Columnar packings of soft spheres in rotating fluids

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Foams & Complex Systems
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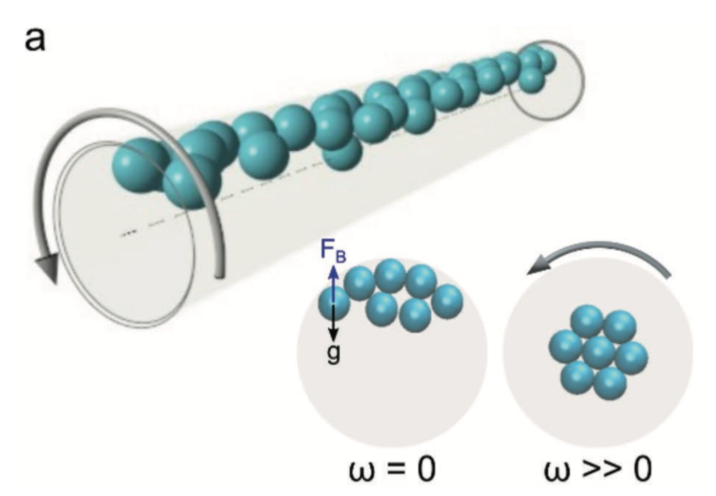
We present the simulation of ordered columnar packings of soft spheres based on enthalpy minimisation. Remarkable similarities have been observed with particles in rotating fluids that self-assemble into such packings.

Self-assembly of spherical particles in rotating fluids (credits to T. Lee et al):



Experiment:

- Polymeric beads of mass m suspended in a fluid of higher density
- Beads and fluid are then rotated with velocity ω inside a lathe

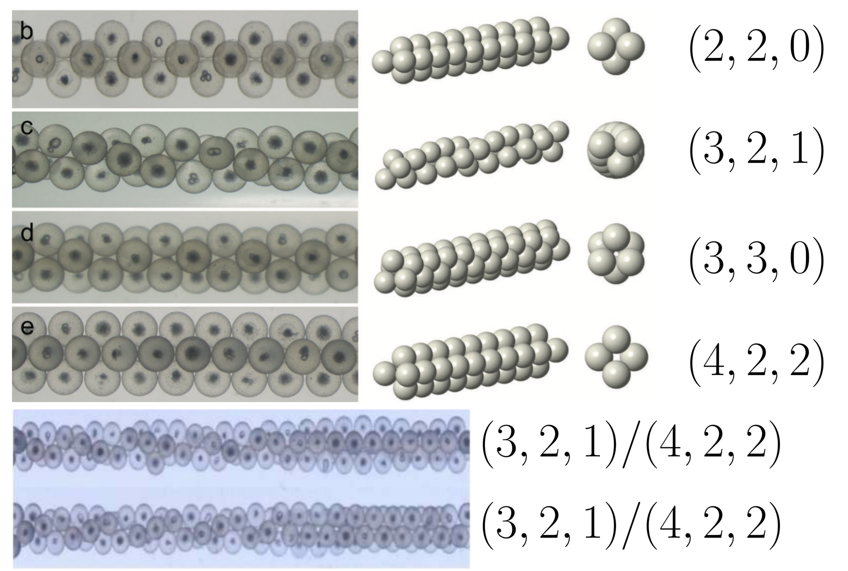
Simulation:

- Computationally intensive molecular dynamics simulation to reproduce experiment
- "partially latching spring model" for bead interaction

- Centripetal force moves beads to the center
- Rotational energy dependent on radial position R

$$E_{\text{rot}} = \frac{1}{2} m\omega^2 R^2$$

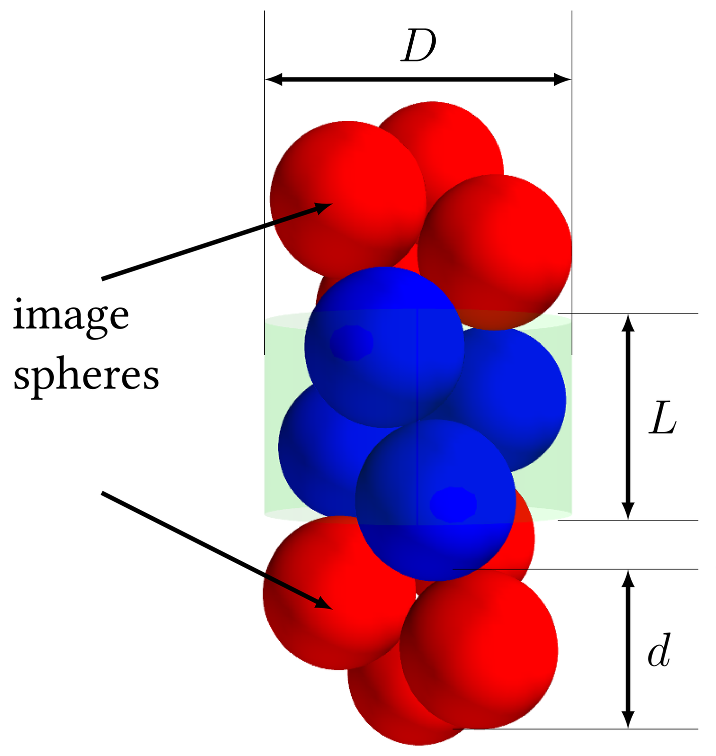
- **Self-assembled packings remarkably similar to ordered uniform structures**
- Mixed structures were observed



Different structures observed by Lee et al.

T. Lee, K. Gizynski, B.A. Grzybowski, *Non-equilibrium Self-Assembly of Monocomponent and Multicomponent Tubular Structures in Rotating Fluids.* Adv. Mater. **29**, 1704274, (2017).

Simulation based on enthalpy minimisation



Unit cell (blue) with image spheres (red).

- Enthalpy H:

$$H(\{\vec{r}_i\}, L) = \underbrace{\frac{1}{2}\sum_{ij}^{N} \varepsilon \delta_{ij}^2}_{\text{soft interaction}} + \underbrace{\frac{1}{2}\sum_{i}^{N} \varepsilon \rho_i^2}_{\text{wall confinement}} + \underbrace{pV}_{\text{pressure term}}$$

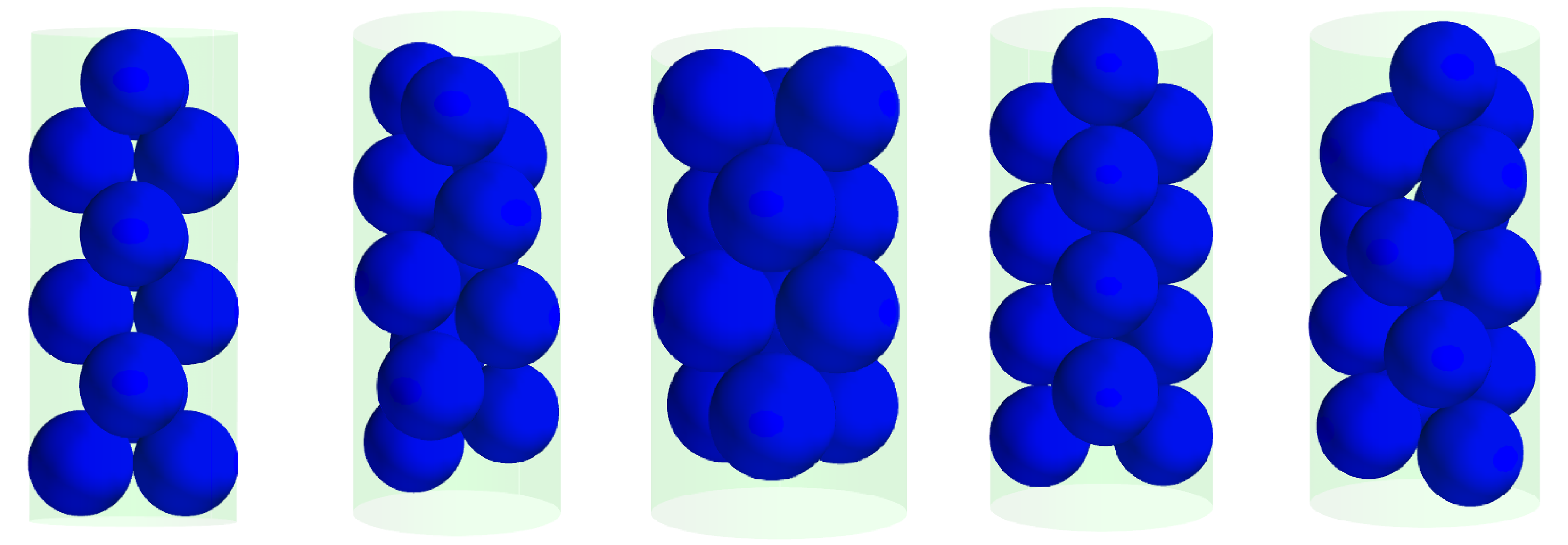
- Soft interaction depends on overlap δ_{ij}
- Soft wall confinement depends on wall overlap ρ_i
- Pressure term $pV = p\pi \left(\frac{D}{2}\right)^2 L$

- Periodic boundaries at top and bottom of unit cell

The Algorithm: Energy minimisation

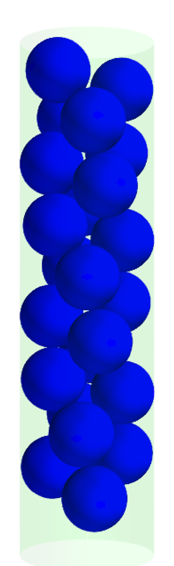
- Find energy minimum for given pressure p
- Basin-Hopping algorithm
  - Global Monte-Carlo type algorithm
- Conjugate Gradient algorithm
  - Local direct minimisation routine

Ordered uniform packings

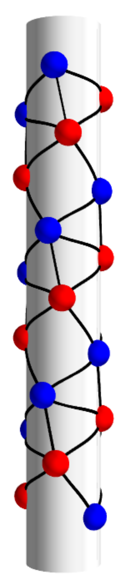


(2, 2, 0) (3, 2, 1) (3, 3, 0) (4, 2, 2) (4, 3, 1)

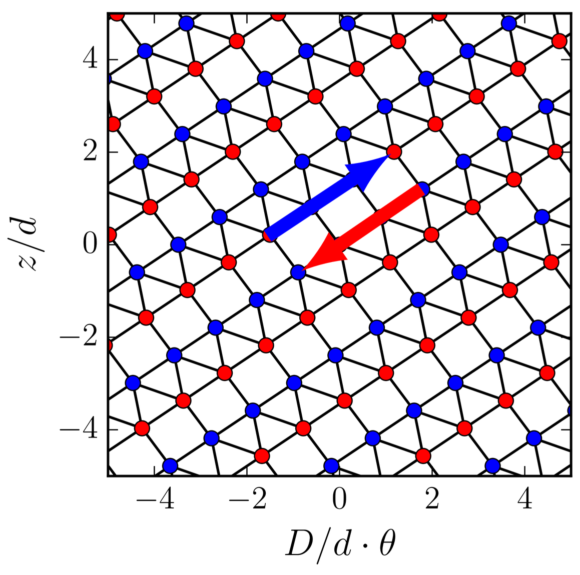
What is a line-slip structure?



Example of a line-slip packing.



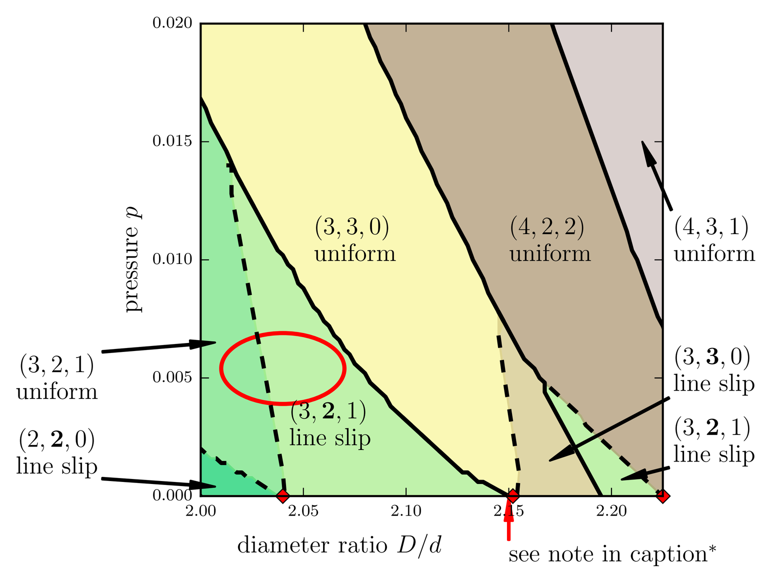
Contact network of the line slip.



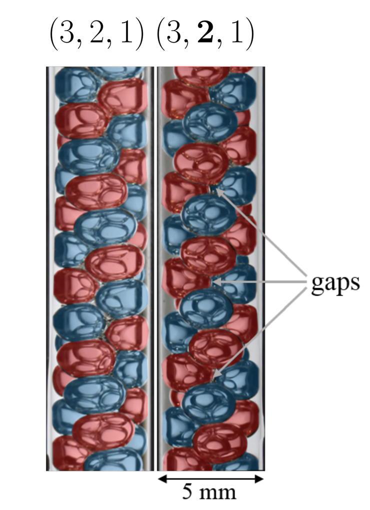
Rolled-out pattern of the contact network of the line slip.

- Line slips differ from ordered uniform structures by a loss of contact
- they are intervening structures between uniform structures
- Uniform packings are generated by sliding the red and blue line along the arrows

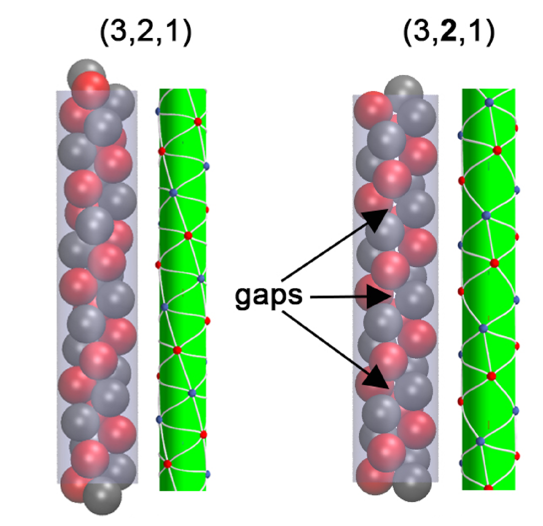
The simulation and observation of a $(3, 2, 1)$ line slip



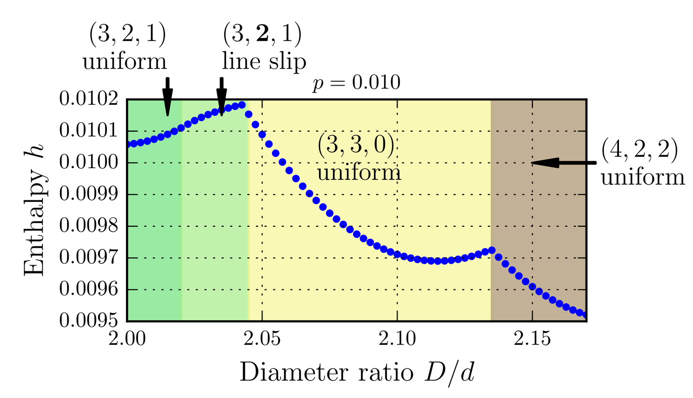
Computed phase diagram around the $(3, \mathbf{2}, 1)$ line slip. (*) $(\mathbf{3}, 2, 1)$ line slip (expected by hard sphere limit) not visible because of finite pressure.



Exp. observation of a $(3, \mathbf{2}, 1)$ in wet foams.



Simulation and contact network of a $(3, \mathbf{2}, 1)$ line slip.



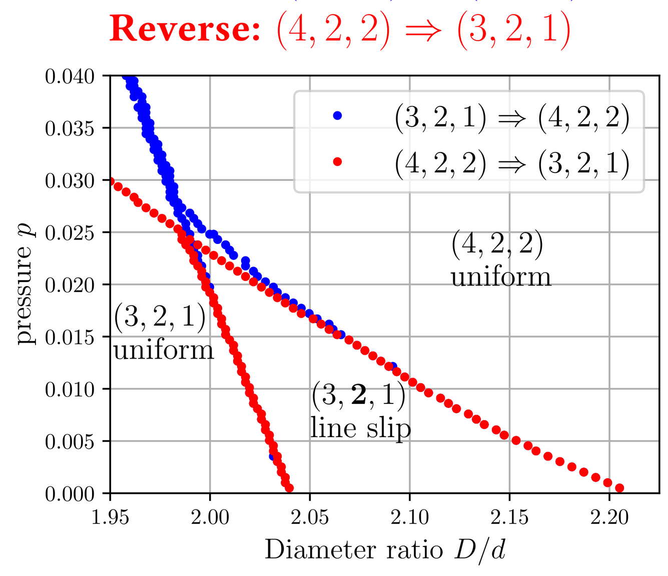
- Red circle represents position of exp. observation of the $(3, \mathbf{2}, 1)$ line slip
- $p = 0$ corresponds to hard sphere limit [7]
- Continuous transitions:
  - dashed lines in phase diagram
  - discontinuity in 2nd derivative of enthalpy
- discontinuous transitions:
  - solid lines in phase diagram
  - discontinuity in derivative of enthalpy

J. Winkelmann, B. Haffner, D. Weaire, A. Mughal and S. Hutzler, *Simulation and observation of line-slip structures in columnar structures of soft spheres.* Phys Rev E **96**, 012610, (2017).

Stability maps for a reversible transition

- Packings can be stable outside of regions given in phase diagram
- Experiments show **different transition sequence** from phase diagram due to local equilibrium
- Stability regions depend on history of structure ⇒ *Hysteresis*
- *Hysteresis* appears at the apex of the line slip region and above

Forward: $(3, 2, 1) \Rightarrow (4, 2, 2)$
Reverse: $(4, 2, 2) \Rightarrow (3, 2, 1)$



Stability regions for the $(3, 2, 1)$, $(3, \mathbf{2}, 1)$, and $(4, 2, 2)$ structures.

Coming soon: Columnar structures in a harmonic potential

Columnar sphere packings in rotating fluids can be simulated by confining the structures in a harmonic potential.

Full Simulation:

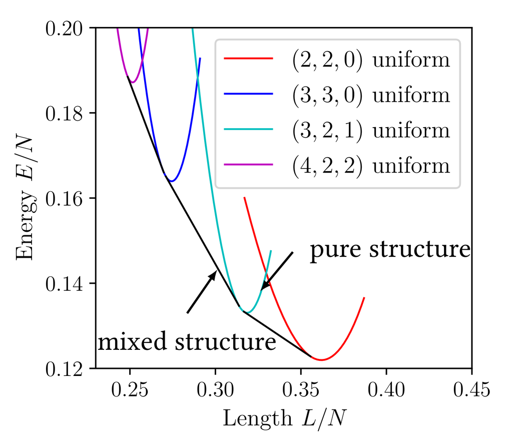
- Total energy E:

$$E(\{\vec{r}_i\}) = \underbrace{\frac{1}{2}k\sum_{ij}^{N} \delta_{ij}^2}_{\text{soft interaction}} + \underbrace{\frac{1}{2}m\omega^2 \sum_{i}^{N} r_i^2}_{E_{\text{rot}}}$$

- Periodic boundaries at top and bottom
- Minimise energy for given tube length L
- Simulates finite size system
- Use Basin-Hopping algorithm

Semi-analytic approach:

- Calculate energy $E(R)$ for specific structure and minimise with respect to R



- Mixed structures lie on common tangent
- Calculation for infinite systems

Do line slips appear in the self-assembly of spherical particles in rotating fluids?

References

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