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

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• Motivation.

• **Spheres**: the Bernal packing

• **Thin rods**: the *ideal* gas in random packings

• **Near-spheres**: density maximum + *ideality*  
  (packing surprise #1)

• **Mixtures**: universality + *ideality*  
  (packing surprise #2)
Motivation

Packings in

• **Nature:**
  - sand, gravel, etc.

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

• **Technology:**
  - catalyst carriers
  - food technology
  - reinforced composites
Kepler’s conjecture: you can’t pack spheres denser than to a solid volume fraction of $\frac{\pi}{\sqrt{18}} = 0.7405$. 
Disordered, ‘random’ sphere packing

Disordered spheres pack at a lower density of about 0.64 (the Bernal sphere packing).
Hard sphere phase diagram

a) Colloids

b) Granular matter

Classical reference system for amorphous matter, colloidal glasses, etc.
Bernal random sphere packing

volume fraction = 0.63

$0.60 < \phi < 0.64$

radial distribution function

Spheres are exceptional ...

Colloidal silica ellipsoids

Granular matter

Failure to analyse these packings in terms of ‘effective spheres’
Generalize ‘Bernal’ to particles of any shape

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

Colloidal silica ellipsoids

Granular matter

Where and how to start?

Colloidal silica ellipsoids

Granular matter


Is any of these (or other) random packings truly random, in the sense that all spatial and orientational correlations are absent?
- **Thermal gas:**
  Reference is an ideal gas of uncorrelated thermal particles.

- **Granular matter:**
  Reference: an ideal packing of uncorrelated mechanical contacts.


Particle contacts

Counting uncorrelated contacts:

\[ f(\vec{r}) = 1 \quad \text{inside } V_{ex} \]
\[ f(\vec{r}) = 0 \quad \text{outside } V_{ex} \]

Orientationally averaged exclude volume:

\[ V_{ex} = \int_{V} f(\vec{r}) d\vec{r} \]
Ideal packing law

Contact number \( c_T = \int_{V} f(r) \rho(r) d\vec{r}; \rho(r) = \text{local nr. density} \)

\[ \sim \rho \int_{V} f(\vec{r}) d\vec{r}; \rho = \text{average nr. density} \]

\[ = \rho V_{ex} \]

Ideal packing law for uncorrelated contacts:

\[ \rho = \frac{<c>}{V_{ex}} \]
Ideal packing law

Ideal packing law for uncorrelated contacts:

\[ \rho = \frac{\langle c \rangle}{V_{ex}} \]

\[ \langle c \rangle = \text{average contact number on a particle} \]

Particle volume fraction:

\[ \Phi = \rho V_p \]

\[ V_p = \text{particle volume} \]

\[ \Phi = \langle c \rangle \frac{V_p}{V_{ex}} \]

\[ \frac{V_p}{V_{ex}} = \text{fixed by particle shape.} \]

But do uncorrelated contacts exist in dense granular packings?
Long thin rods

Simulations

Experiments
Long thin rods

Random rod packing in the thin-rod limit.

Contact surface fraction \( \sim \frac{D^2}{DL} \sim \frac{D}{L} \); vanishes for \( \frac{L}{D} \to \infty \)

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

So for thin rods the ideal packing law \( \Phi = \frac{V_p}{V_{ex}} \) 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.
Random contact equation:

\[ 2\phi \frac{L}{D} \approx c \]

for \( L/D \gg 1; \; <c> \approx 10 \)
Random contact equation:

\[ 2\phi \frac{L}{D} \approx c \]

for \( L/D \gg 1; \quad <c> \approx 10 \)
Packing (ellipsoids)

Is there universality in the density maximum?
Colloidal rods (spheroids)

Experimental data at different [LiNO$_3$]:

- 10 mM
- 500 μM
- 150 μM
- no Salt

Simulations:

- Dorev et al.
- Wouterse et al.
Packing (rod-sphere mixture)

rod/sphere mixture:

\[ \sigma \uparrow \quad \text{sphere} \quad + \quad \text{spherocylinder} \]
Mechanical contraction method (MCM)

System:

\[ \sigma \uparrow \bigcirc \quad \text{(a) spheres} \]

\[ \text{D} \quad \text{L} \quad \text{(b) spherocylinders} \]

Procedure:

\[ V = 10^5 - 10^7 \]

\[ V - \Delta V \]

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

Dilute system is mechanically contracted until overlaps cannot be removed anymore. Result is a reproducible random packing density.
rate of overlap changing:

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

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 \(\rightarrow\) direction of overlap removal:

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

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

Packing (binary sphere mixture)


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

\[ \frac{D_l}{D_s} = 2.6 \]
Packing (binary sphere mixture)

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

M. Clusel et al., Nature, 2009

Packing (rod-sphere mixture)

composition: $x = 0.1$

L/D = 0
L/D = 1
L/D = 5
L/D = 10
Packing (rod-sphere mixture)

Composition: $x = 0.5$
Packing (rod-sphere mixture)

composition: $x = 0.5$
Packing (rod-sphere mixture)

composition: $x = 0.9$
Packing (rod-sphere mixture)

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 !
Packing (rod-sphere mixture)

composition: $x = 0.5$
Packing (bidisperse rod mixture)

Composition: \( x = 0.5 \)

\[ \frac{L_1}{D_1} = 3 \]

\( D_1 = D_2 \)

\( L_2 = 1 \)

A.V. Krylyuk and A.P. Philipse, in preparation
Packing (polydisperse rods)

Uniform length distribution

\[ f(L) = \frac{1}{L_{\text{max}} - L_{\text{min}}} \]

Averaged Aspect Ratio

Packing Fraction

Uniform length distribution
\((L_{\text{min}} = 0.1, L_{\text{max}} = 0.3 - 5.9)\)
Glass transition of near-spheres

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


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

Ideal MCT glass transition for hard ellipsoids

Ideal MCT glass transition for symmetric hard dumbbell systems

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

Ideal glass transition for rod-like particles

Conclusions

• Bernal packing of spheres: no ideality

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

• Non-monotonic 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