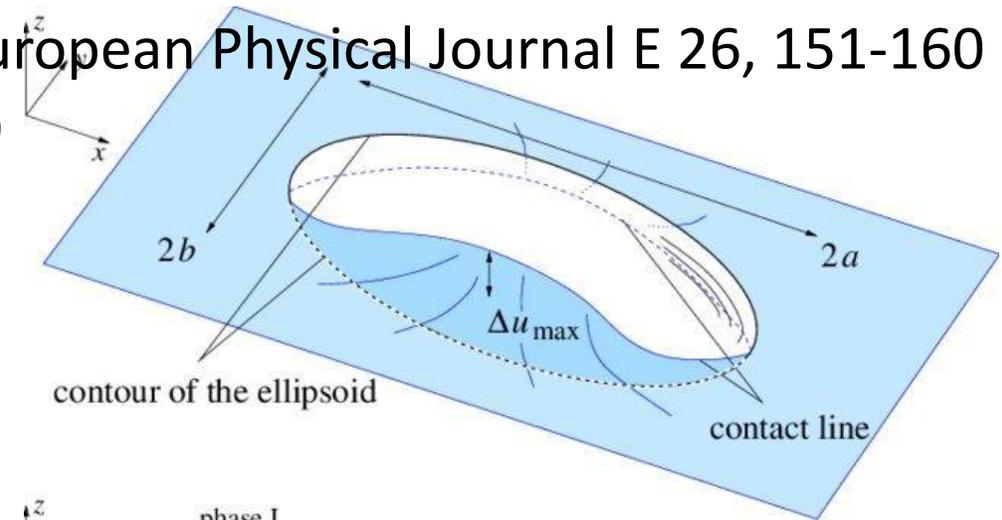


FIG. 3 (color online). Experimental image plots of the interfacial distortions $z = h(x, y)$ around floated particles calculated from PSI sequences. (a) Ellipsoid. (b) Sphere. The particle bodies were artificially colored in gray.

$$h(r, \theta) = A_0 \ln r + A_1 r^{-1} \cos(\theta + \alpha_1) + A_2 r^{-2} \cos(2\theta + \alpha_2) + \dots$$

The European Physical Journal E 26, 151-160 (2008)



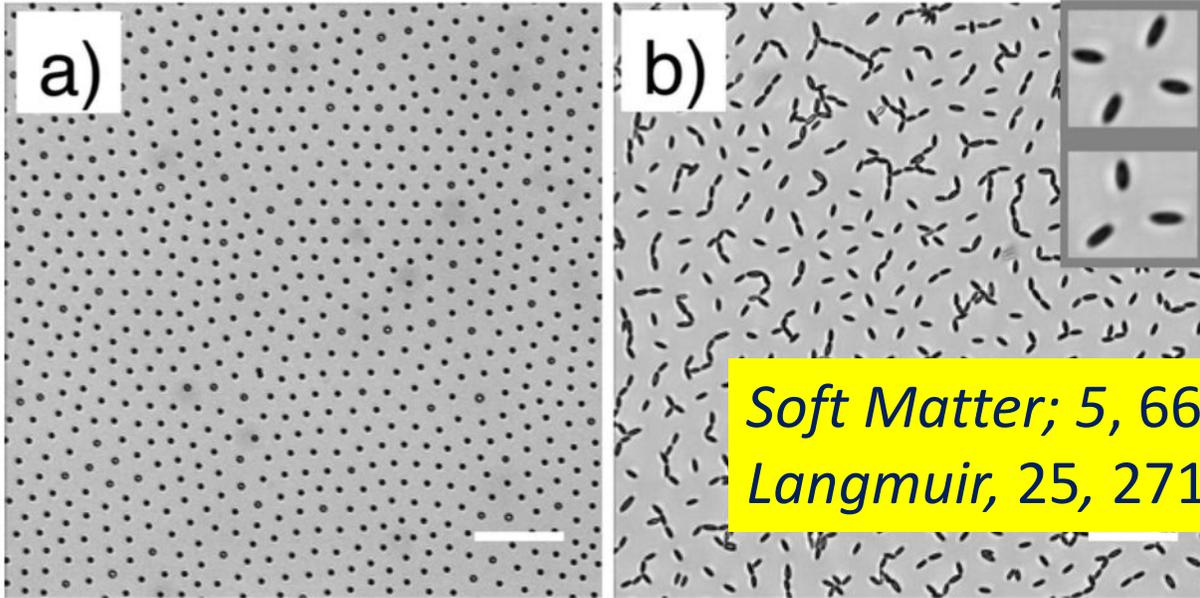
Enhanced deformation at tip

$$\nabla^2 h = 0$$

Soft Matter, 2012, 8, 9957-9971

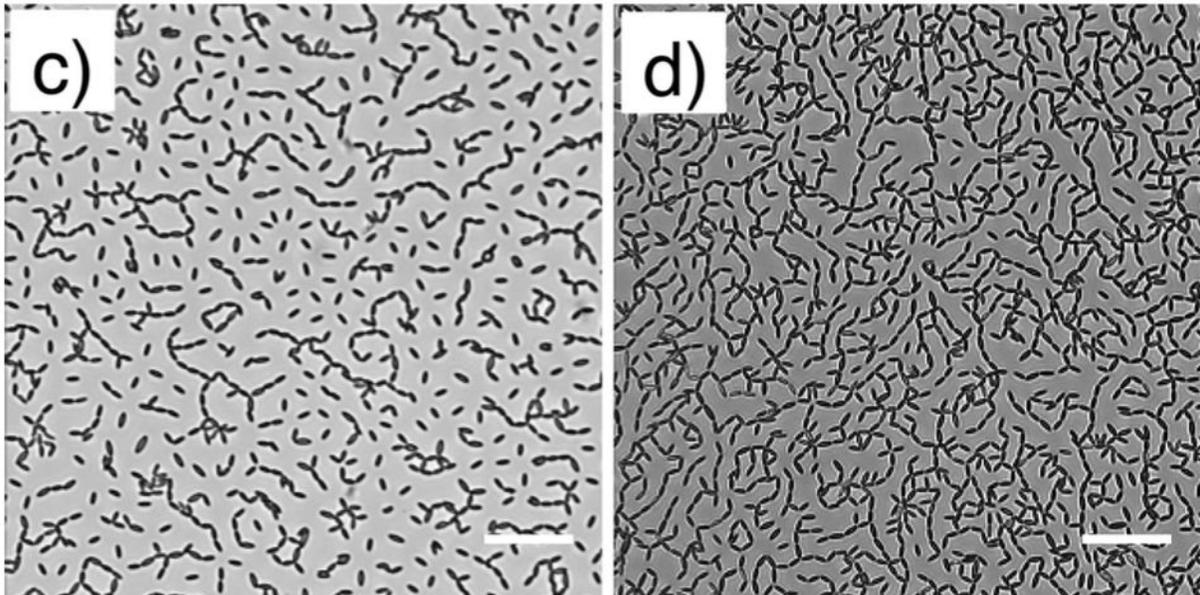
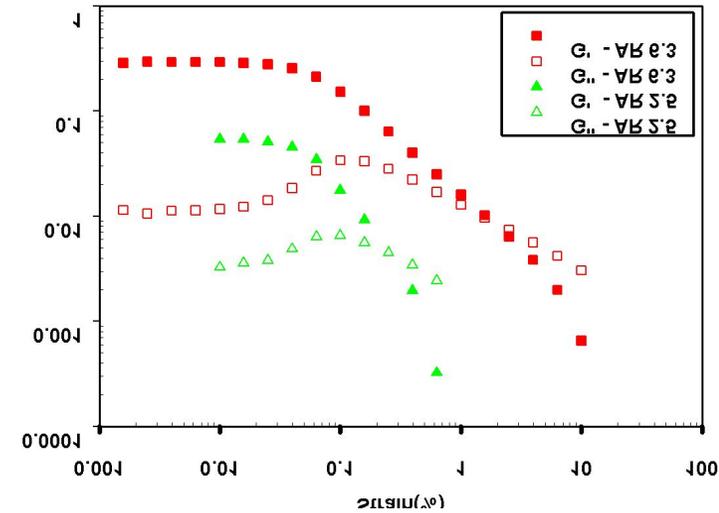
PRL 97, 018304 (2006)

Shape effects – self-assembly at interface

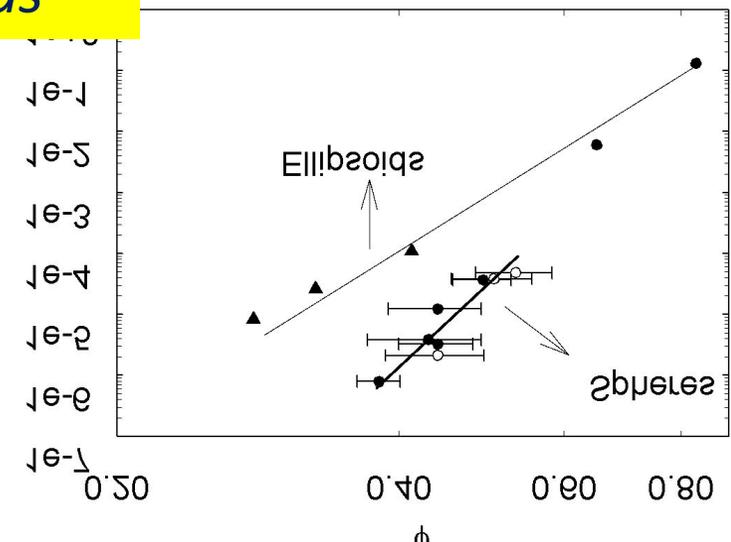


Soft Matter; 5, 6605 – 6612 (2009)
Langmuir, 25, 2718 – 2728 (2009)

Modulus vs. strain (%) via interfacial rheology



Spheres vs. Ellipsoids



Shape effects exploited in interfacial engineering

Pendant Drop Compression



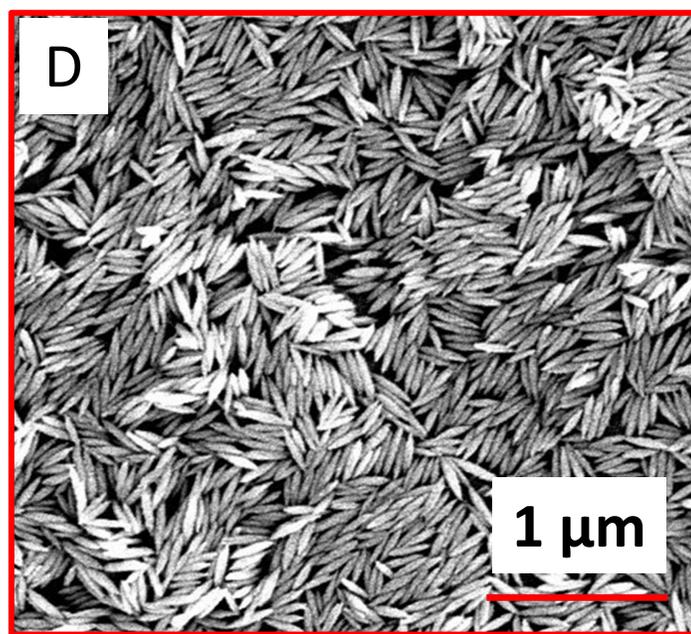
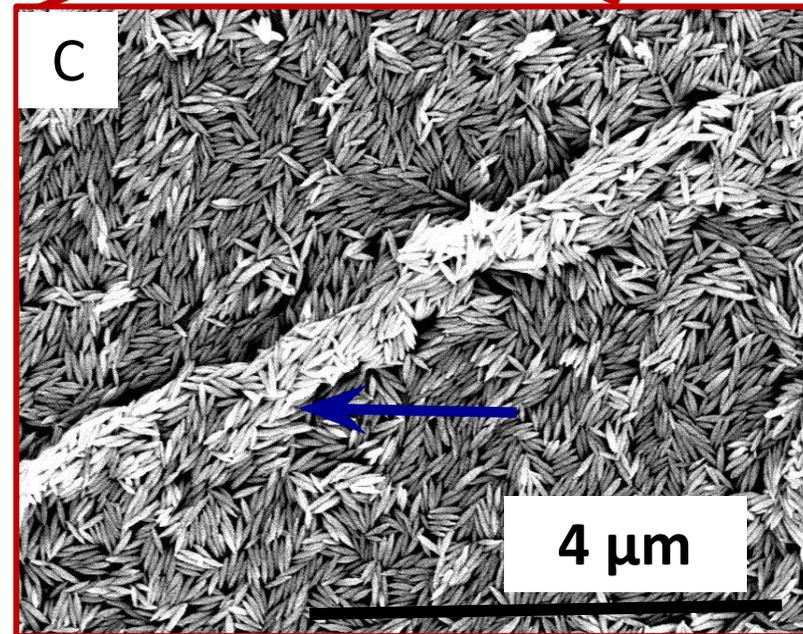
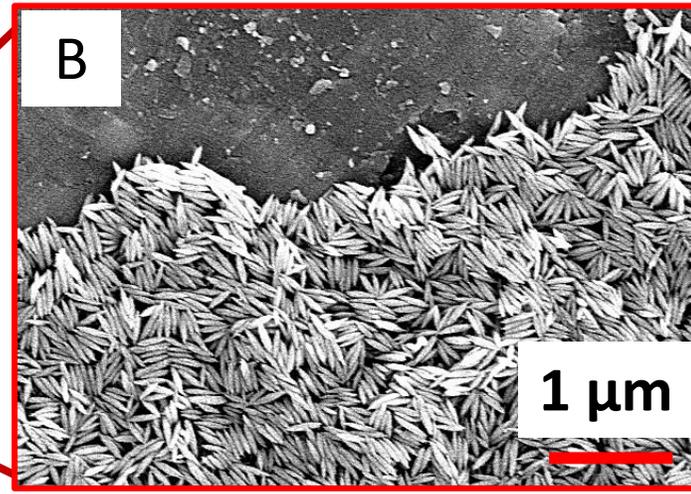
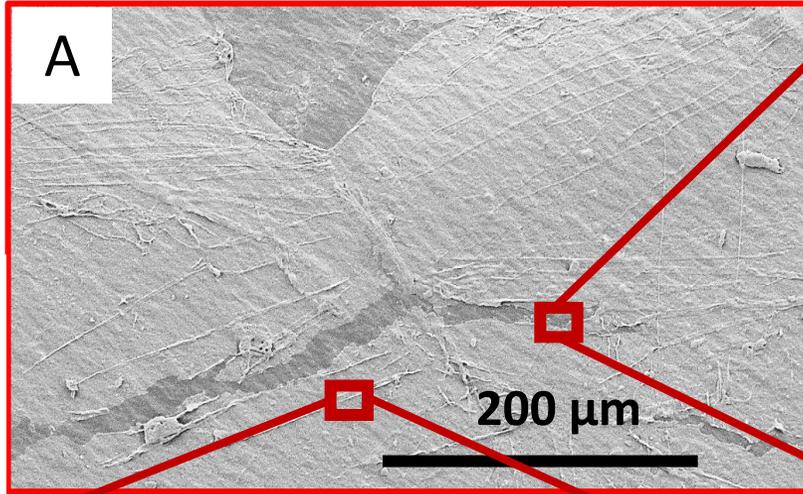
Dugyala, Venkateshwar Rao, et al. Faraday discussions 186 (2016): 419-434.



Pristine oil-water interface

Interface coated with ellipsoids

Shape effects exploited in interfacial engineering



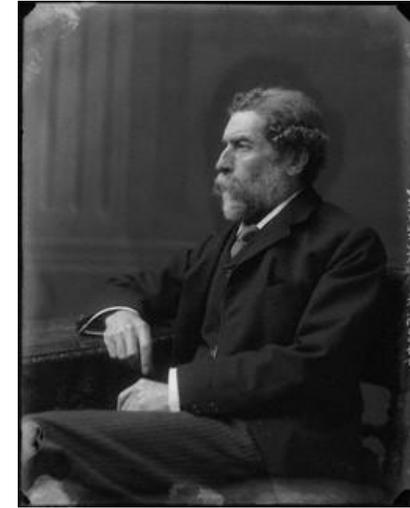
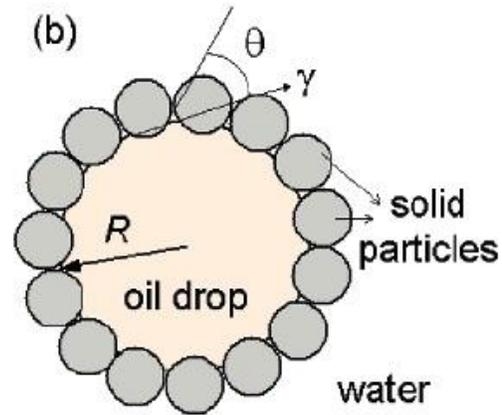
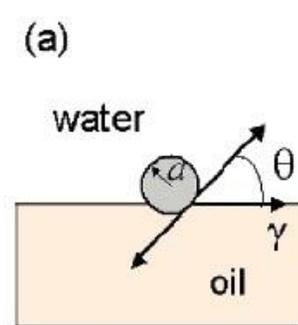
Faraday discussions
186 (2016): 419-434.

Solid stabilized emulsions – particles as emulsifiers

Stabilized by particles adsorbed on the interface



W. Ramsden



S.U. Pickering

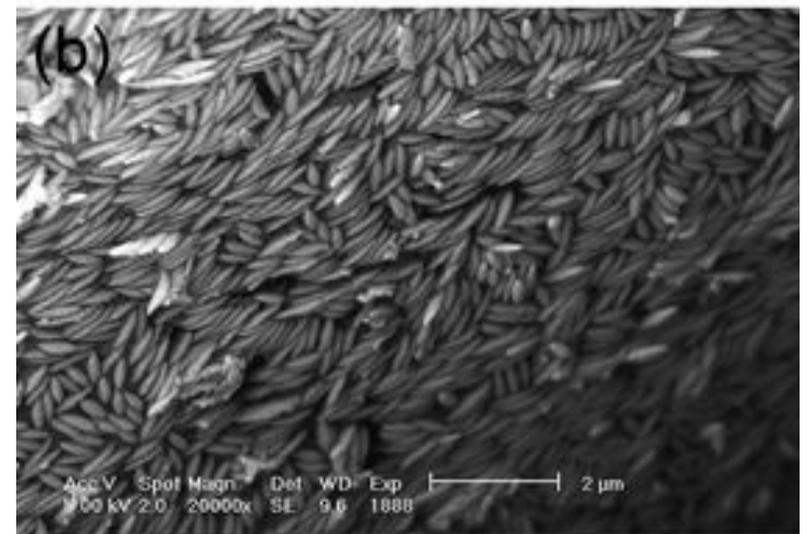
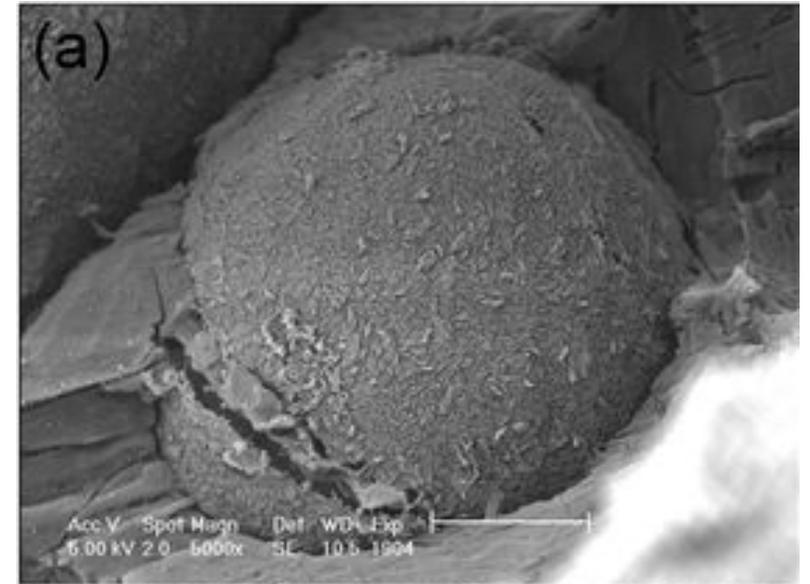
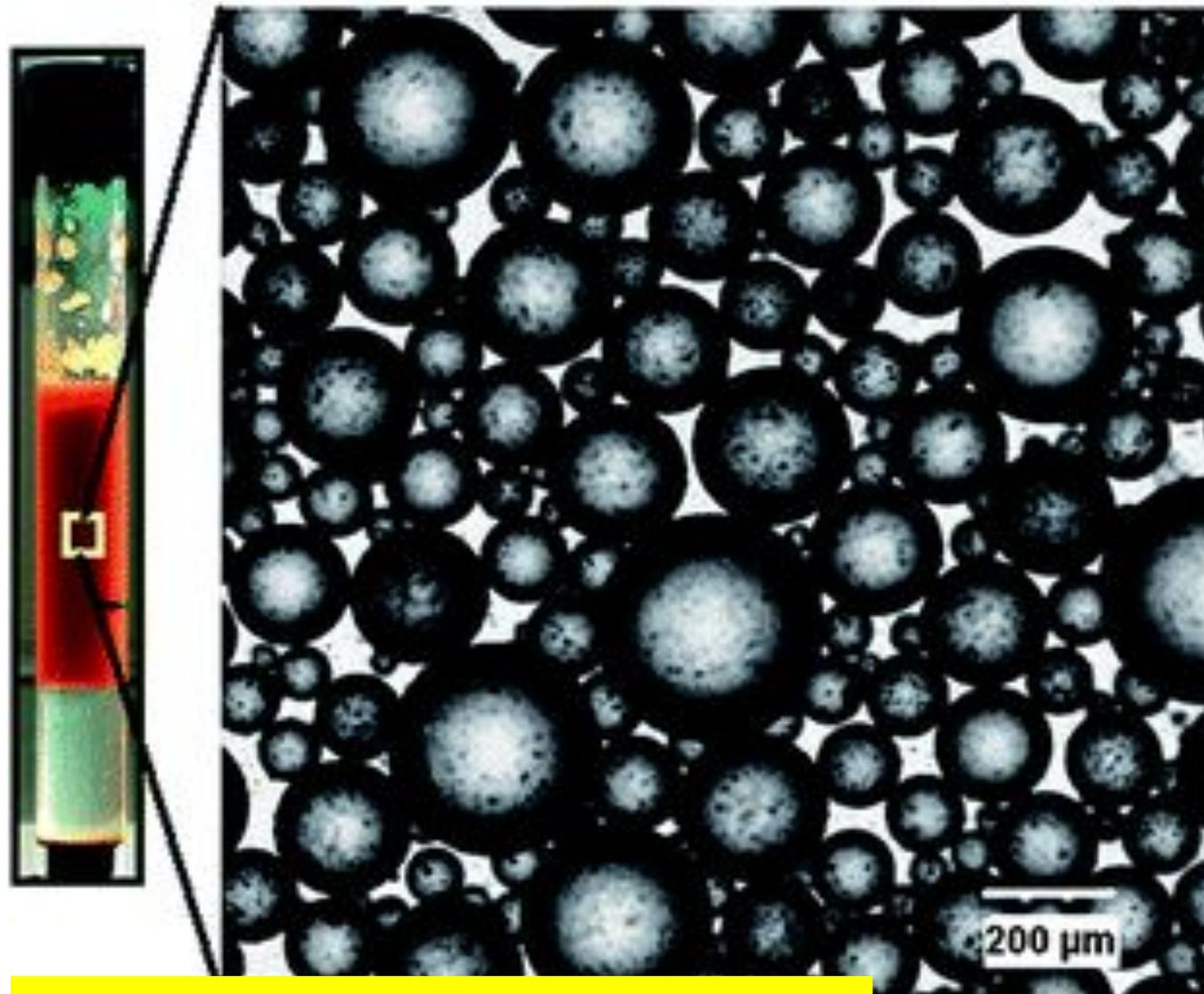
First described by:

W. Ramsden, Proc. R. Soc., London (1903)

Later studied by:

S.U. Pickering, J. Chem. Soc. 91, 2001 (1907)

Microstructure and particle arrangement

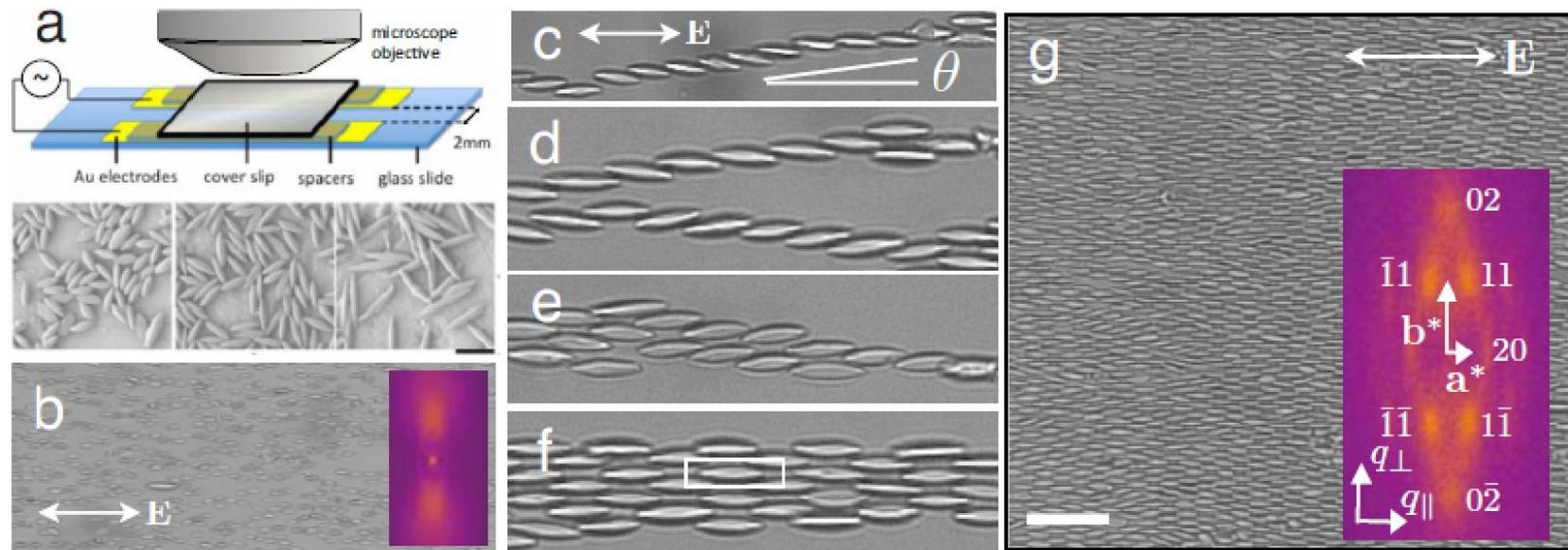


Soft Matter; 5, 6605 – 6612 (2009)

Outline of the Review

- **Literature review (10 pages)**
- **Classification of anisotropic particles (5 pages)**
- **Particle shape analysis by scattering (15 pages)**
- **Particle shape descriptors (5 pages)**
- **Exploiting particle effects - some examples (35 pages)**

Thank You



John P. Singh, Pushkar P. Lele, Florian Nettesheim, Norman J. Wagner, and Eric M. Furst Phys. Rev. E 79, 050401(R)