Formation of Complex Spherical Packing Phases in Hard Spheres with SALR Interactions

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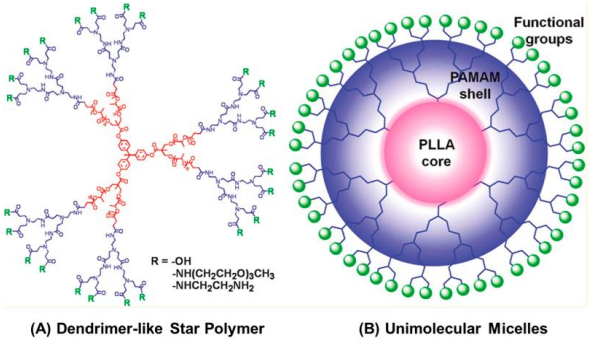
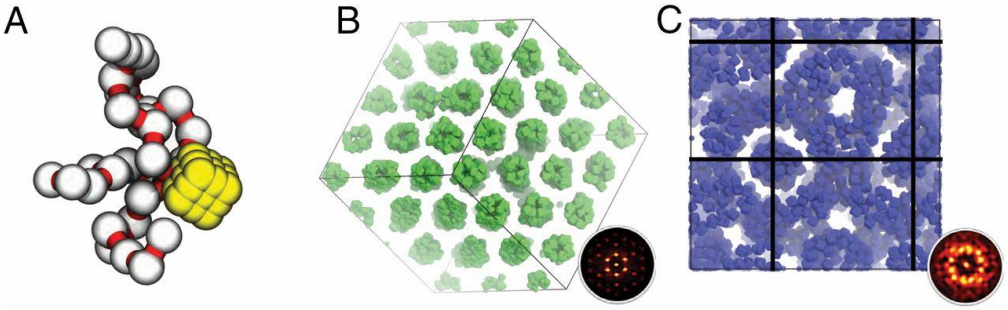
Introduction

Self-Assembly & Spherical Packing

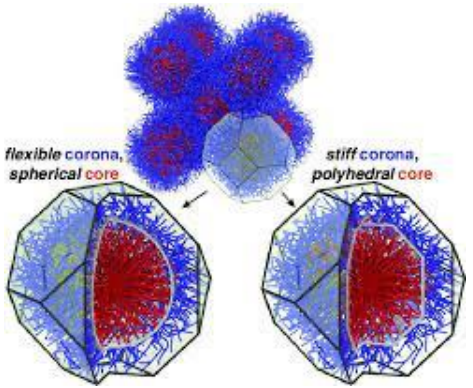
- Order from disorder
- Spherical packing hierarchy:
  - Clustered ‘Mesoatoms’ form
  - Mesoatoms deform and pack onto crystal lattice



D.A. Tomalia, L.S. Nixon, and D.M. Hedstrand, Biomolecules **10**, 642 (2020).



K. Yue *et al.*, Proc. Nat. Acad. Sci. USA **113**, 50 (2016).

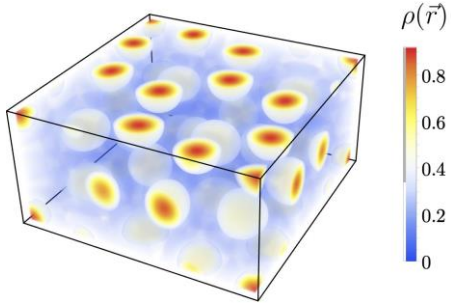


A. Reddy *et al.*, Proc. Nat. Acad. Sci. USA **115**, 41 (2018).

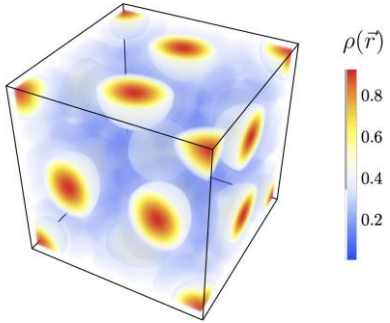
Introduction

Frank-Kasper Phases

- Class of complex spherical packing phases with 2 or more unique units.
  - Di-block copolymers
  - Giant surfactants
  - Aqueous surfactant solutions
- Stability depends on the cost to form domains of different sizes and shapes.



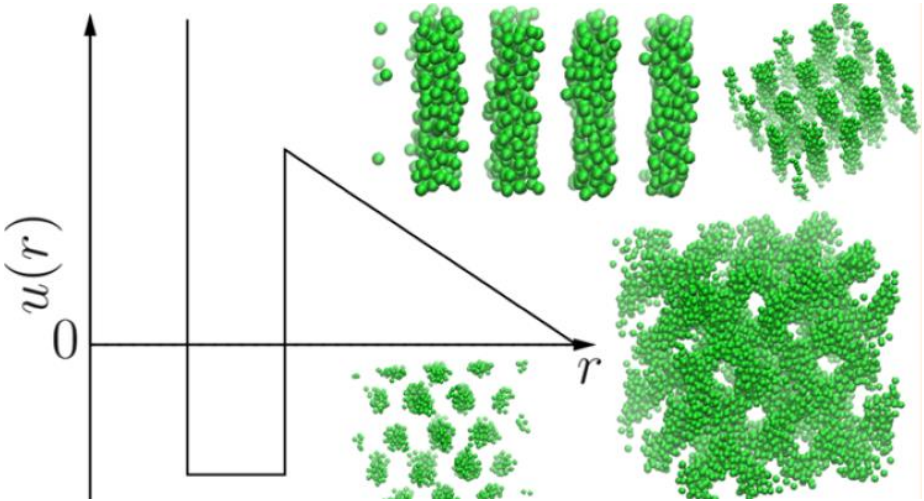
σ Phase



A15 Phase

Model

Colloidal Hard-Spheres with SALR



- Cluster crystal spherical packing phases can be formed by colloids with inter-particle interactions.
- Short-range attraction long-range repulsion (SALR) interaction potential
- Do F-K phases appear in this generic system?

Y. Zhuang, and P. Charbonneau, J. Phys. Chem. B **120**, 32 (2017).

Method

Density Functional Theory

- Classical DFT: Free energy as a functional of the density profile.

Grand potential density:

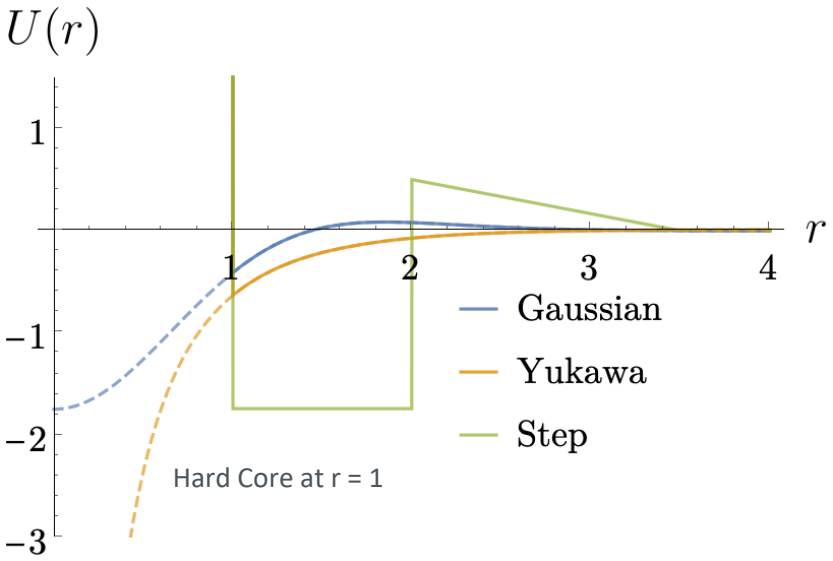
$$\eta = \frac{\pi \rho(\vec{r}) \sigma^3}{6}$$

$$\Omega = \frac{\Phi}{k_B T V} = \frac{1}{V} \int d\vec{r} \rho(\vec{r}) \left[\ln \rho(\vec{r}) - \mu - 1 + \frac{\eta(4-3\eta)}{(1-\eta)^2} \right] + \frac{1}{2 k_B T V} \int d\vec{r} \int d\vec{r'} \rho(\vec{r}) \rho(\vec{r'}) U(\vec{r} - \vec{r'})$$

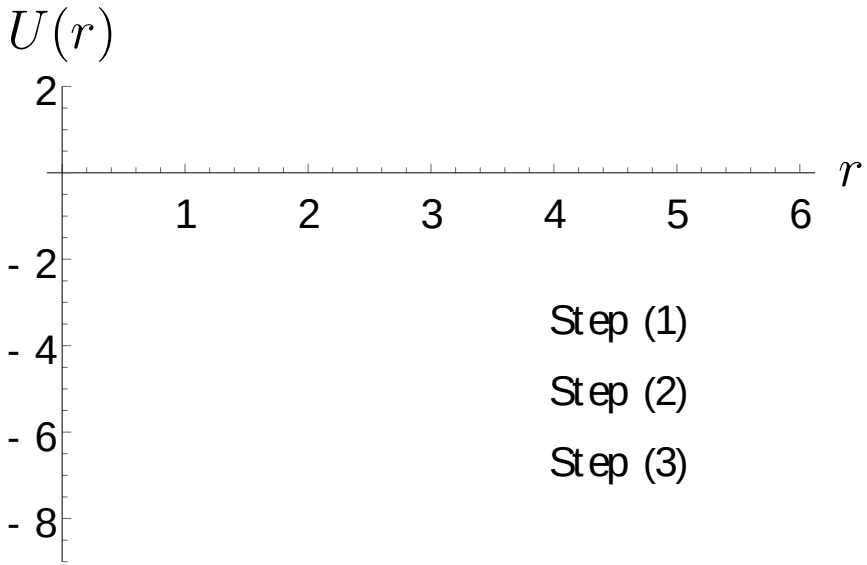
- Initialize with a density profile → iterative minimizing algorithm → converge stable/meta-stable cluster crystal phase.
- Search for F-K Stability

Method

SALR Interaction Potentials



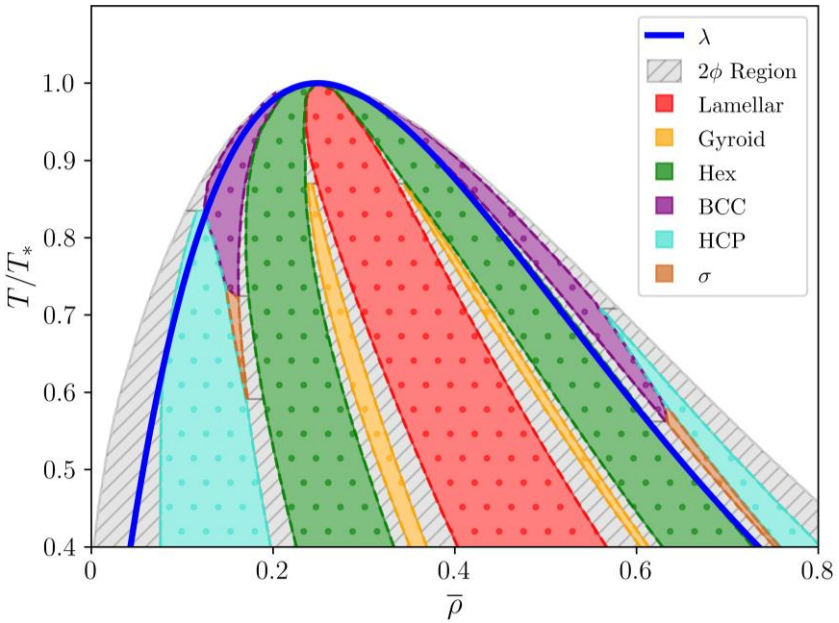
3 SALR Potentials



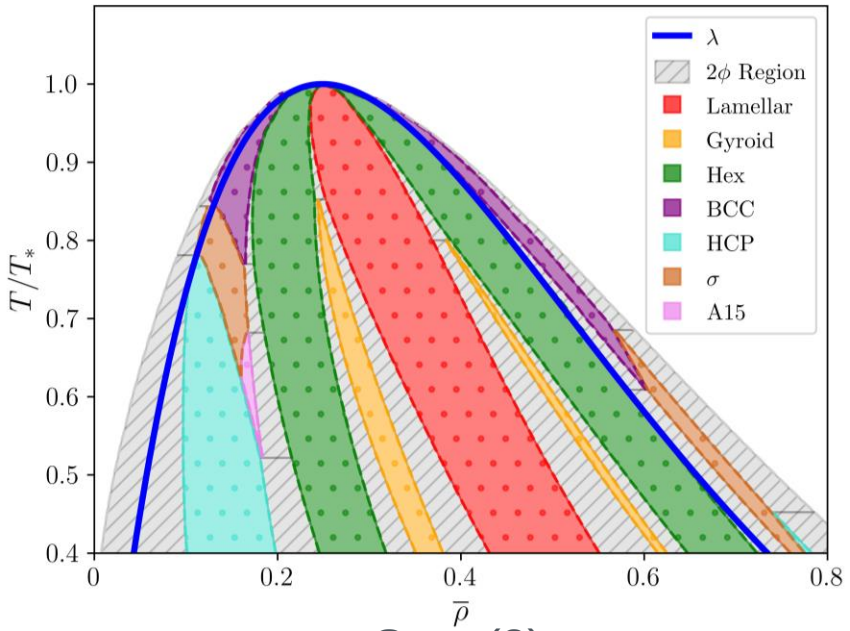
Specific Generic Step Potentials

Results

Phase Diagrams



Step (1)

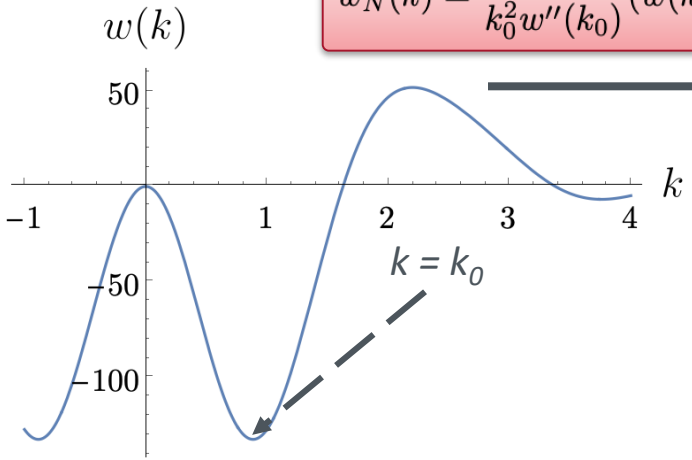


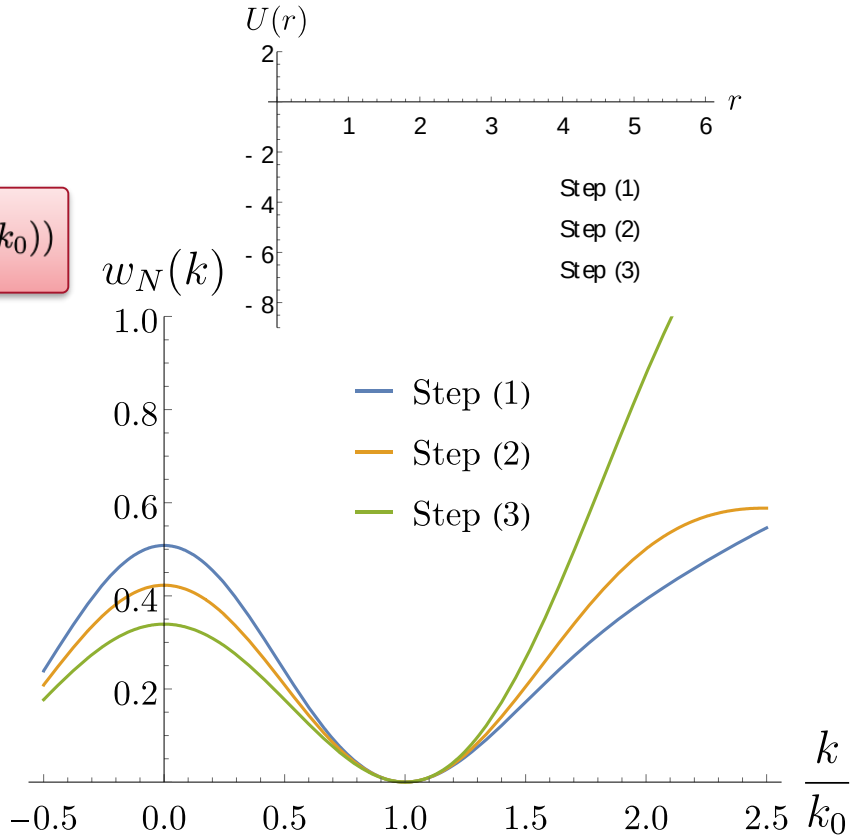
Step (3)

Results

Potentials in Fourier Space

$$w_N(k) = \frac{2}{k_0^2 w''(k_0)}(w(k_0 k) - w(k_0))$$





Interparticle Potential After Fourier Transform

Summary

- F-K A15 and σ phases are stable for some SALR interaction potentials
- The windows of stability are sensitive to the interaction potential parameters
- Analyzing the Fourier Transform of the potential may offer predictive power for the stability of F-K phases.