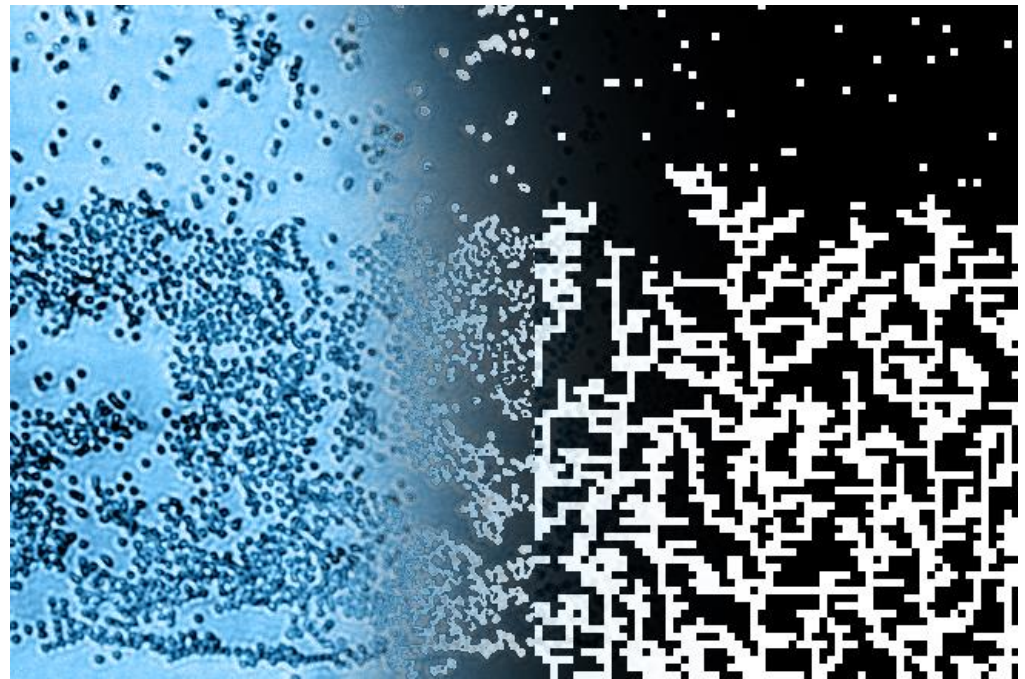
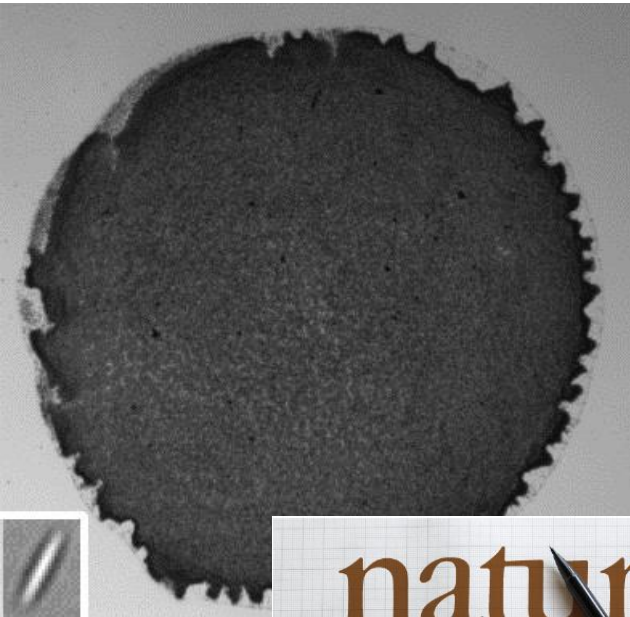


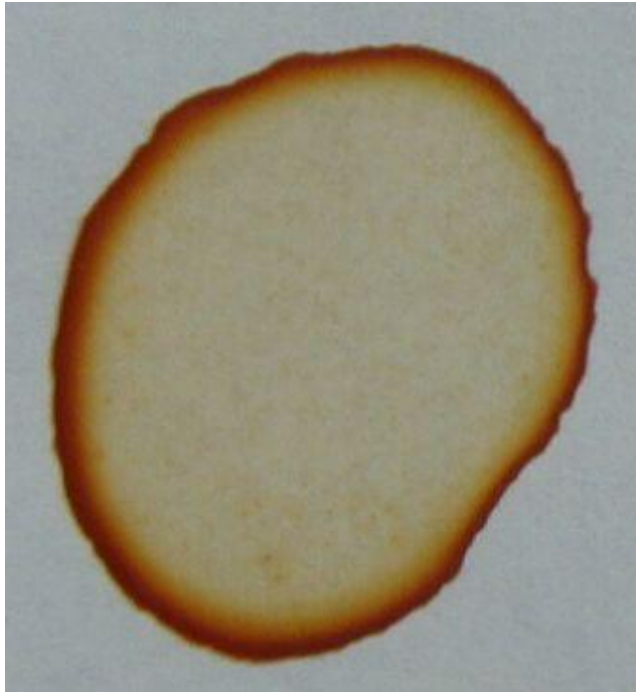
Growth Processes in Evaporating Drops



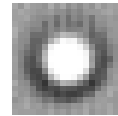
**Peter Yunker (Harvard, UPenn, GT)
Tim Still, Matt Lohr,
Arjun Yodh, Doug Durian (UPenn)
Alexei Borodin (MIT)**

P.J. Yunker, T. Still, M.A. Lohr, and A.G. Yodh, *Nature* 476, 308 (2011).
P.J. Yunker, *et al.*, PRL (2012).
P.J. Yunker, *et al.*, PRL (2013). P.J. Yunker, *et al.*, *Physics Today* (2013).

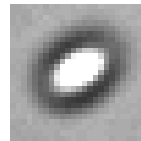
Growth process depends on particle shape



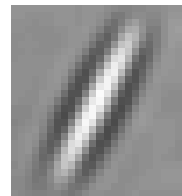
Coffee-ring effect



Poisson Process



KPZ Process



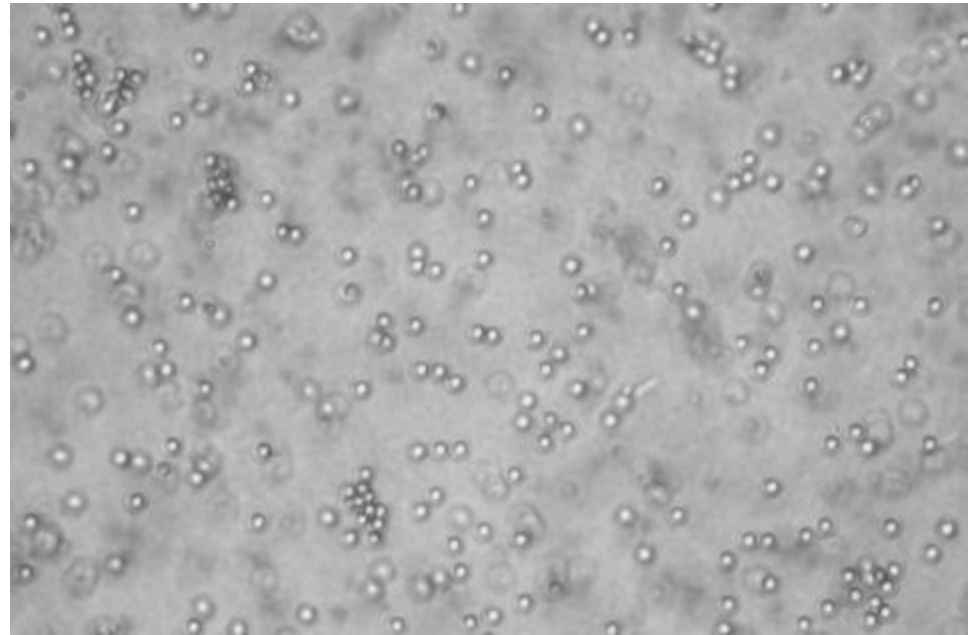
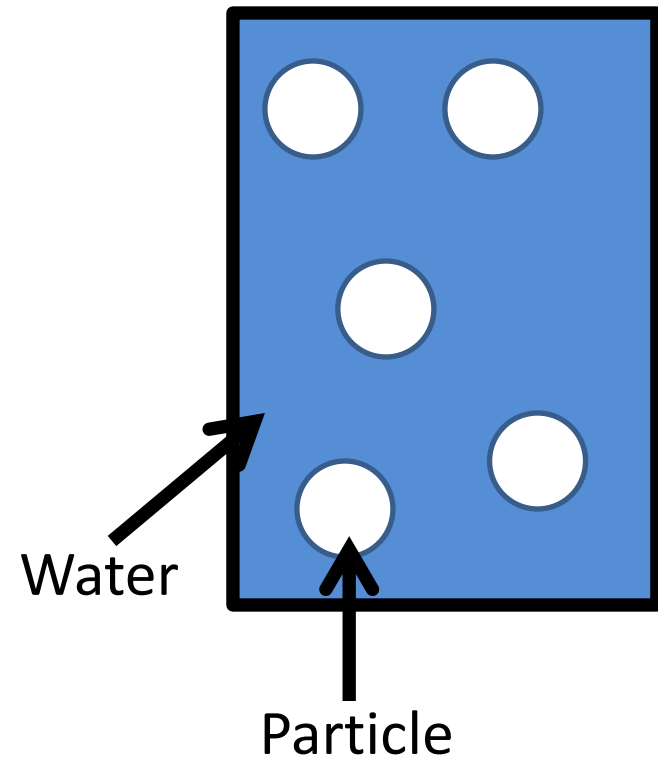
Colloidal Matthew Effect

Which growth processes?

Why particle shape?



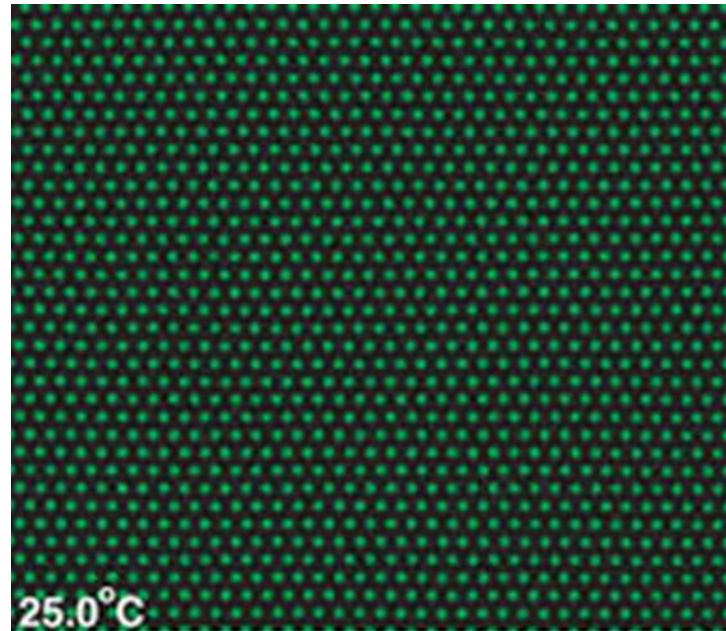
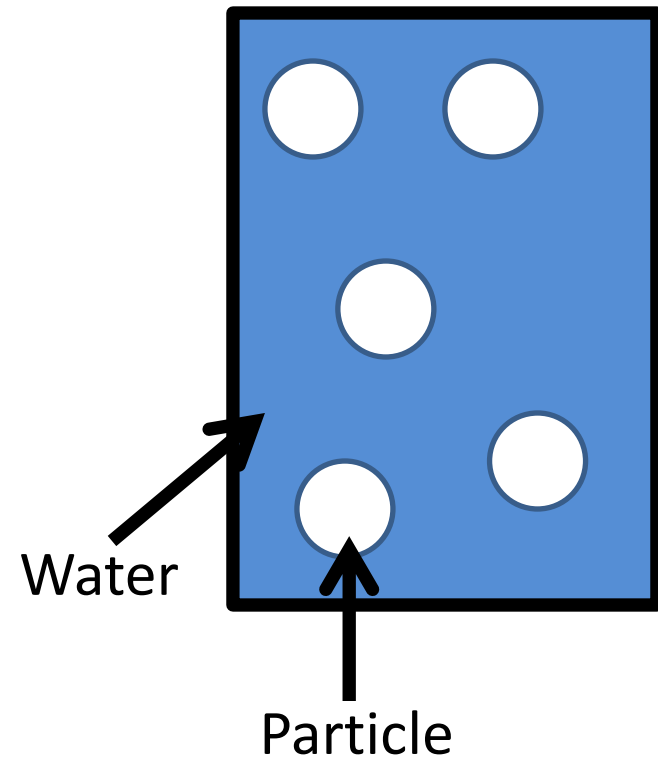
Colloidal particles: a convenient experimental tool



Colloidal Fluid



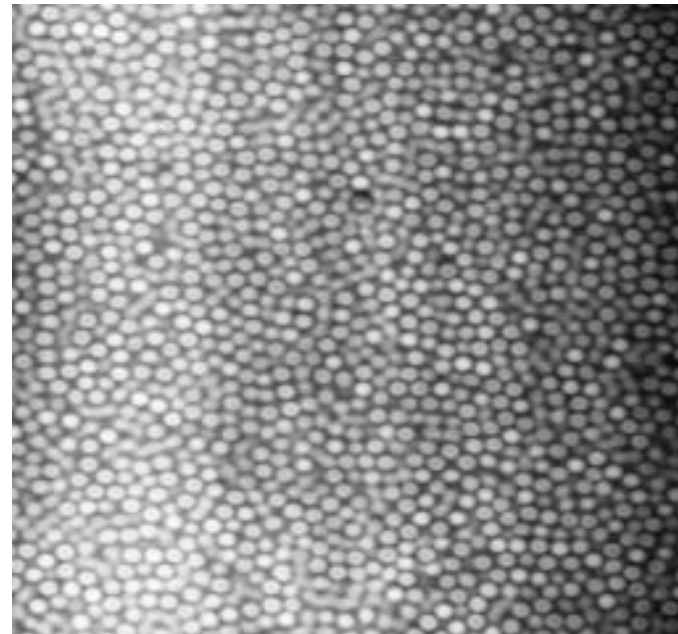
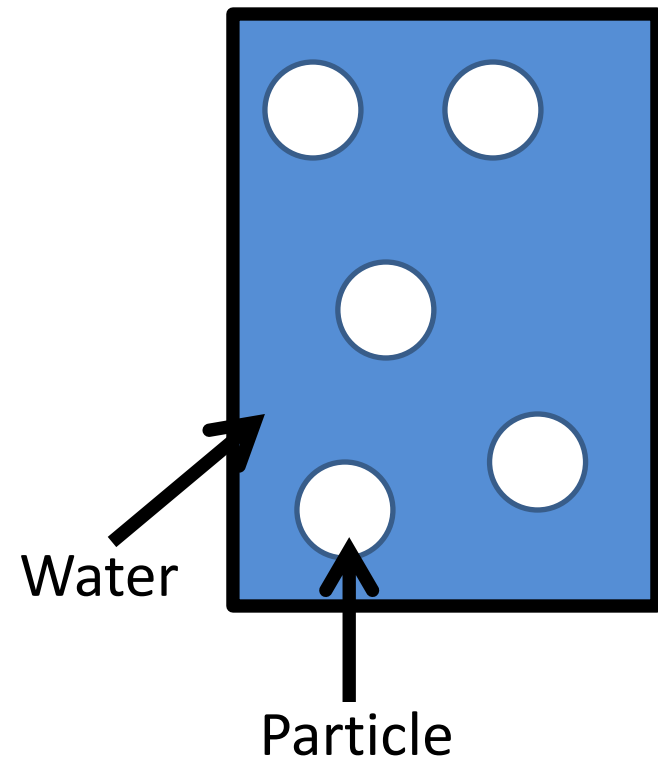
Colloidal particles: a convenient experimental tool



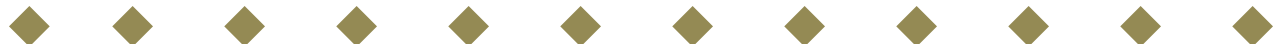
Colloidal Crystal



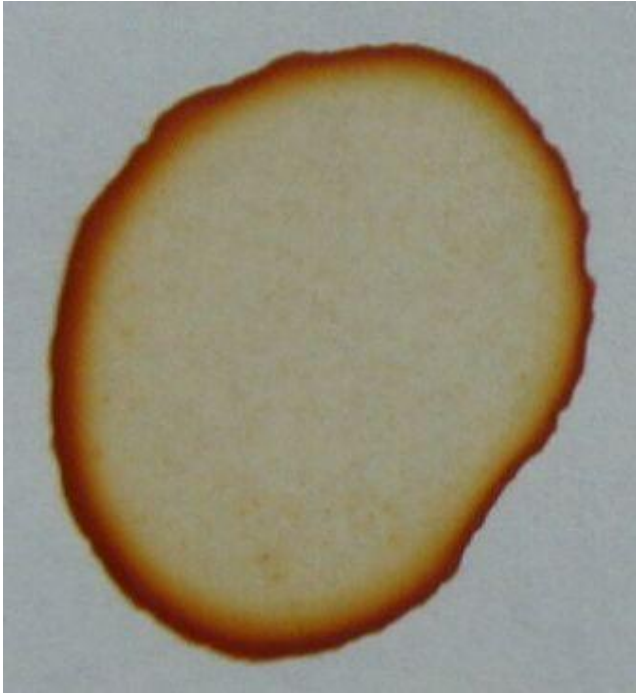
Colloidal particles: a convenient experimental tool



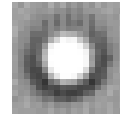
Colloidal Glass



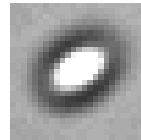
Growth process depends on particle shape



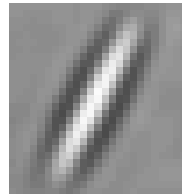
Coffee-ring effect



Poisson Process



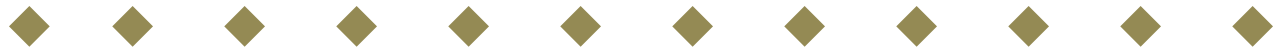
KPZ Process



Colloidal Matthew Effect

Which growth processes?

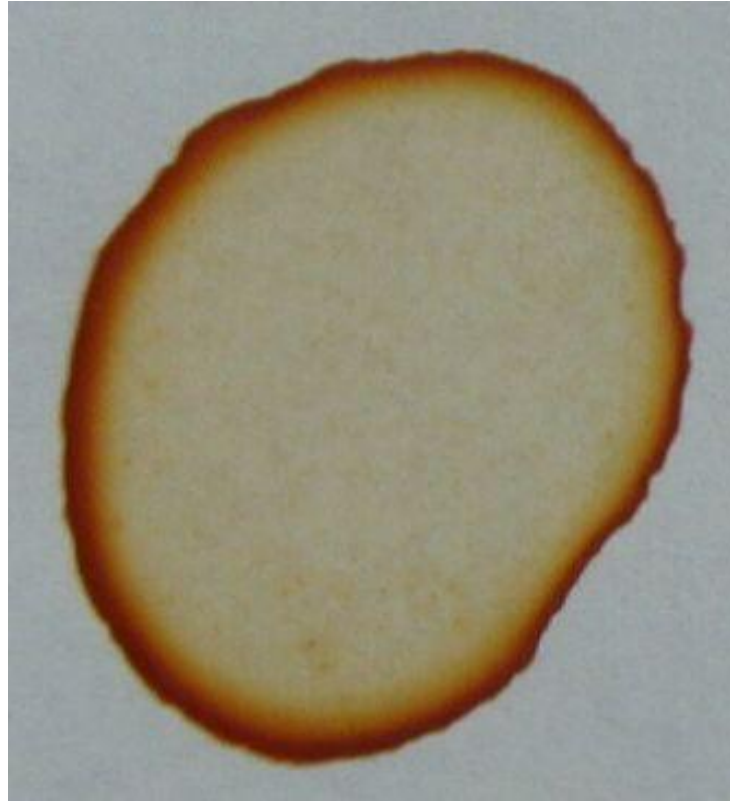
Why particle shape?



The Coffee Ring Effect



The Coffee Ring Effect



coffee

Robert D. Deegan, Olgica Bakajin, T.F. Dupont, G.Huber, Sidney R. Nagel , Thomas A. Witten, *Nature* (1997).

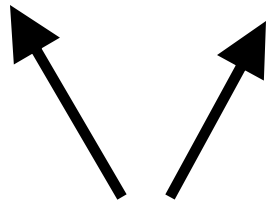


Drop Edges Pinned During Evaporation

Edges Unpinned – Diameter Decreases



Edges Pinned – Contact Angle Decreases



Drop edges pinned



Convective Fluid Flow from Middle of Drop to Edges

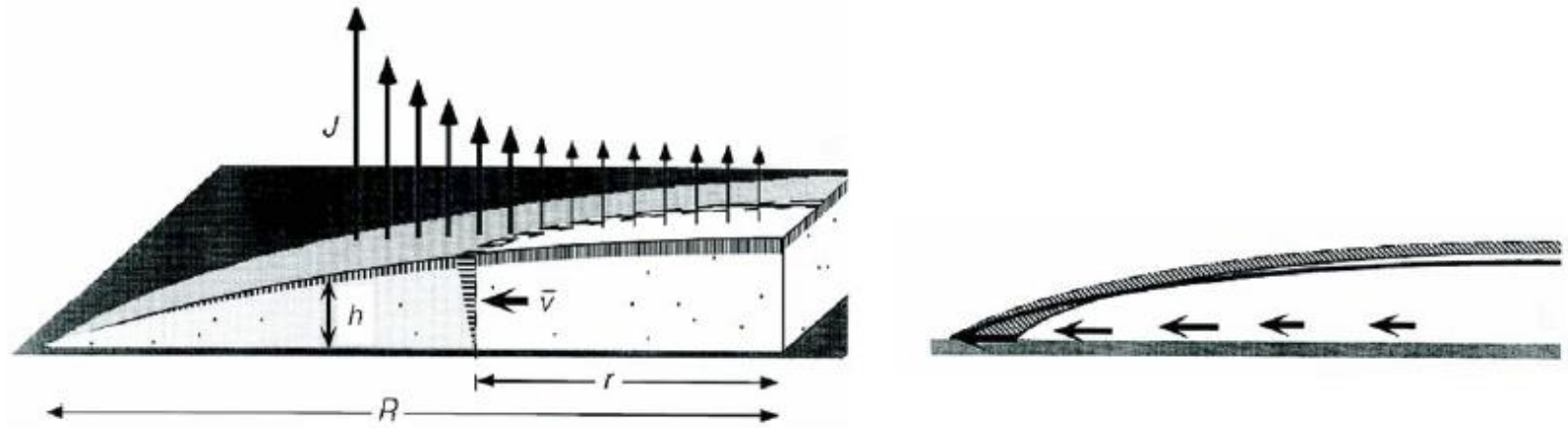
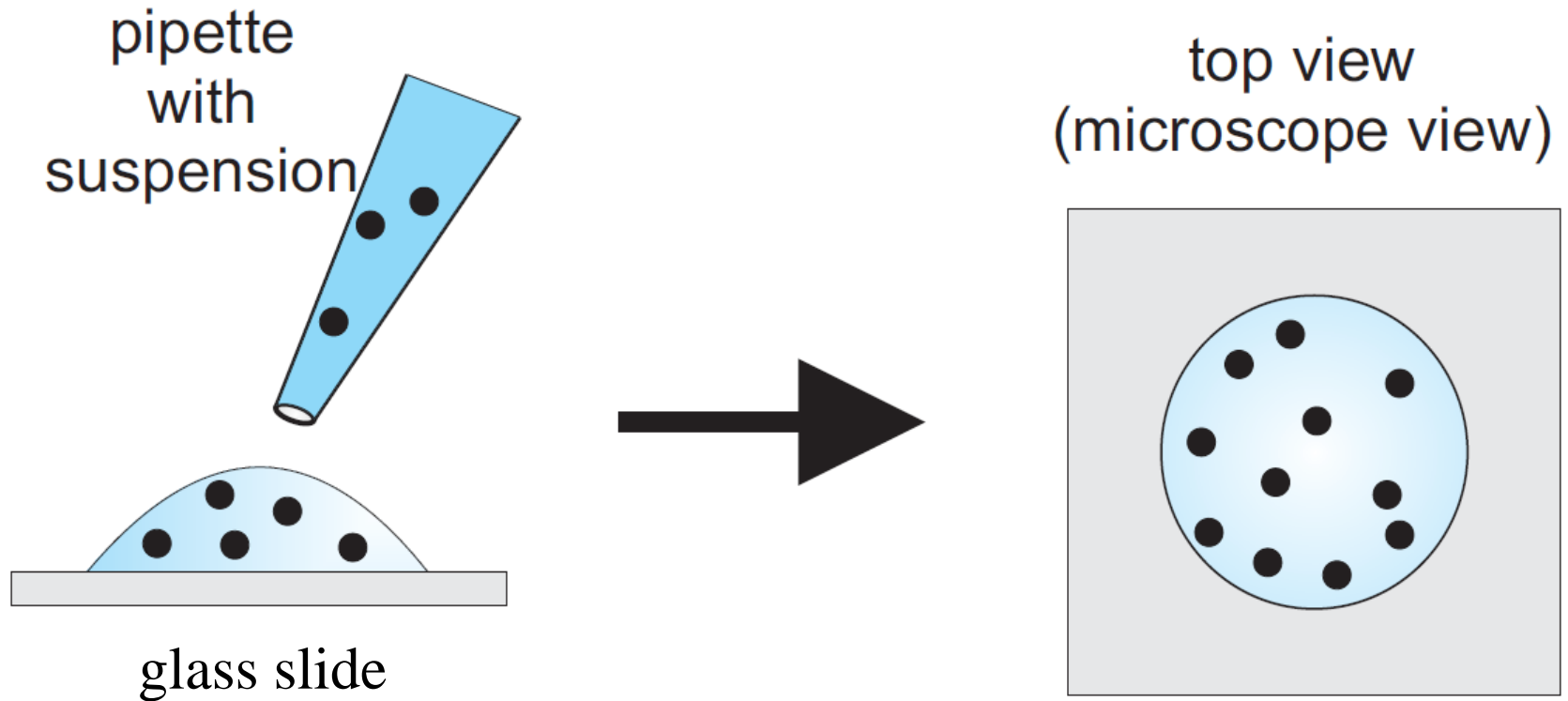


Figure from R. D. Deegan et al., Nature **389**, 827 (1997).




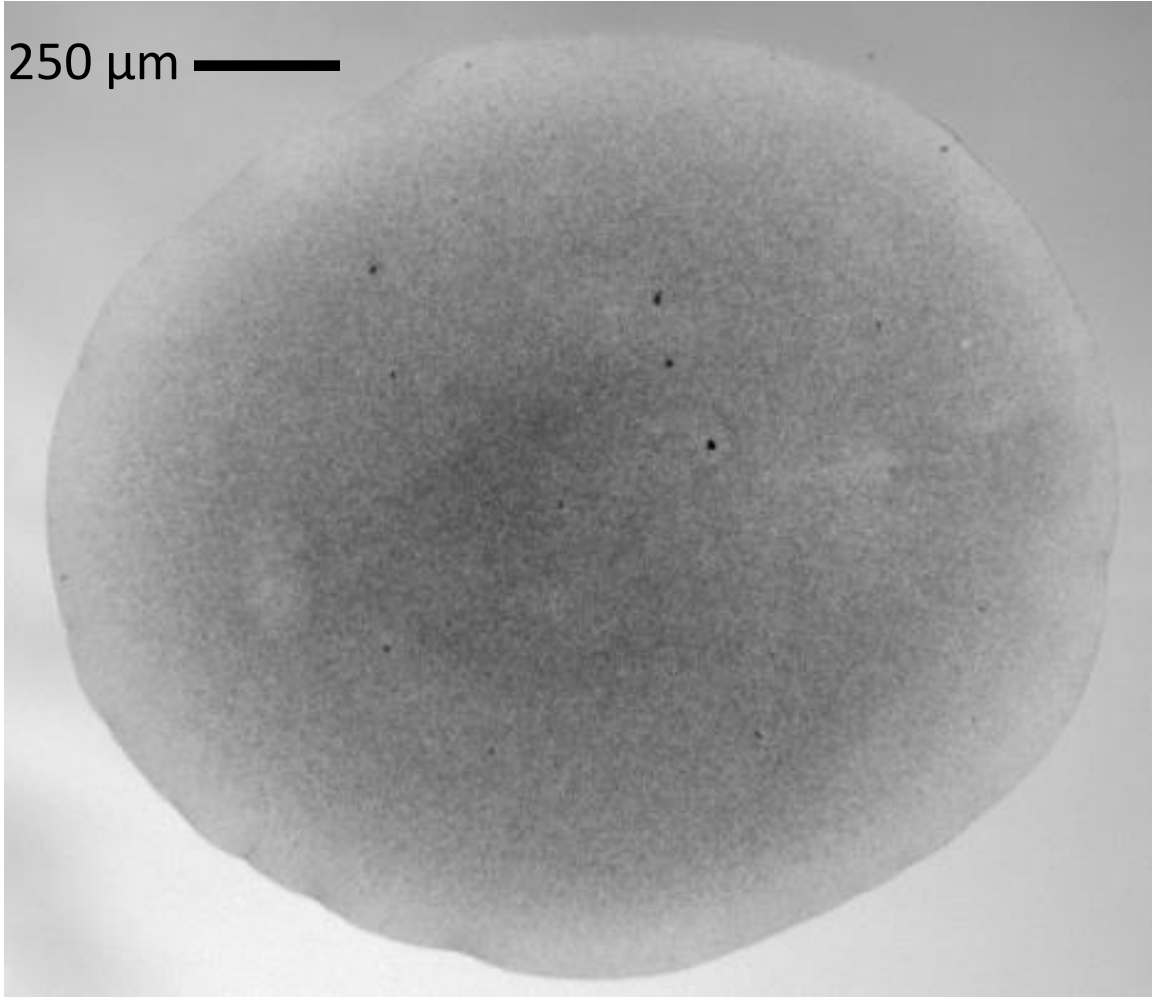
Basic Experiment



Drying Drops Containing Polystyrene Spheres

(20x faster)

250 μm 



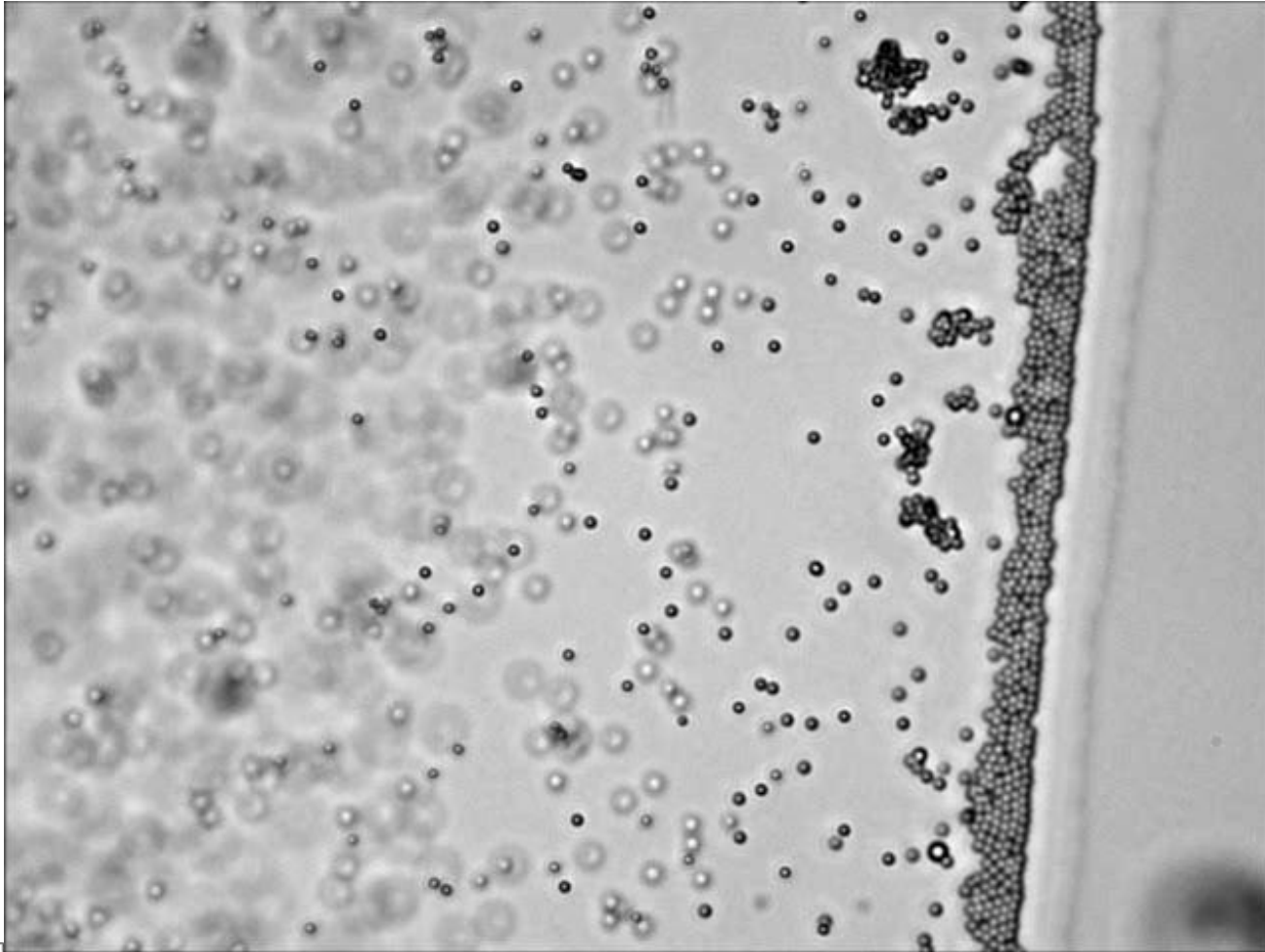
Initial
Volume
Fraction
 $\phi = 0.005$



Drying Drops Containing Polystyrene Spheres

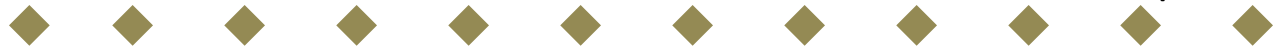
10 μm 

(10x faster)

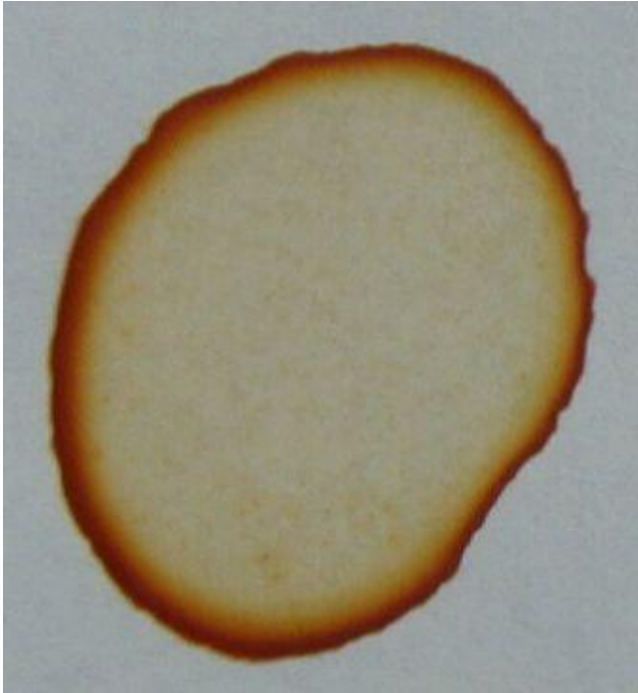


Drop
Edge

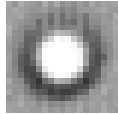
Initial
Volume
Fraction
 $\phi = 0.005$



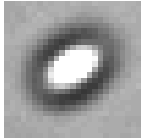
Growth process depends on particle shape



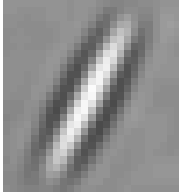
Coffee-ring effect



Poisson Process



KPZ Process



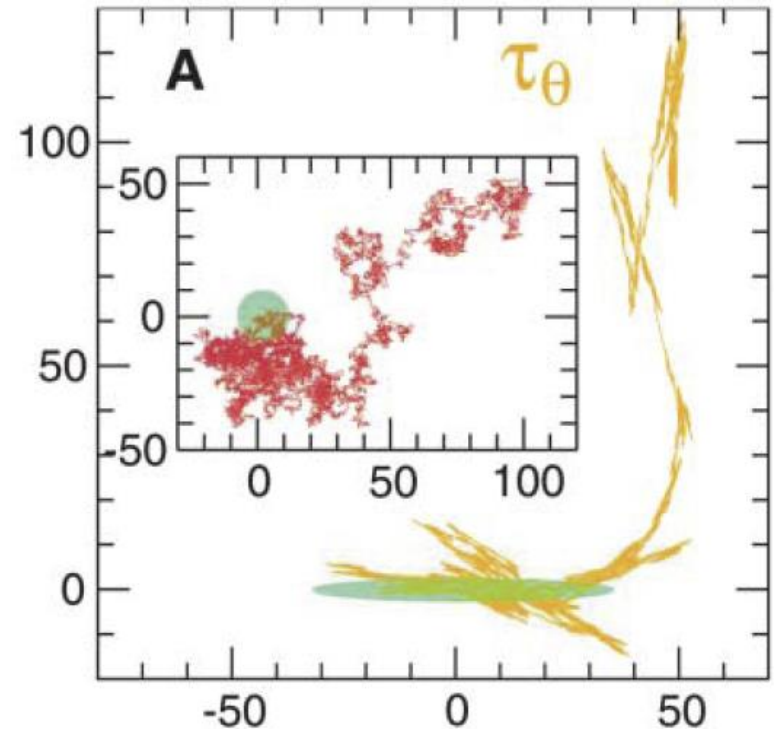
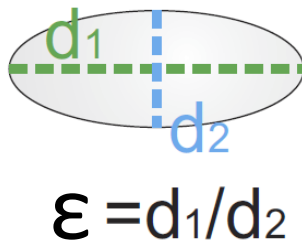
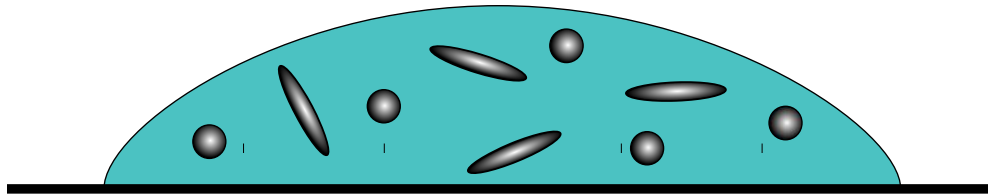
Colloidal Matthew Effect

Which growth processes?

Why particle shape?



Why Does Particle Shape Matter?

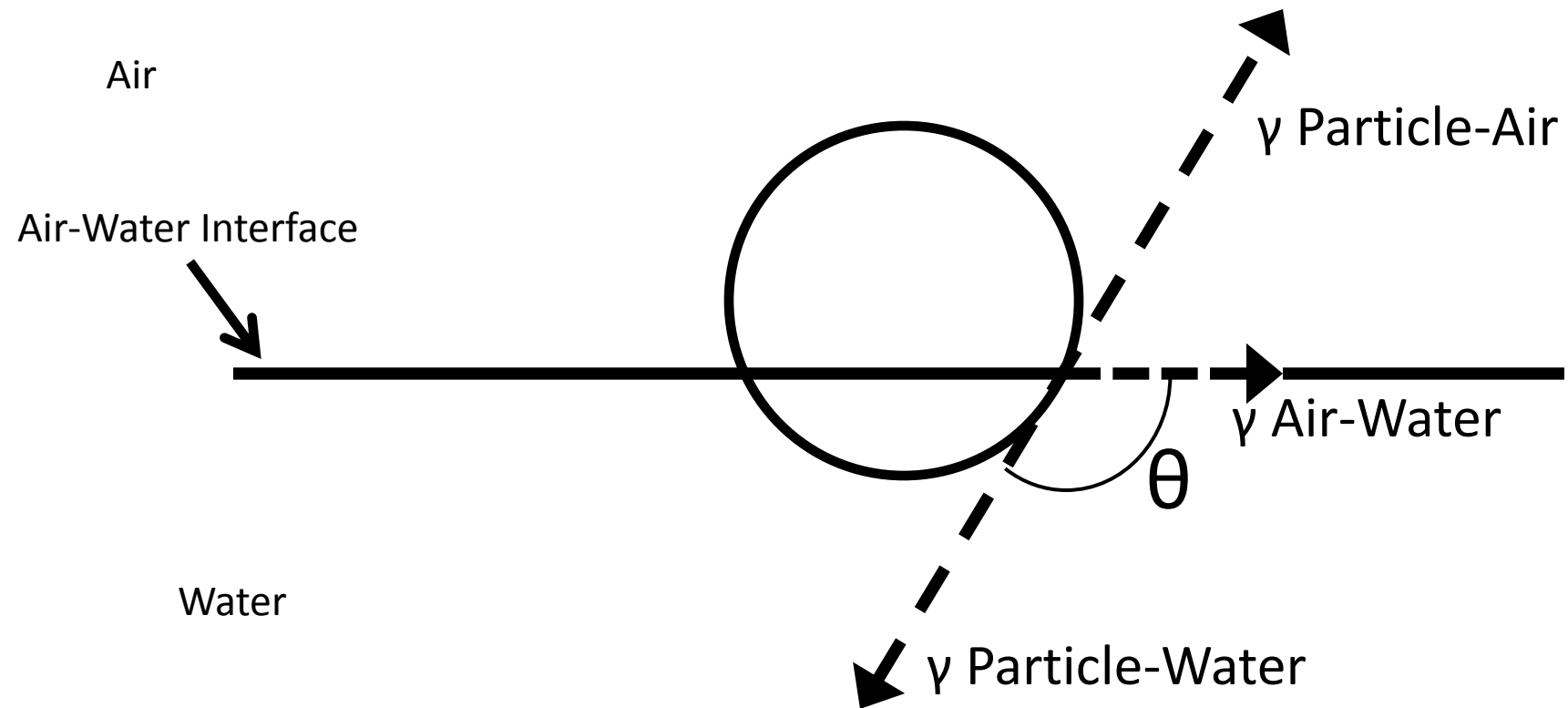


Han, Y., Alsayed, A.M., Nobili, M., Zhang, J., Lubensky, T.C., & Yodh, A.G., Brownian motion of an ellipsoid. *Science* (2006).

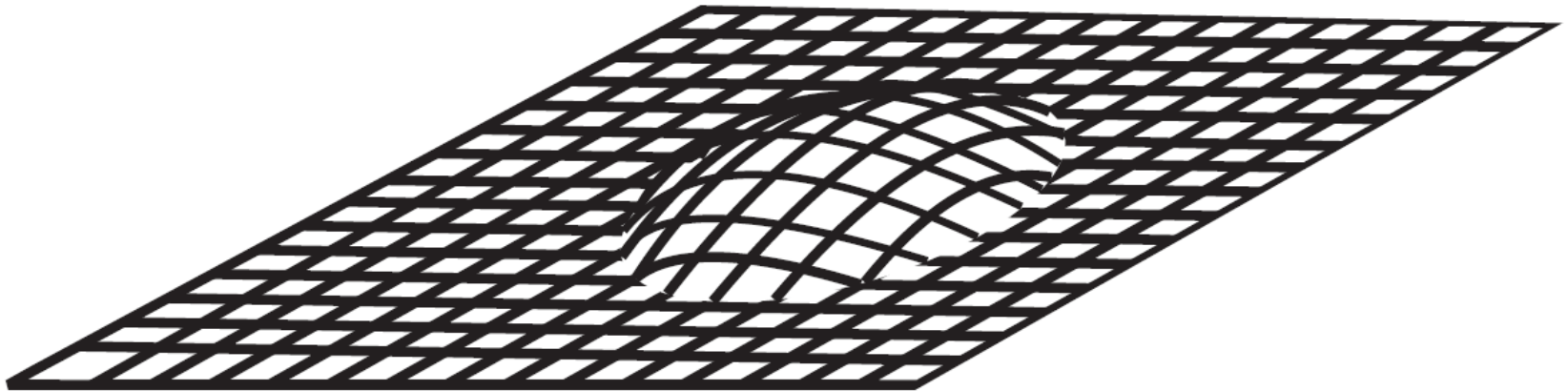
**“Spheres” and “Ellipsoids” at low volume fraction
will have fairly similar bulk behaviors.**



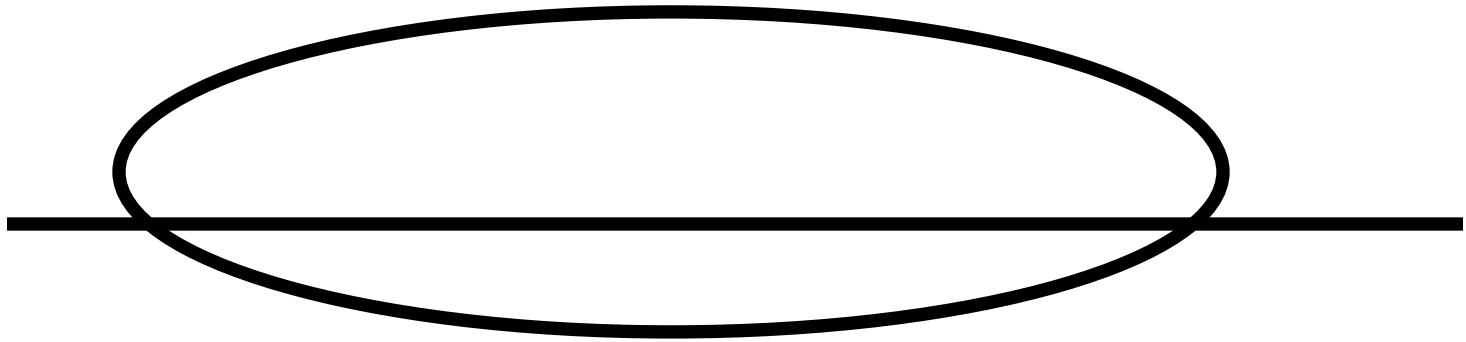
Interfacial tensions balance at equilibrium contact angle



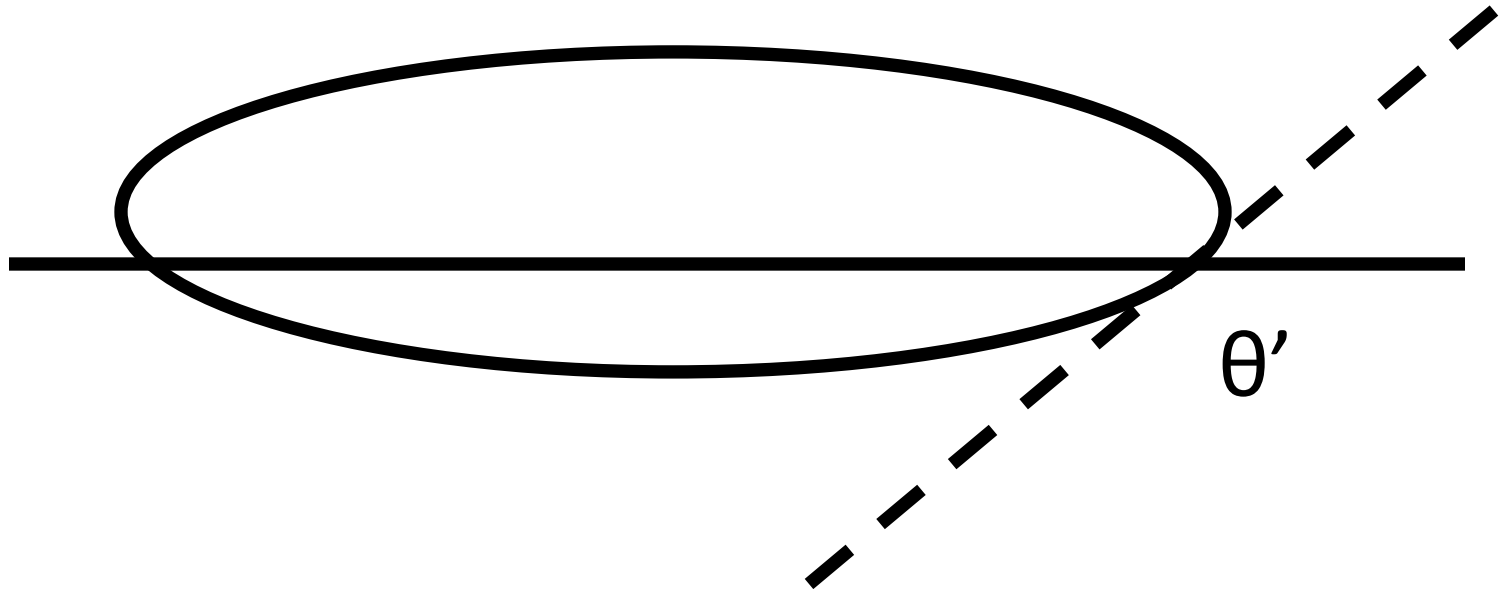
Interfacial tensions balance at equilibrium contact angle



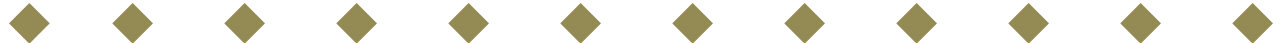
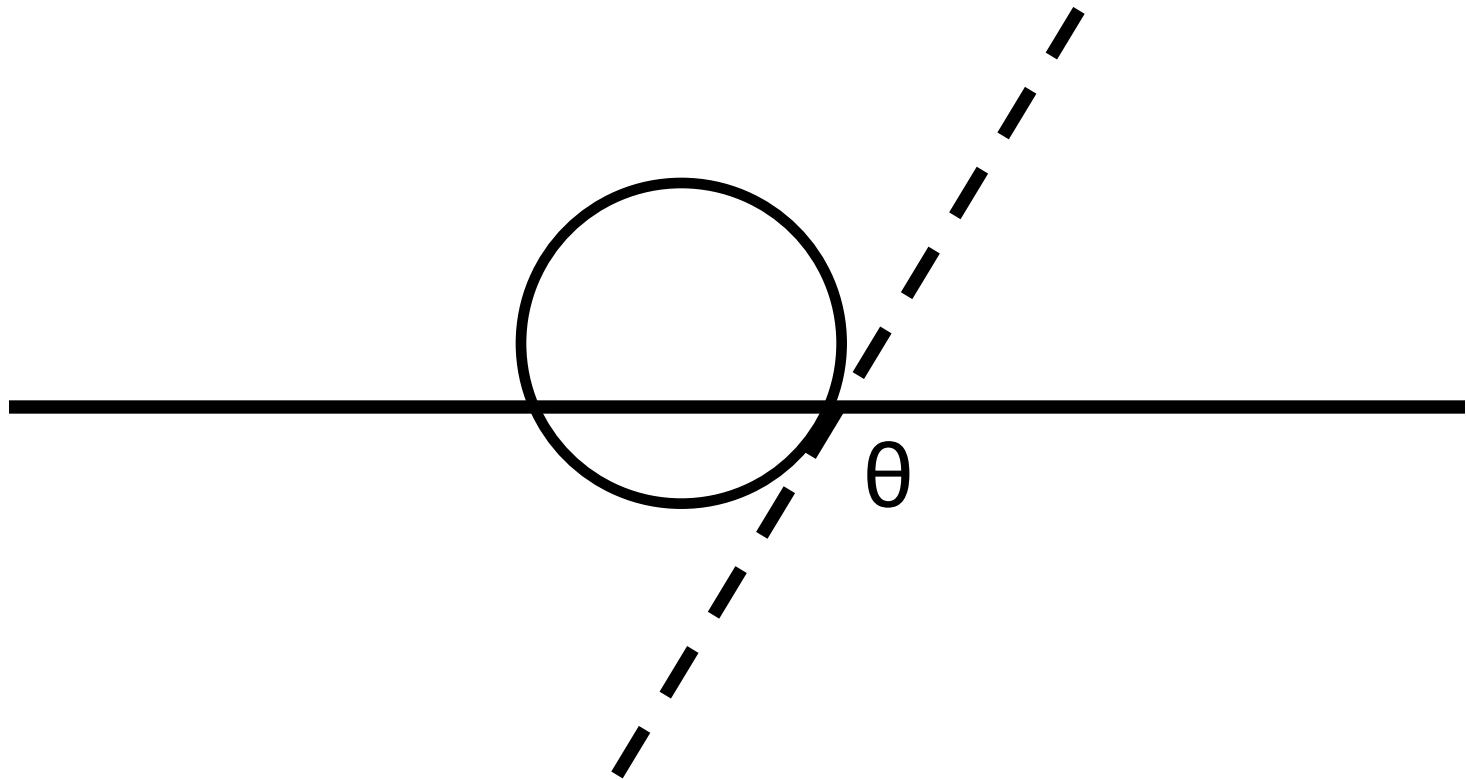
Interfacial tensions balance at equilibrium contact angle



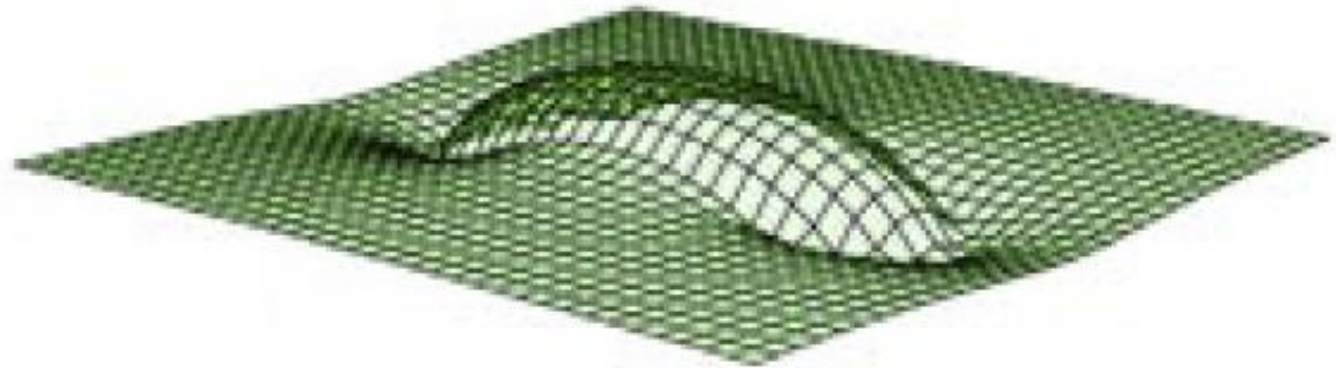
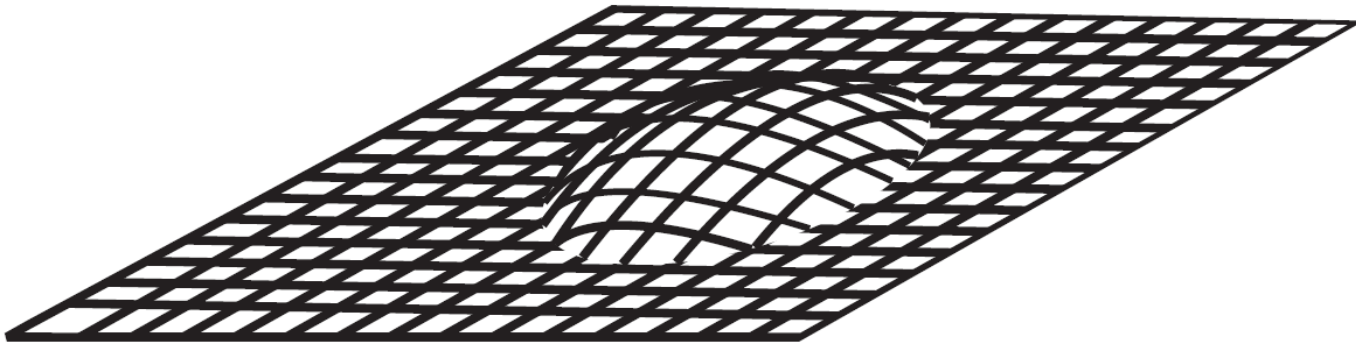
Interfacial tensions balance at equilibrium contact angle



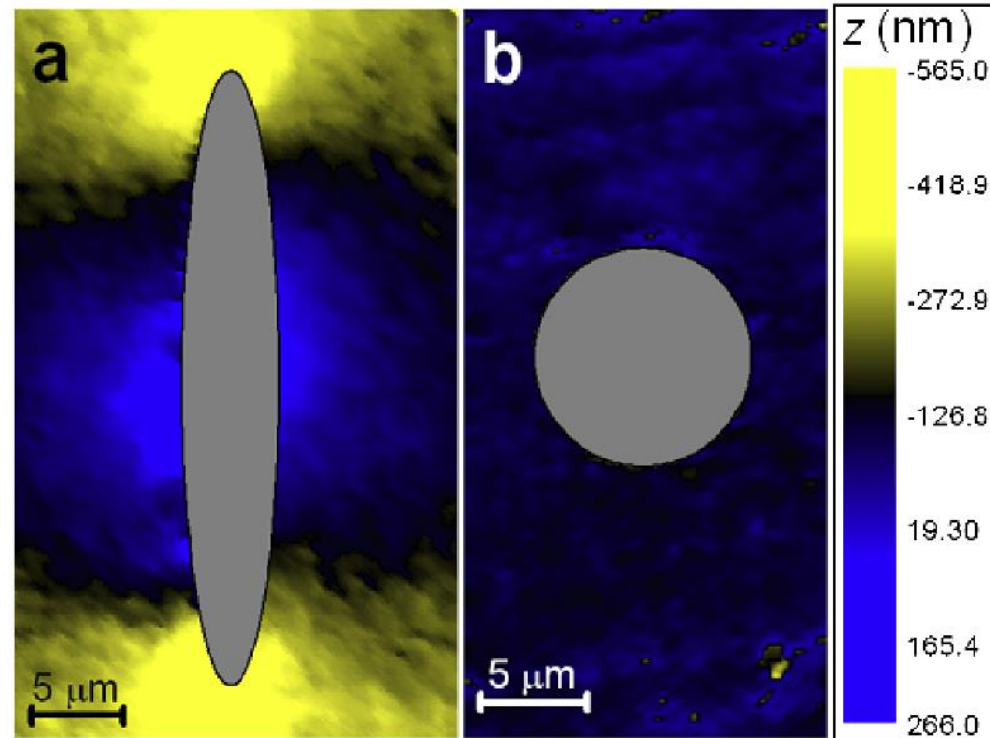
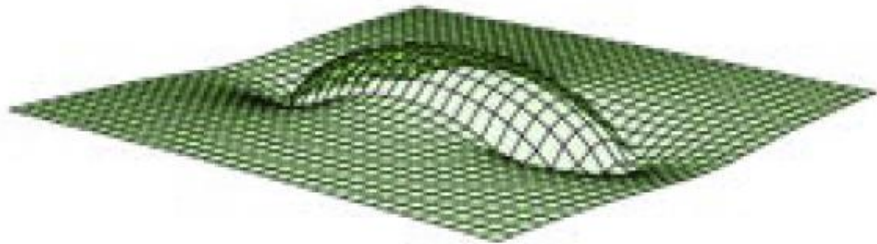
Interfacial tensions balance at equilibrium contact angle



Interfacial tensions balance at equilibrium contact angle



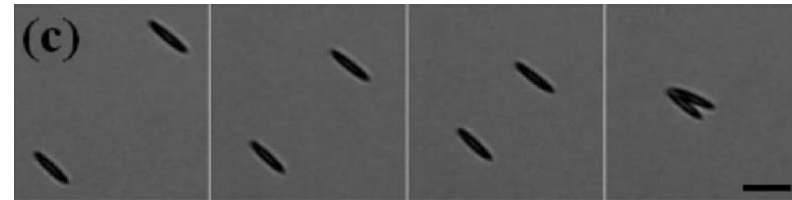
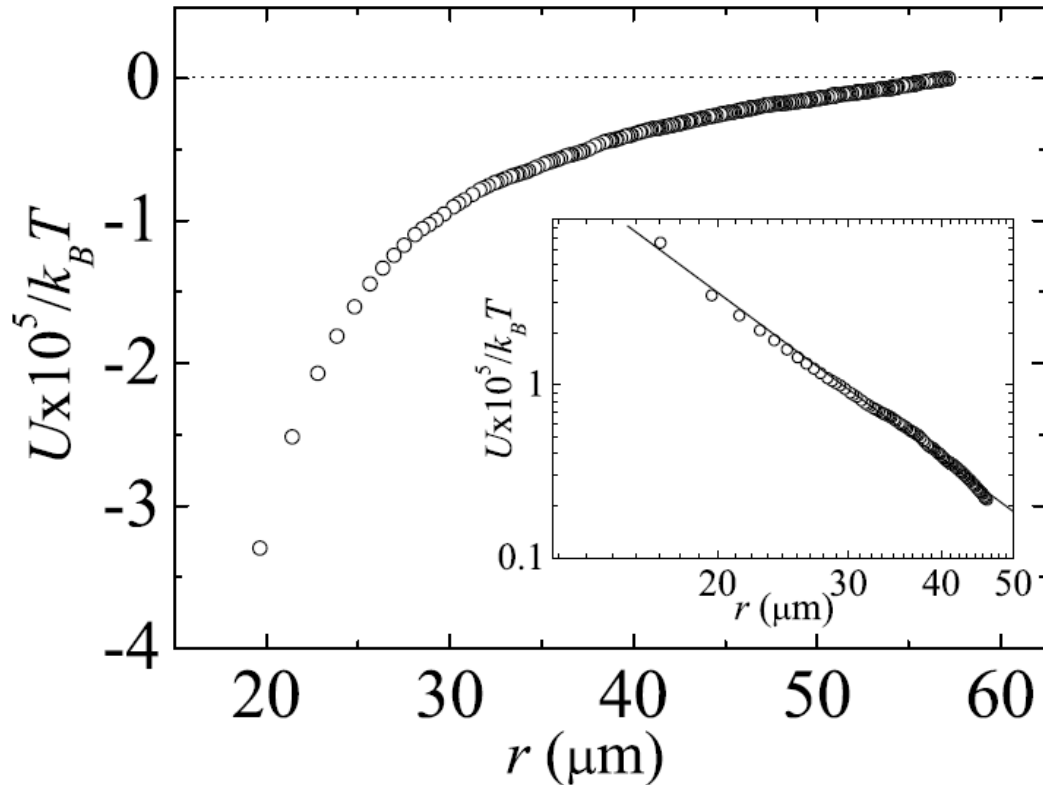
Shape Anisotropy Deforms Interface



Loudet, J.C., Alsayed, A.M., Zhang, J., and Yodh, A.G., *Phys Rev Lett* (2005); Loudet J.C., Yodh A.G., Pouligny B., *Phys Rev Lett* (2006); Kralchevsky, Paunov, Ivanov and Nagayama, *J. Coll. Inter. Sci.*, (1992)



Interfacial Forces Depend on Particle Shape

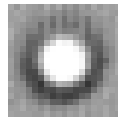


$$U \propto r^2 (\epsilon - 1)^2$$

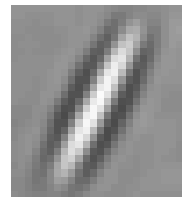
Loudet, J.C., Alsayed, A.M., Zhang, J., and Yodh, A.G., *Phys Rev Lett* (2005);
Loudet J.C., Yodh A.G., Pouligny B., *Phys Rev Lett* (2006); Kralchevsky, Paunov,
Ivanov and Nagayama, *J. Coll. Inter. Sci.*, (1992)



Outward flows drive coffee ring-effect



Spheres

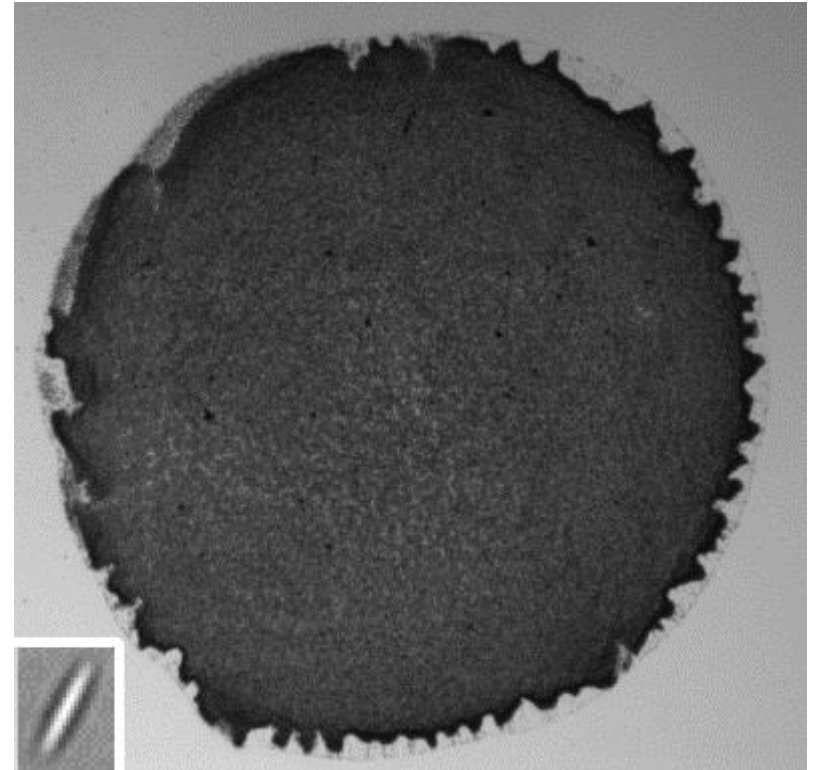
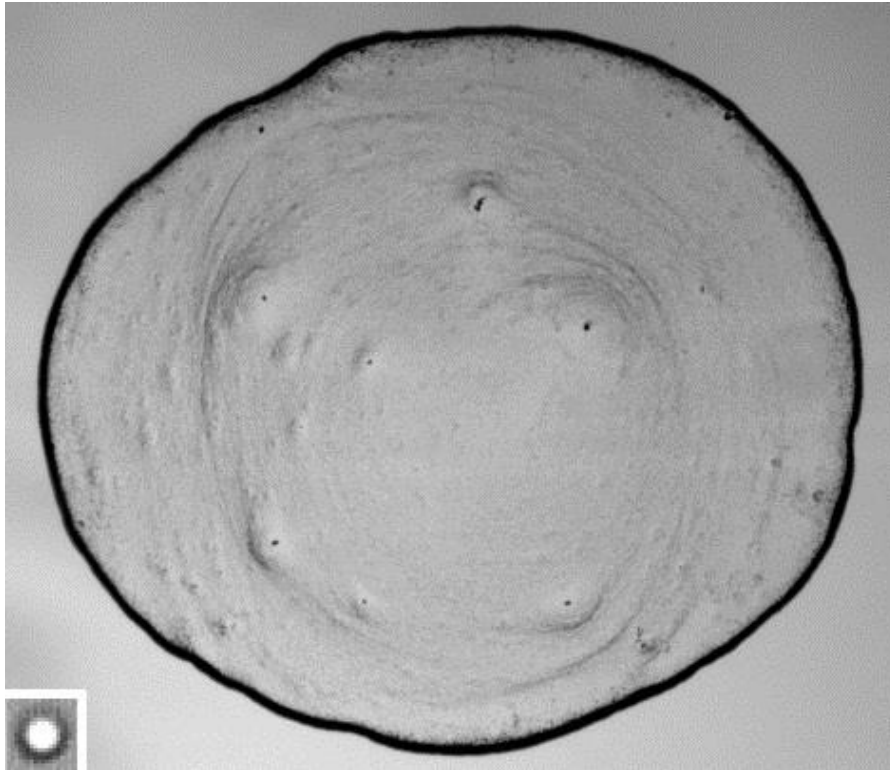


Ellipsoids

Robert D. Deegan, Olgica Bakajin, T.F. Dupont, G.Huber, Sidney R. Nagel , Thomas A. Witten, *Nature* (1997).



Coffee Rings for Spheres but not Ellipsoids!

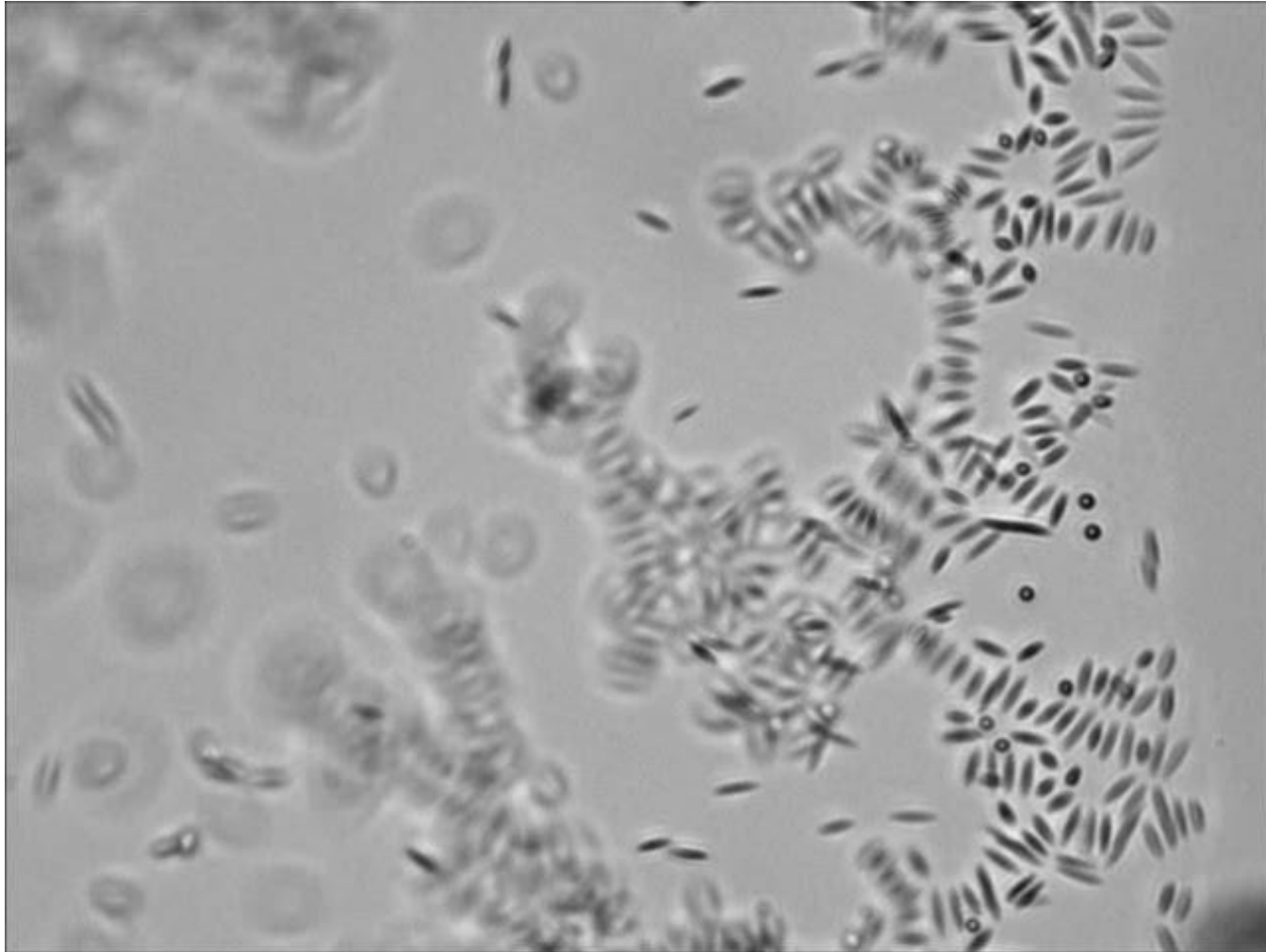


250 μm —

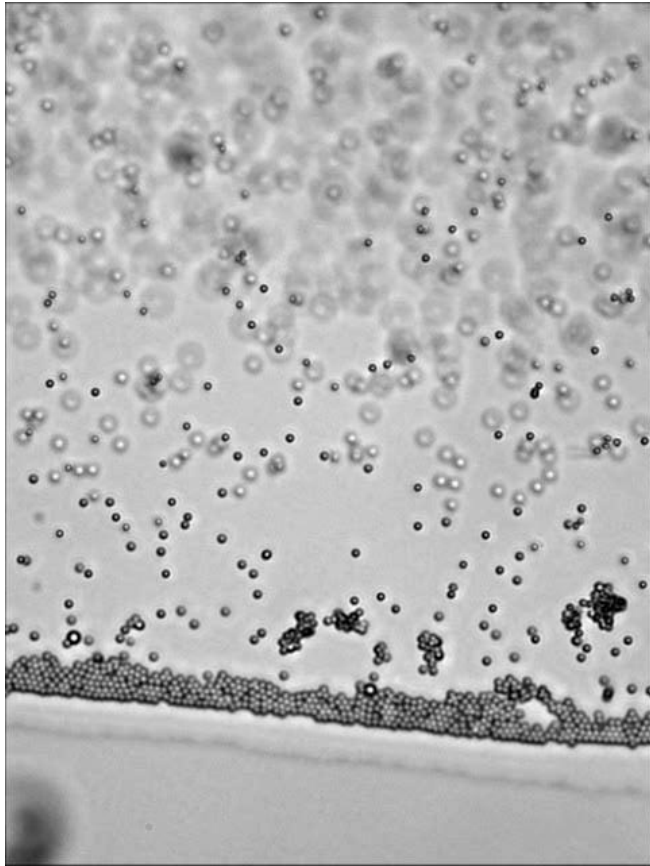
Yunker, P.J., Still, T., Lohr, M.A., and Yodh, A.G., *Nature* (2011).



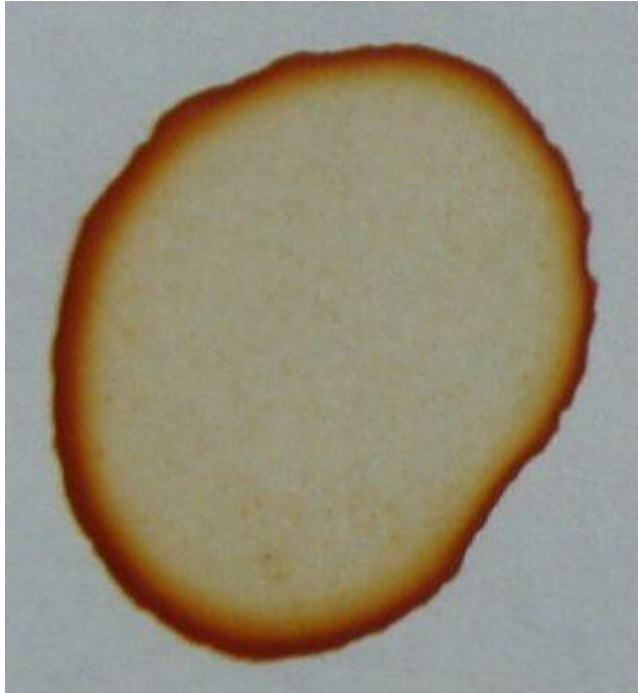
Ellipsoids form loosely-packed, open network



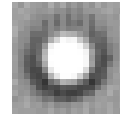
Reminiscent of growth process simulation



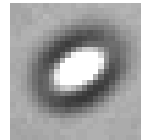
Growth process depends on particle shape



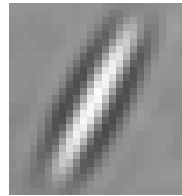
Coffee-ring effect



Poisson Process



KPZ Process



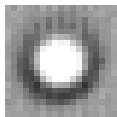
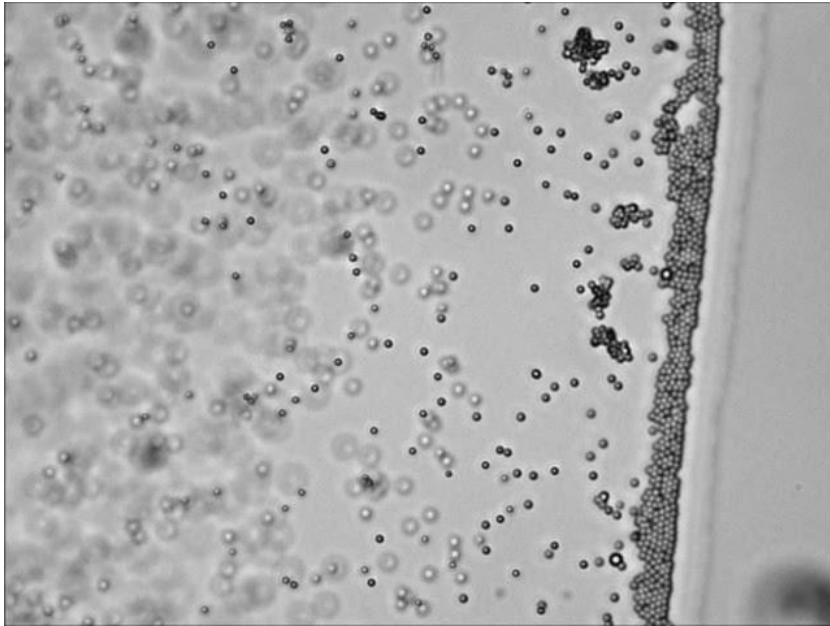
Colloidal Matthew Effect

Which growth processes?

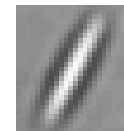
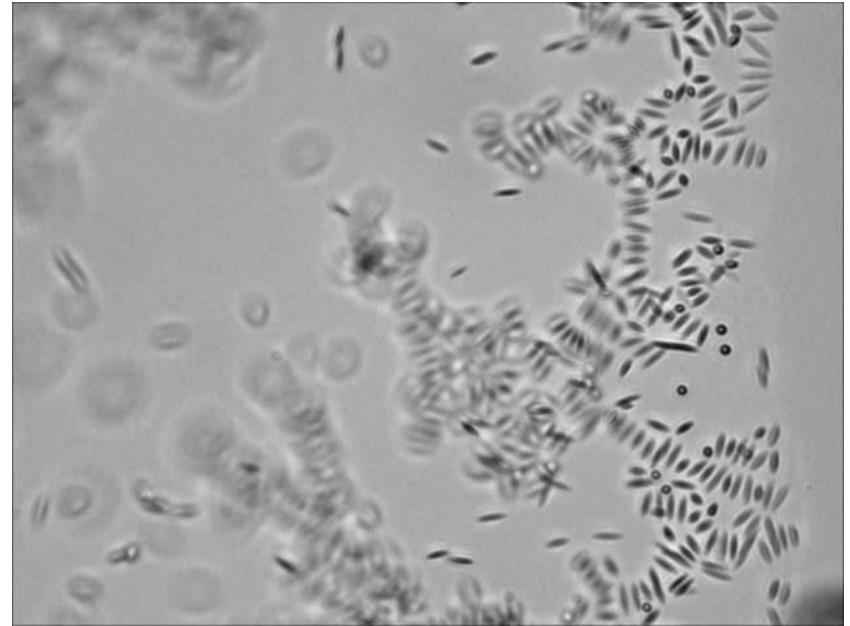
Why particle shape?



How do deposits grow during evaporation?



Spheres



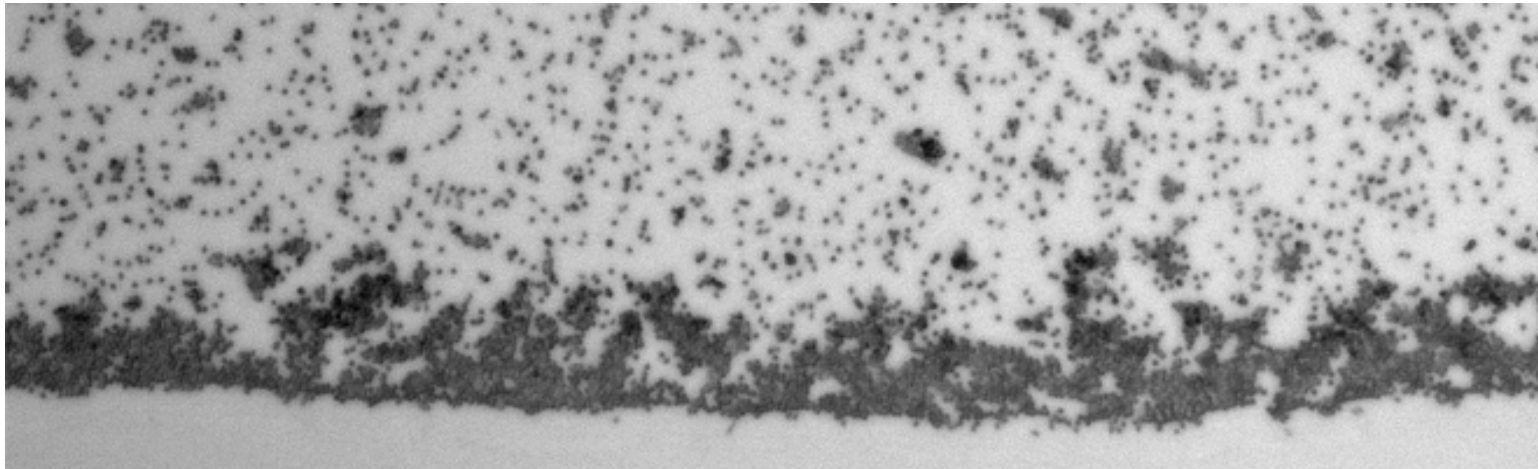
Ellipsoids

What types of growth processes occur?

How does growth process depend on particle shape?



Deposit Characterization



25 μm —



Deposit Characterization



25 μm —



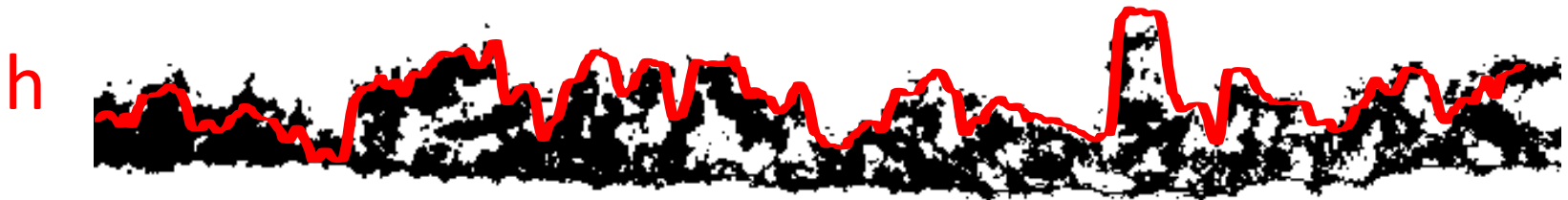
Deposit Characterization



h I
25 μm —



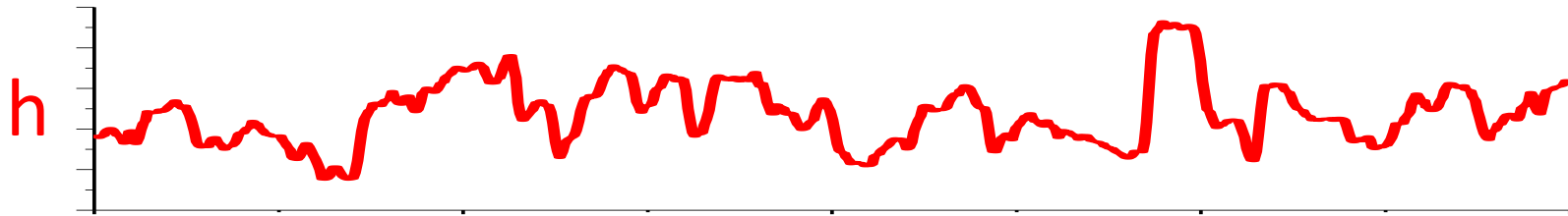
Deposit Characterization



25 μm —



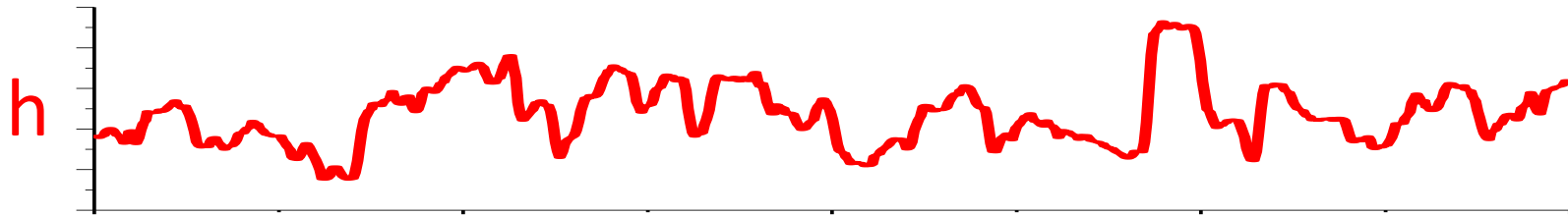
Deposit Characterization



25 μm —



Deposit Characterization



25 μm —

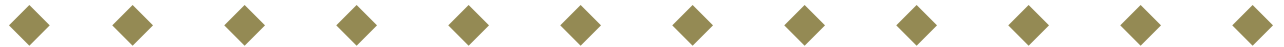
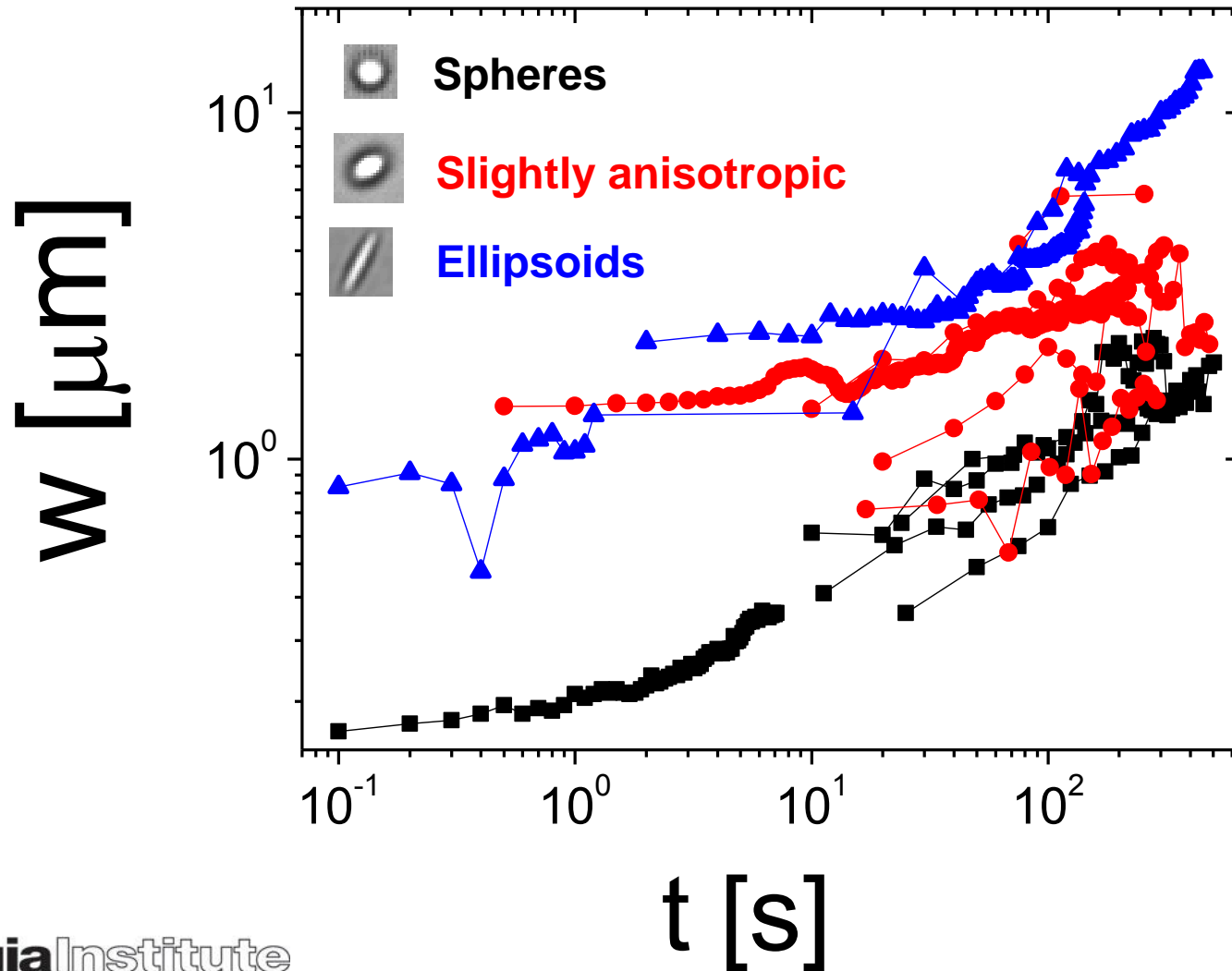
$$\text{Width, } w = \left\langle \sqrt{\langle (h - \langle h \rangle)^2 \rangle} \right\rangle \sim t^\beta$$

Slightly anisotropic particles

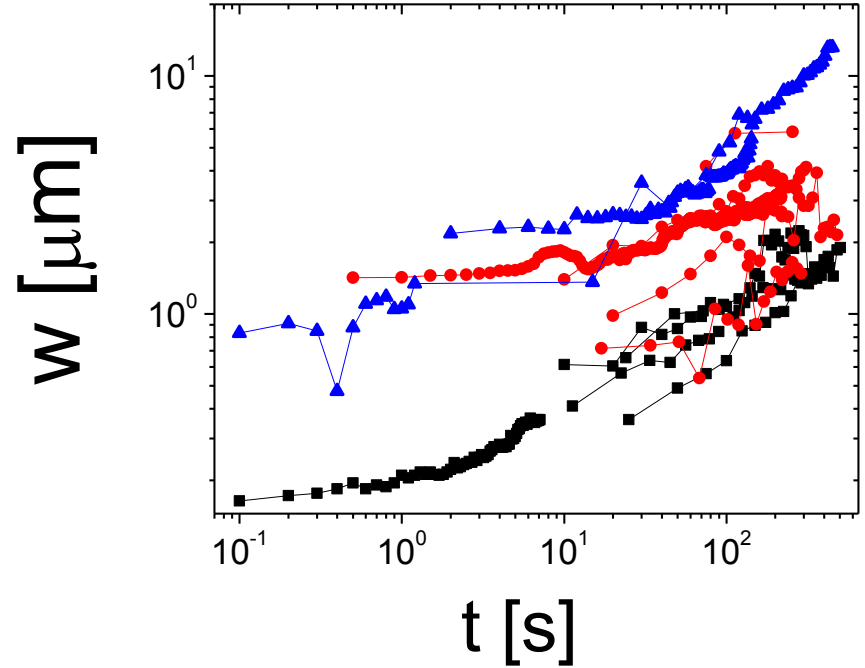
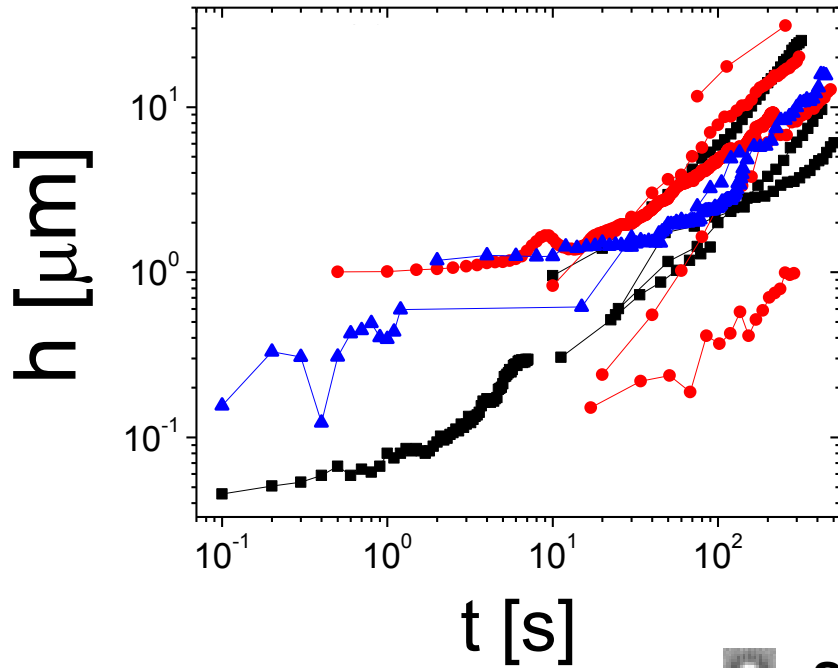
$\alpha = 1.2$



Deposit width increases over time



Use h instead of t



Spheres



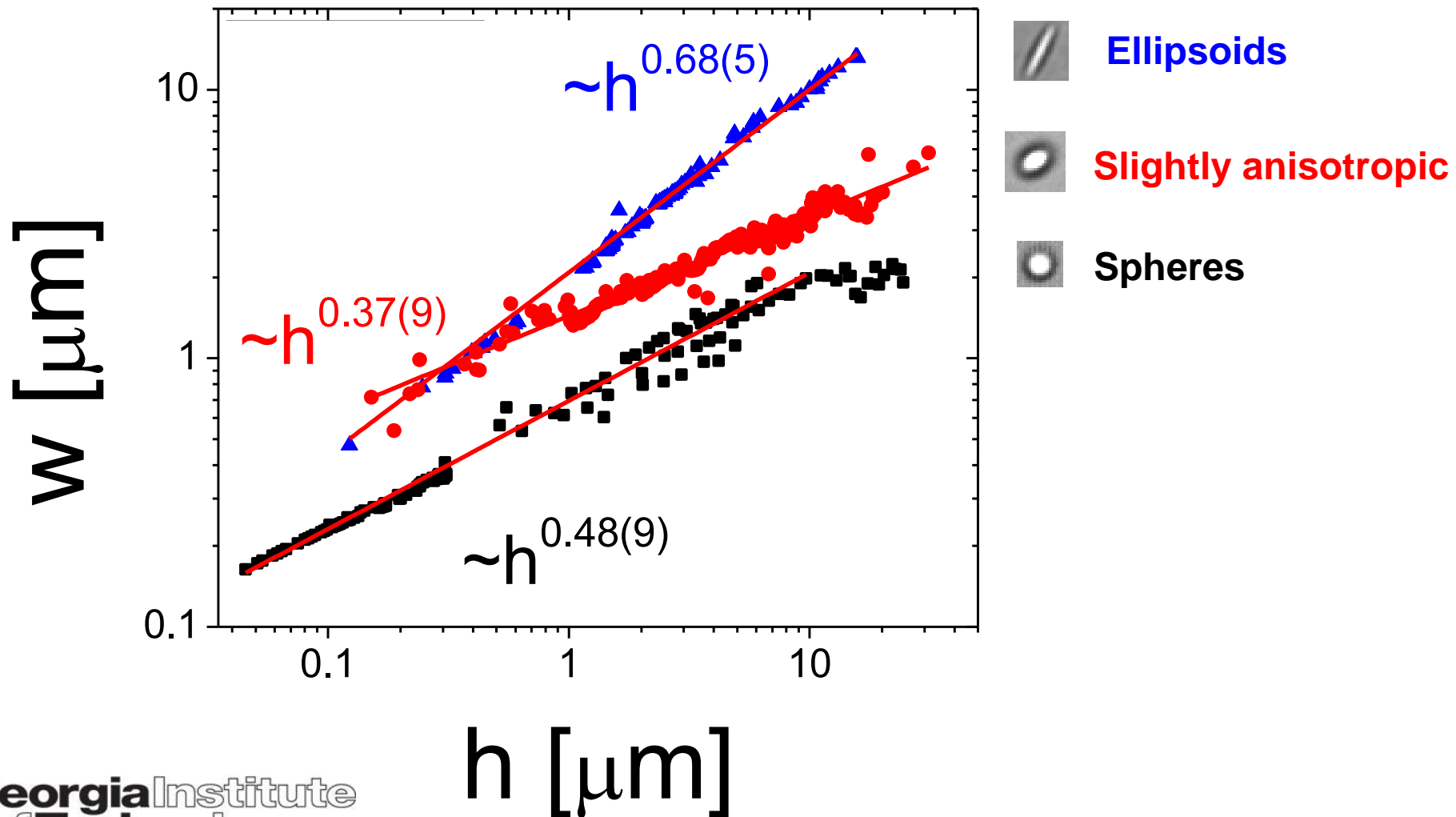
Slightly anisotropic



Ellipsoids



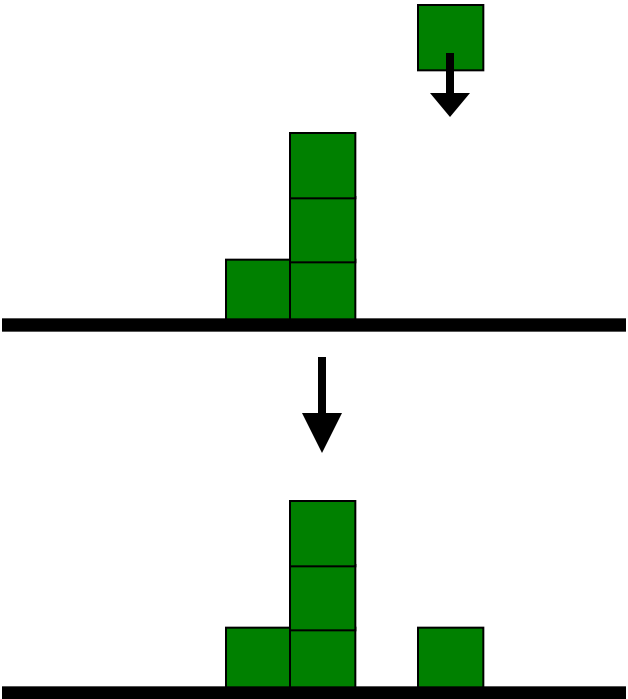
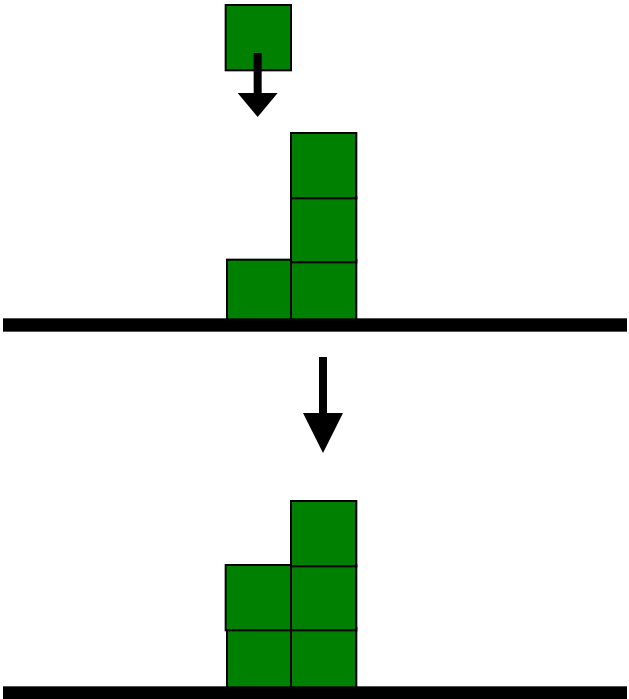
Data collapse into distinct trends based on particle shape



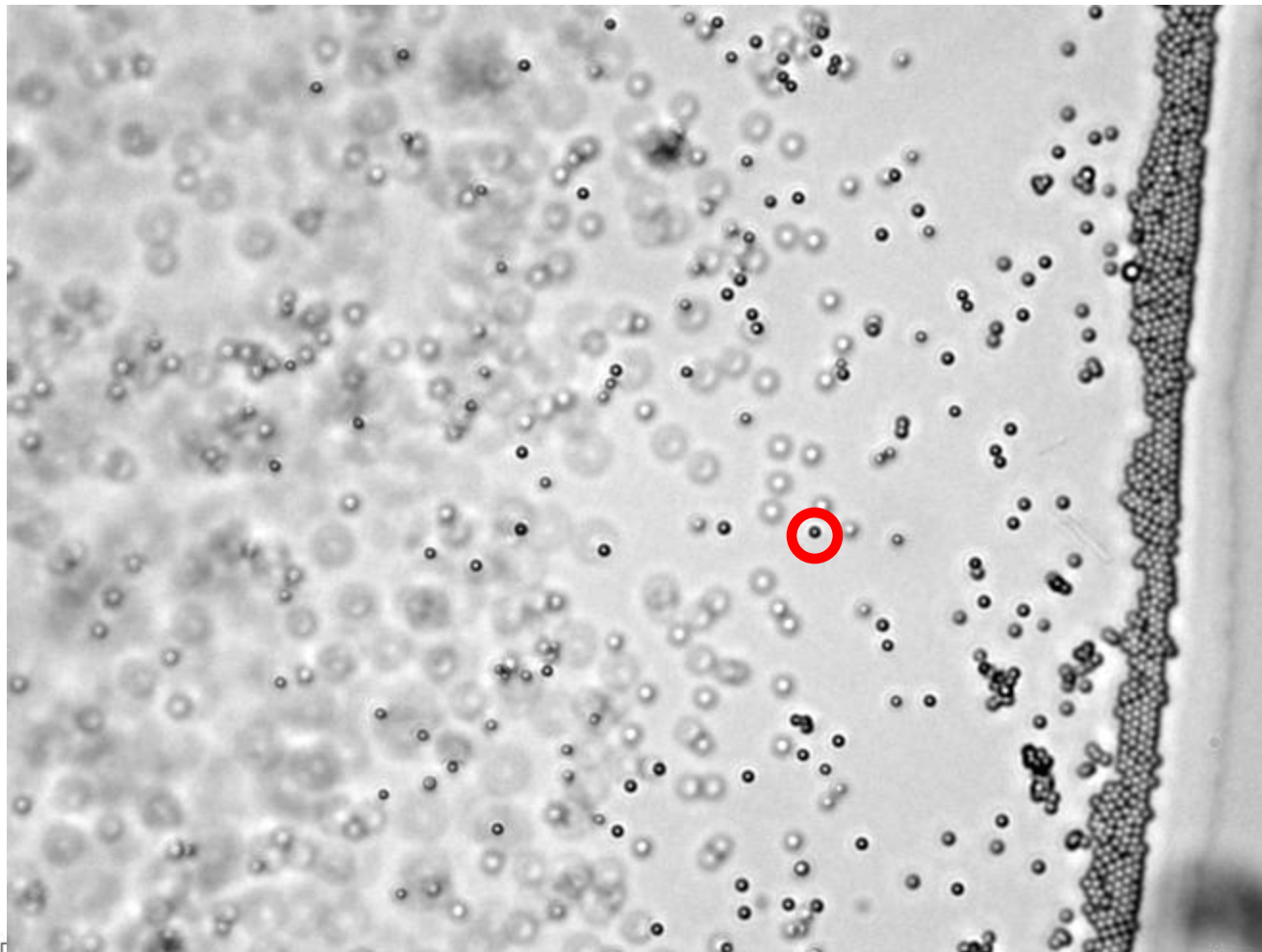
Spheres
 $\varepsilon = 1.0, 1.05$
Poisson Process



Random deposition – Poisson process



Spheres densely pack at drop edge



Drop
Edge

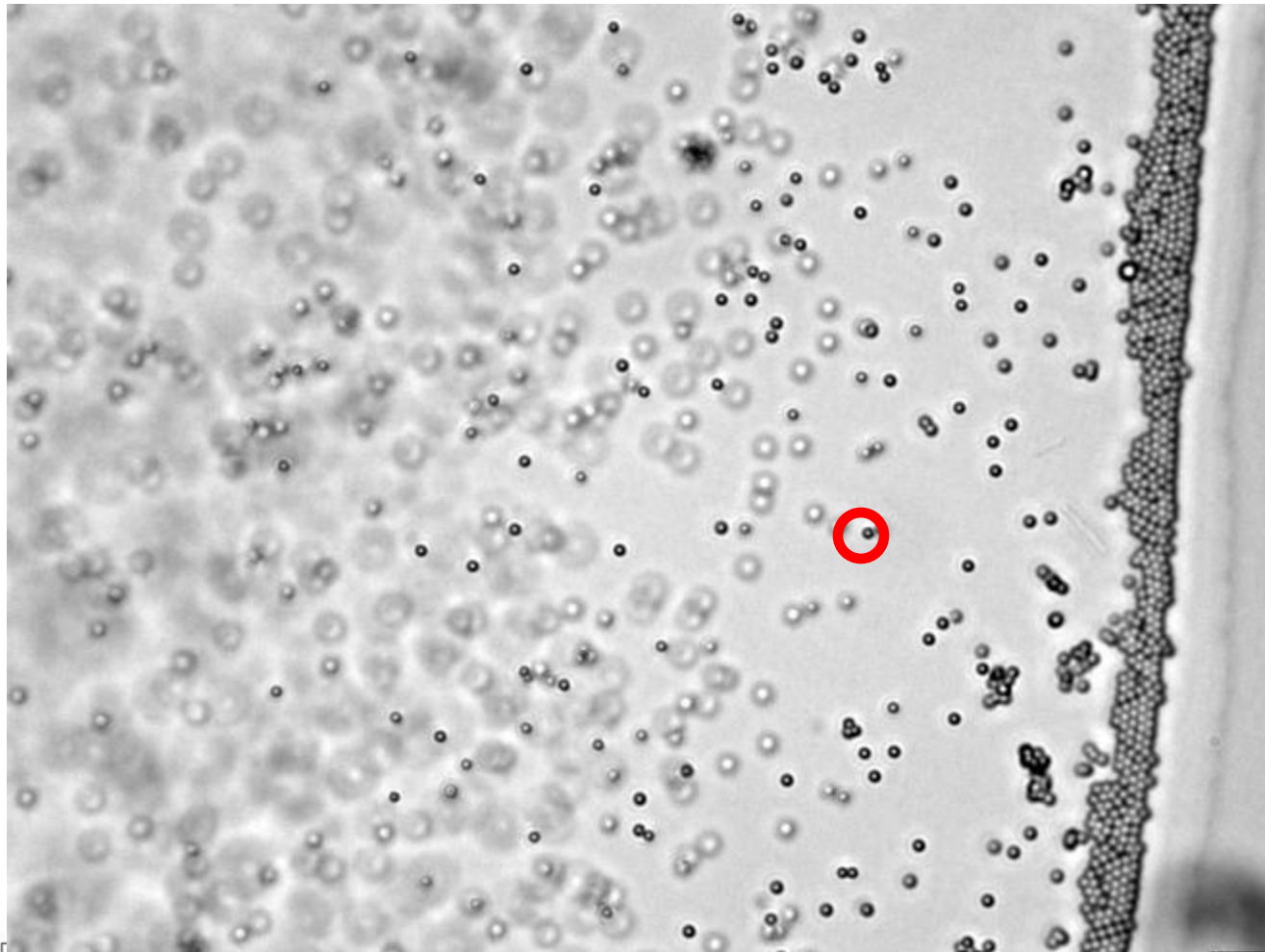
5 μm —

$t = 1 \text{ s}$

Initial
Volume
Fraction
 $\phi = 0.005$



Spheres densely pack at drop edge



Drop
Edge

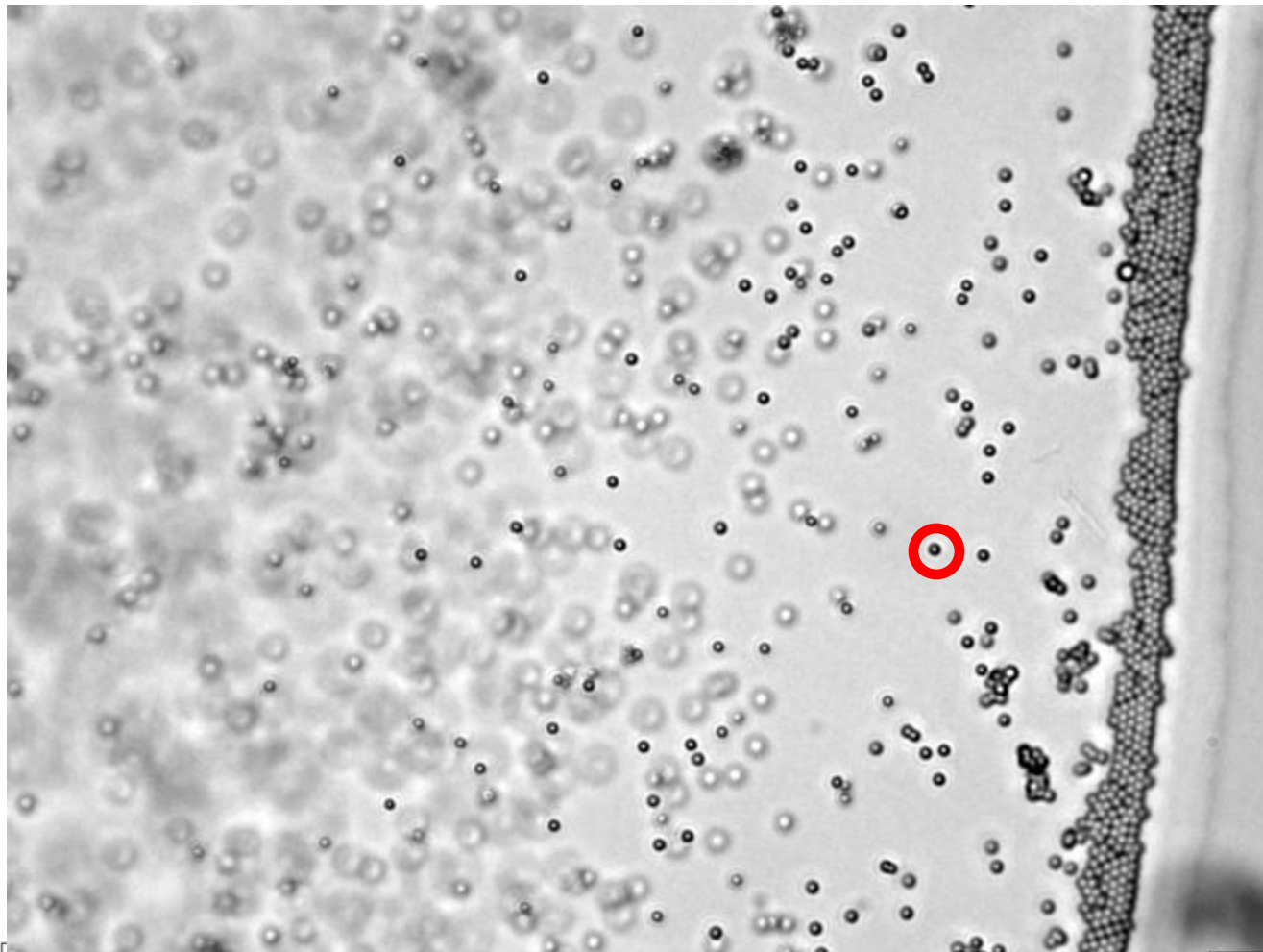
5 μm —

$t = 2 \text{ s}$

Initial
Volume
Fraction
 $\phi = 0.005$



Spheres densely pack at drop edge



Drop
Edge

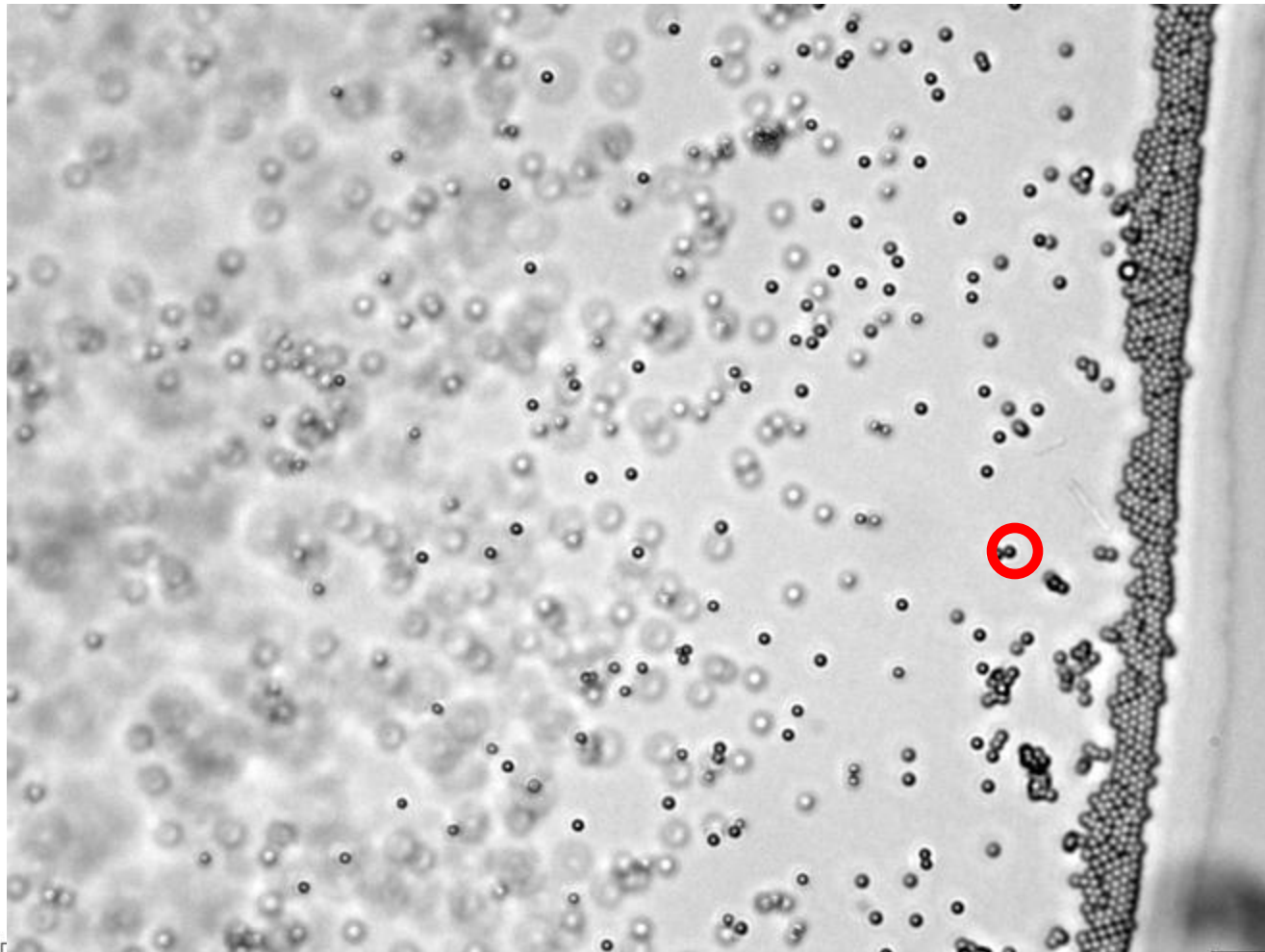
5 μm —

$t = 3 \text{ s}$

Initial
Volume
Fraction
 $\phi = 0.005$



Spheres densely pack at drop edge



Drop
Edge

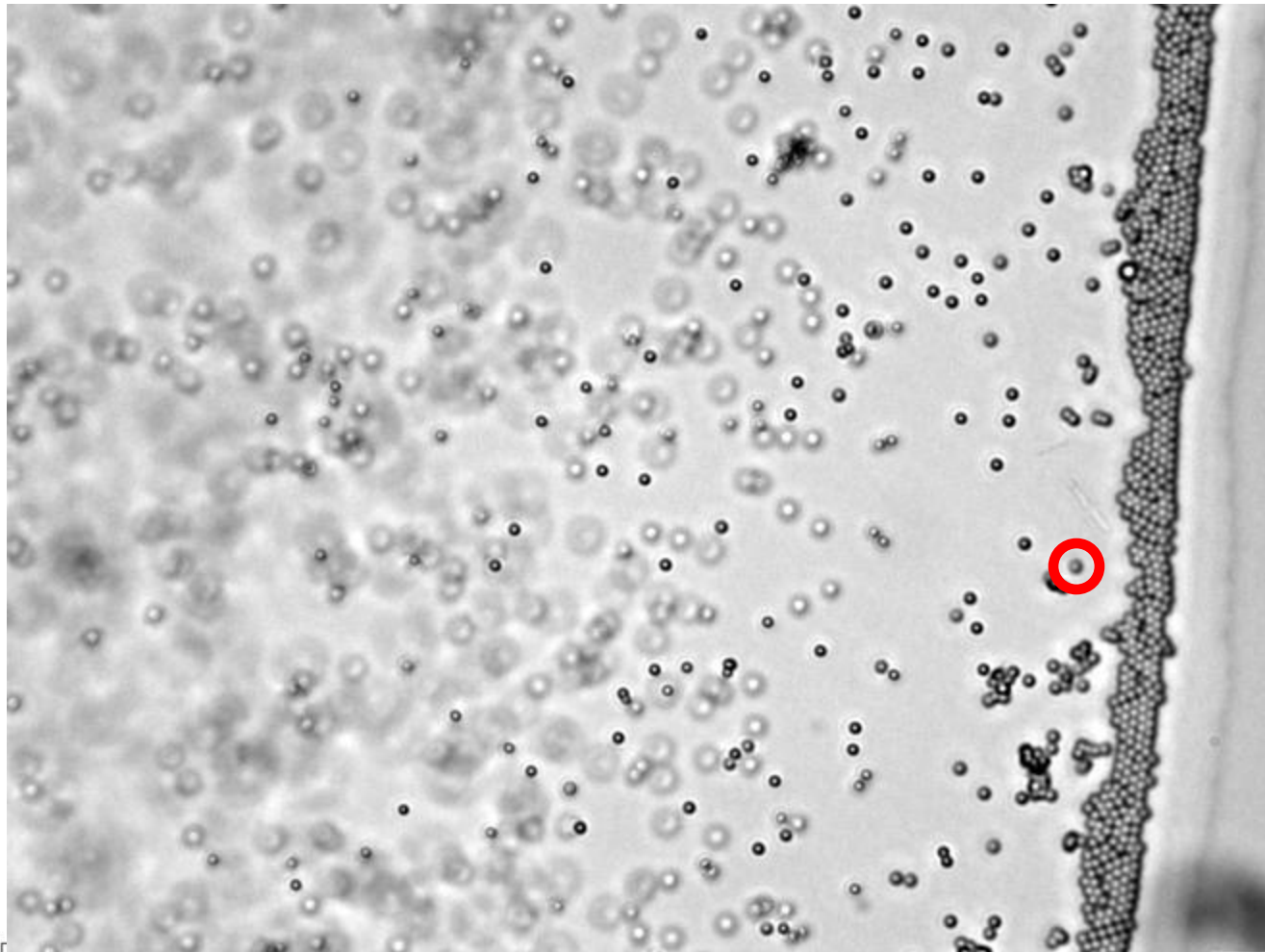
5 μm —

$t = 4 \text{ s}$

Initial
Volume
Fraction
 $\phi = 0.005$



Spheres densely pack at drop edge



Drop
Edge

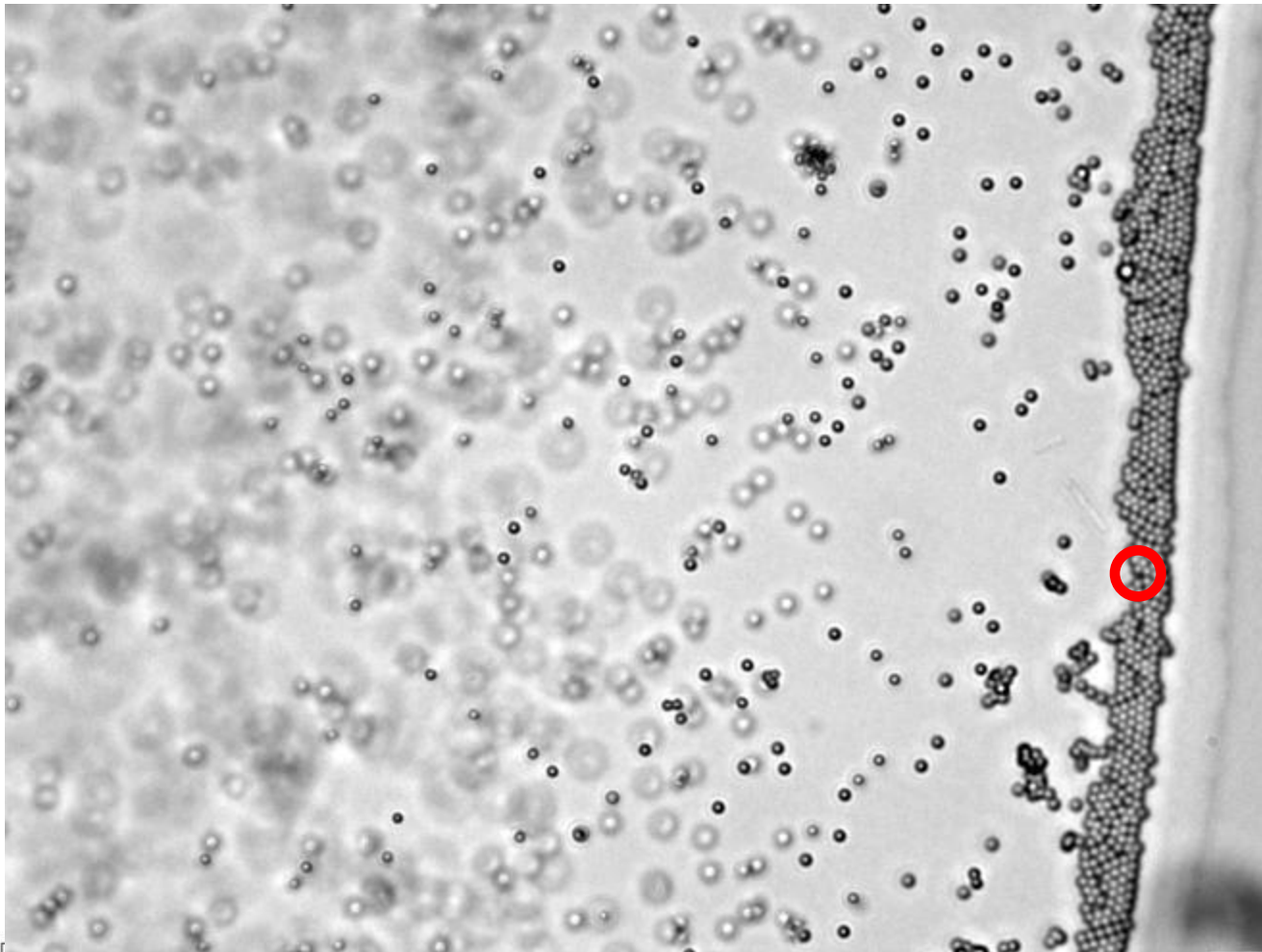
5 μm —

$t = 5 \text{ s}$

Initial
Volume
Fraction
 $\phi = 0.005$



Spheres densely pack at drop edge



Drop
Edge

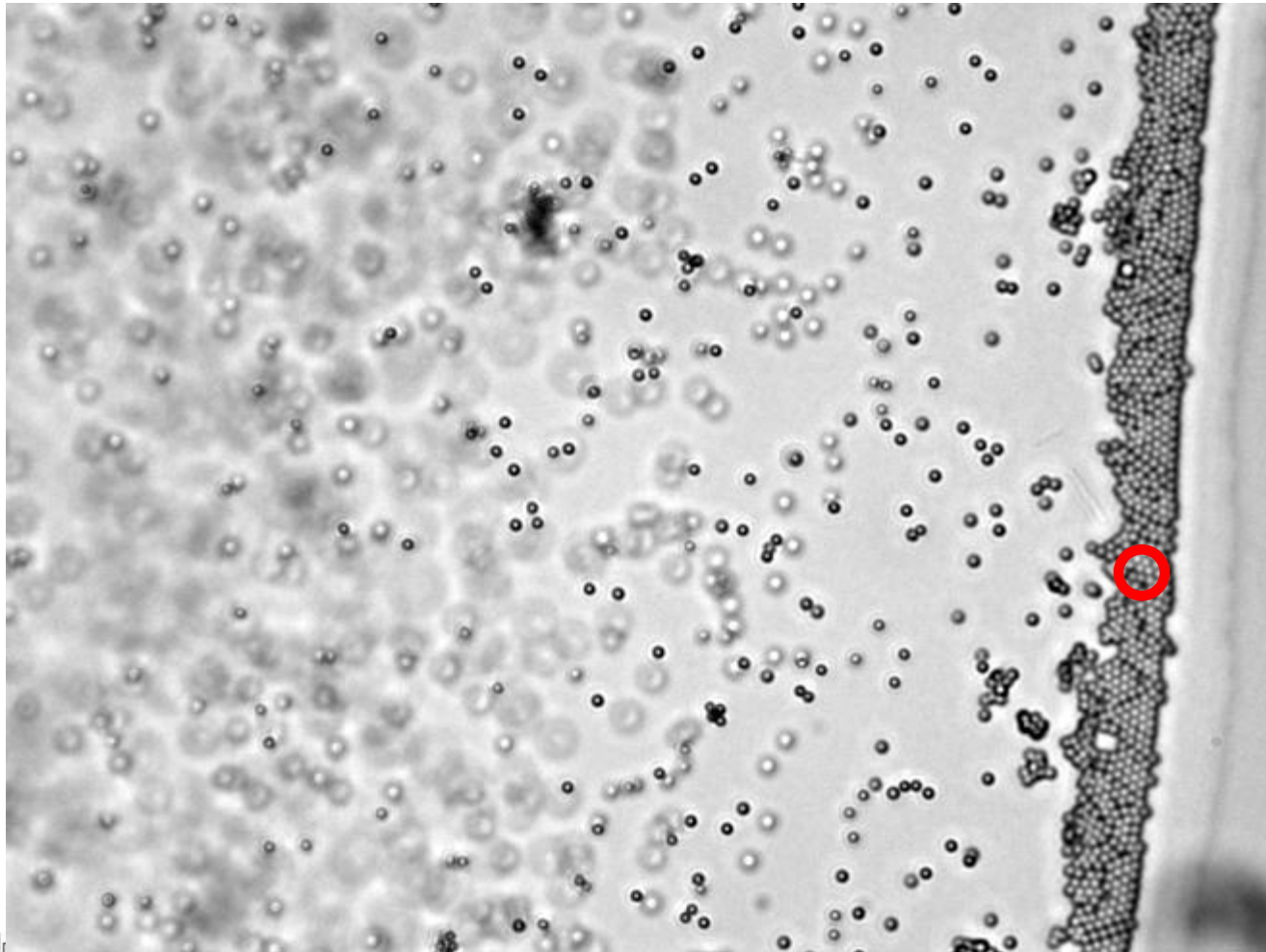
5 μm —

$t = 6 \text{ s}$

Initial
Volume
Fraction
 $\phi = 0.005$



Spheres densely pack at drop edge



Drop
Edge

5 μm —

$t = 26 \text{ s}$

Initial
Volume
Fraction
 $\phi = 0.005$



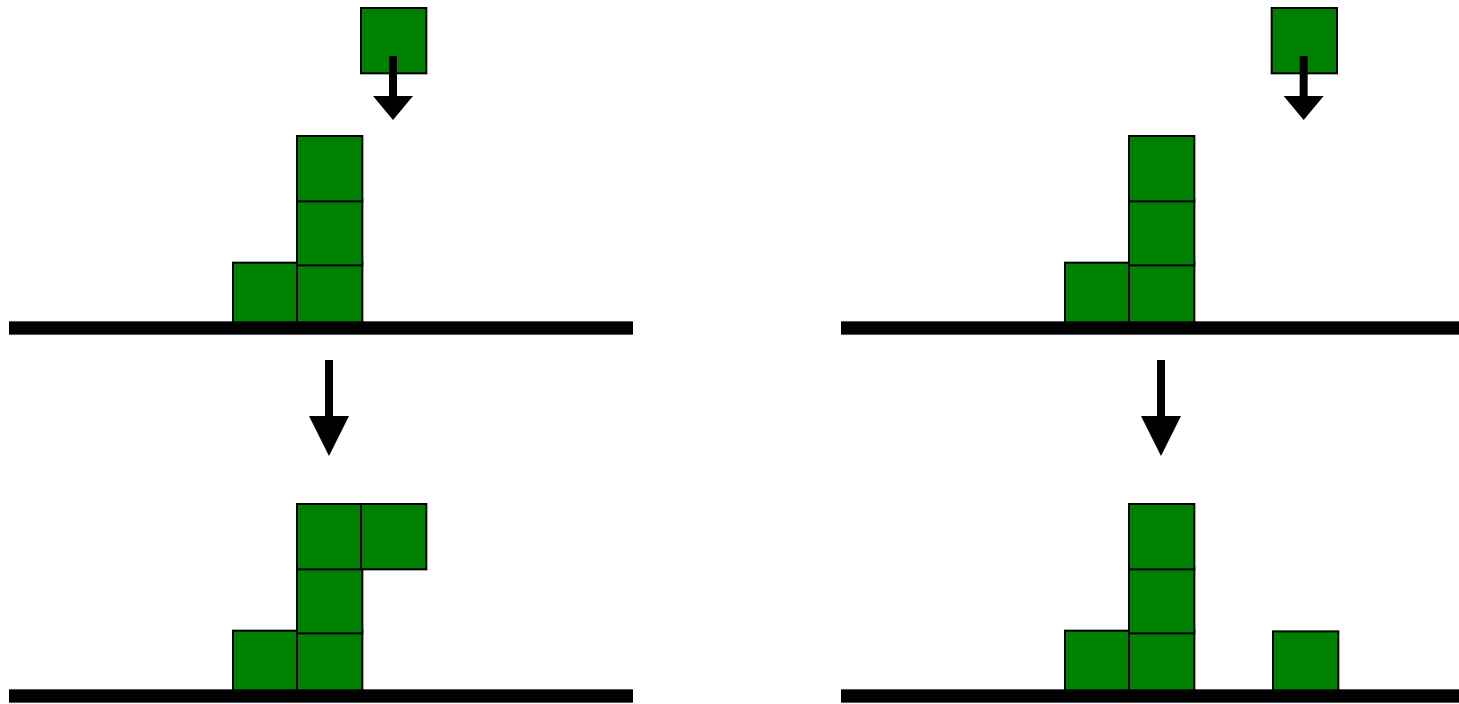
Slightly anisotropic particles

$\varepsilon = 1.1, 1.2$

KPZ Process



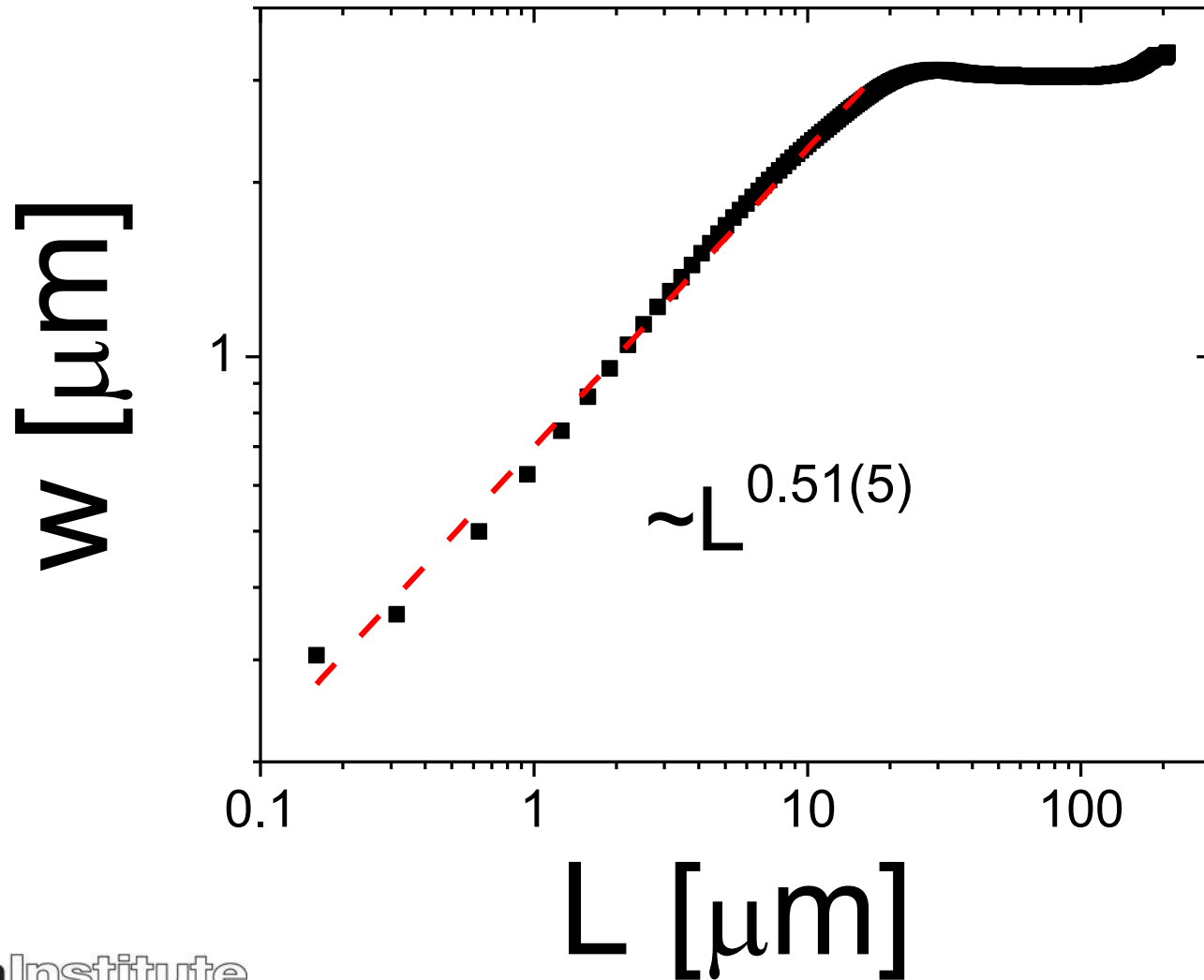
Slightly stretched particle deposition similar to ballistic deposition



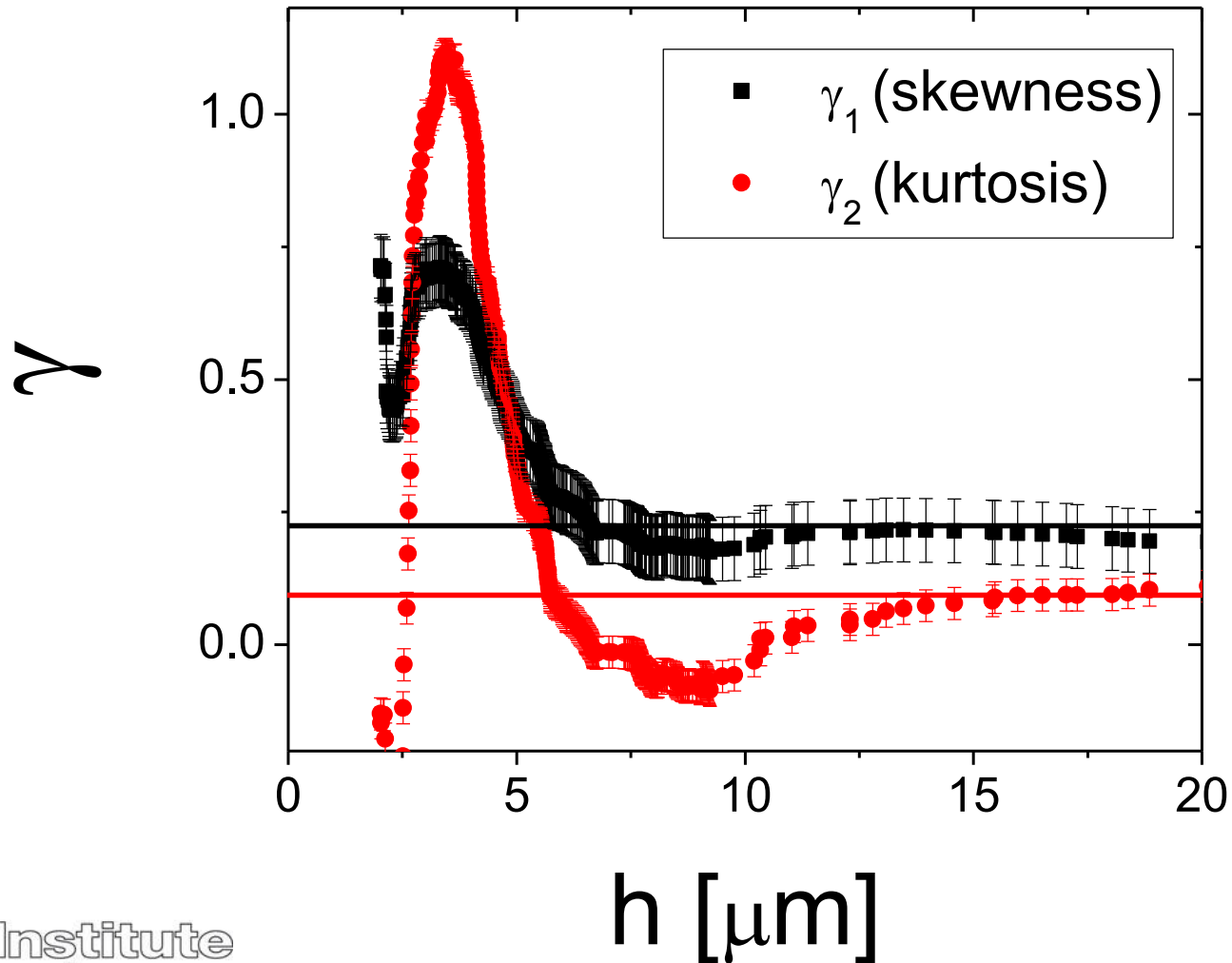
Interparticle interaction is $\gg 1 k_B T$ for nearest neighbors only



Roughness exponent α agrees with KPZ



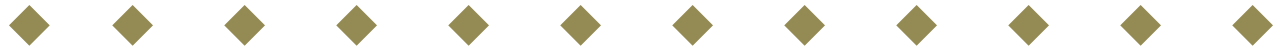
Skewness and Kurtosis approach KPZ values



Very anisotropic ellipsoids

$$\varepsilon > 1.2$$

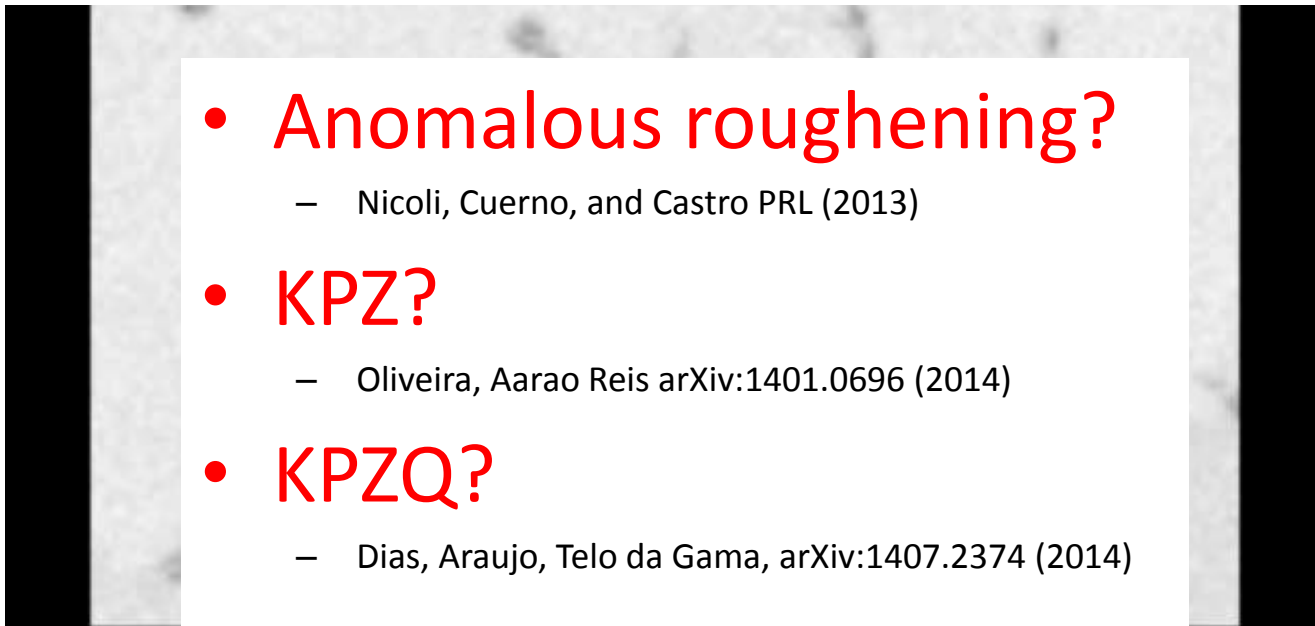
Colloidal Matthew Effect



Particle-rich regions get richer



What type of growth process is this?



- Anomalous roughening?

- Nicoli, Cuerno, and Castro PRL (2013)

- KPZ?

- Oliveira, Aarao Reis arXiv:1401.0696 (2014)

- KPZQ?

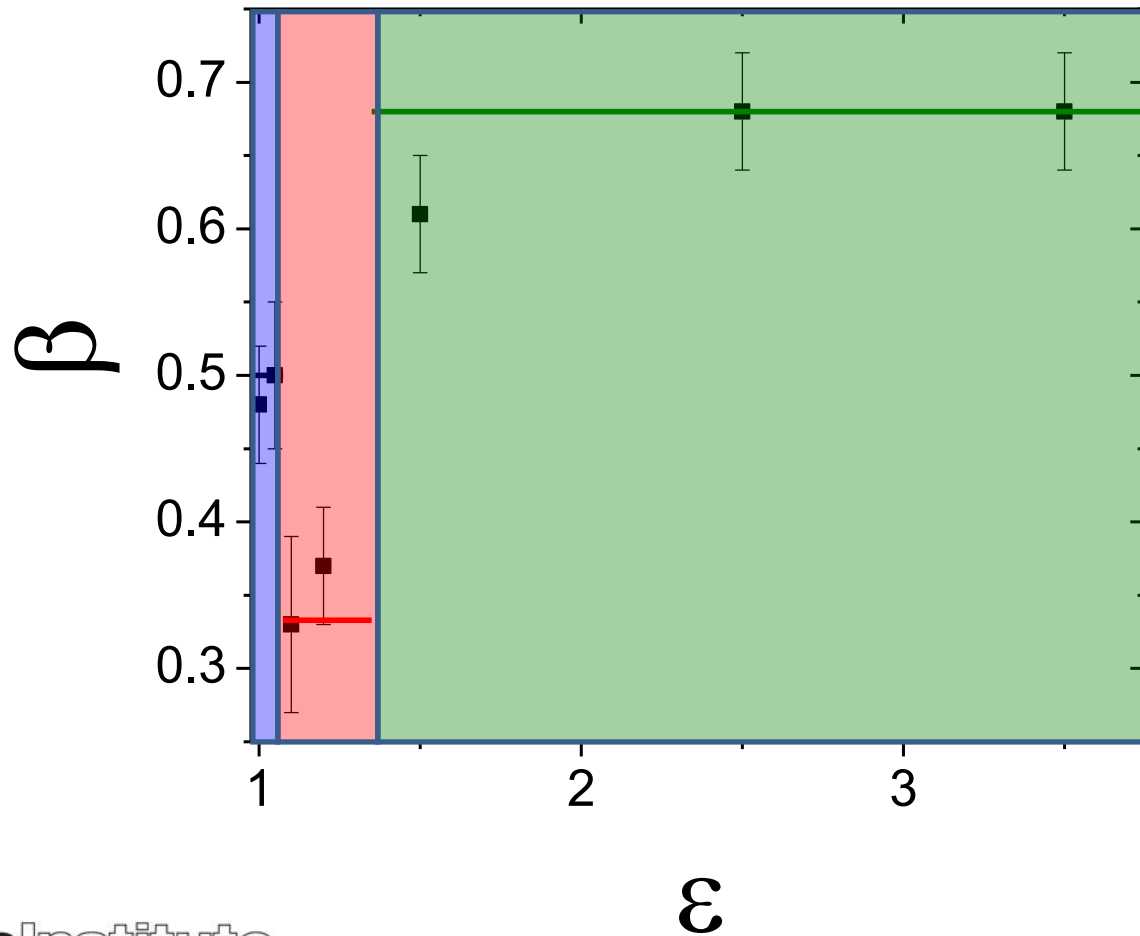
- Dias, Araujo, Telo da Gama, arXiv:1407.2374 (2014)

Drop Edge

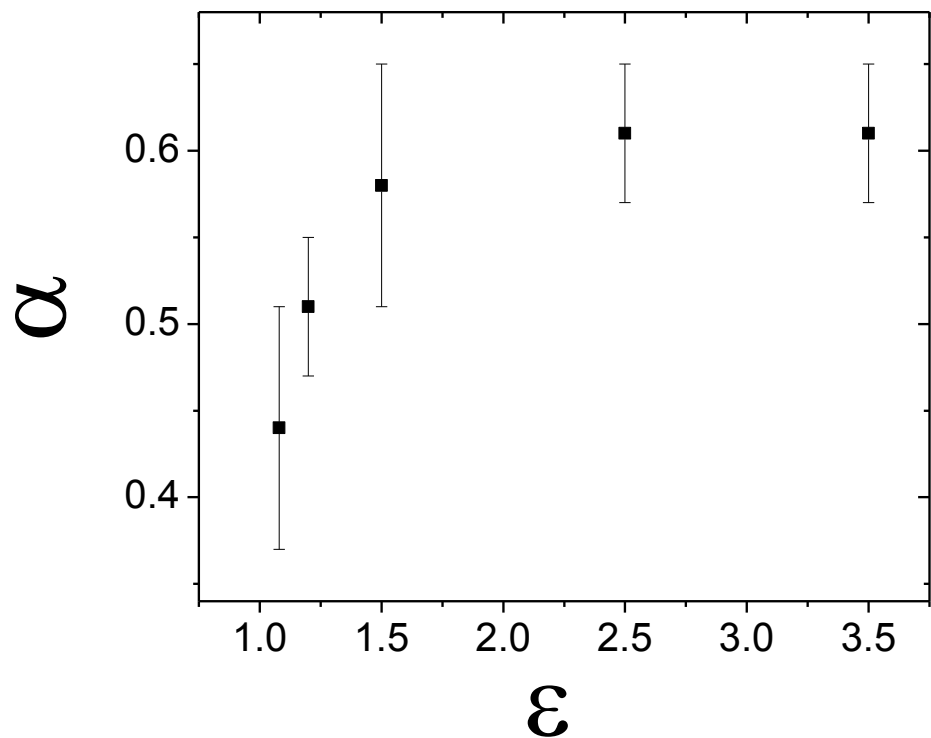
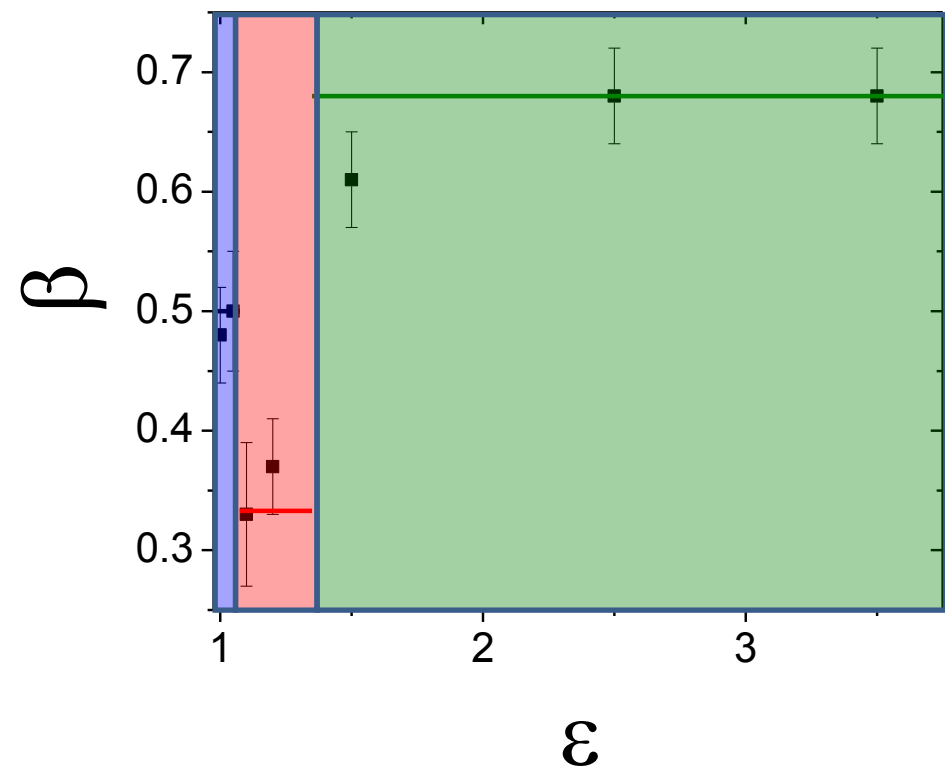
10 μm 



Must explain abrupt transition



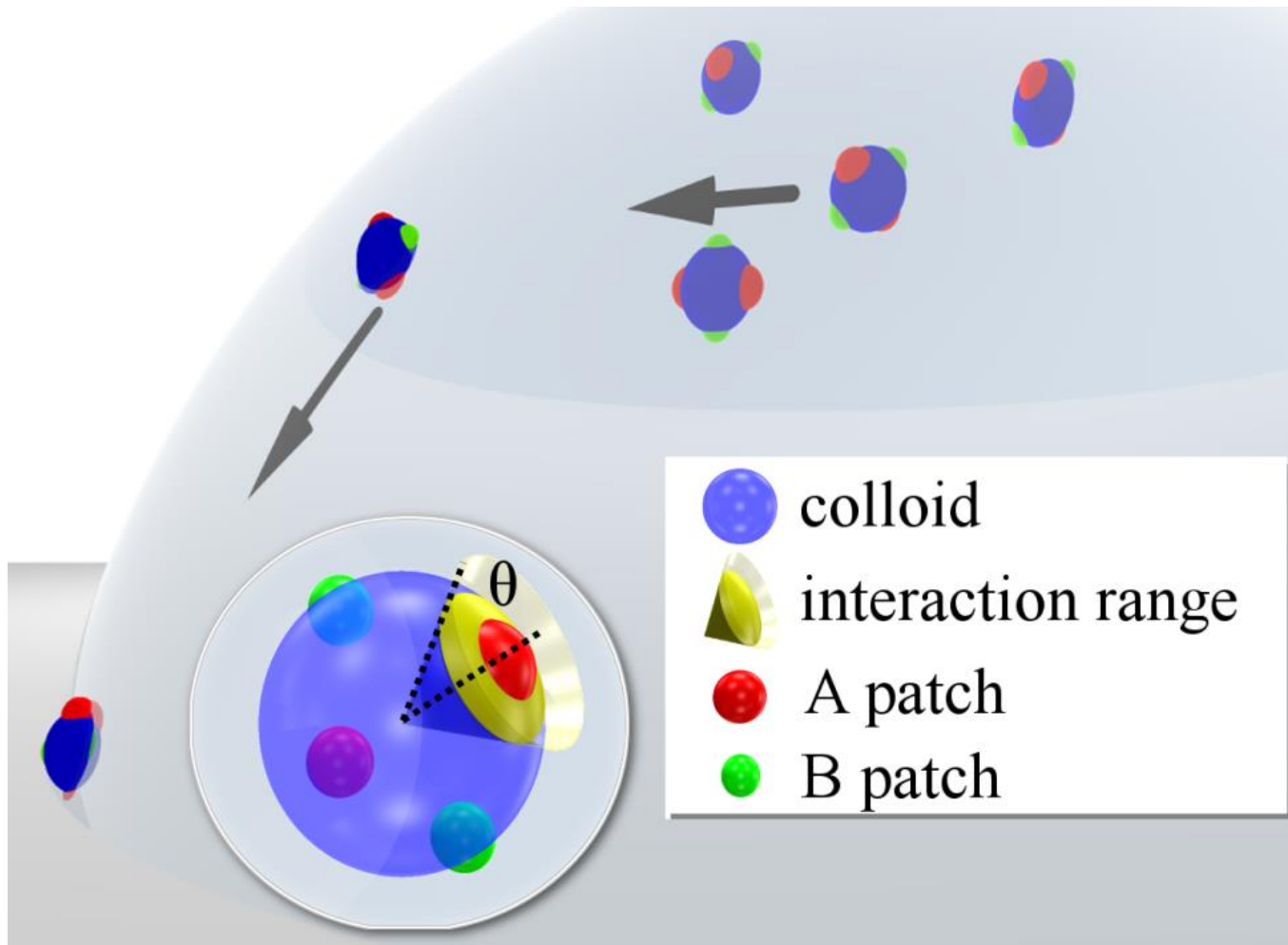
Must explain abrupt transition



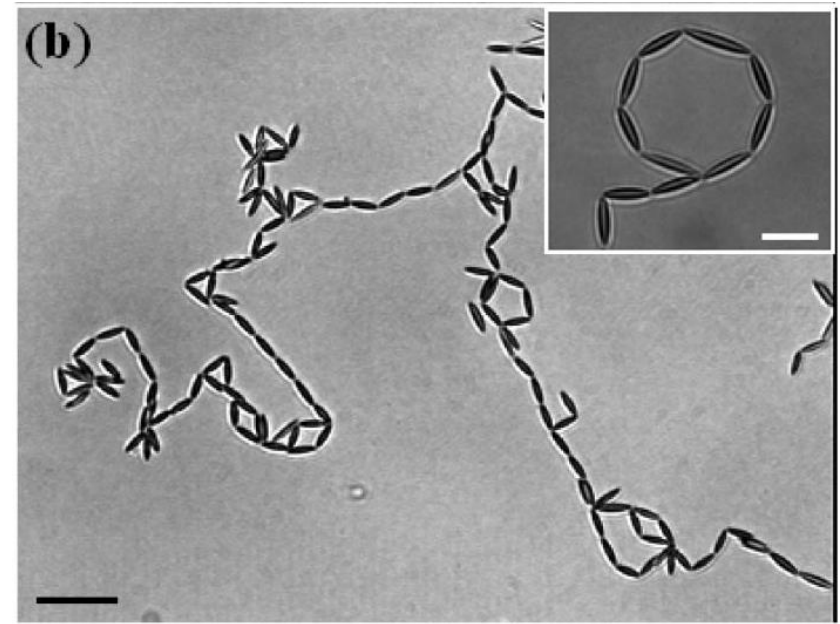
Minimal simulation?



Simulation of patchy colloids

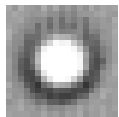


Highly anisotropic ellipsoids prefer tip-to-tip or side-to-side

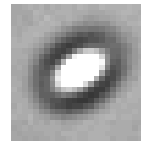


Summary

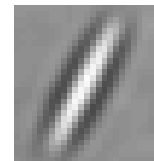
- Changing particle shape selects 3 distinct growth processes



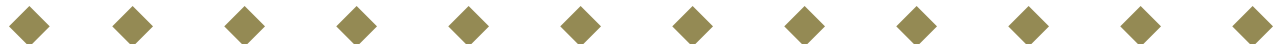
Poisson
Process



KPZ
Process



Colloidal Matthew
Effect
(other universal
process?)



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- Collaborators: Alexei Borodin, Doug J. Durian, Tom Lubensky, Matthew A. Lohr, Tim Still



 **Physics: Coffee Stains Test Universal Equation**

January 18, 2013



An equation that describes a wide array of phenomena can be directly tested by wa
the equivalent of a drying coffee drip.

[Focus on Phys. Rev. Lett. **110**, 035501 (2013)]

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P. J. Yunker, T. Still, M.A. Lohr, A.G. Yodh, *Nature* (2011)

P. J. Yunker, M. Gratale, T. Still, M.A. Lohr, T.C. Lubensky, A.G. Yodh, *PRL* (2012)

P. J. Yunker, T. Still, M.A. Lohr, D.J. Durian, Alexei Borodin, A.G. Yodh, *PRL* (2013)

P. J. Yunker, D.J. Durian, A.G. Yodh, *Physics Today* (2013)

