Random Packing Density of Colloids and Granular Matter

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Outline

- **Motivation.**
- **<u>Spheres</u>: the Bernal packing .**
- **<u>Thin rods</u>: the ideal gas in random packings.**
- **<u>Near-spheres</u>: a packing surprise.**
- **Conclusions and outlook.**

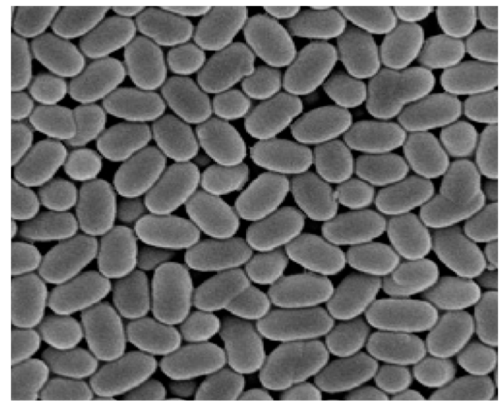
- **Extra: something on random *bio*-packings.**

Motivation

Packings in

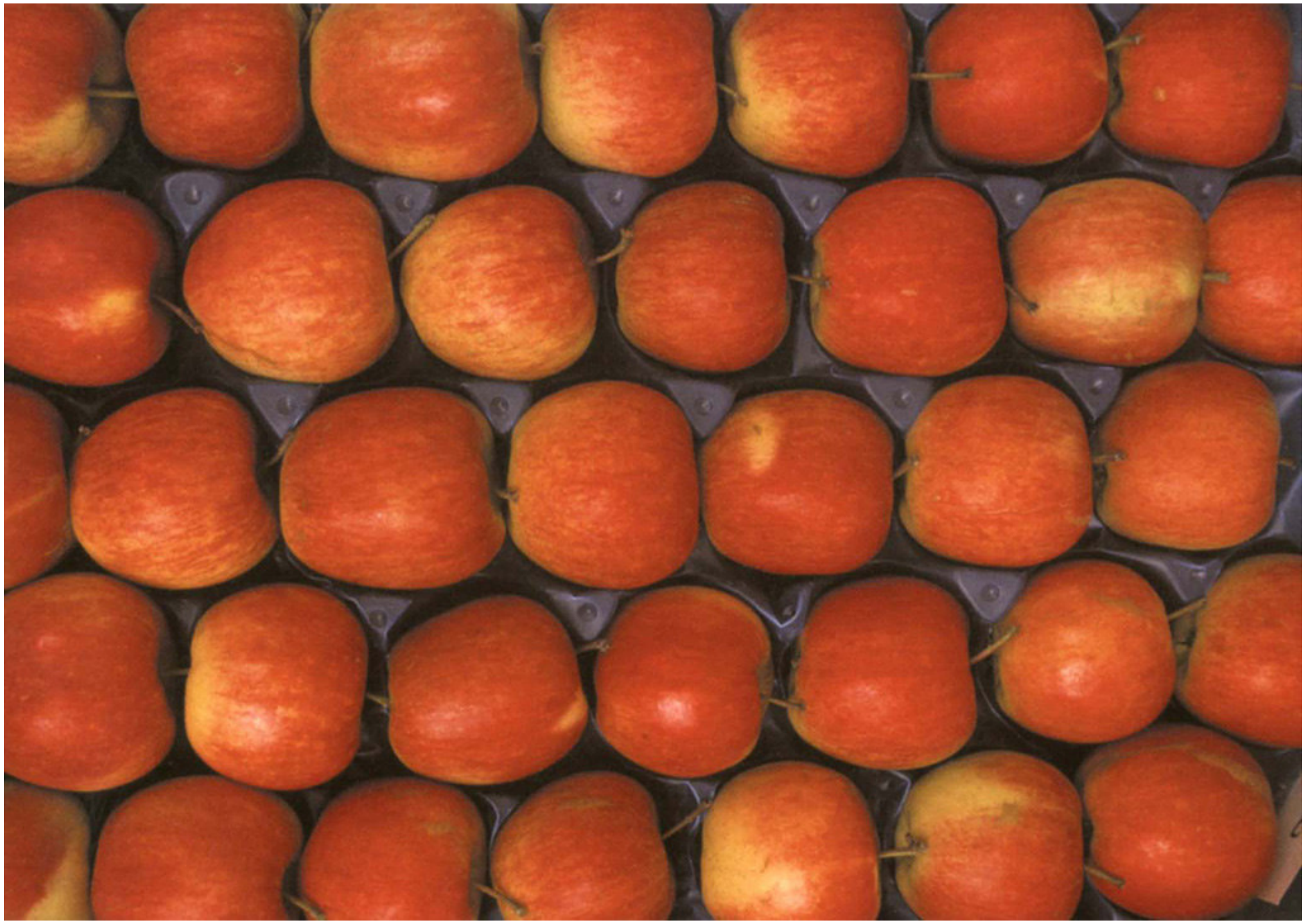
- **Nature:**
  - sand, gravel, etc.

- **Colloid science:**
  - colloidal ellipsoids



- **Technology:**
  - food technology
  - catalyst carriers ( )

Ordered sphere packing

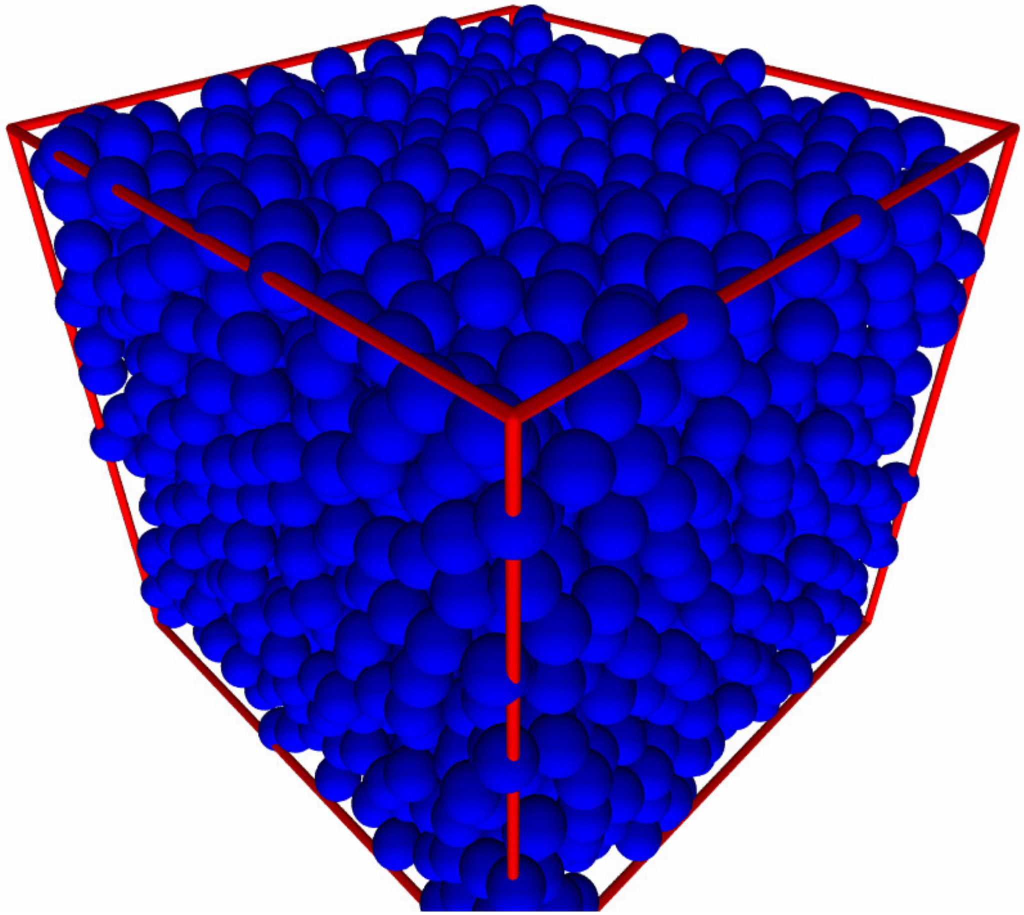


Kepler's conjecture : you can't pack spheres denser than to a solid volume fraction of $\pi / \sqrt{18}$ **= 0.7405.**

Disordered, ‘random’ sphere packing

Disorded spheres pack at a lower density of about 0.64 (the Bernal sphere packing).

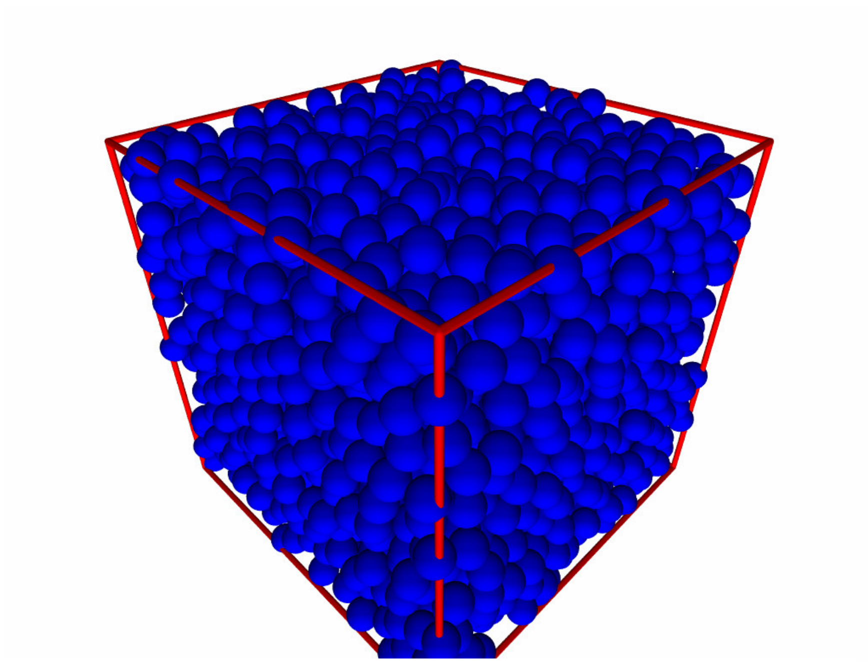
The Bernal random sphere packing



Classical reference system for amorphous matter, colloidal glasses etc.

The Bernal random sphere packing

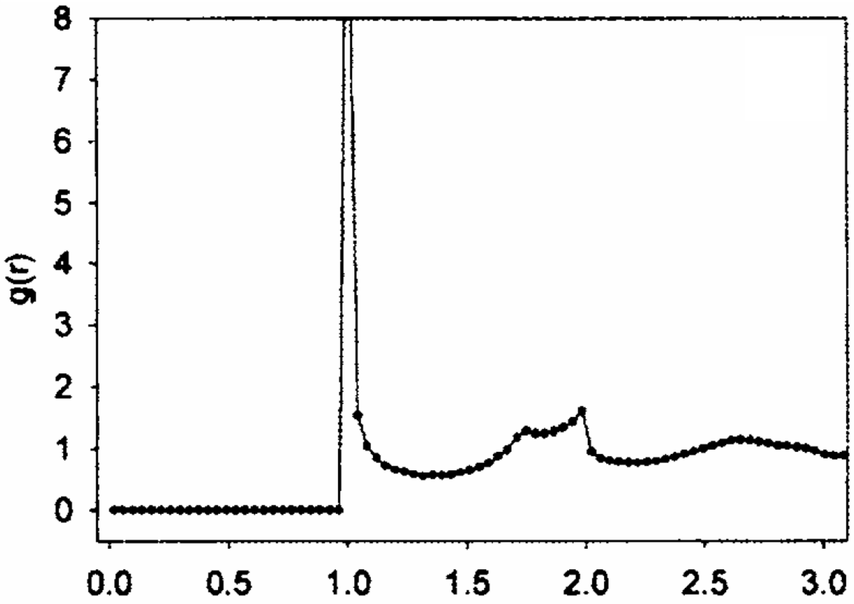
S.R. Wiliams and A.P. Philipse, *Phys. Rev. E*, 2003
A. Wouterse et al., *J. Chem. Phys.*, 2006



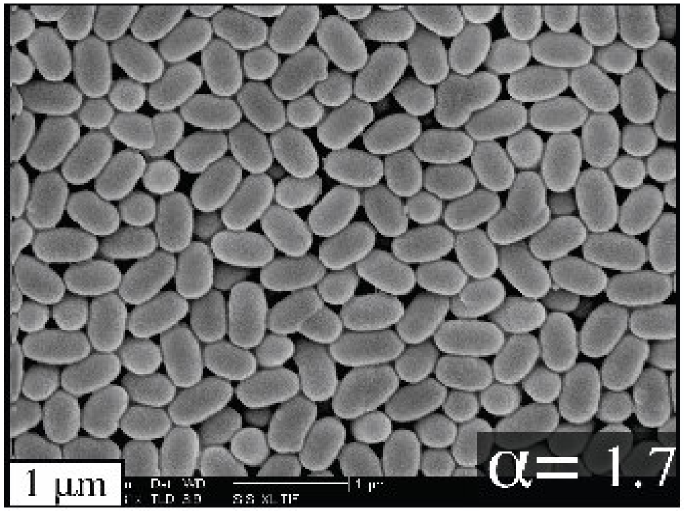
volume fraction = 0.62

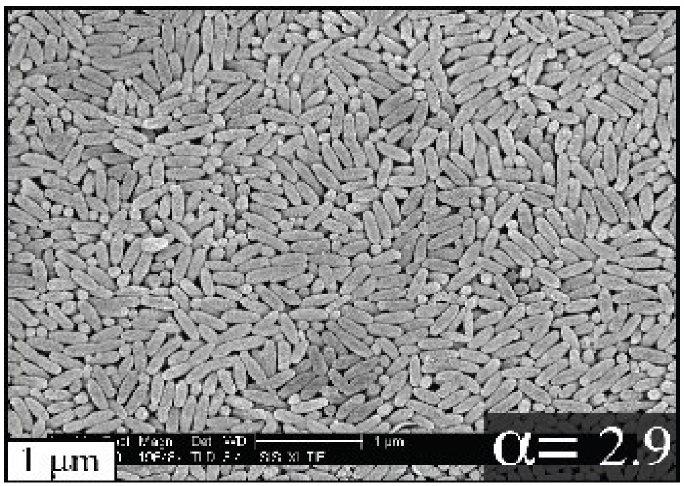
$$0.60 < \phi < 0.64$$

radial distribution function



Spheres are exceptional.........

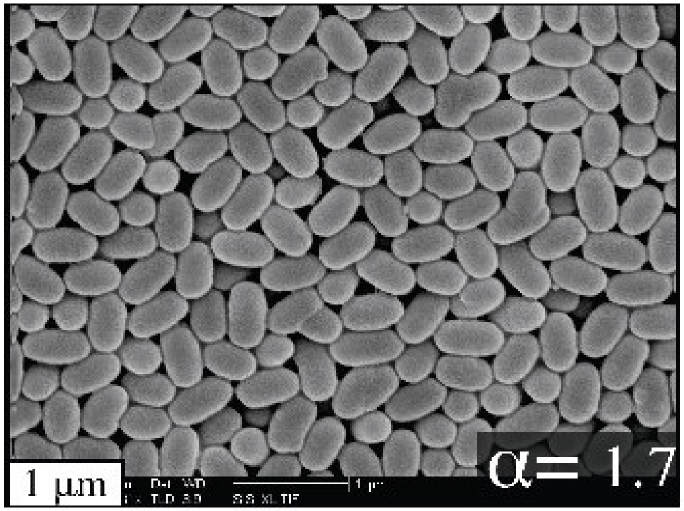


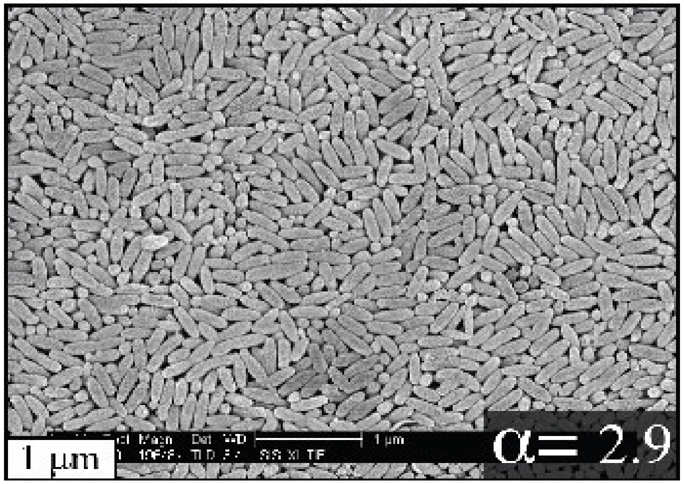


Failure to analyse these packing in terms of 'effective spheres'.

(Thesis Alan Wouterse, 2008)

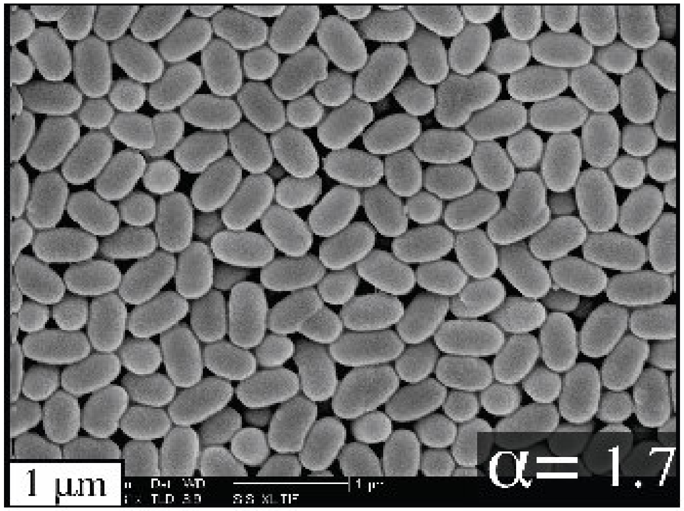
Generalize 'Bernal' to particles of any shape.

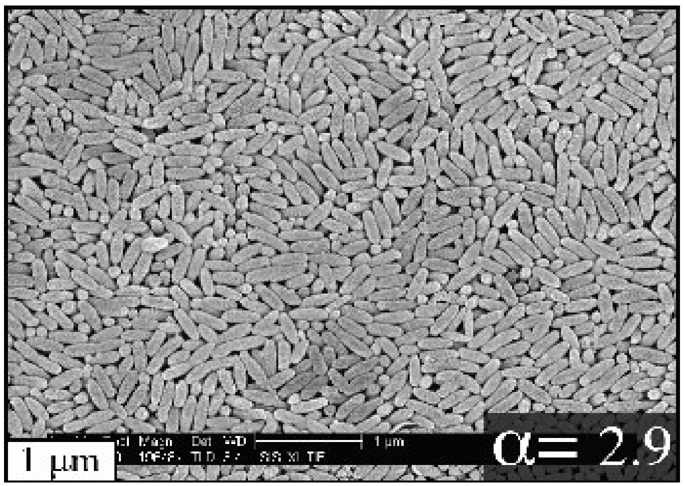




Conjecture: any particle shape has a unique, size-invariant maximum random packing density.

Where and how to start?





Is any of these (or other) random packings truly random, in the sense that all spatial and orientational correlations are absent ?

The Ideal Packing

- **Thermal gas:**

  Reference is an ideal gas of uncorrelated thermal particles.

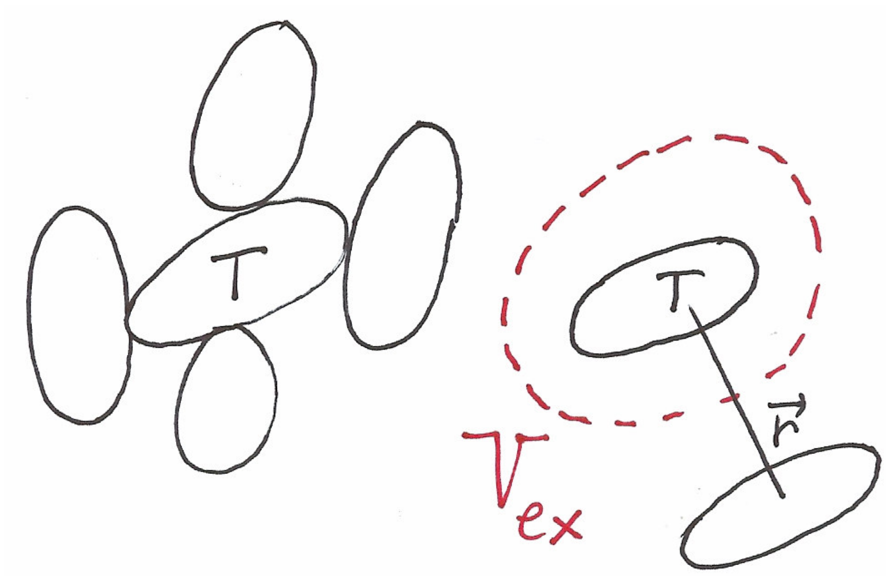
- **Granular matter:**

  Reference: an ideal packing of uncorrelated mechanical contacts.

A.Philipse, Langmuir 12, 1127 (1996)

A. Wouterse, Thesis (2008)

Counting uncorrelated contacts:



$f(\vec{r}) = 1$ **inside *V*ex**

$f(\vec{r}) = 0$ **outside *V*ex**

Orientationally averaged exclude volume:

$$V_{ex} = \int_V f(\vec{r})\, d\vec{r}$$

Contact number $c_T = \int_V f(\vec{r})\rho(\vec{r})d\vec{r}; \rho(\vec{r}) =$ **local nr.density**

$\sim \rho \int_V f(\vec{r})d\vec{r}; \rho =$ ***average* nr. density**

$$= \rho V_{ex}$$

Ideal packing law for uncorrelated contacts:

$$\rho = \frac{< c >}{V_{ex}}$$

Ideal packing law for uncorrelated contacts:

$$\rho = \frac{< c >}{V_{ex}}$$

$< c >$ **= average contact number on a particle**

Particle volume fraction : $\Phi = \rho V_p$

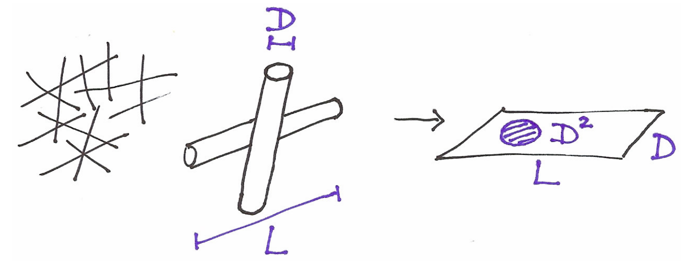
V_p **= particle volume**

$$\Phi = < c > \frac{V_p}{V_{ex}}$$

$\frac{V_p}{V_{ex}}$ **= fixed by particle *shape.***

But do uncorrelated contacts exists in dense granular packings ?

Random rod packing in the thin-rod limit.



Contact surface fraction $\sim \dfrac{D^2}{DL} \sim \dfrac{D}{L}$ **; vanishes for** $\dfrac{L}{D} \to \infty$

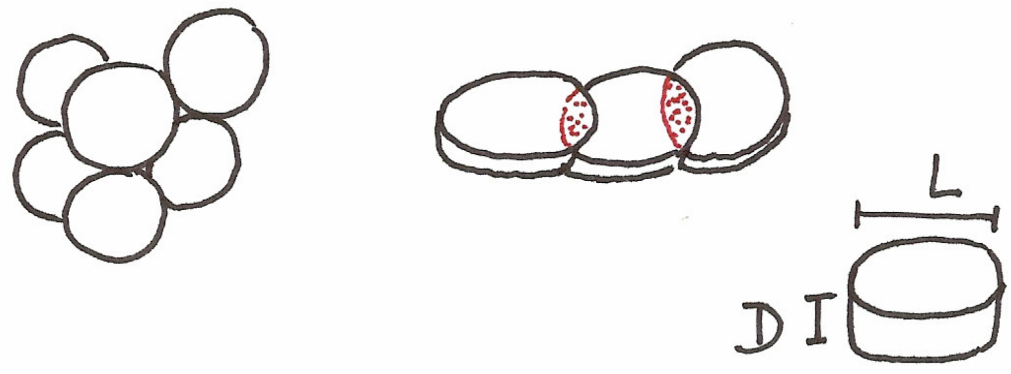
For thin rods: $\dfrac{V_{ex}}{V_p} \sim 2\dfrac{L}{D};\dfrac{L}{D} \gg 1$ **(Onsager 1949)**

So for thin rods the ideal packing law $\Phi = < c > \dfrac{V_p}{V_{ex}}$ **becomes:**

$$\Phi \frac{L}{D} \sim \frac{1}{2} < c >; \frac{L}{D} \gg 1$$

(A. Philipse, Langmuir 1996)

Clearly, as a rule, packings are *non*-ideal :



In the Bernal sphere packing, contacts are highly correlated.

In the random disc packing, correlations do *not* vanish in the thin-disc limit.

Experimental check of the thin-rod limit.

(A.Philipse, Langmuir 1996)

1 cm

$\frac{L}{D} = 10$

Granular Cocktail Matter

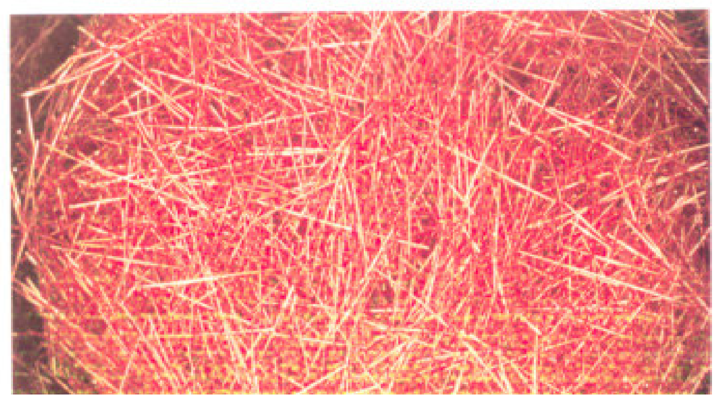
1 cm

$\frac{L}{D} = 34$

Copper wire

1 cm

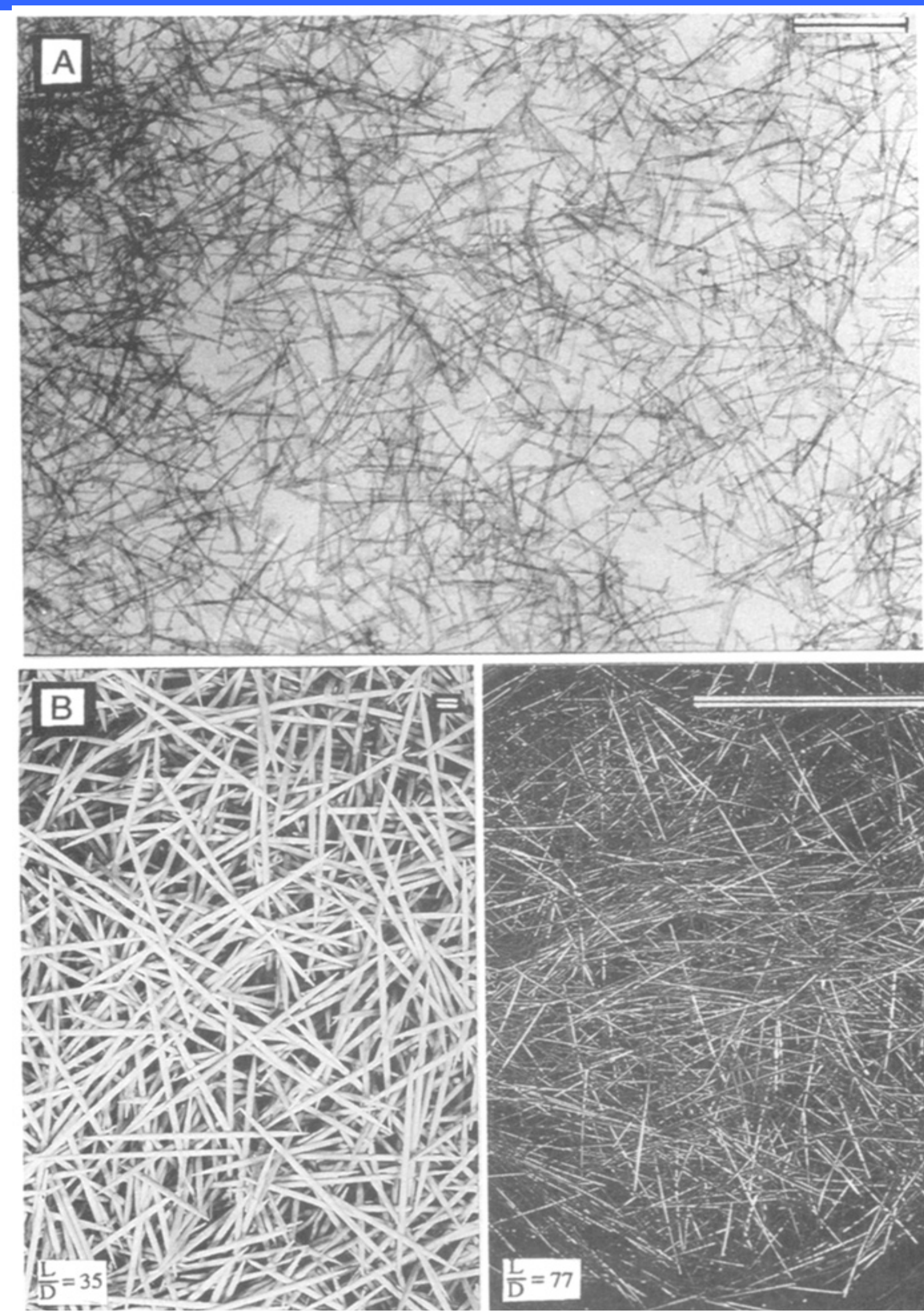
$\frac{L}{D} = 77$



Comparison colloidal and granular rods

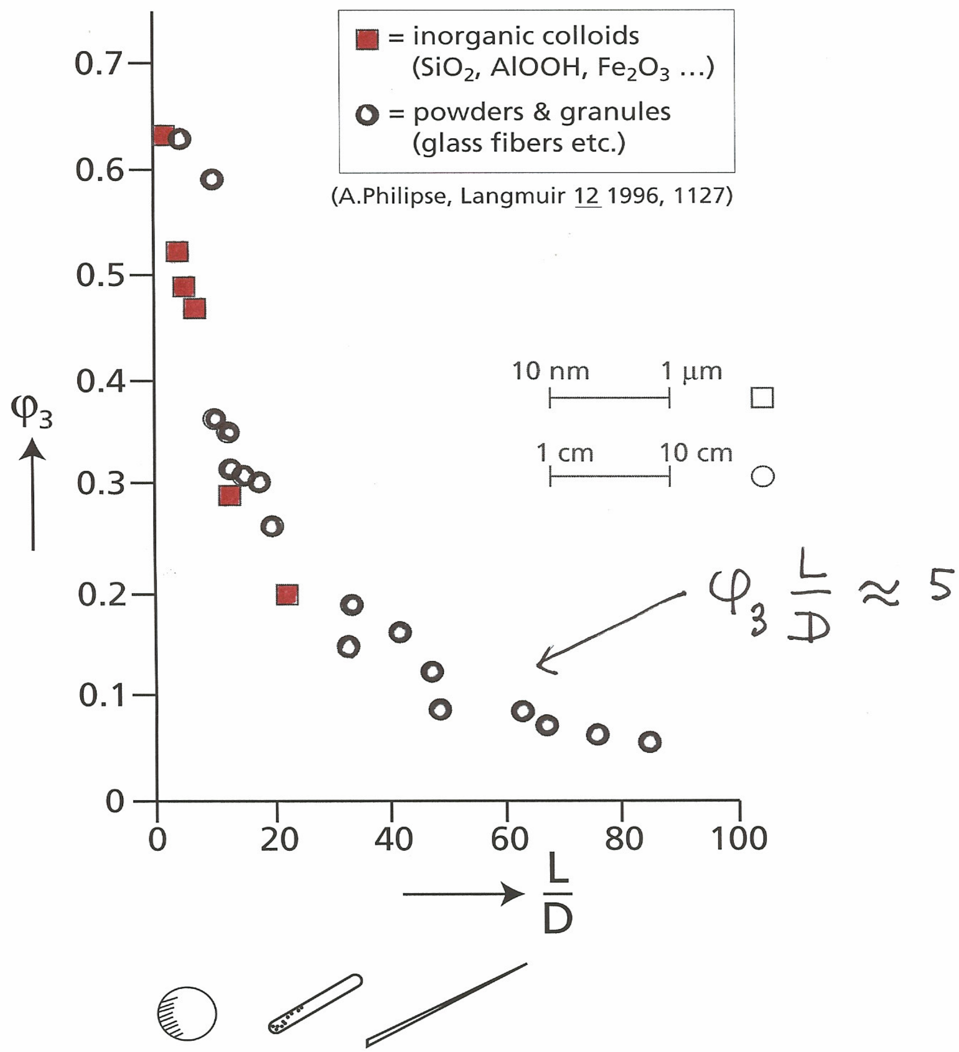
Colloidal AlOOH needles (*L* = 100 nm)

Granular rods

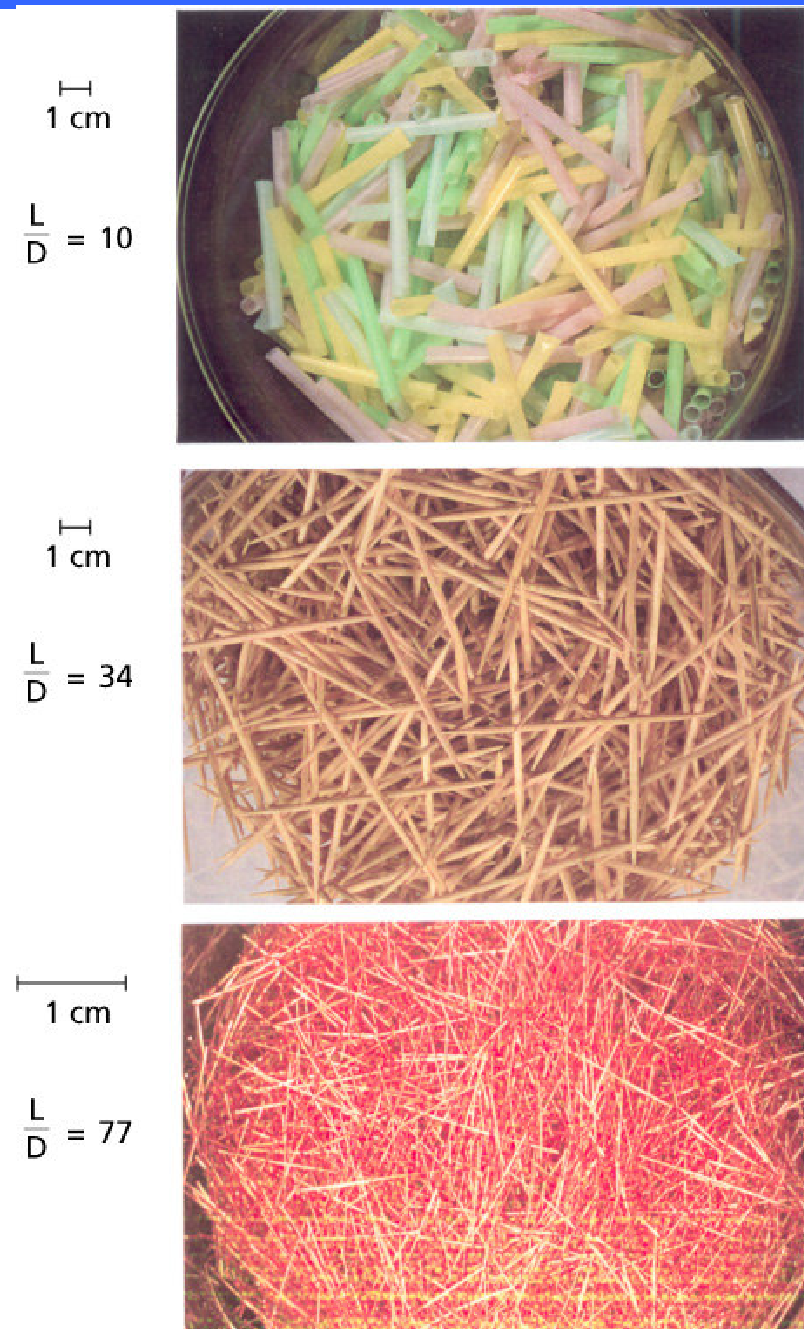


Experimental packing densities of colloids and granular matter

• Volume fractions φ_3 of 3-d packings



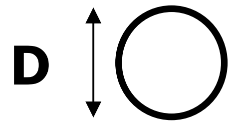
Experimental check of the thin-rod limit.



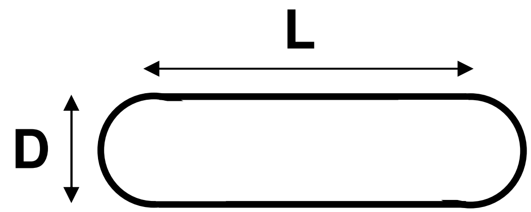
Can't go to much higher *L*/*D* without introducing flexibility

Mechanical contraction method

System:

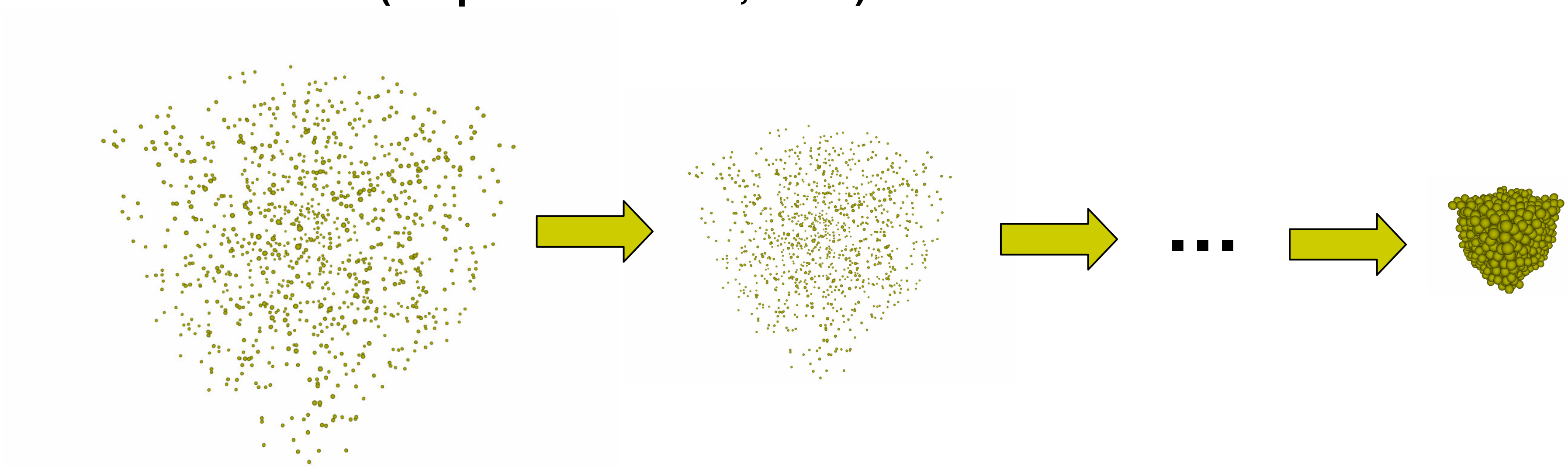


(a) spheres



(b) spherocylinders

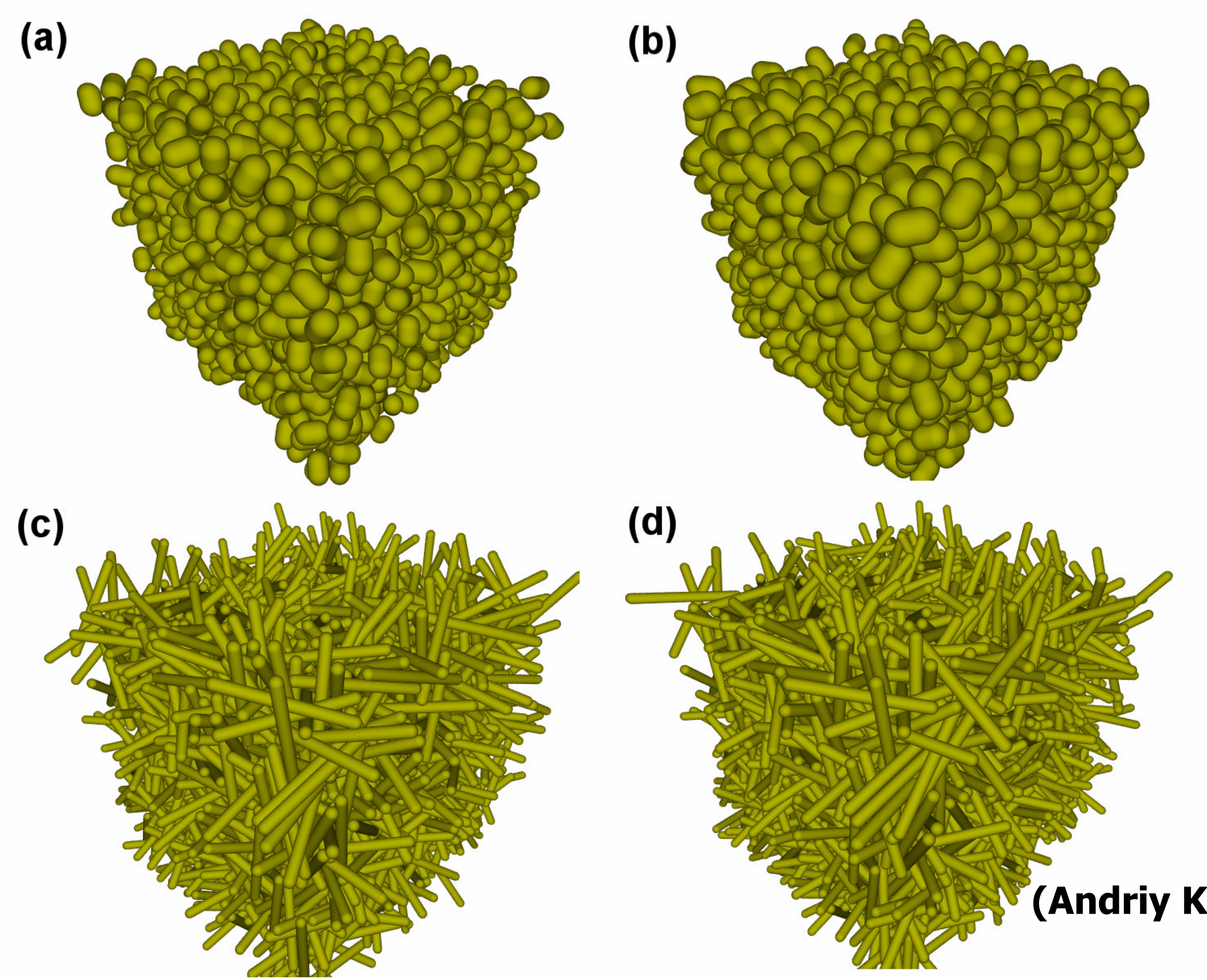
Procedure (Stephen Williams, 2003)



Dilute system is mechanically contracted until overlaps cannot be removed anymore. Result is a reproducible random packing density.

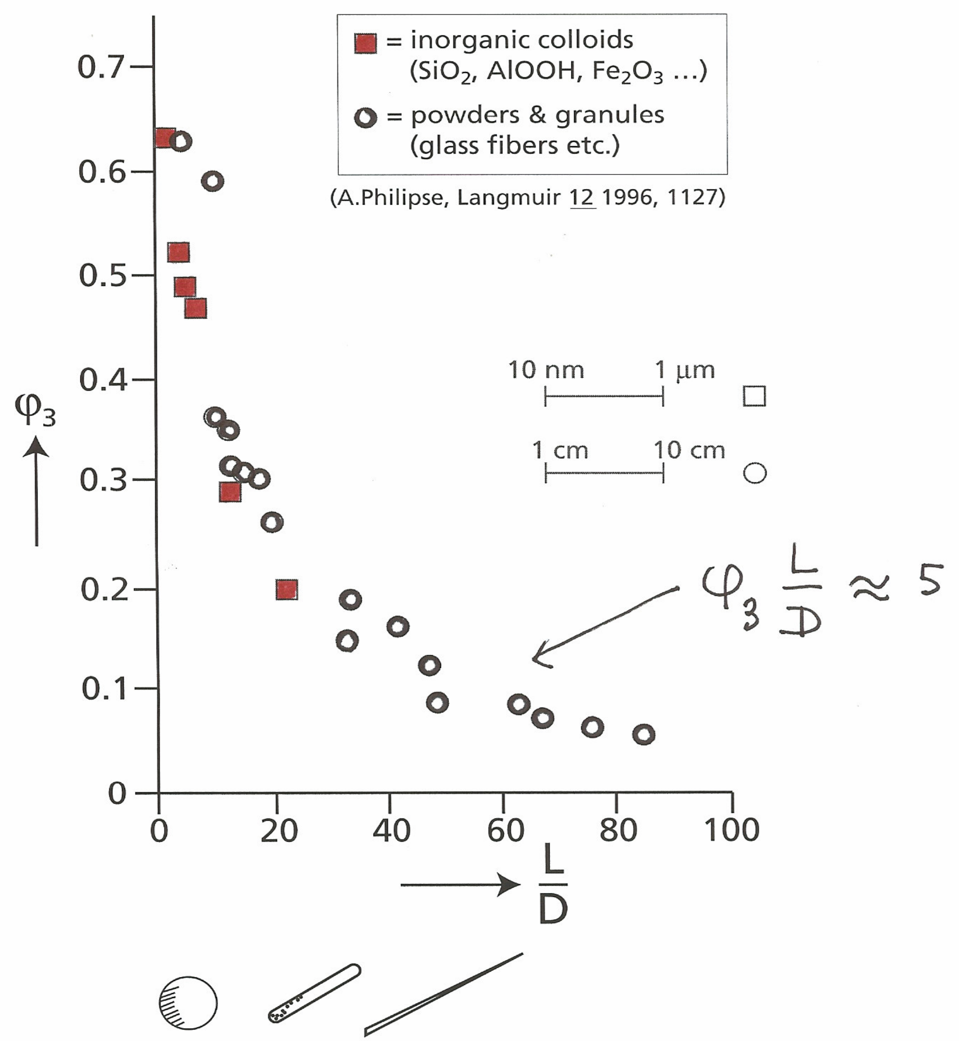
S.R. Williams and A.P. Philipse, *Phys. Rev. E*, 2003 ; A. Wouterse et al., *J. Chem. Phys.*, 2006

Randomly packed sphero-cylinders



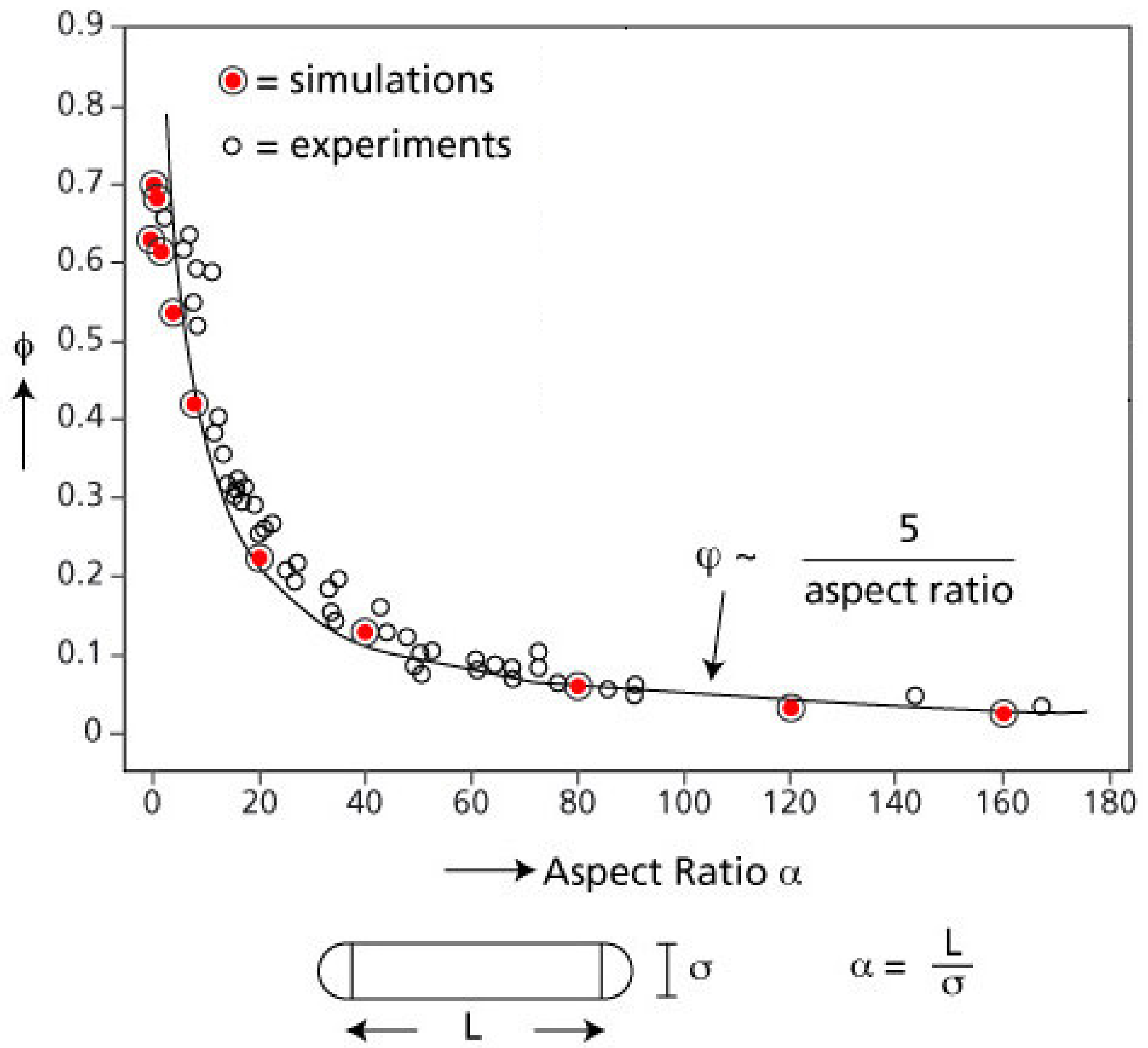
(Andriy Kyrylyuk)

- Volume fractions φ_3 of 3-d packings

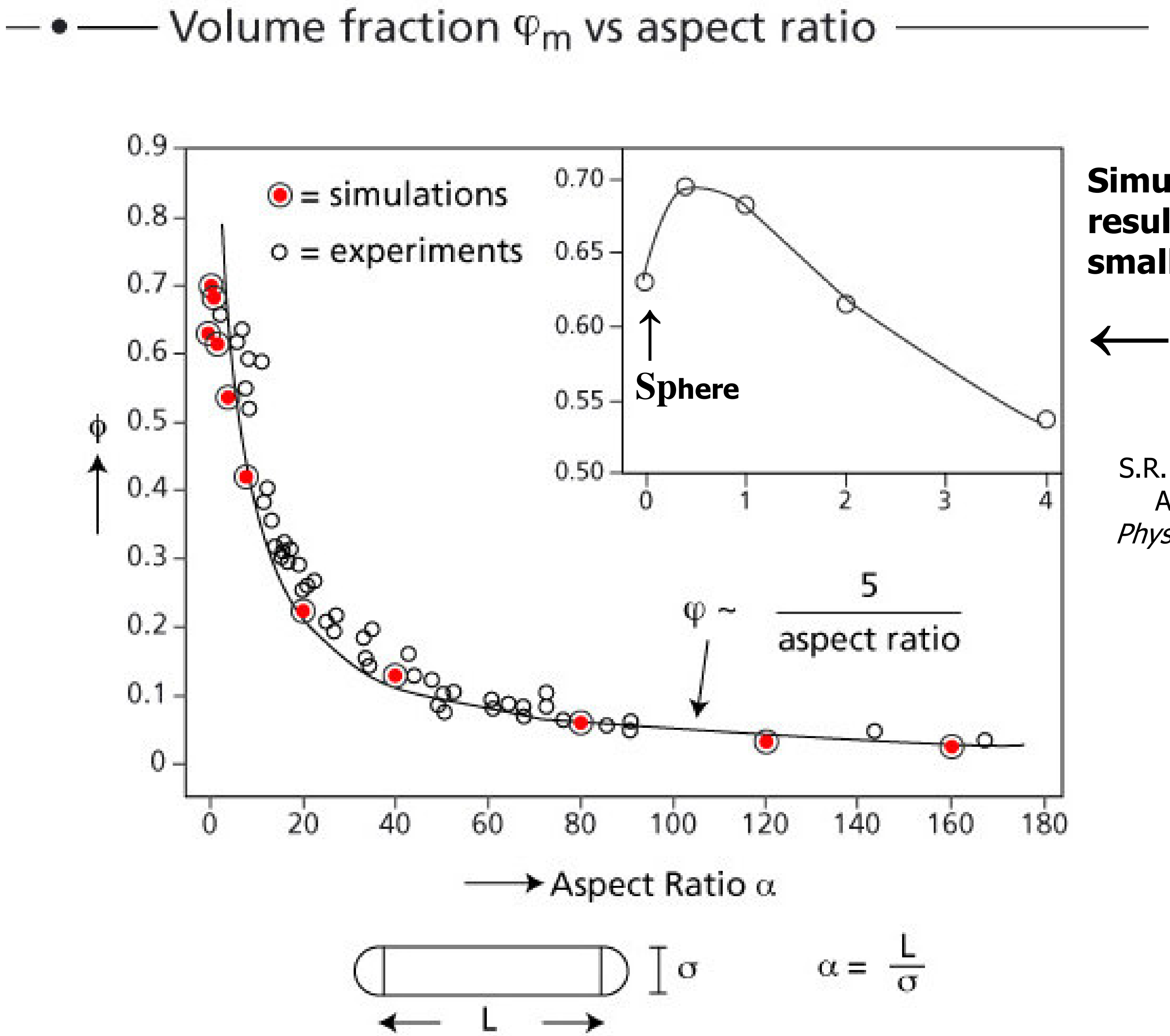


Overview experiments and simulations

Volume fraction φ_m vs aspect ratio



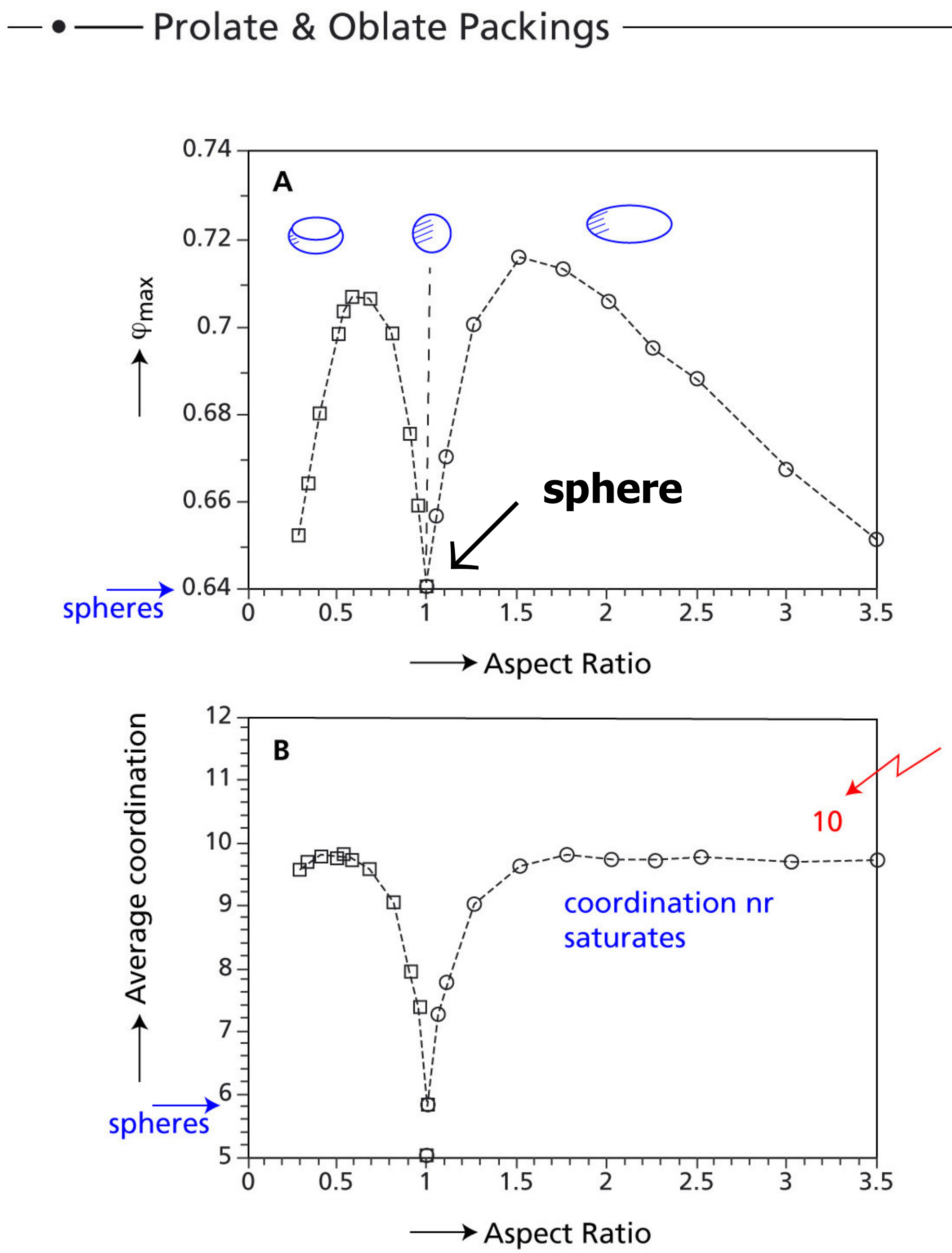
Overview experiments and simulations



Simulation results at small aspect ratio.

S.R. Williams and A.P. Philipse *Phys. Rev. E*, 2003

Bernal packing is local minimum……

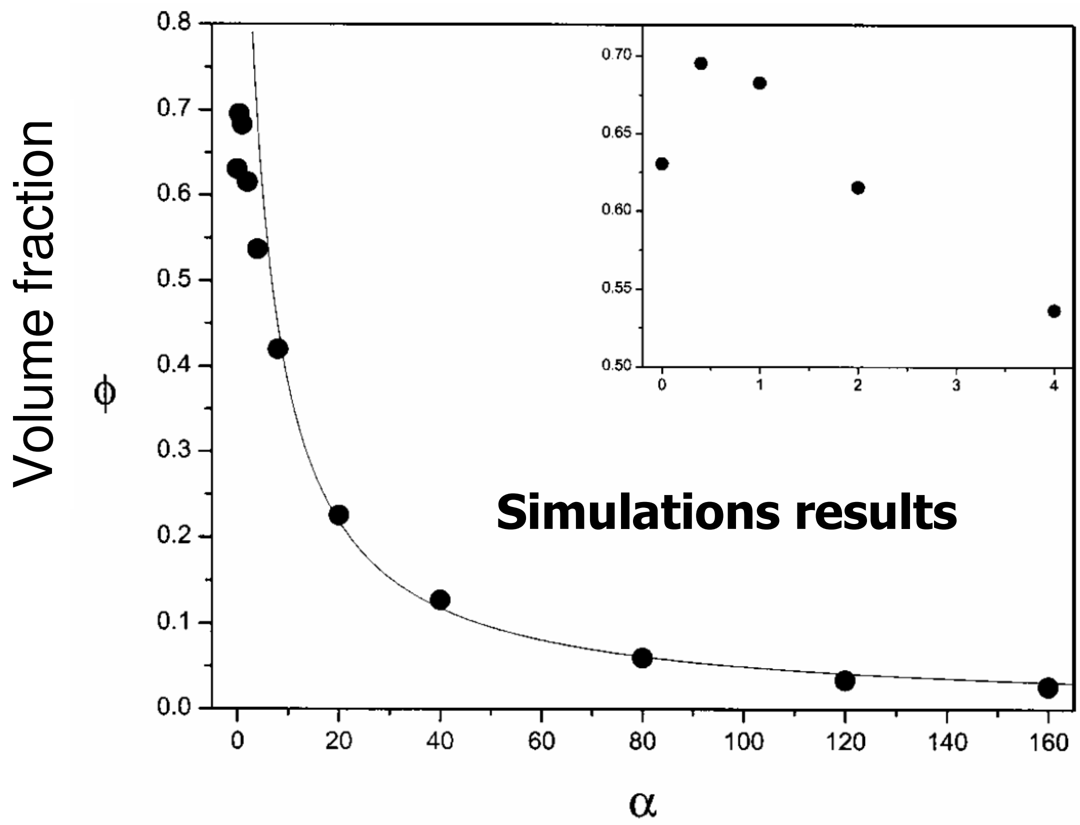


Donev *et al,*
Science 303 (2004) 990

- On this density maximum for near-spheres see also:

S.Sacanna, L.Rossi, A.Wouterse, and A.P, *Observation of a shape-dependent maximum in random packings and glasses of colloidal silica ellipsoids*, J.Phys.:Condes. Matter 19 (2007) 406215.

Volume fraction versus aspect ratio



Aspect ratio

Drawn line: $\phi \dfrac{L}{D} \approx 5$

S.R. Williams and A.P. Philipse, *Phys. Rev. E*, 2003

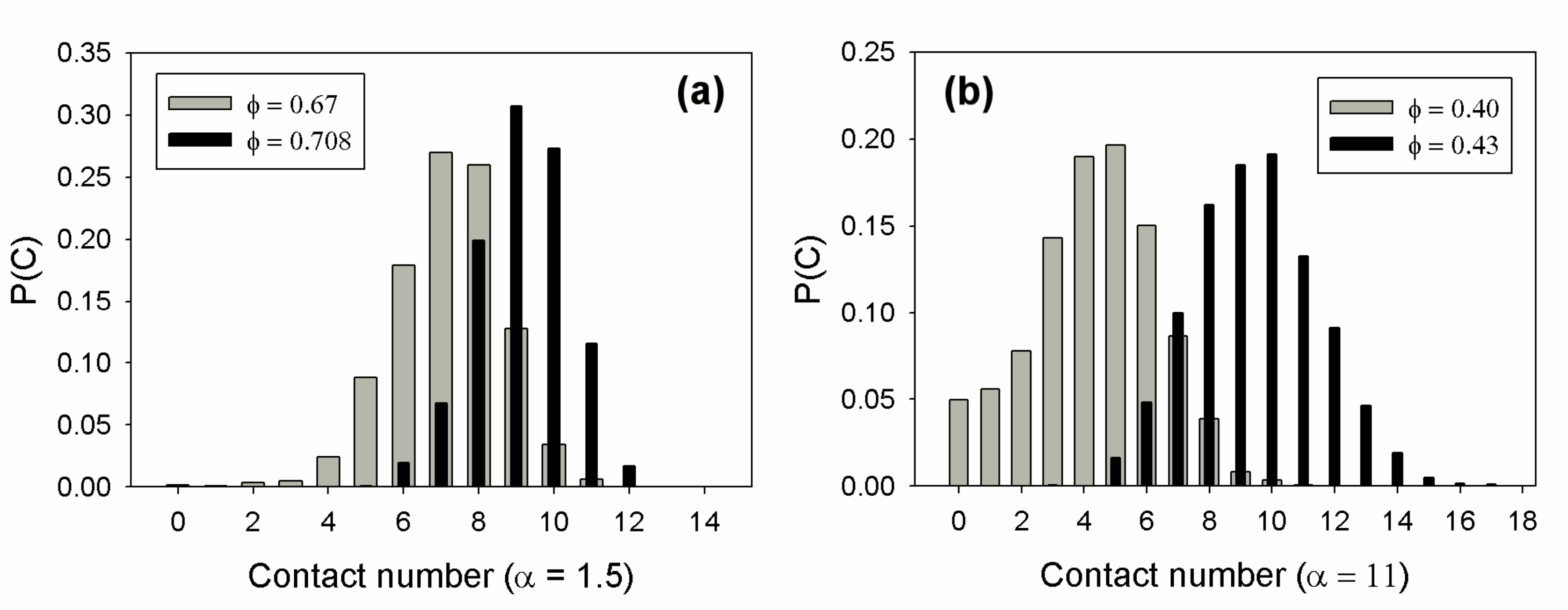
The ideal packing law: $\Phi = \langle c \rangle \frac{V_p}{V_{ex}}$

For thin rods: $\Phi \frac{L}{D} \sim \frac{1}{2} \langle c \rangle ; \frac{L}{D} \gg 1$

Experiments and simulations: $\Phi \frac{L}{D} \approx 5$

Is indeed $\langle c \rangle \approx 10$ **, and what does it mean?**

Contact numbers in packings of sphero-cylinders

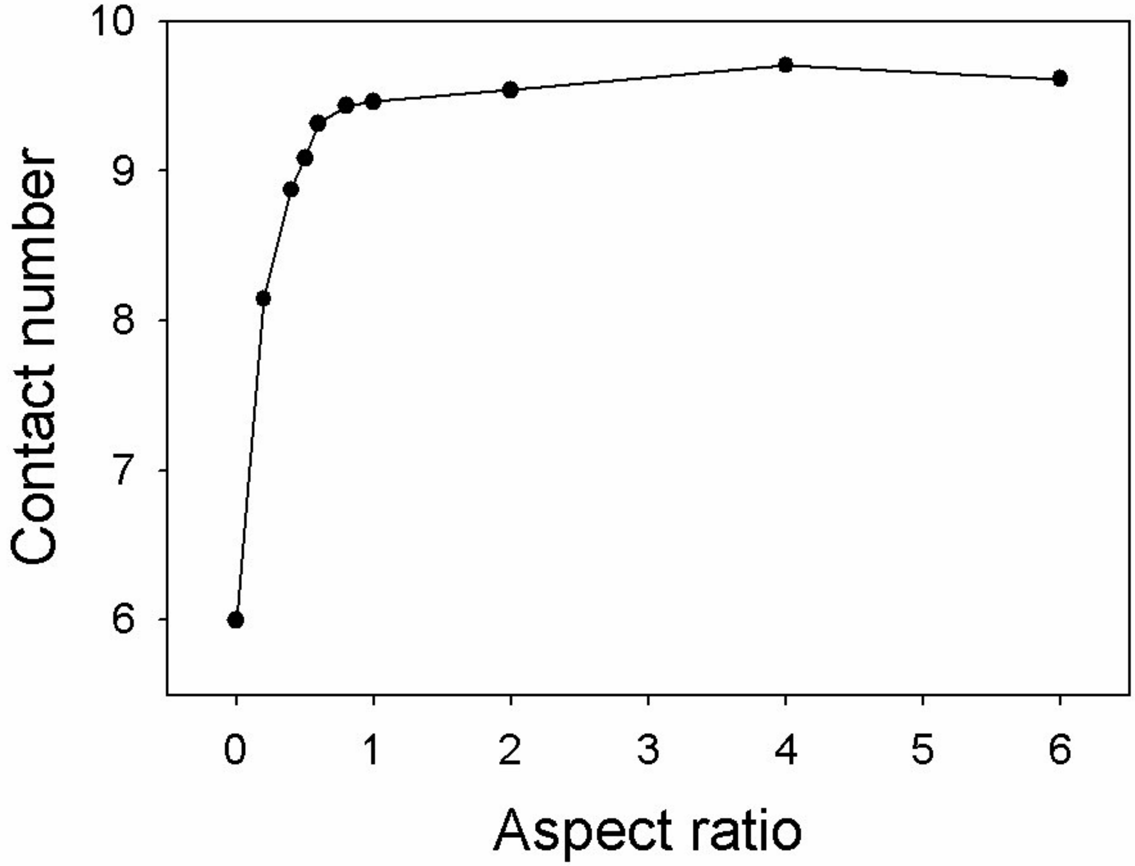


Near-spheres

Rods with aspect ratio 11

(Thesis Alan Wouterse, 2008)

Contact number versus aspect ratio



Contact numbers for sphero-cylinders indeed asymptote to $< c > \approx 10$

And why is that?

Rod packing is dominated by *local* caging effects.

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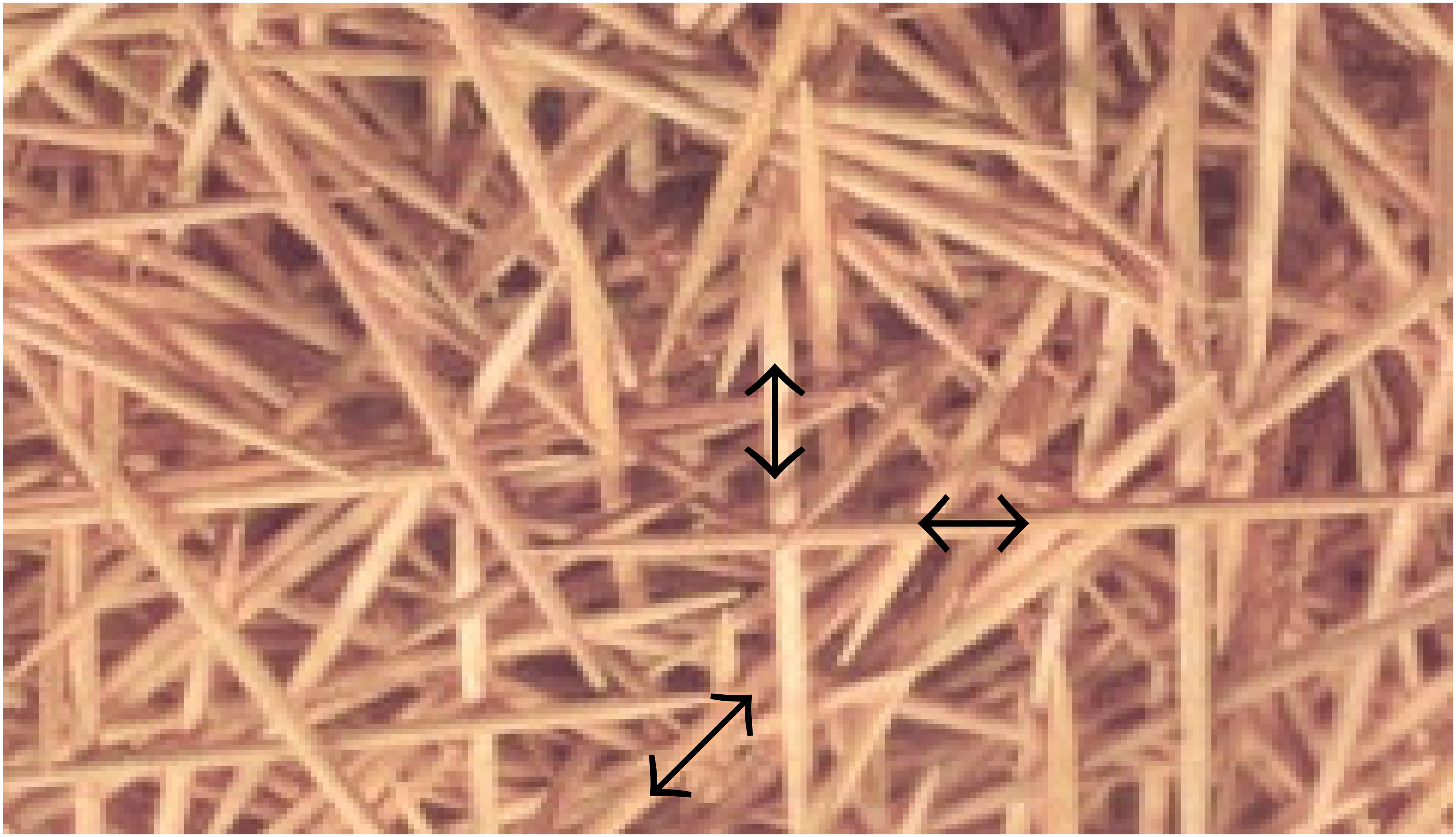
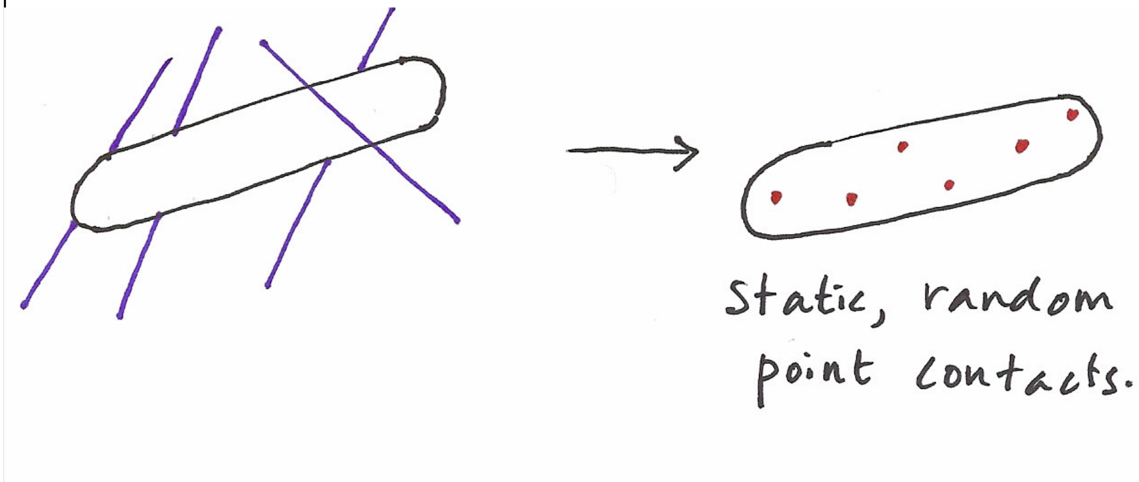


The caging number: a geometrical minimization problem

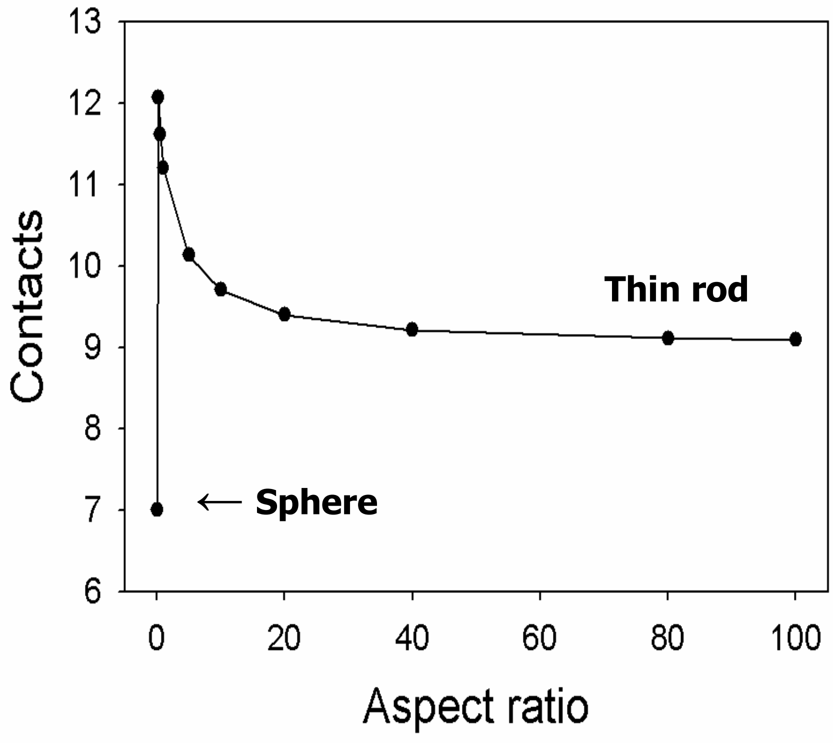
- **Cage = the *minimal* configuration of static contacts that block all translational and rotational motion.**

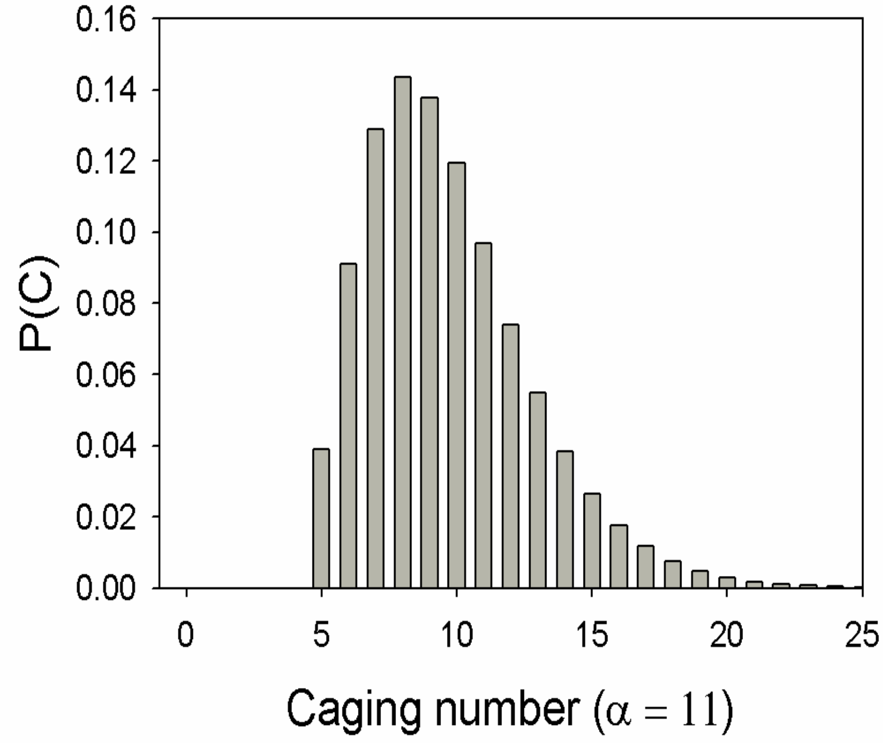


- ***c* contacts cage a particle; *c* – 1 still allow translation or rotation.**

- **Caging number =** $<c>_{cage}$ **No analytical solution yet…….**

Caging number for uncorrelated contacts



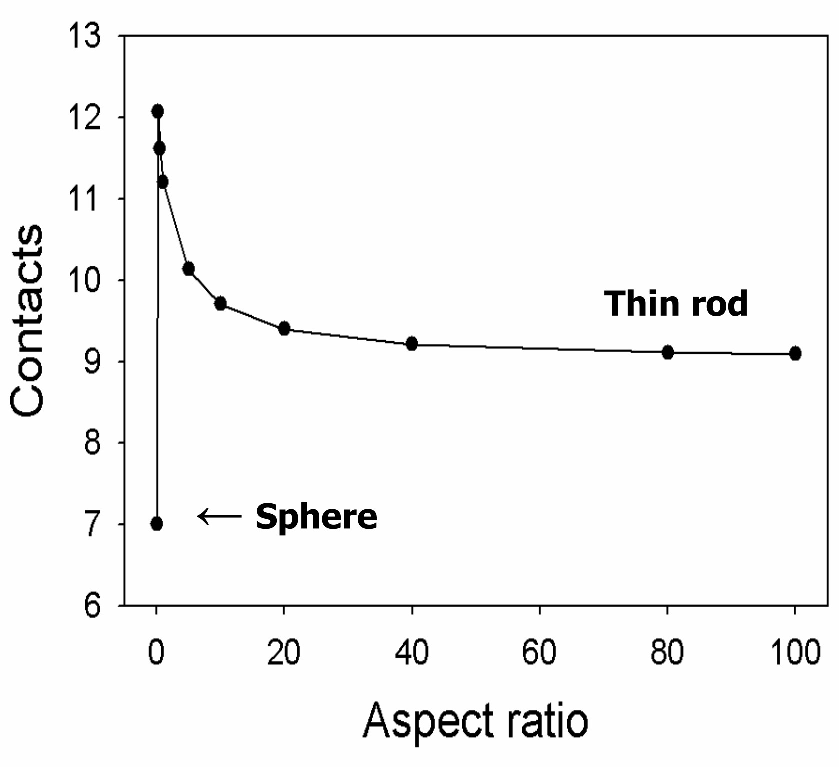


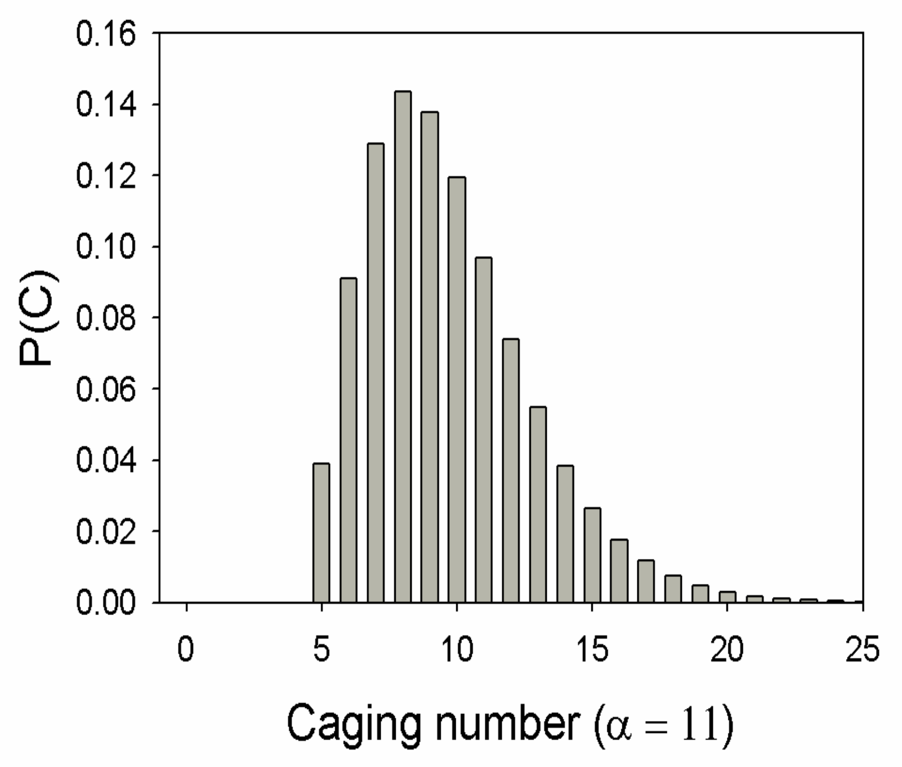
For thin rods: $< c >_{cage} \approx 9$

Probability distribution for caging number of a thin rod.

(A.Wouterse, 2008)

Caging number for uncorrelated contacts





For thin rods: $< c >_{cage} \approx 9$

Probability distribution for caging number of a thin rod.

Corresponding density: $\Phi \frac{L}{D} \approx 4.5$

(A.Wouterse, 2008)

Some conclusions

- The ideal packing law explains the aspect ratio dependence of granular rod-packings.

- The rod caging number accounts fairly well for the absolute random rod packing density.

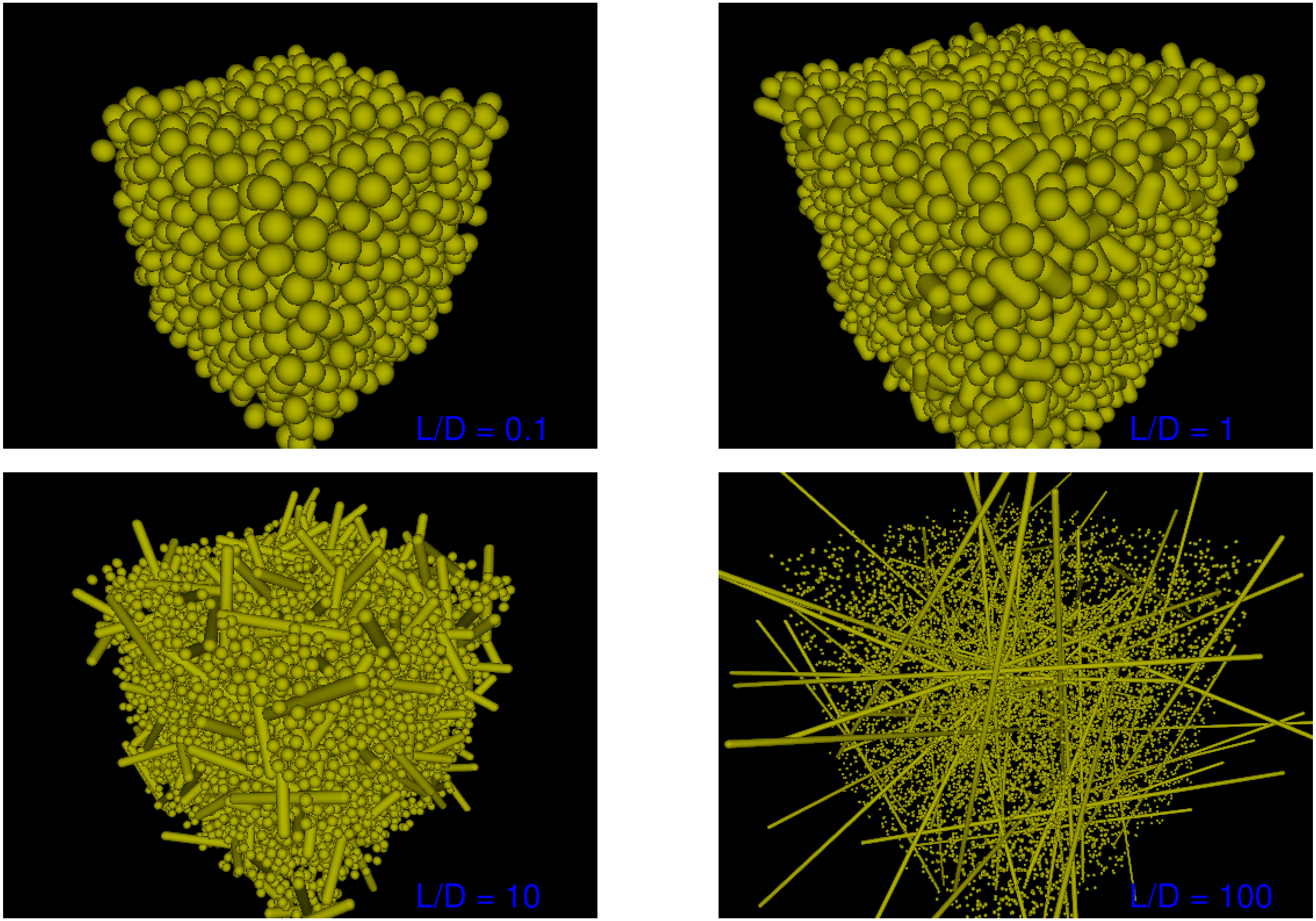
- Random packing has a density maximum for near-spheres; the Bernal sphere packing is a singularity in packing space.

Outlook

- Effect of planar faces such as in random packing of coins. (see thesis Alan Wouterse).

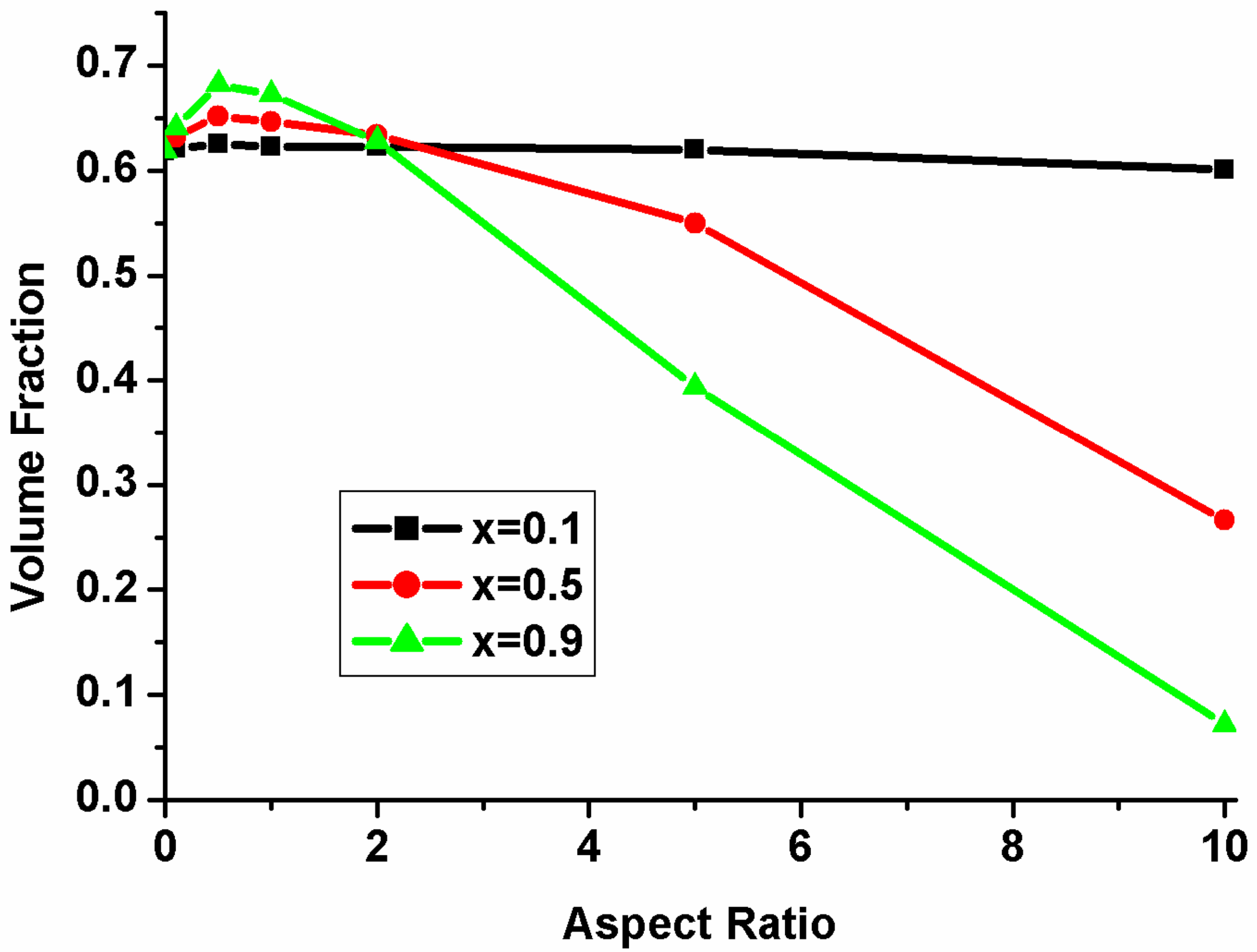
- Mixtures of sphero-cylinders : is there universality in the density maximum? (work in progress by Andriy Kyrylyuk)

Results (mixture)



composition: x = 0.5

Results (mixture)



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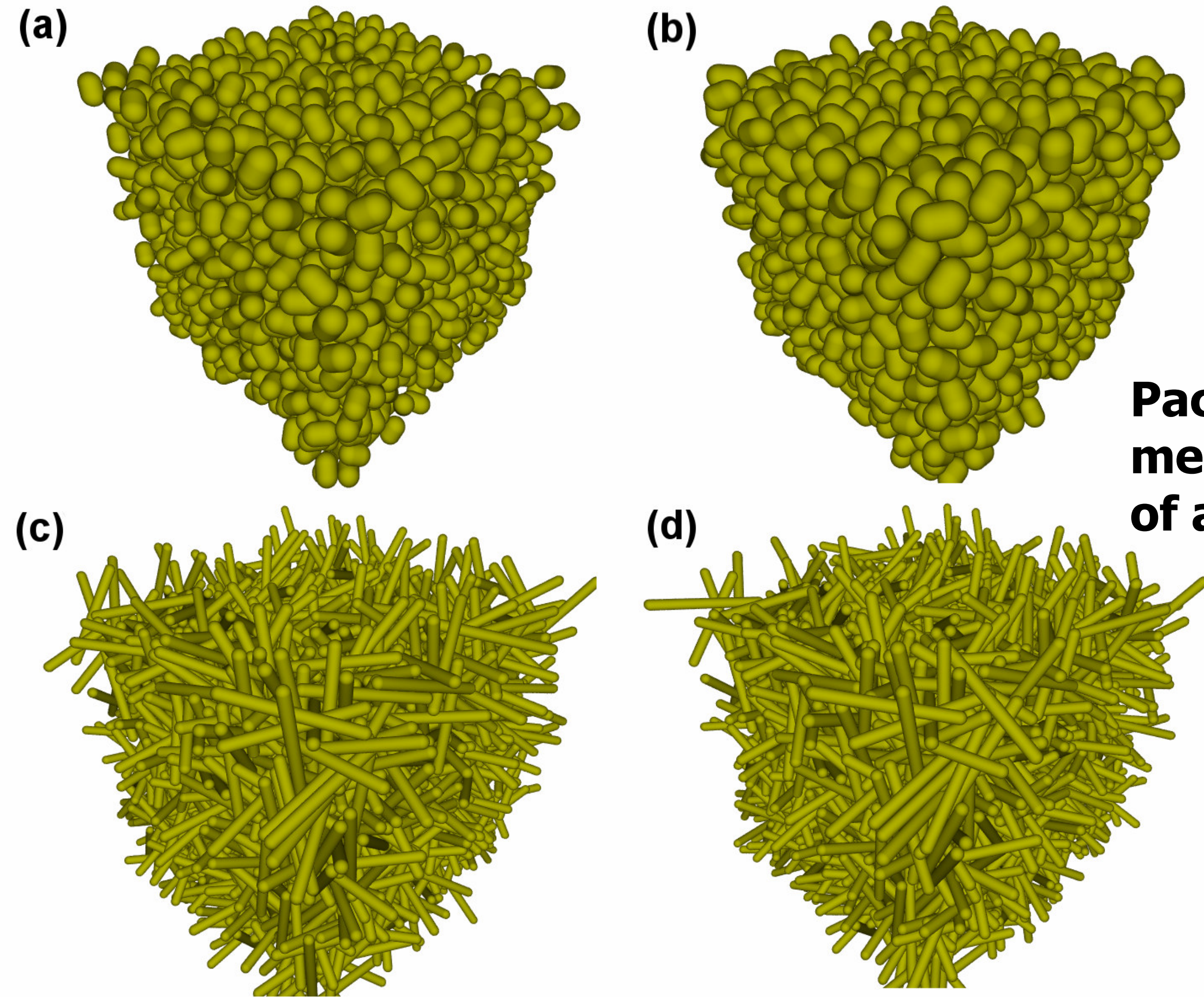
- **Near-spheres: a packing surprise.**
- **Conclusions and outlook.**

- **Extra: something on random *bio*-packings.**

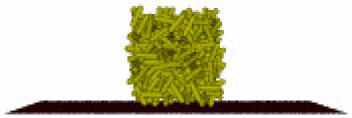
Are these random packings ‘geometrical states’?



Packings prepared by mechanical contraction of a dilute rod system.

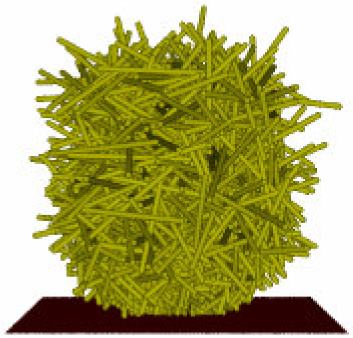
(Andriy Kyrylyuk)

If so, *growth* of random rods out of a ‘point gas’ should eventually produce the same density.



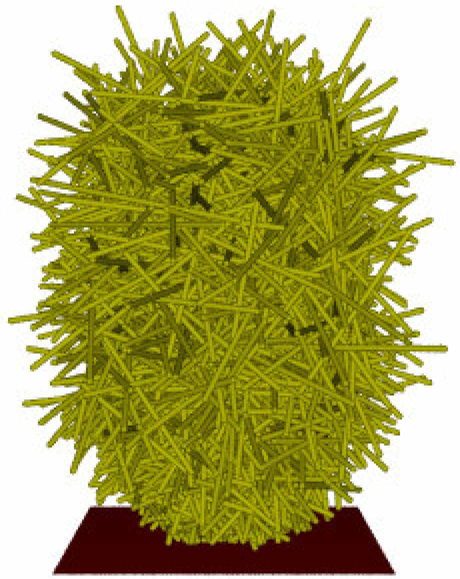
In a random distribution of particle centers, rods start to grow in random directions.

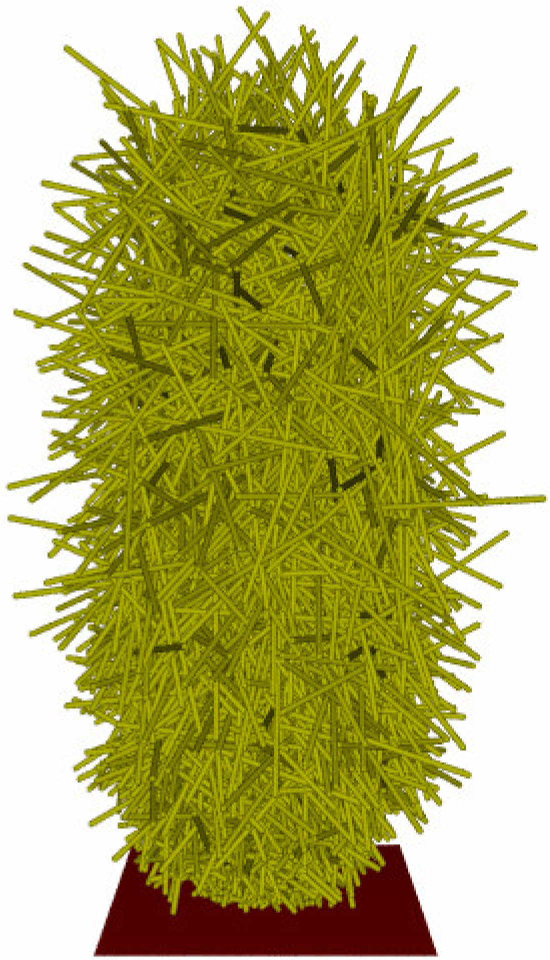
Thesis Alan Wouterse (2008)



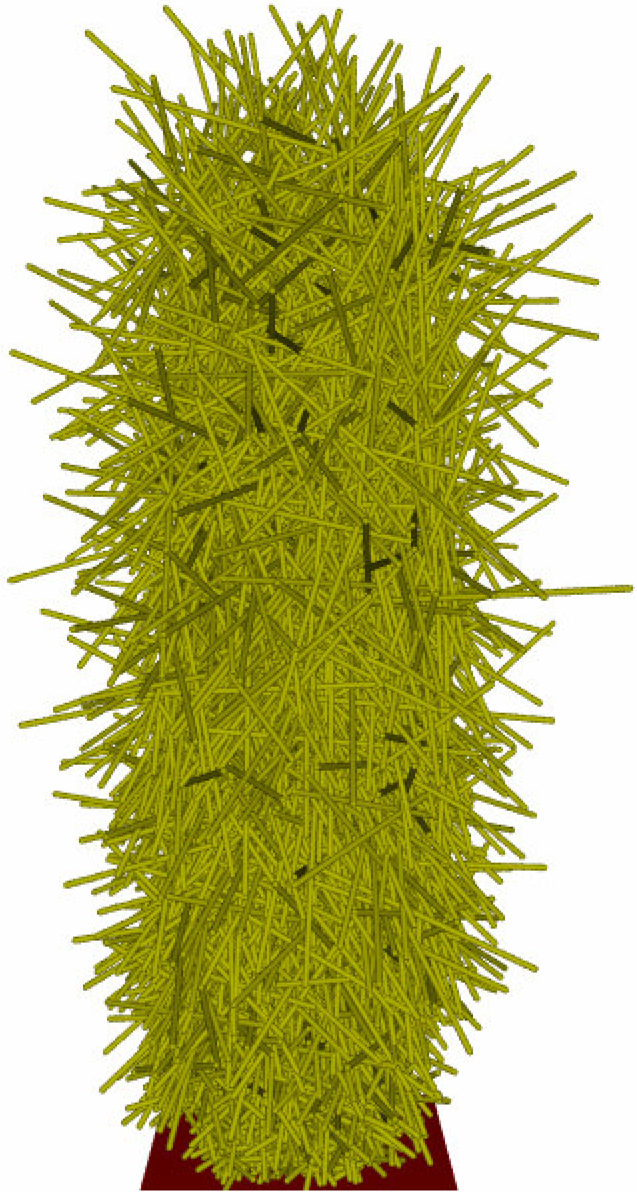
Volume expansion to accommodate the growing rods.

The density follows the ideal packing law, and is inversely proportional to the aspect ratio.





Do such growing rod packings occur in Nature?

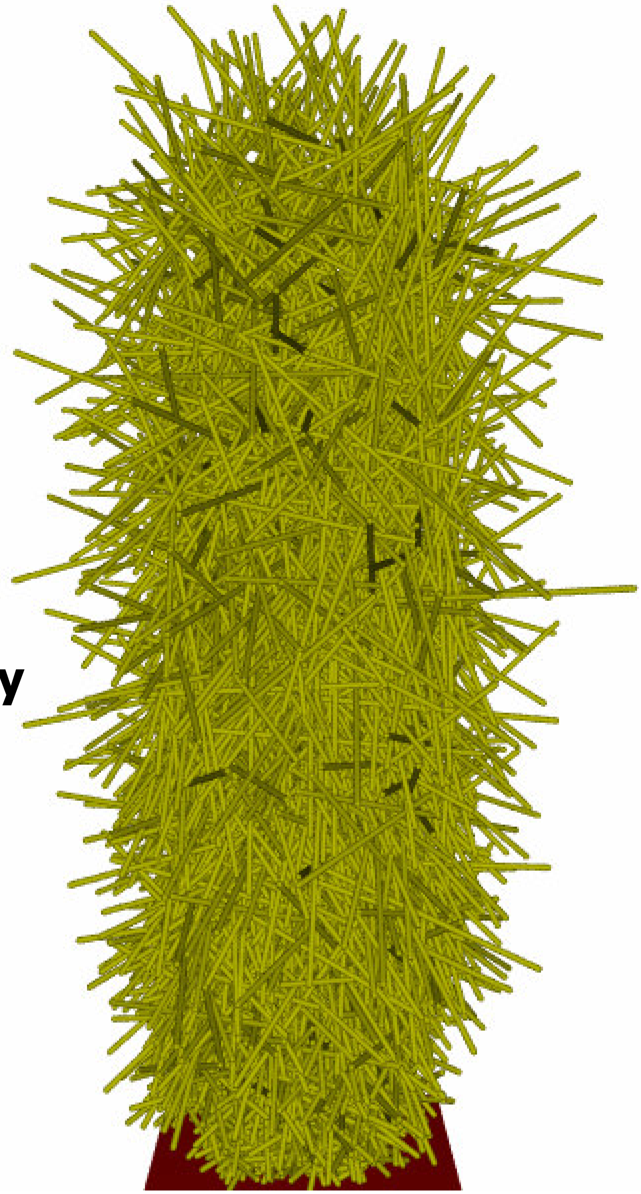


Prehnite crystals.

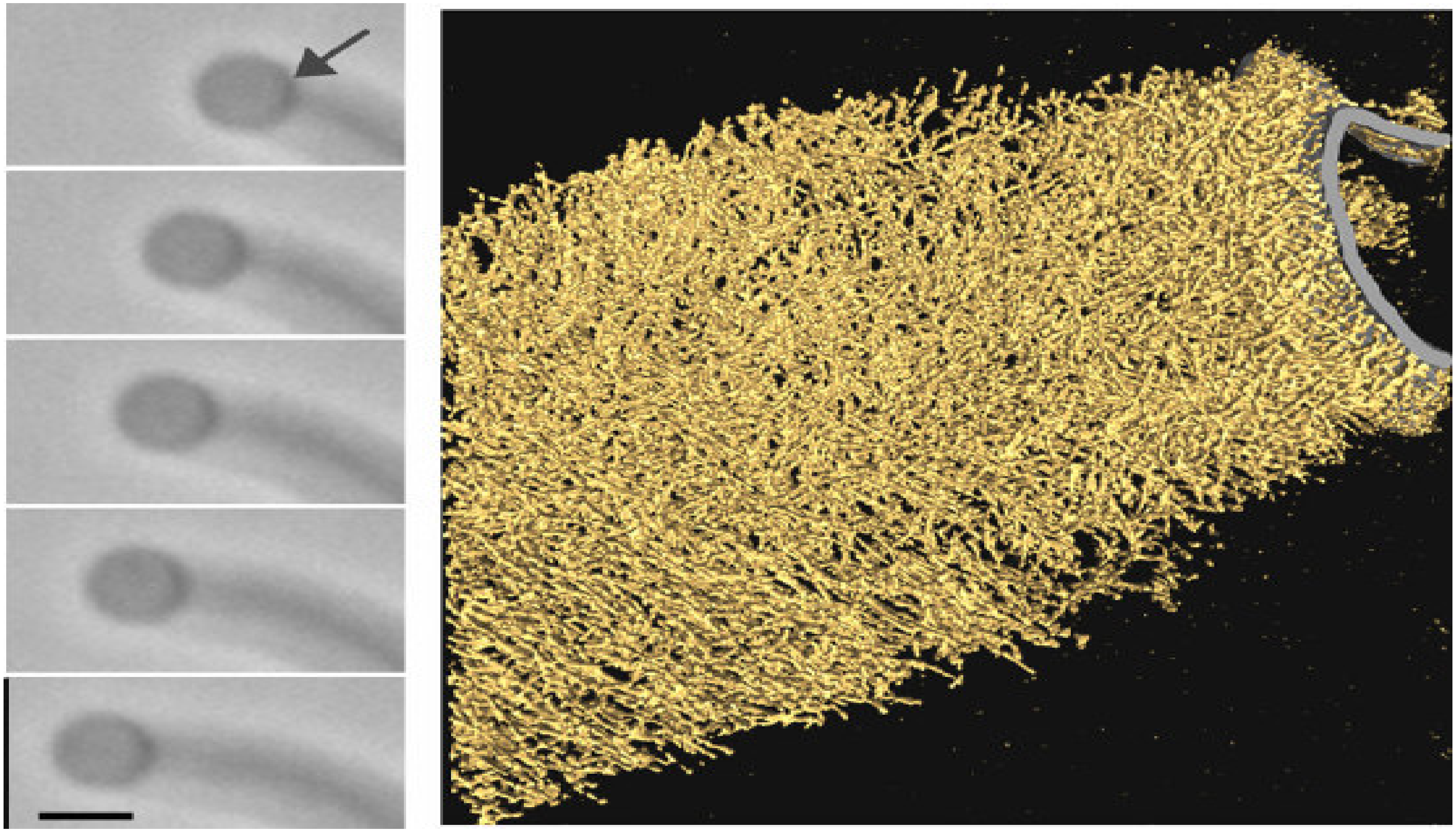
Pale green tubular epimorphs after laumontite (Maharashtra, India)

Murray Stewart
(MRC Lab for Molecular Biology, Cambridge UK)

"Growing random rod packings might be a mechanism for motility of biological cells"



Growing random packing causes self-motion.



Vesicle from cell membrane produces randomly growing rods. Volume expansion occurs on reaching the random packing density which pushes the cell.

(Long Miao *et al,* PNAS , 2008)

Acknowledgements

- Andriy Kyrylyuk (UU/Shell).
- Alan Wouterse (UU/FOM).
- Steven Williams & Stefan Luding.
- Photography: Jan den Boesterd, Ingrid van Rooijen.

•Thanks also to Karel Planken and Alexander Nechifor.

- For further information see also:

Alan Wouterse, *Random Packing of Colloids and Granular Matter,* Thesis, Utrecht University, 2008.

The ‘nesting effect’.

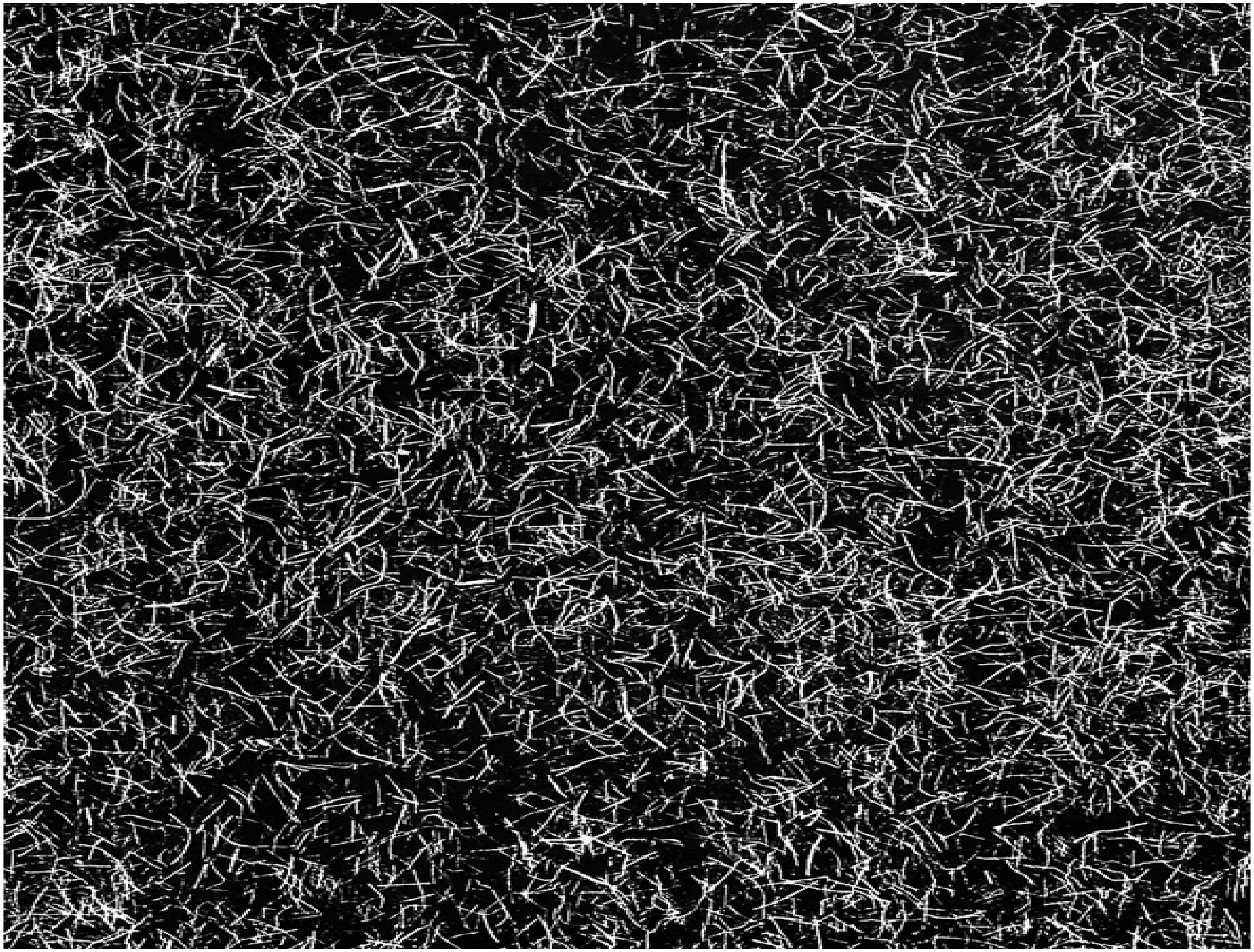
At sufficiently low aspect ratio (left) granular rods are able to flow.
At sufficiently high aspect ratio’s the rods form a stiff, entangled solid.

Such a ‘nested’ structure can also be observed in the packing of pins on the first slide of this presentation; see also the copper wire rods on the next slide

(A.Philipse, Langmuir 1996)

Some more examples of random packings of non-spherical particles.

Hand-made paper



(P. Bodatz)

Paper: randomly packed cellulose fibers deposited from water onto a filter.