

Coarse-grained modelling of complex systems:

From molecular fluids to colloidal particles

Carlos Avendaño

Department of Chemical Engineering and Analytical Science

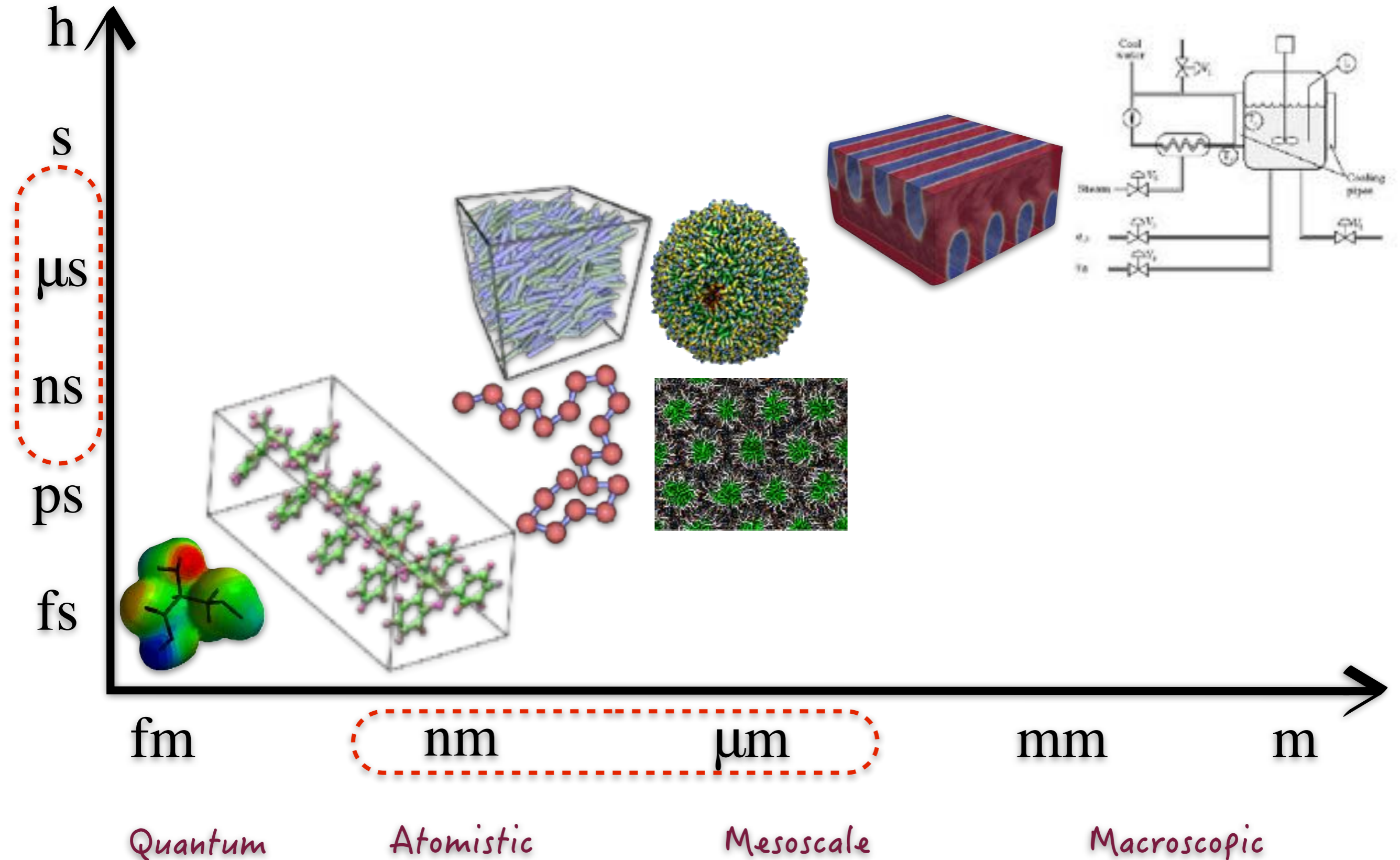
The University Manchester

carlos.avendano@manchester.ac.uk

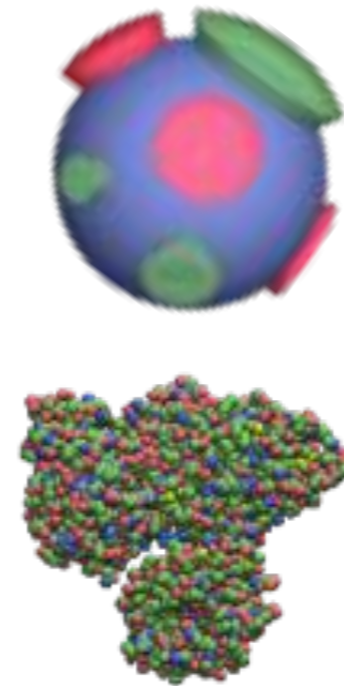
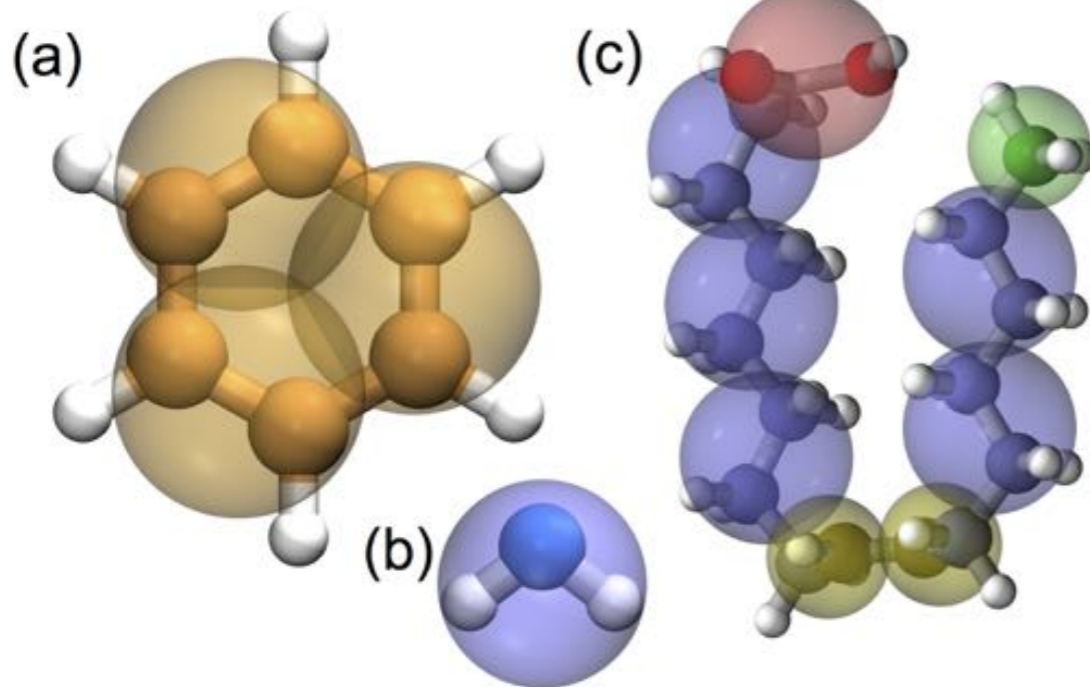
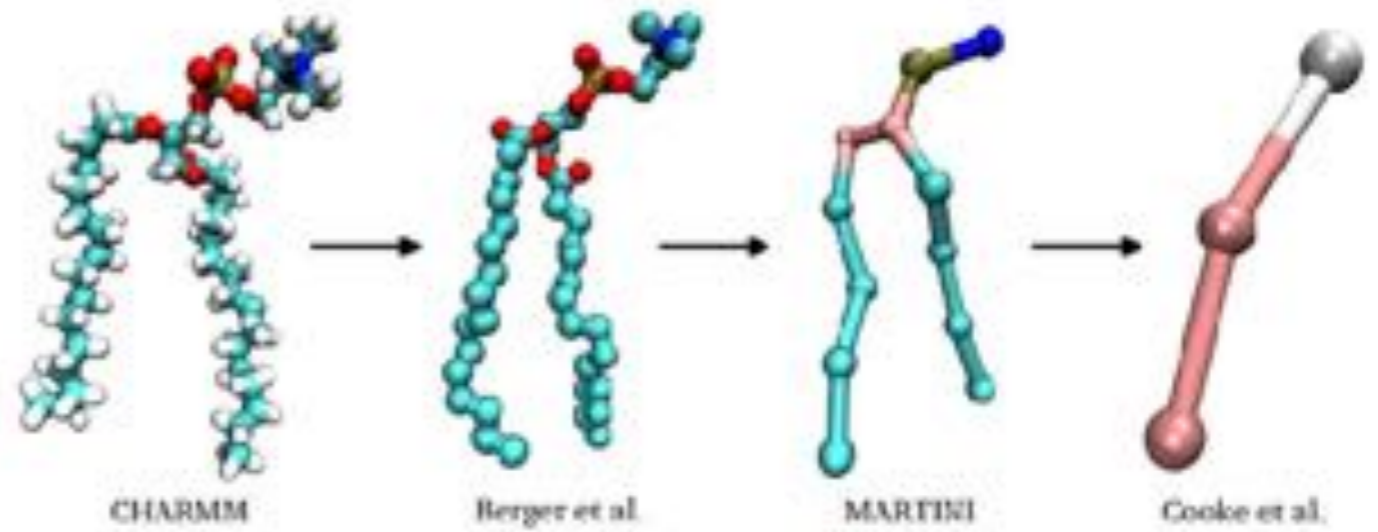
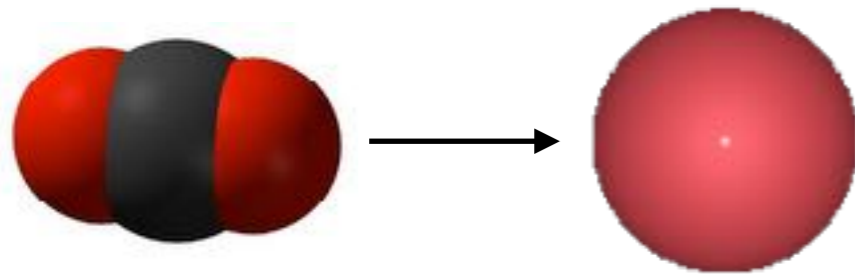
- **Coarse-grained (CG) models**
- **Self-assembly of colloidal particles**
 - ▷ Self-assembly of convex particles
 - ▷ Self-assembly of non-convex particle: Engineering macroporous ordered materials
- **CG models for molecular system**
 - ▷ Statistical Associating Fluid Theory
 - ▷ SAFT- γ force field

Coarse-grained (CG) modelling

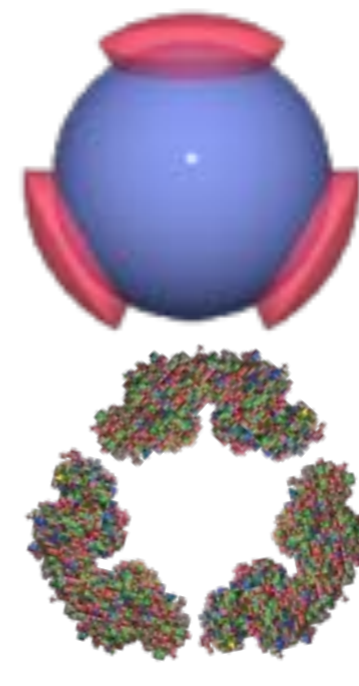
The University of Manchester



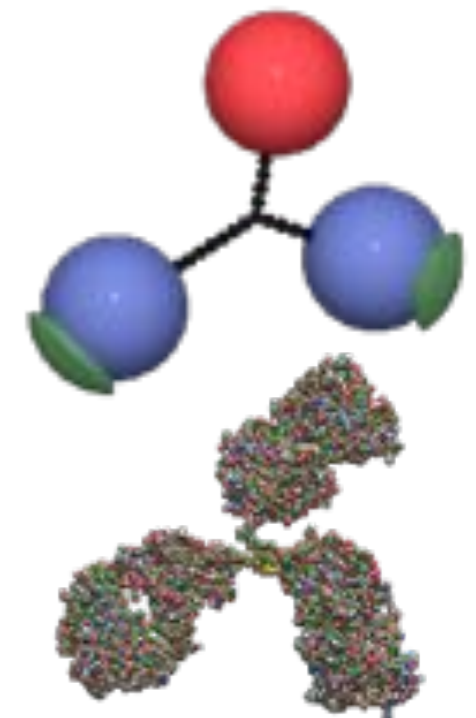
Coarse-grained (CG) modelling



Globular protein
(serum albumin)



Trimer protein aggregate
(annexin V)



Antibody
(Immunoglobulin G)

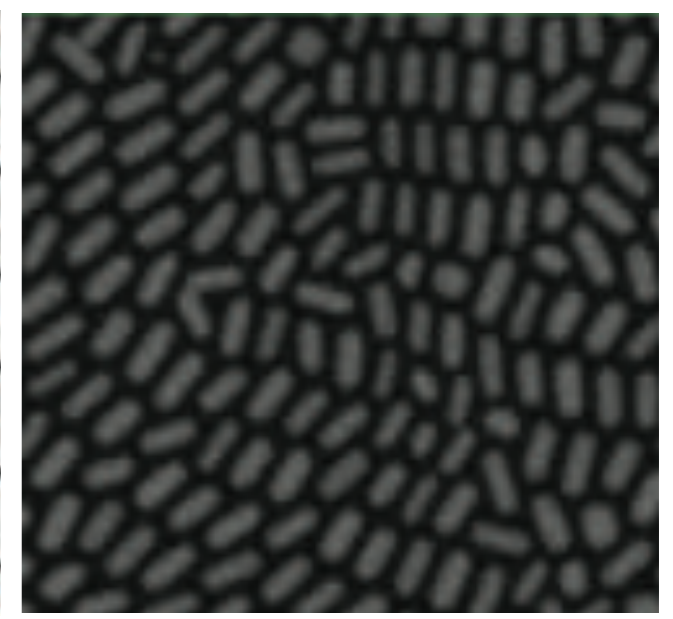
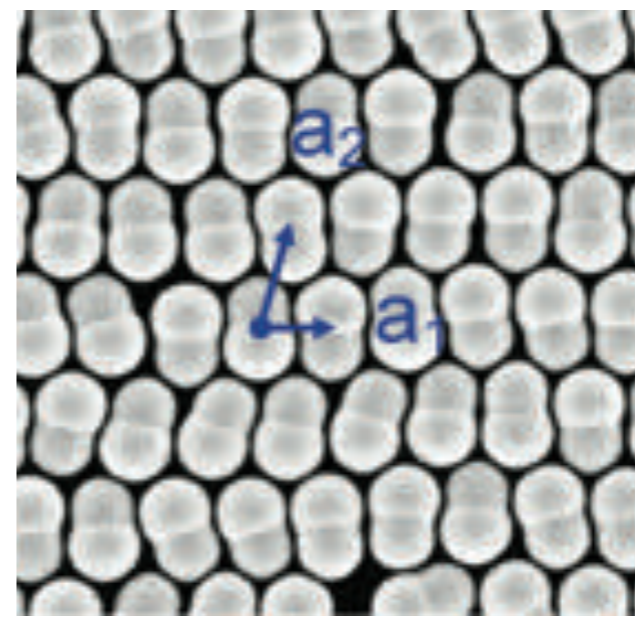
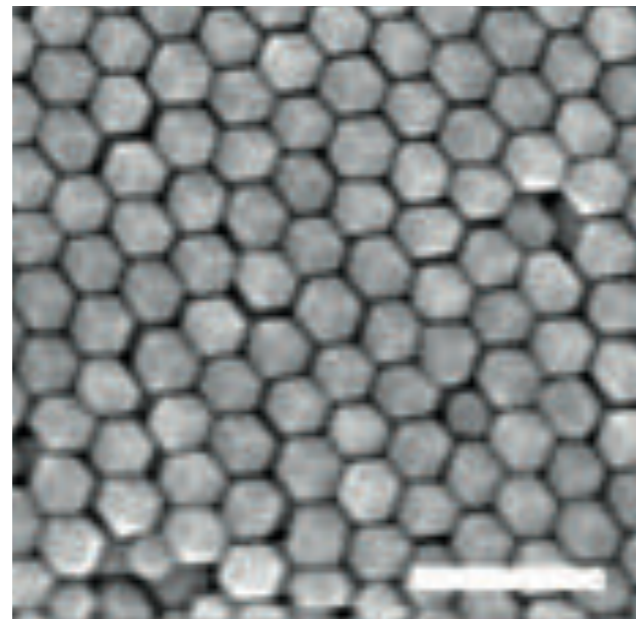
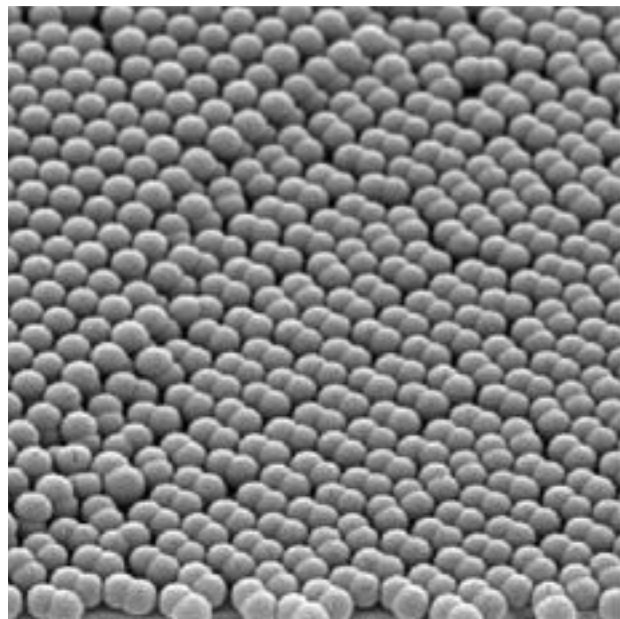
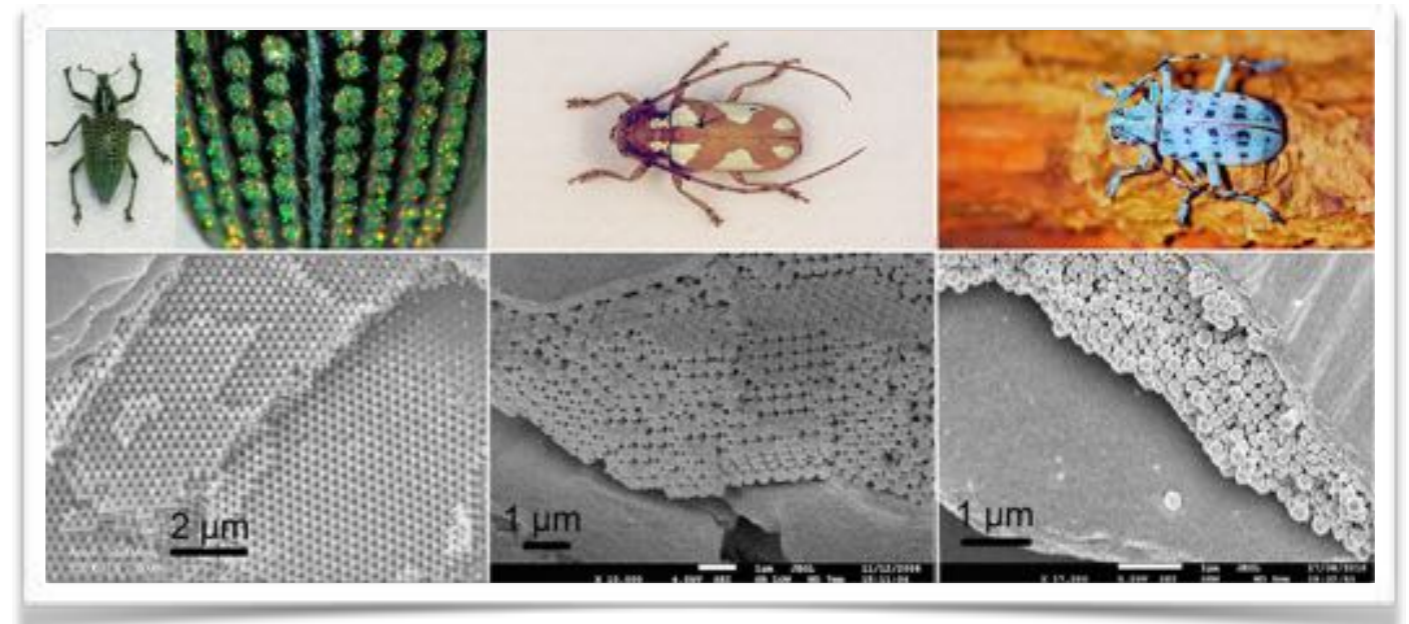
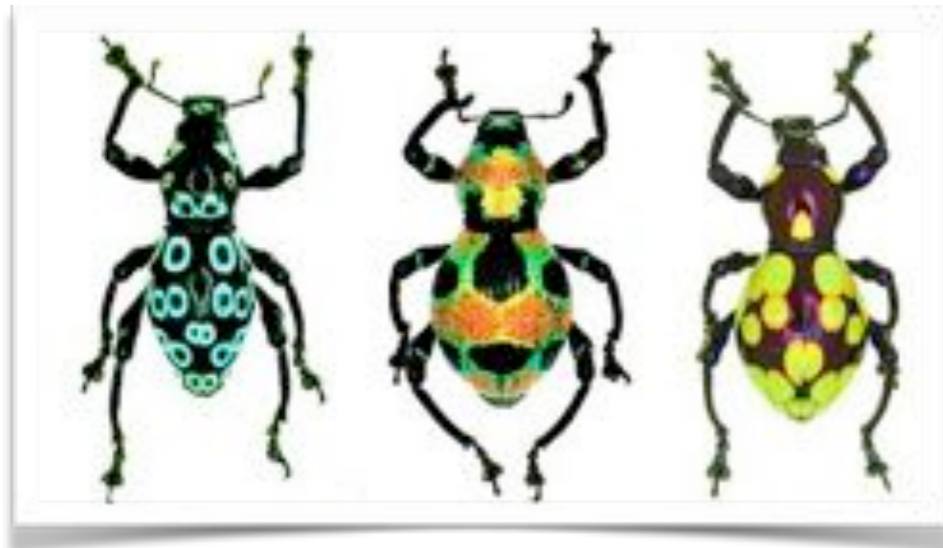
Coarse-grained (CG) modelling



Museo del Prado, Madrid
Museo Picasso, Barcelona

Self-assembly of colloidal particles

Self-assembly of colloidal particles



JP Vigneron and P Simonis, *Physica B*, 2012, 407, 4032

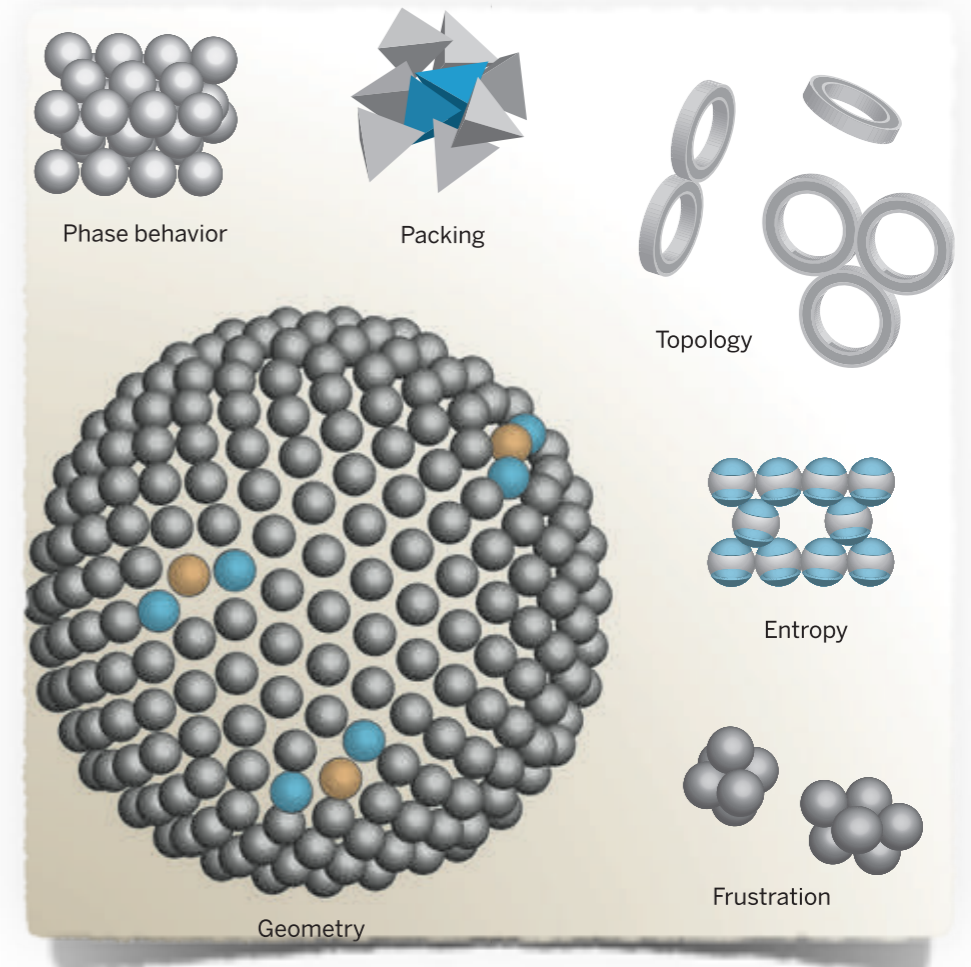
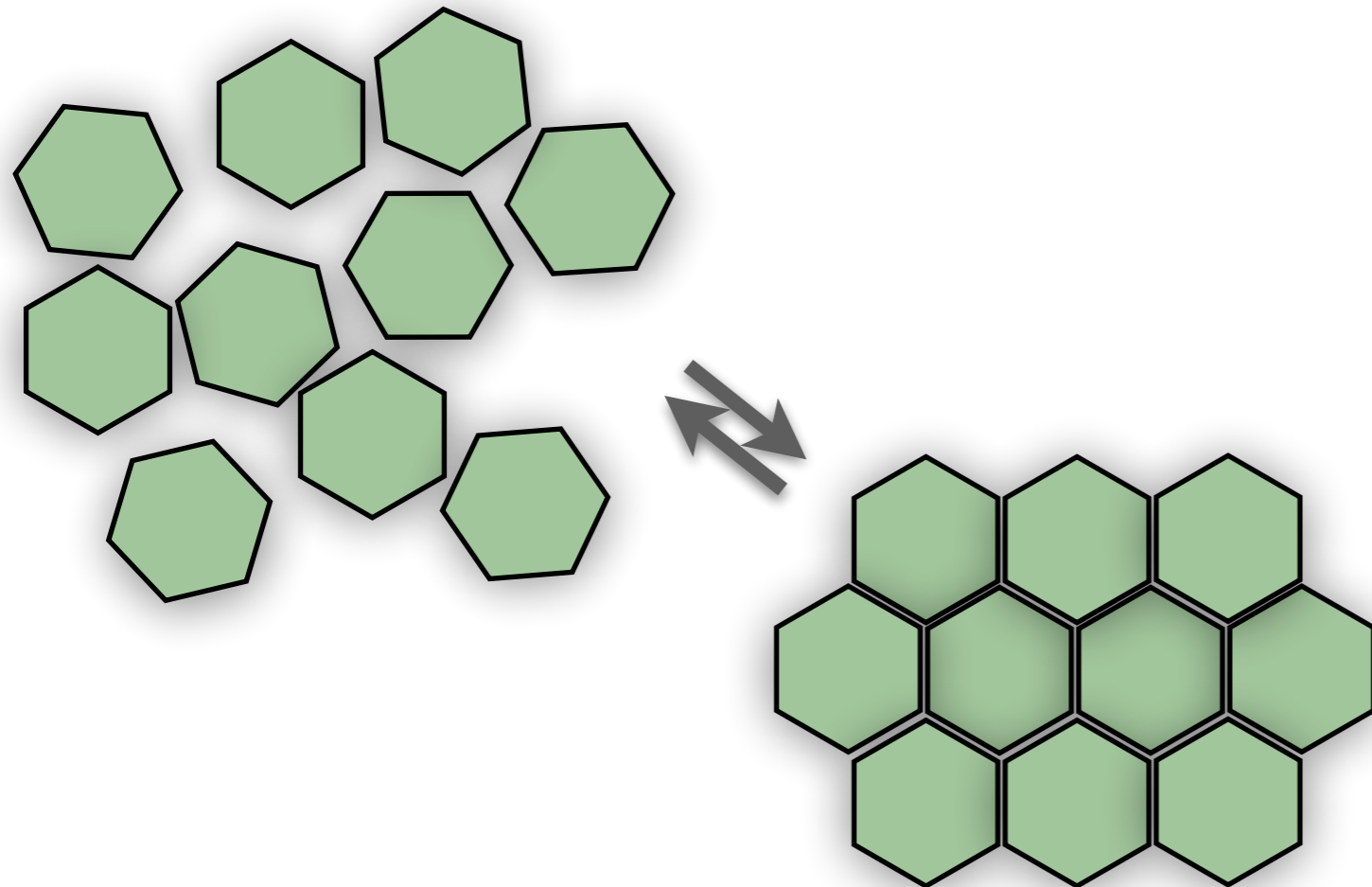
Young et al., *Angew. Chem. Int. Ed.* 2013, 52, 13980

Hosein and Liddell, *Langmuir* 2007, 23, 10479

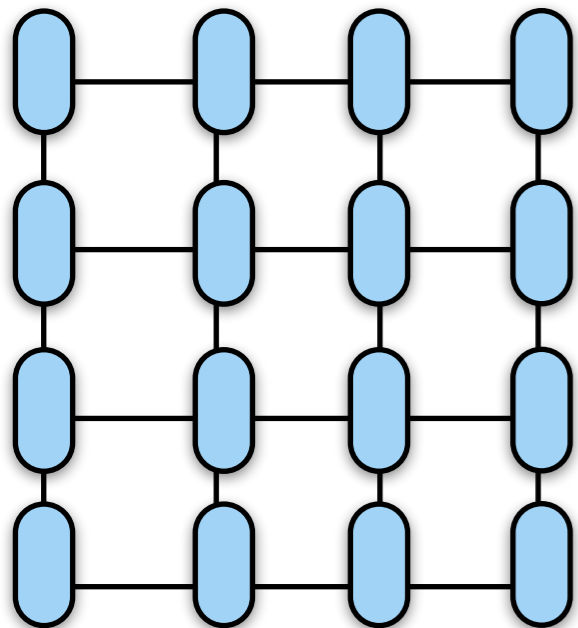
Ng et al, *ACS Nano* 2012, 6, 925

Whitesides and Boncheva, *PNAS*, 2002, 99, 4769

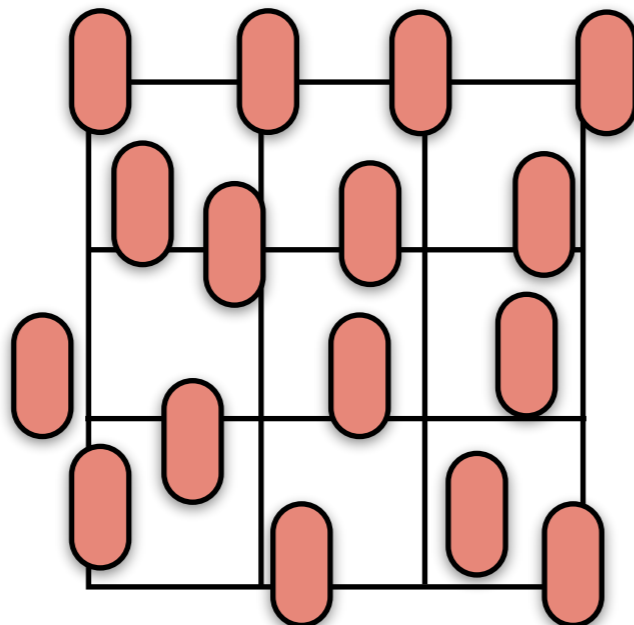
Self-assembly of colloidal particles



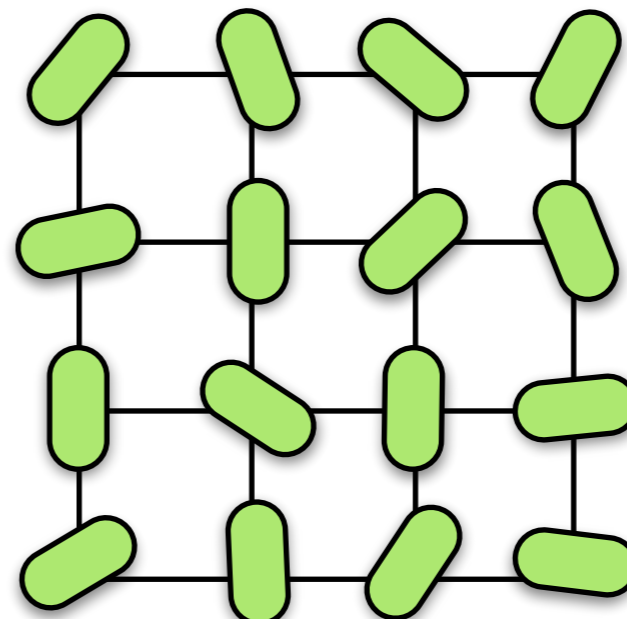
Crystal



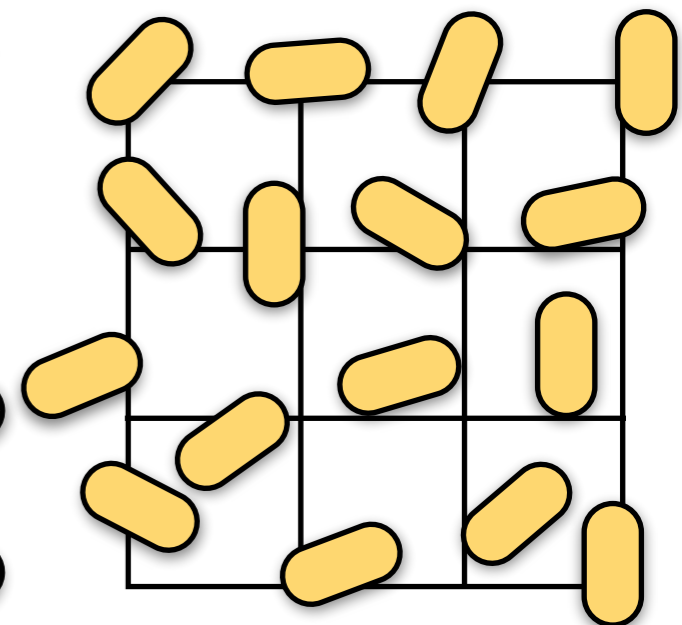
Liquid crystal



Plastic crystal

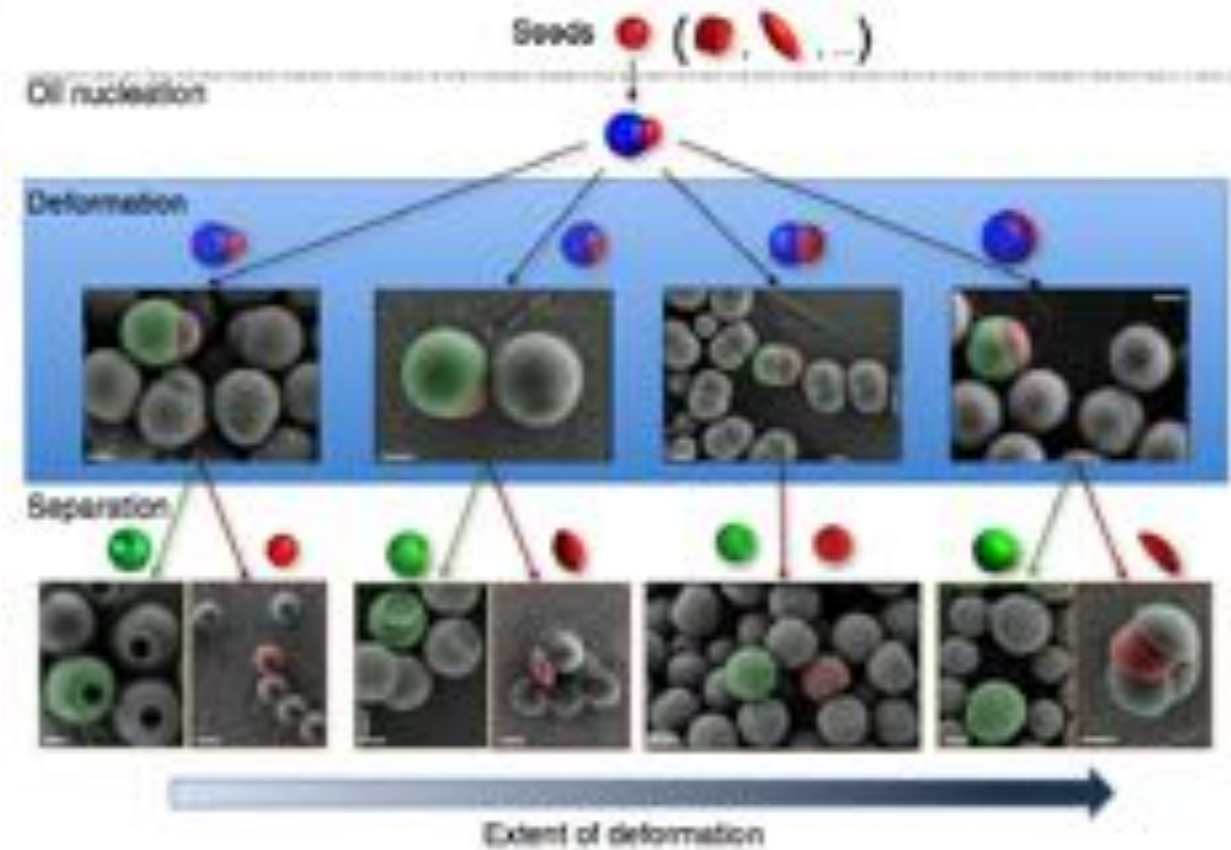
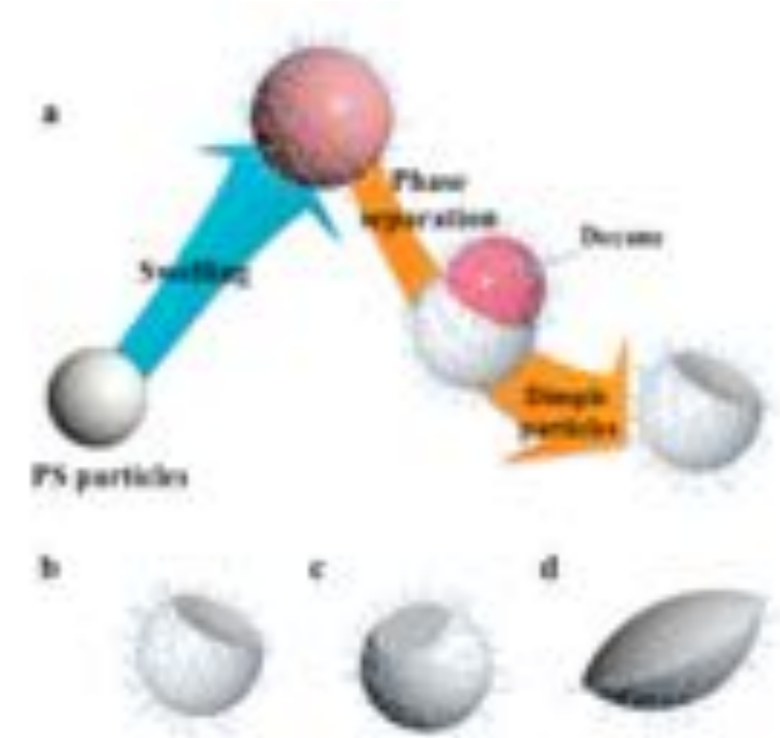
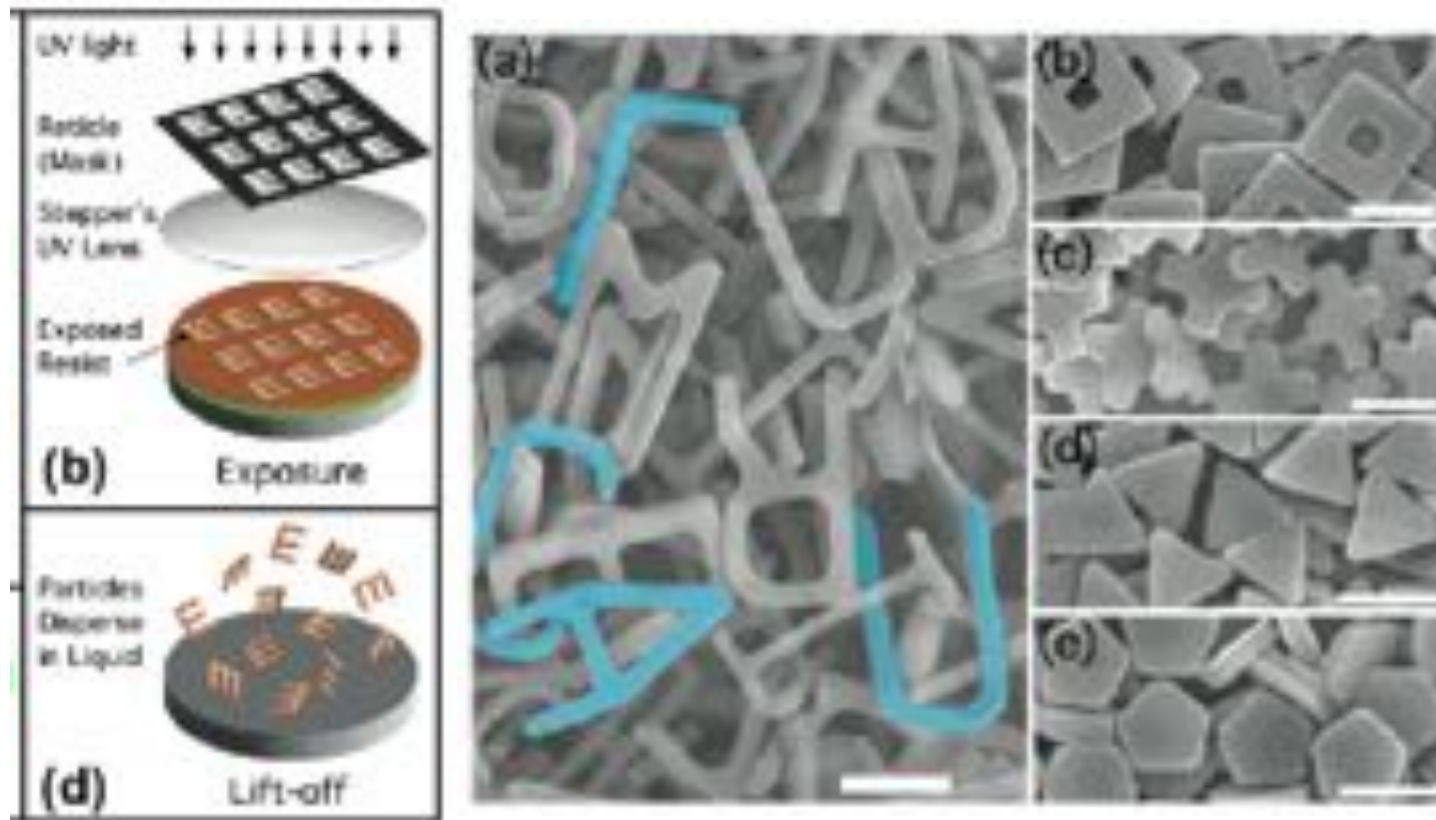


Isotropic



Lithography

Mason's group @ UCLA



Swelling and phase separation

Pine's group @ NYU

Self-assembly of colloidal particles



$$\phi = \frac{\pi}{3\sqrt{2}} \approx 0.74048\dots$$



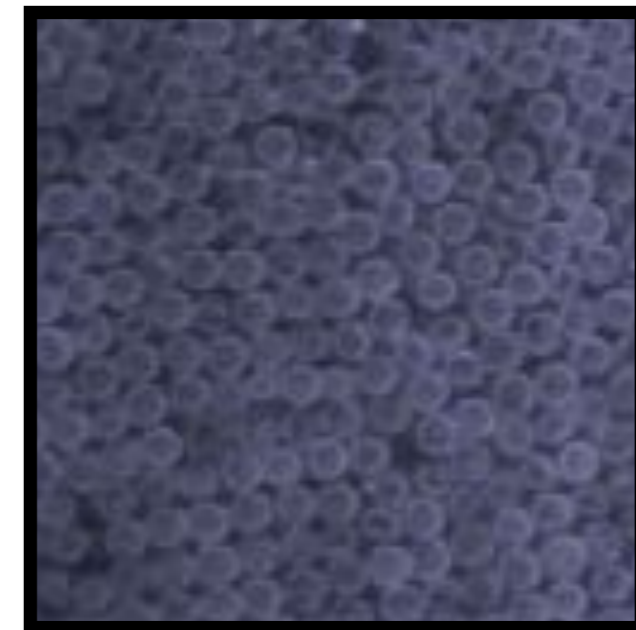
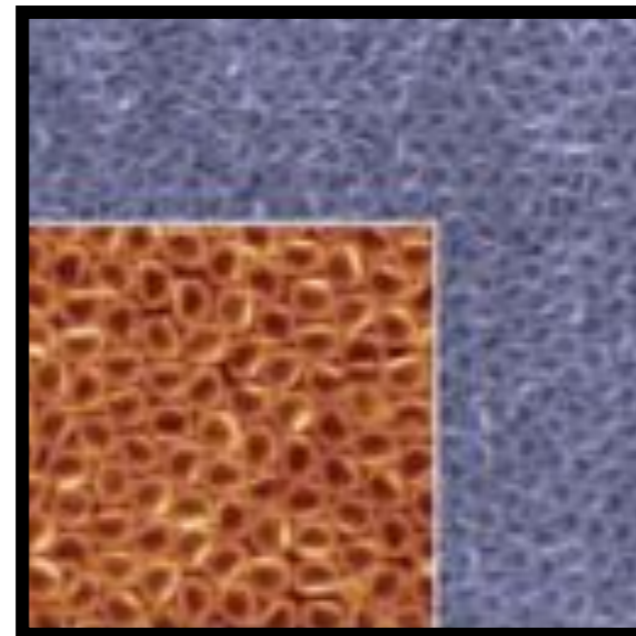
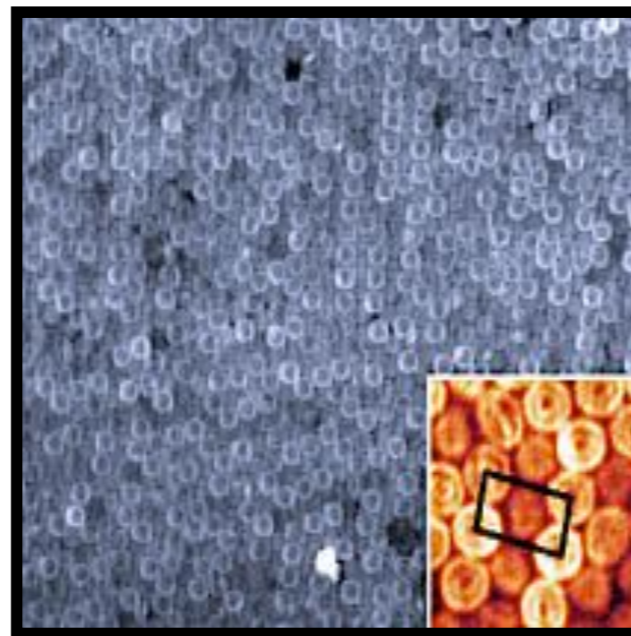
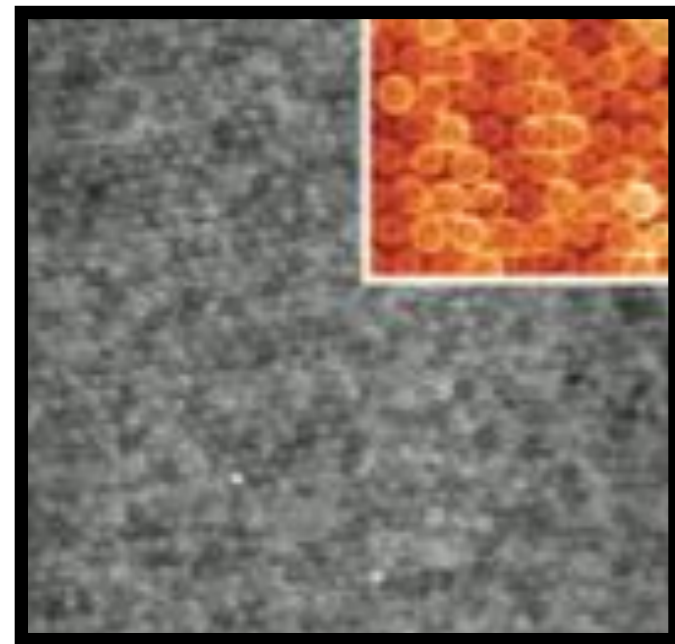
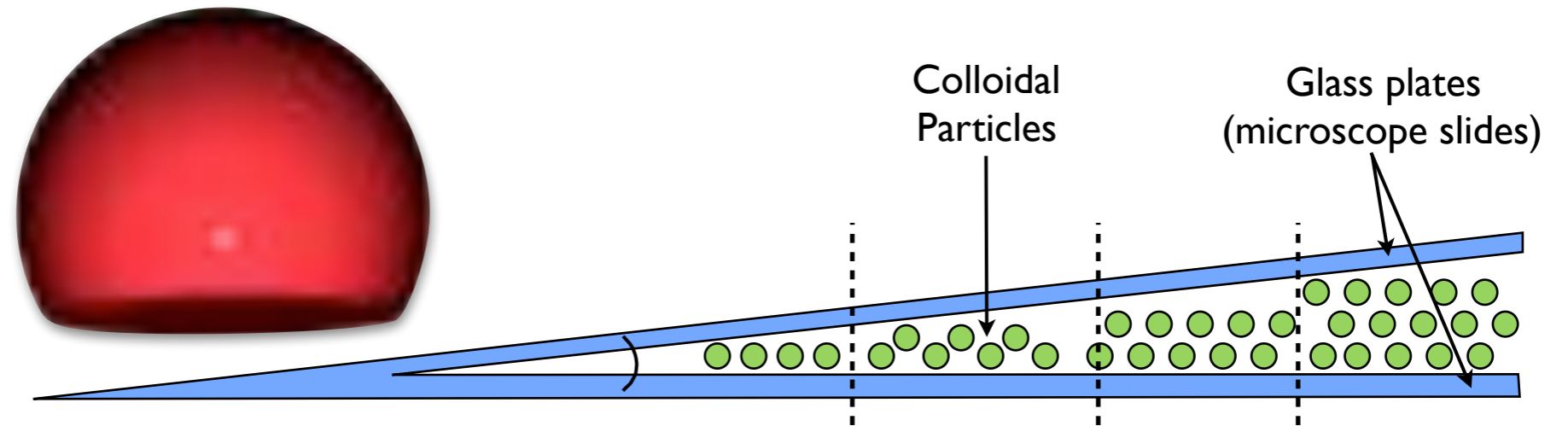
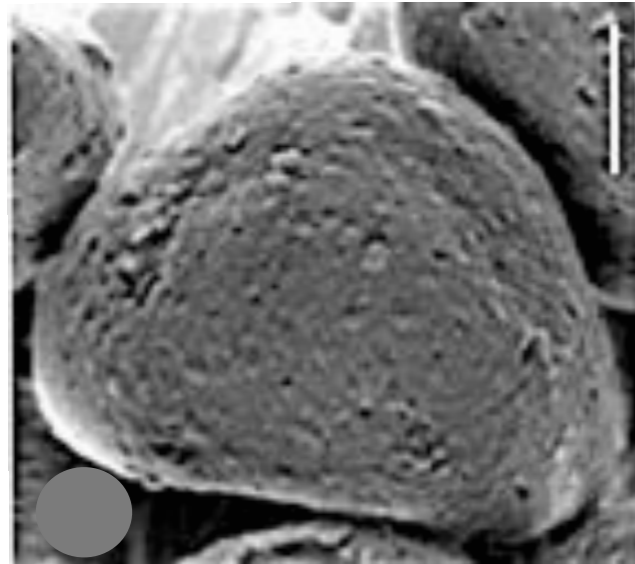
Kepler (1611) conjecture.

Proved by Thomas Hale (1998)

$$\min - \phi(r_1^\lambda, r_2^\lambda, r_3^\lambda, \dots, r_N^\lambda; \theta_1, \theta_2, \theta_3, \dots, \theta_N; \Gamma)$$

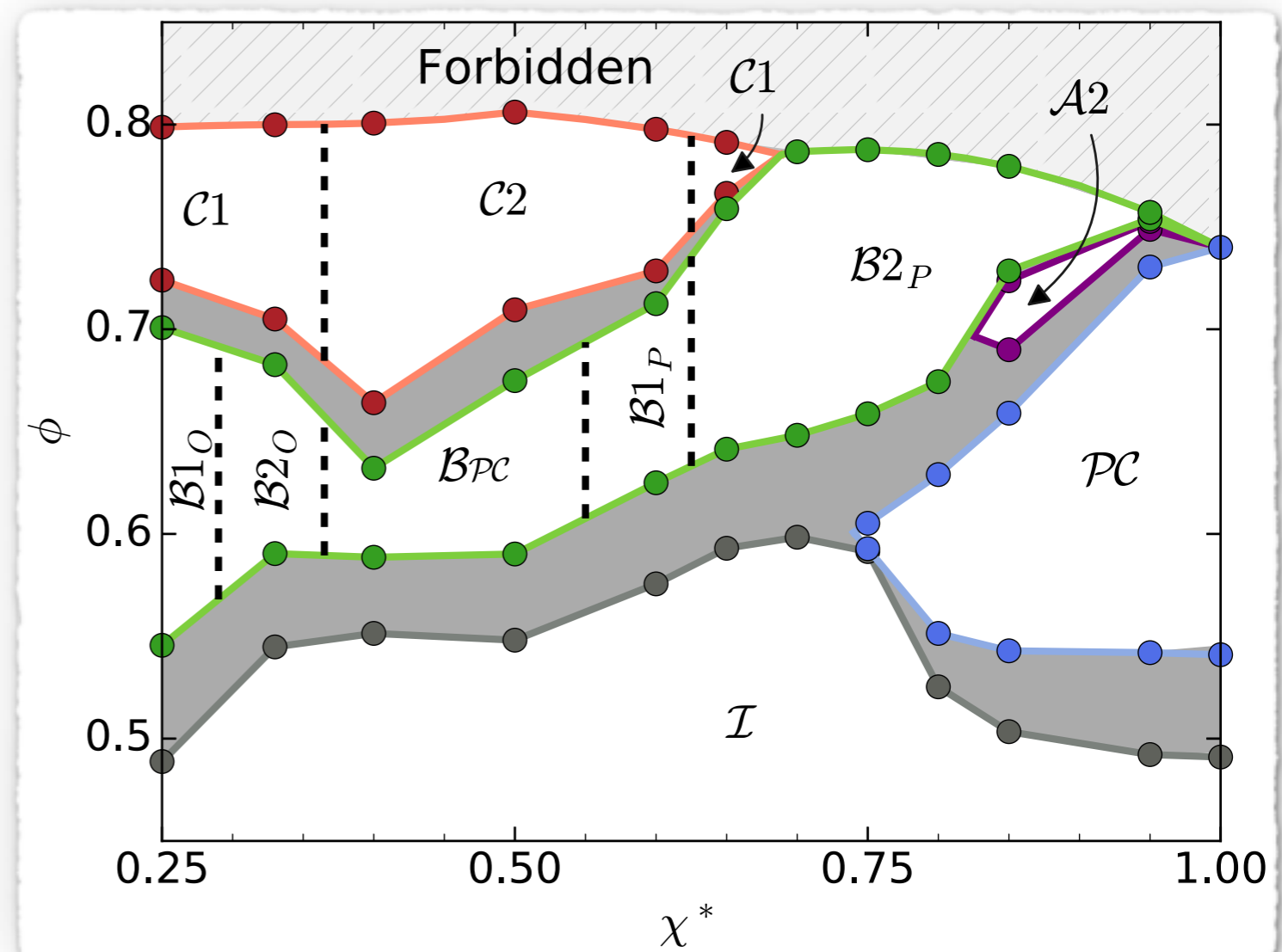
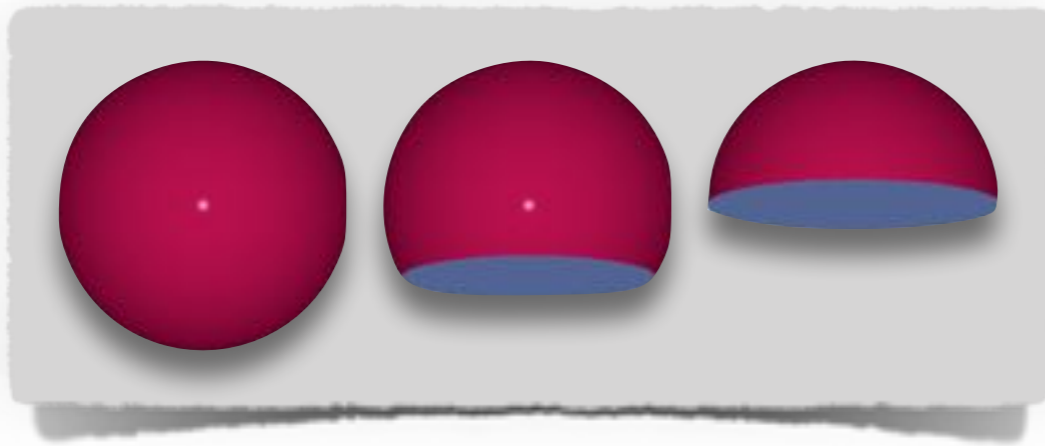
such that $(S_i \cap S_j) \subseteq (\Gamma_i \cup \Gamma_j) \quad \forall i, j = 1, 2, 3, \dots, N, i \neq j$

Self-assembly of convex particles

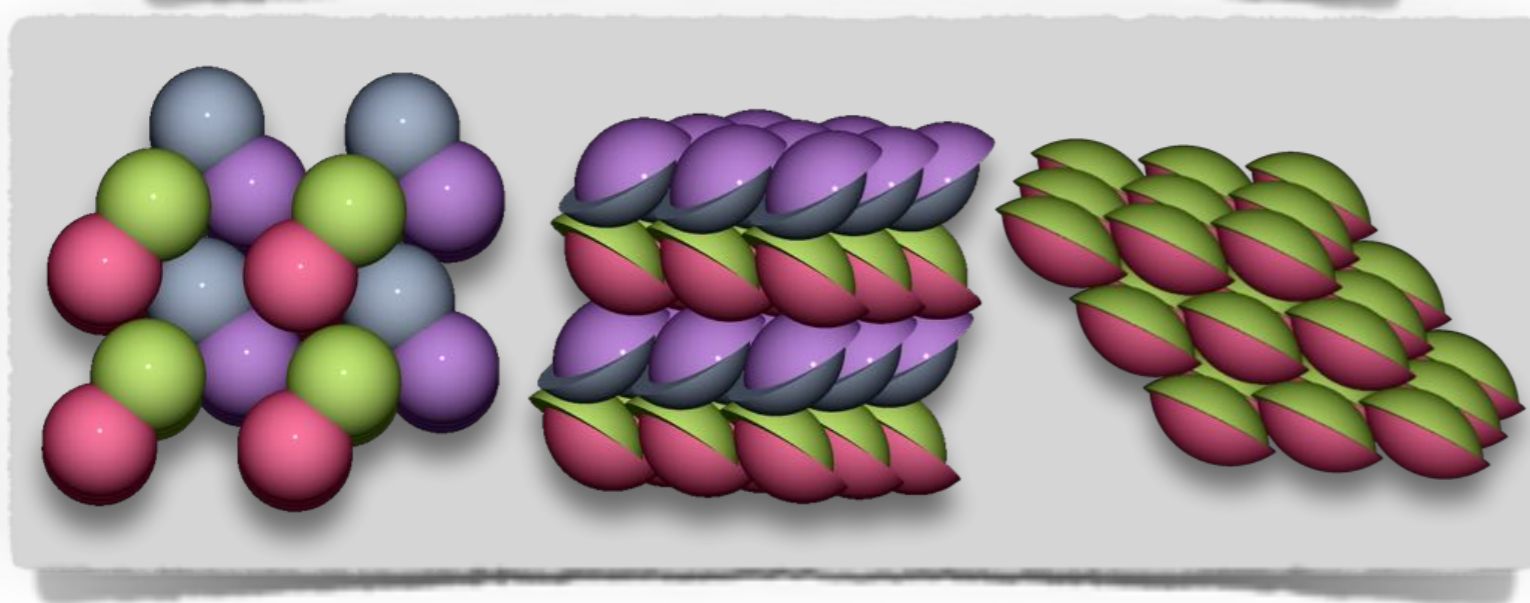
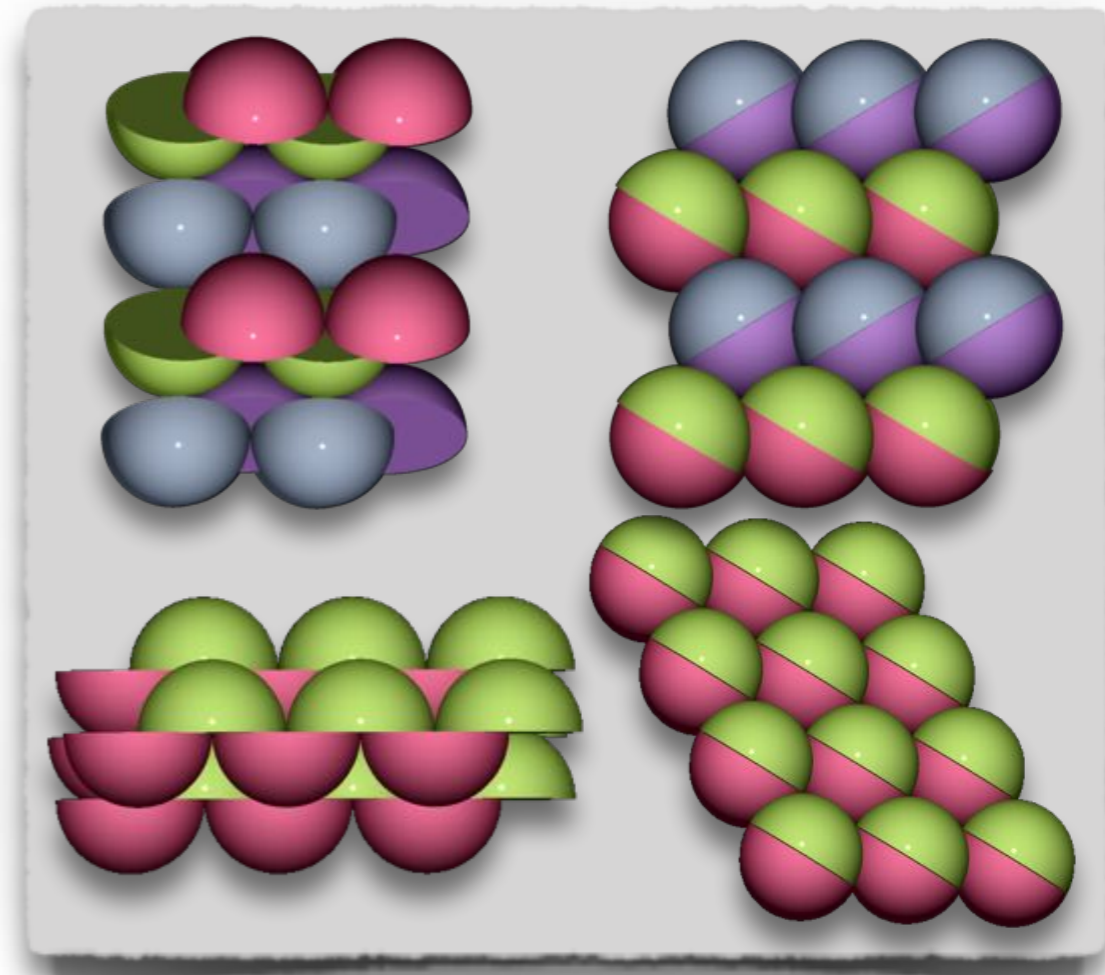
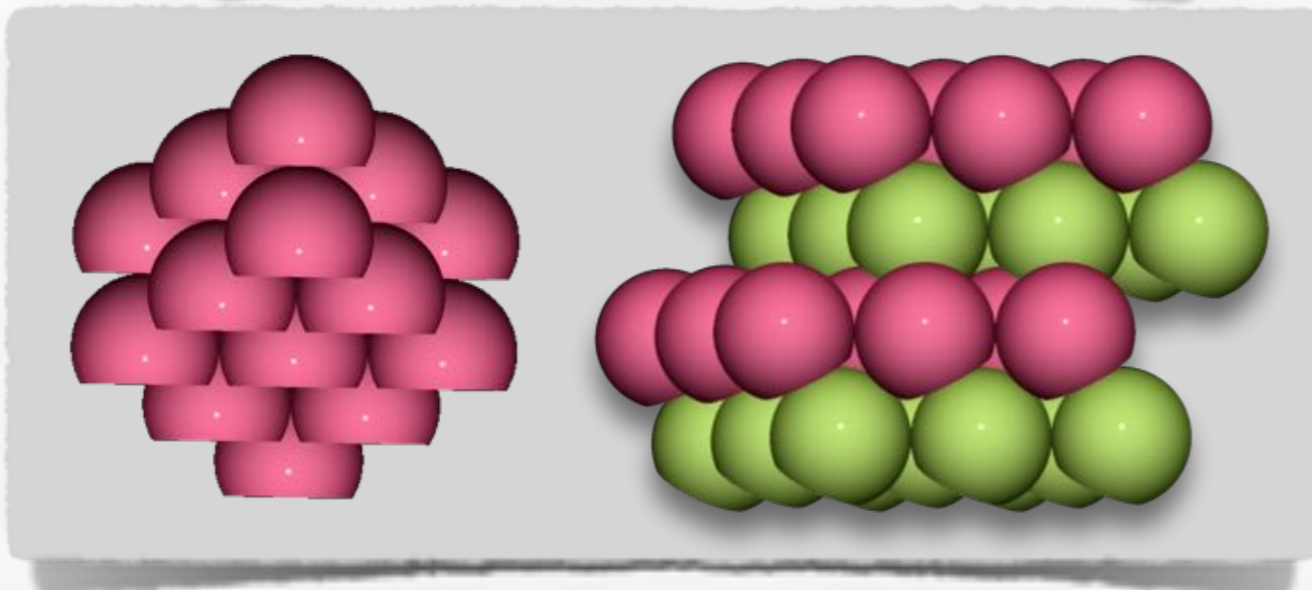
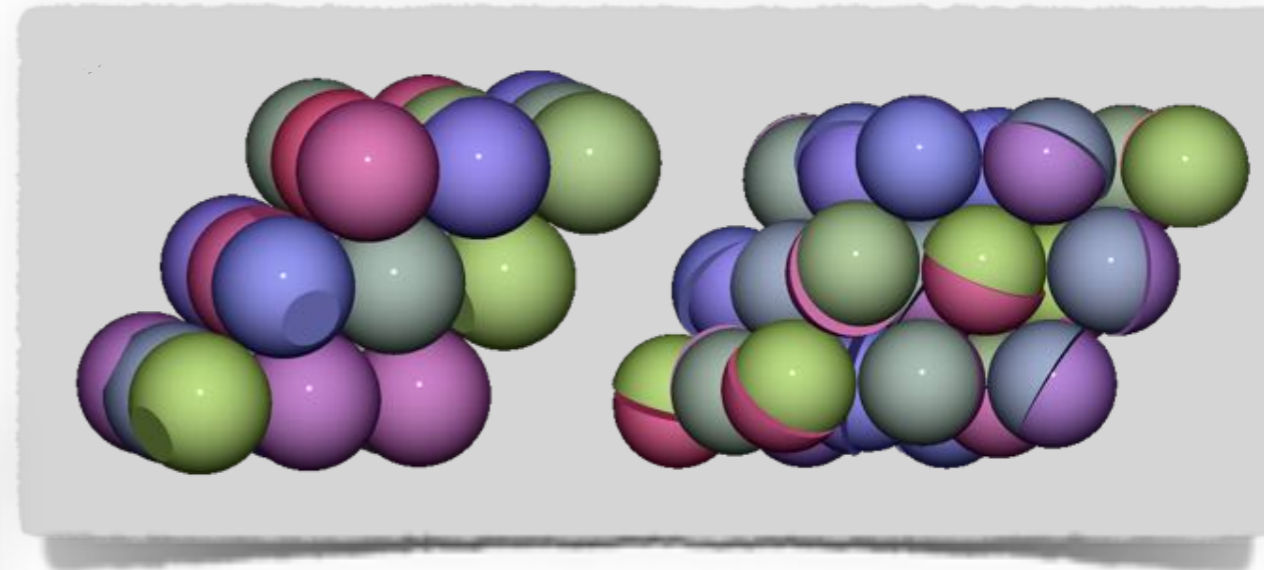
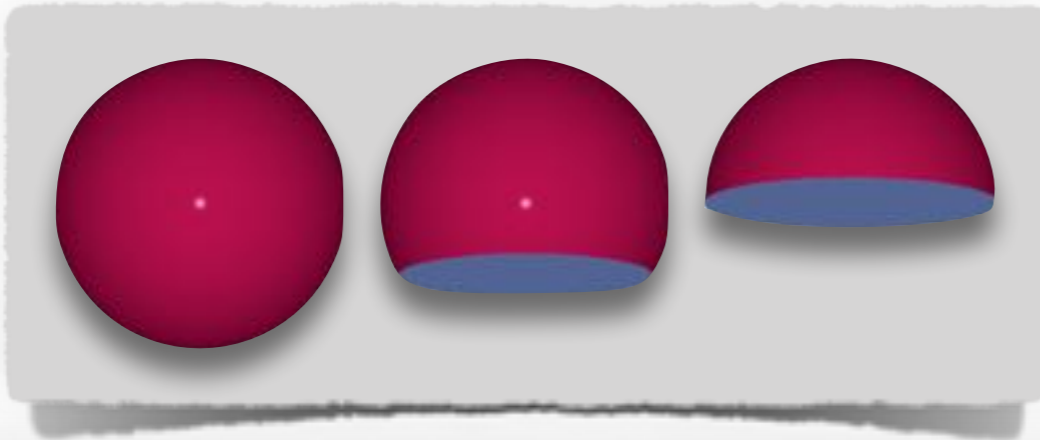


E. K. Riley and C. M. Liddell, *Langmuir*, 2010, 26, 11648
Lowen, *J. Phys. Condens. Matter*, 2009, 20, 404201
Avendano, Liddell, Escobedo, *Soft Matter*, 2013, 9, 9153

Self-assembly of convex particles

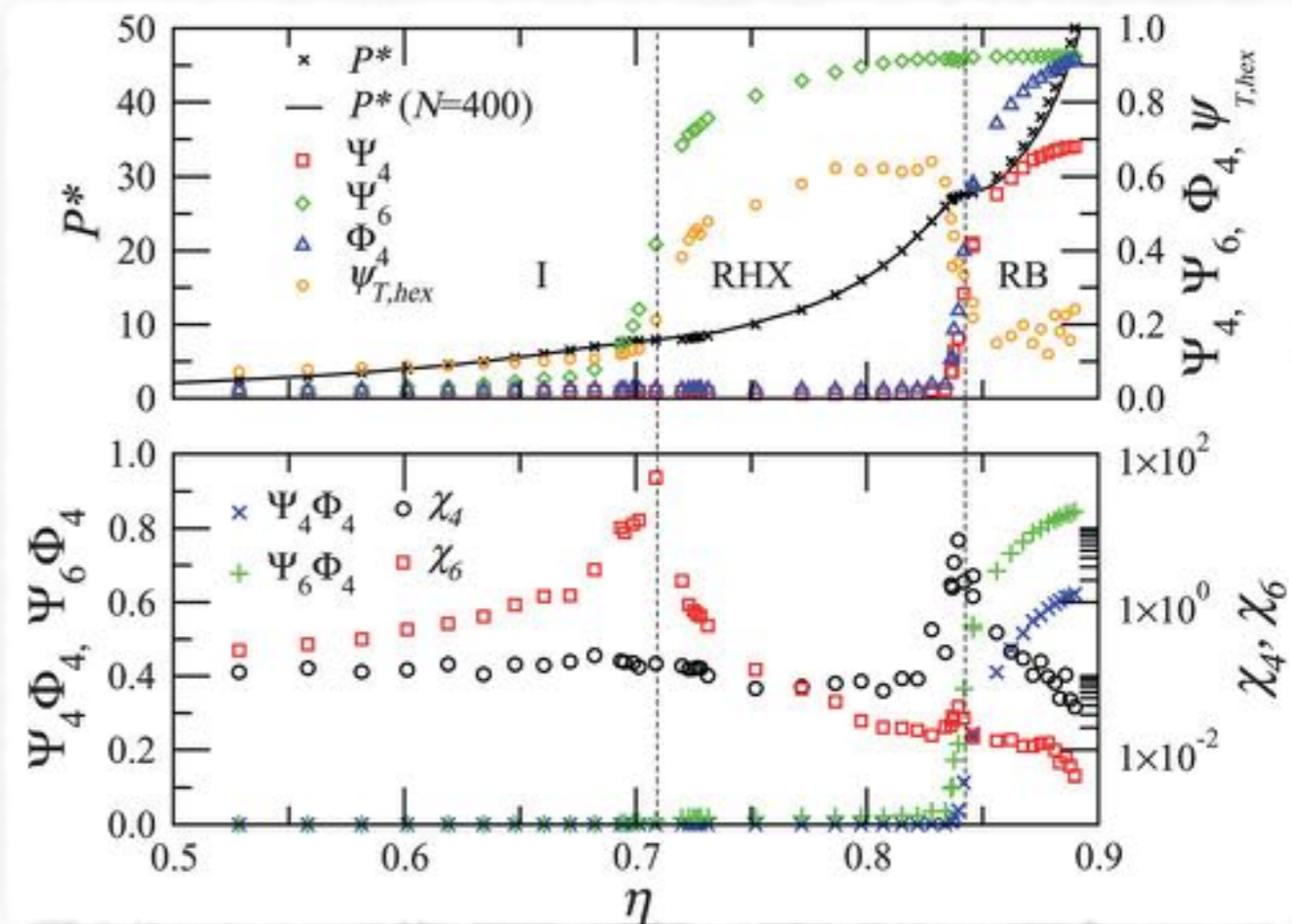
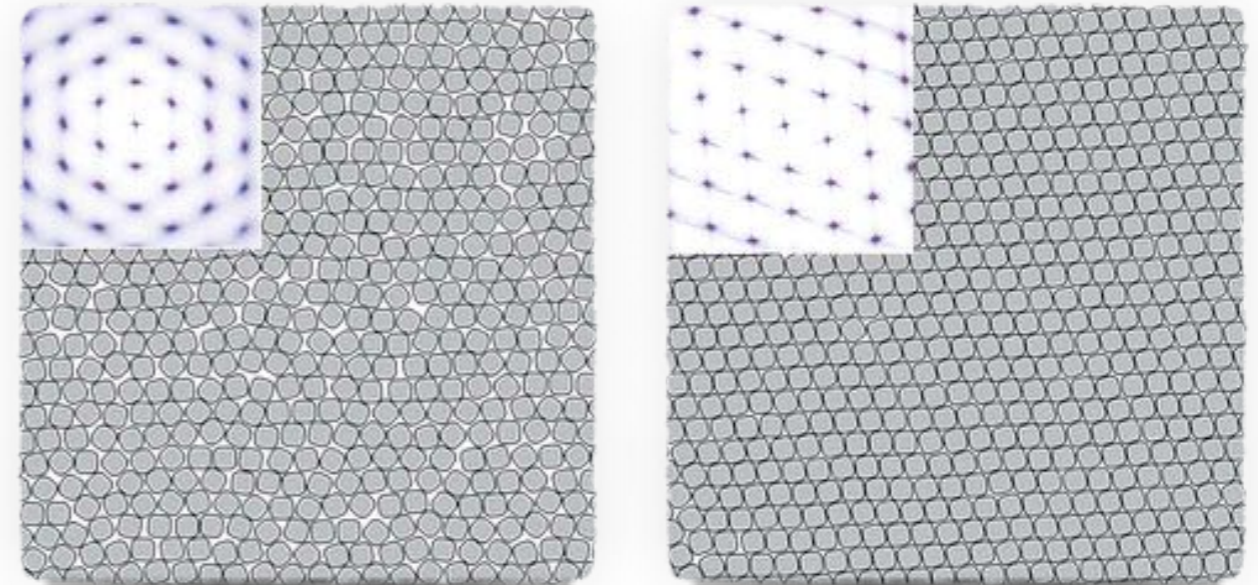
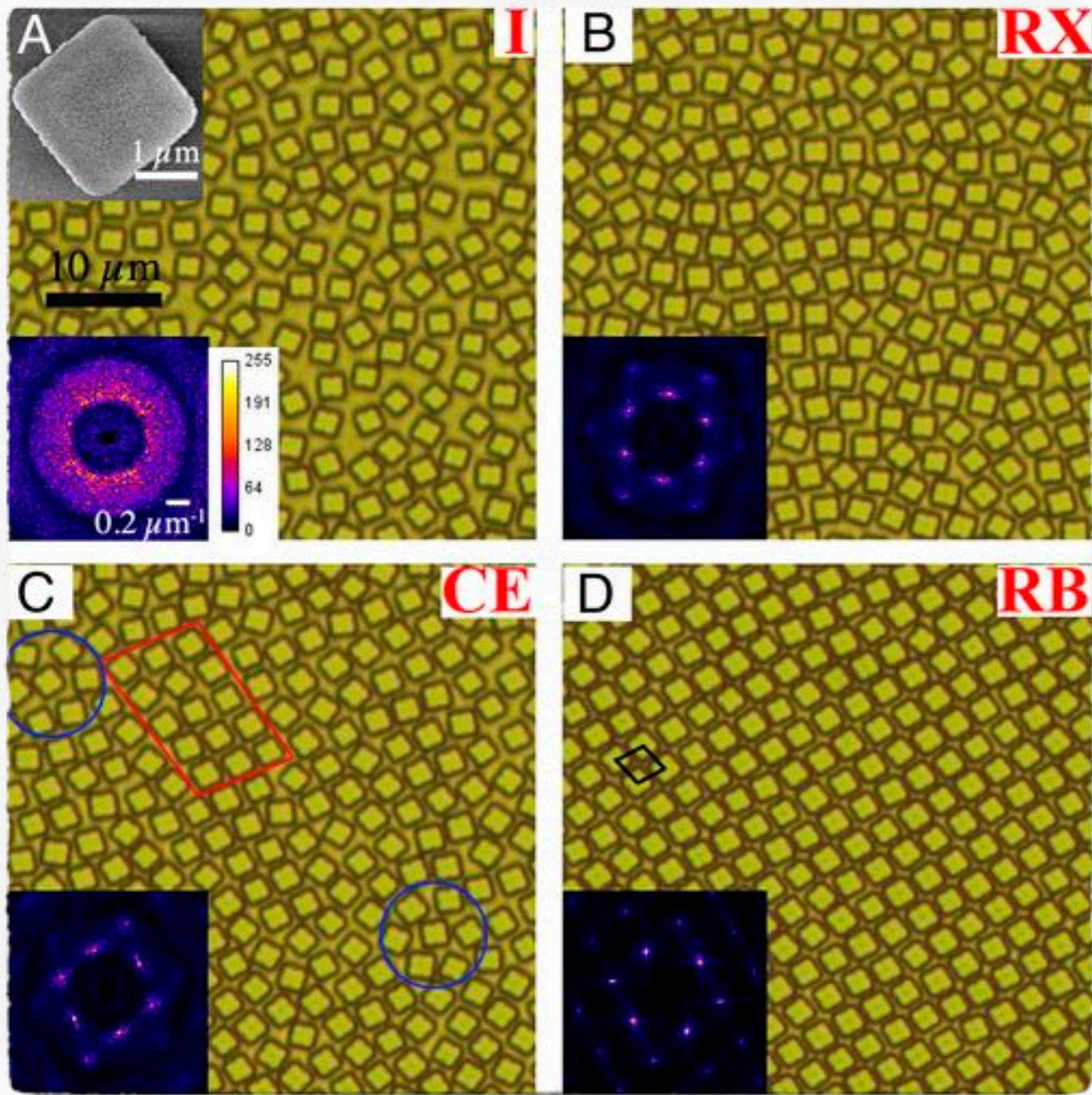


Self-assembly of convex particles



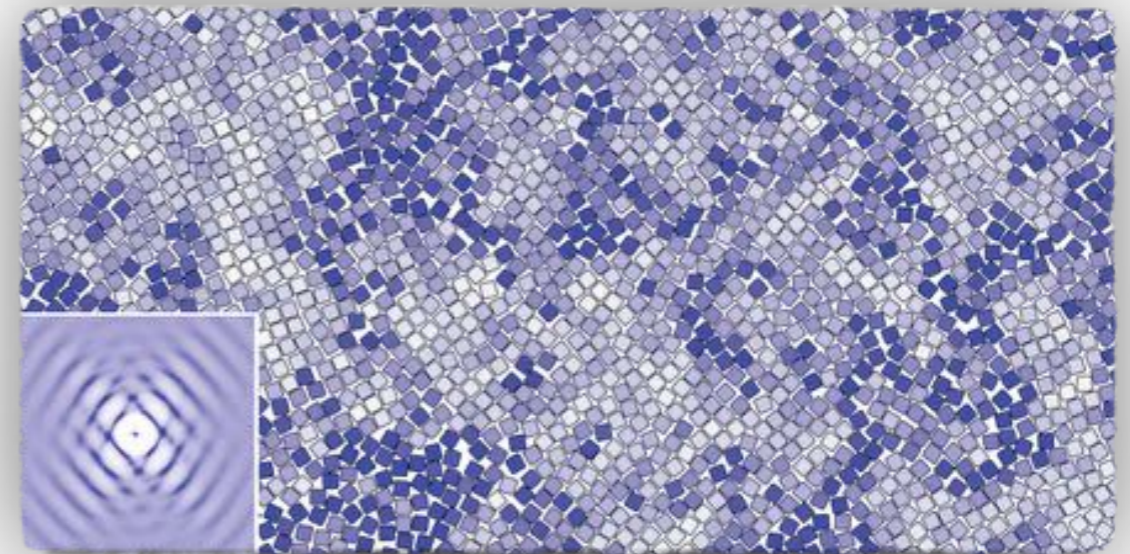
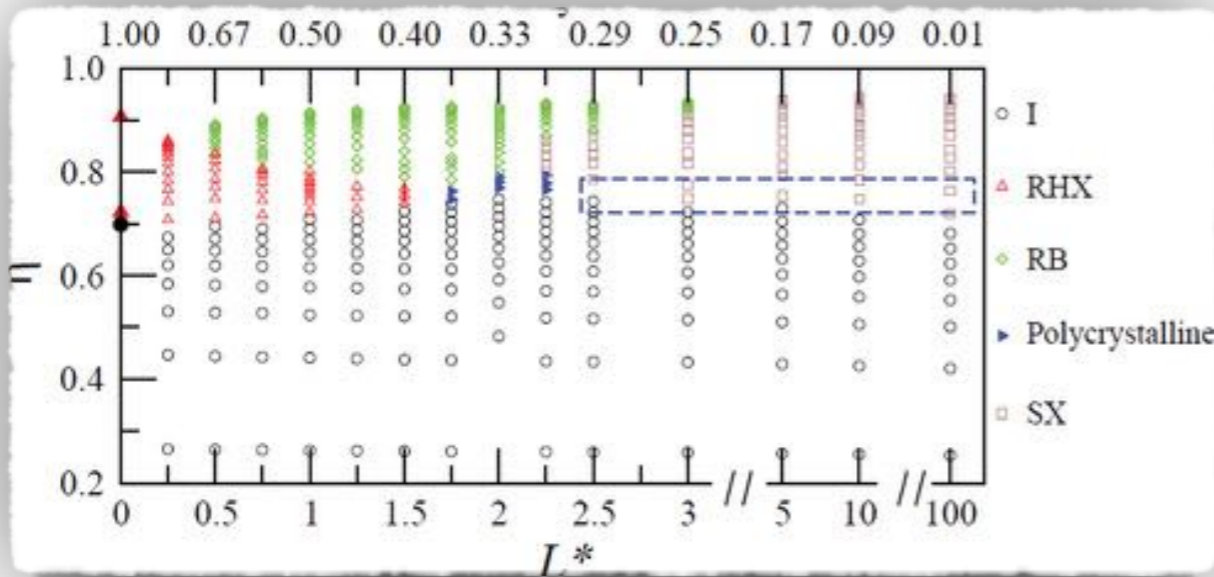
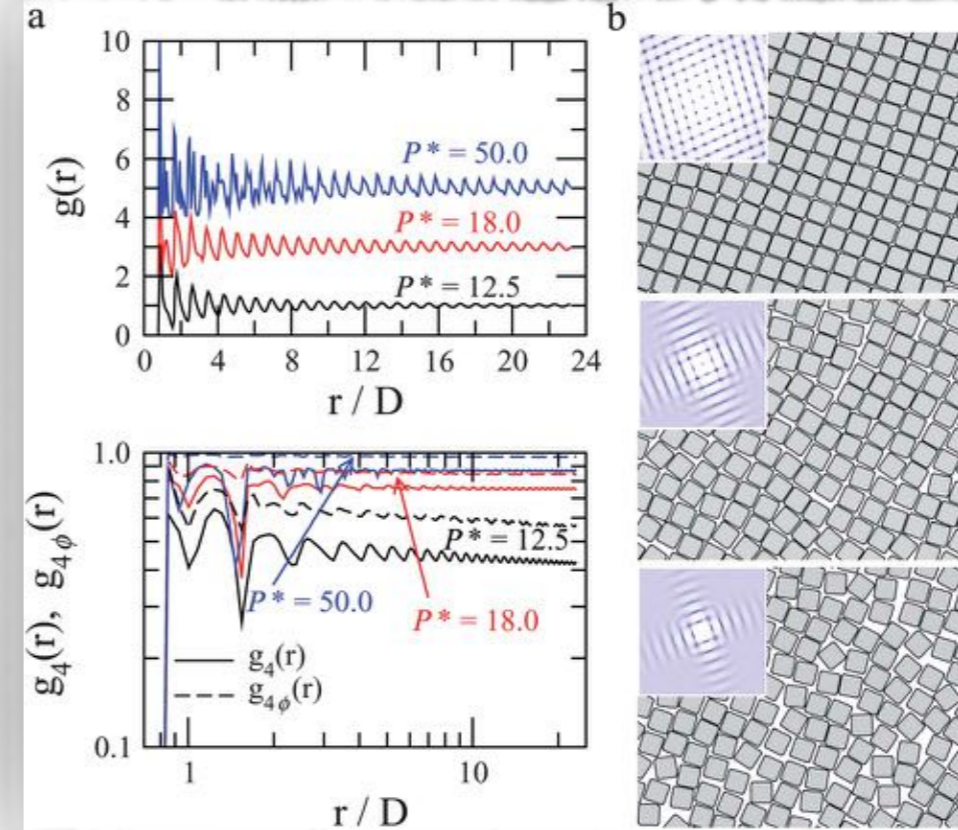
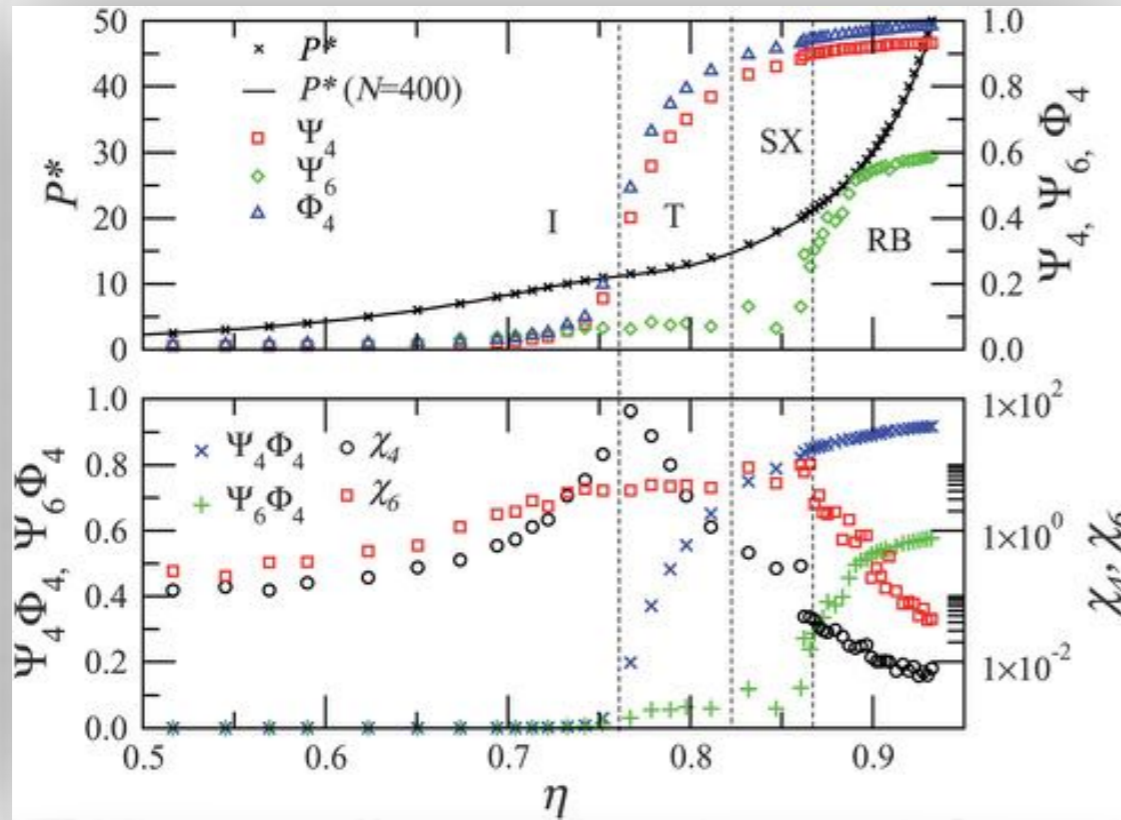
Self-assembly of convex particles

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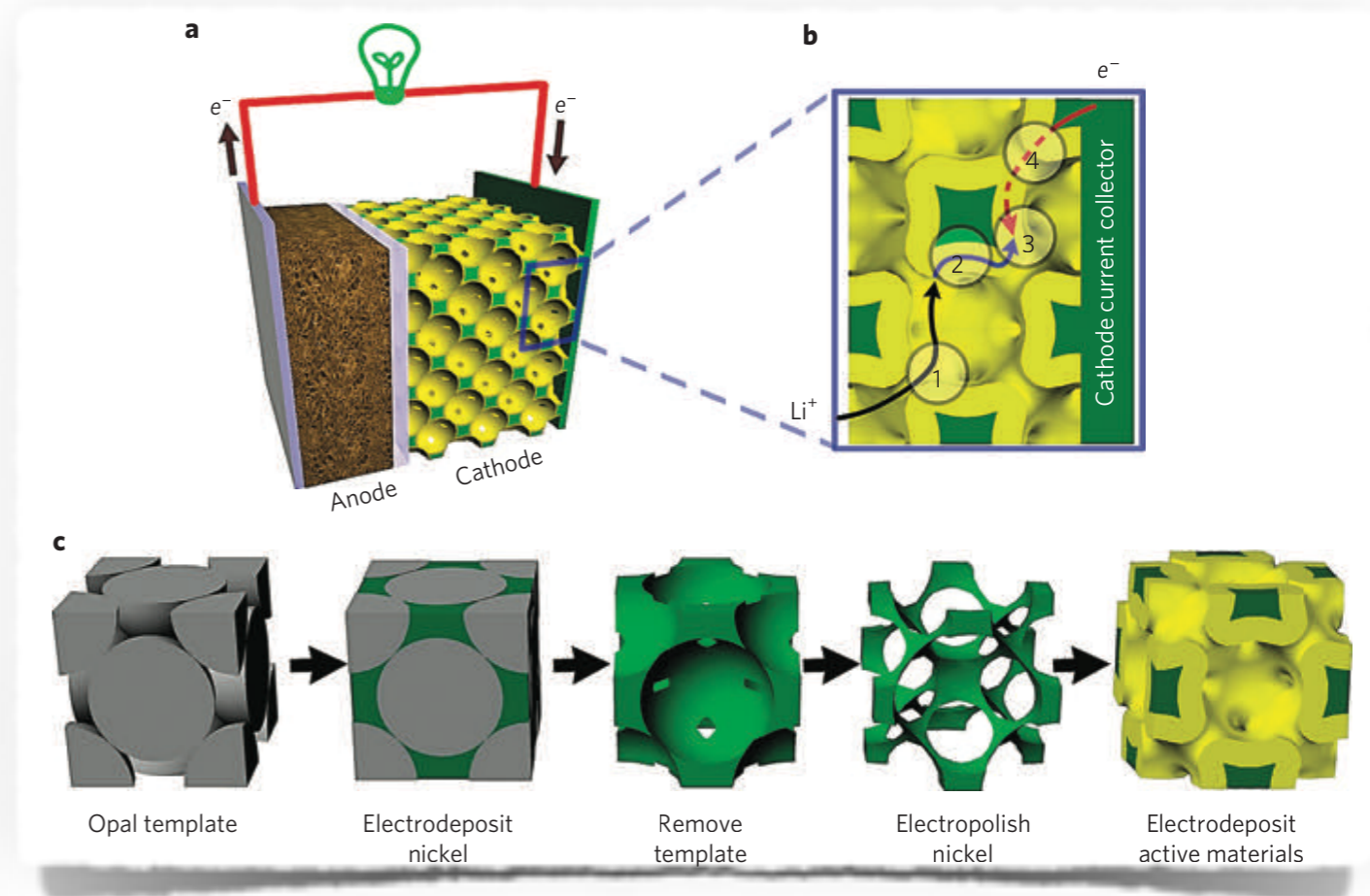
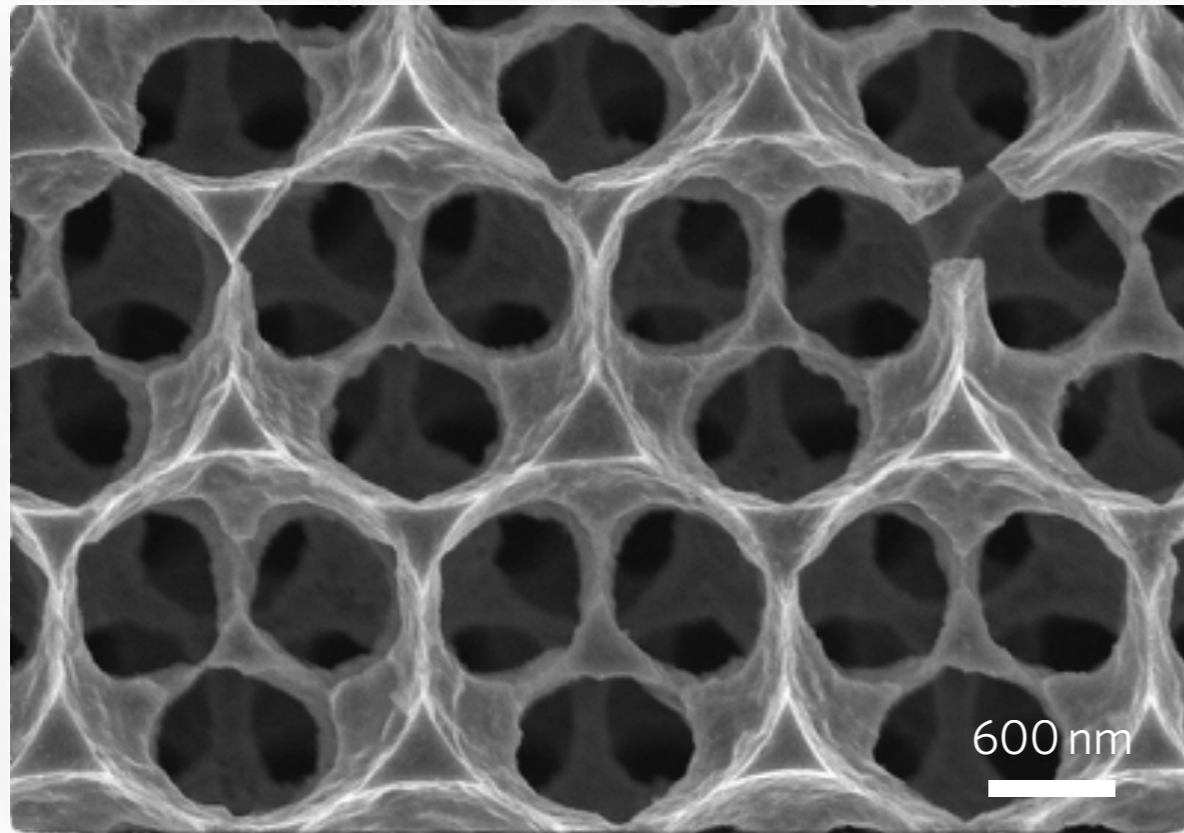


Self-assembly of convex particles

The University of Manchester

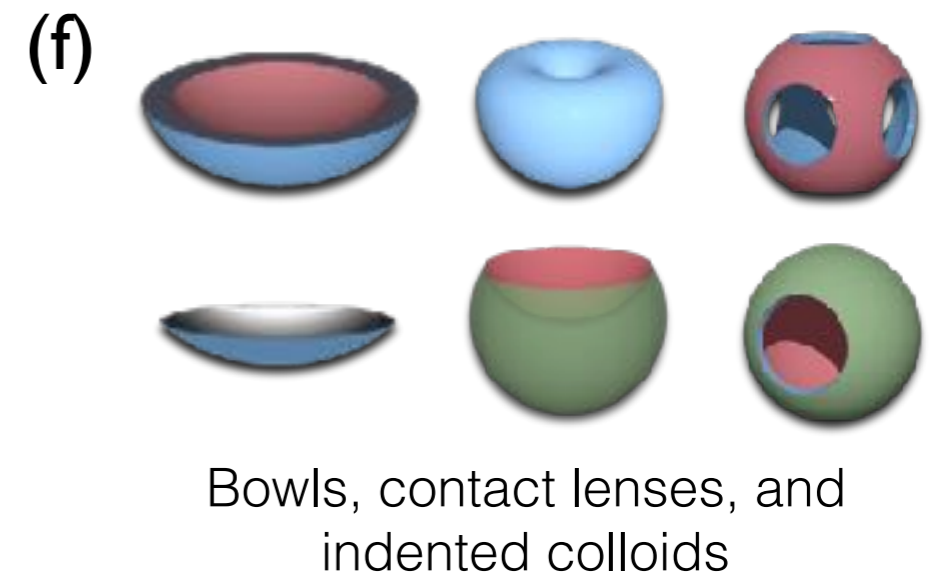
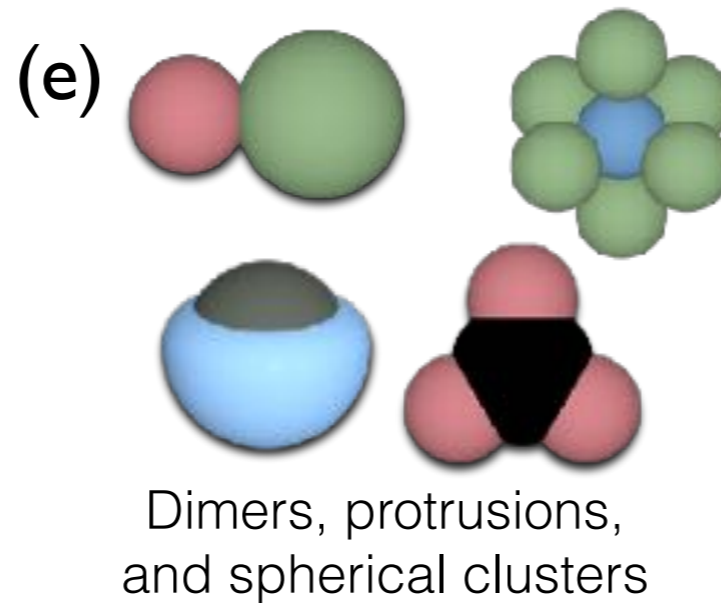
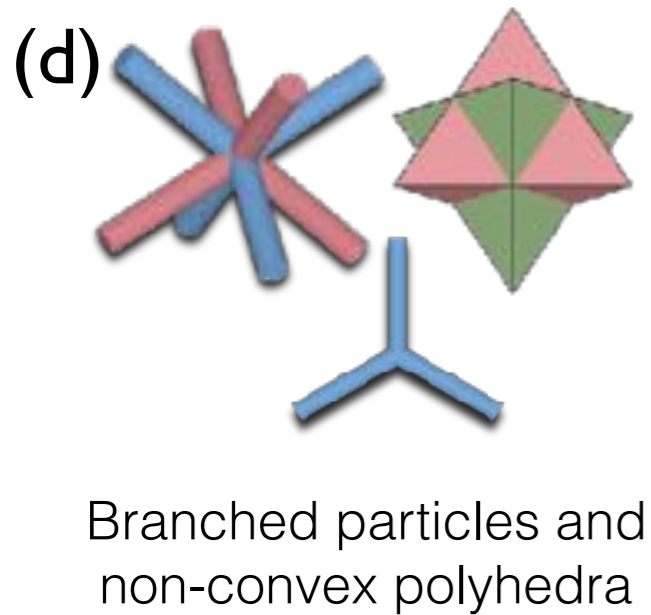
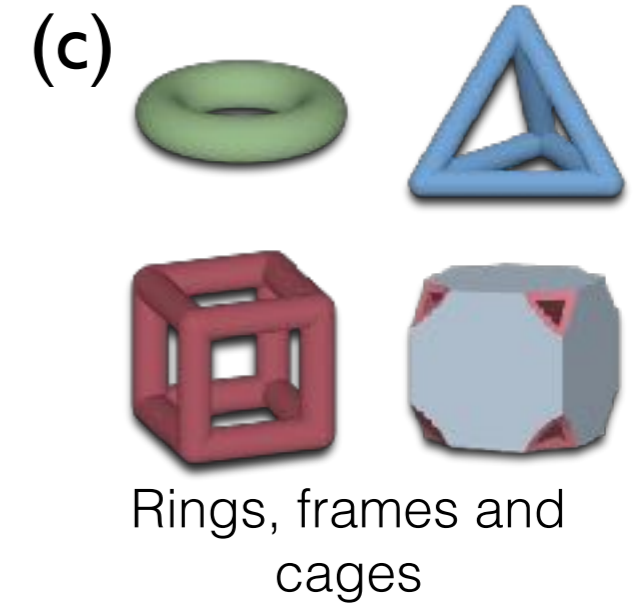
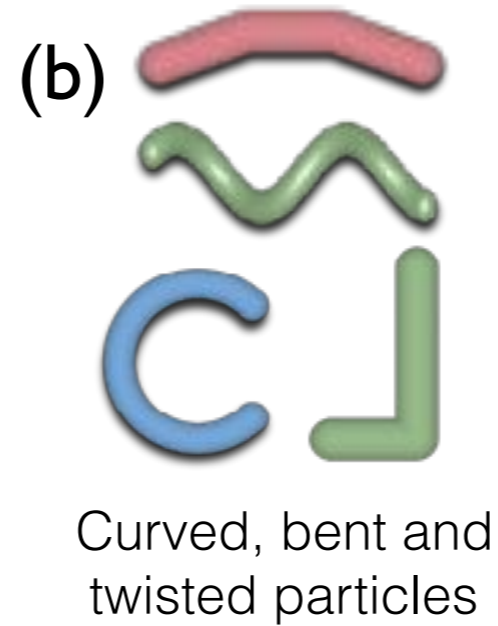
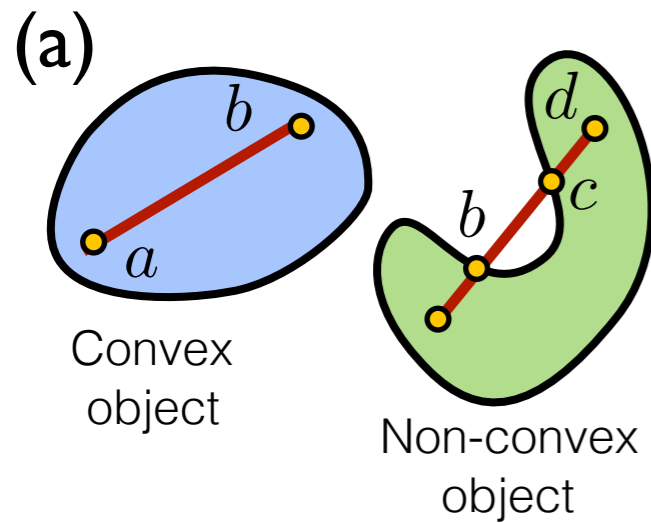


Engineering ordered macroporous materials

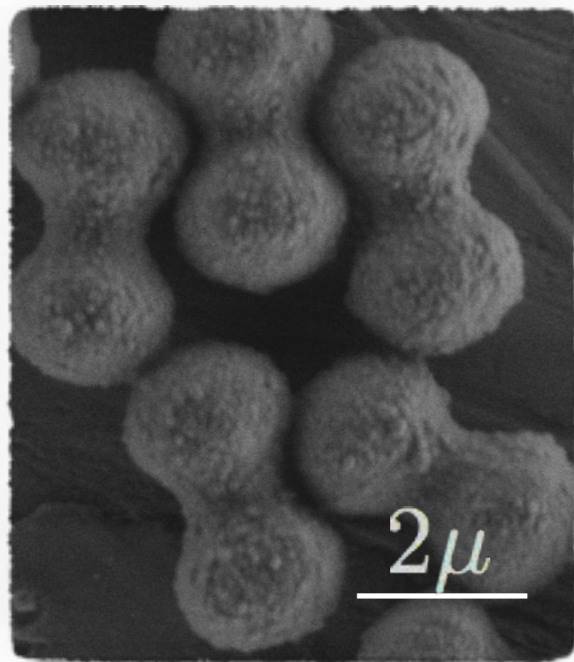


- Photocatalysis (light scattering)
- Liquid phase catalysis (reduction of diffusion limitation)
- Battery electrodes (reduction of ion-transport resistance)
- Tissue engineering
- Thermal, acoustic, and electrical insulators
- Photonic materials

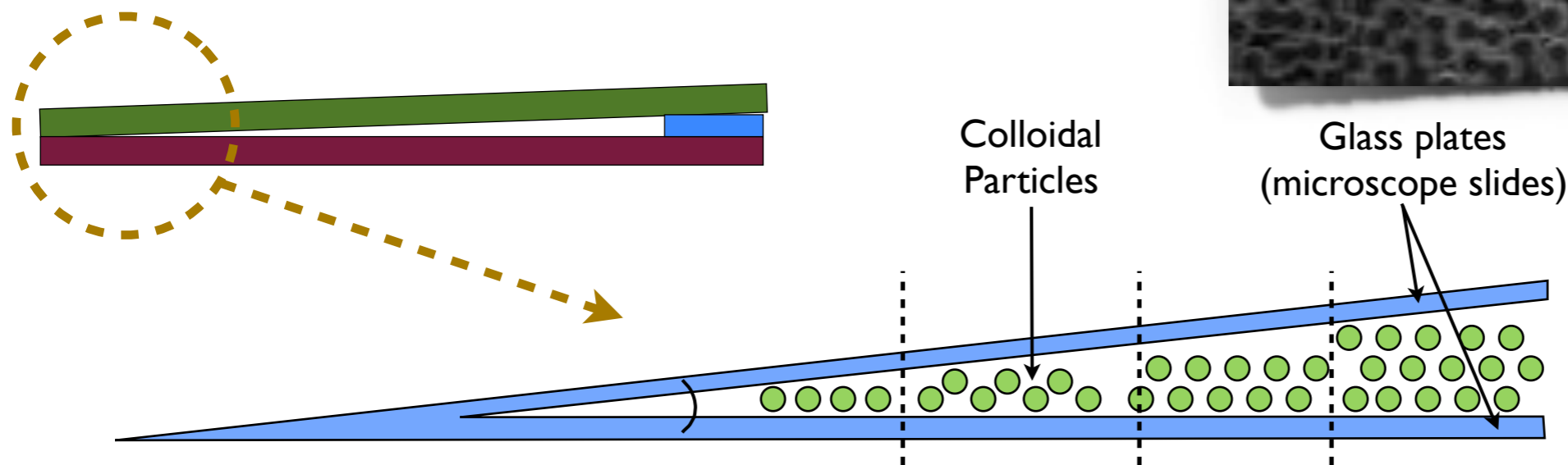
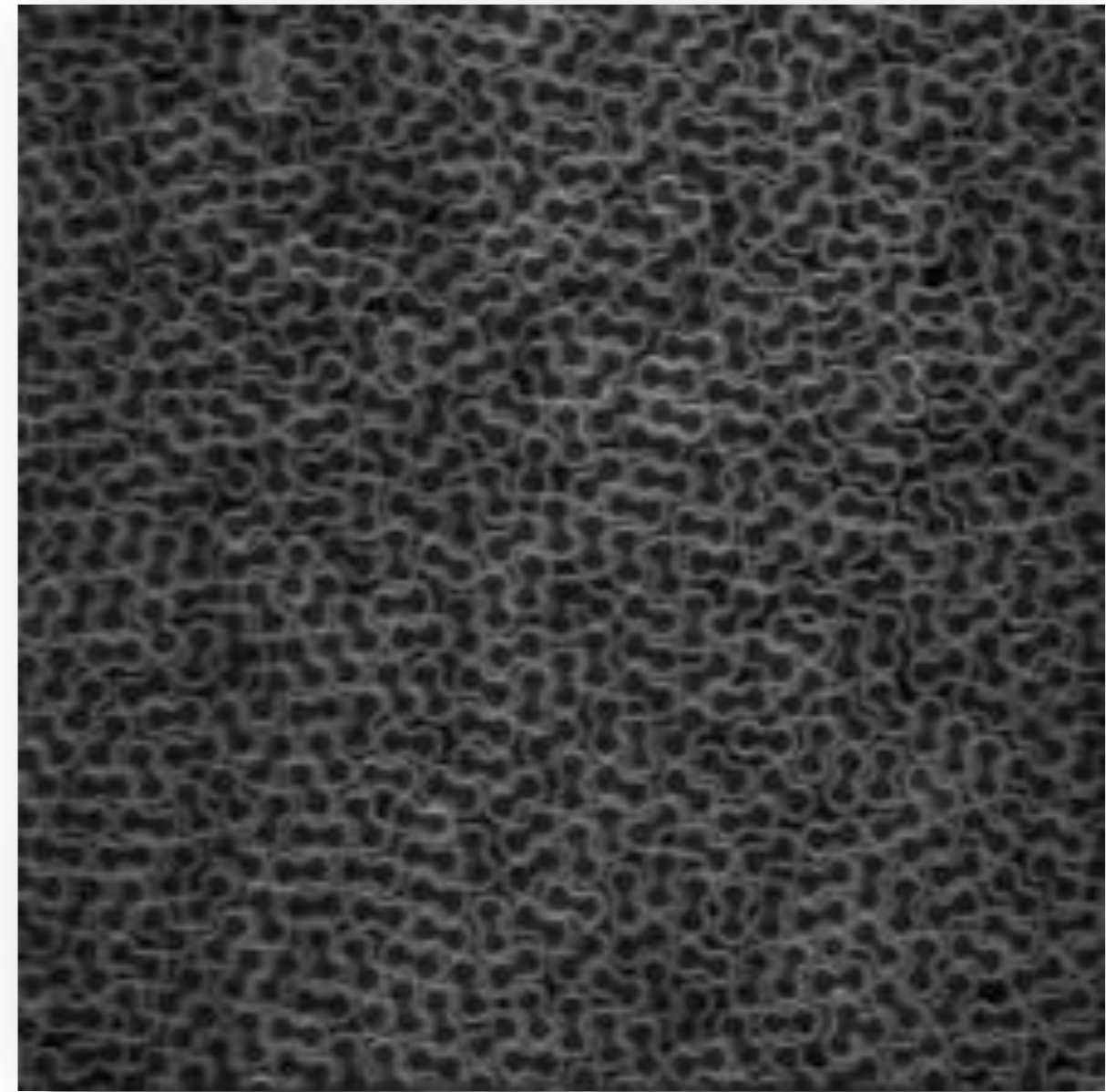
Non-convex particles



Self-assembly of colloidal dimers



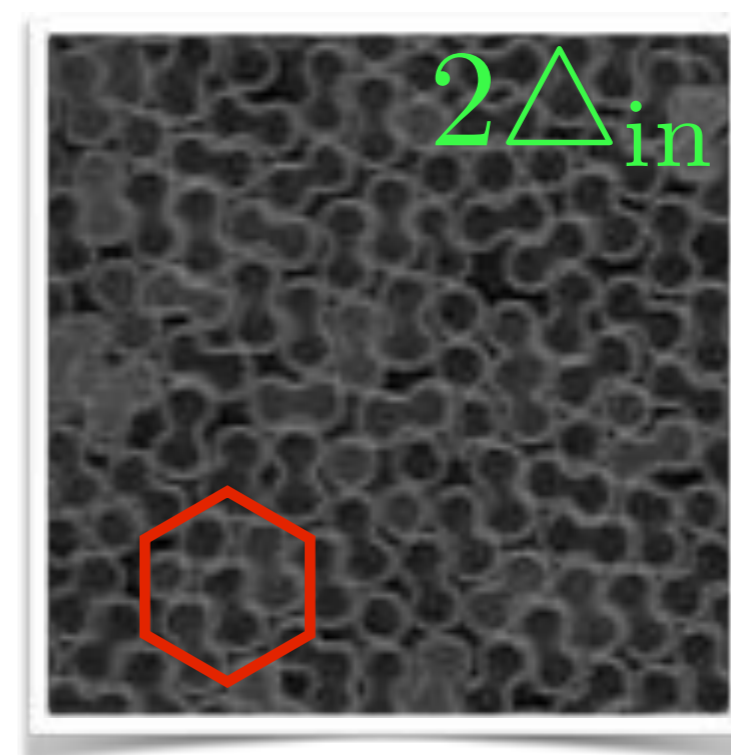
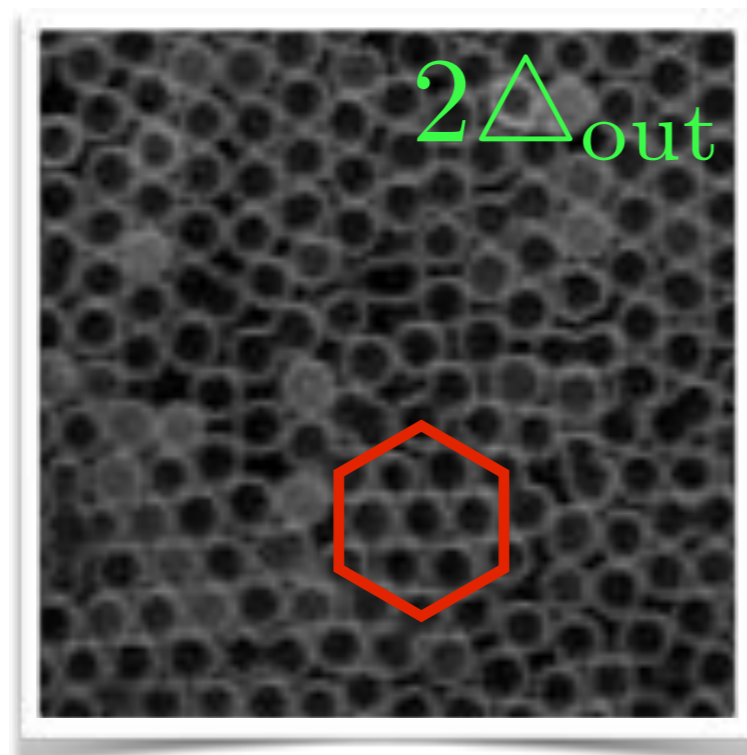
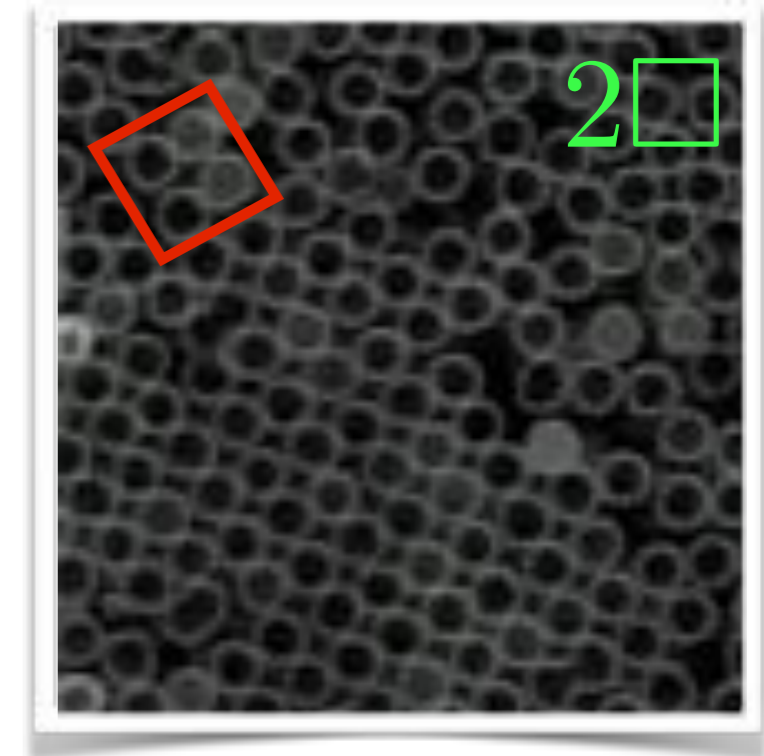
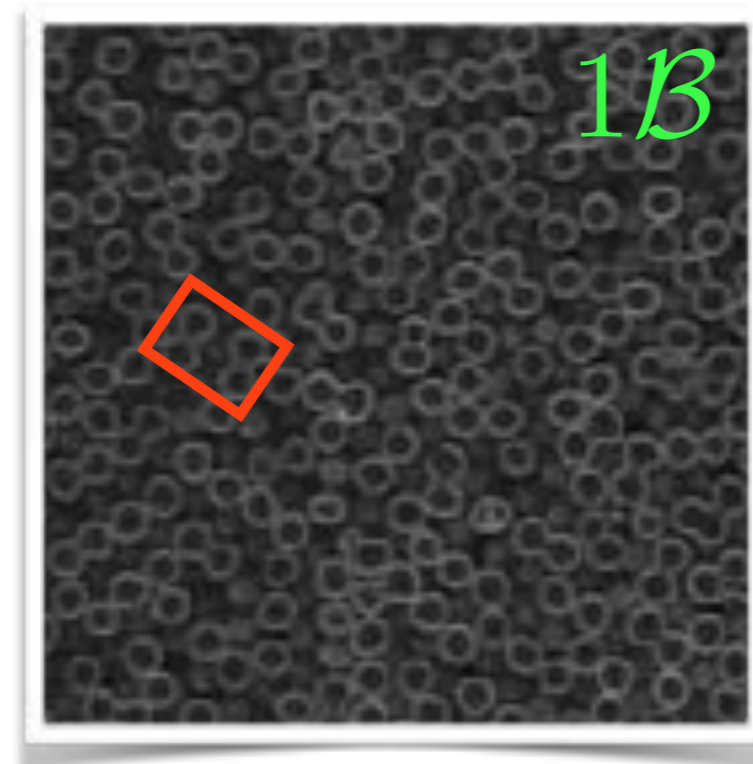
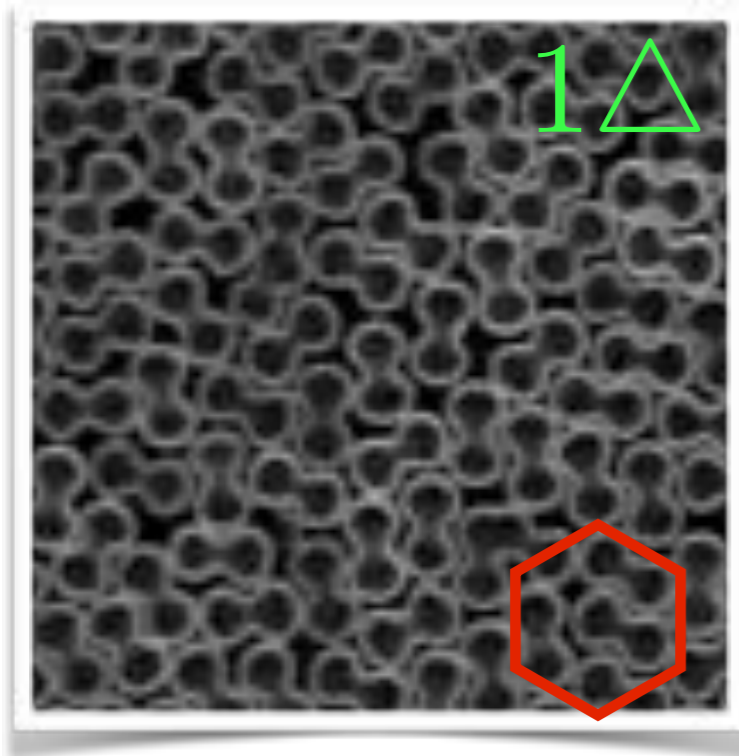
Liddell group @ Cornell



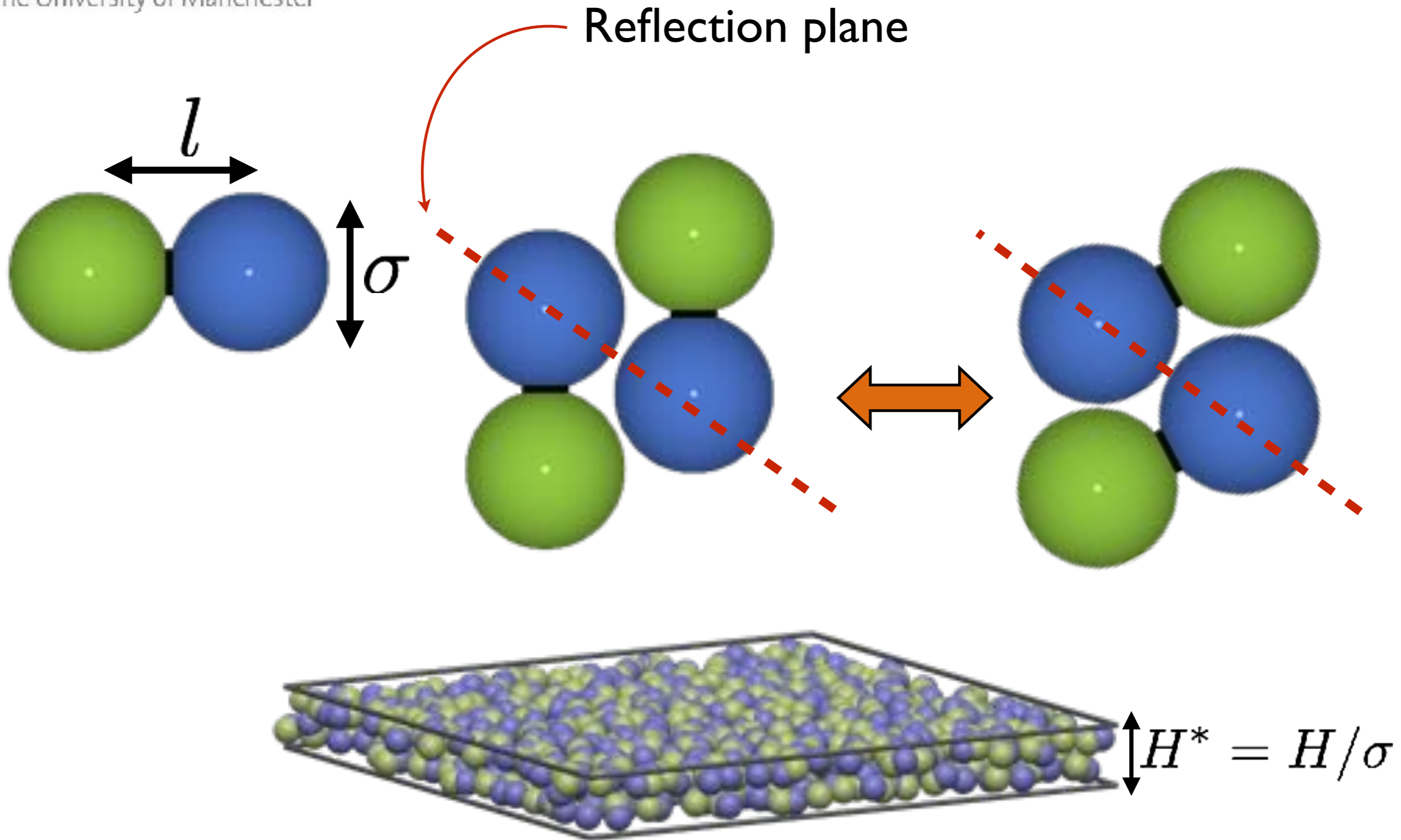
SH Lee et al., *J. Mater. Chem.*, **41**, 4881 (2008)

K Muangnapoh, C Avendano, C Liddell, and FA Escobedo, *Soft Matter*, **10**, 9729 (2014)

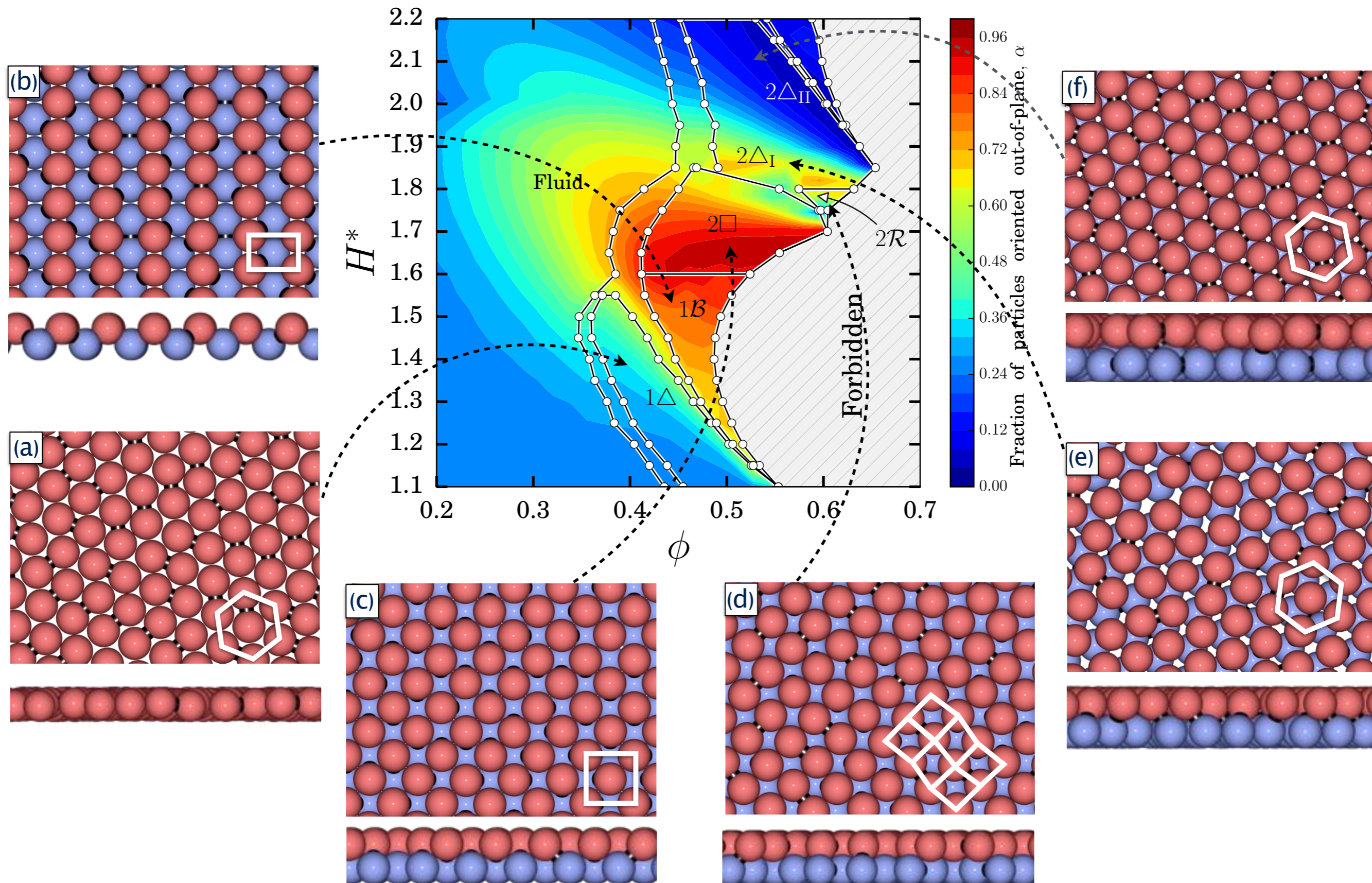
Self-assembly of colloidal dimers



Self-assembly of colloidal dimers

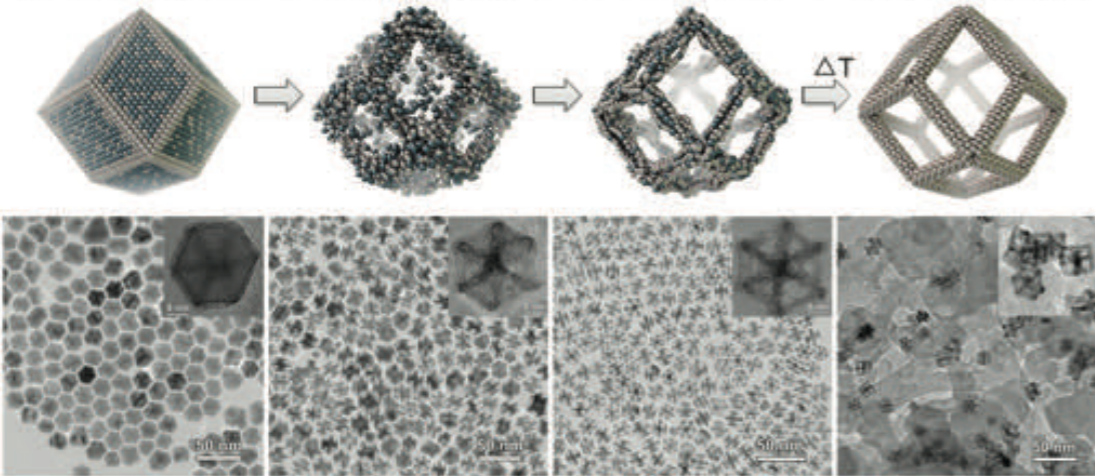


Self-assembly of colloidal dimers

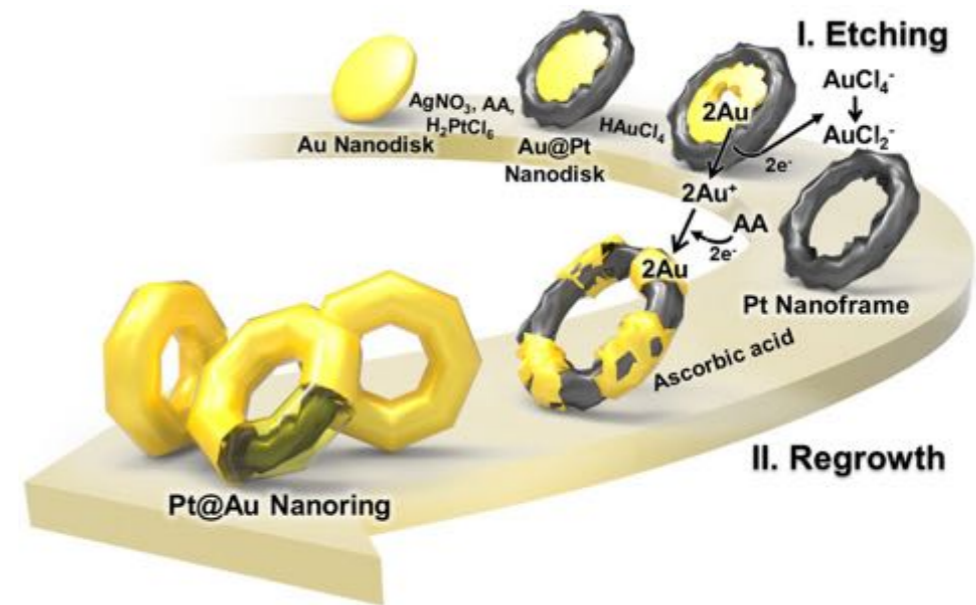


Non-convex particles

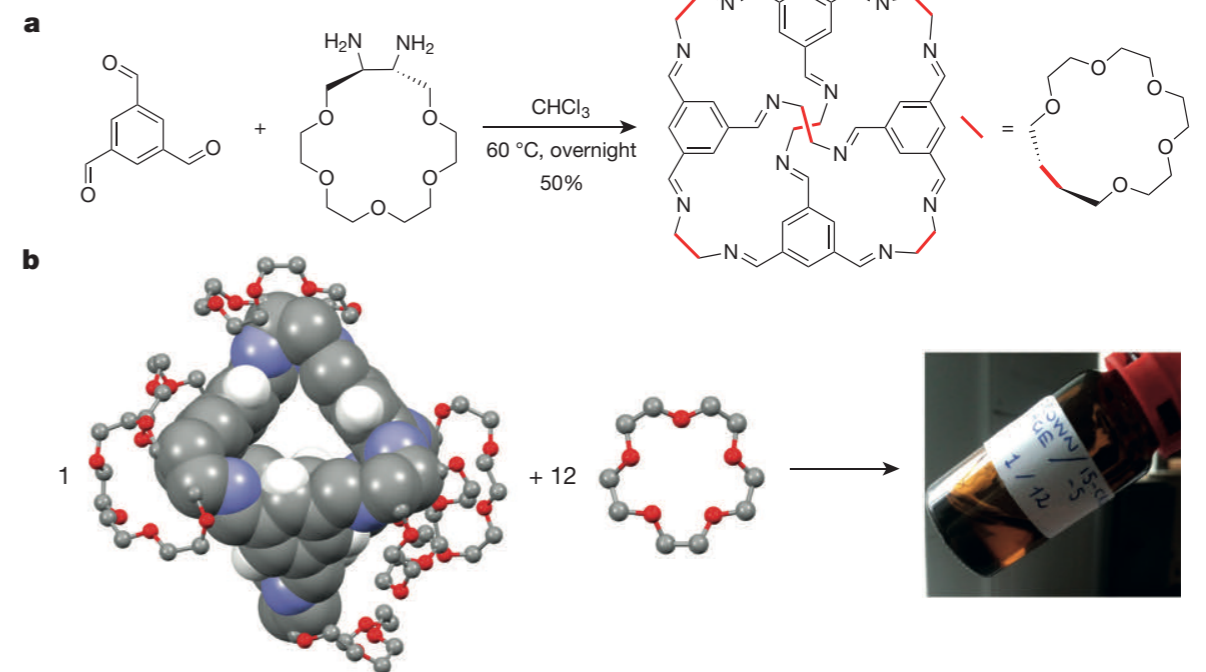
A PtNi₃ Polyhedra B PtNi Intermediates C Pt₃Ni Nanoframes D Pt₃Ni nanoframes/C with Pt-skin surfaces



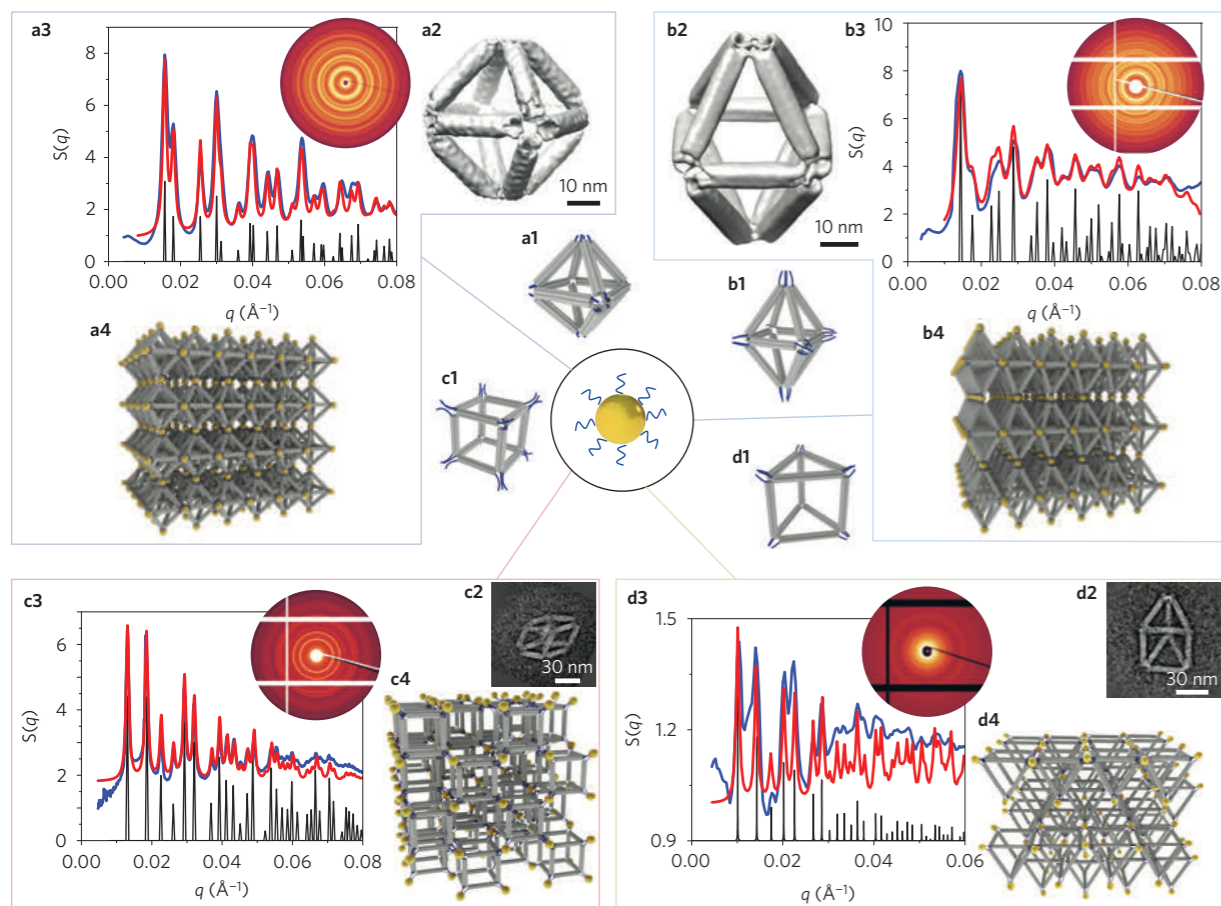
C Chen *et al.*, *Science*, **343**, 1339 (2014)



HH Jang *et al.*, *JACS*, **136**, 17674 (2014)

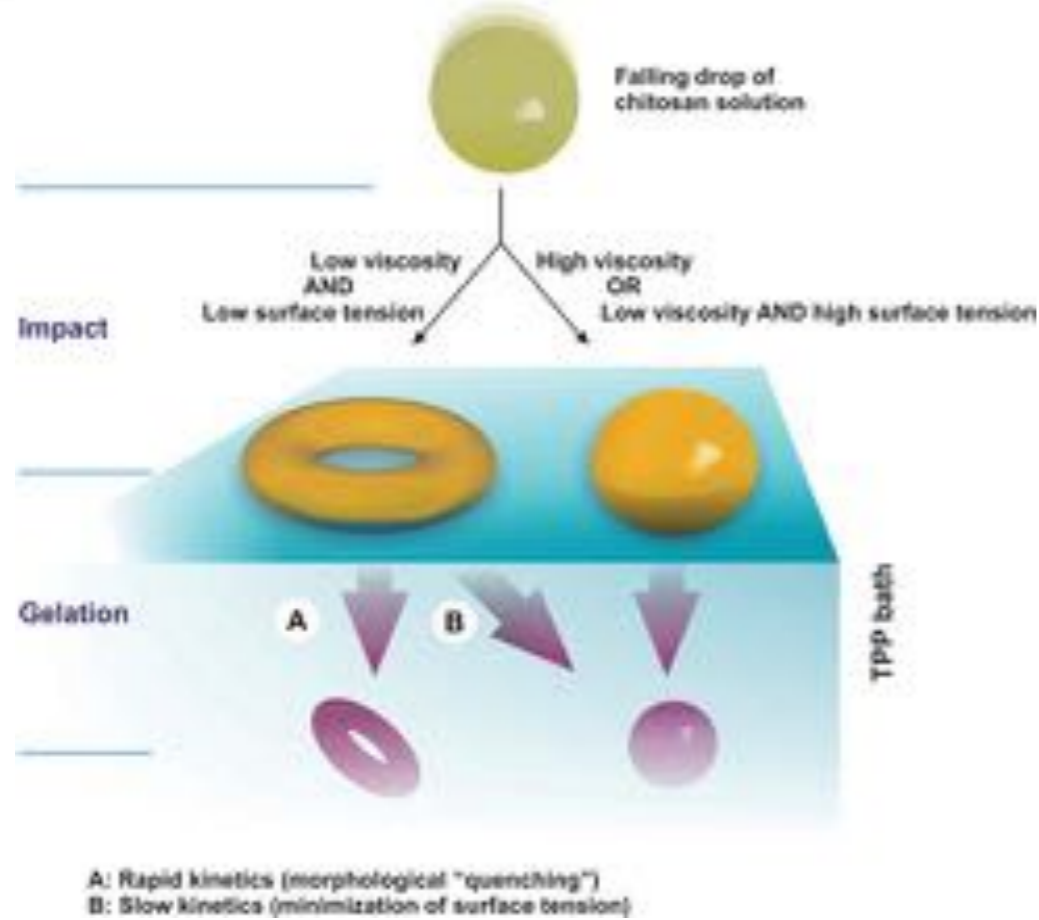


Giri, Cooper, *Nature* (2015)

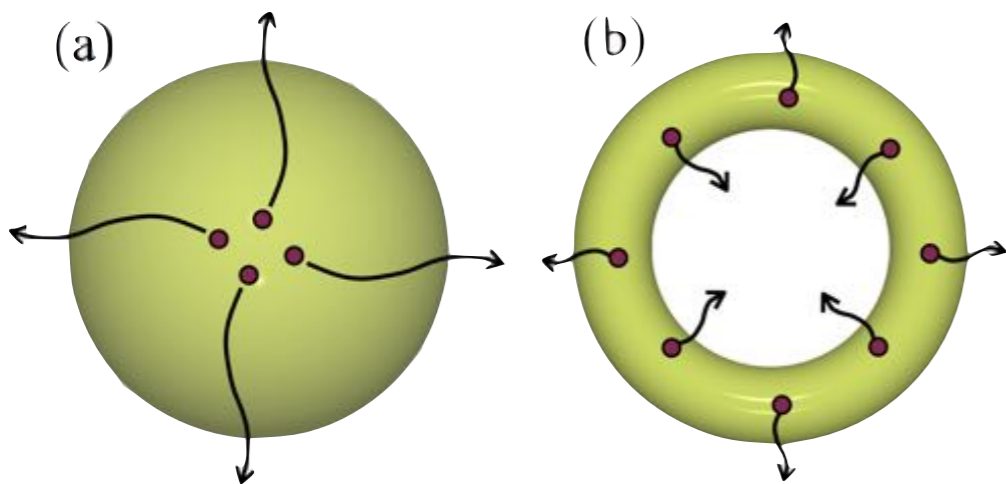


Y Tian *et al.*, *Nat. Mater.* **15**, 654 (2014)

Non-convex particles

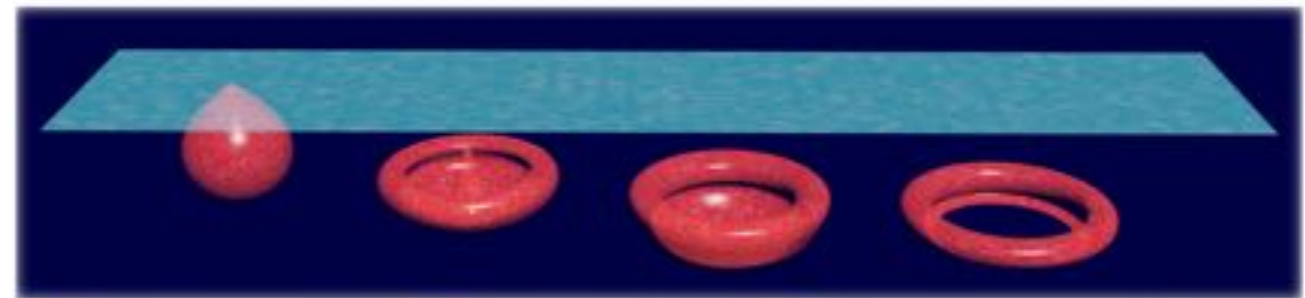
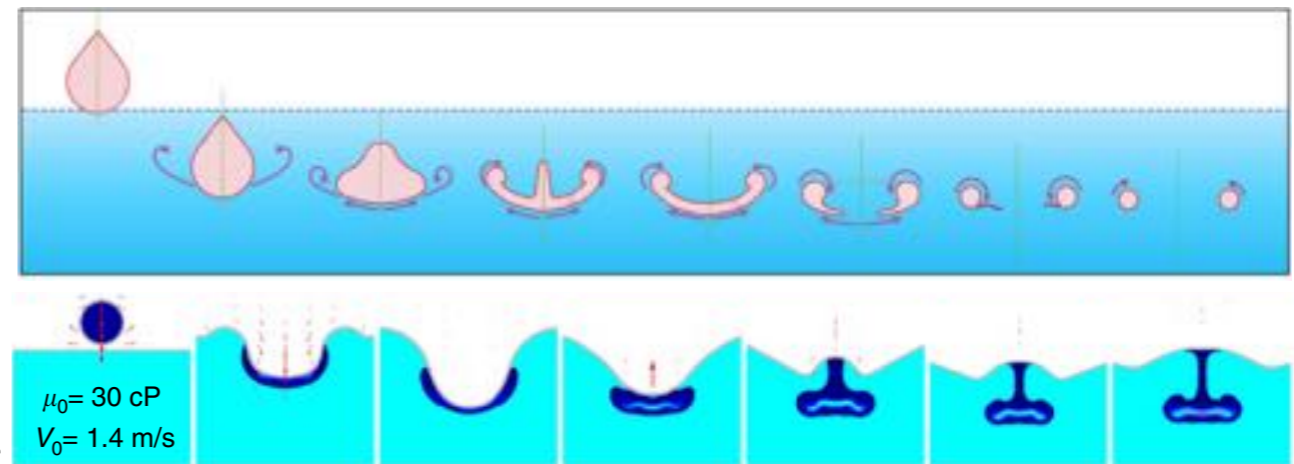
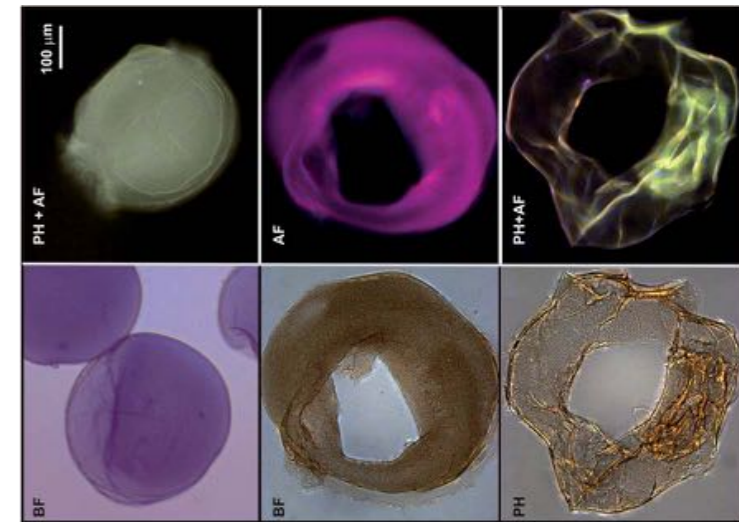


Ungphaiboon, *Soft Matter* (2010)



RG Gabrielli, Y Jiao, S. Torquato, *Phys. Rev. E*, **89**, 022133 (2014)

S Ungphaiboon *et al.*, *Soft Matter*, **6**, 4070 (2010)



D An *et al.*, *Nat. Comm.* **7**, 12401 (2016)

Self-assembly of colloidal rings

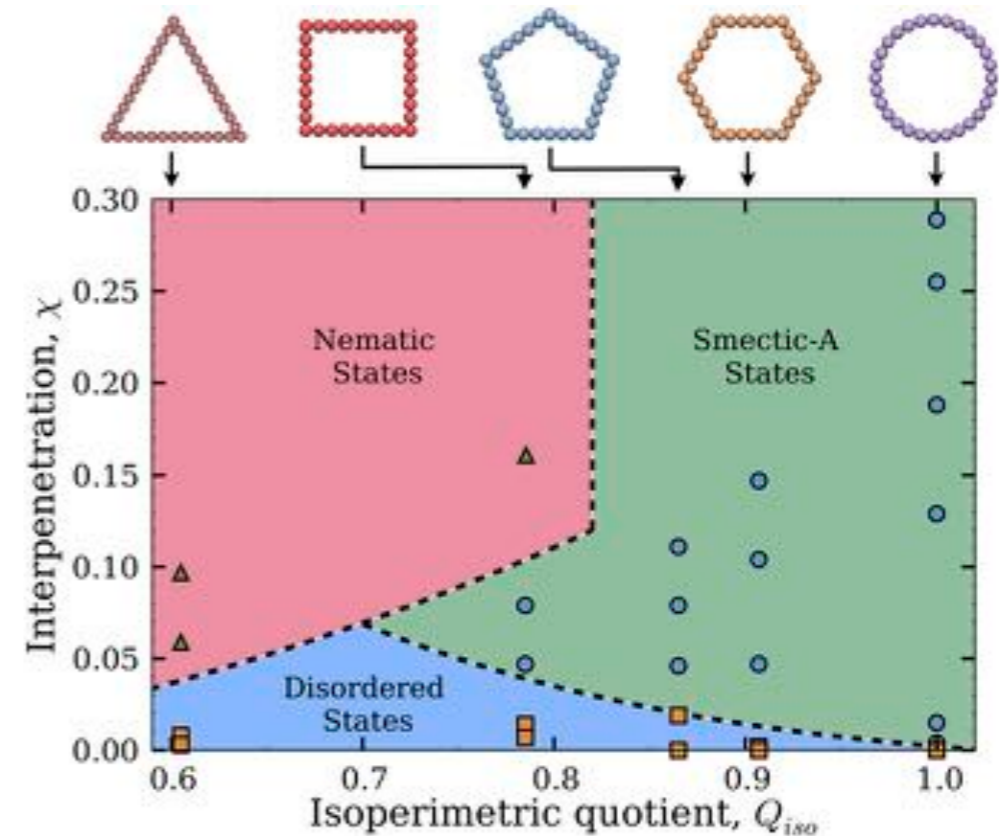
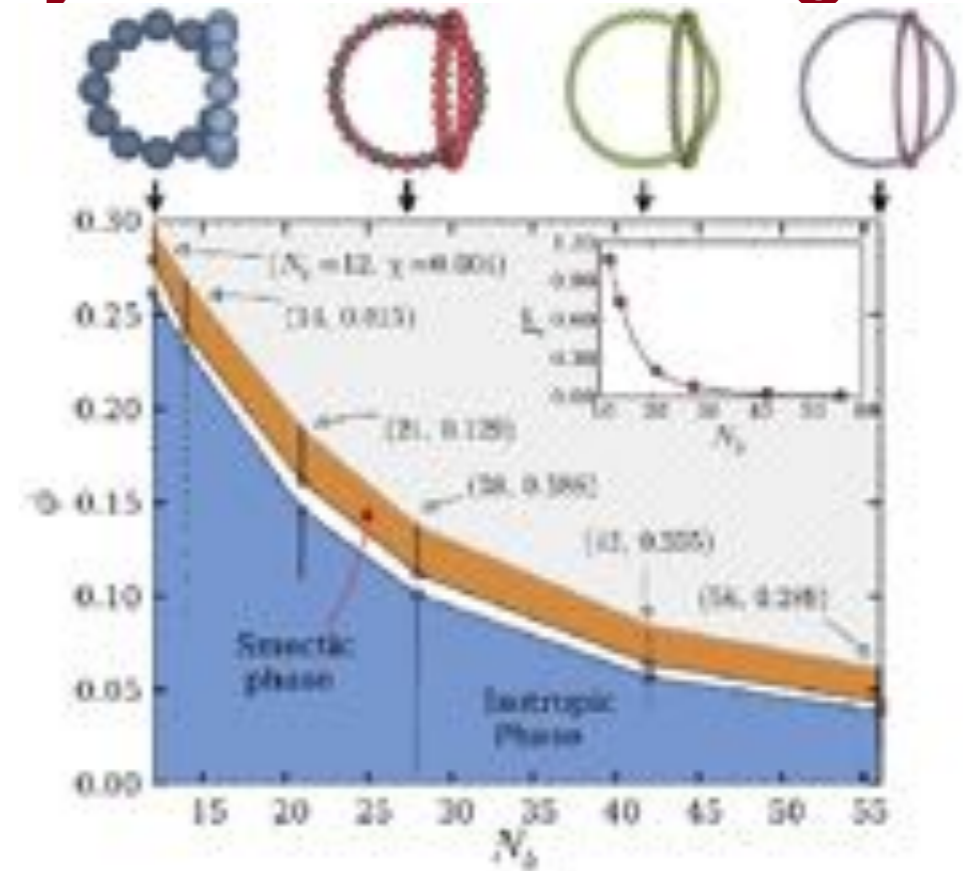
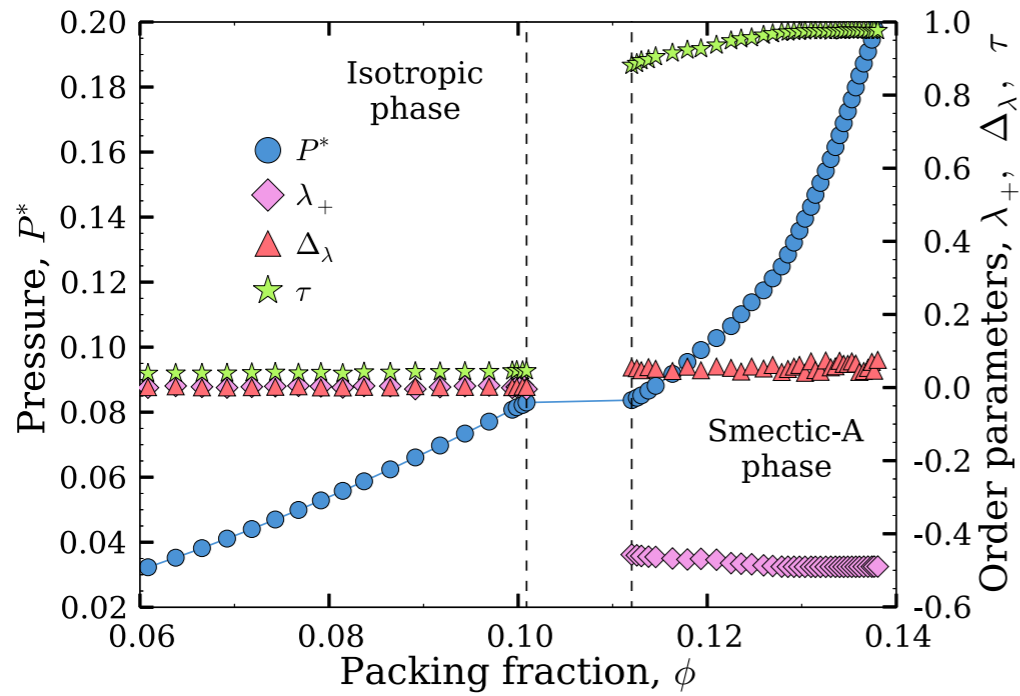
Rings of type 1

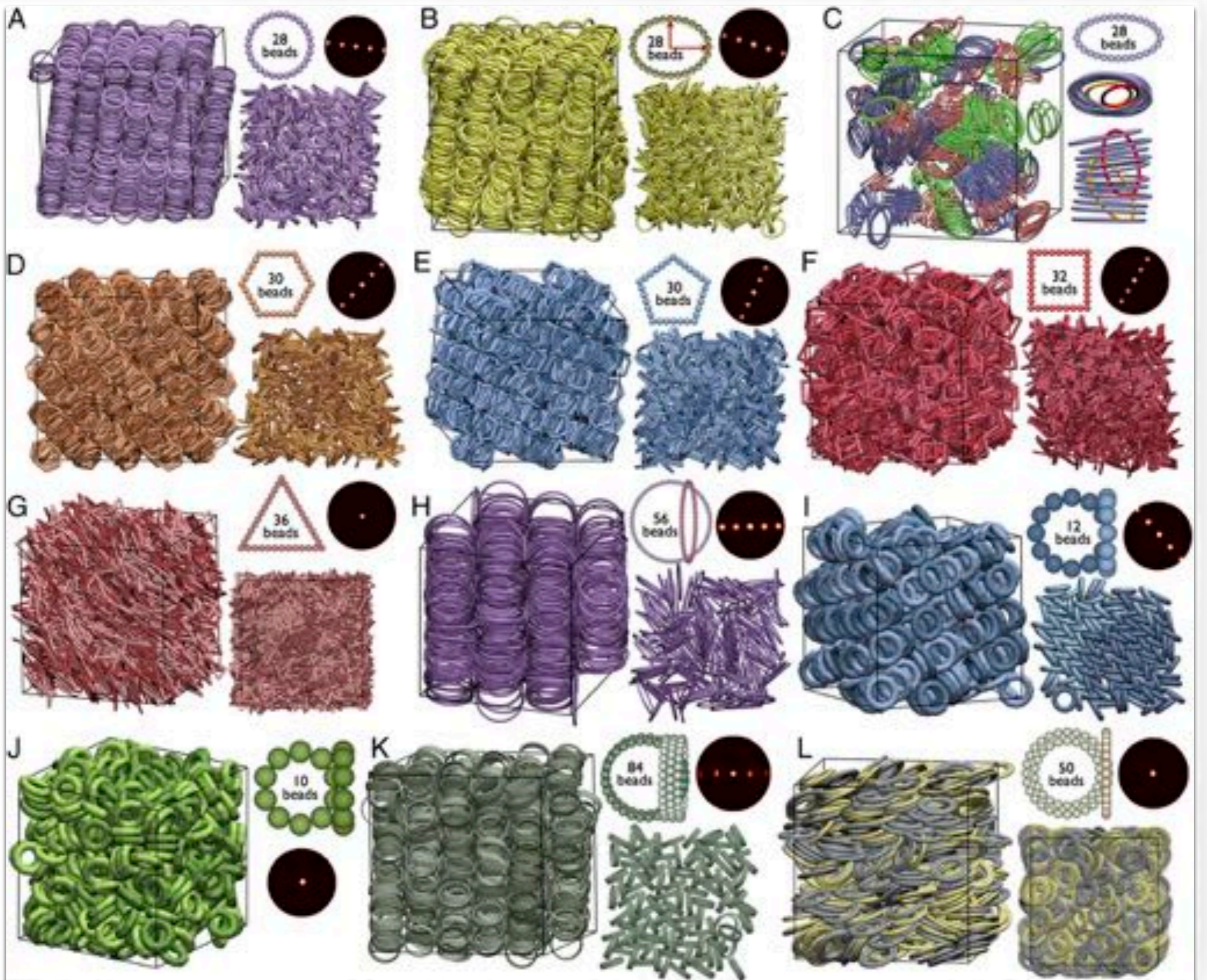


Rings of type 2



Self-assembly of colloidal rings





Colloidal rings confined in a planar slit

The University of Manchester

$$L/r_p = 11.2 \quad L_z/r_p = 65.4$$

$$L/r_p = 11.2 \quad L_z/r_p = 59.2$$

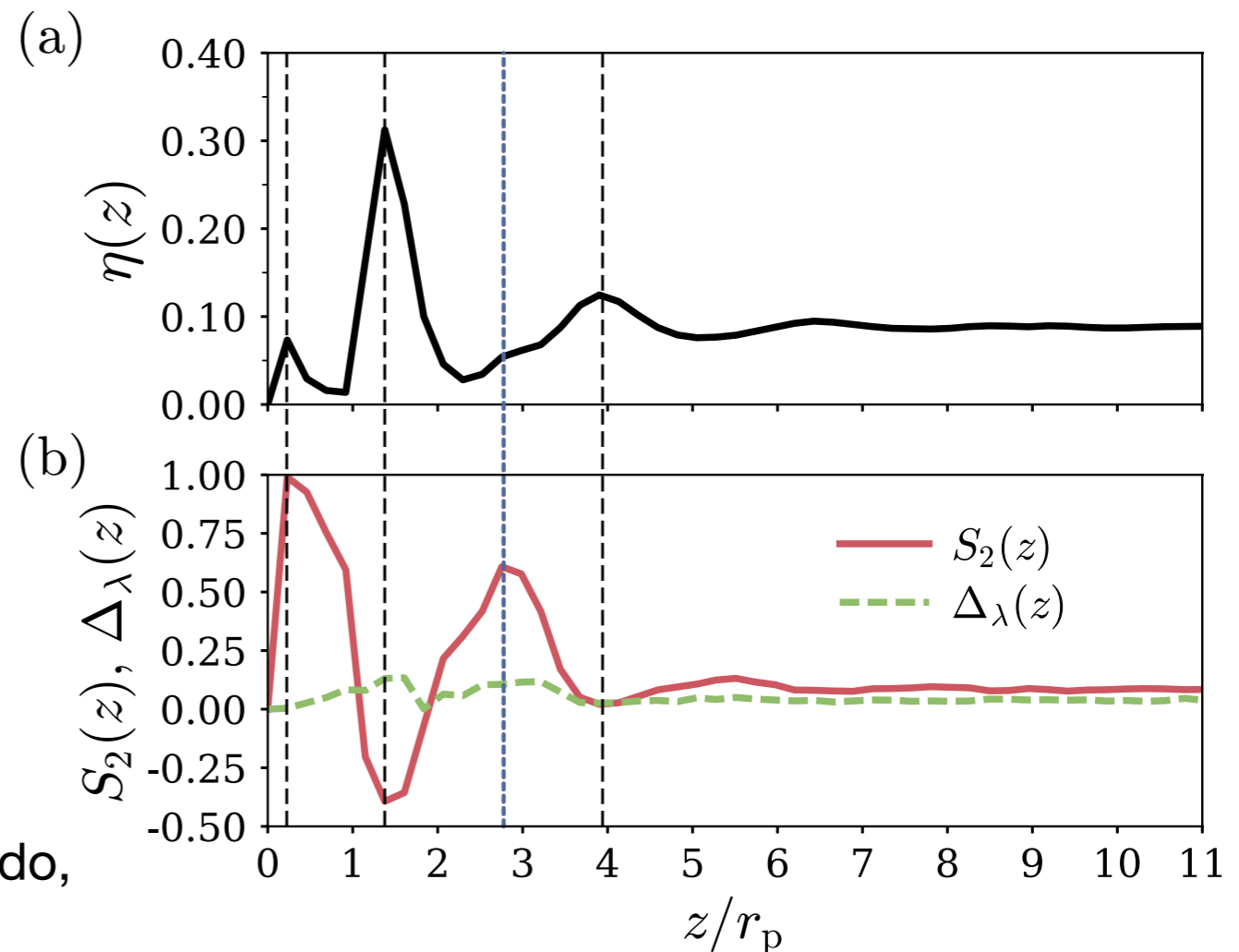


$$\eta(z_j) = \frac{N_s \sigma^3 \pi \langle N(z_j) \rangle}{6 L^2 \delta z}$$

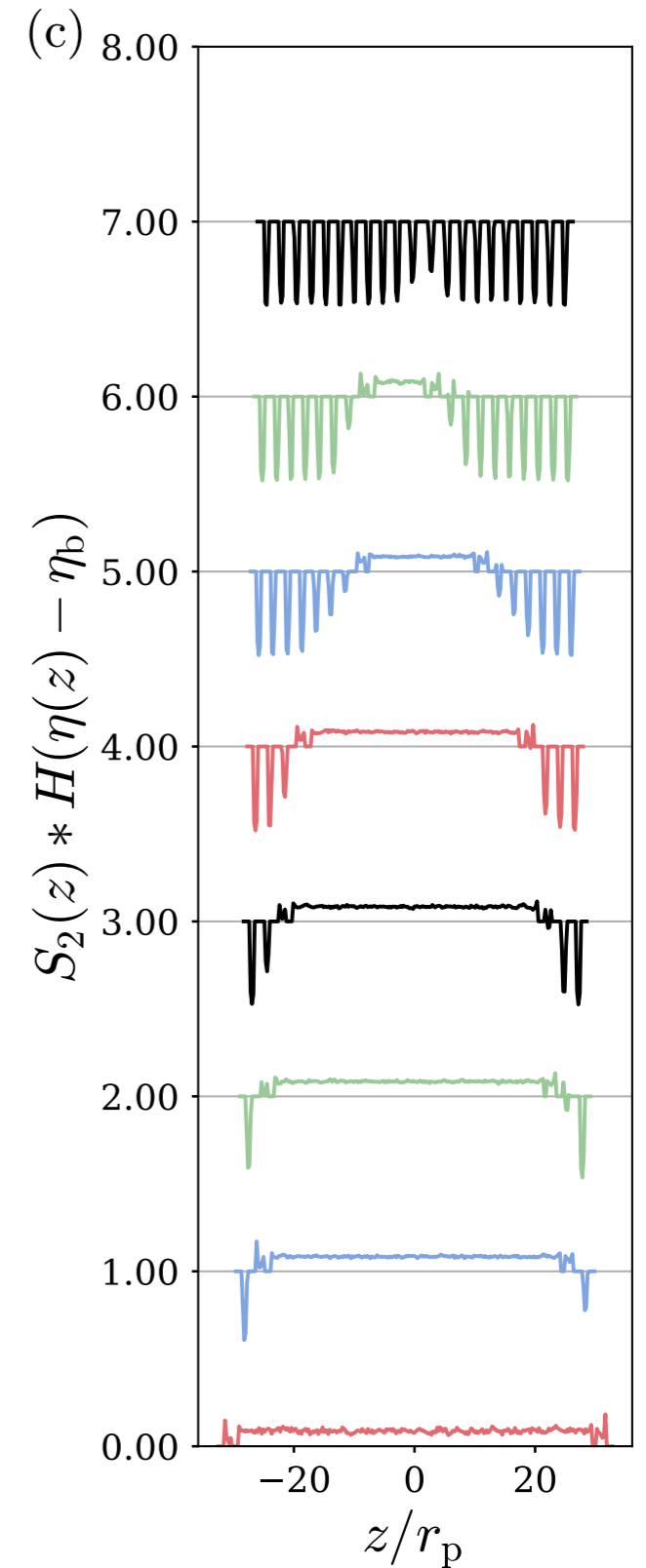
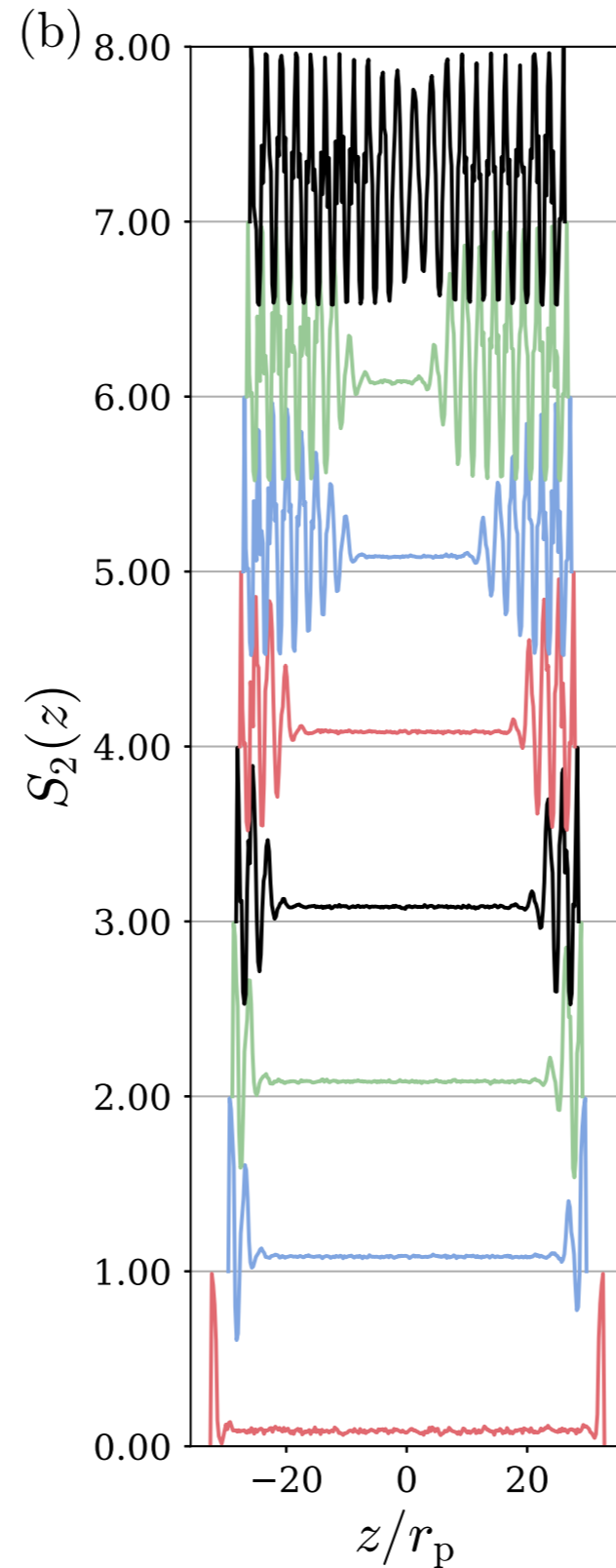
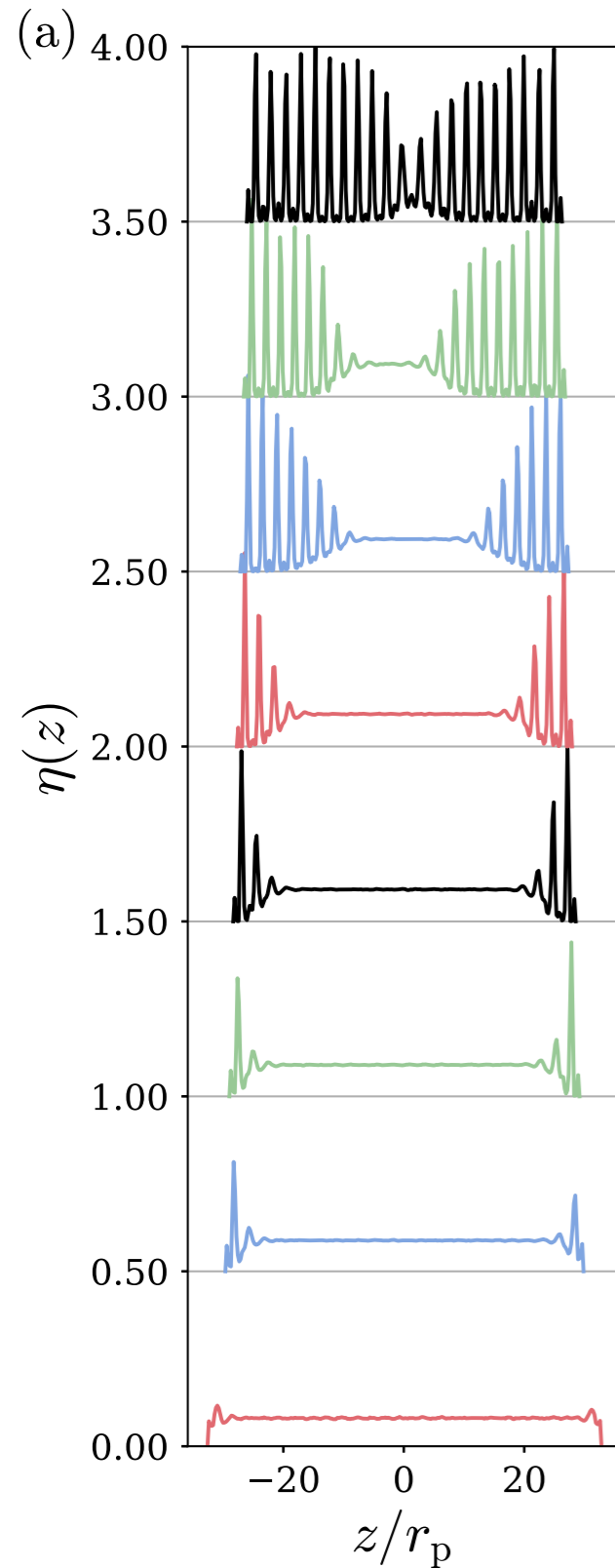
$$\mathbf{Q}(z_j) = \frac{1}{N(z_j)} \sum_{i=1}^{N(z_j)} \left(\frac{3 \hat{\mathbf{u}}_i \otimes \hat{\mathbf{u}}_i}{2} - \frac{\mathbf{I}}{2} \right)$$

C Avendaño, G Jackson, and HH Wensink,
Mol. Phys. (2018)

C Avendaño, EA Müller, G Jackson, and FA Escobedo,
PNAS, **113**, 9699 (2016)



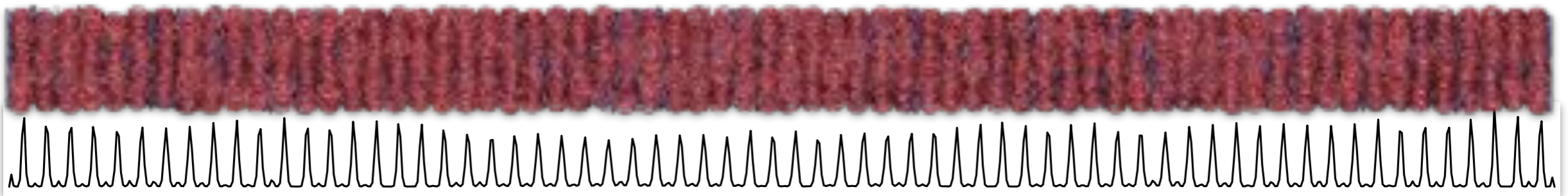
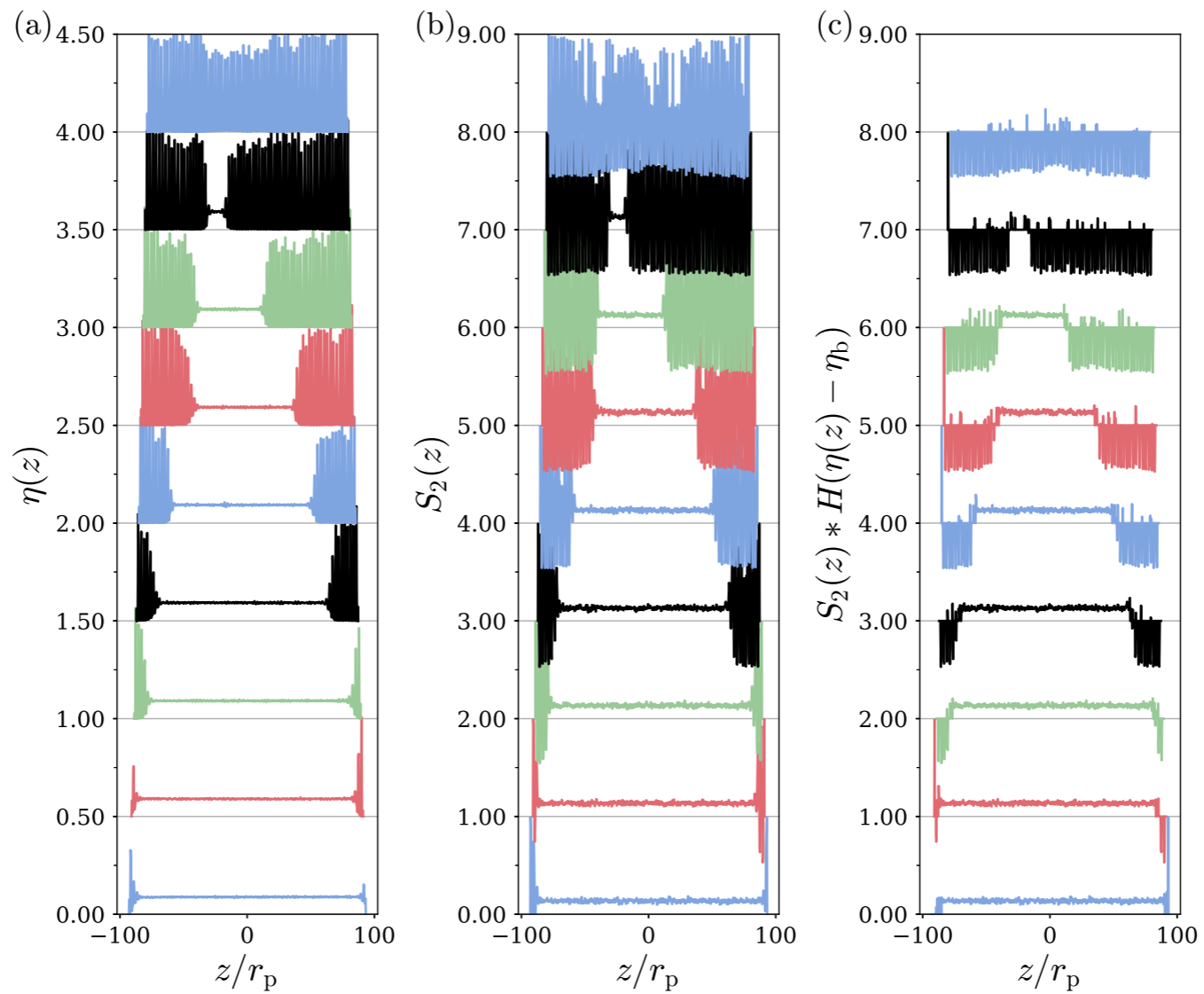
Colloidal rings confined in a planar slit



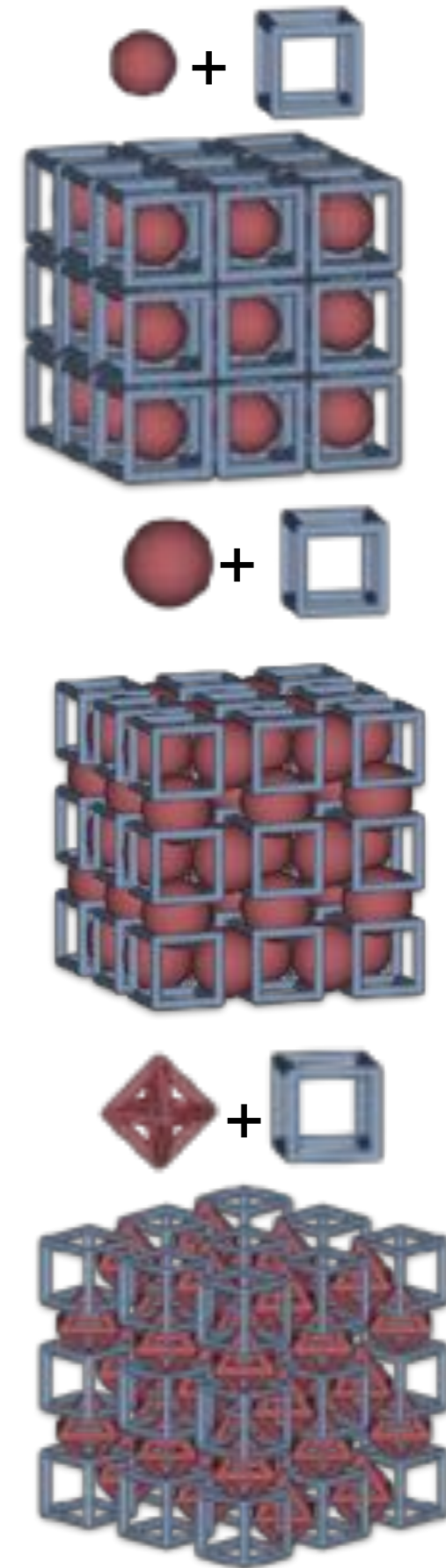
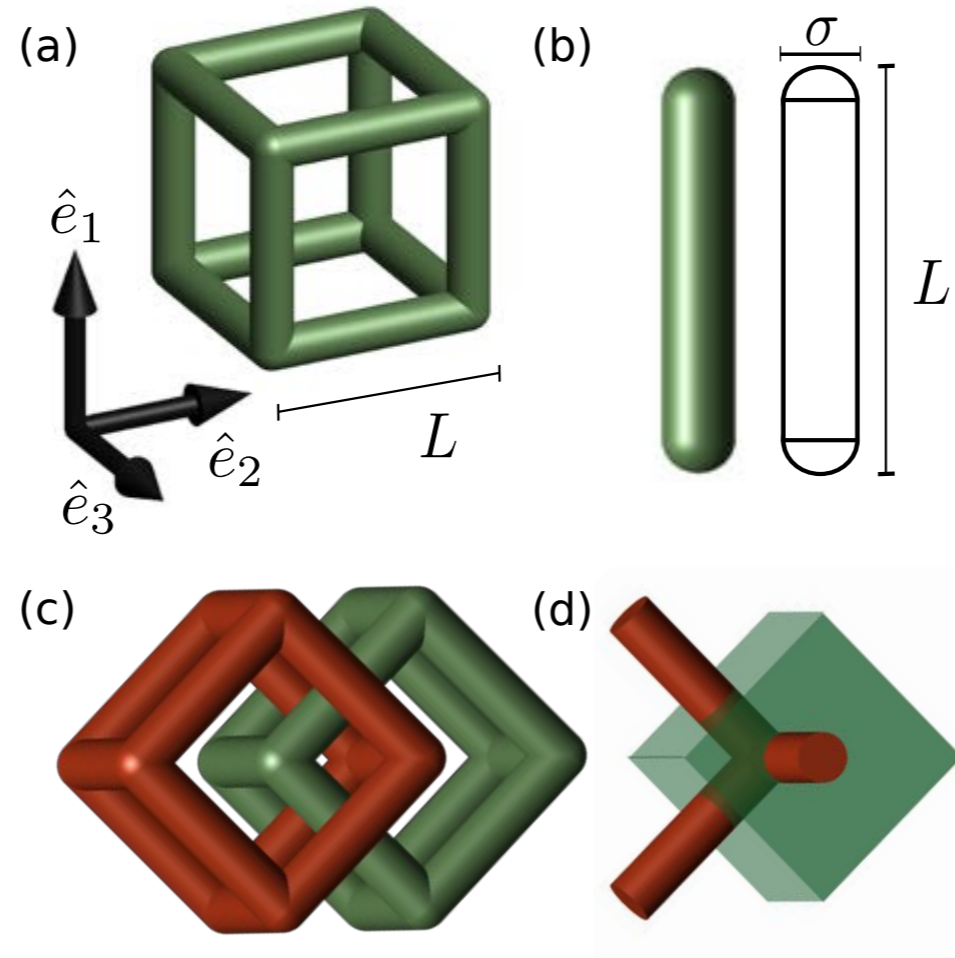
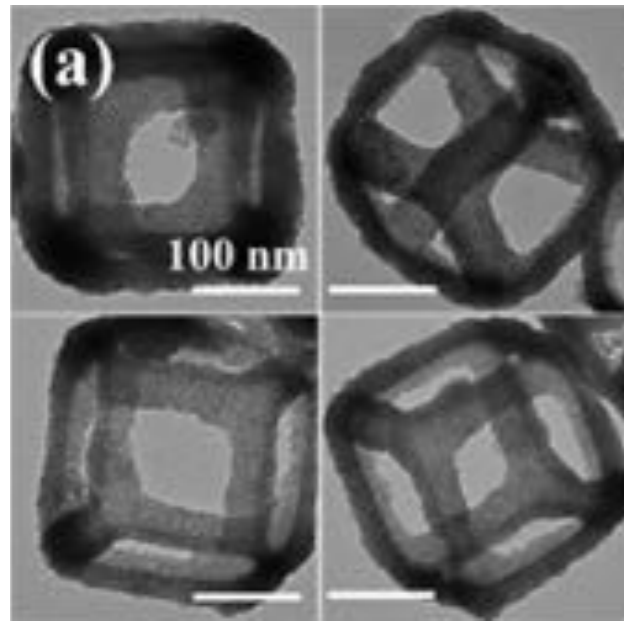
Colloidal rings confined in a planar slit



Colloidal rings confined in a planar slit



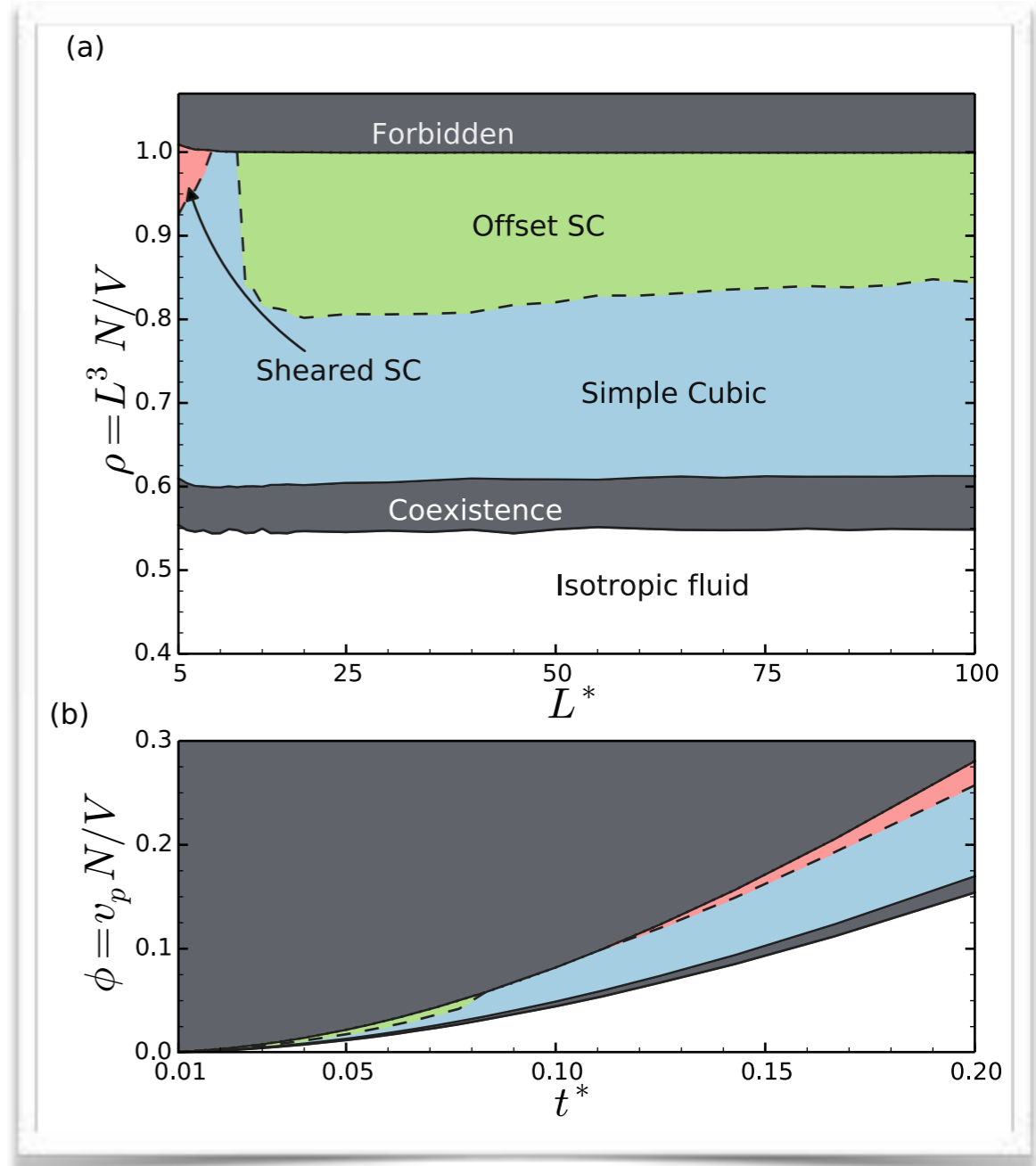
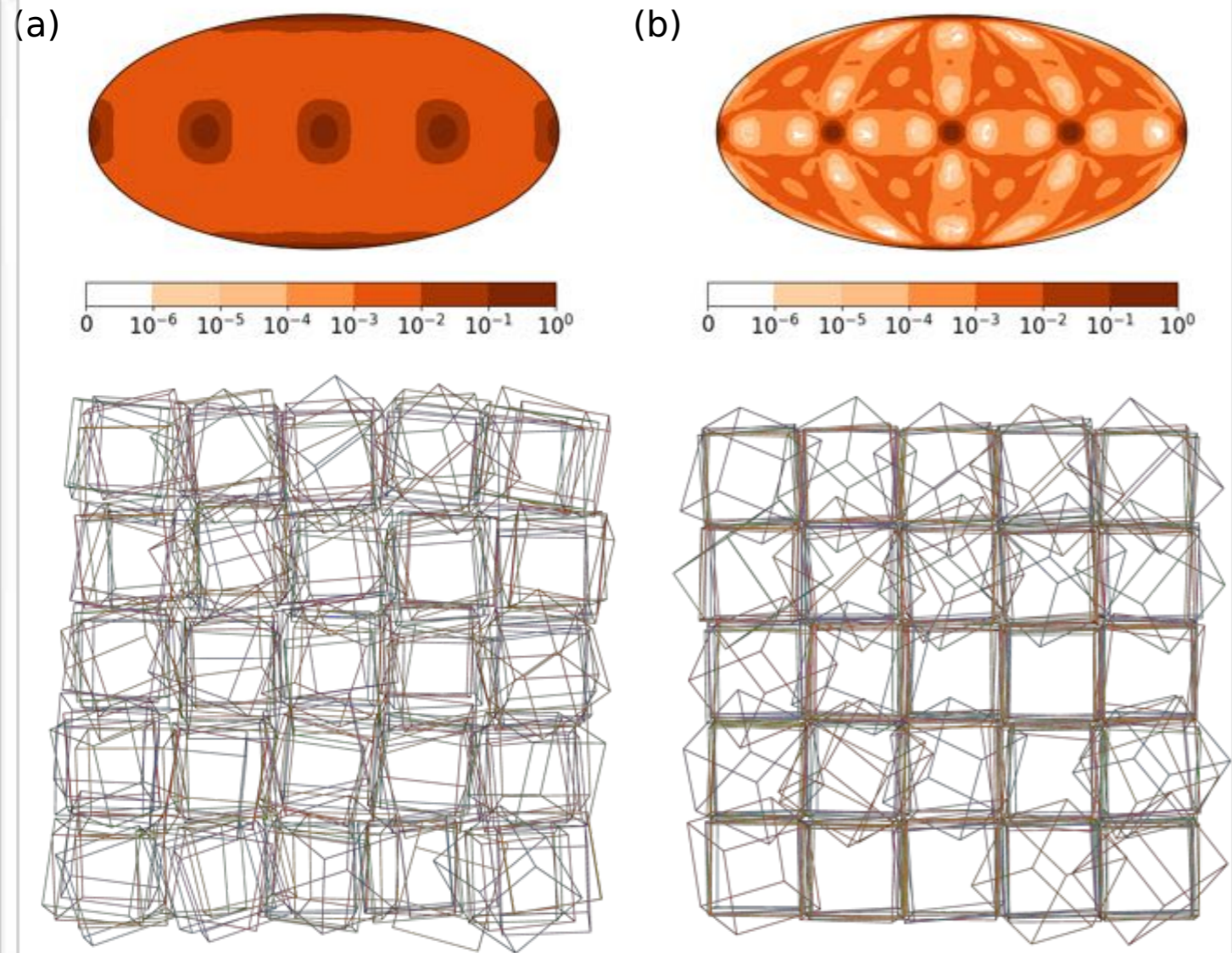
Self-assembly of colloidal frames



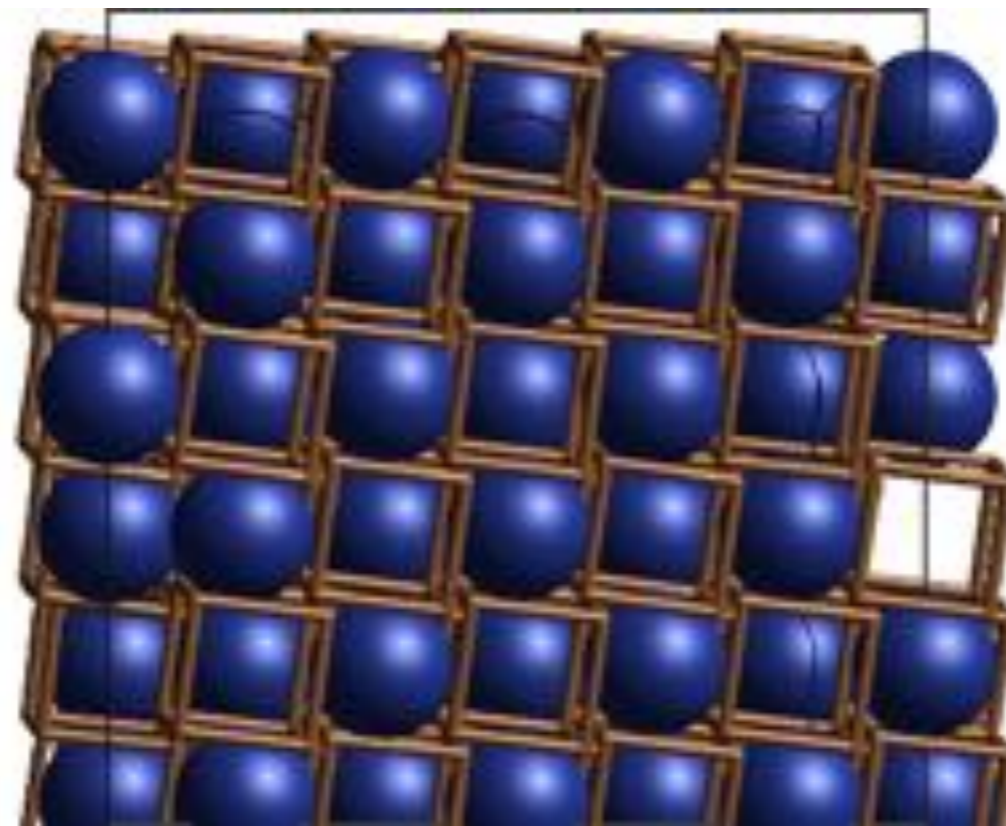
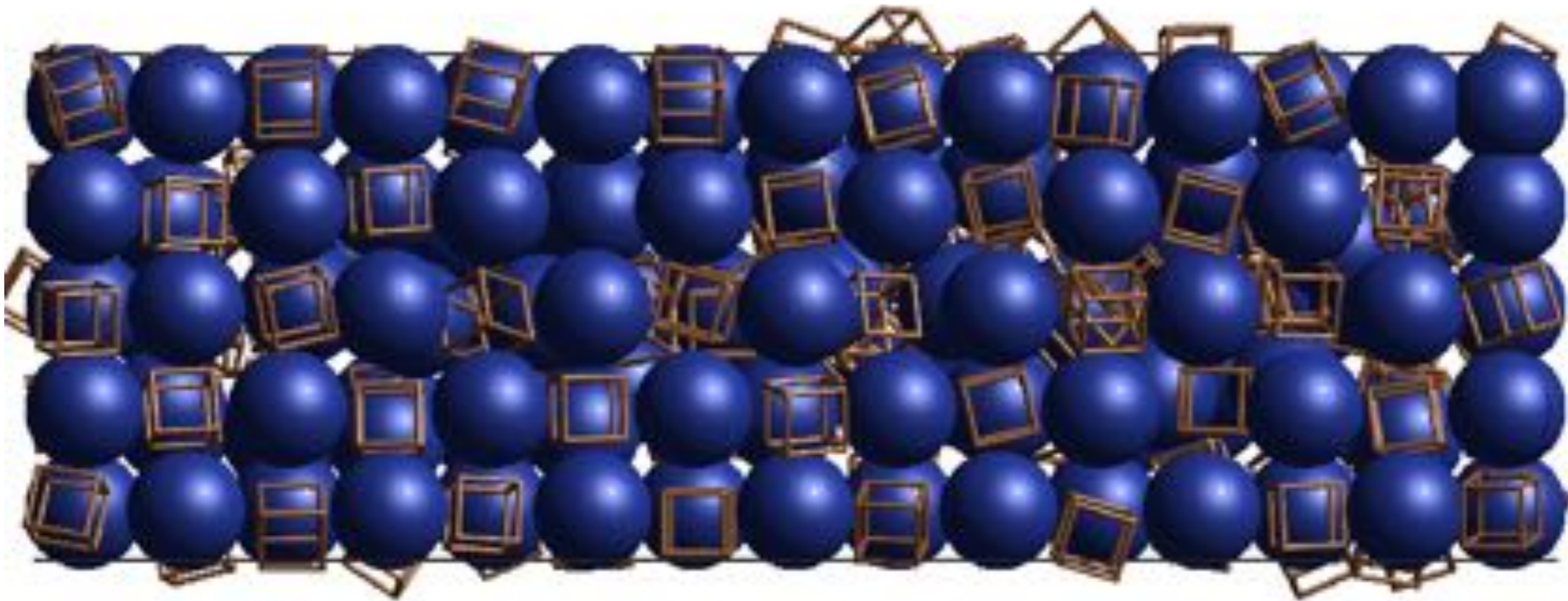
Porosity of self-assembled superlattices increases

- JM McBride and C Avendaño, *Phys. Rev. Mater.*, 2018, **2**, 055601
 H Wang et al., *ACS Appl. Mater. Interfaces*, 2017, **9**, 26897
 S Ciarella, O Gang, and F Sciortino, *Eur. Phys. J. E*, 2016, **39**, 131
 C Avendaño and FA Escobedo, *Soft Matter*, 2012 **8**, 4675

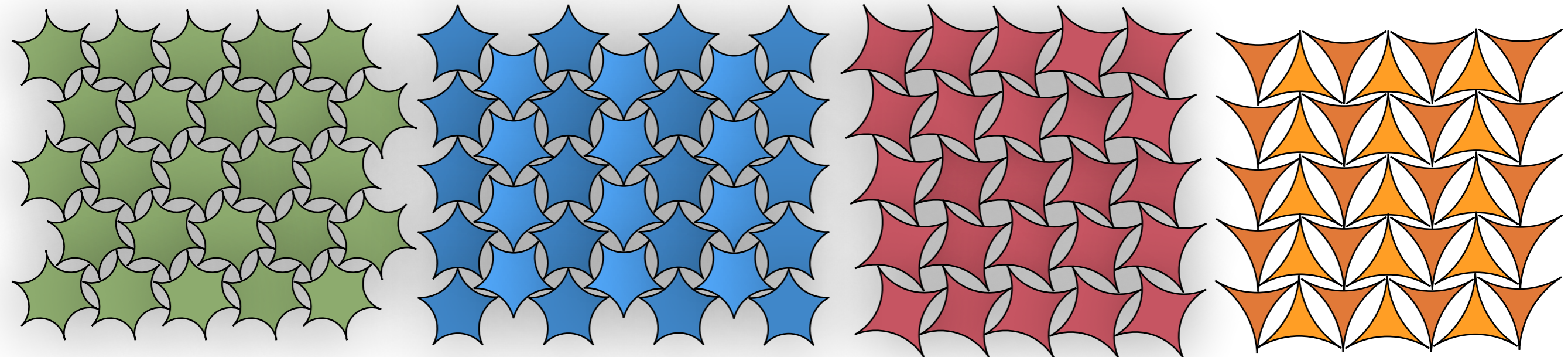
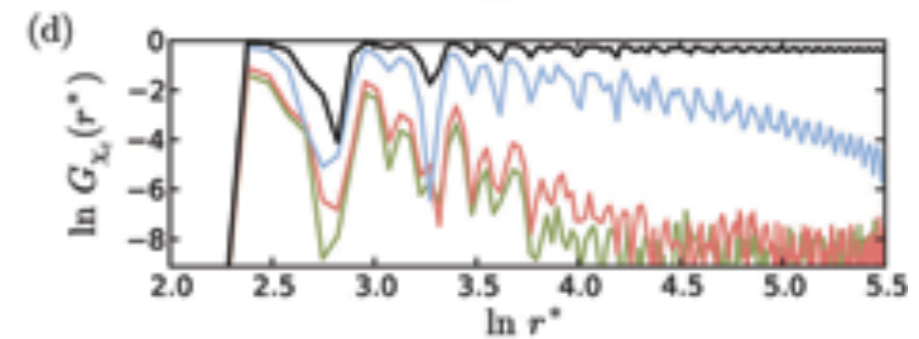
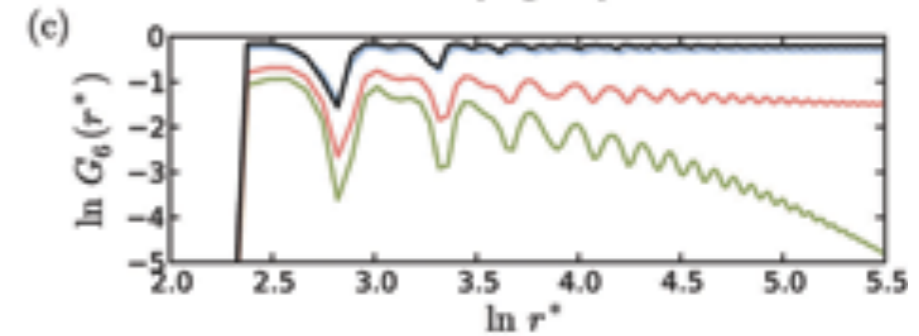
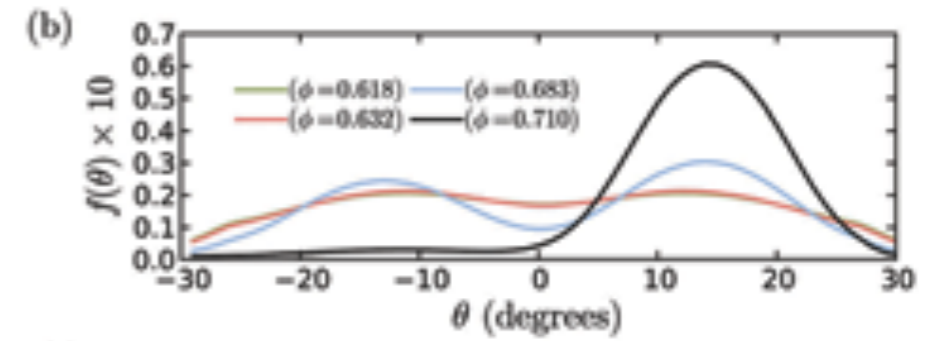
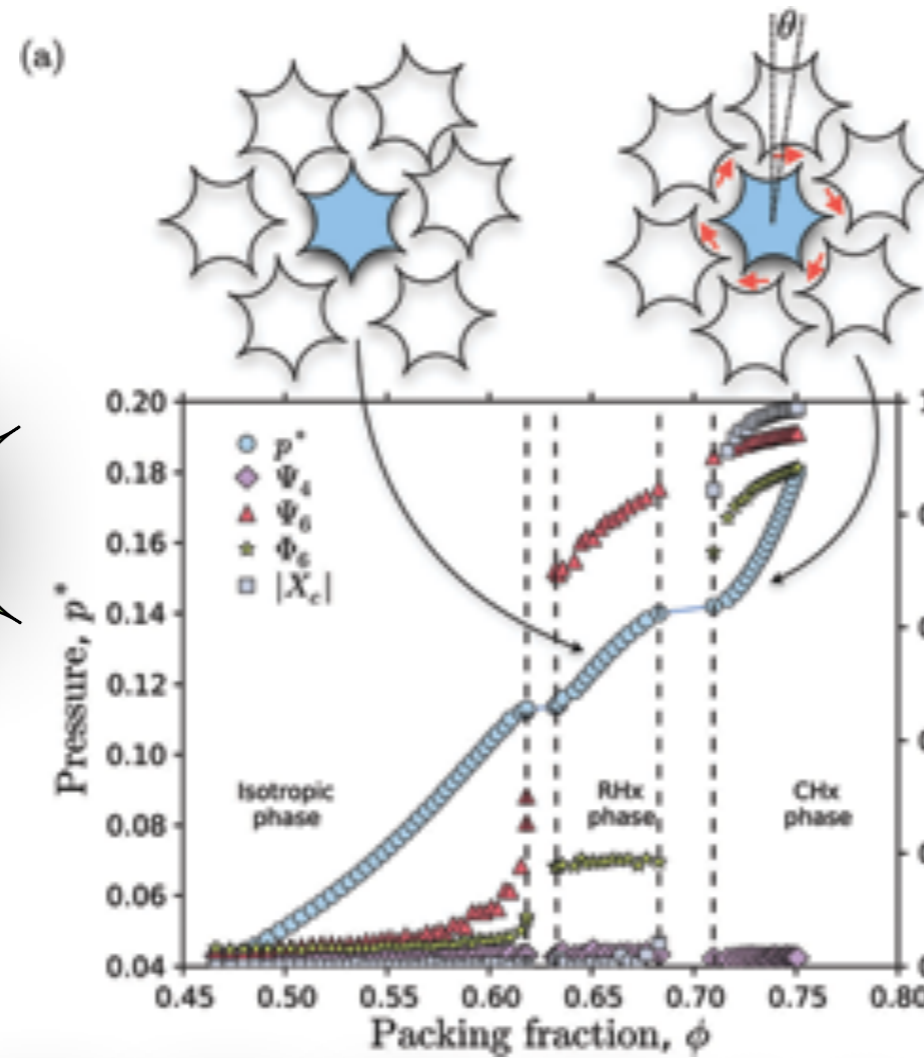
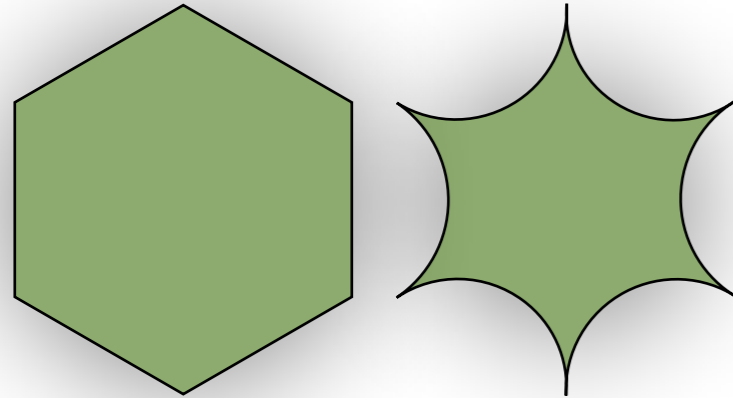
Self-assembly of colloidal frames



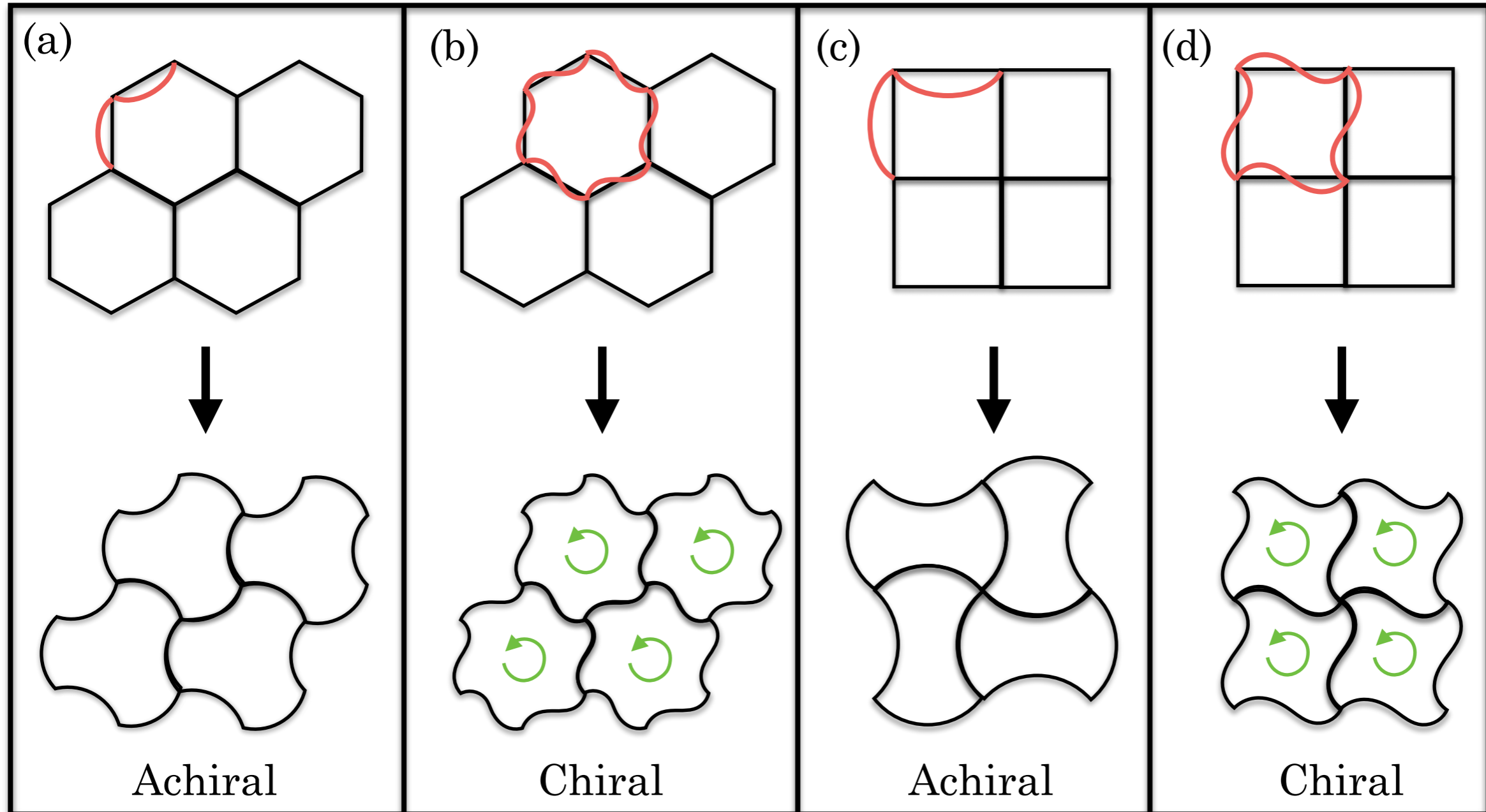
Self-assembly of colloidal frames



Self-assembly of non-convex polygons

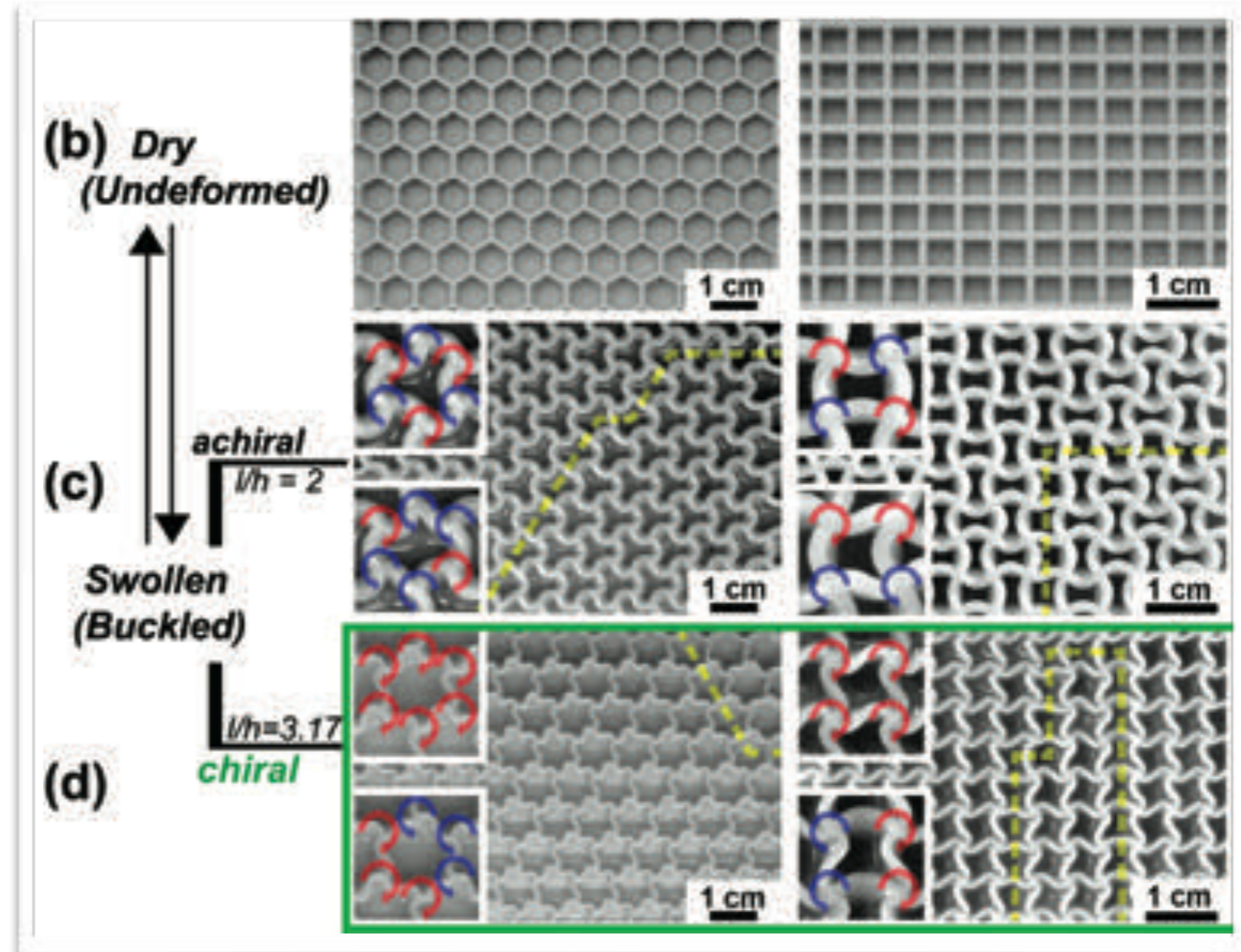
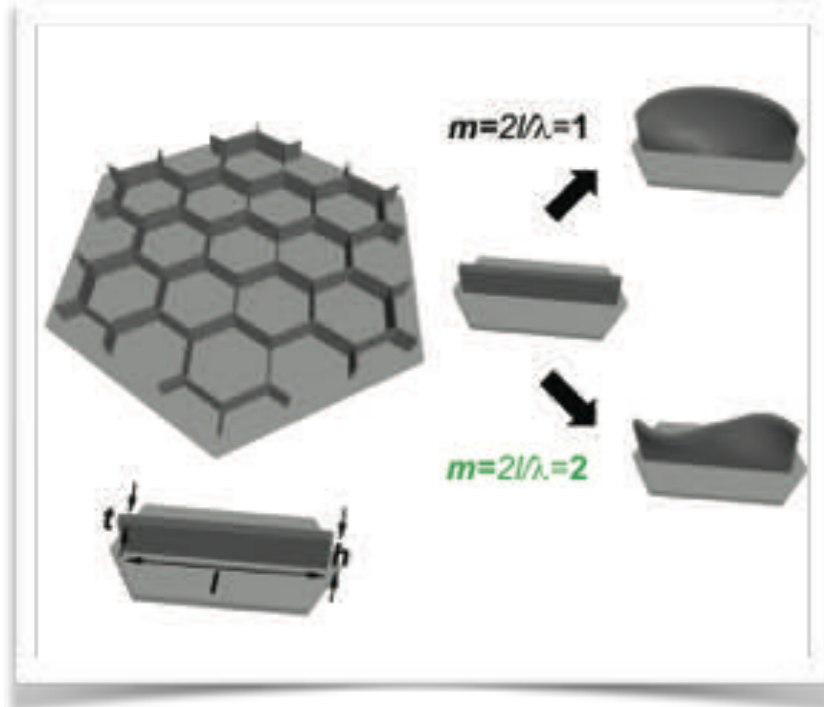


Self-assembly of non-convex polygons



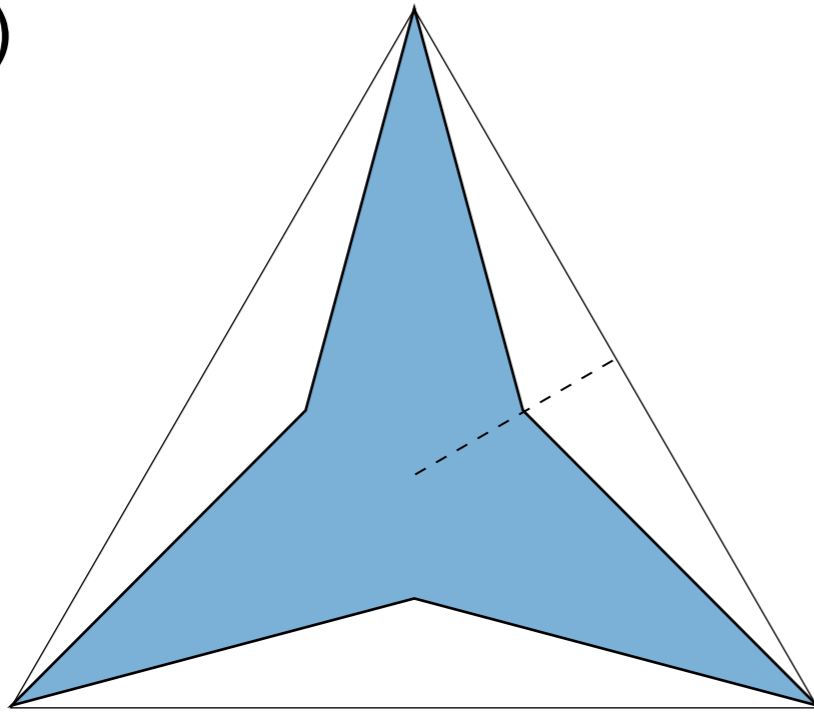
Self-assembly of non-convex polygons

The University of Manchester

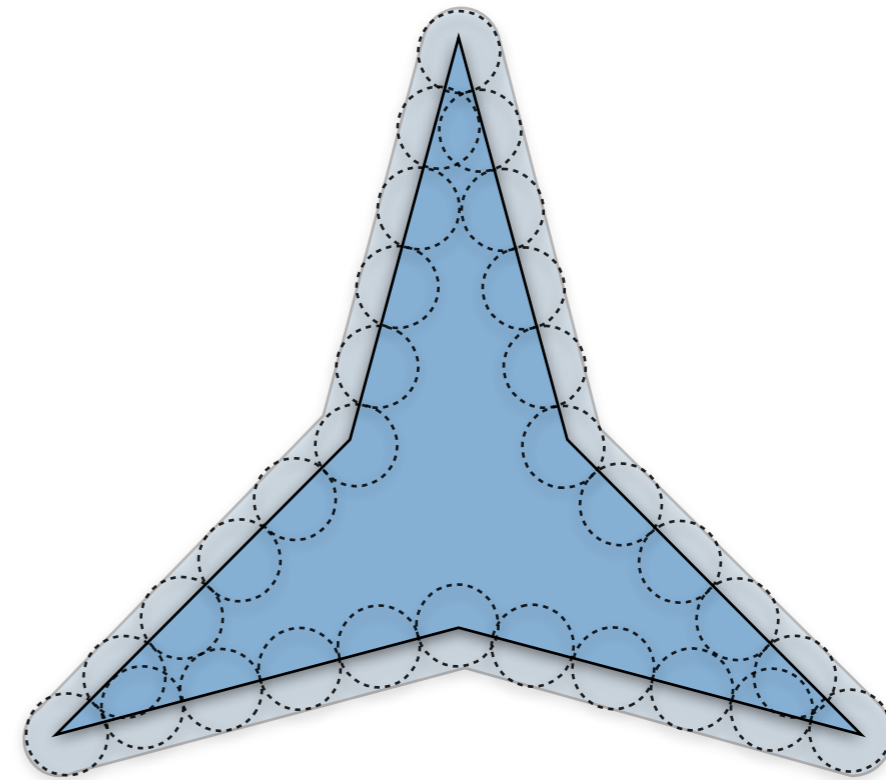


Self-assembly of non-convex polygons

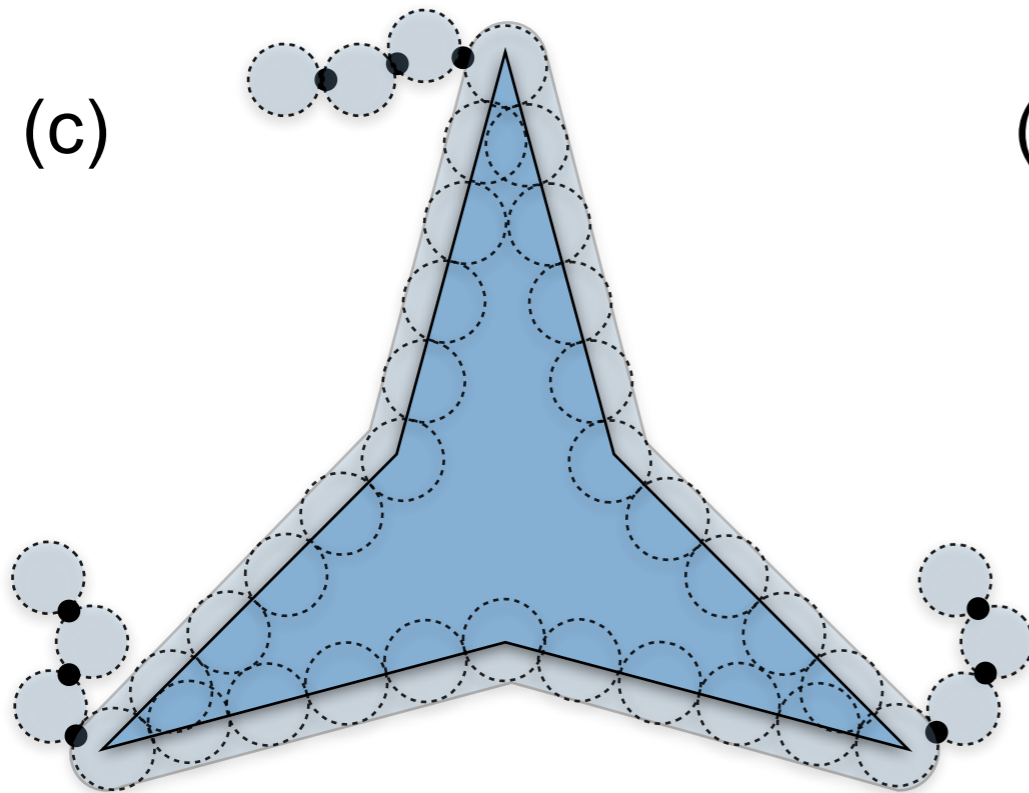
(a)



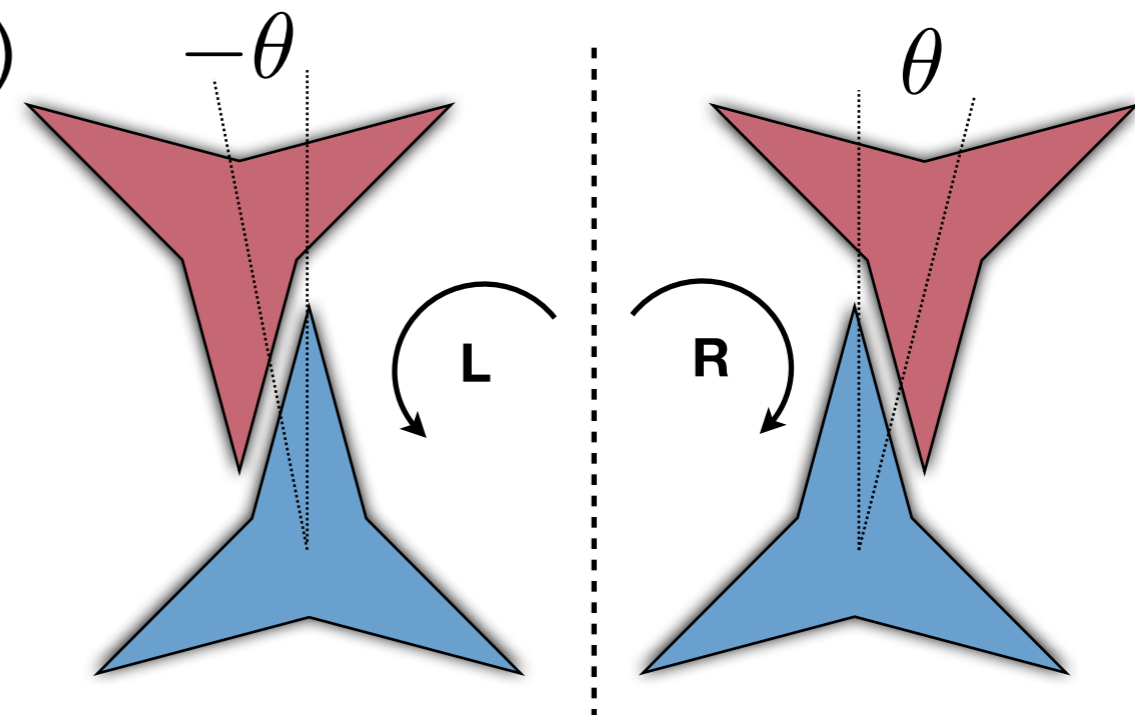
(b)



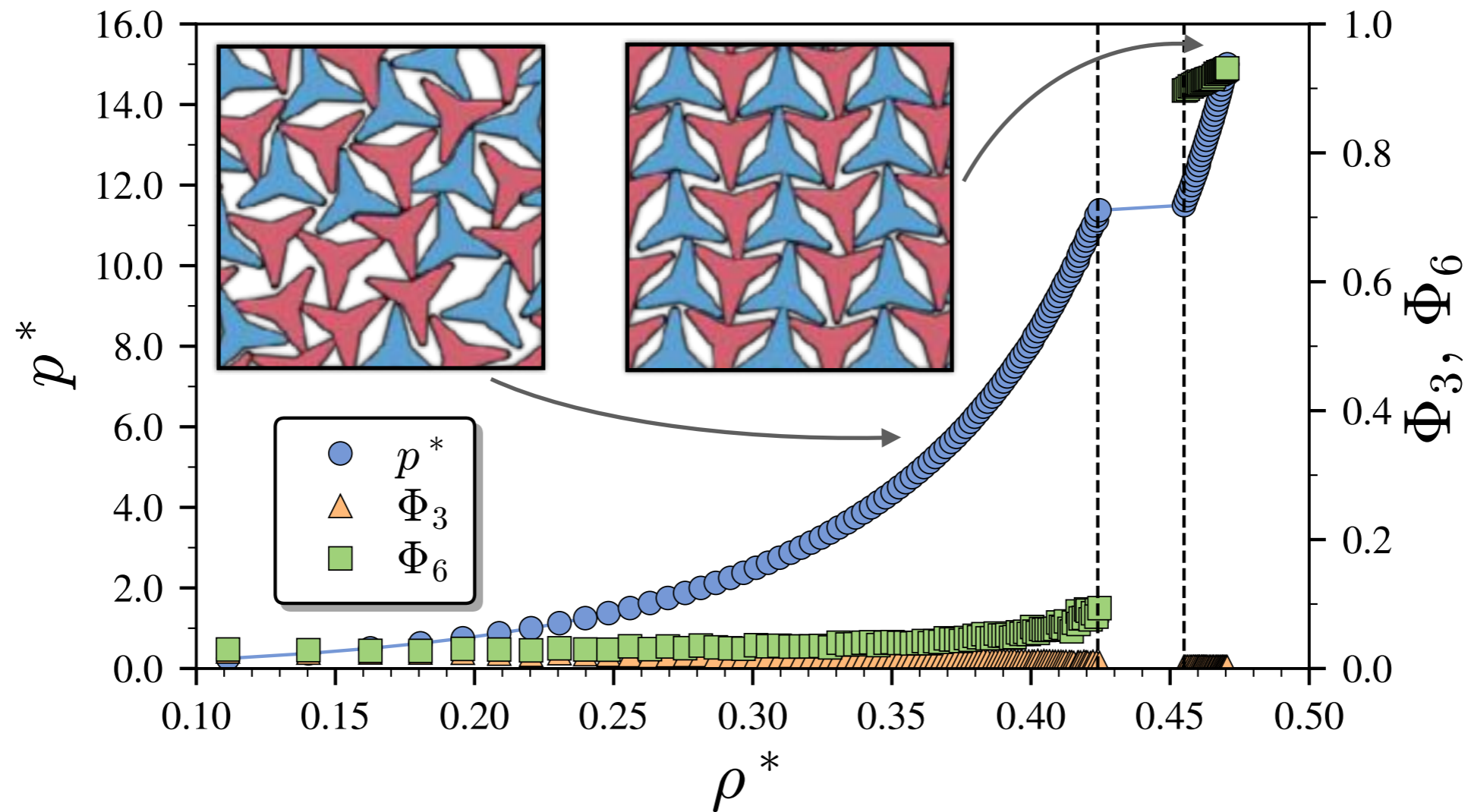
(c)



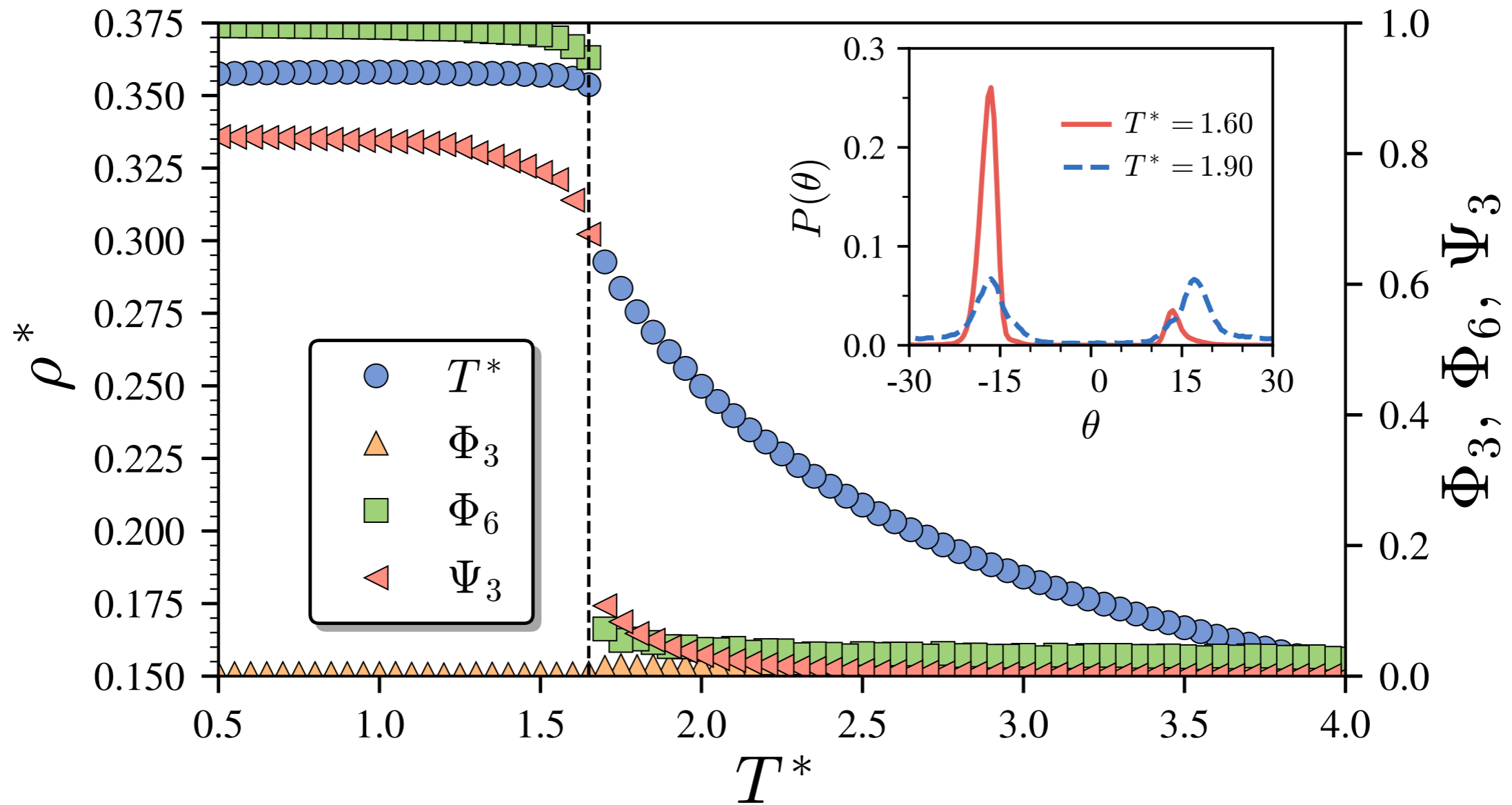
(d)



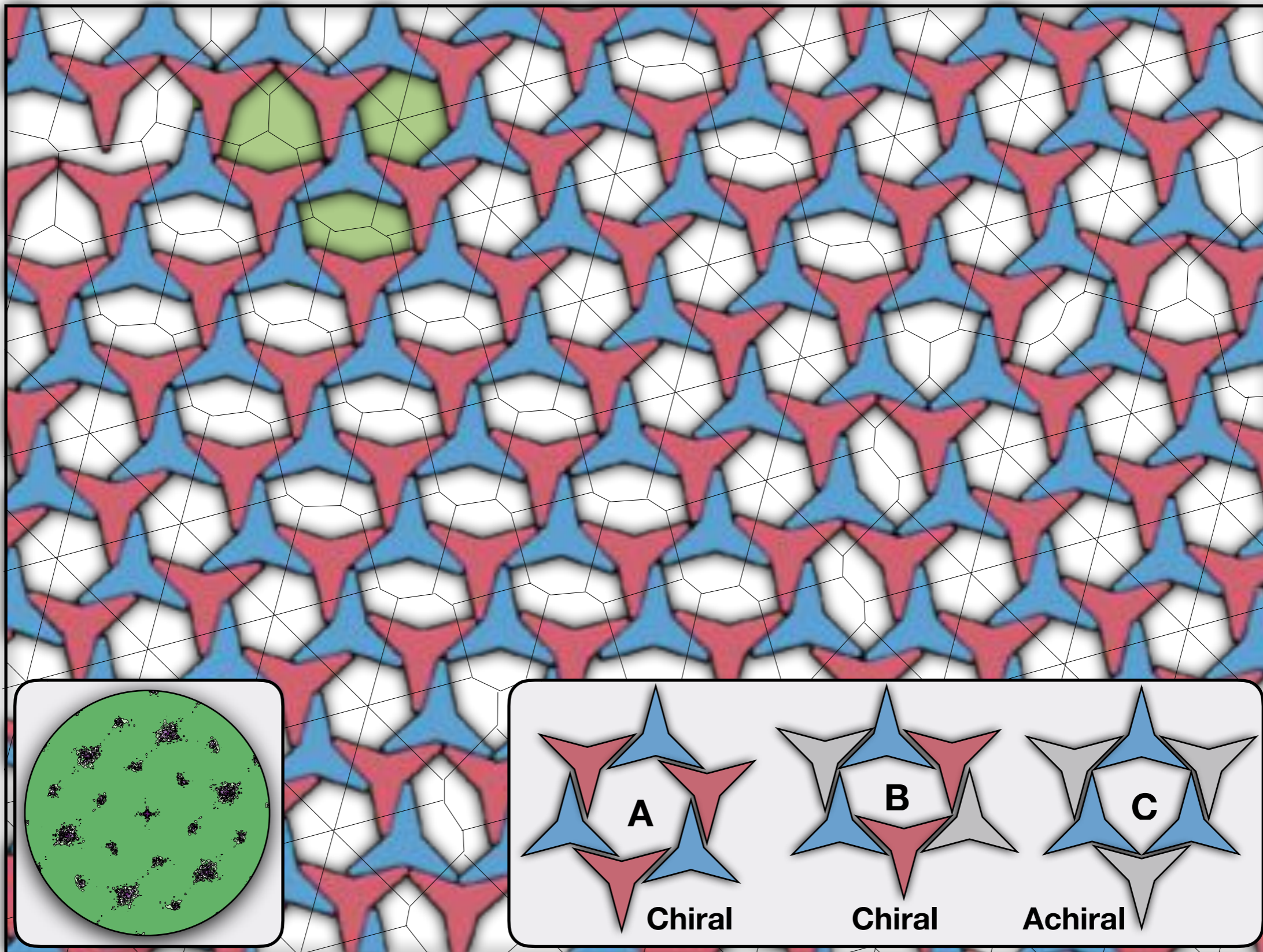
Self-assembly of non-convex polygons



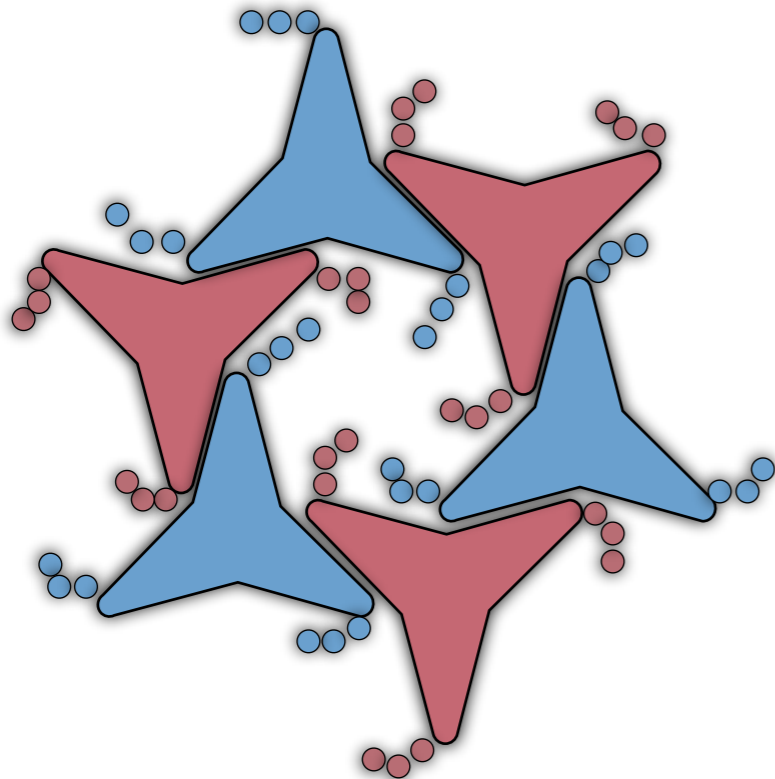
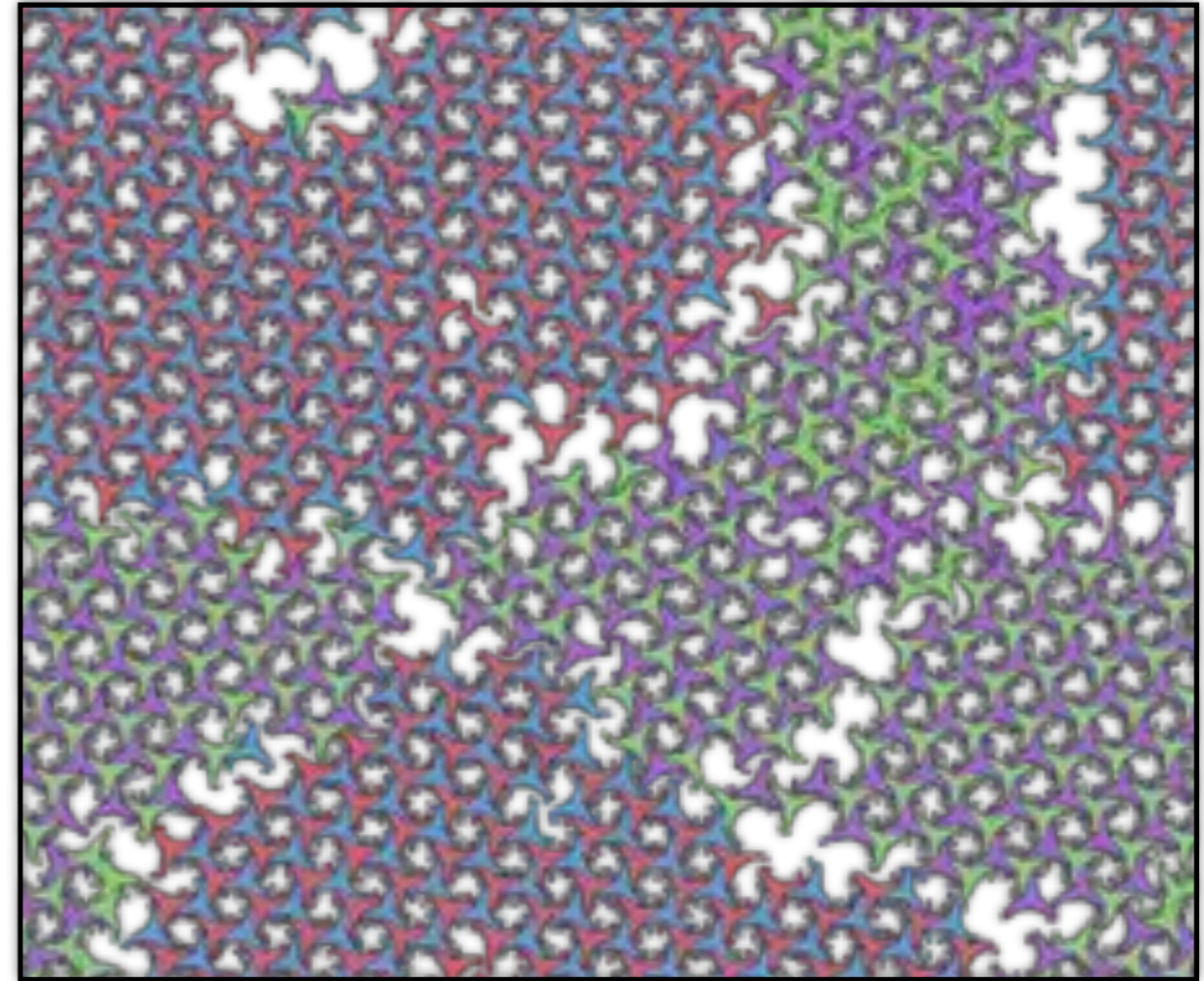
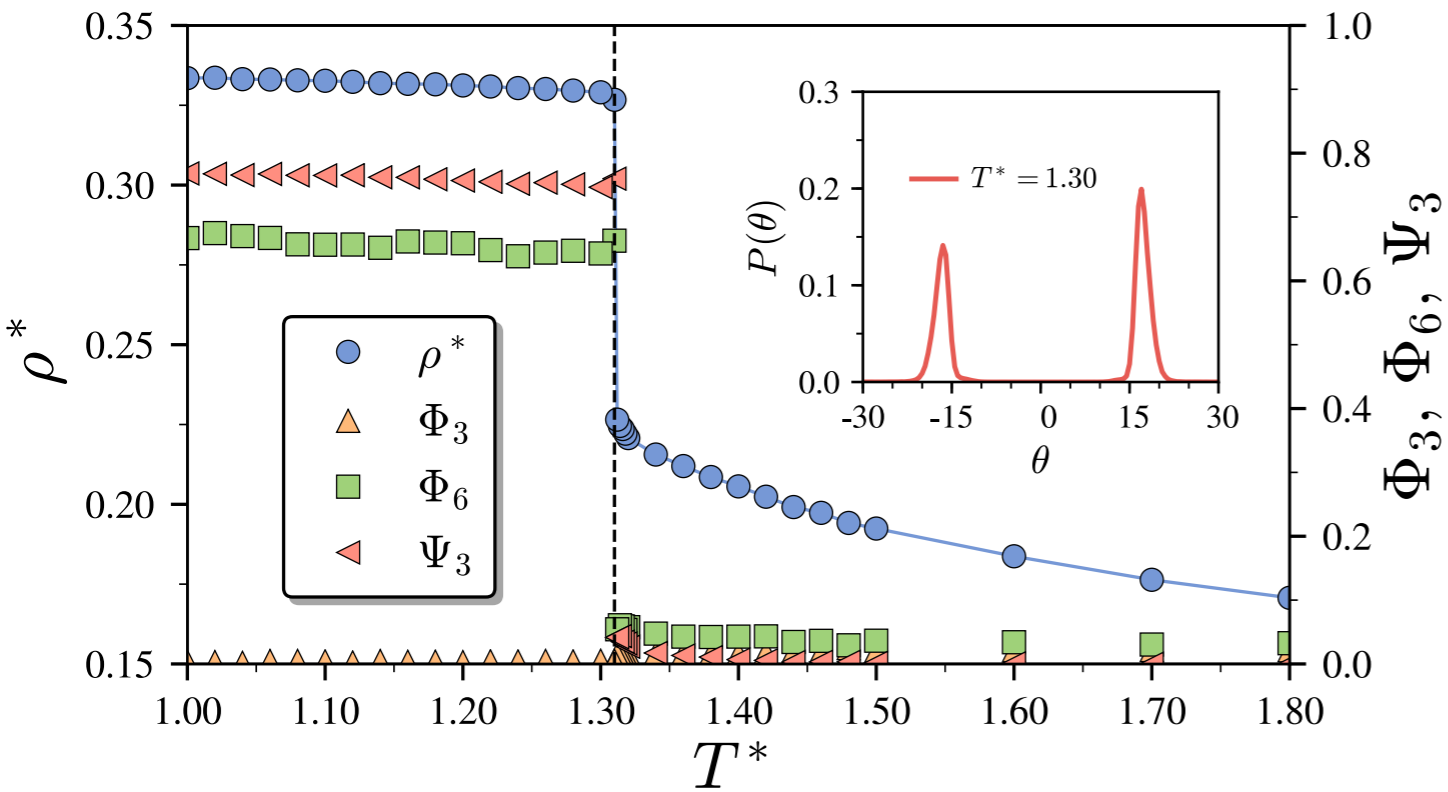
Self-assembly of non-convex polygons



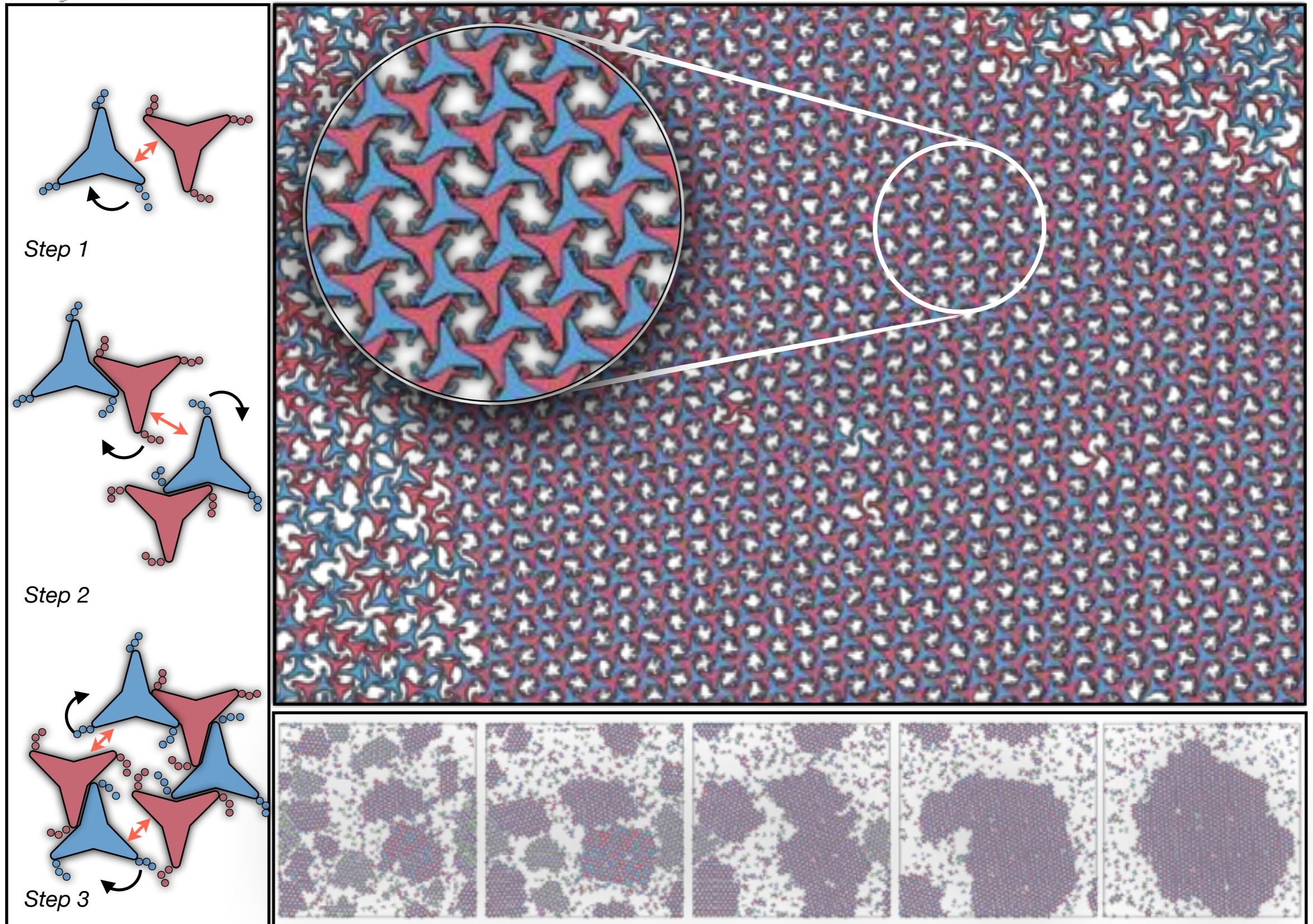
Self-assembly of non-convex polygons



Self-assembly of non-convex polygons

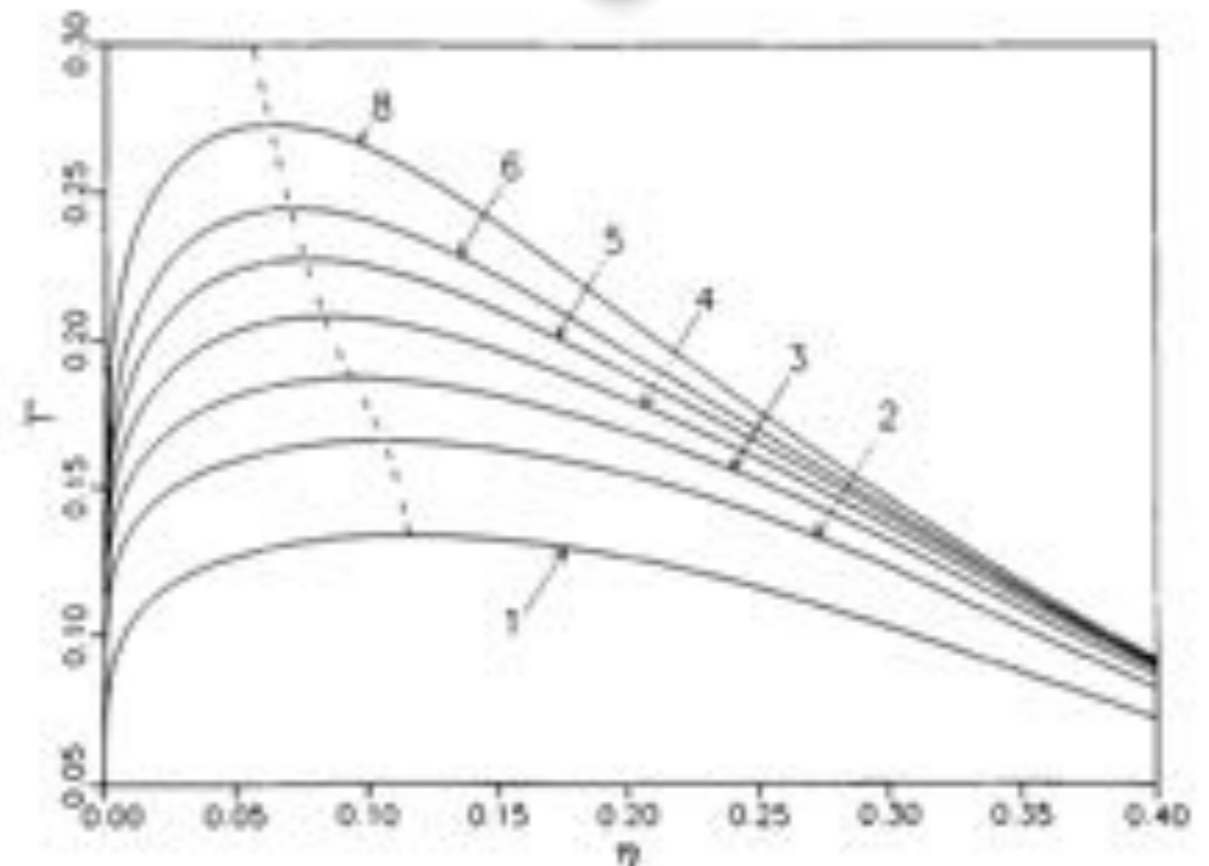
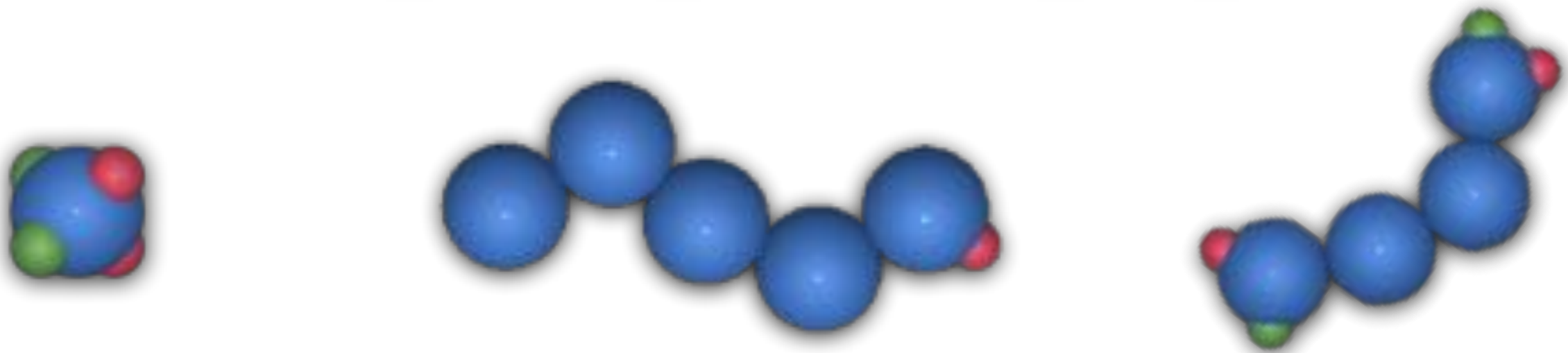
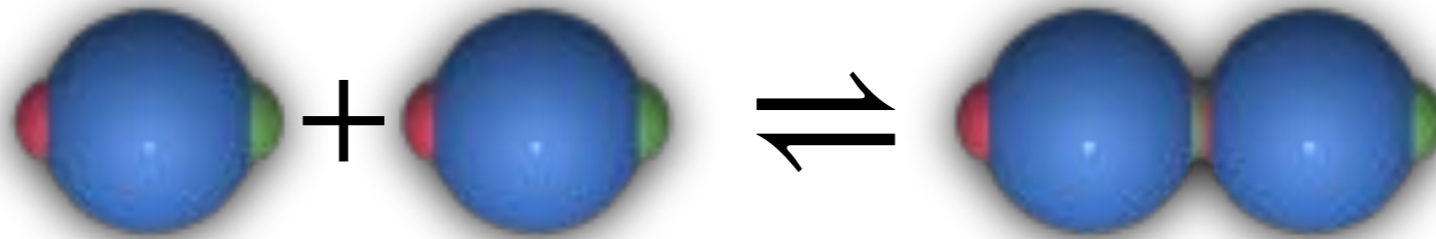


Self-assembly of non-convex polygons



SAFT- γ coarse grained

Statistical Associating Fluid Theory (SAFT)



Keith Gubbins' group

@ Cornell University

Chapman, Jackson, Gubbins, Radosz,

Fluid Phase Equil **52**, 31 (1989);

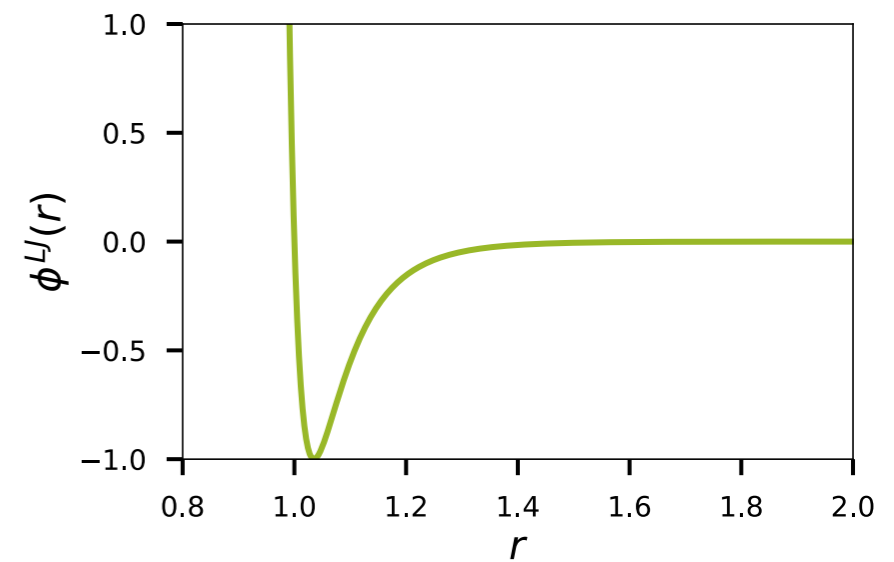
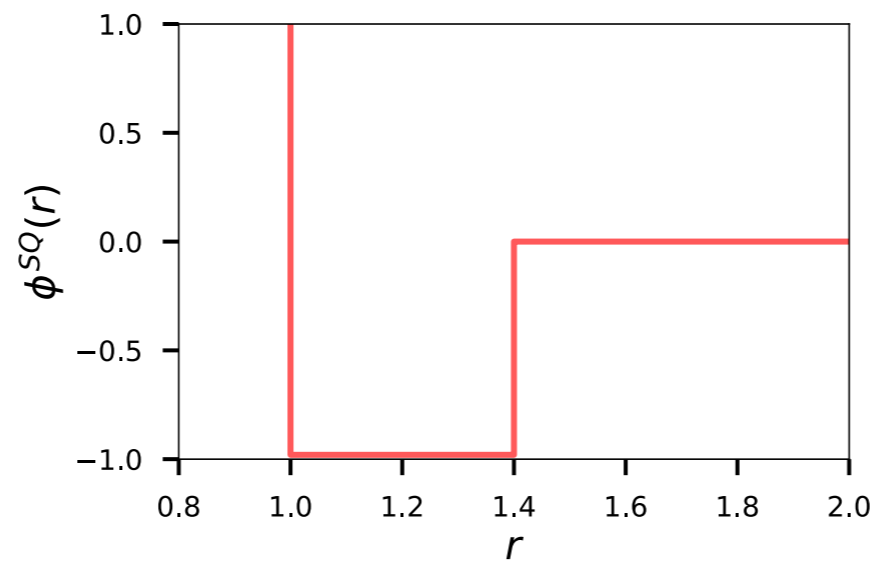
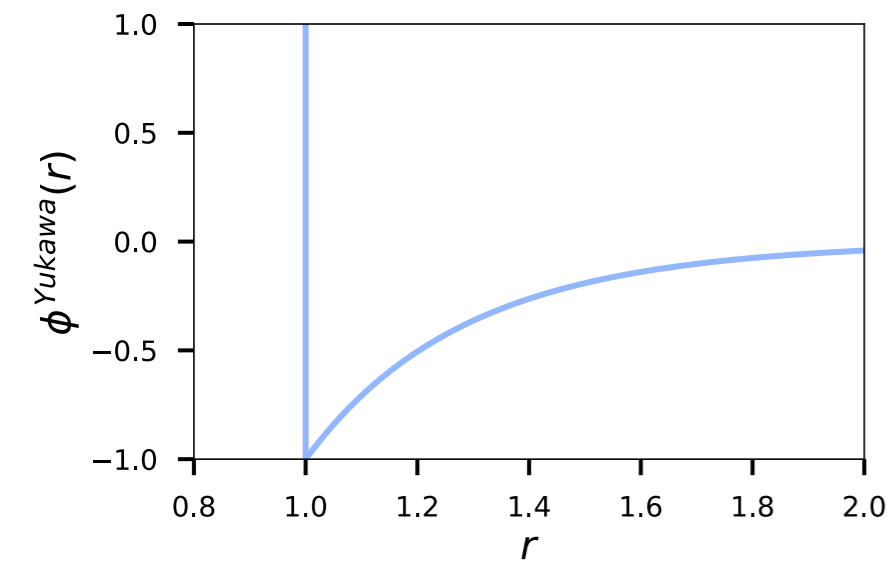
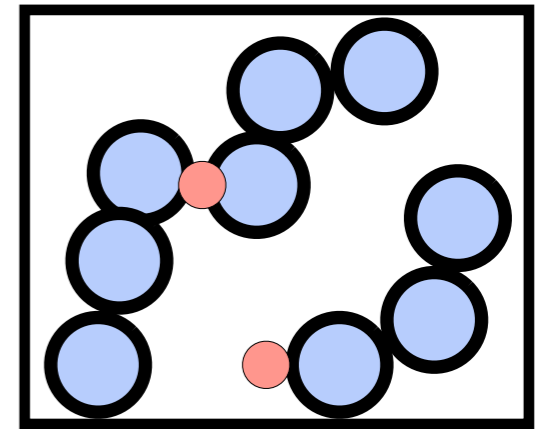
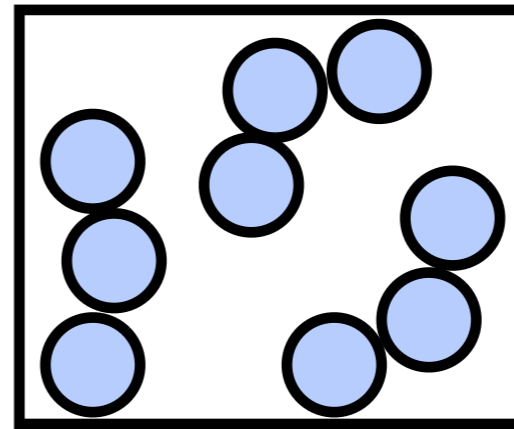
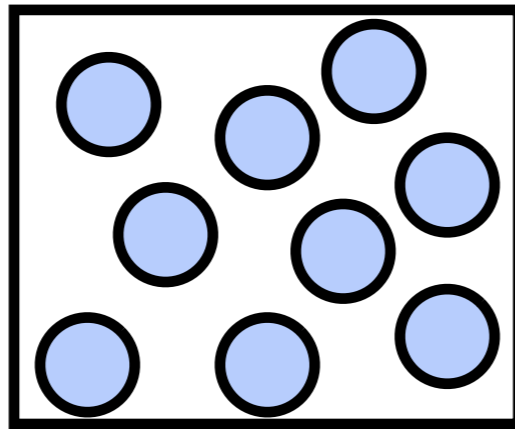
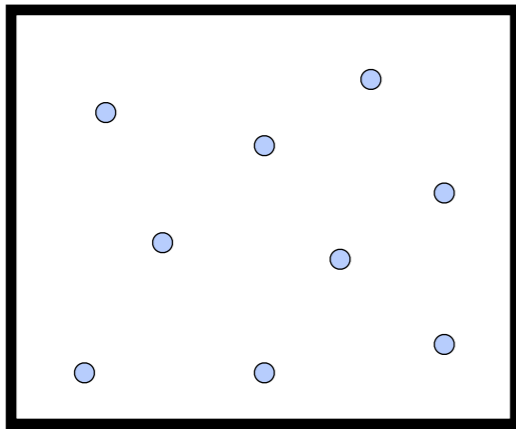
Mol Phys **65**, 1 (1988);

Mol Phys **65** 1057 (1988);

Ind. Eng. Chem. Res **29** 1709 (1990)

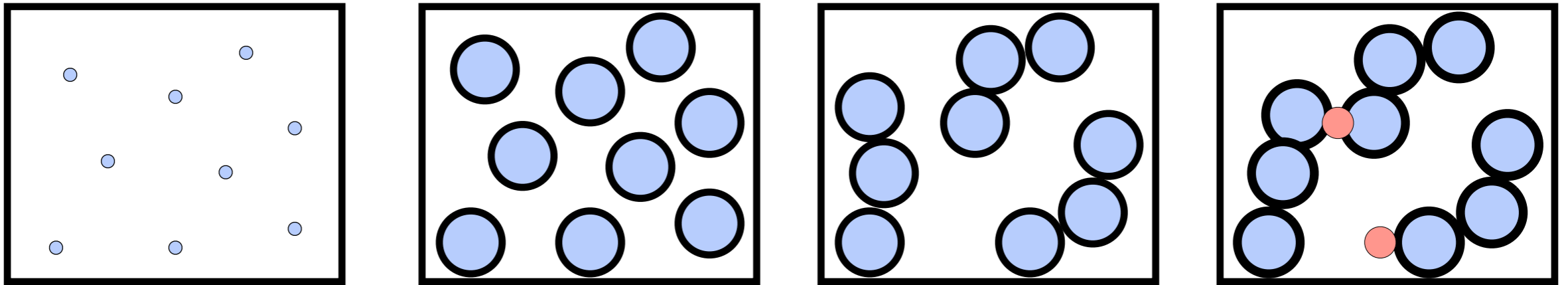
SAFT-VR

$$\frac{A^{\text{SAFT}}}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{mono}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc}}}{NkT}$$



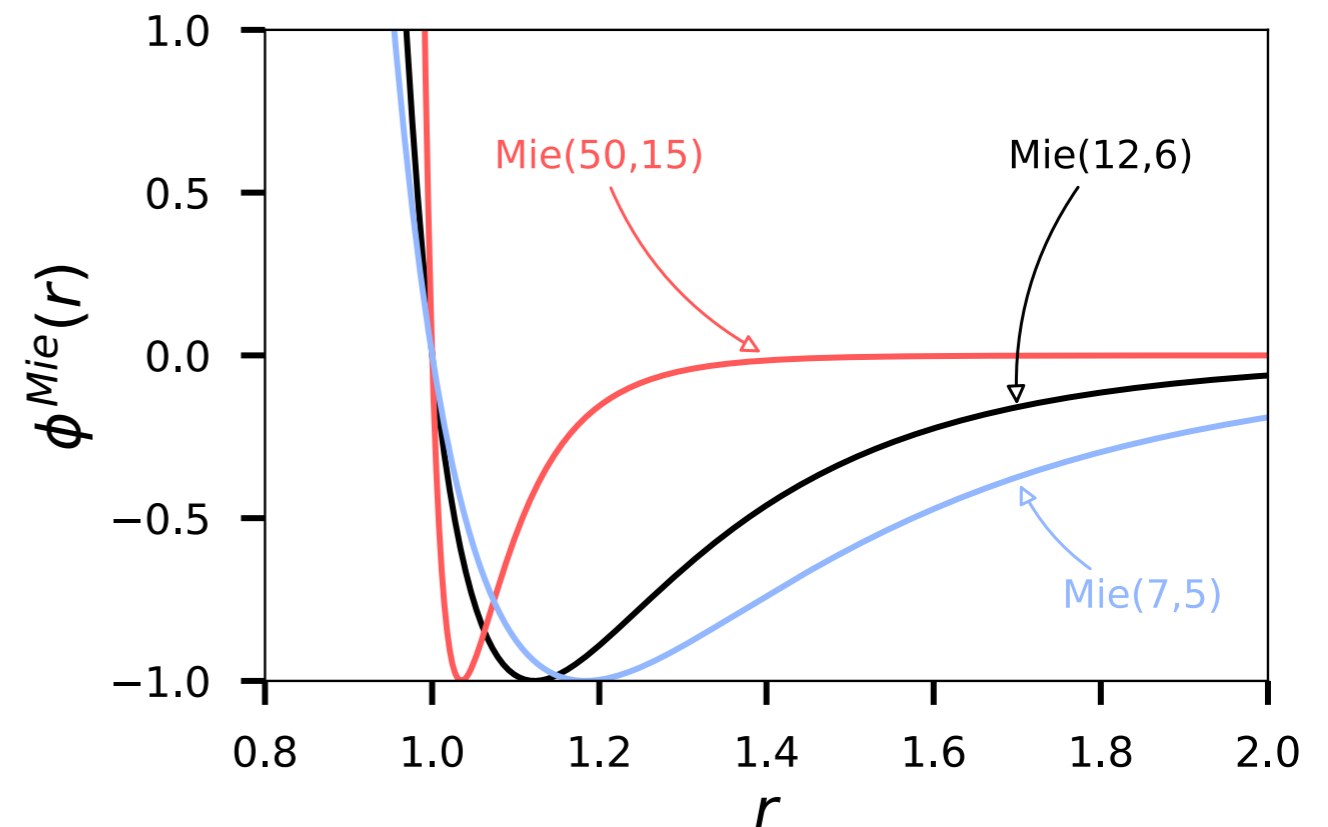
SAFT-VR Mie

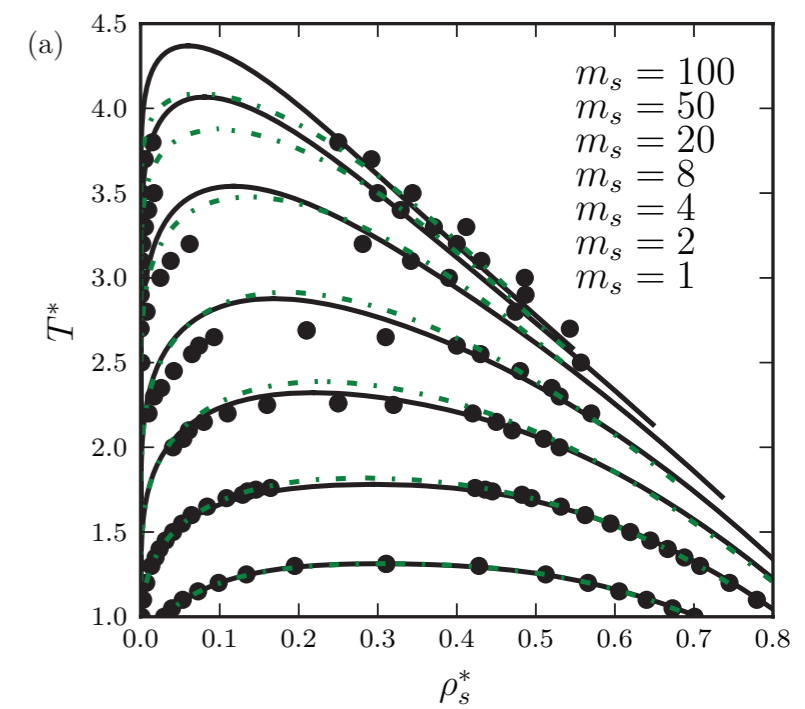
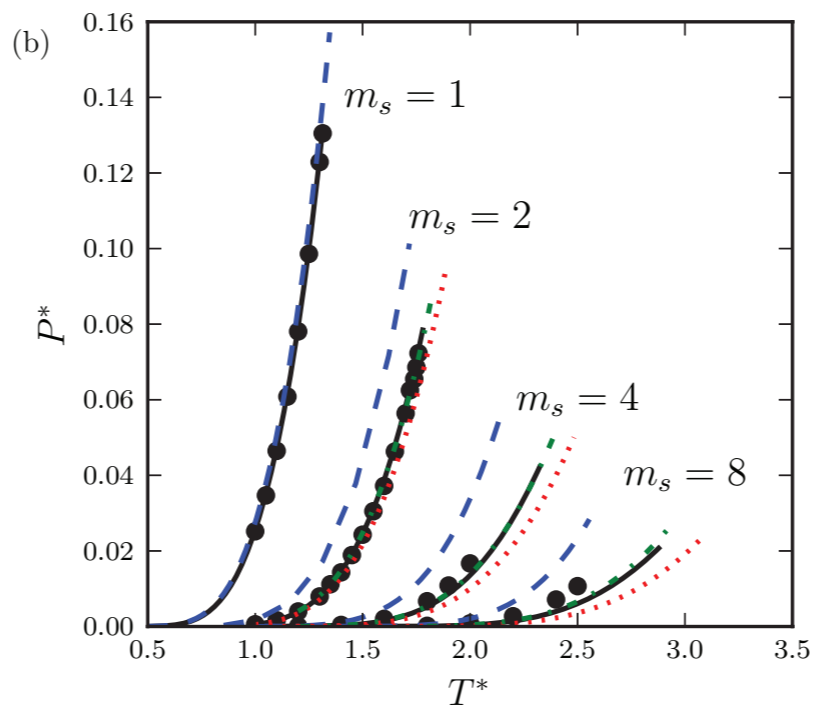
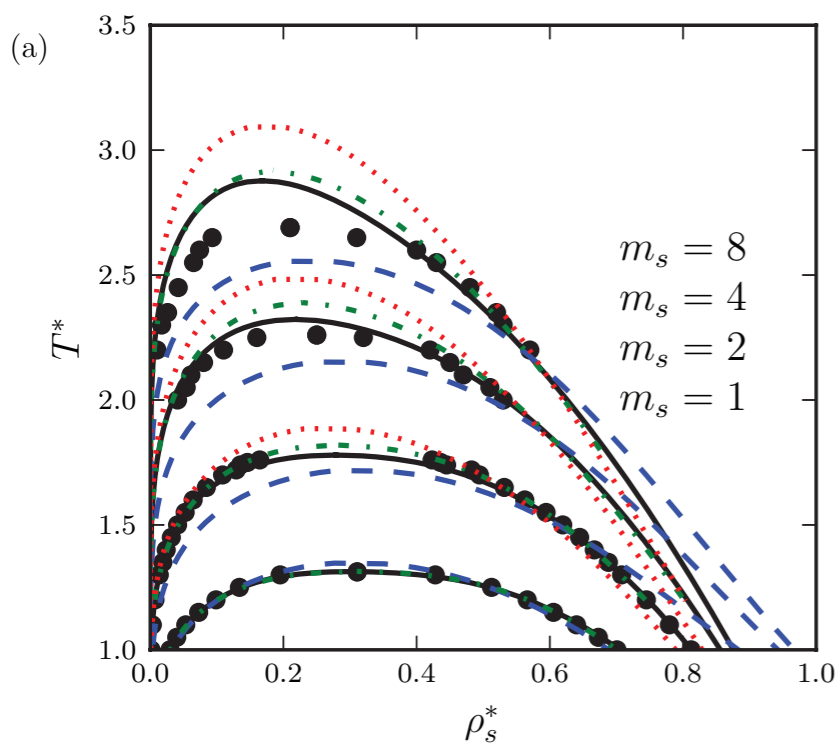
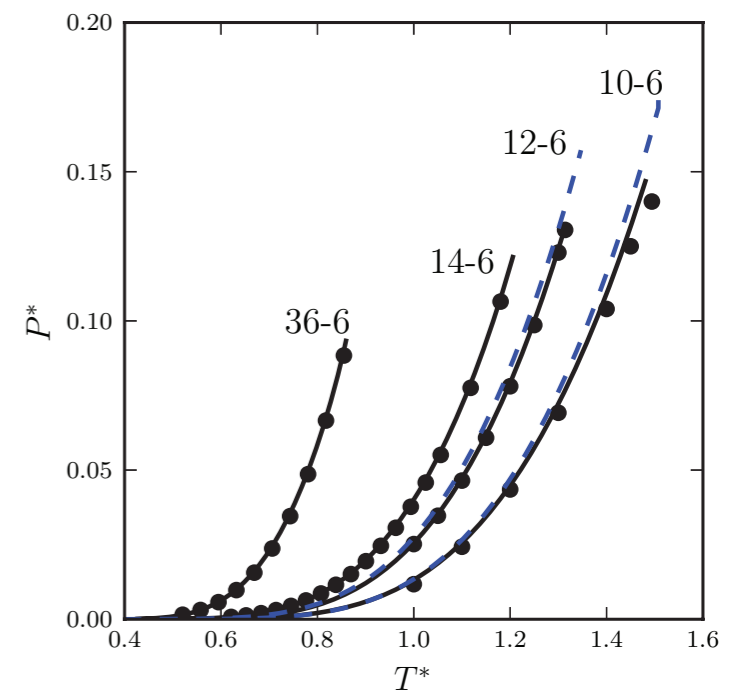
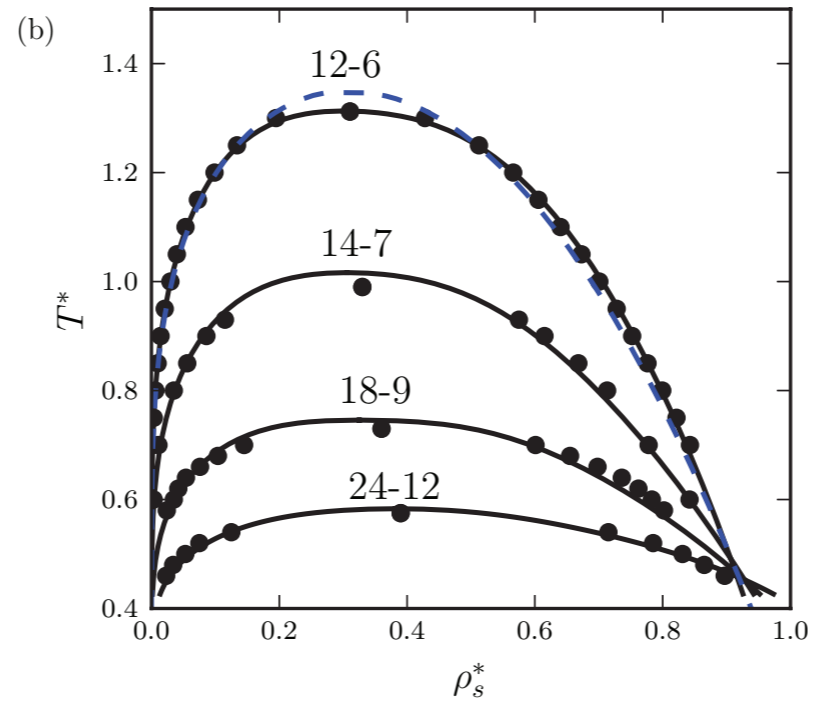
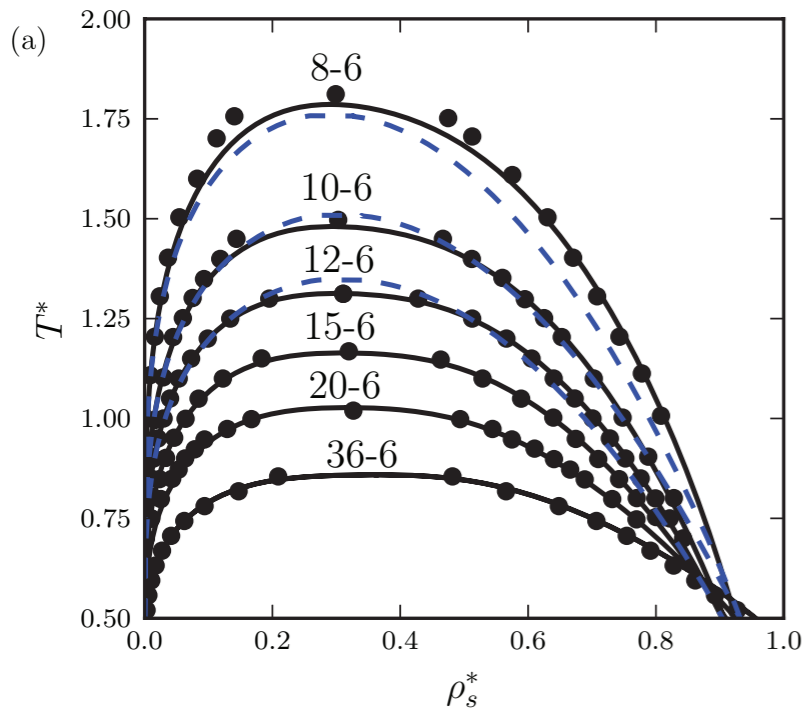
$$\frac{A^{\text{SAFT}}}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{mono}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc}}}{NkT}$$



$$\phi^{\text{Mie}}(r) = \mathcal{C}\epsilon \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^m \right]$$

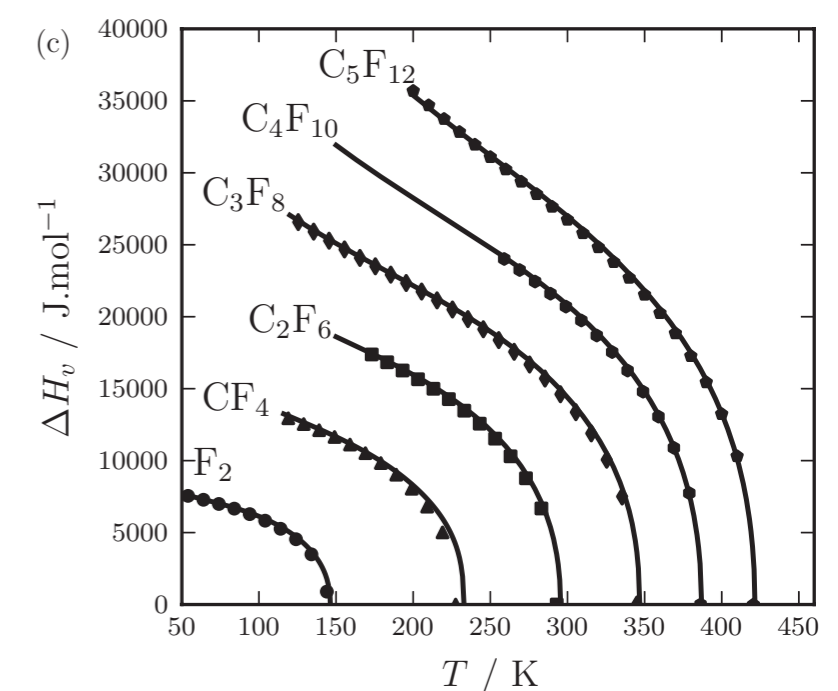
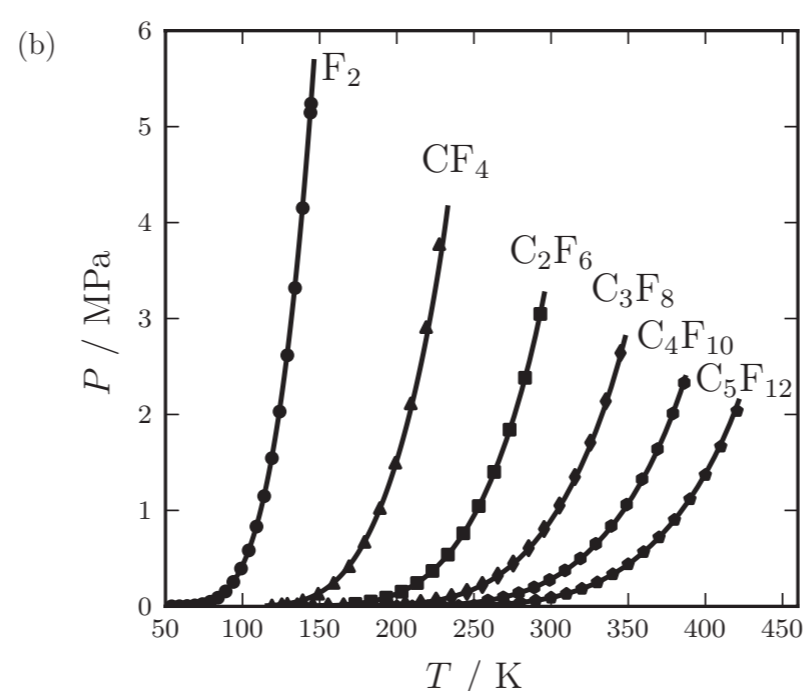
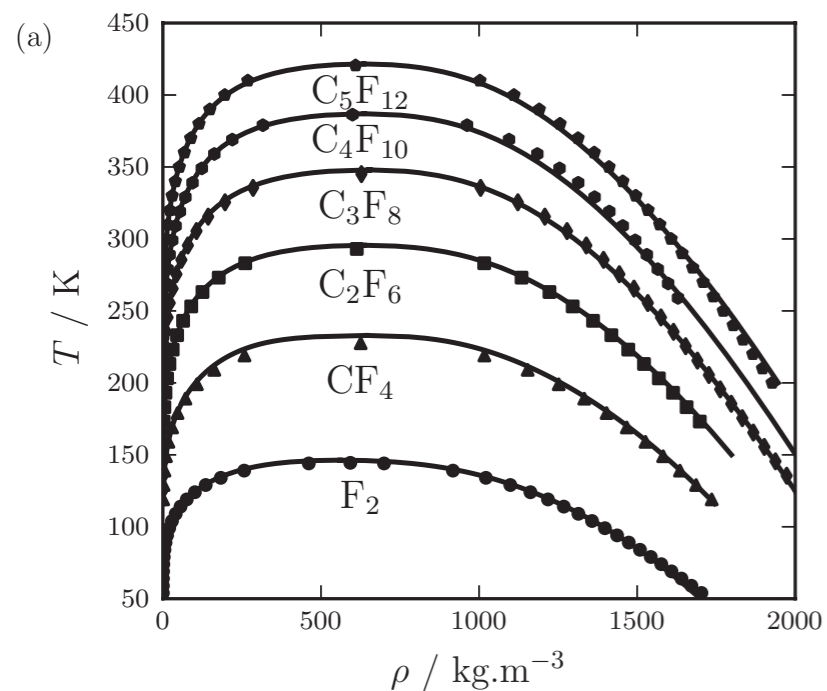
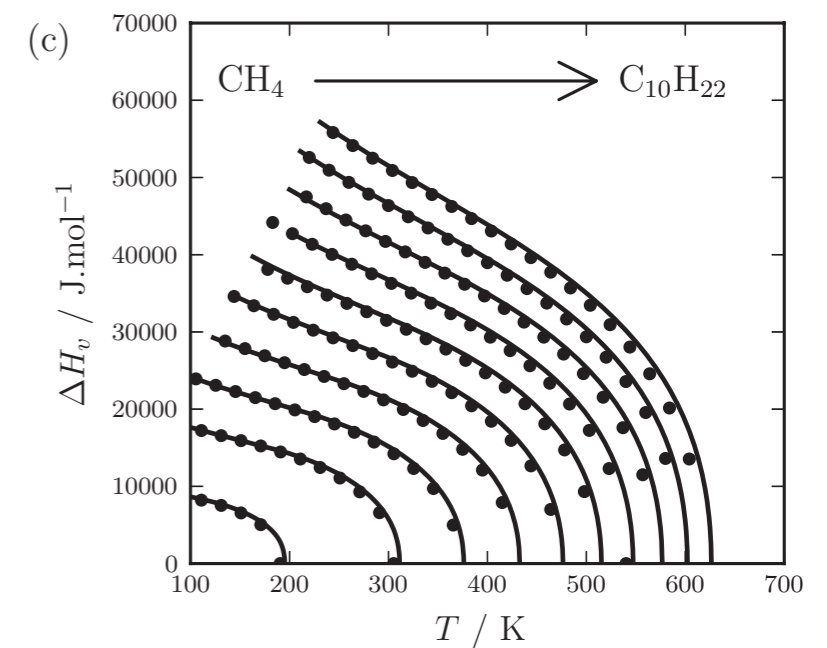
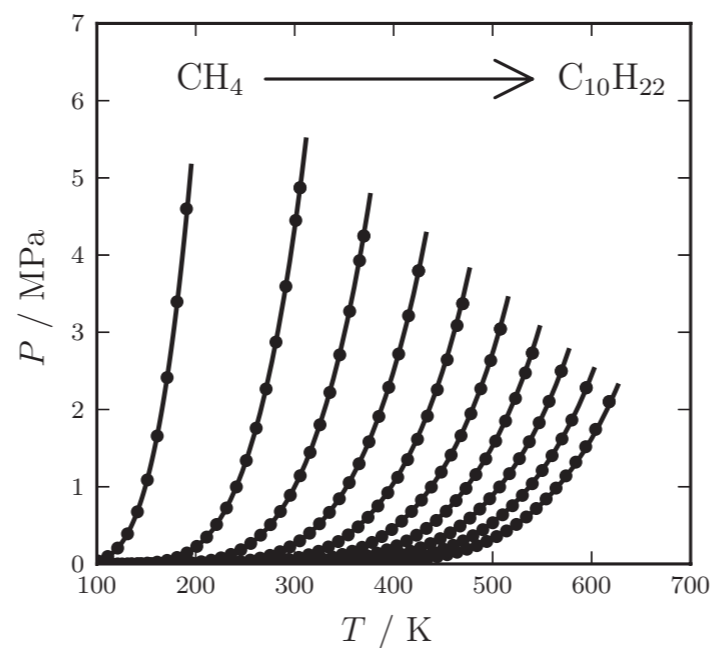
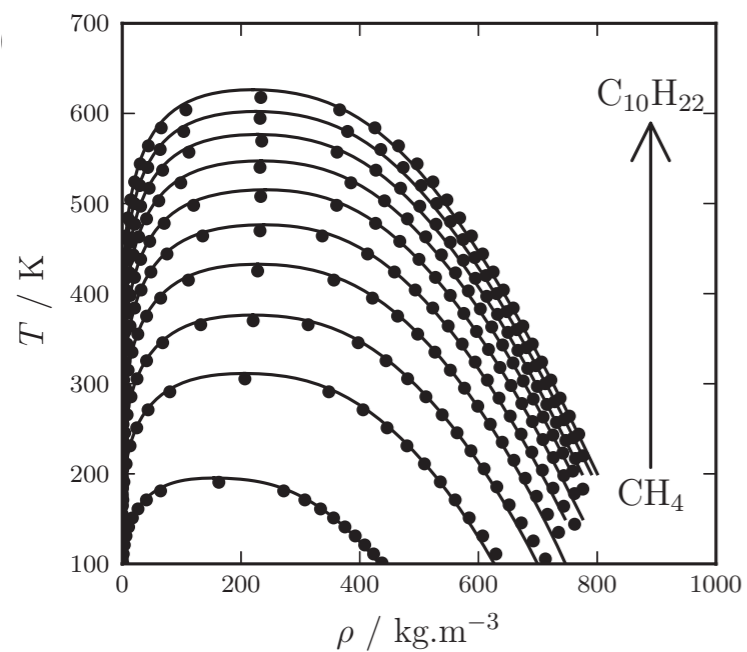
Avendano, Lafitte, Galindo, Adjiman,
Jackson, Muller,
J Phys Chem B **115**, 11154 (2011);
Mol Phys **110**, 1189 (2012);
J Phys Chem B **117**, 2717 (2013);
J Chem Phys **139**, 154504 (2013);
J. Chem. Phys. **140**, 054107 (2014)



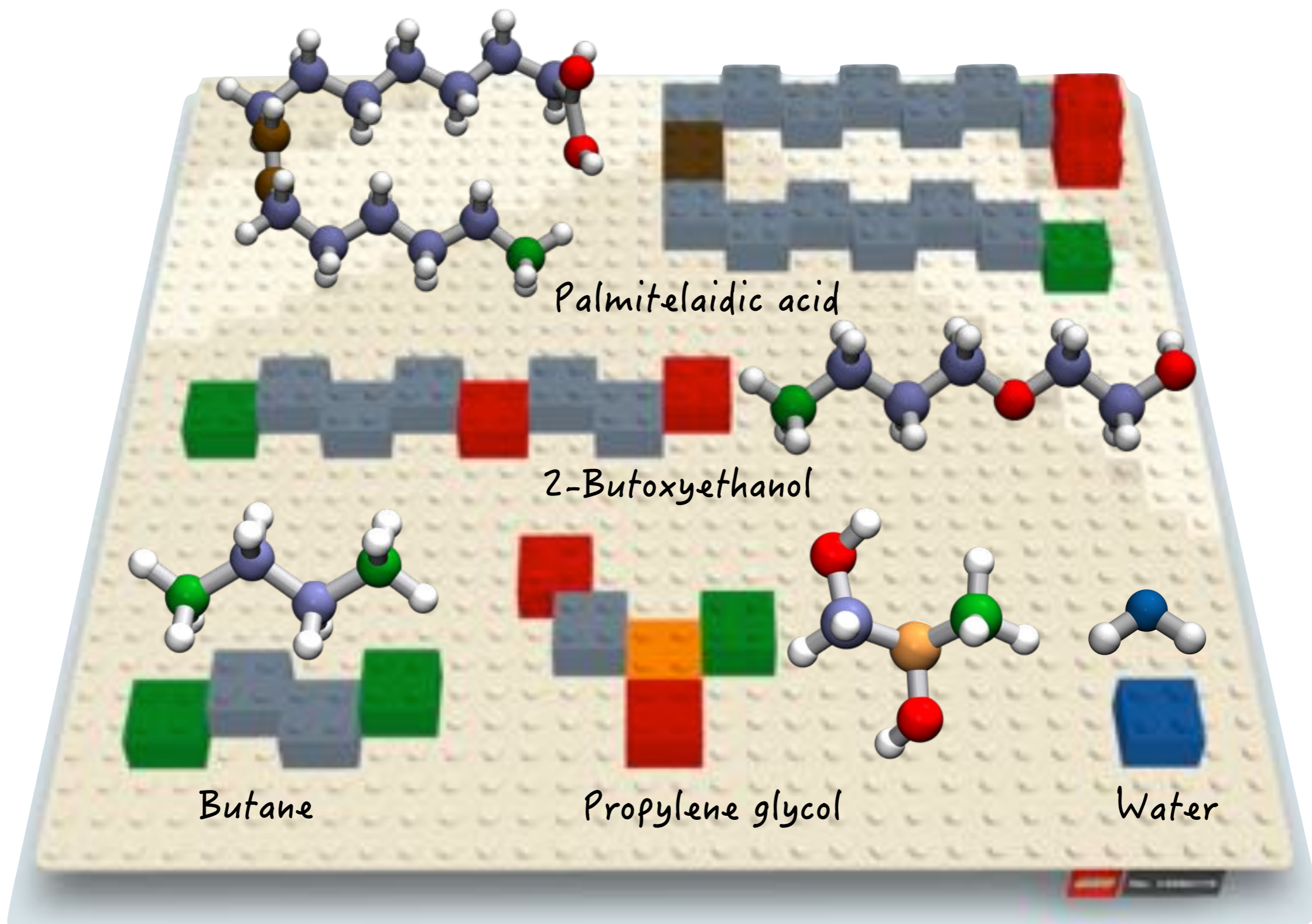


SAFT-VR Mie

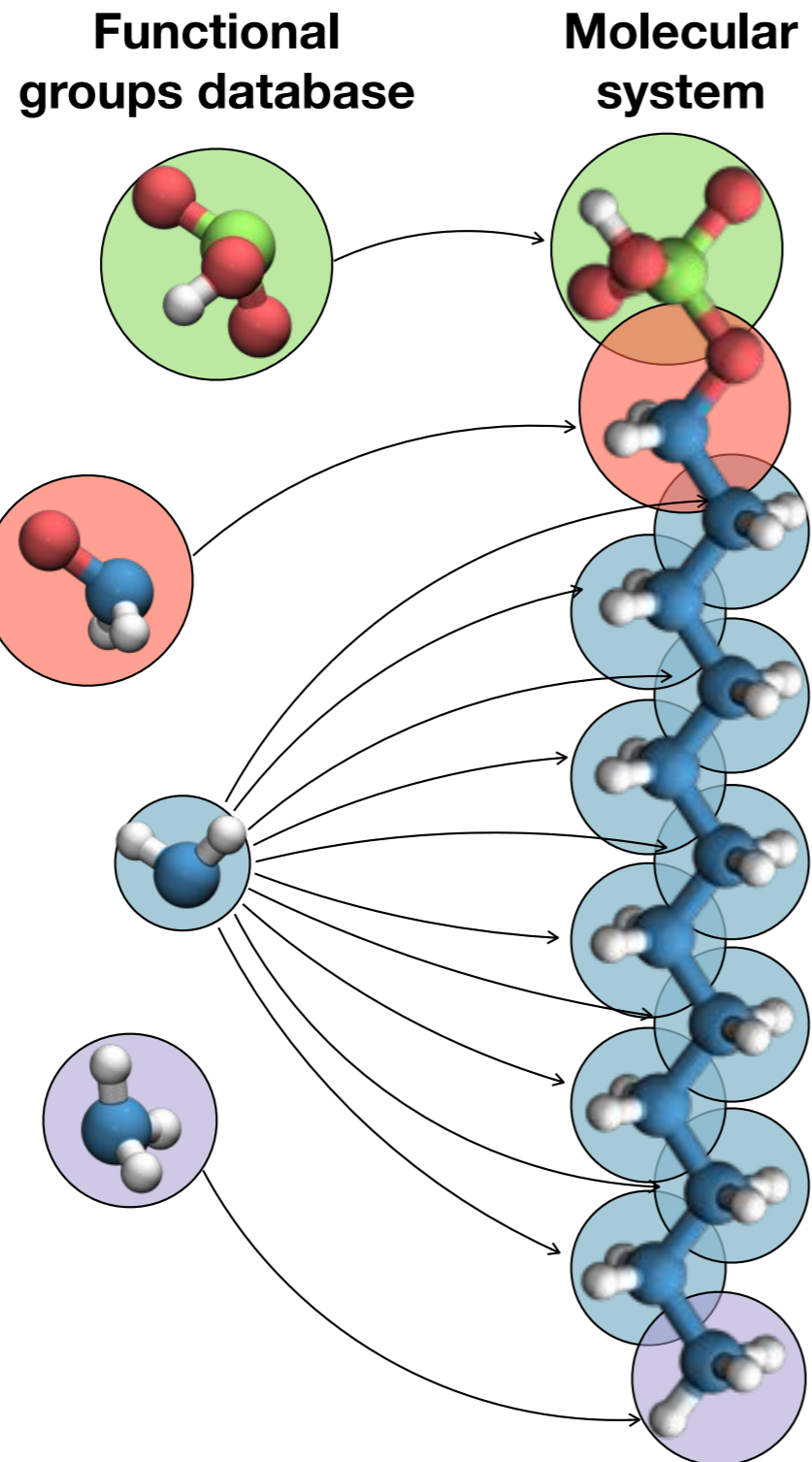
$$\min_{\sigma, \epsilon, n, m} F(\sigma, \epsilon, n, m) = \min_{\sigma, \epsilon, n, m} \left[\sum_{i=1}^{N_p} \left(\frac{P_i^{\text{sat}}(T; \sigma, \epsilon, n, m) - P_i^{\text{sat,exp}}(T)}{P_i^{\text{sat,exp}}(T)} \right)^2 + \sum_{i=1}^{N_d} \left(\frac{\rho_i^{\text{L}}(T; \sigma, \epsilon, n, m) - \rho_i^{\text{L,exp}}(T)}{\rho_i^{\text{L,exp}}(T)} \right)^2 \right]$$



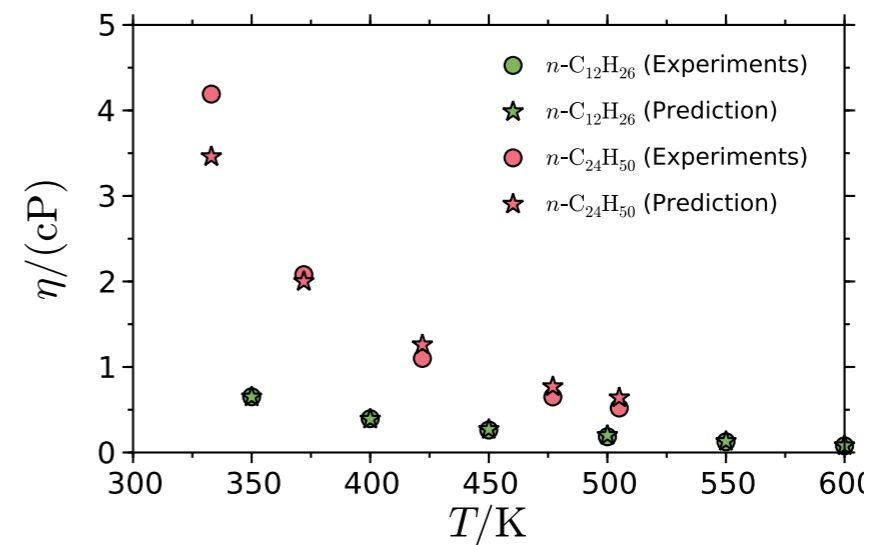
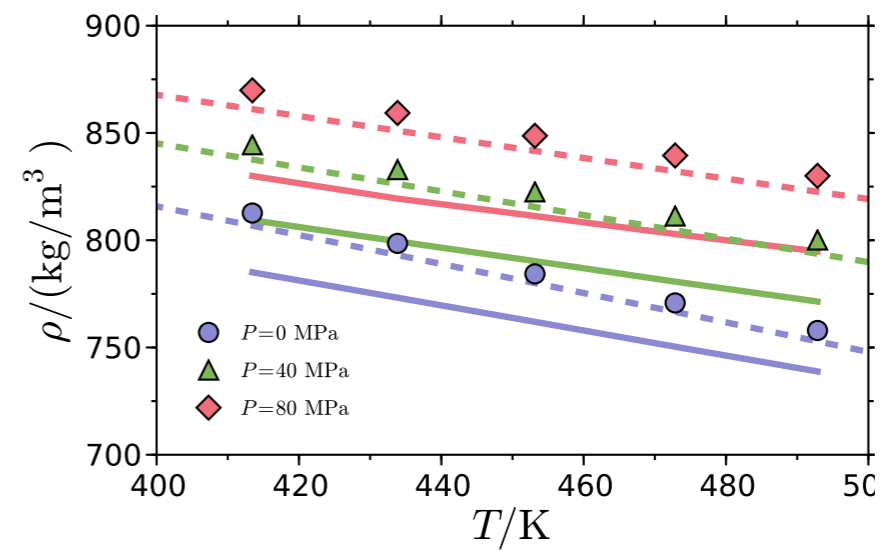
Group contribution methods



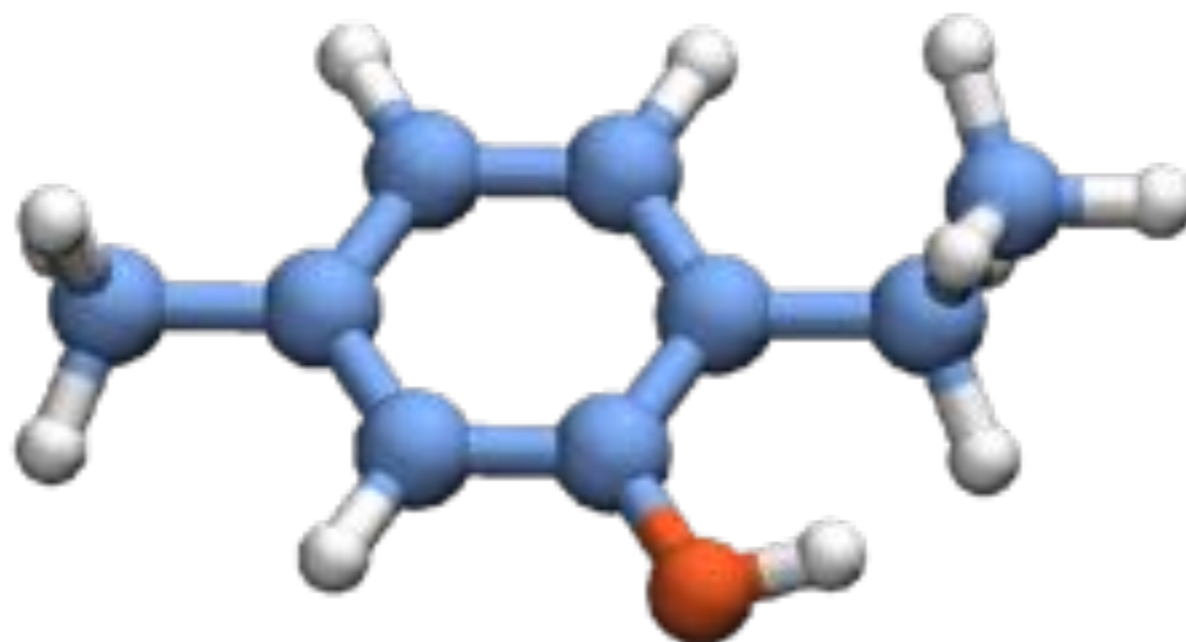
Group contribution methods



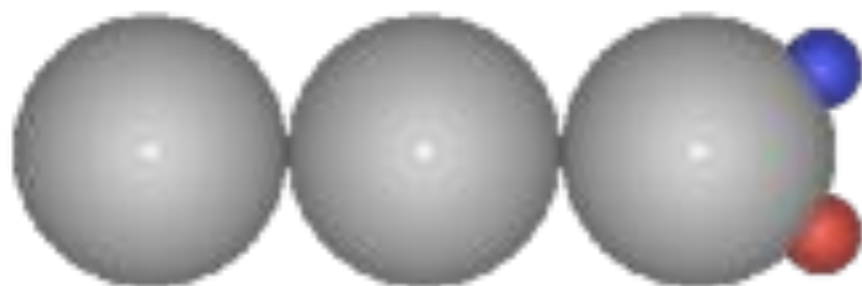
Property prediction



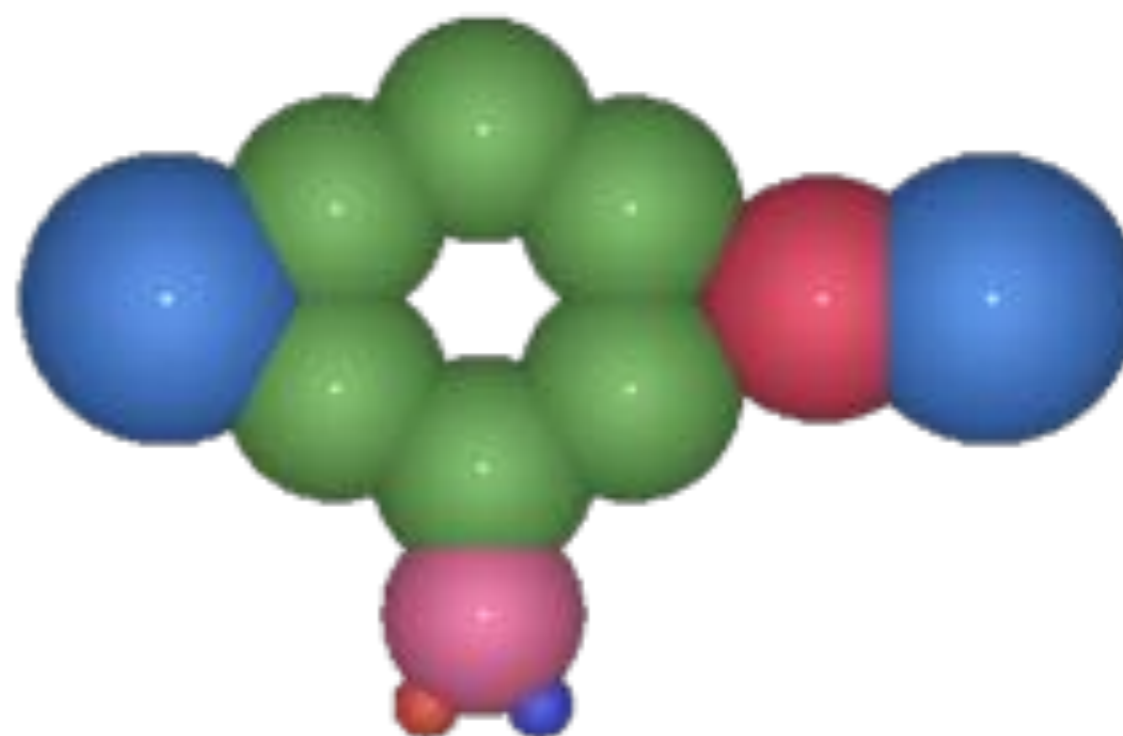
SAFT- γ Mie



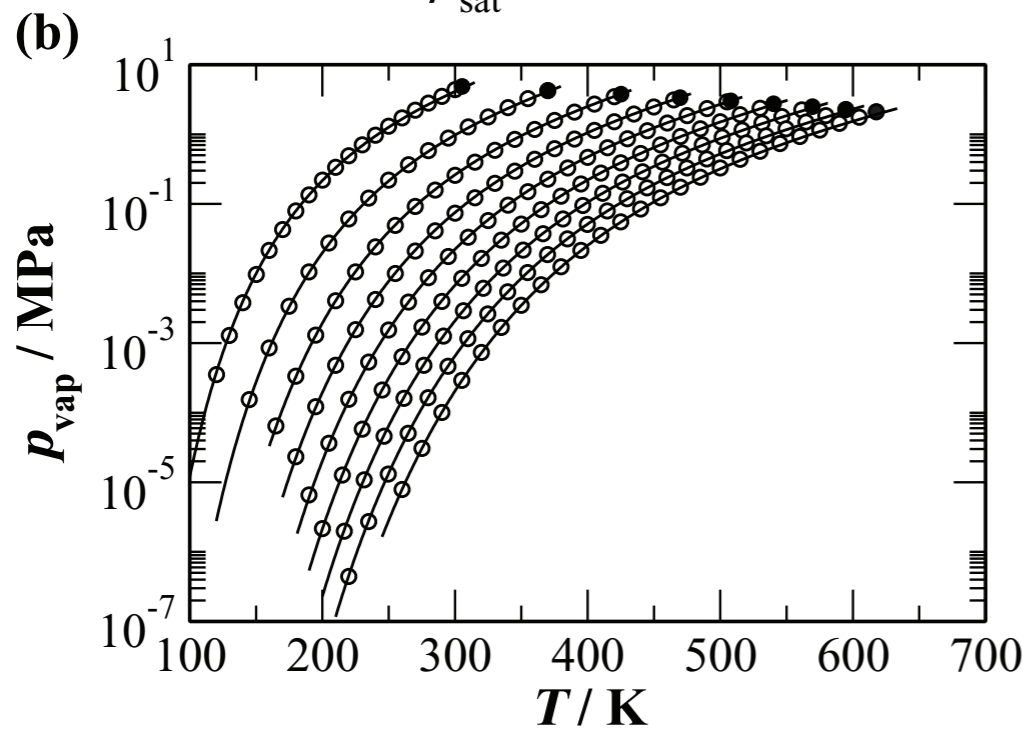
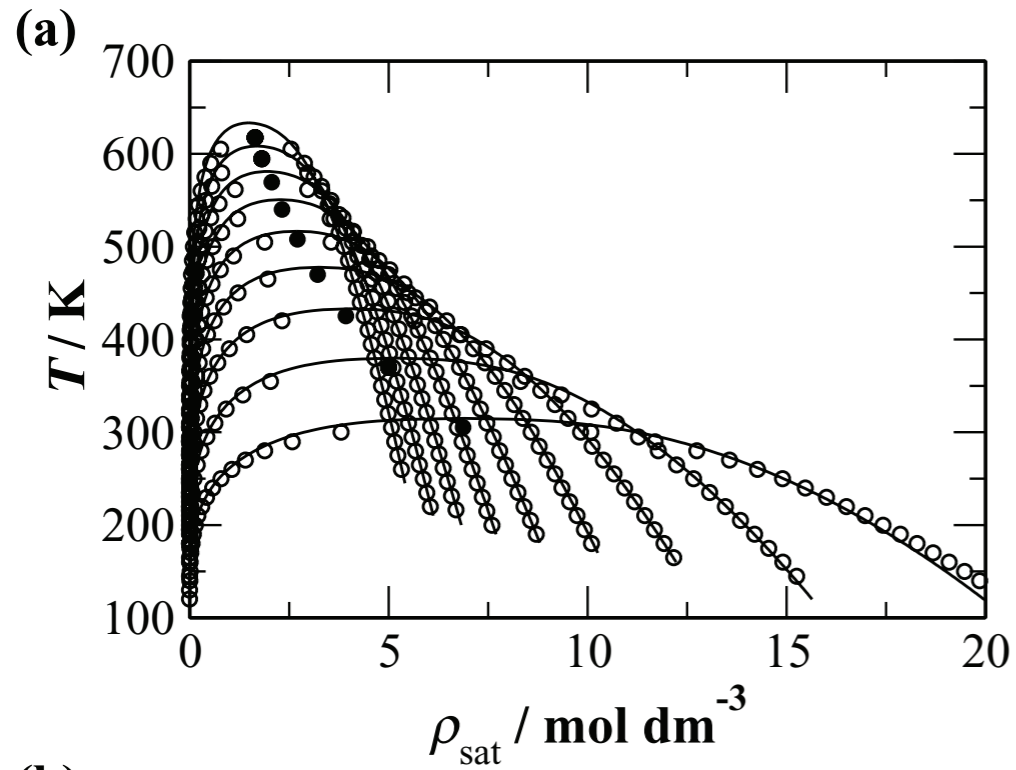
SAFT-VR homonuclear model



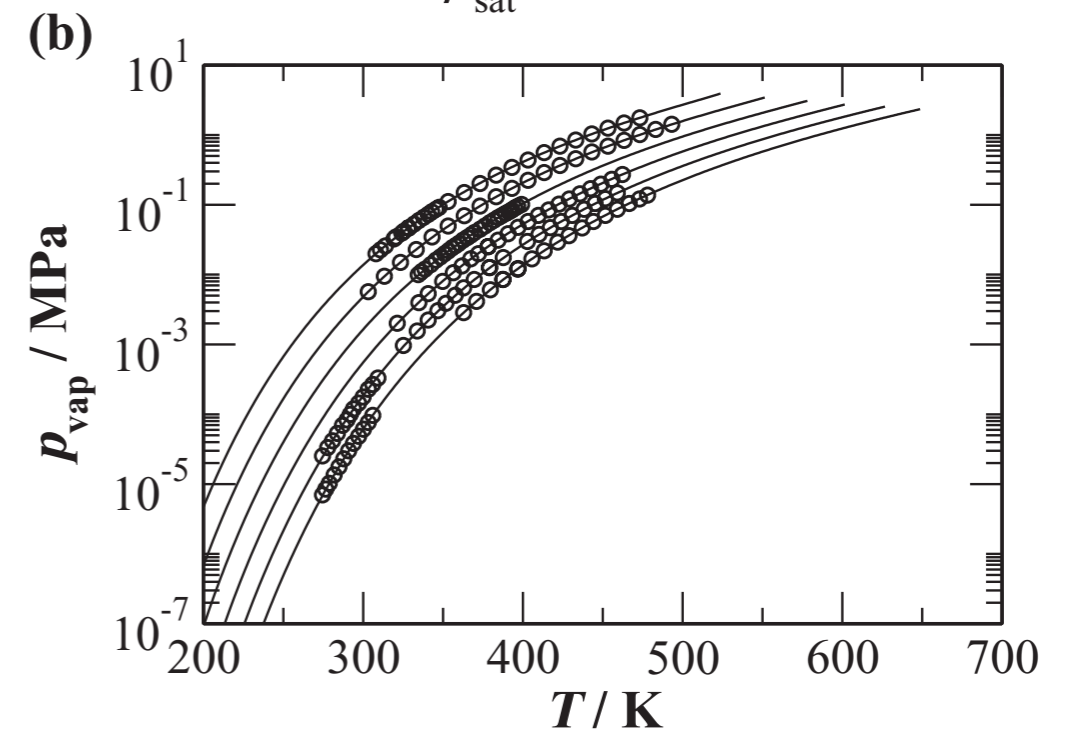
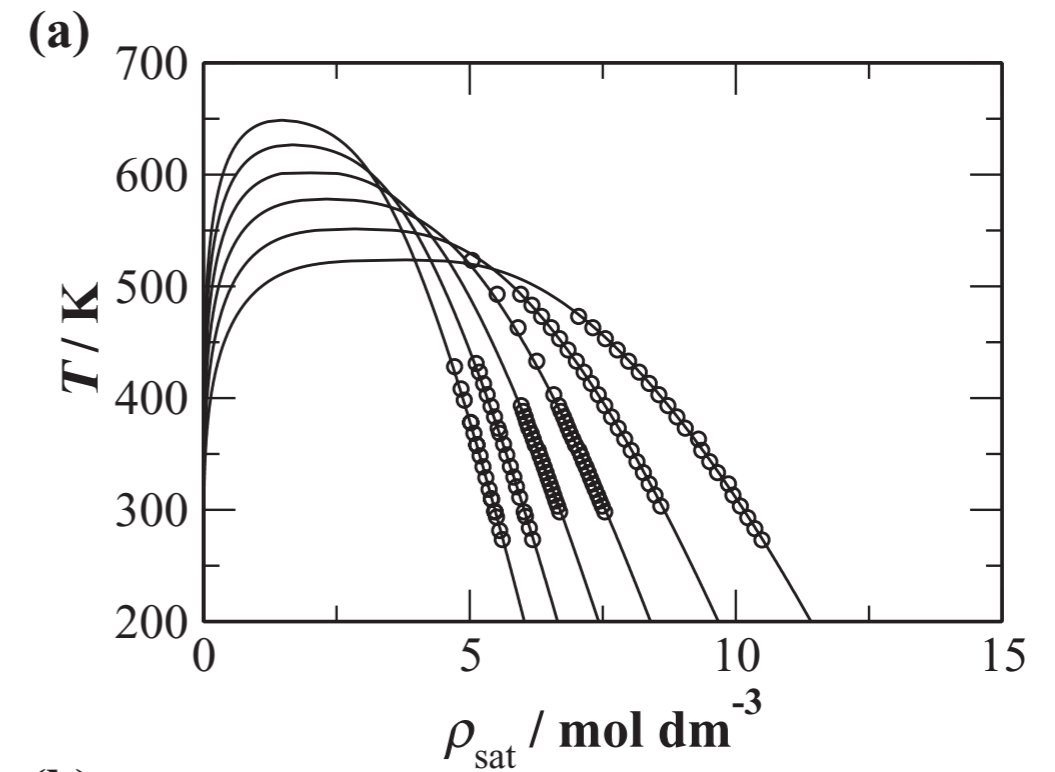
SAFT- γ heteronuclear model



SAFT- γ Mie



Alkane series : CH₃, CH₂



Ester series : COO

SAFT- γ coarse grained force field

Properties of Interest

Molecular
simulation

Coarse-grained model

Experimental structure;
atomistic or QM
calculations

Iterative Boltzmann Inversion
Force Matching method

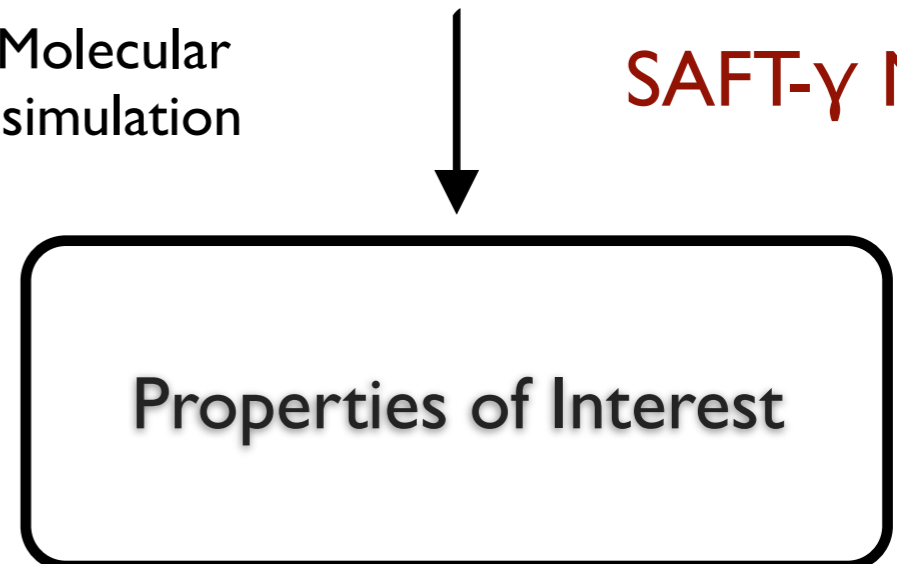
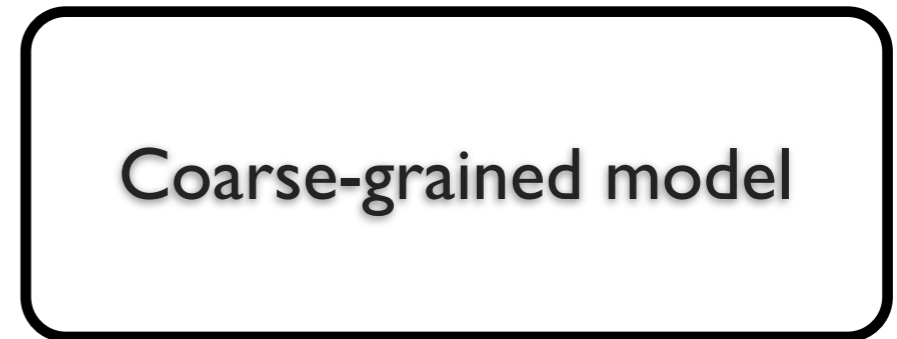
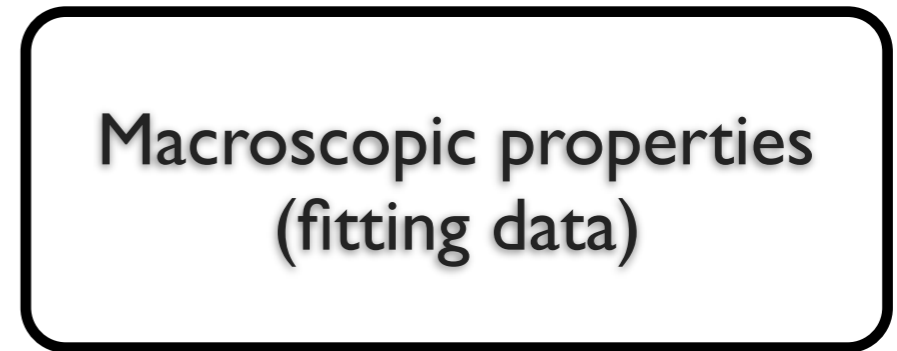
Macroscopic properties
(fitting data)

Coarse-grained model

Molecular
simulation

SAFT- γ Mie

Properties of Interest



SAFT- γ coarse grained force field

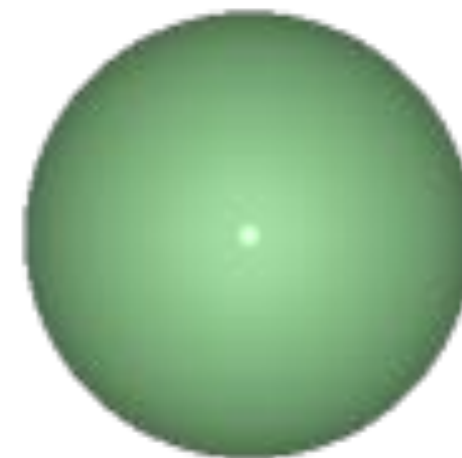
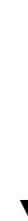
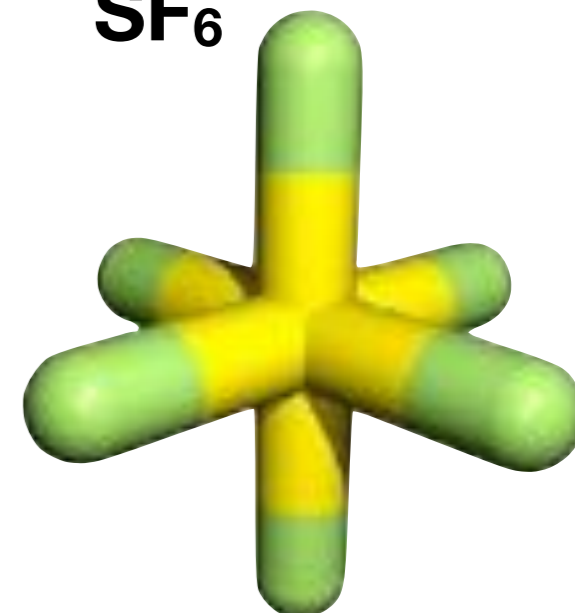
CO₂



CF₄



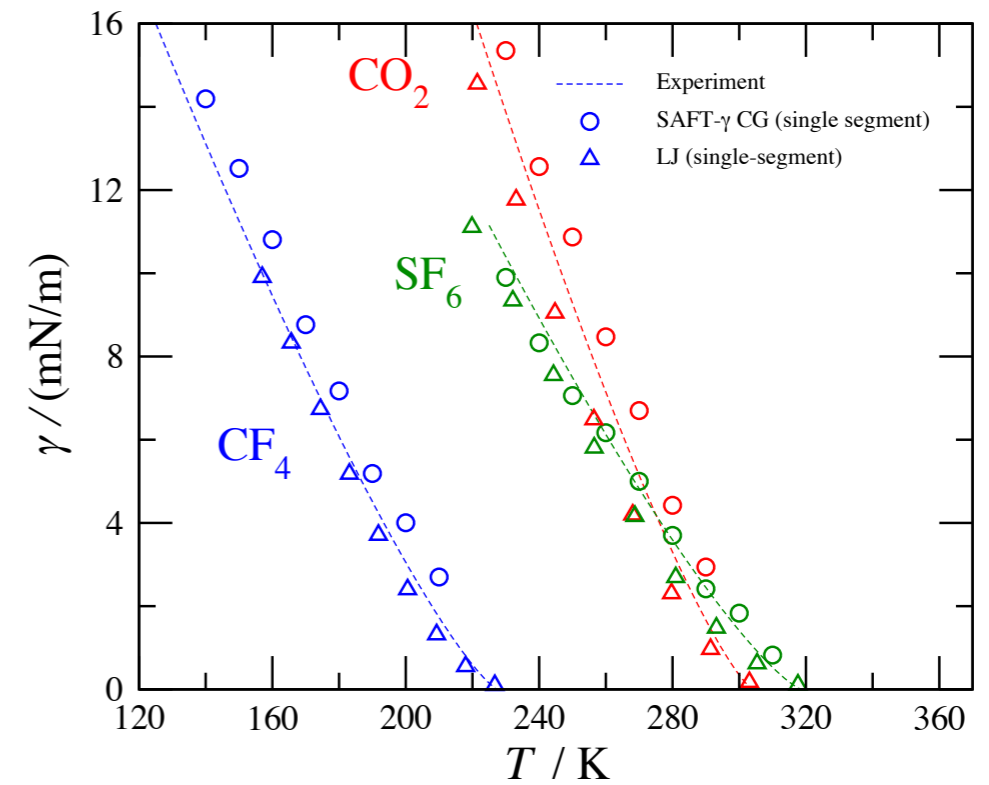
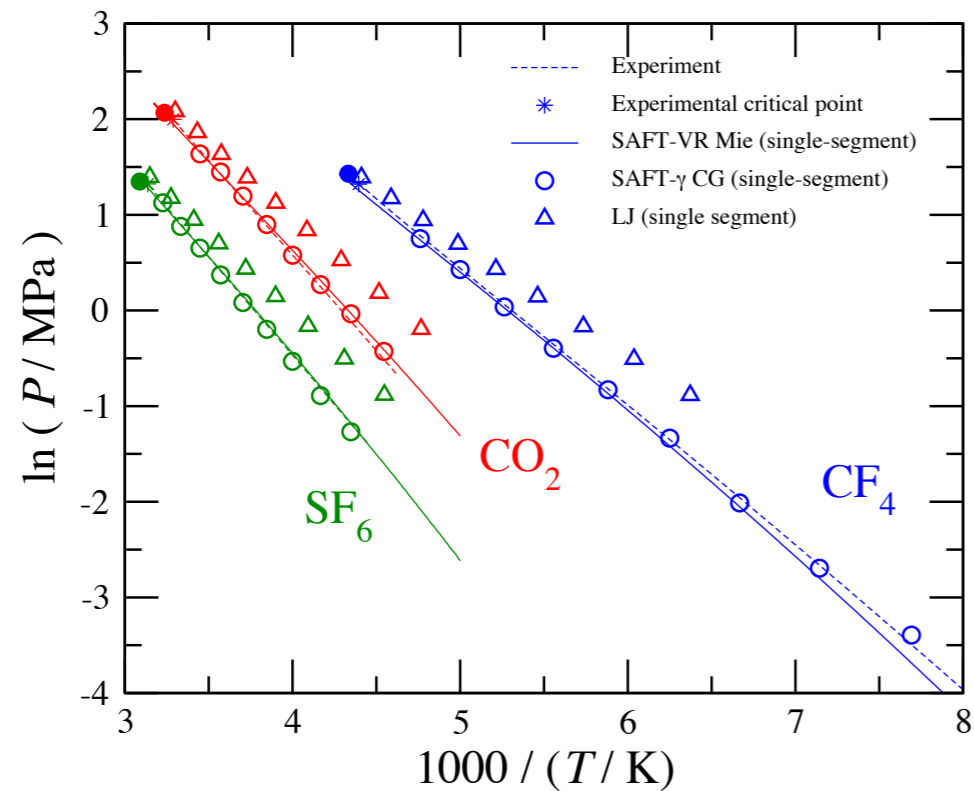
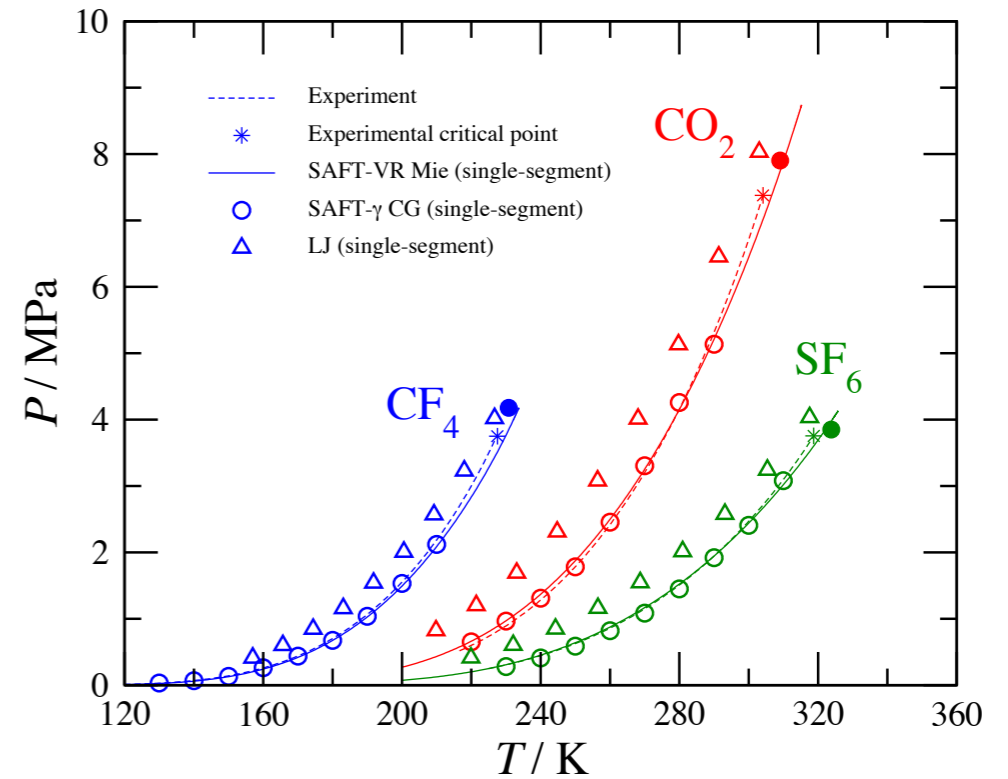
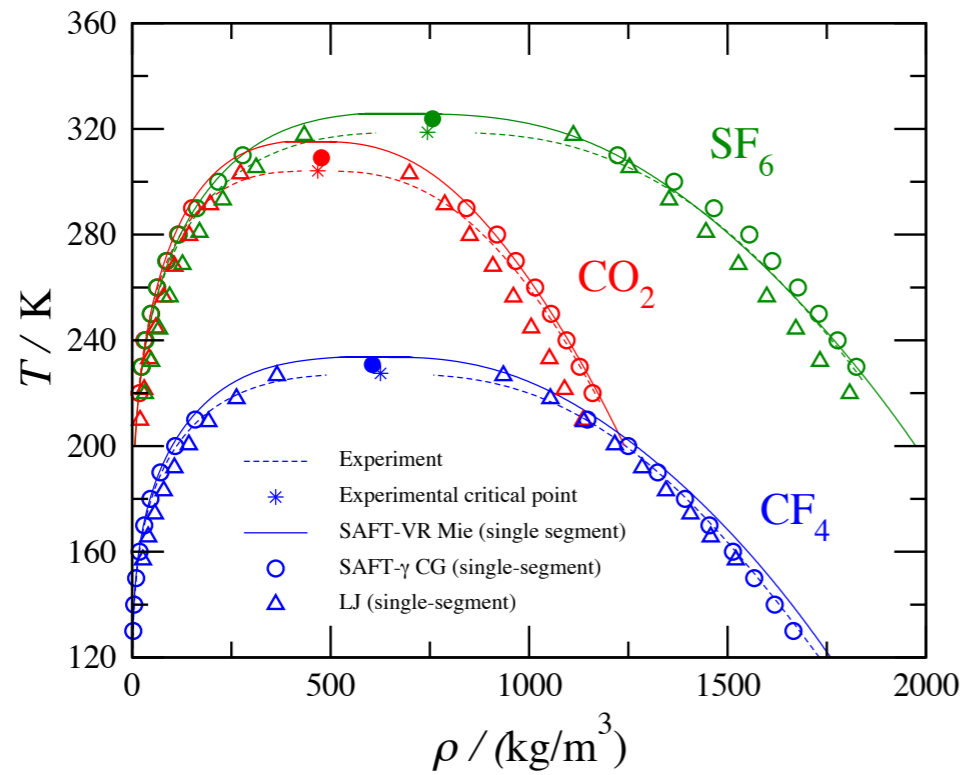
SF₆



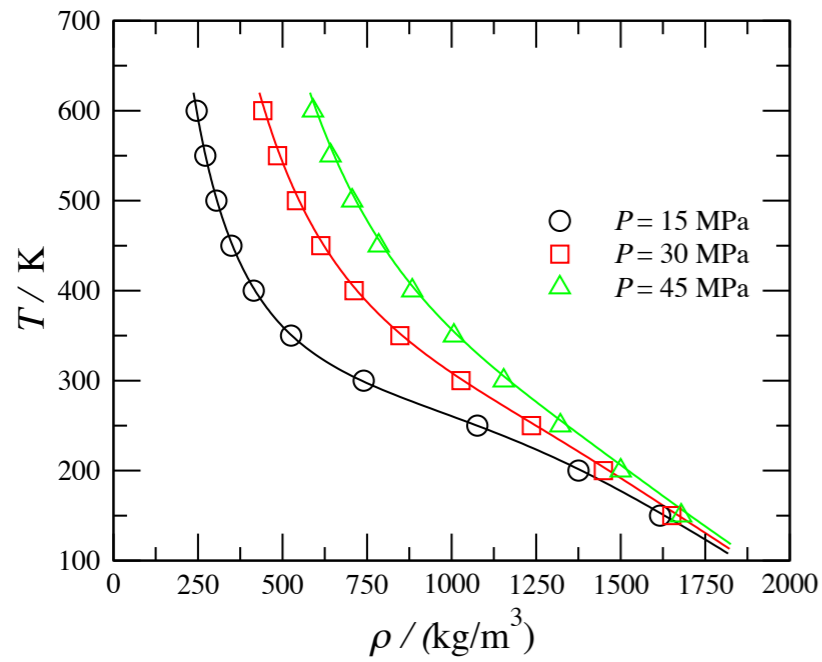
Avendano, Lafitte, Galindo, Adjiman, Jackson, Muller, *J Phys Chem B* (2011)

Avendano, Lafitte, Galindo, Adjiman, Muller, Jackson, *J Phys Chem B* (2013)

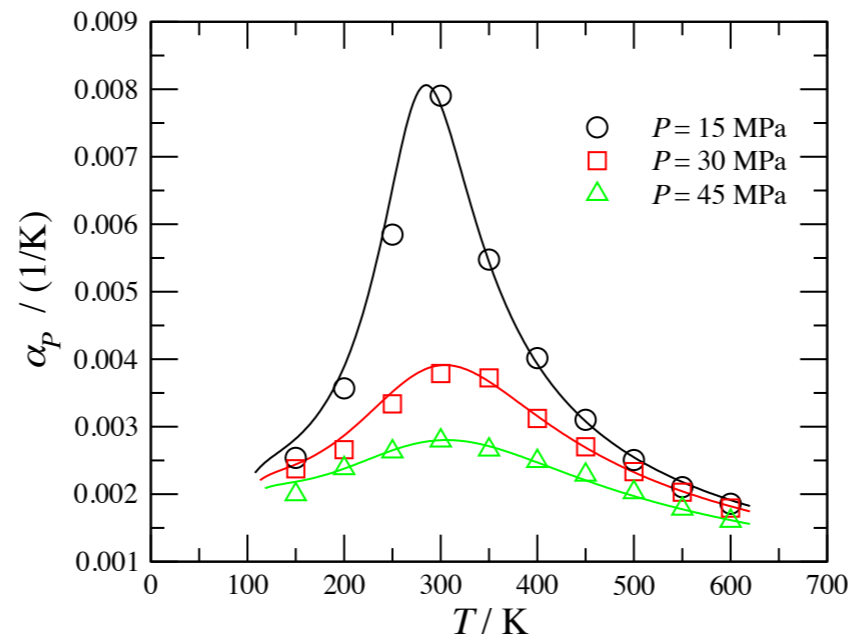
SAFT- γ coarse grained force field



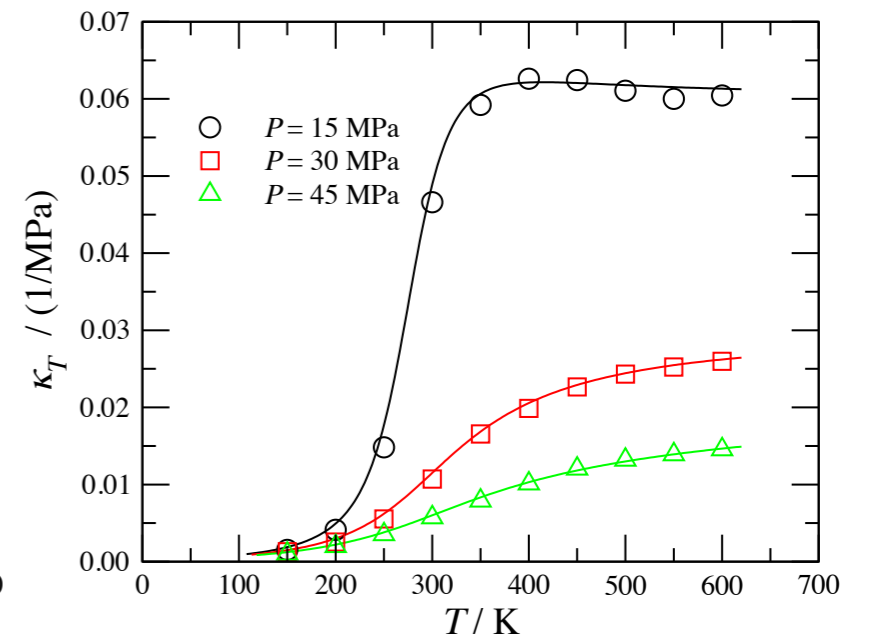
SAFT- γ coarse grained force field



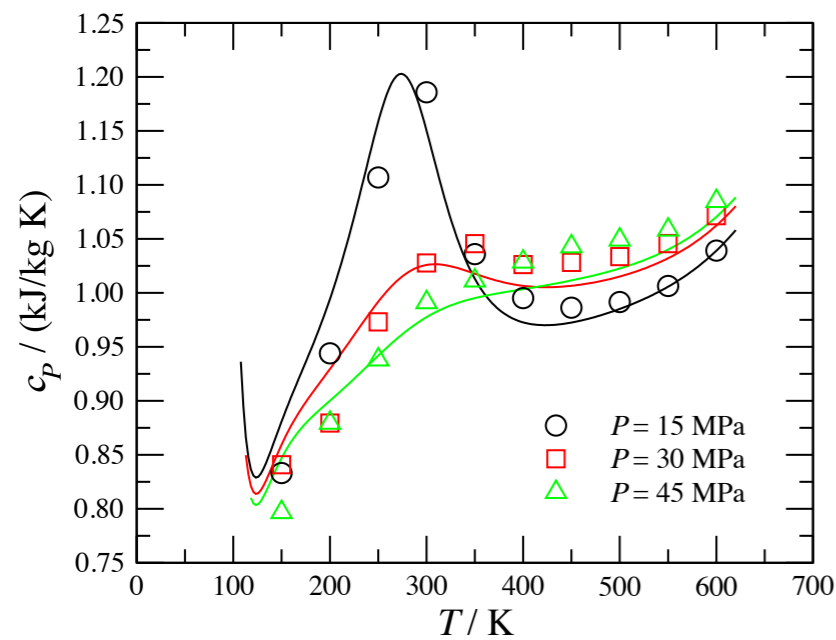
(a)



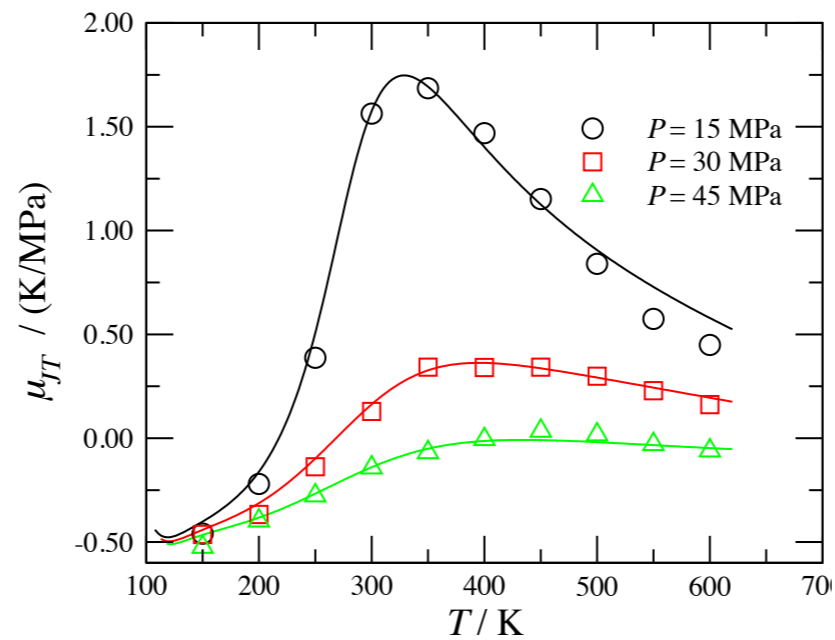
(b)



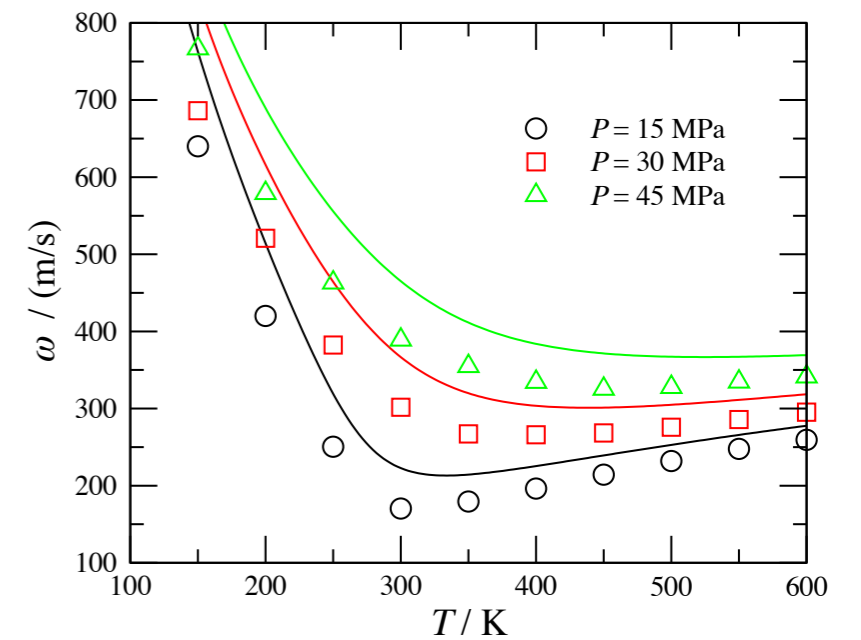
(c)



(d)

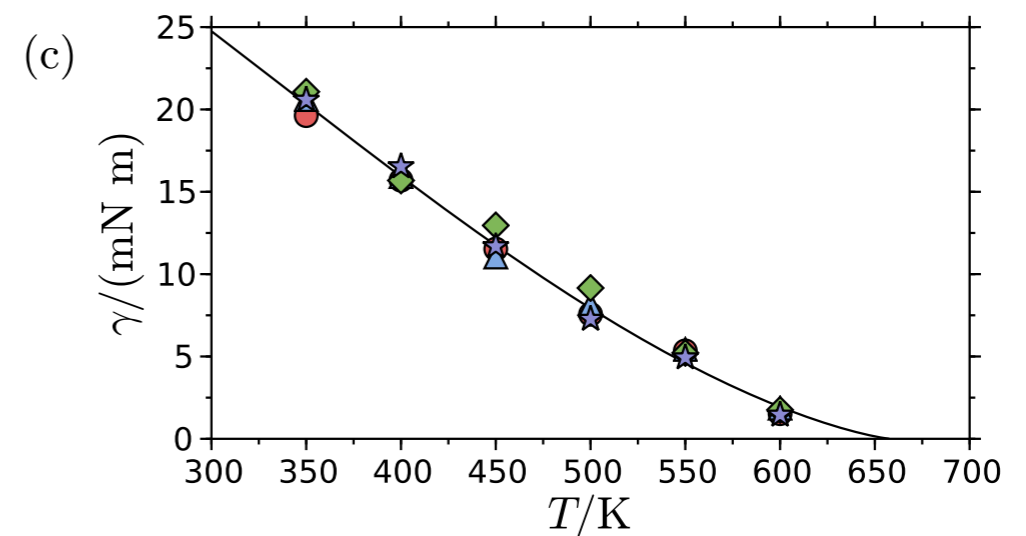
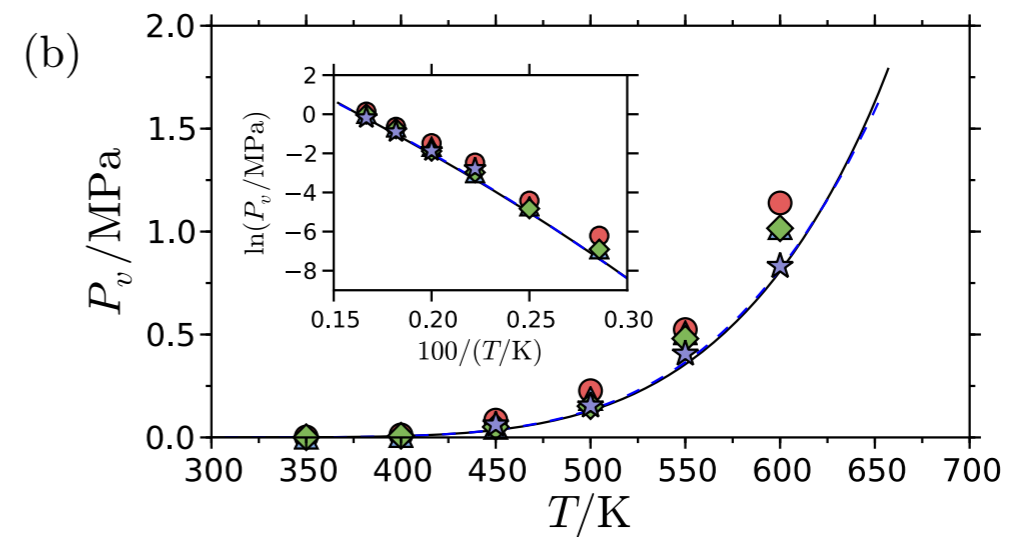
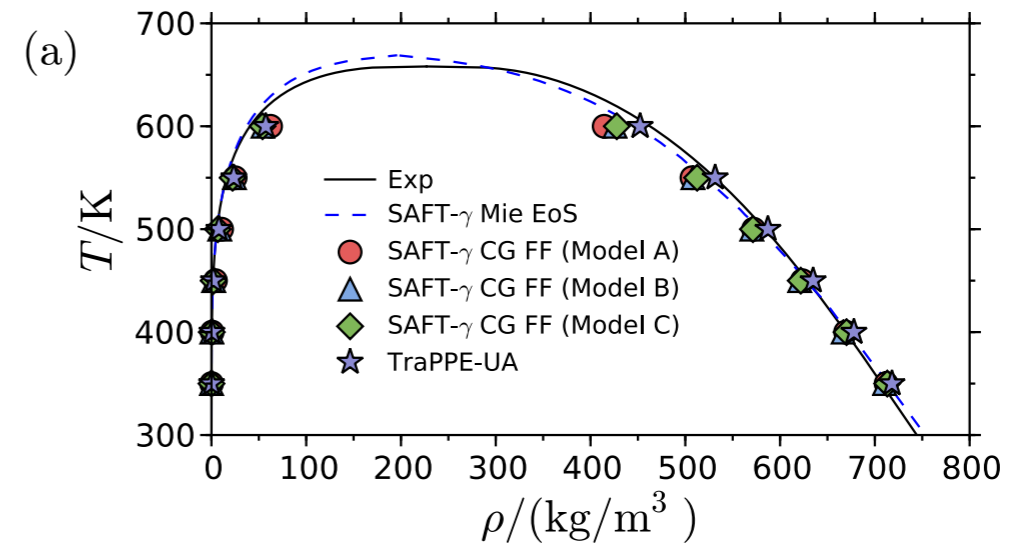
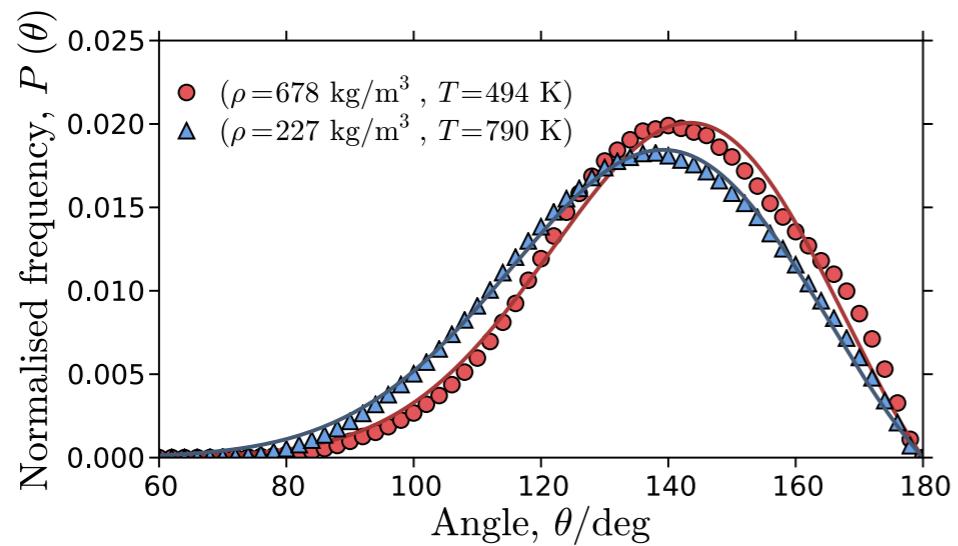
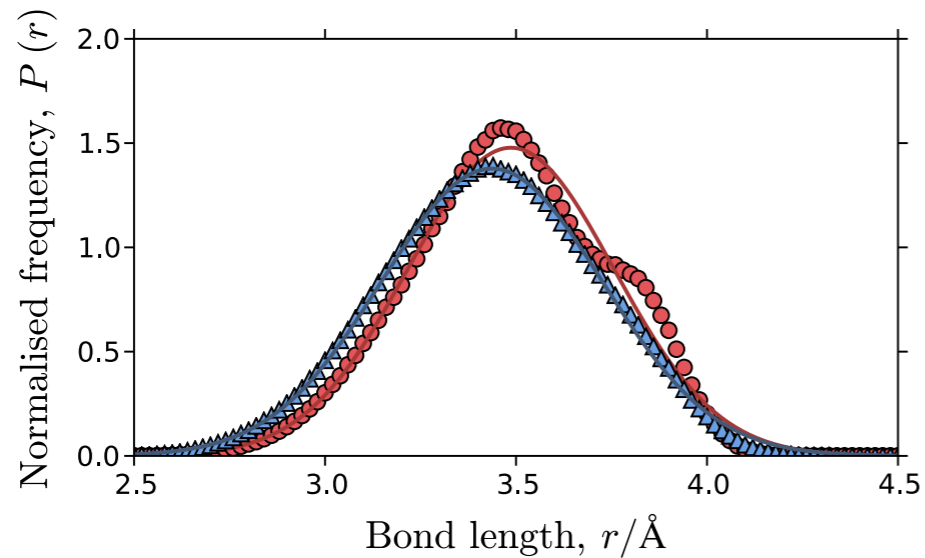
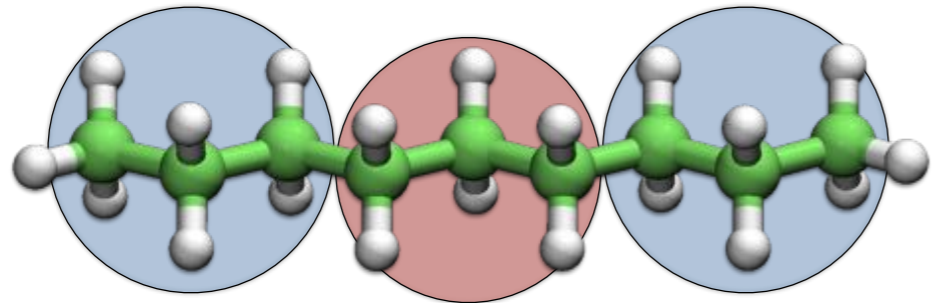


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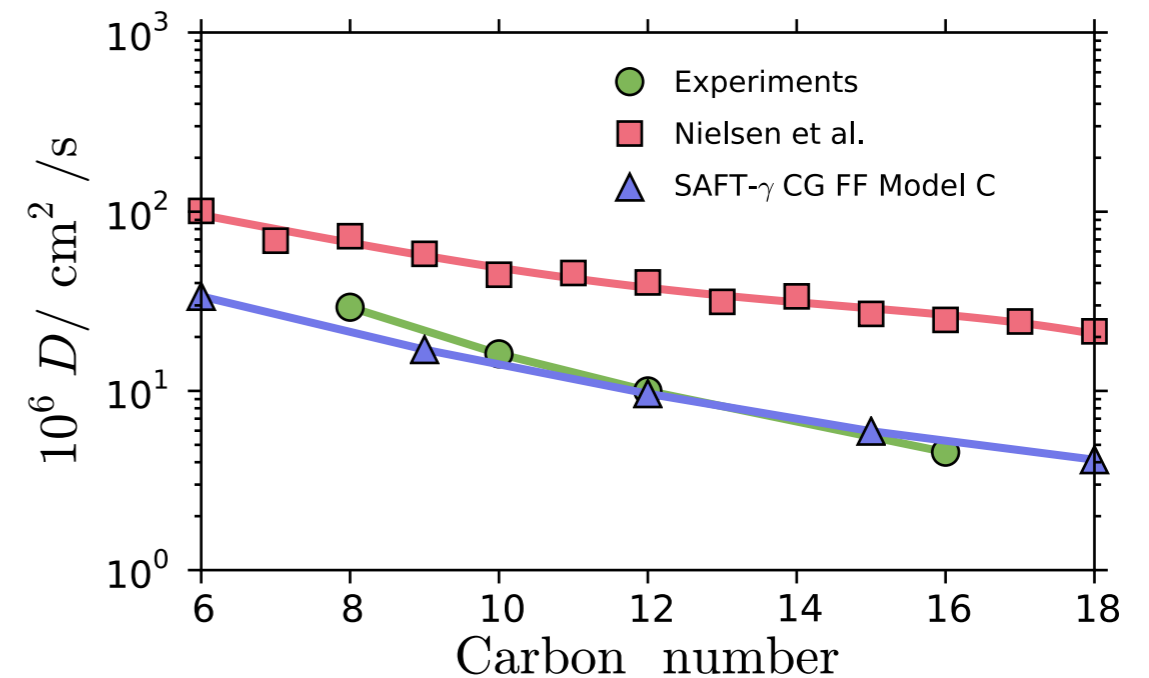
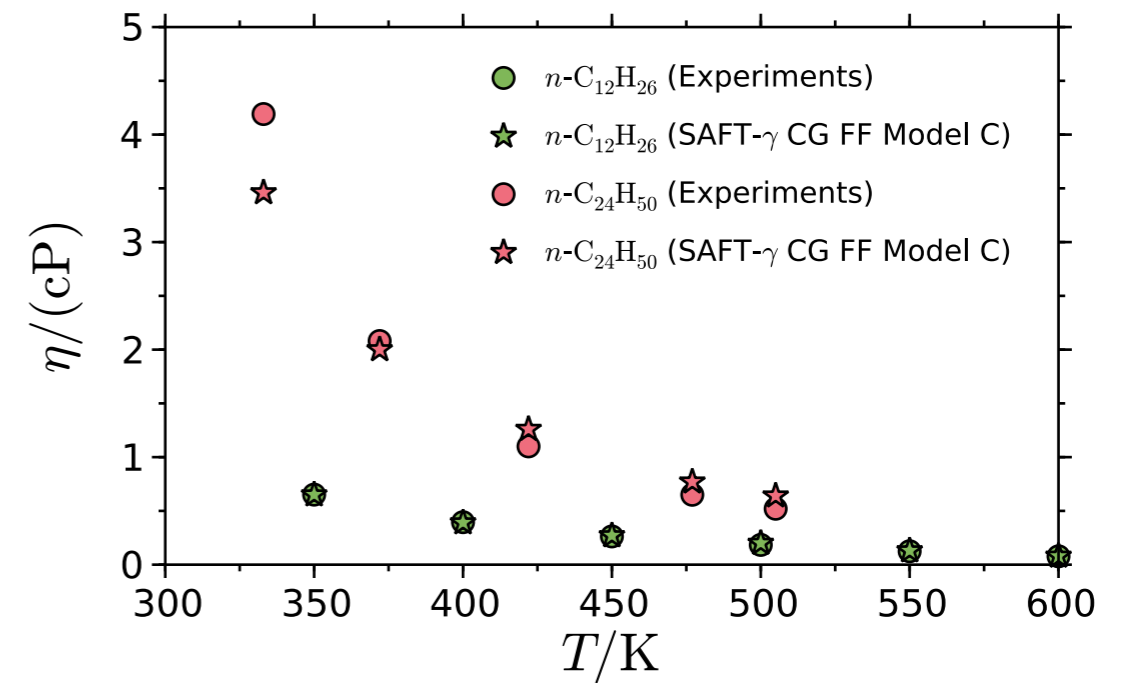
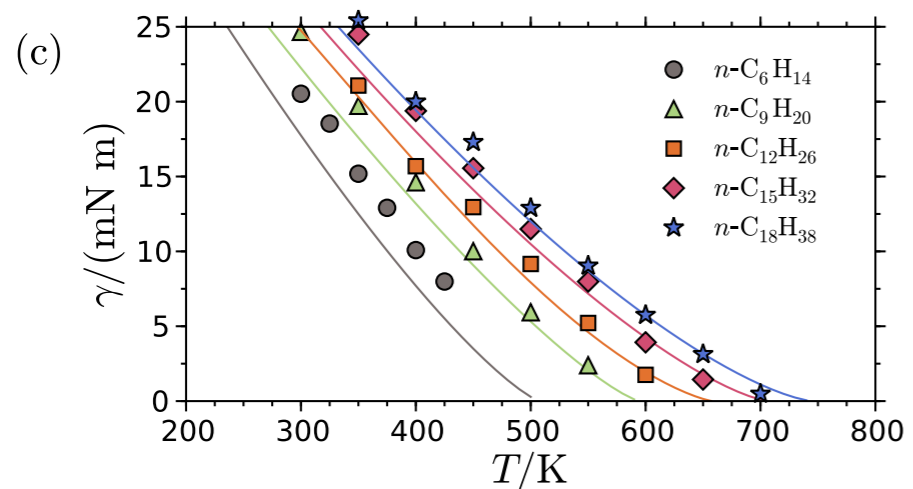
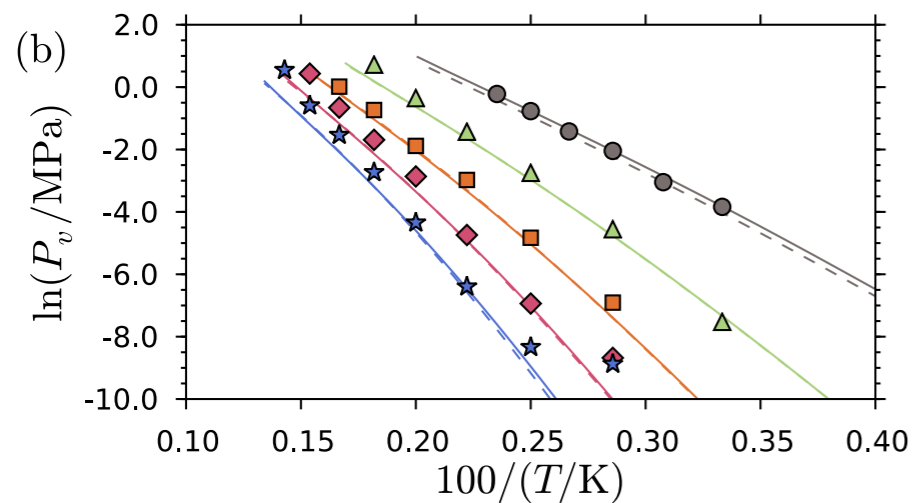
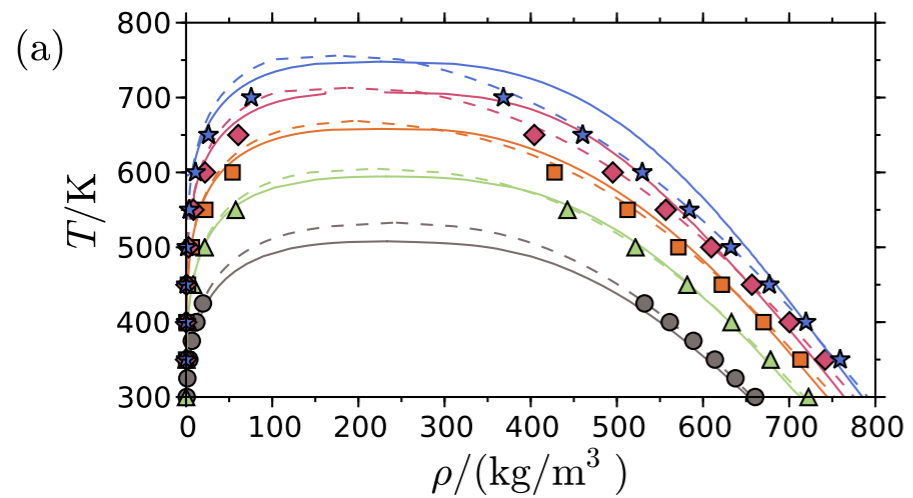


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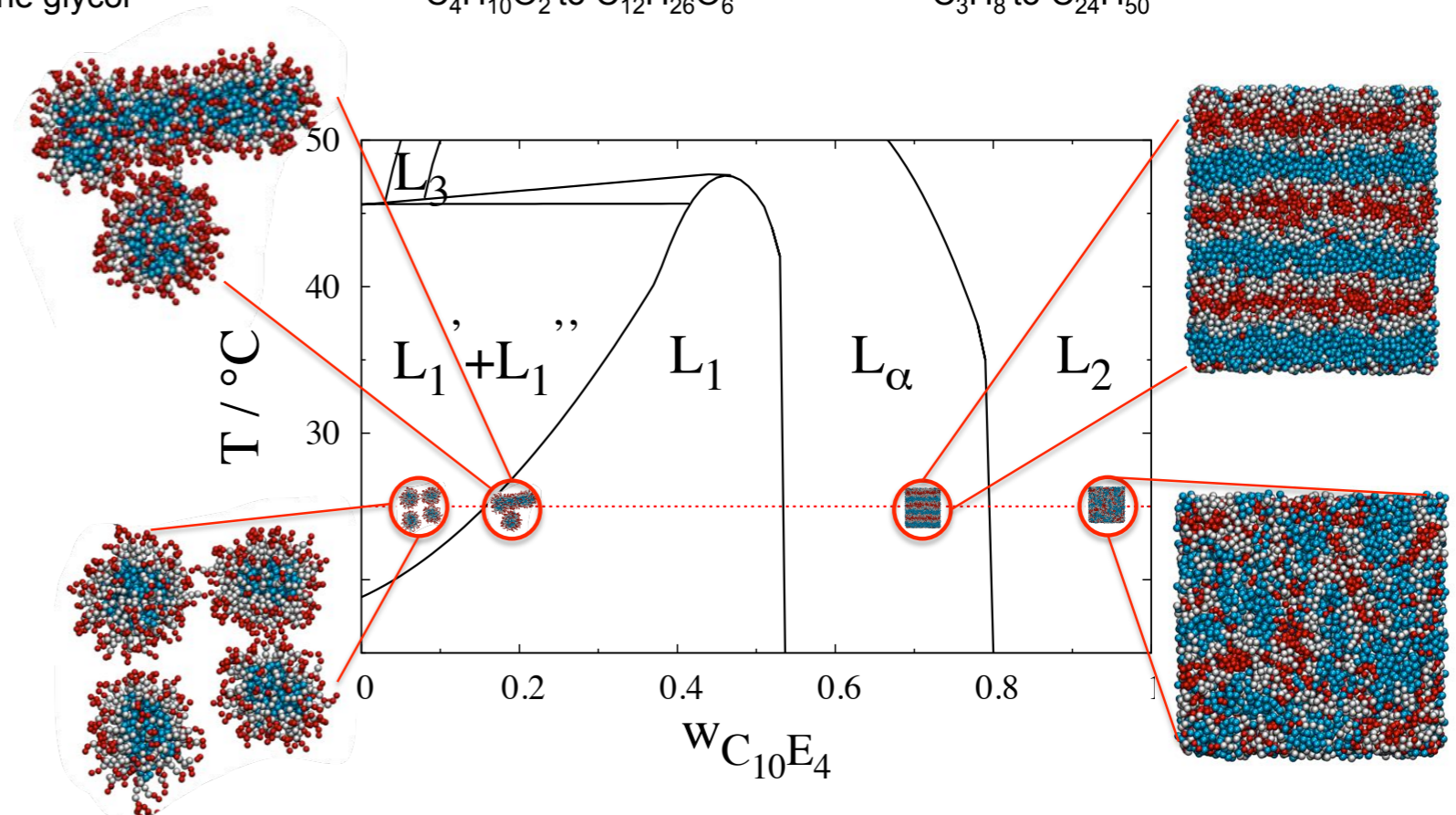
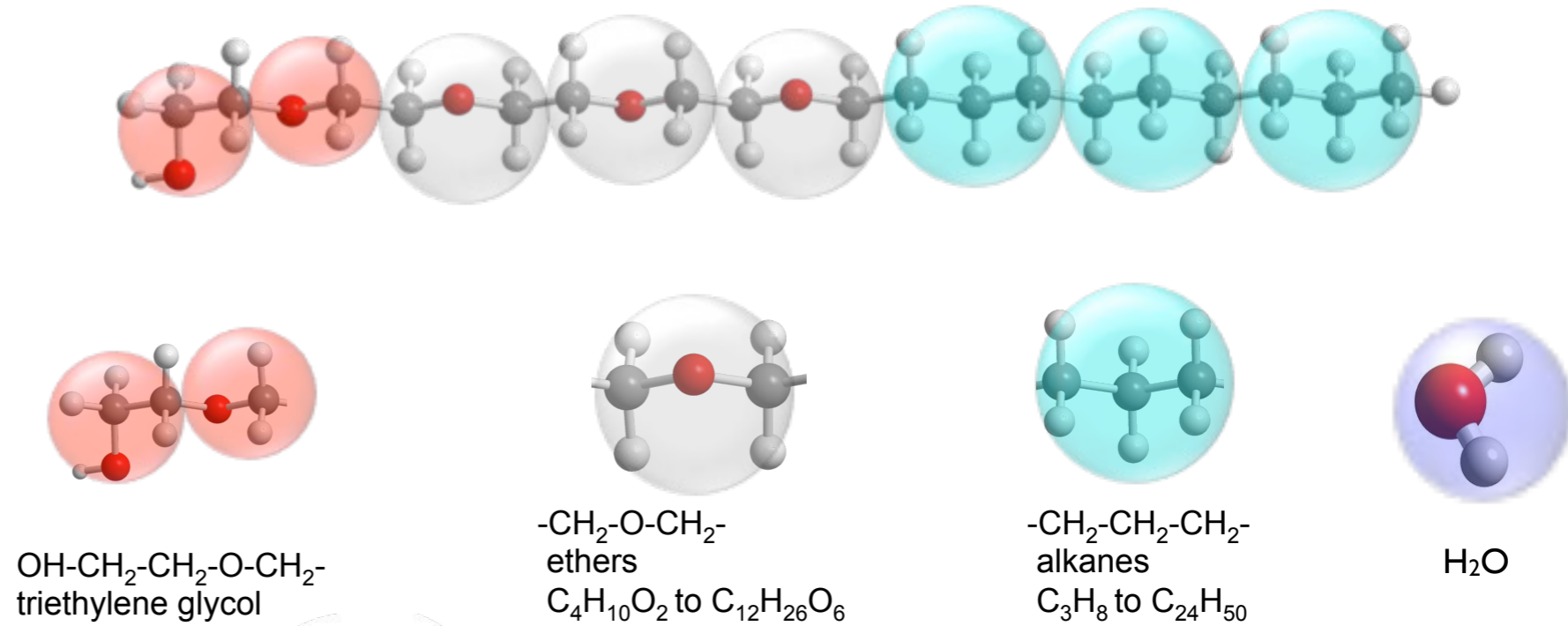
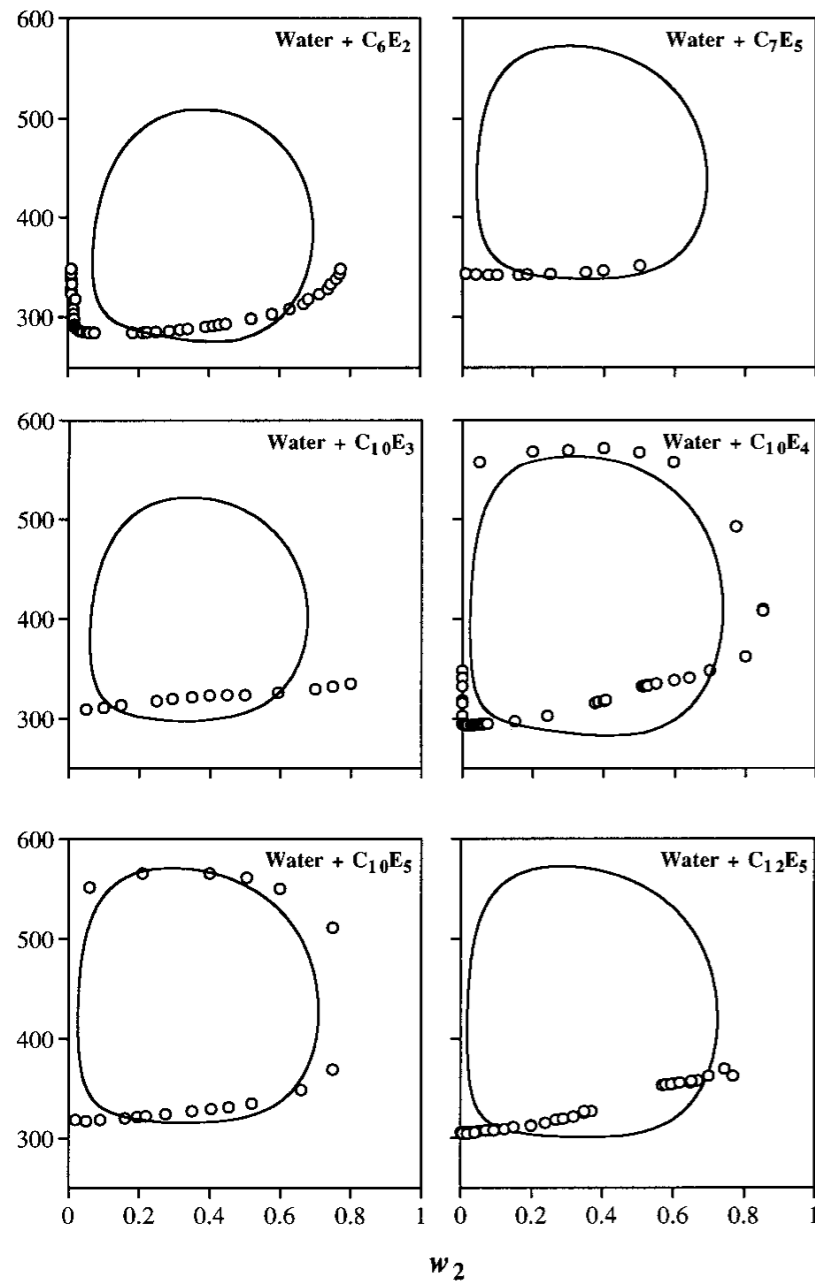
SAFT- γ coarse grained force field



SAFT- γ coarse grained force field



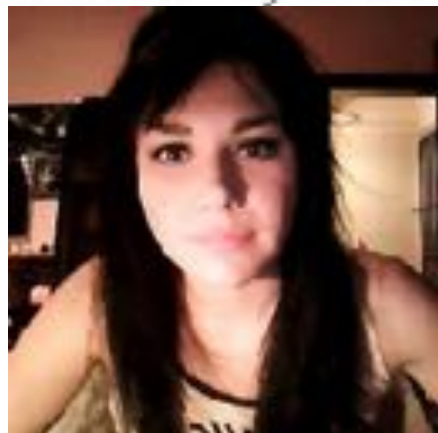
SAFT- γ coarse grained force field



Alkyl Polyoxyethylene Surfactants

MANCHESTER
1824

The University of Manchester



Nikoletta Pakalidou

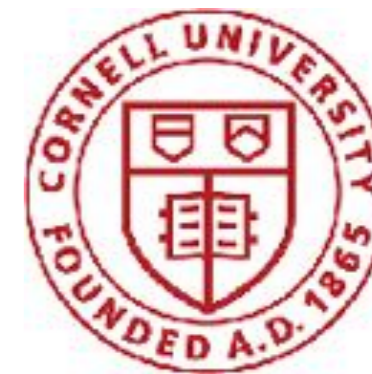


Paola Carbone

**EPSRC
NSF
DoE
Unilever
AstraZeneca**



Fernando Escobedo

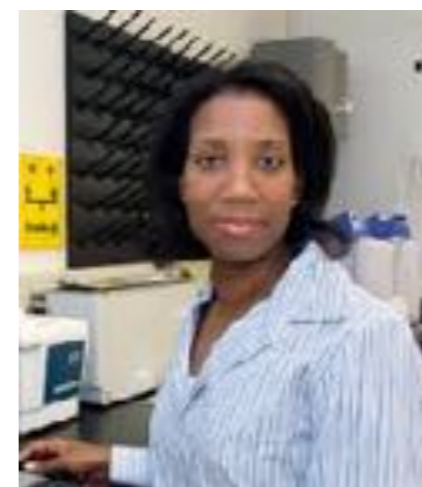


John McBride

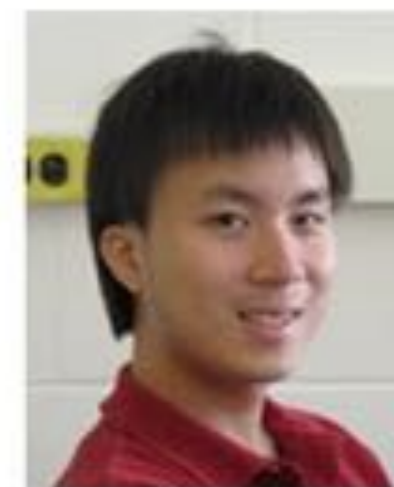


Andrew J. Masters

**Imperial College
London**



Chekesha Liddell



Kullachate Muangnapoh



Erich Muller



George Jackson



Angela Stelson



Erin Riley