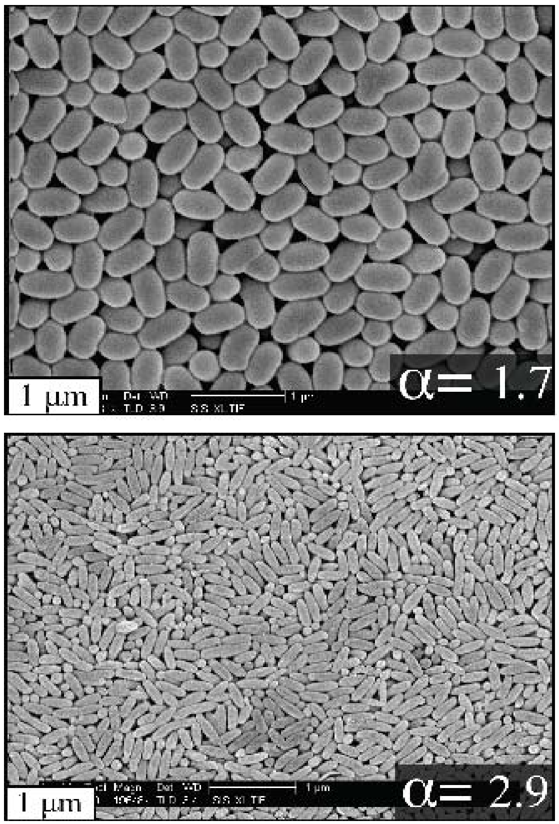
Ideality in Granular Mixtures:
Random Packing of Non-Spherical Particles



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Outline

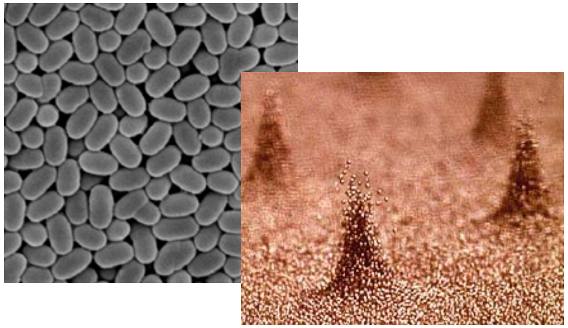
- **Motivation.**
- **<u>Spheres</u>: the Bernal packing**
- **<u>Thin rods</u>: the ideal gas in random packings**
- **<u>Near-spheres</u>: density maximum + ideality (packing surprise #1)**
- **<u>Mixtures</u>: universality + ideality (packing surprise #2)**

Motivation

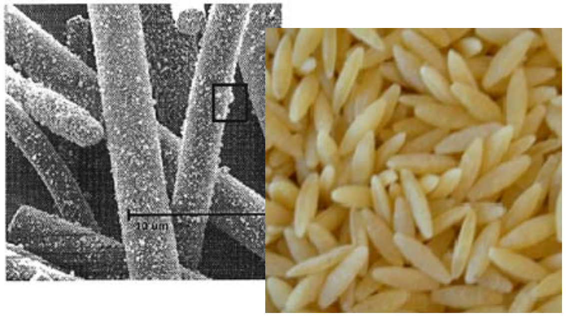
Packings in

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

- **Science:**
  - colloids
  - granular media



- **Technology:**
  - catalyst carriers
  - food technology
  - reinforced composites



Ordered sphere packing

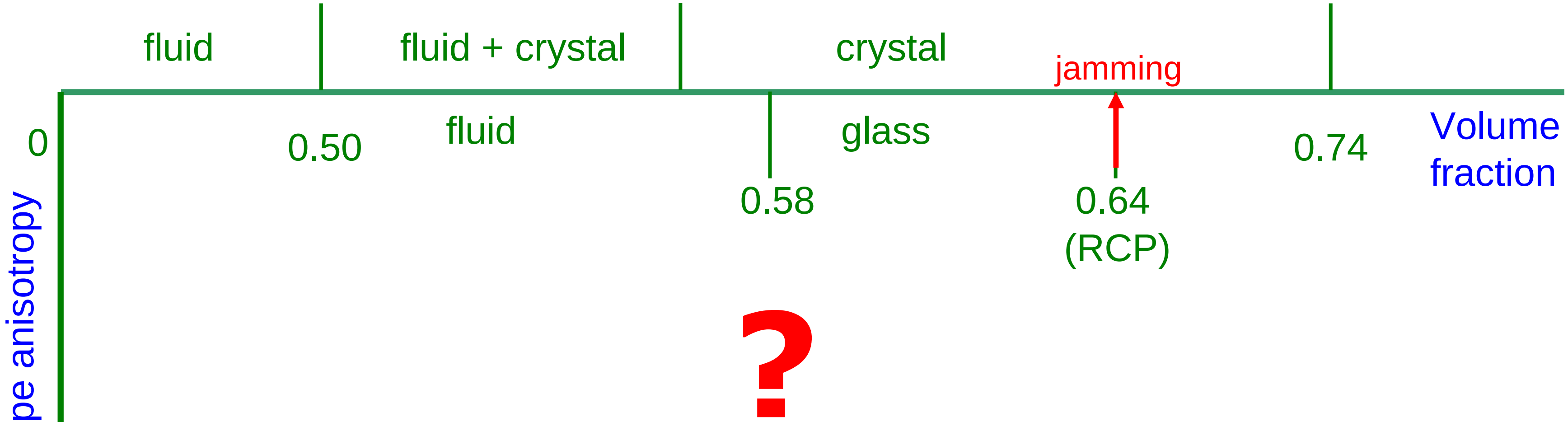
Kepler's conjecture : you can't pack spheres denser than to a solid volume fraction of $\pi / \sqrt{18}$ **= 0.7405.**

Disordered, ‘random’ sphere packing

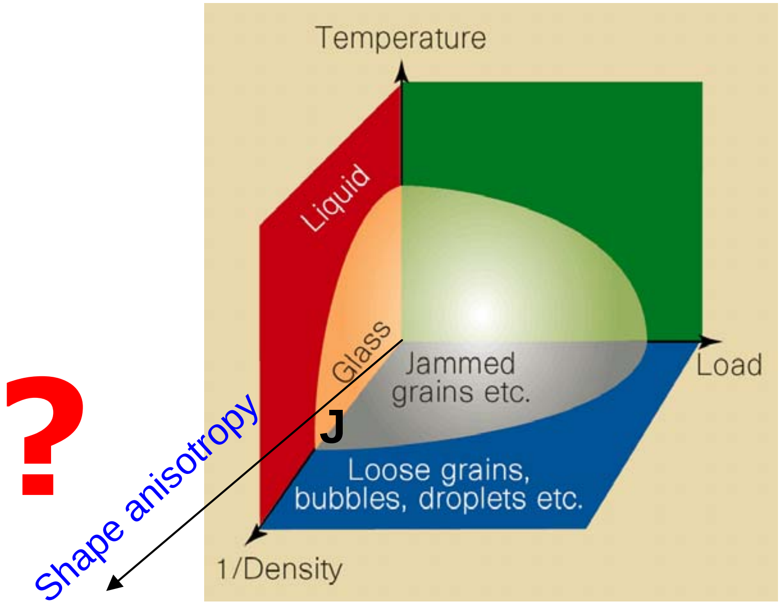
Disorded spheres pack at a lower density of about 0.64 (the Bernal sphere packing).

Hard sphere phase diagram

a) Colloids

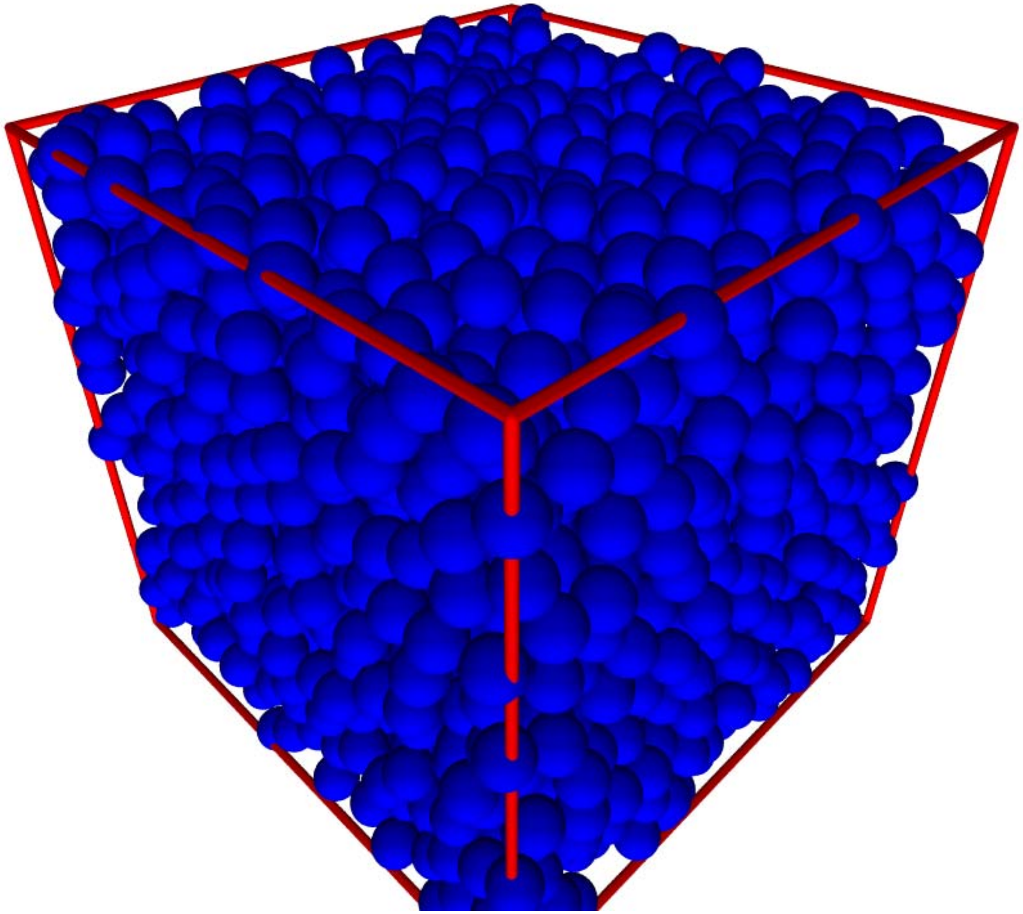


b) Granular matter



A.J. Liu and S.R. Nagel, Nature, 1998

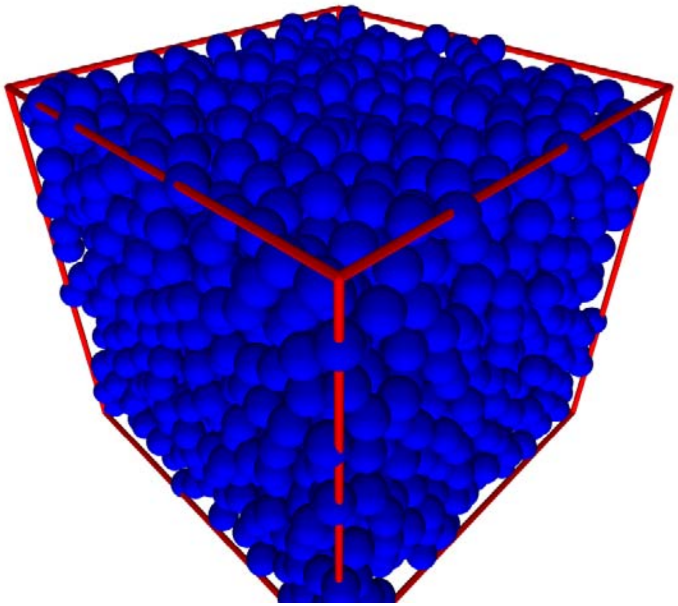
Bernal random sphere packing



Classical reference system for amorphous matter, colloidal glasses, etc.

Bernal random sphere packing

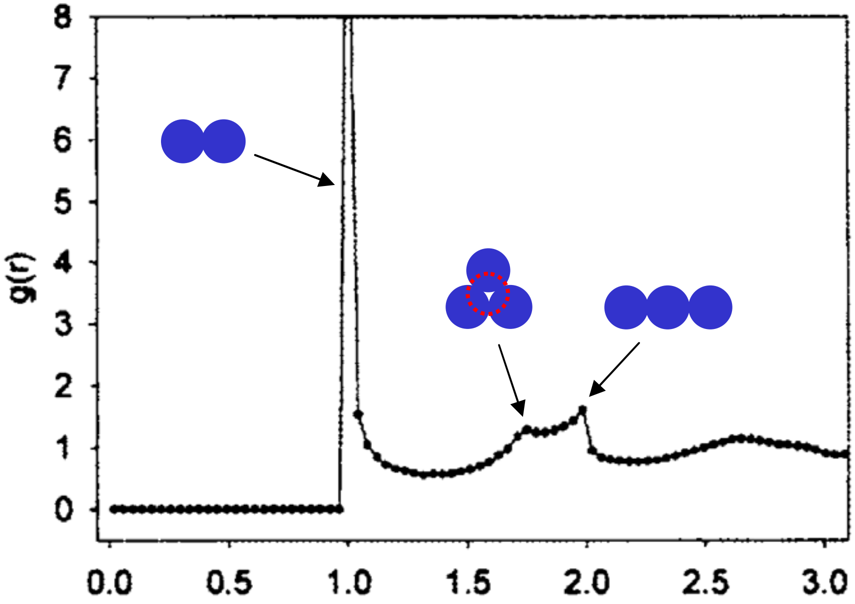
S.R. Wiliams and A.P. Philipse, *Phys. Rev. E*, 2003
A. Wouterse et al., *J. Chem. Phys.*, 2006
J.D. Bernal, *Nature*, 1960



volume fraction = 0.63

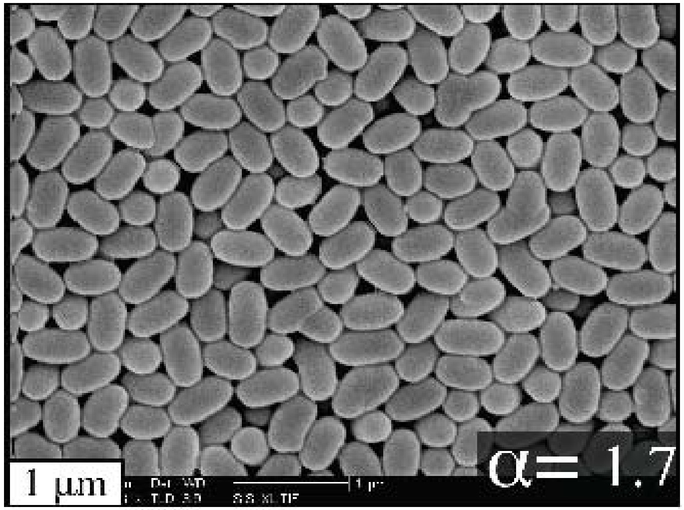
$$0.60 < \phi < 0.64$$

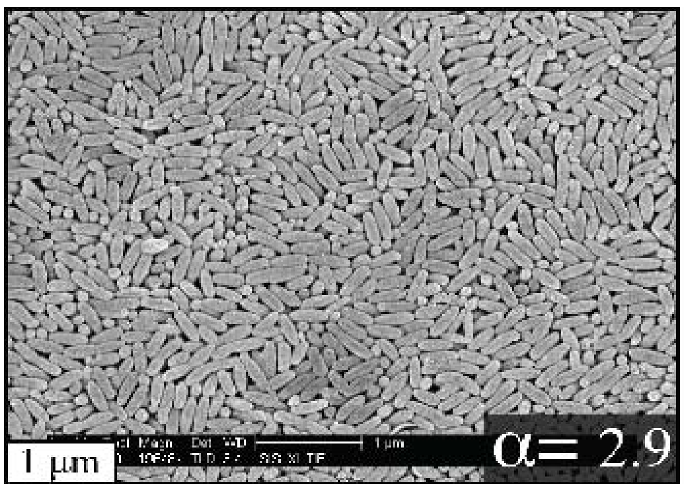
radial distribution function



Spheres are exceptional …

Colloidal silica ellipsoids





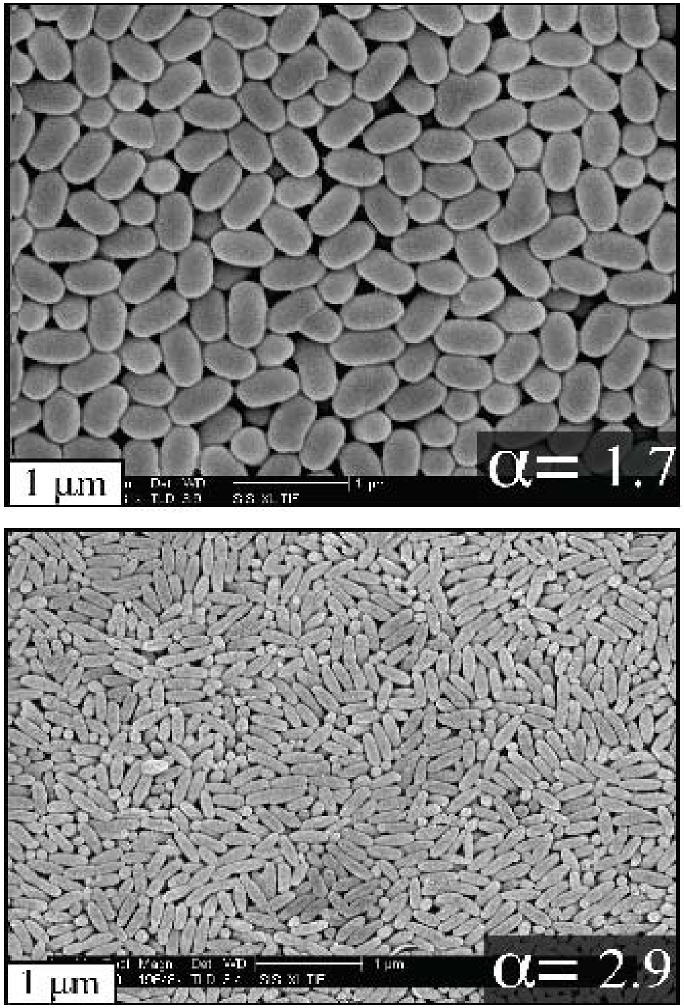
S. Sacanna et al., *J. Phys.: Condens. Matter*, 2007

Granular matter

Failure to analyse these packings in terms of 'effective spheres'

Generalize 'Bernal' to particles of any shape

Colloidal silica ellipsoids



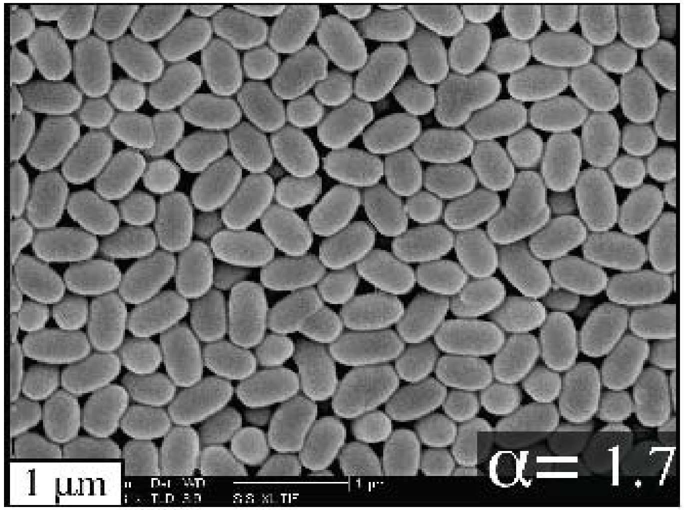
S. Sacanna et al., *J. Phys.: Condens. Matter*, 2007

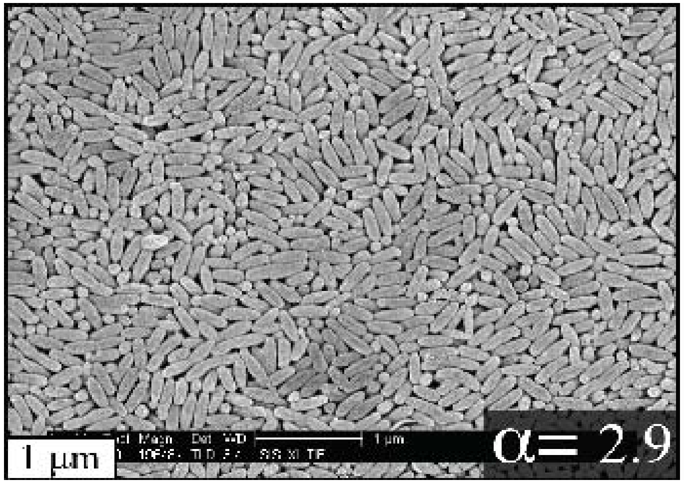
Granular matter

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

Where and how to start?

Colloidal silica ellipsoids





S. Sacanna et al., *J. Phys.: Condens. Matter*, 2007

Granular matter

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:**

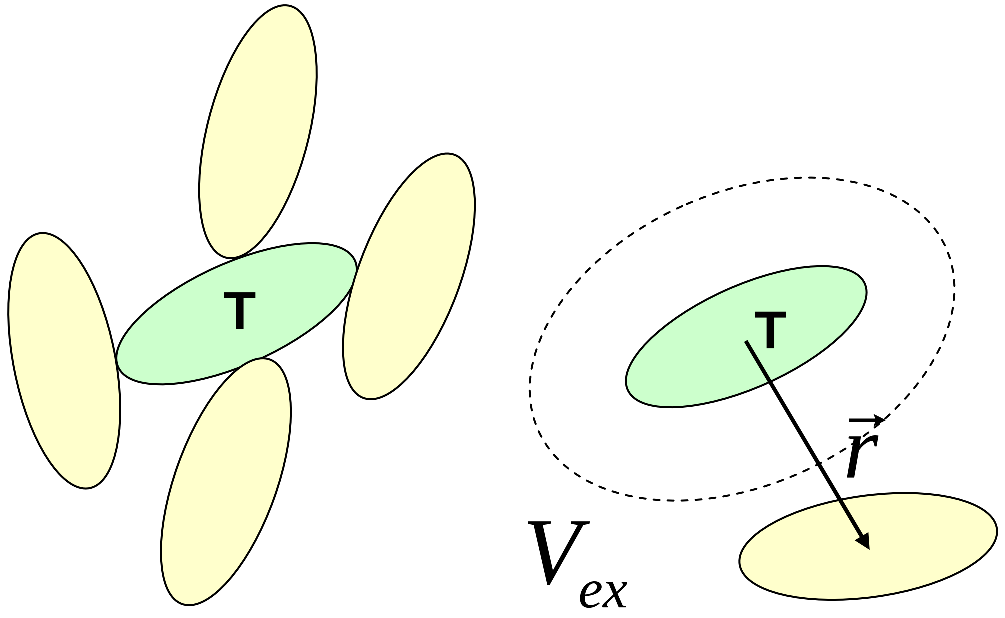
  Reference: an ideal packing of uncorrelated mechanical contacts.

A. Philipse, Langmuir 12, 1127 (1996)

A. Wouterse, Thesis (2008)

Particle contacts

Counting uncorrelated contacts:



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

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

Orientationally averaged exclude volume:

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

Ideal packing law

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

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

$$= \rho V_{ex}$$

Ideal packing law for uncorrelated contacts:

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

Ideal packing law

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**

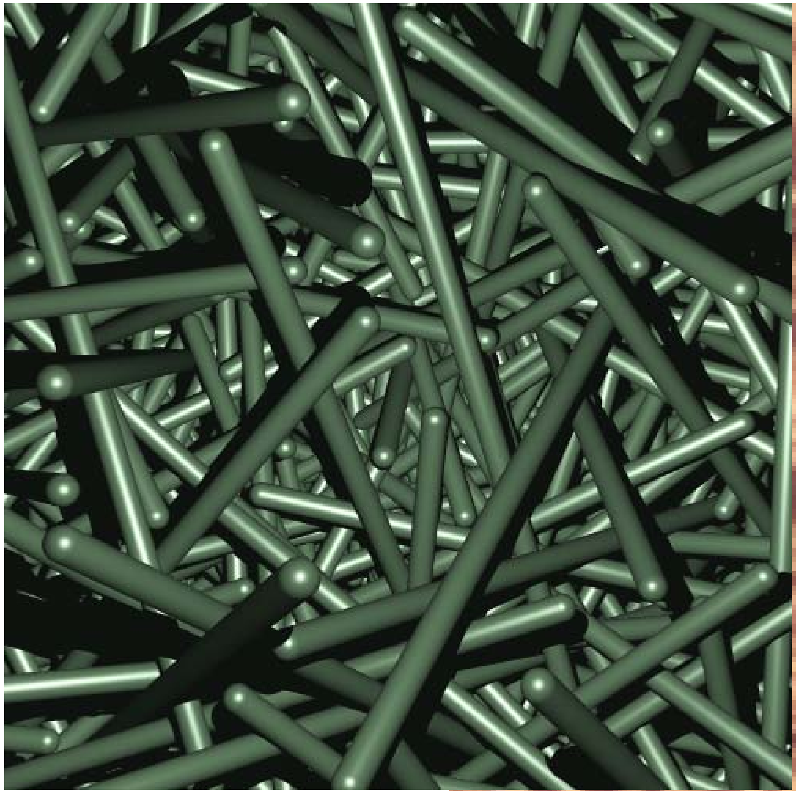
$$\Phi = < c > \frac{V_p}{V_{ex}}$$

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

But do uncorrelated contacts exists in dense granular packings ?

Long thin rods

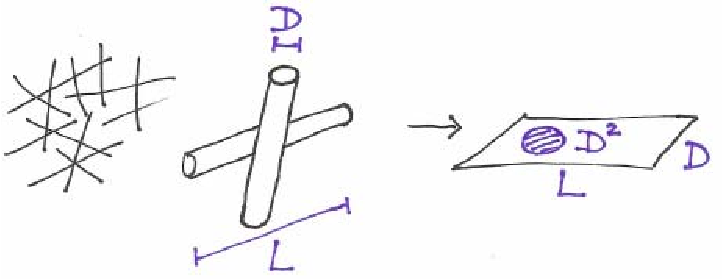
Simulations



Experiments

Long thin rods

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)**

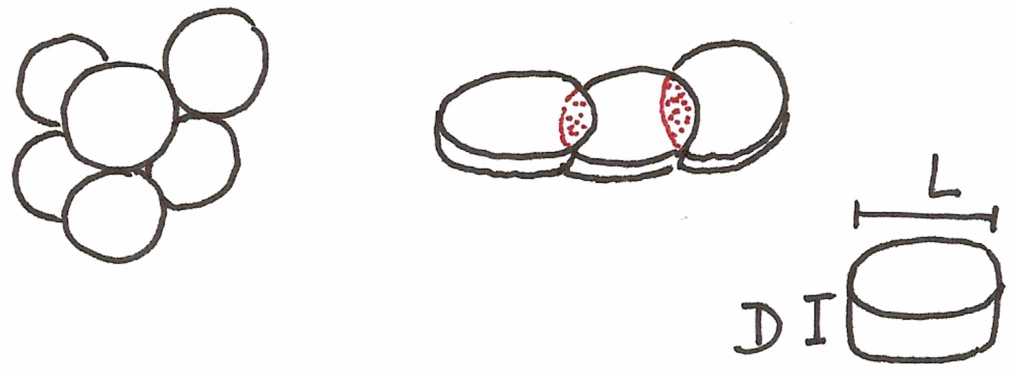
So for thin rods the ideal packing law $\Phi = < c > \dfrac{V_p}{V_{ex}}$ **becomes:**

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

(A. Philipse, Langmuir 1996)

Non-ideal packings

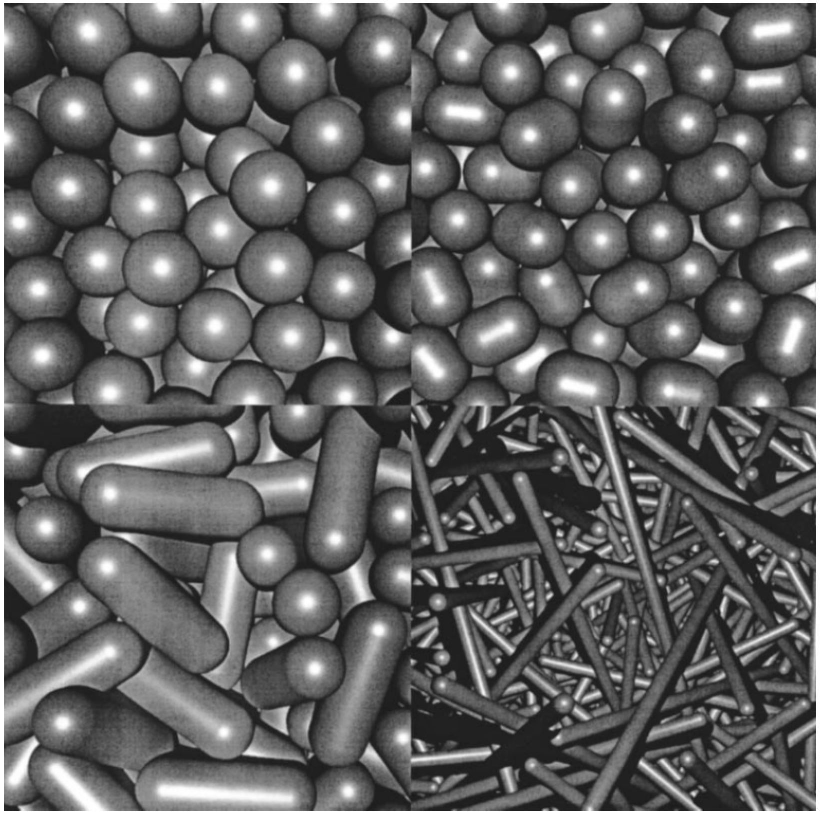
Clearly, as a rule, packings are *non*-ideal :



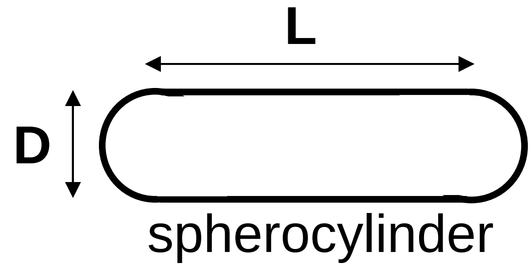
In the Bernal sphere packing, contacts are highly correlated.

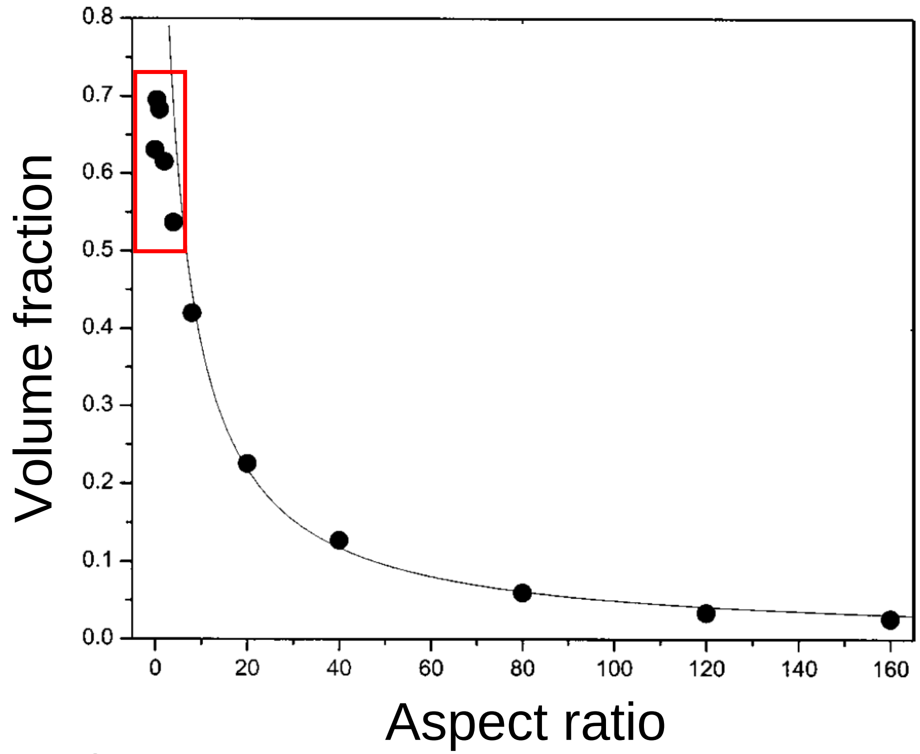
In the random disc packing, correlations do *not* vanish in the thin-disc limit.

Packing (spherocylinders)



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



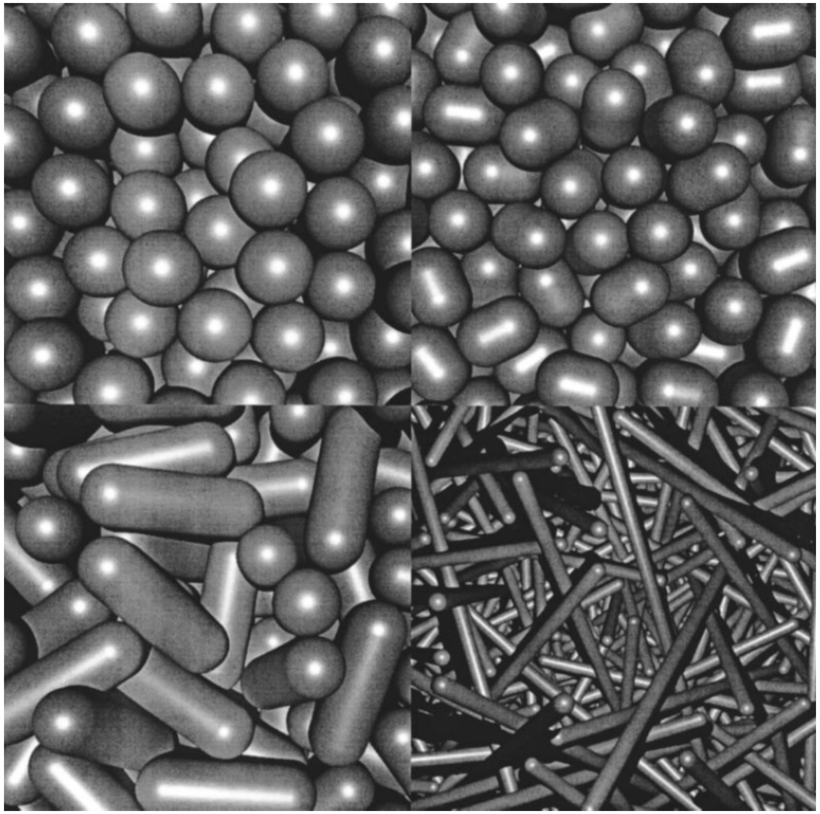


Random contact equation:

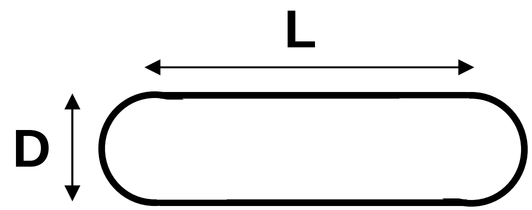
$$2\phi\frac{L}{D}\approx c$$

for L/D >> 1; $<c>\approx$ 10

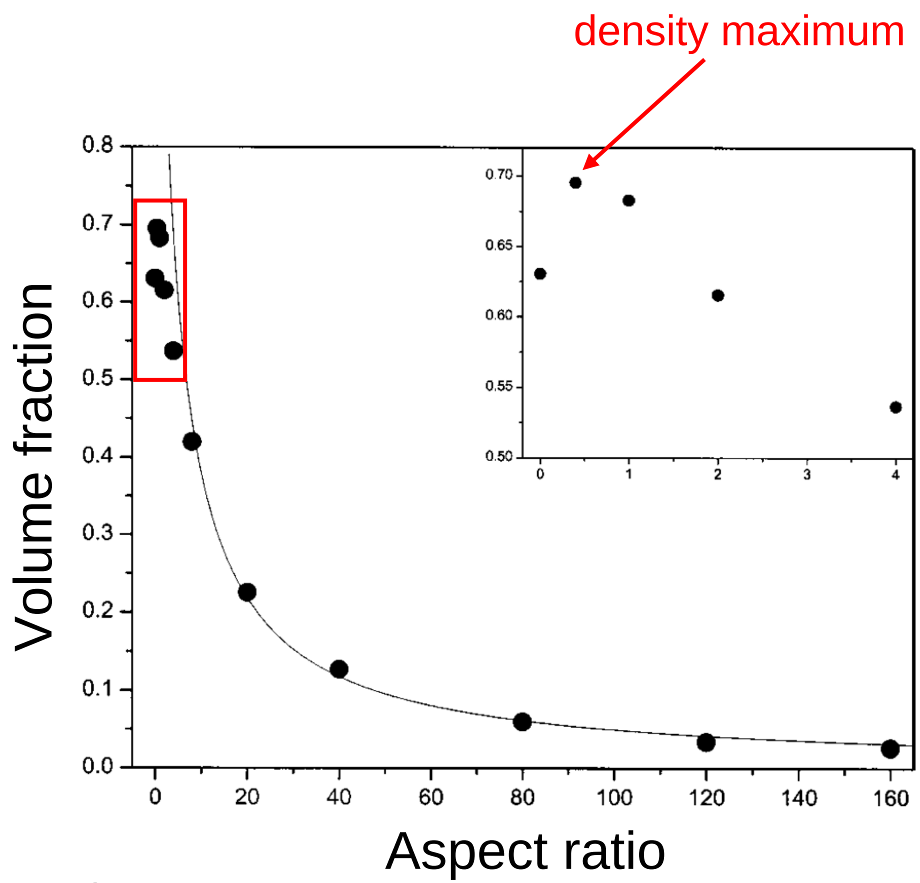
Packing (spherocylinders)



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



spherocylinder



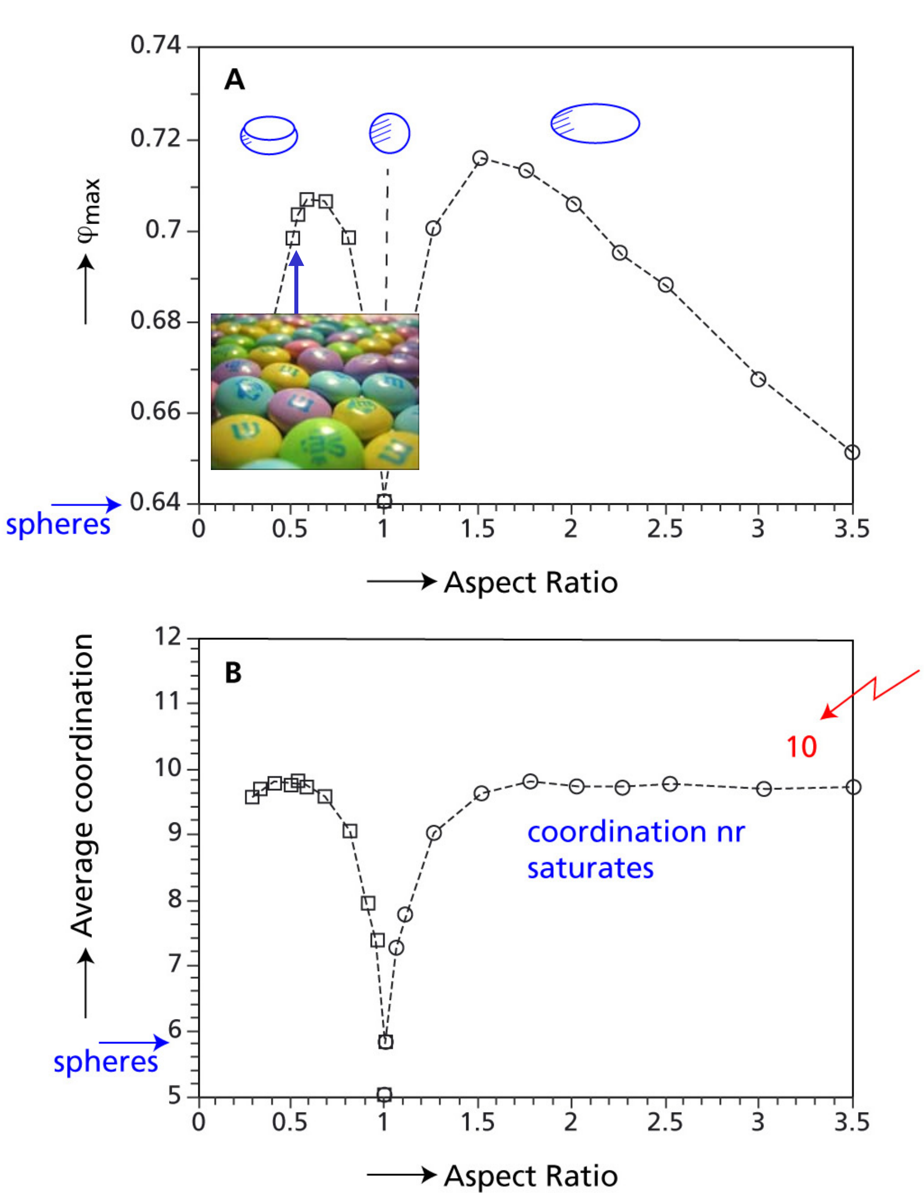
Random contact equation:

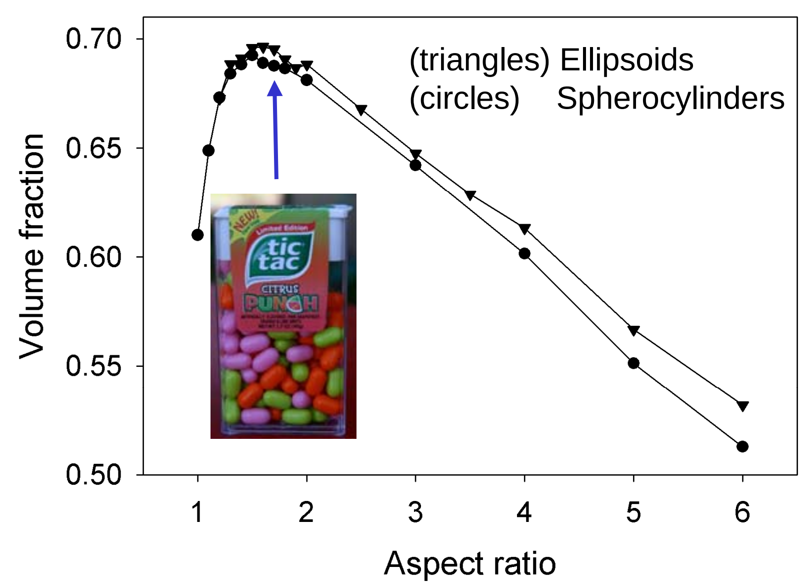
$$2\phi \frac{L}{D} \approx c$$

for L/D >> 1; $< c > \approx$ 10

Packing (ellipsoids)

A. Donev et al., *Science*, 2004

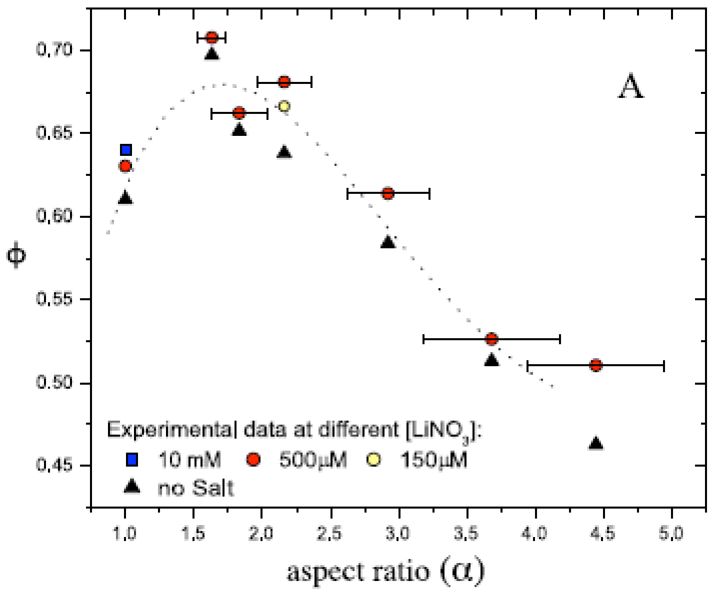


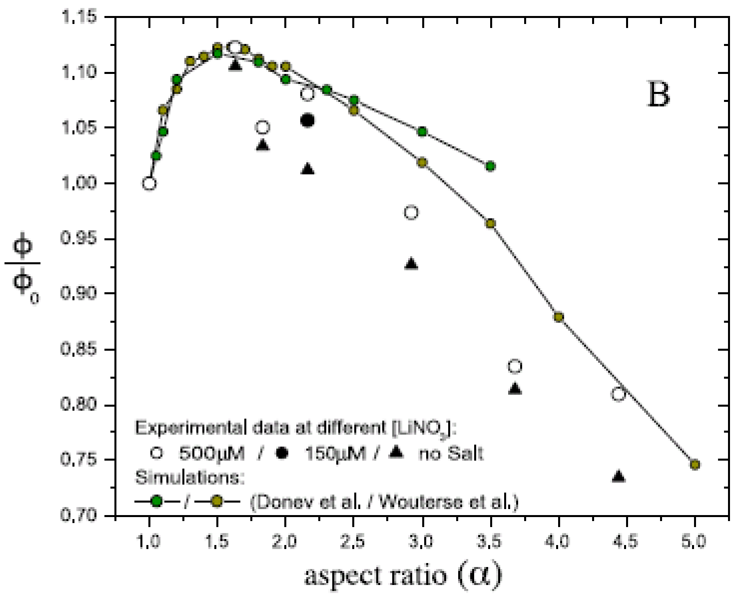


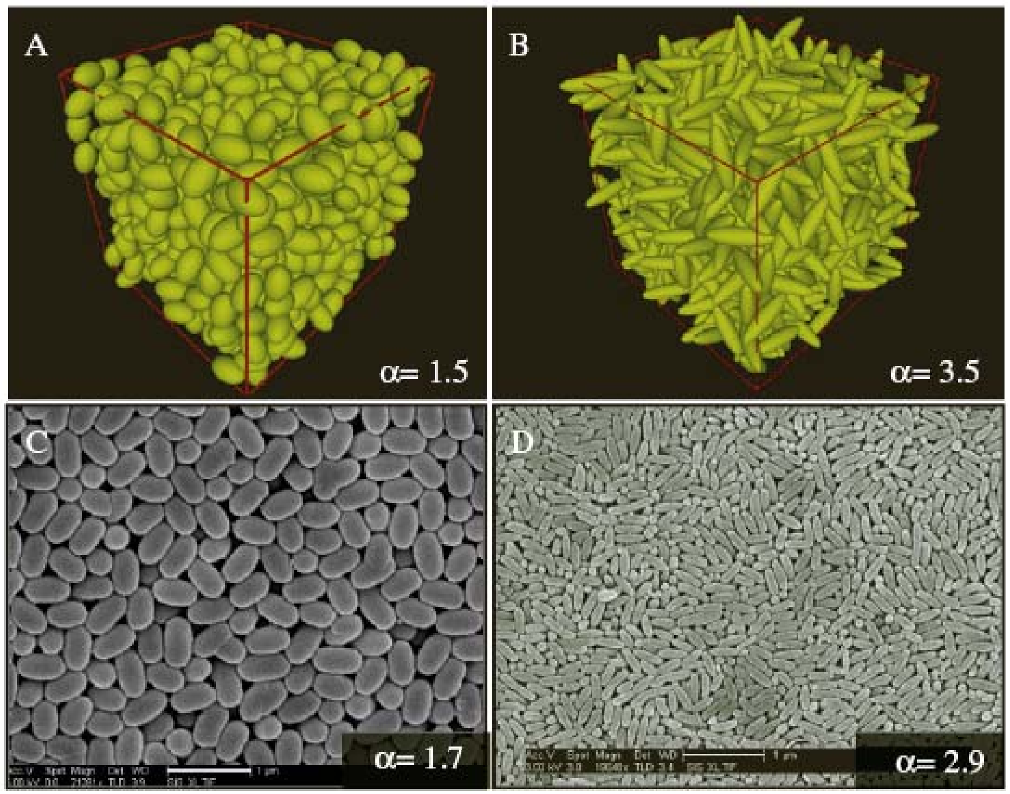
A. Wouterse et al., *J. Phys.: Condens. Matter*, 2007

Is there universality in the density maximum?

Colloidal rods (spheroids)

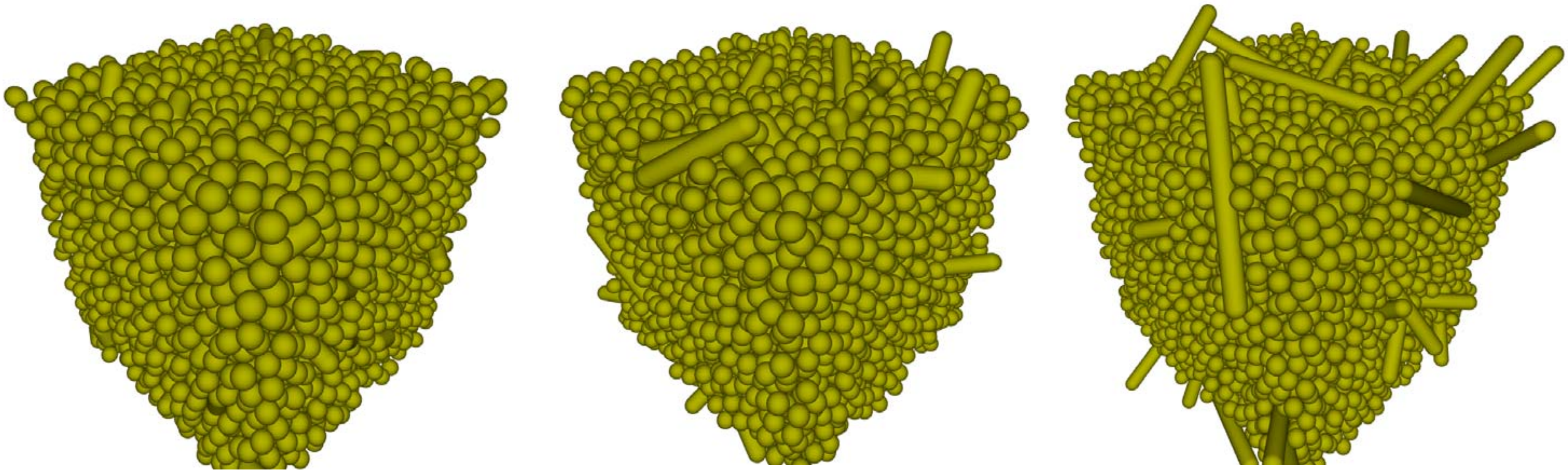




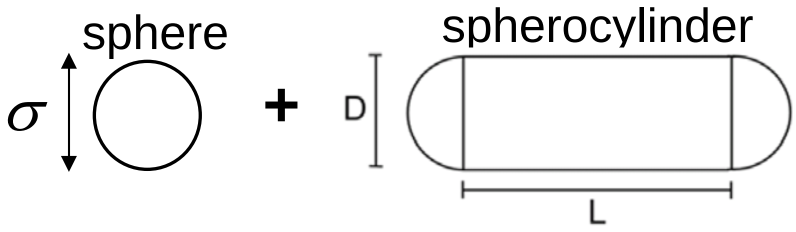


S. Sacanna et al., *J. Phys.: Condens. Matter*, 2007

Packing (rod-sphere mixture)

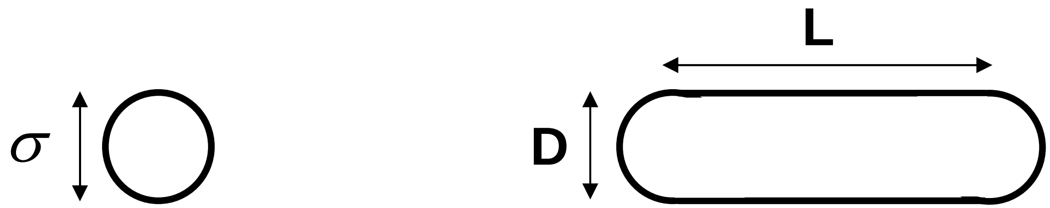


rod/sphere mixture:



Mechanical contraction method (MCM)

System:



(a) spheres (b) spherocylinders

Procedure:

$V = 10^5 - 10^7$

$V - \Delta V$

$$s = \left(1 - \frac{\Delta V}{V}\right)^{1/3}$$

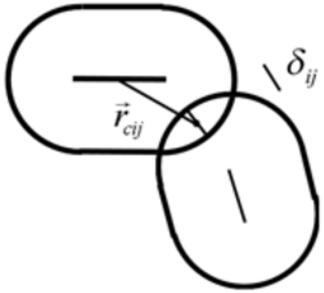
$V = 10^3 - 10^4$

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

Approach

A. Wouterse et al., *J. Phys.: Condens. Matter*, 2007

rate of overlap changing:



$$\frac{\partial \delta_{ij}}{\partial t} = \left(\vec{v}_i + \vec{\omega}_i \times r_{cij}\right) \cdot \hat{\vec{n}}_{ij}$$

overlap removal speed:

$$s_i = \sum_{j=1}^{C} \delta_{ij} \frac{\partial \delta_{ij}}{\partial t}$$

constraint:

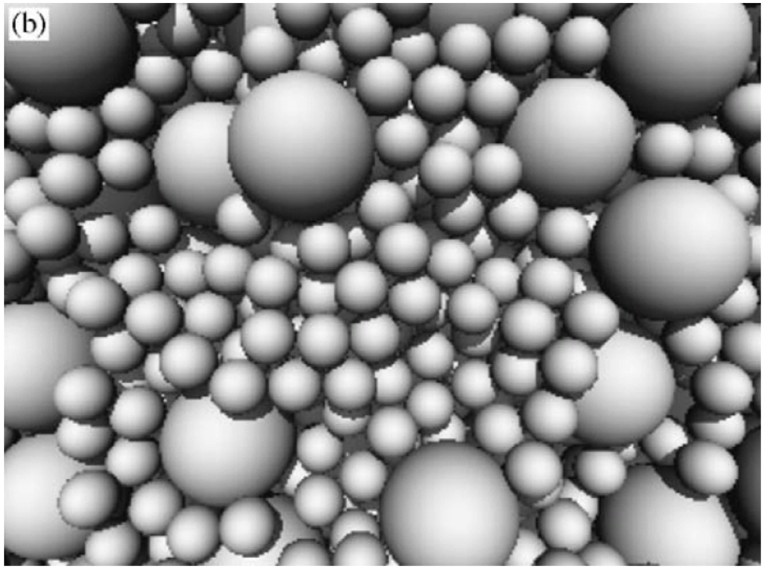
$$\vec{v}_i \cdot \vec{v}_i + \vec{\omega}_i I \vec{\omega}_i = 1$$

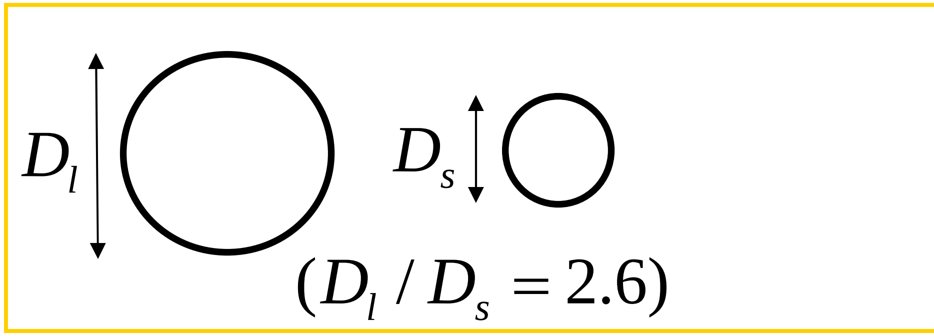
Lagrange multiplier method $\Longrightarrow$ direction of overlap removal:

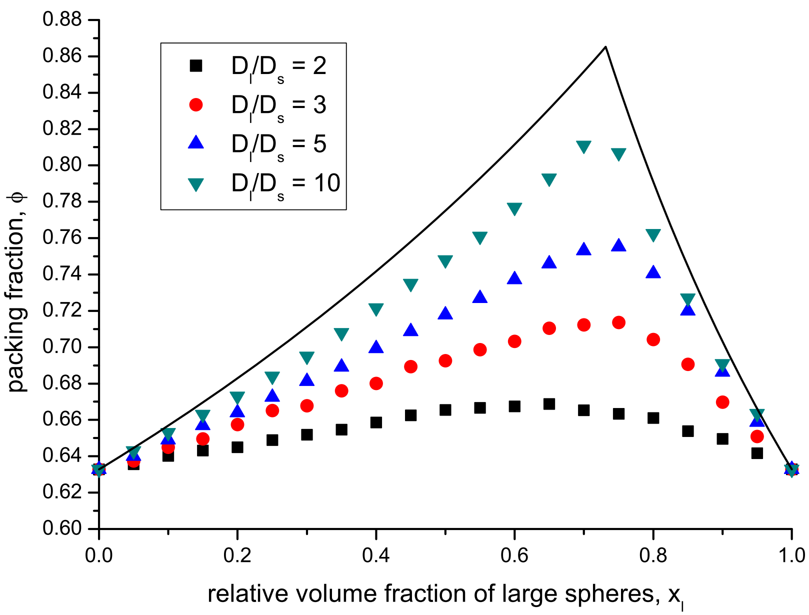
$$\vec{v}_i = \sum_{j=1}^{C} \delta_{ij} \hat{\vec{n}}_{ij}$$

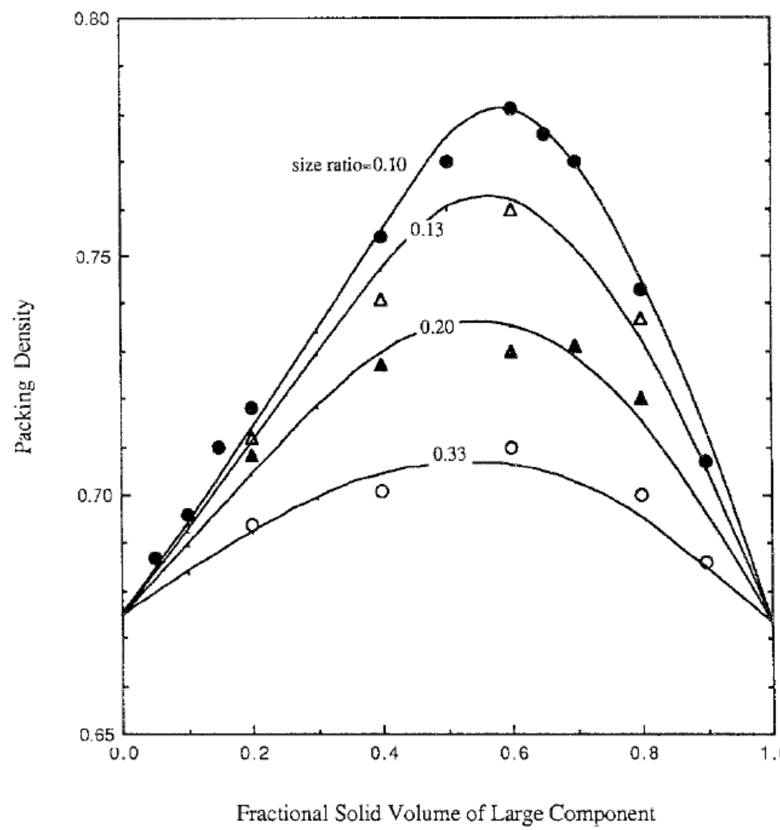
$$\omega_i^{(\alpha)} = \frac{1}{I_{\alpha\alpha}} \sum_{j=1}^{C} \delta_{ij} \left(n_{ij}^{(\gamma)} r_{cij}^{(\beta)} - n_{ij}^{(\beta)} r_{cij}^{(\gamma)}\right), \quad \alpha, \beta, \gamma = x, y, z$$

Packing (binary sphere mixture)







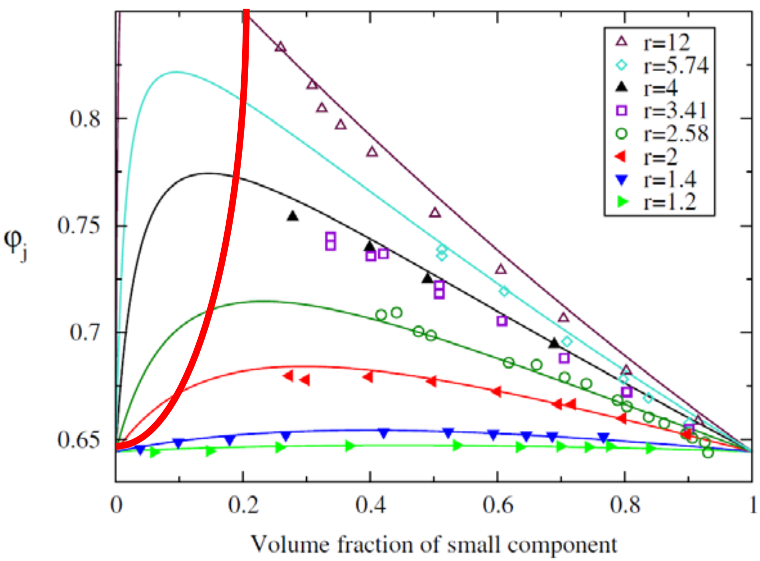


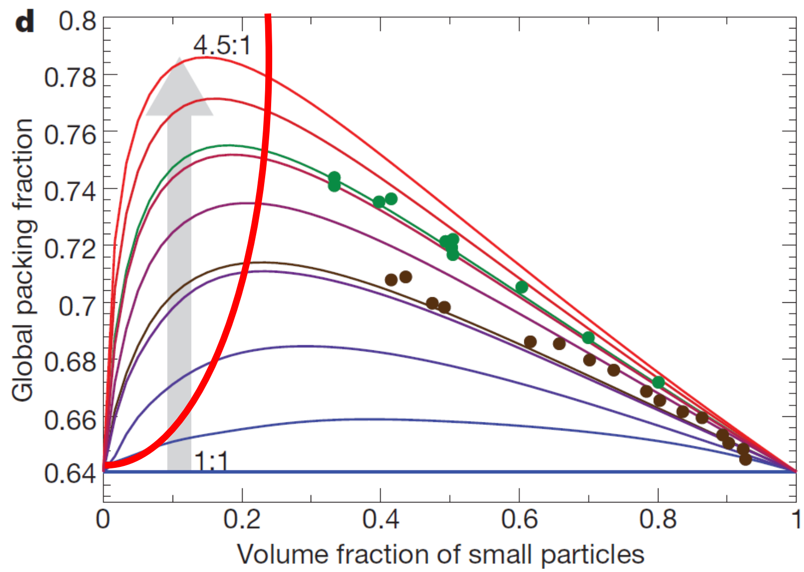
A.B. Yu and N. Standish., *Powder Tech.*, 1993

A.V. Kyrylyuk, A. Wouterse and A.P. Philipse, *Prog Colloid Polym Sci*, 2010

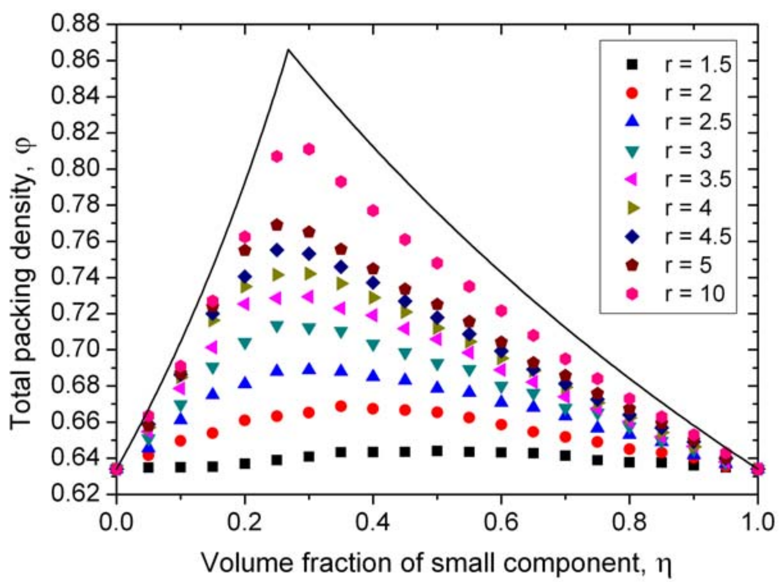
Packing (binary sphere mixture)

I. Biazzo et al., *Phys Rev Lett*, 2009



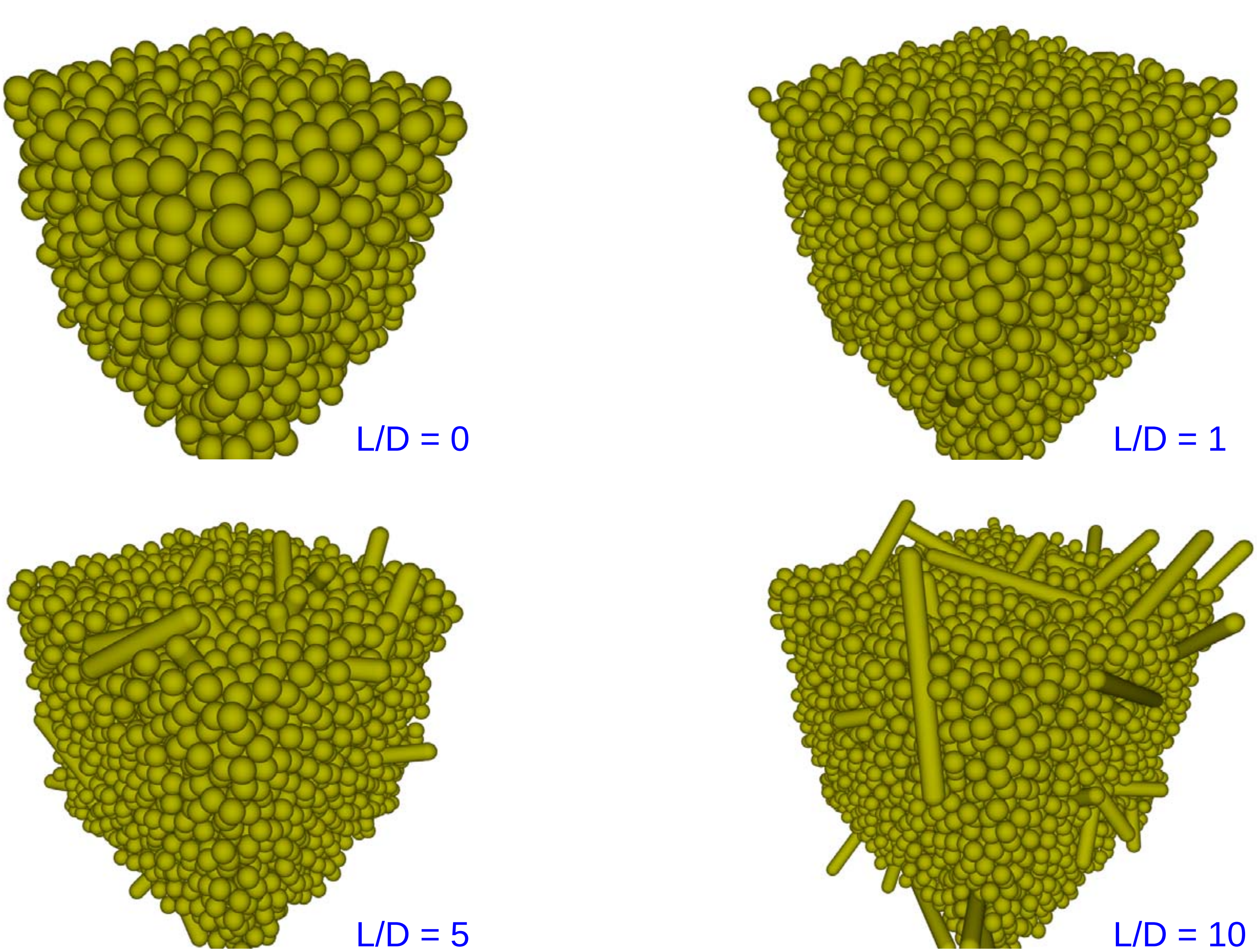


M. Clusel et al., *Nature*, 2009



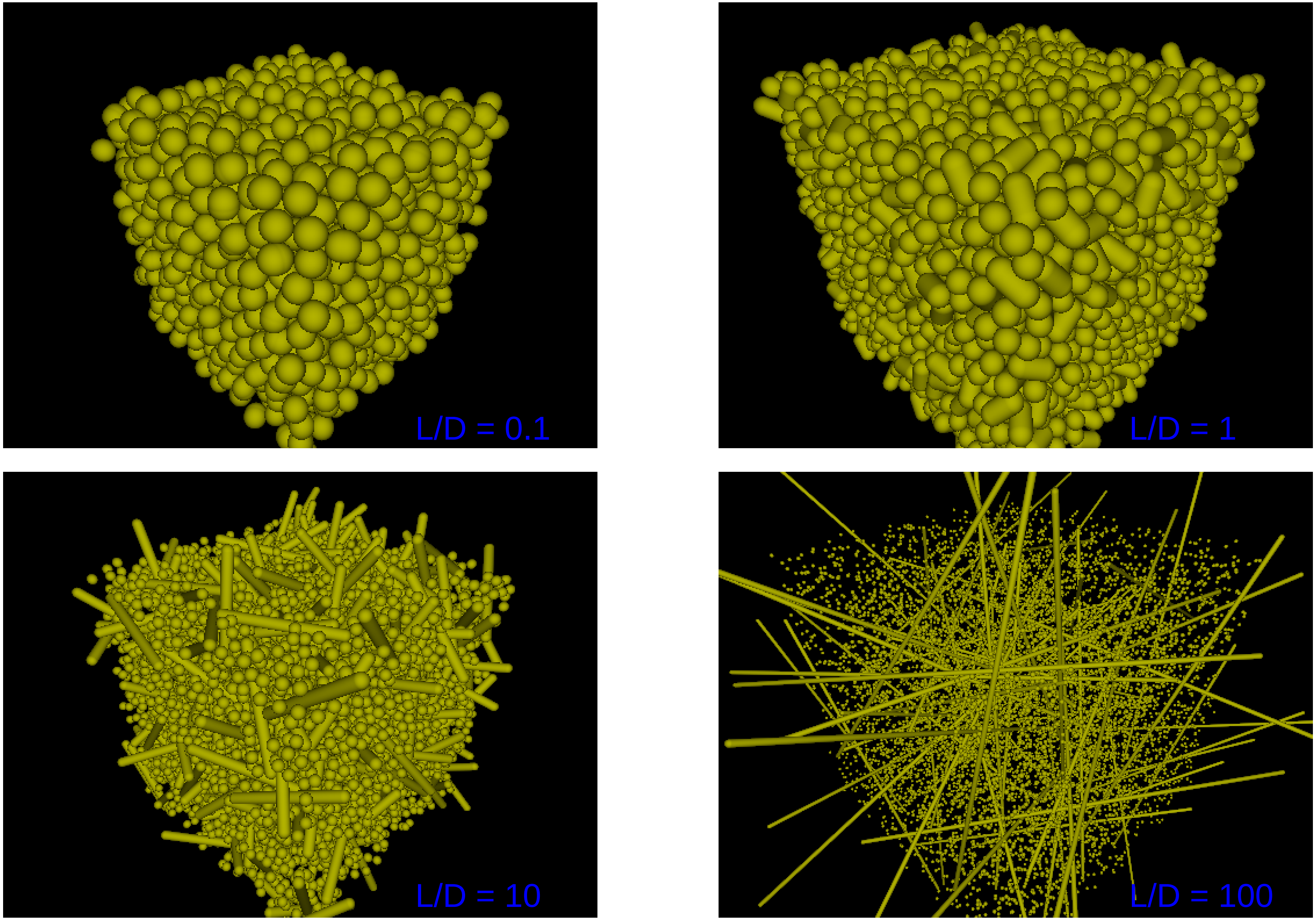
A.V. Kyrylyuk, A. Wouterse and A.P. Philipse, *Prog Colloid Polym Sci*, 2010

Packing (rod-sphere mixture)



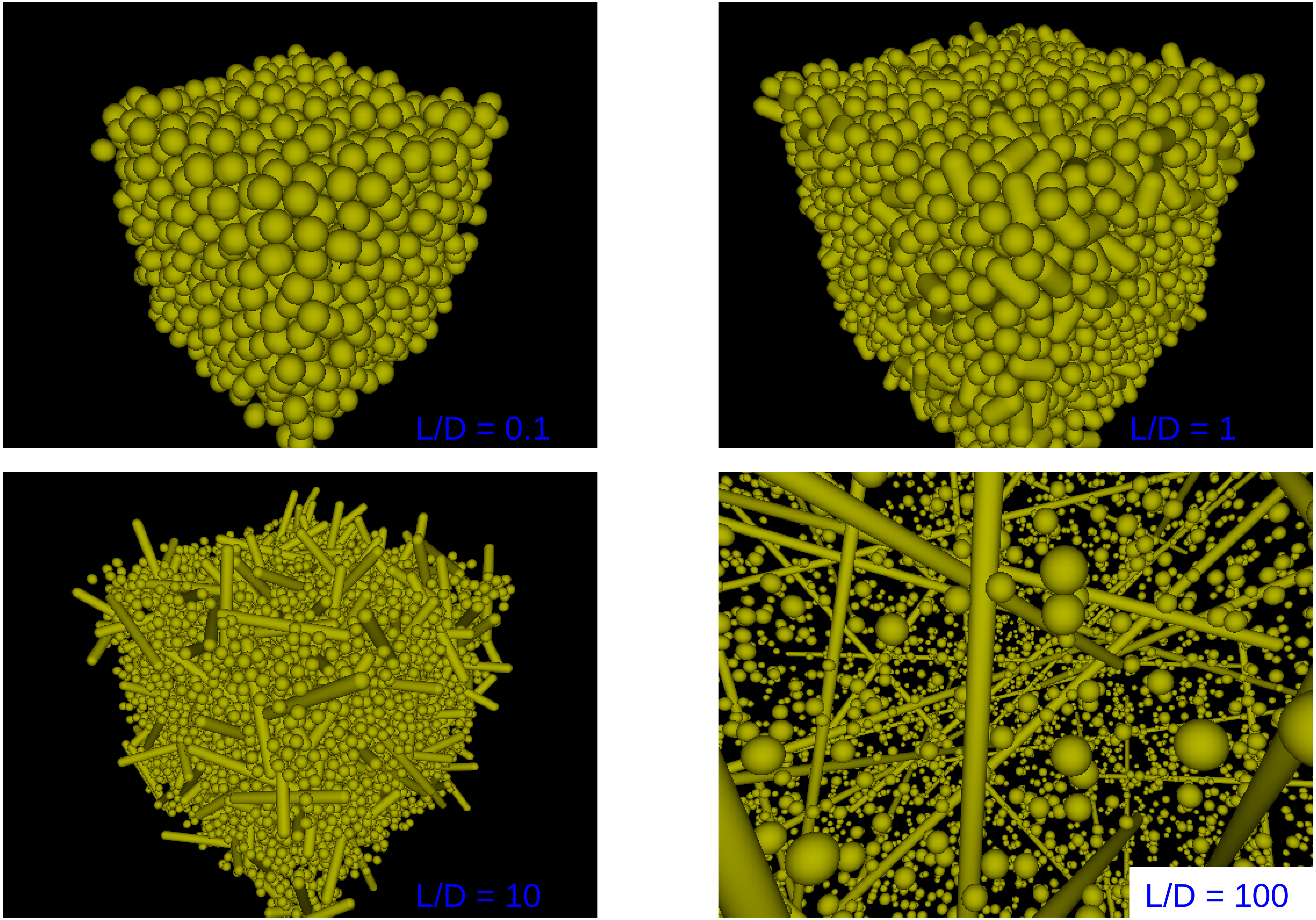
composition: x = 0.1

Packing (rod-sphere mixture)



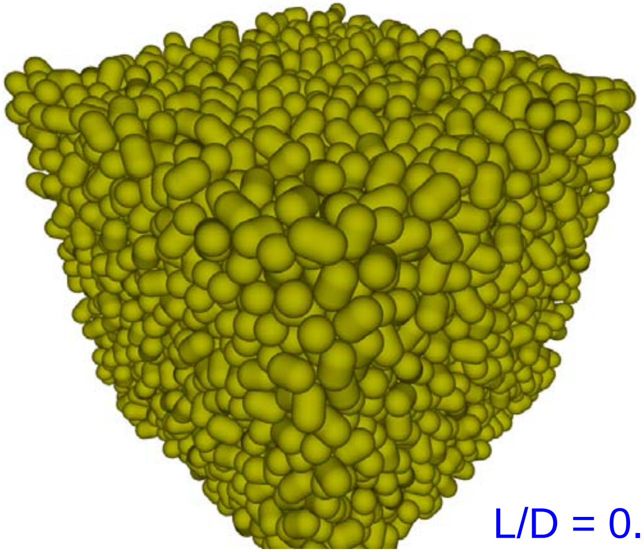
composition: x = 0.5

Packing (rod-sphere mixture)

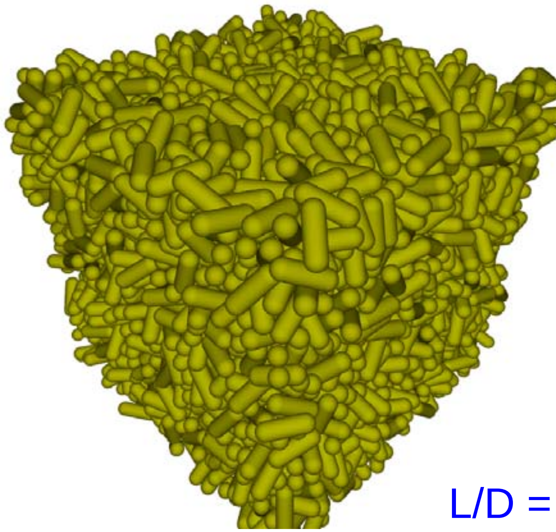


composition: x = 0.5

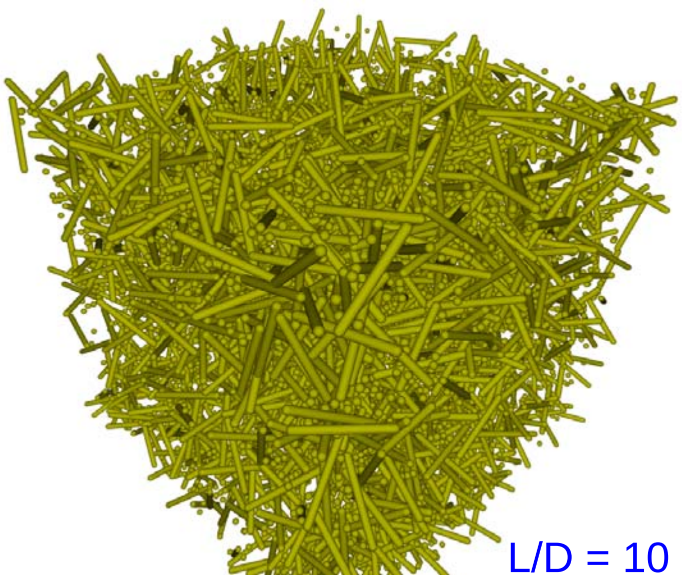
Packing (rod-sphere mixture)



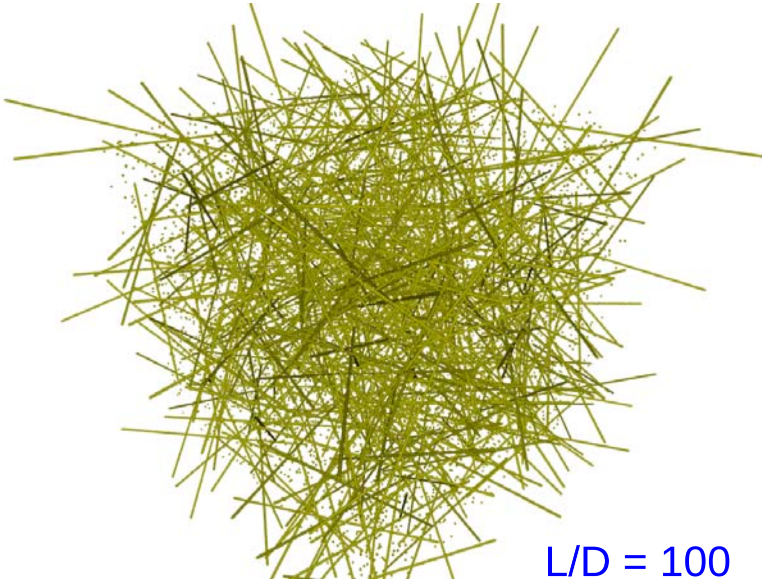
L/D = 0.5



L/D = 2



L/D = 10

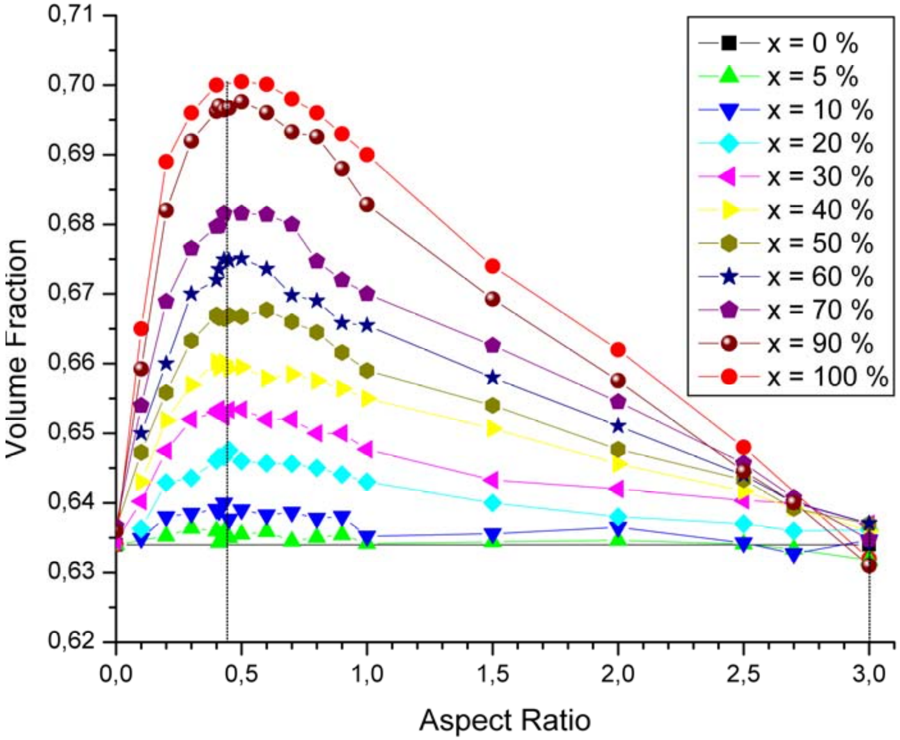


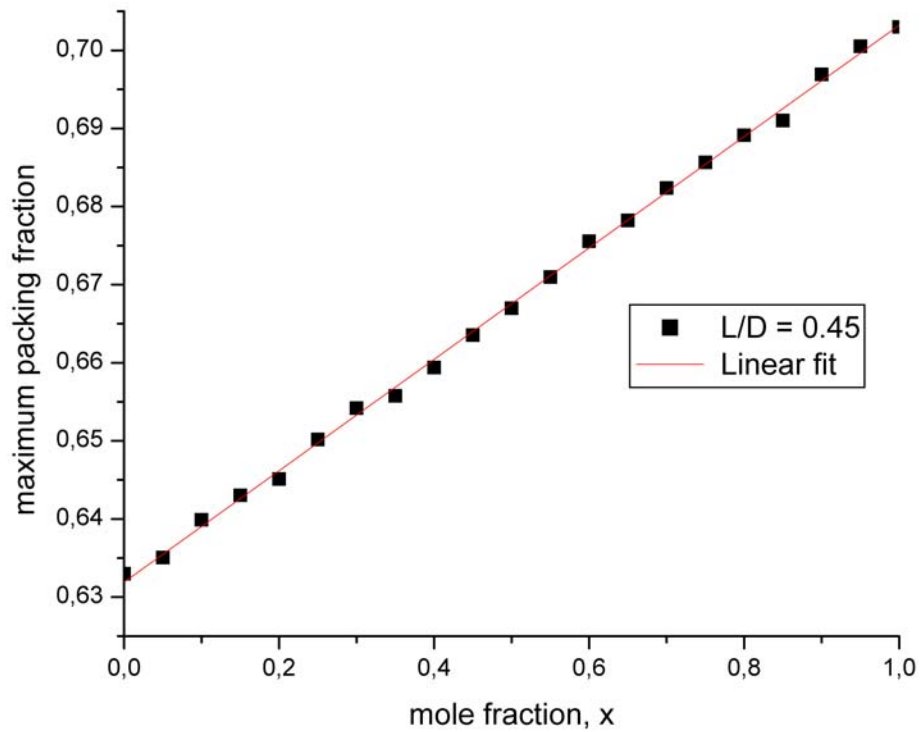
L/D = 100

composition: x = 0.9

Packing (rod-sphere mixture)

A.V. Kyrylyuk, A. Wouterse and A.P. Philipse, *AIP Conf. Proc.*, 2009





Universality + Ideality: the value of the density maximum depends linearly on the mixture composition

Packing (rod-sphere mixture)

- Linearity for aspect ratios up to 1.7

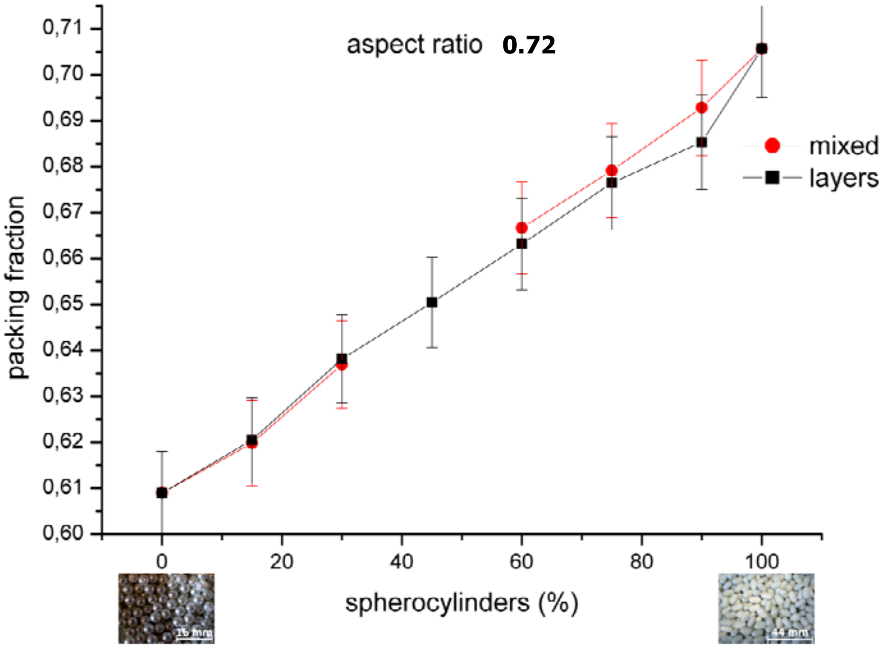
 +  =  = 

$$\Phi = \Phi_s x_s + \Phi_r (1-x_s)$$ (law of mixtures)

- Equality of mixed and demixed packings

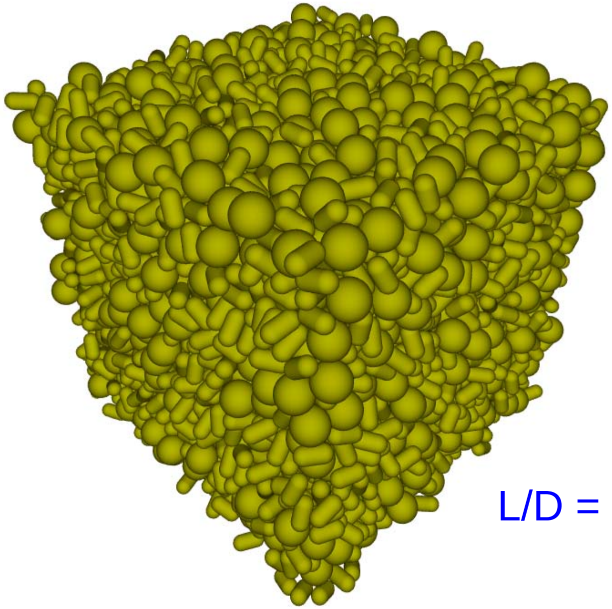
⇓

Mixing Entropy = 0 !

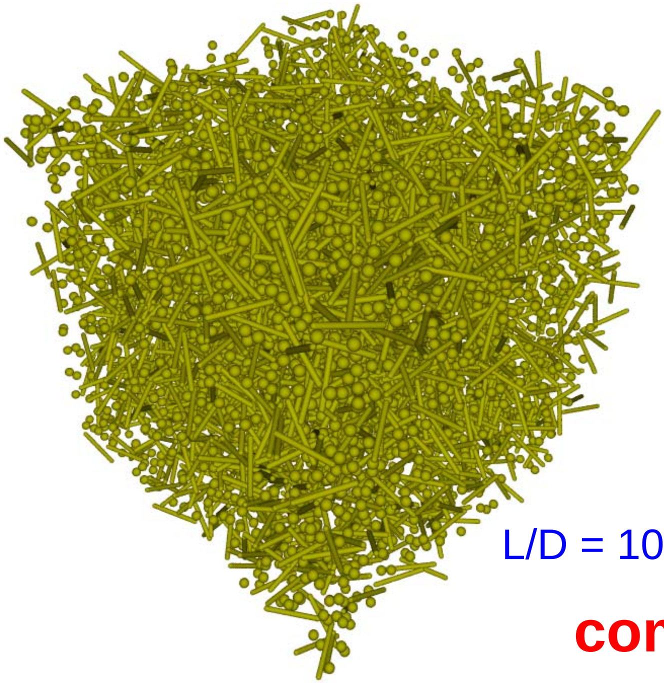


A.V. Kyrylyuk et al., in preparation

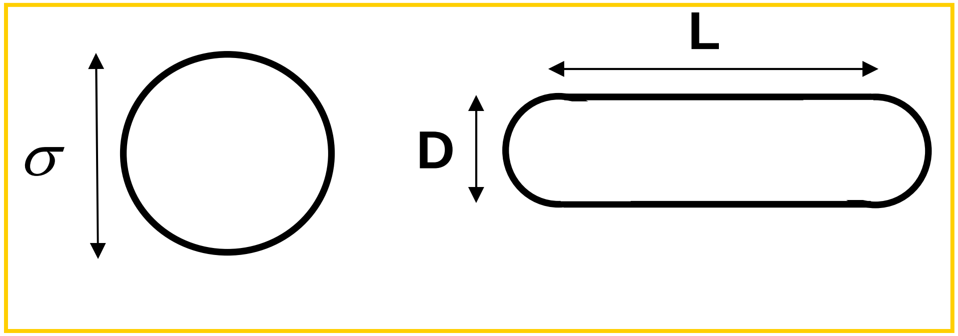
Packing (rod-sphere mixture)

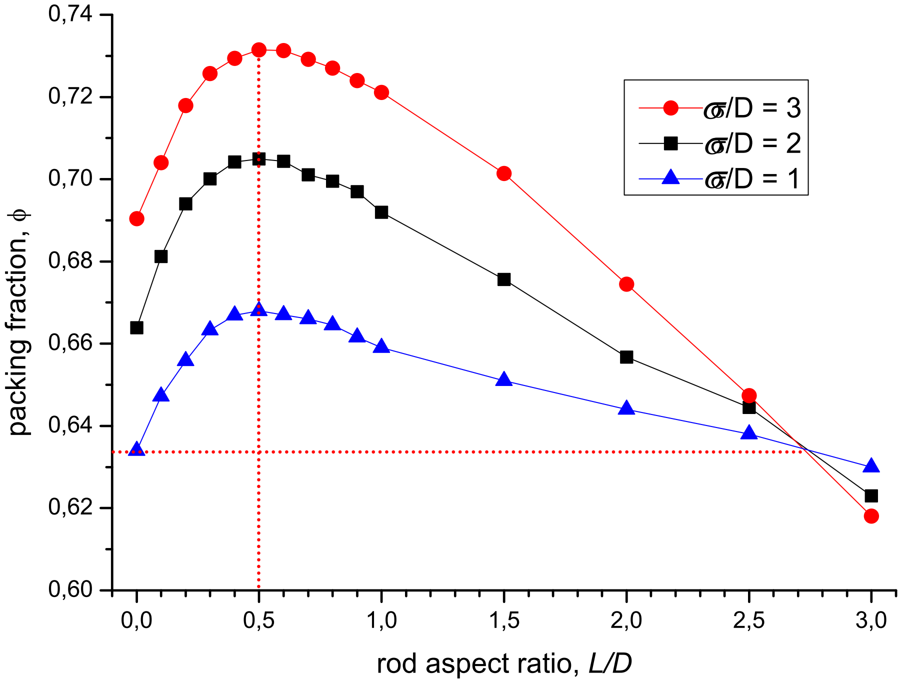


L/D = 1



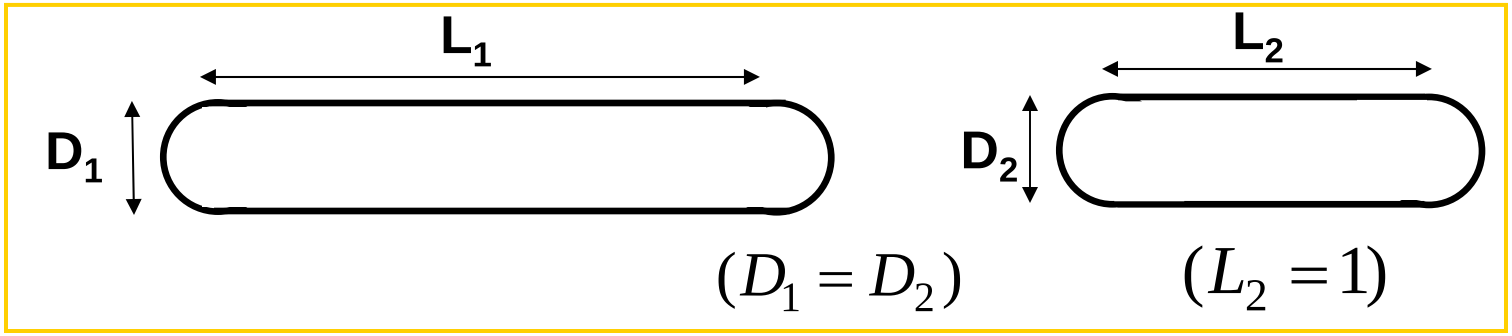
L/D = 10

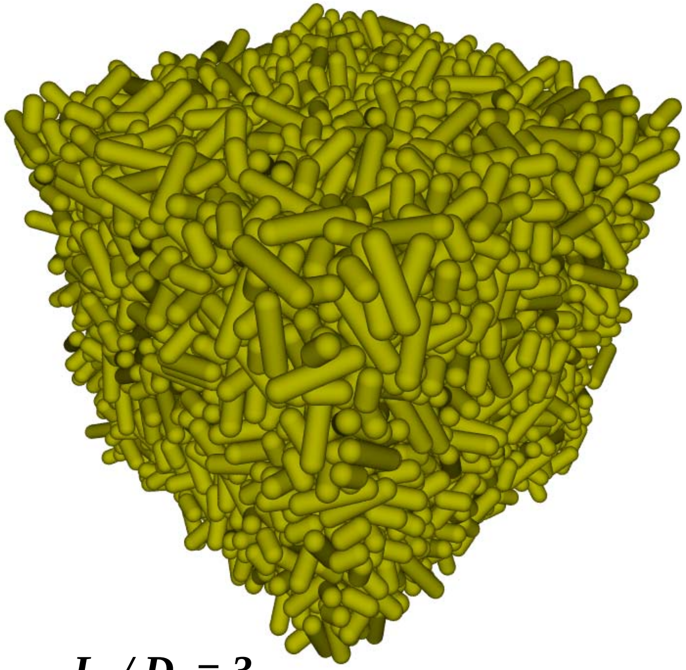




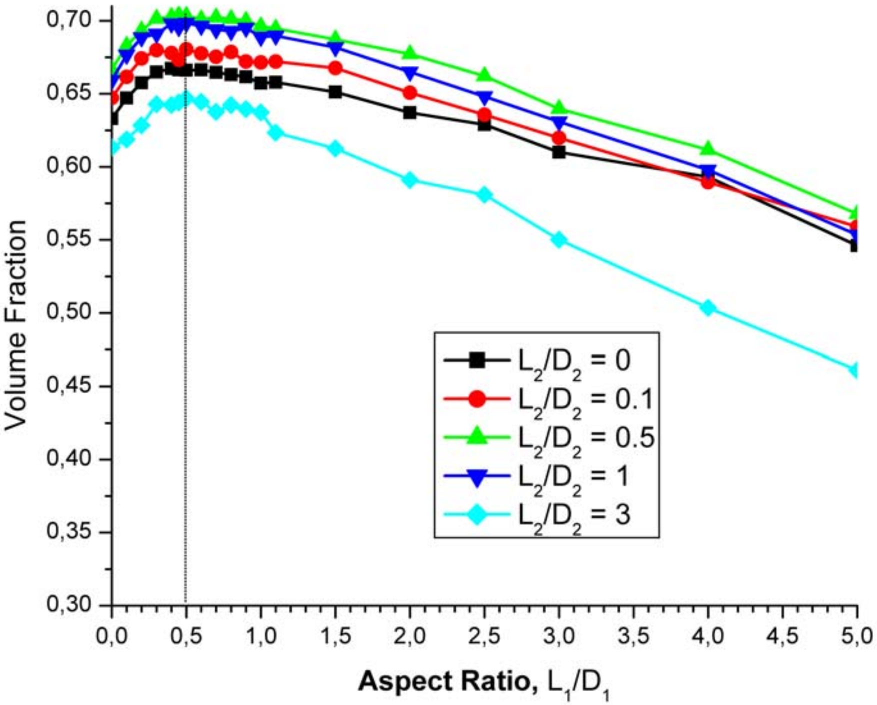
composition: x = 0.5

Packing (bidisperse rod mixture)





$L_1 / D_1 = 3$

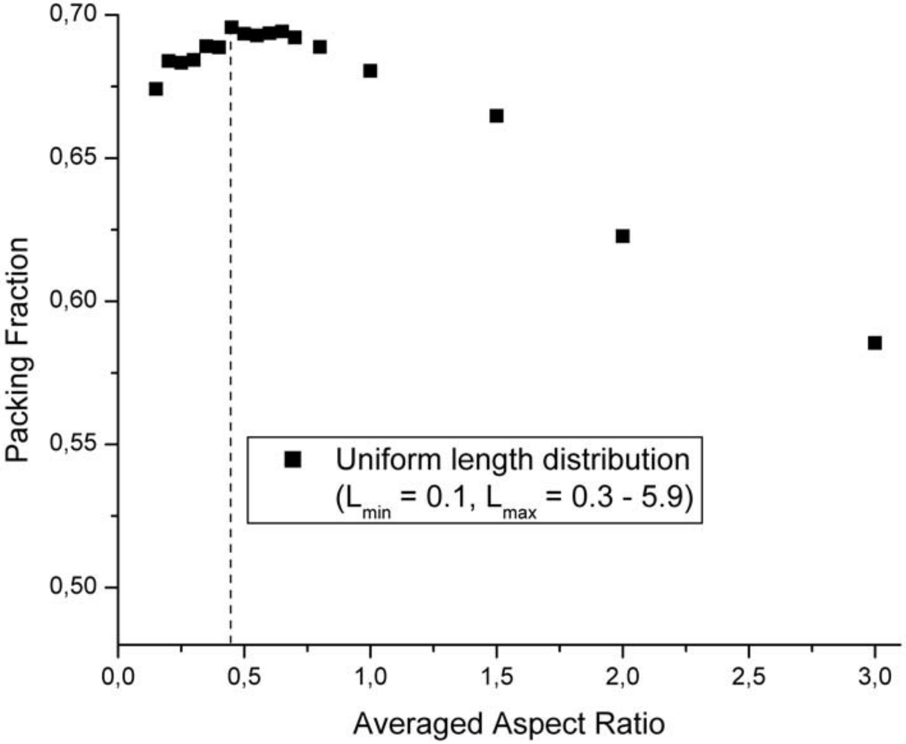


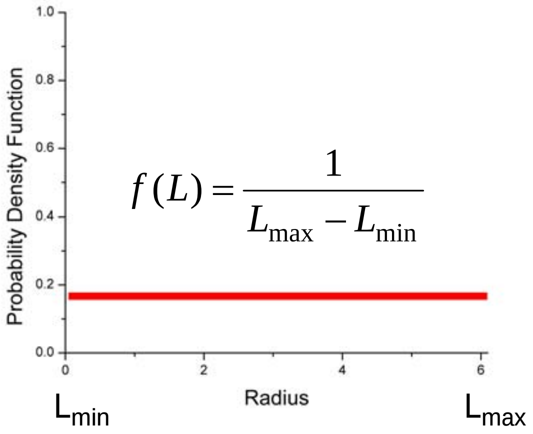
A.V. Kyrylyuk and A.P. Philipse, *in preparation*

composition: x = 0.5

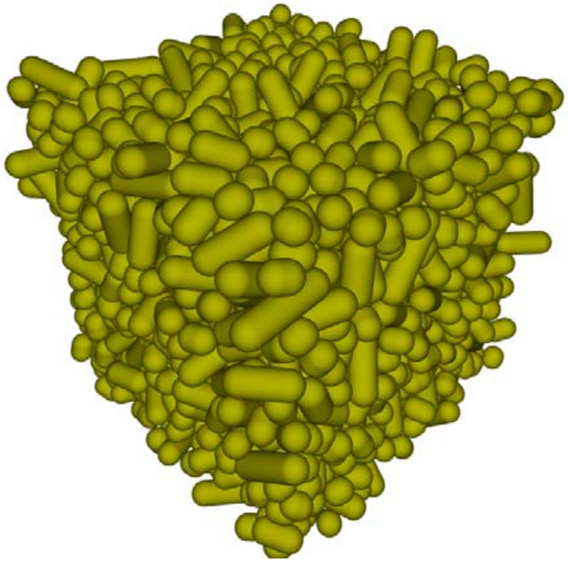
Packing (polydisperse rods)

Uniform length distribution



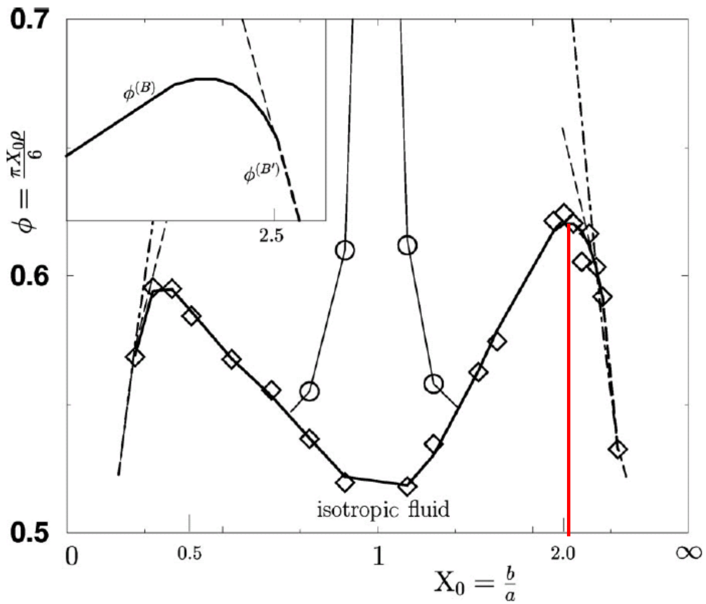


$$f(L) = \frac{1}{L_{max} - L_{min}}$$

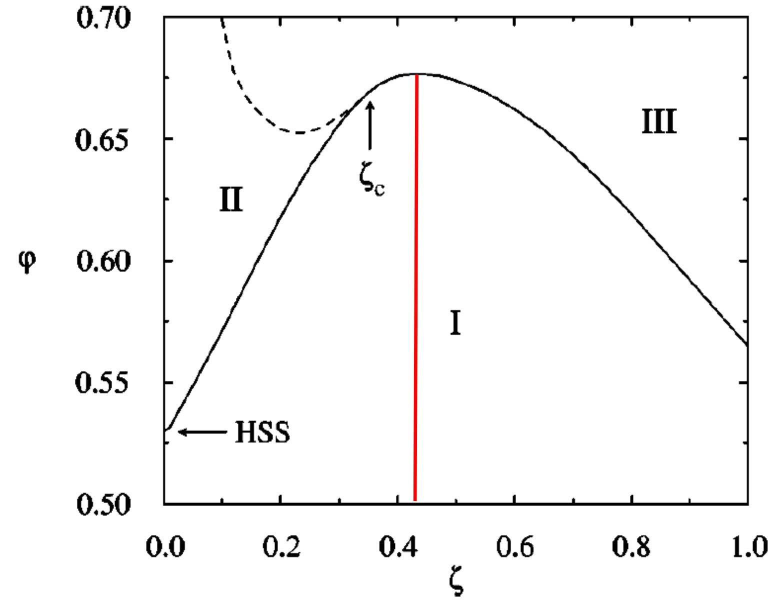


Glass transition of near-spheres

M. Letz, R. Schilling and A. Latz, *PRE*, 2000



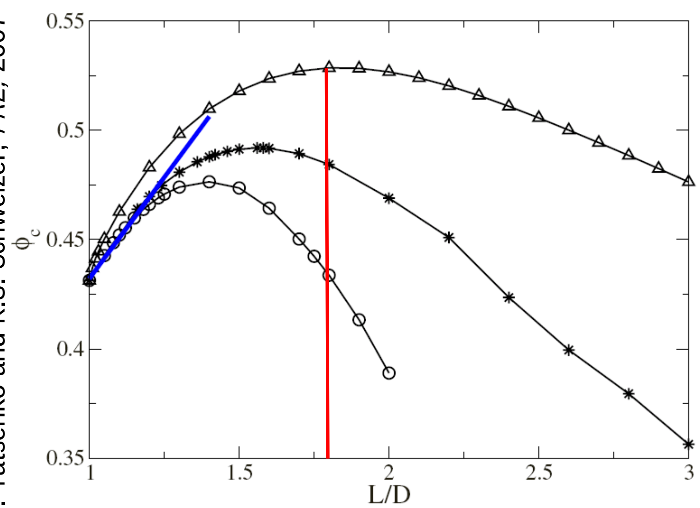
Ideal MCT glass transition for hard ellipsoids



S.H. Chong and W. Gotze, *PRE*, 2002

Ideal MCT glass transition for symmetric hard dumbbell systems

G. Yatsenko and K.S. Schweizer, *PRE*, 2007



Ideal glass transition for rod-like particles

F. Sciortino and P. Tartaglia, *Adv. Phys.*, 2005

Conclusions

- Bernal packing of spheres: no ideality

- Long thin rods: an ideal packing of uncorrelated mechanical contacts

- Non-monitonic packing behavior: deviation from spheres to near-spheres produces a density maximum

- Random packing of a rod-sphere mixture also has a density maximum for near-spheres:

  - Universality: Positions of the density maximum and intersection point depend only on the rod aspect ratio and not on the composition

  - Ideality: the height of the maximum depends linearly on the rod-sphere mixture composition

- The density maximum is also present in bidisperse and polydisperse rod mixtures

↓

Universality: Position of the density maximum holds for one **unique** rod aspect ratio and does not depend on the rod aspect ratio of the second component