Theory of rotational columnar structures of soft spheres

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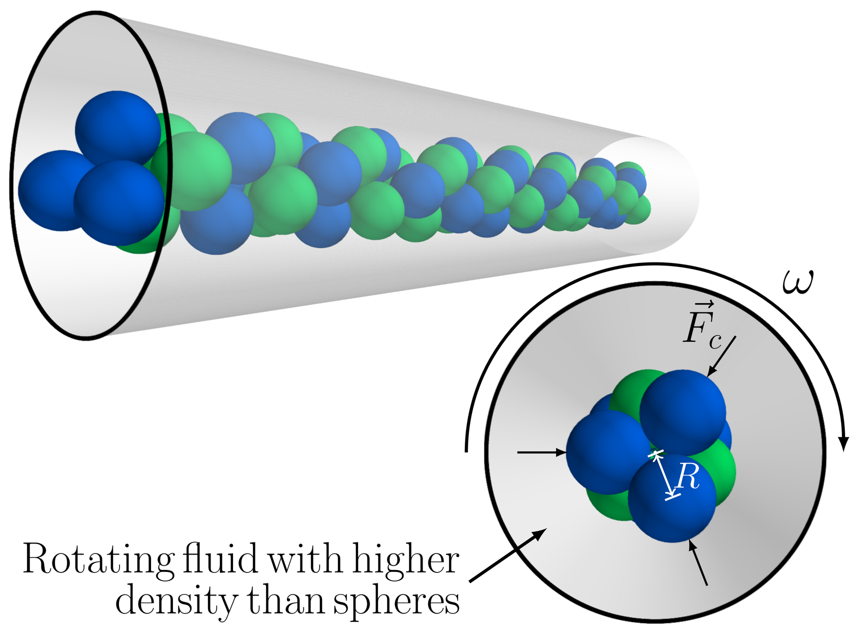
Experiments & simulations by Lee *et al.*: Columnar structures in a rotating fluid



A novel self-assembly method

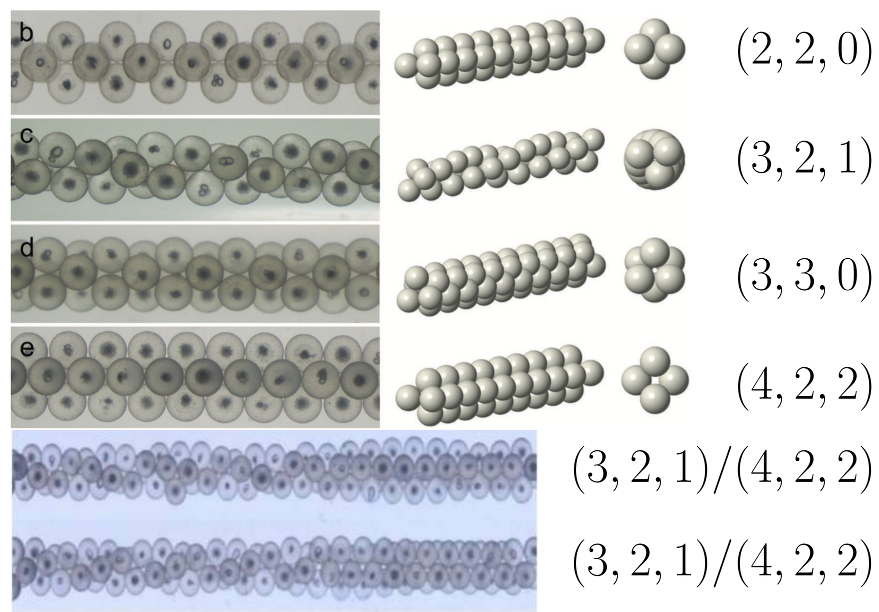
Experiment:
- Polymeric beads of mass M and diameter d suspended in a fluid of higher density
- System rotates with velocity ω inside lathe

Simulation:
- *Intensive* molecular dynamics simulation to reproduce experiment
- Bead interaction: hard sphere model

- Centripetal force $\vec{F}_c$ moves beads to the centre
- Rot. energy depends on radial displacement R

$$E_{\mathrm{rot}}(R) = \frac{1}{2} M\omega^2 R^2$$

- Homogeneous structures and binary mixtures observed for varying ω and number density ρ

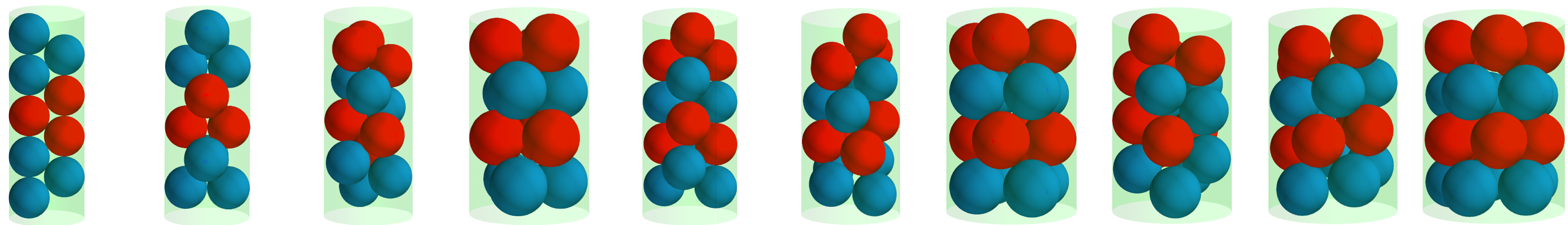


Homogeneous columnar packings and binary mixtures [Lee *et al.*].

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).

We present comprehensive *analytic* energy calculations for self-assembled columnar packings, based on a generic soft sphere model, from which we obtain a phase diagram with *peritectoid* transition points.

Ordered homogeneous packings



$(2,1,1)$ $(2,2,0)$ $(3,2,1)$ $(3,3,0)$ $(4,2,2)$ $(4,3,1)$ $(4,4,0)$ $(5,3,2)$ $(5,4,1)$ $(5,5,0)$

Analytic soft sphere energy calculations

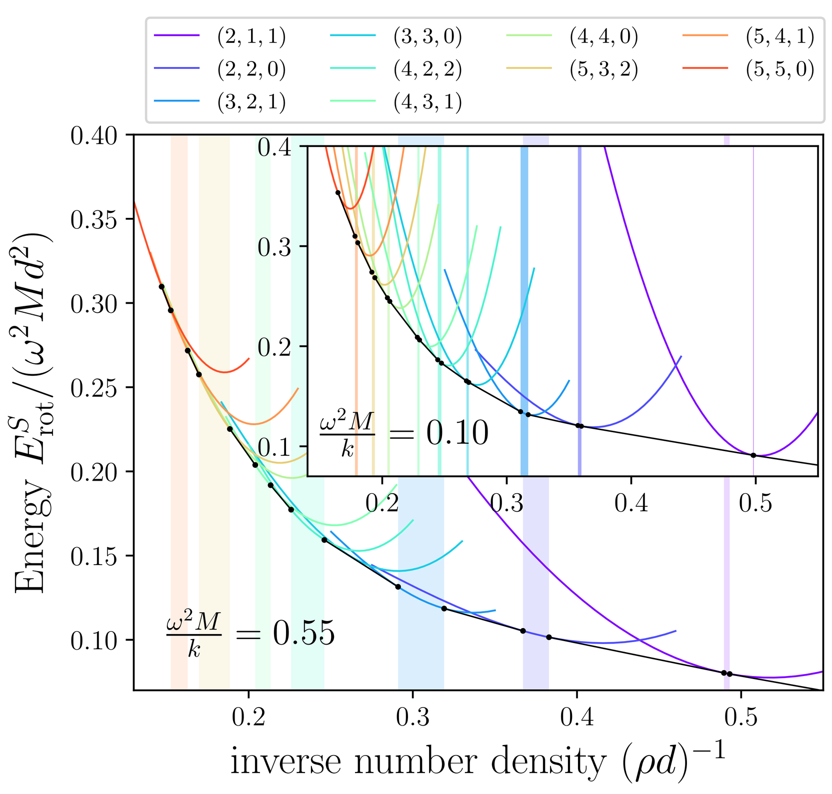
A comprehensive way to describe columnar structures

- Energy for homogeneous structures

$$\frac{E^S(R)}{M\omega^2 d^2} = \underbrace{\frac{1}{2}\frac{R^2}{d^2}}_{\text{rot. Energy}} + \underbrace{\frac{1}{2}\frac{k}{M\omega^2}\left\langle \left(\frac{\delta_{ij}}{d}\right)^2 \right\rangle}_{\text{soft sphere energy}}$$

  - soft sphere energy depends on overlap δ_{ij}
  - $\left\langle (\delta_{ij}/d)^2 \right\rangle$ calculated for each structure
- Energy minimisation w.r.t. to only R

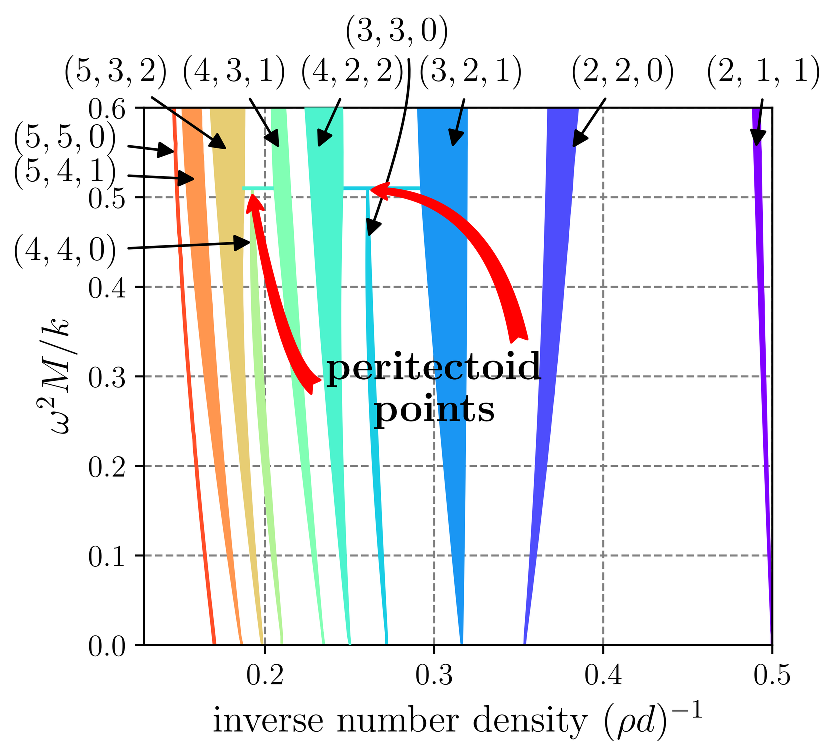
- Homogeneous structures: Minimal energies given by coloured curves within coloured regions
- Binary mixtures: Energies given by **common tangent** within white regions (Maxwell construction)



Minimal energies of homogeneous (coloured) and mixed (black) structures.

The phase diagram

Which structures occur under what conditions?



- Homogeneous structures: coloured area
- Binary mixtures: white area in-between

- Chiral structure can store energy by twisting, but achiral structure cannot

$\Rightarrow$ Achiral $(3,3,0)$ and $(4,4,0)$ structures vanish in peritectoid points

⋆ **Peritectoid point**:
  - Homogeneous structure vanish together with adjacent binary mixtures
  - New binary mixture of adjacent homogeneous structure occurs above

- $(5,5,0)$ last structure without inner spheres $\Rightarrow$ no left hand boundary

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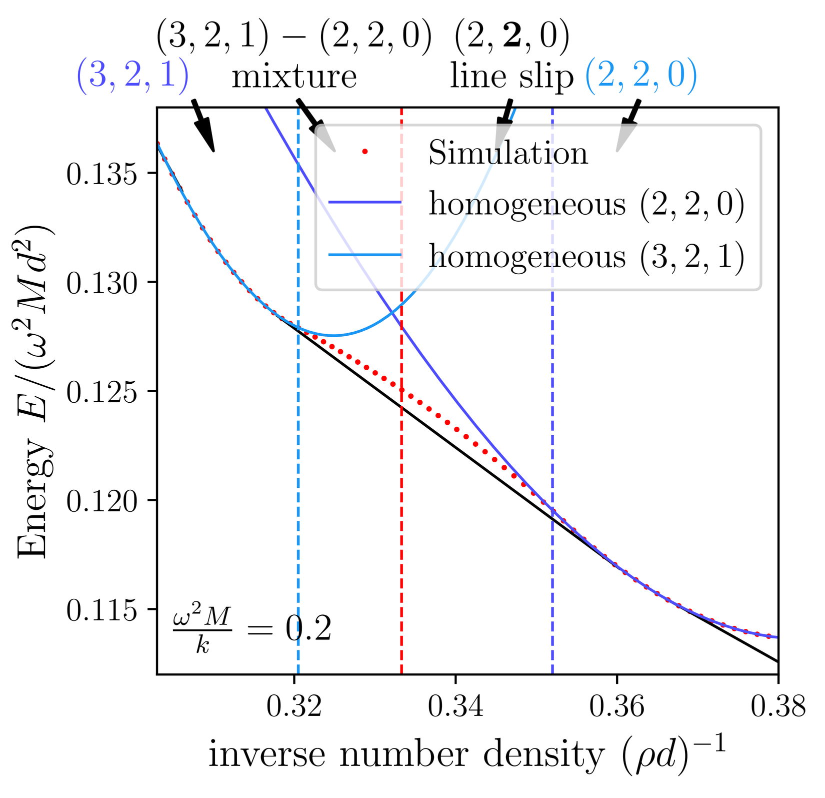
Soft sphere simulations for finite sample size



Energies of finite-size simulation (red dots) and analytic calculations (blue/purple curves).

The "full" soft sphere energy model:

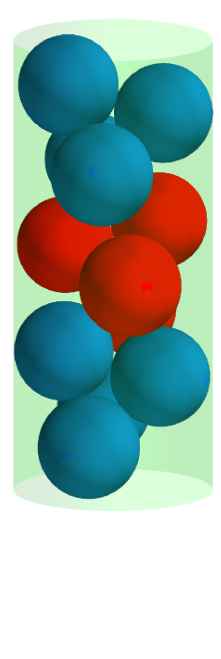
$$\frac{E(\{\vec{r}_i\},\alpha)}{M\omega^2 d^2} = \frac{1}{2}\sum_i^N \left(\frac{R_i^2}{d^2}\right)^2 + \frac{1}{2}\frac{k}{M\omega^2}\sum_{ij}^N \frac{|\vec{r}_i - \vec{r}_j|^2}{d^2}$$

- Simulation cell length L containing N spheres $\Rightarrow \rho = N/L$
- periodic boundaries with translated and twisted image spheres
- Energy minimisation w.r.t. to *all* sphere positions $\vec{r}_i$ and twist angle α

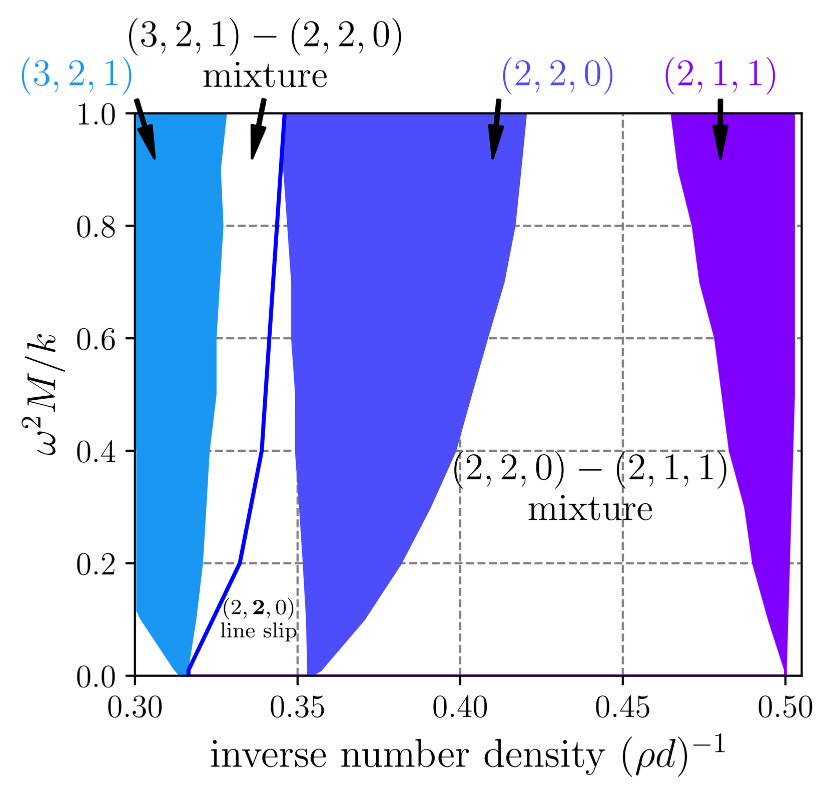
Energy and phase diagram comparison:
- Energy deviations for binary mixtures due to **interface energies**
- New structure occurs due to finite-size effect: homogeneous $(2,\mathbf{2},0)$ line slip

To-do list for the future:

1. Finit-size simulations: Extend phase diagram
2. Lathe experiments with soft spheres: Compare with theory



$(2,\mathbf{2},0)$ line slip



Phase diagram of the finite-size simulations.

References

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