Soft Nanopolyhedra

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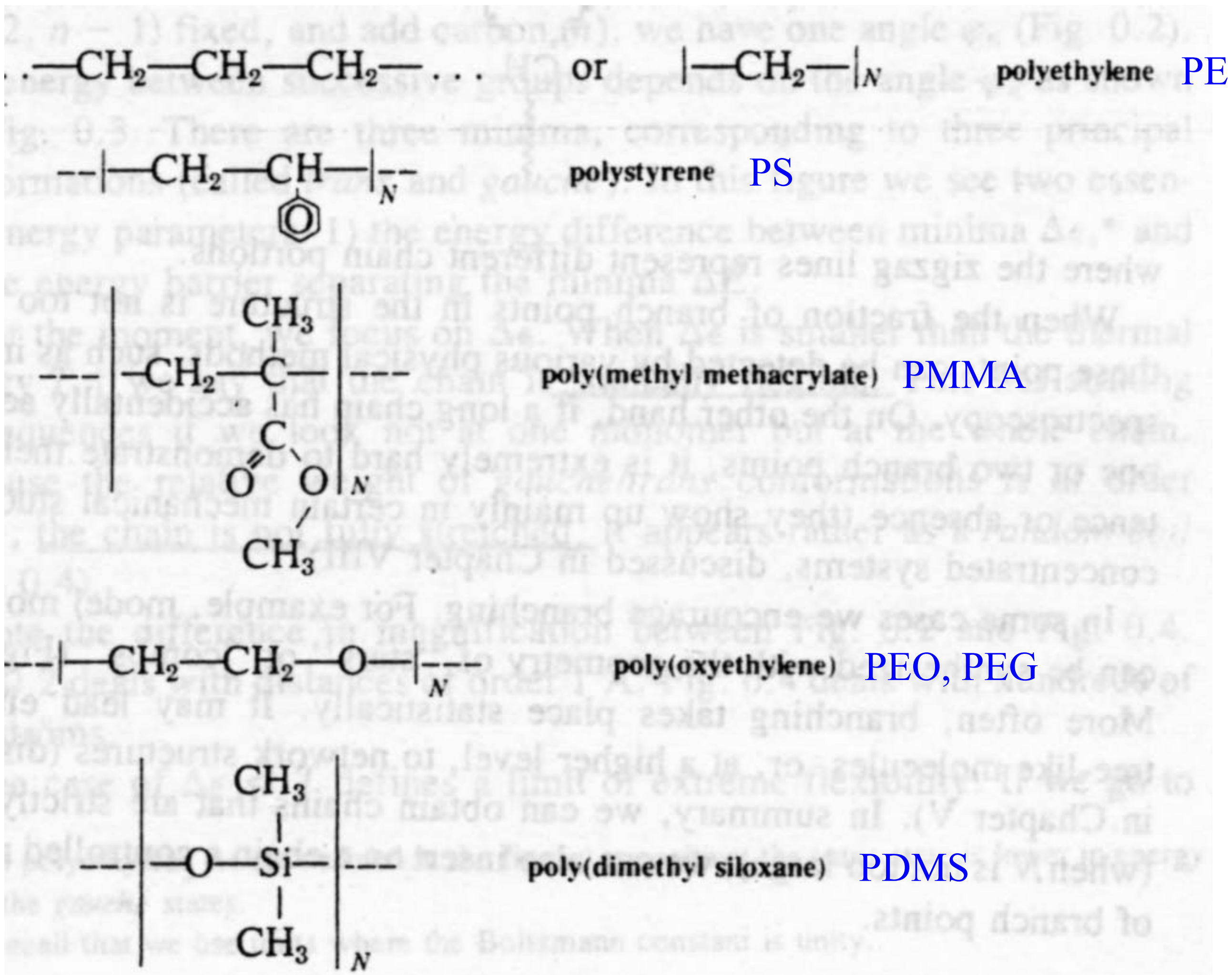
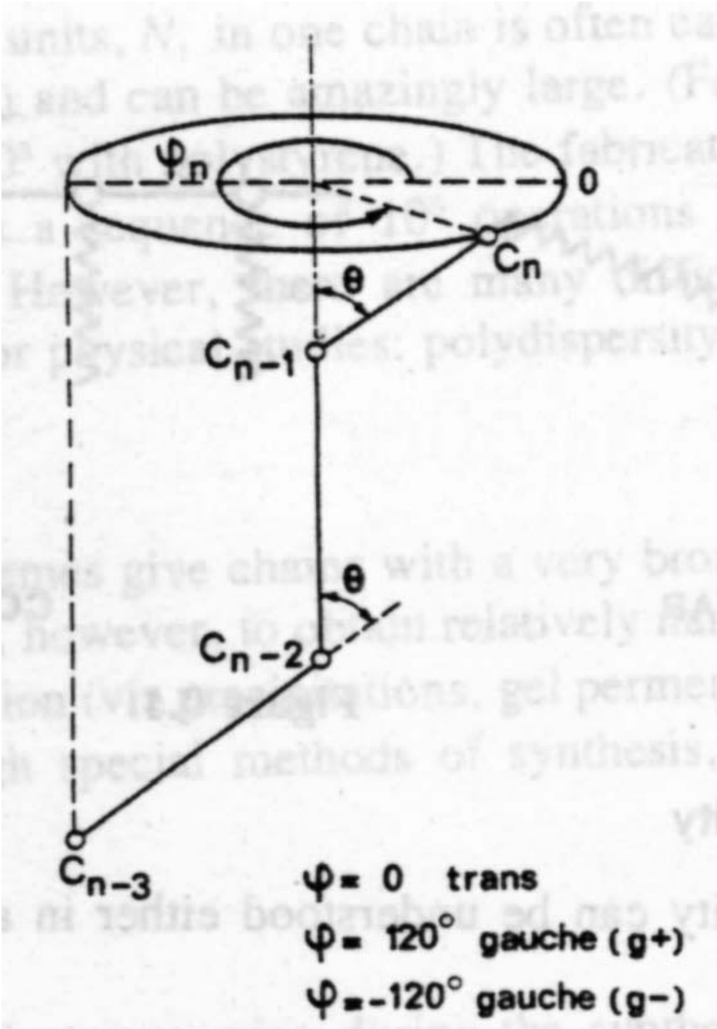
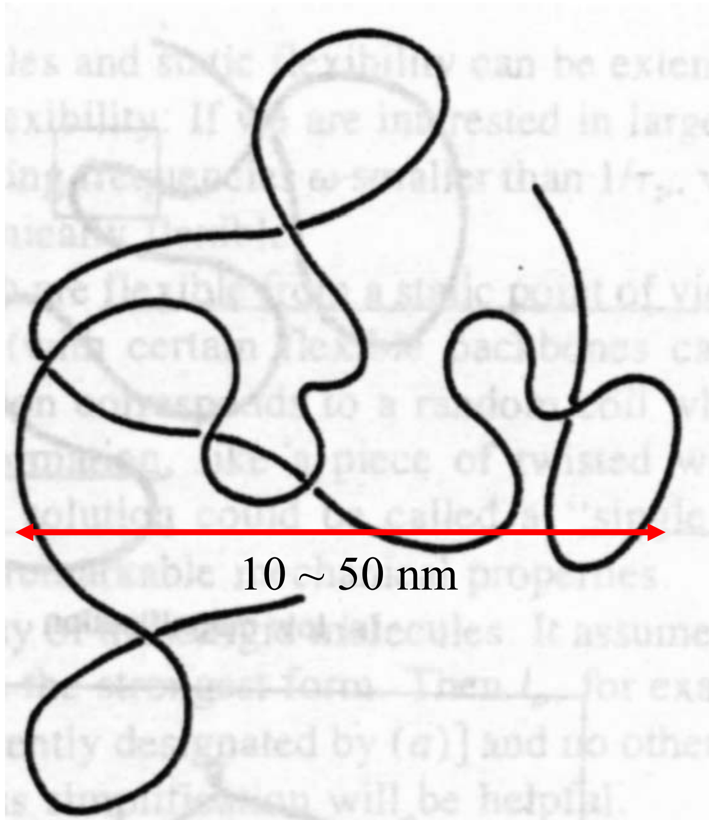
Polymers as flexible chains



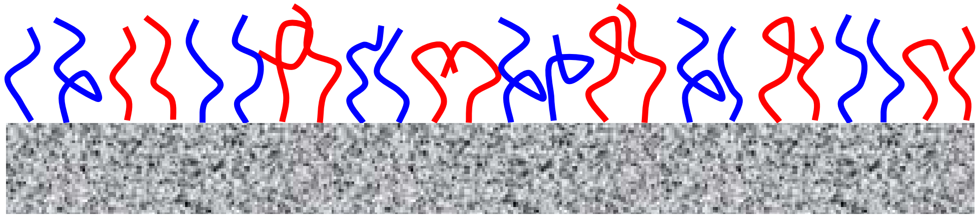
From P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca (1979).



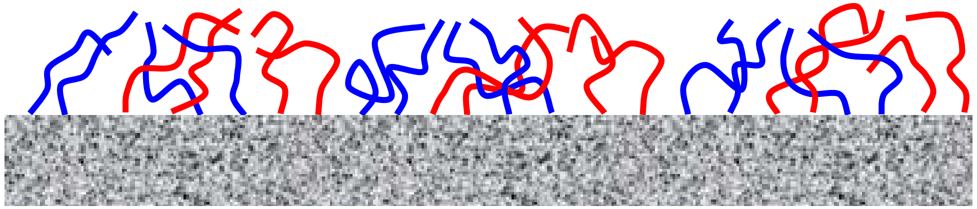


From P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca (1979).

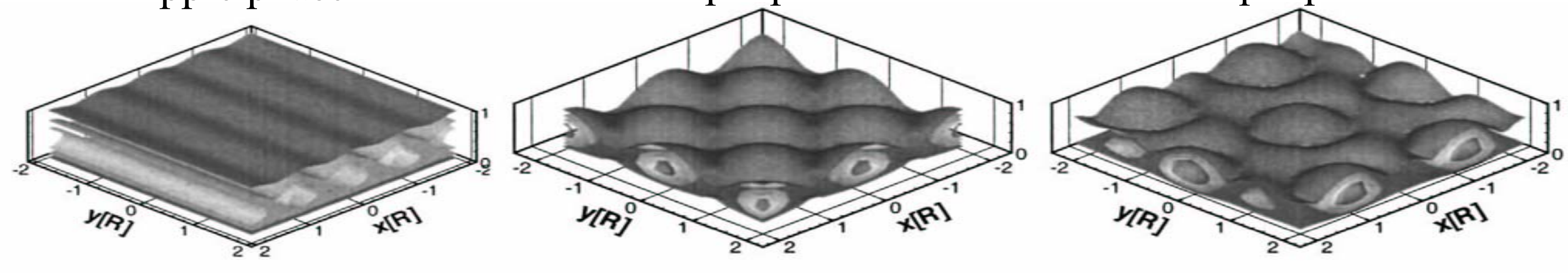
Structured planar brushes



Binary brush

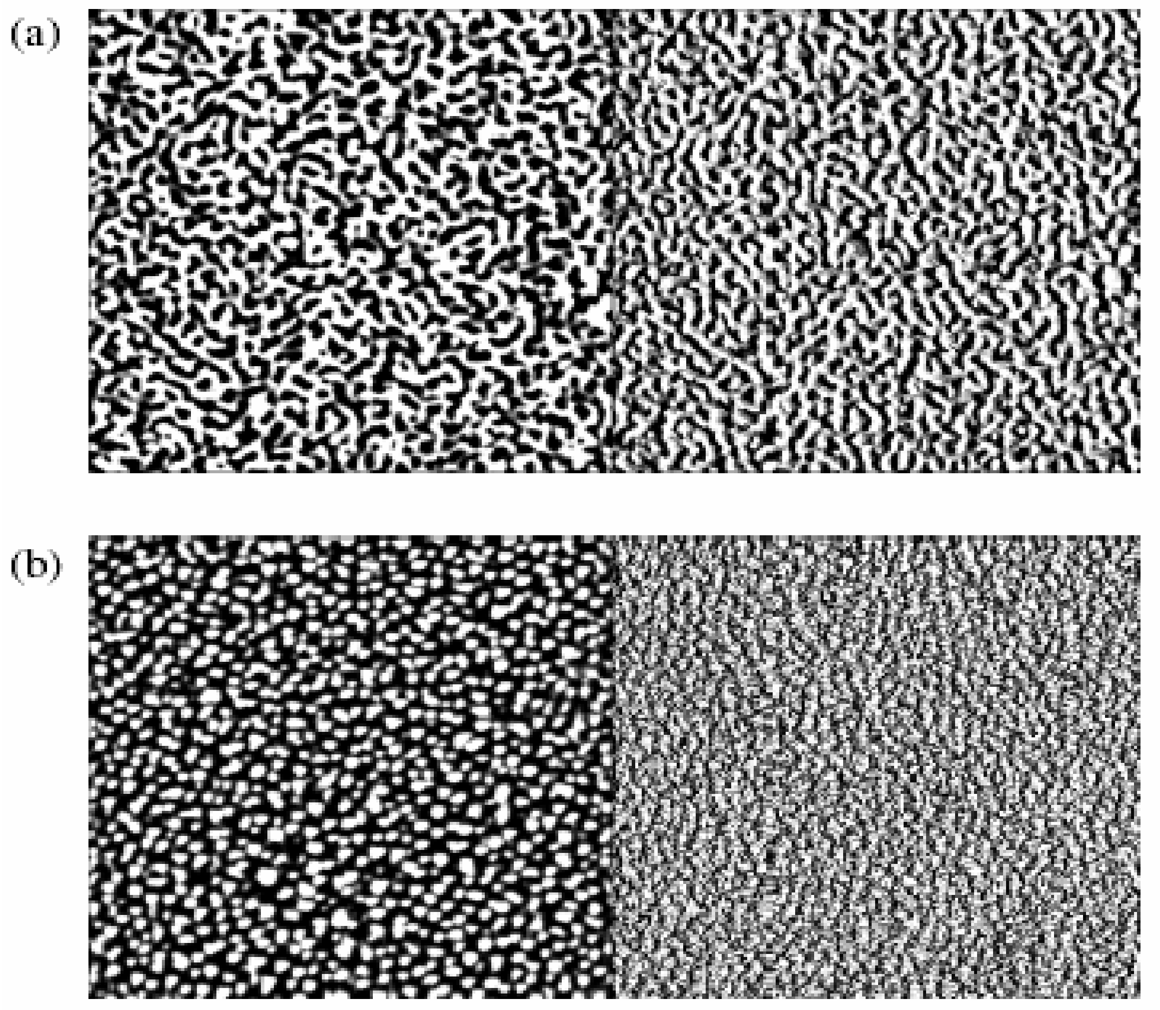


Ripple phase Dimple phase Dimple phase



From M. Müller, *Phys. Rev.* **E65**, 030802(R) (2002).

Real structured planar brushes



From S. Minko *et al*., *Phys. Rev. Lett.* **88**, 035502 (2002).

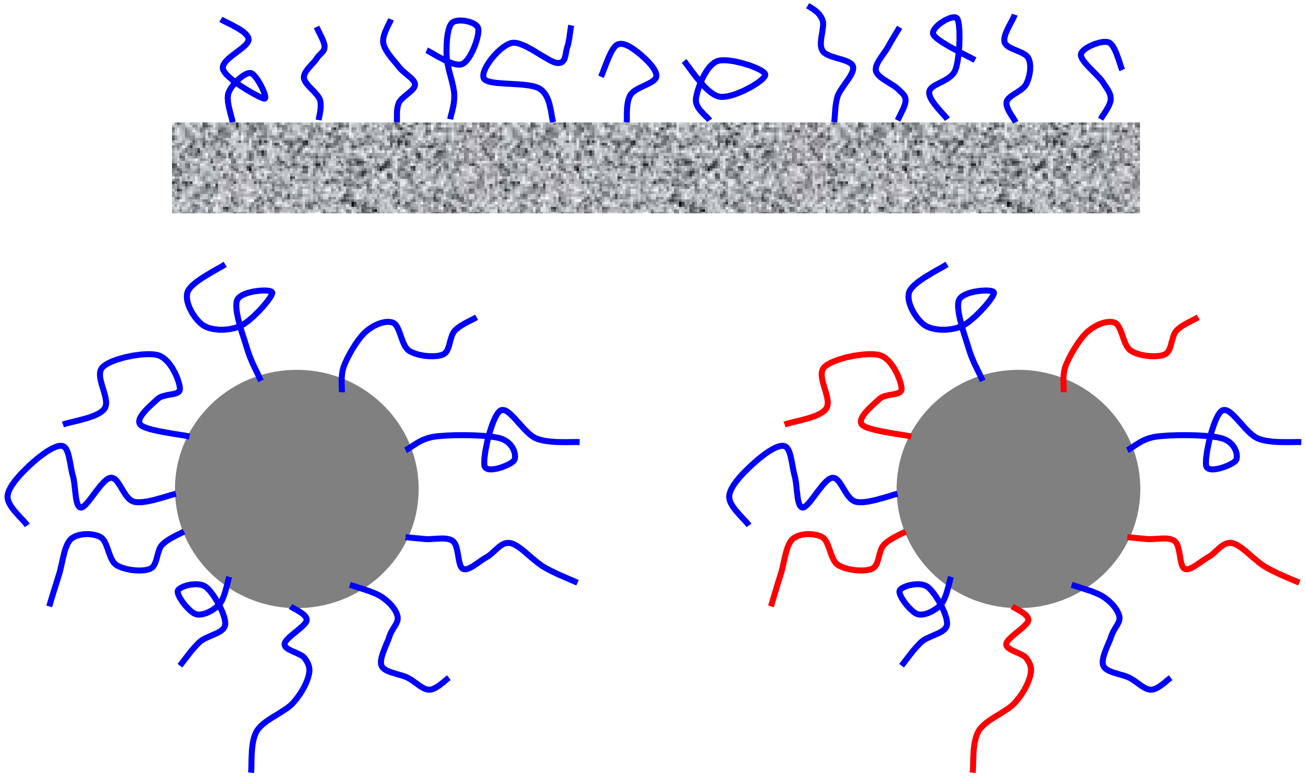
What if the substrate is a nanoparticle?

Spherical polymeric assemblies

Typical polymer size: 10 ~ 50 nm

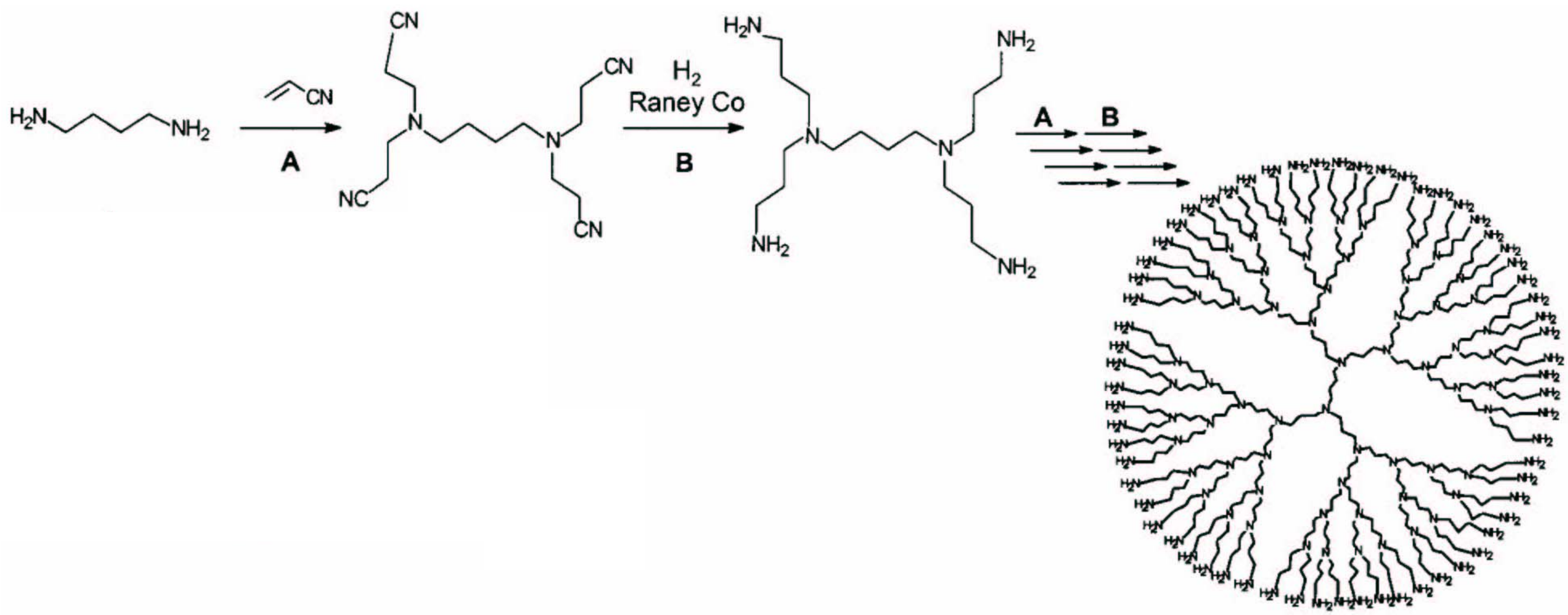
Micron-sized particle ⇨ Planar assemblies

Nanoparticle ⇨ Spherical assemblies

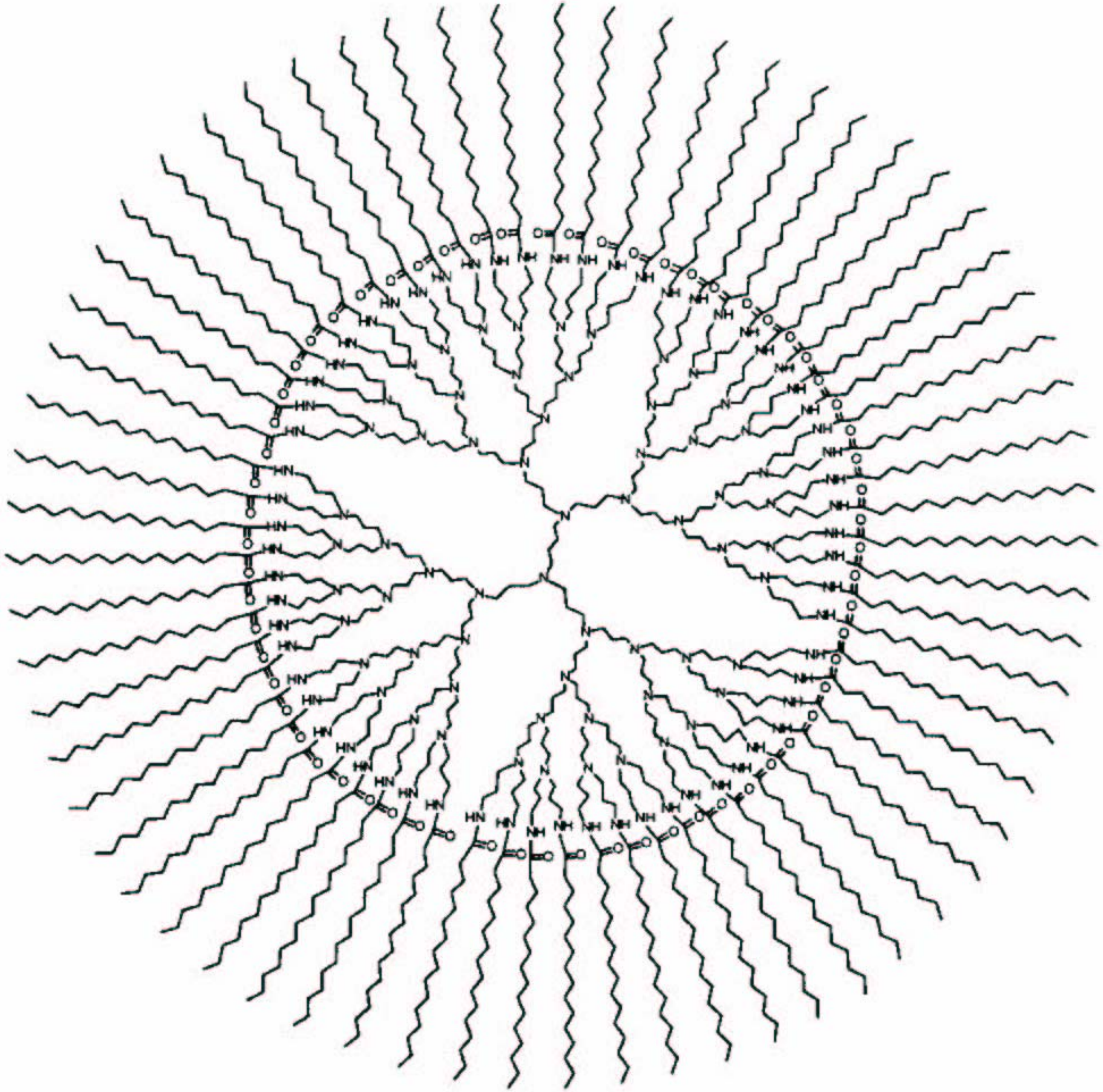


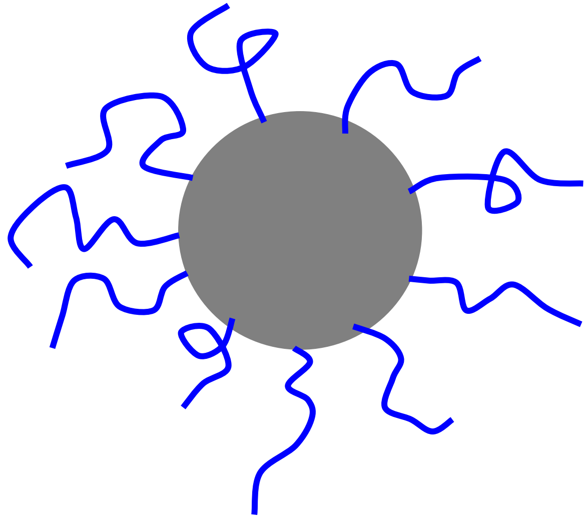
Real spherical polymeric assemblies

Dendrimers

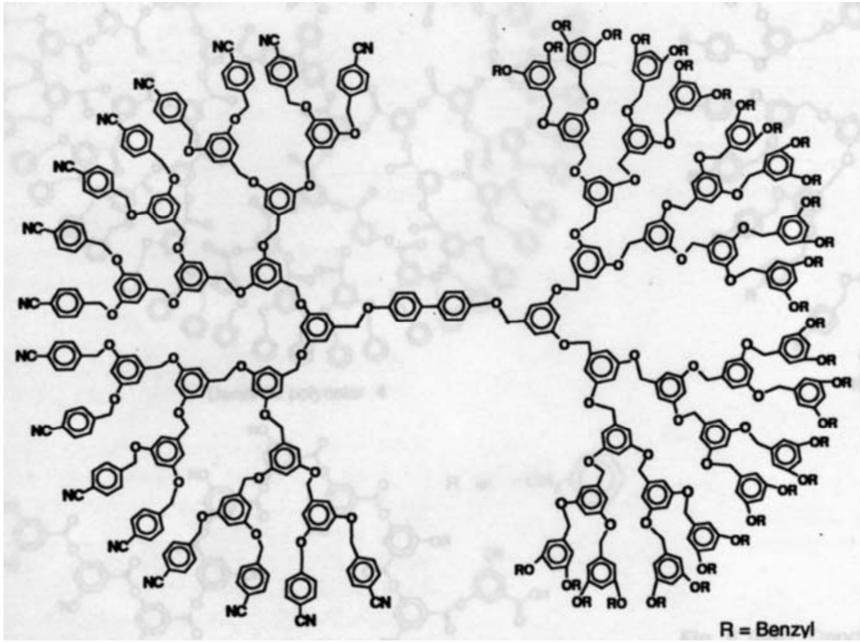


From A. W. Bosman *et al*., *Chem. Rev.* **99**, 1665 (1999).

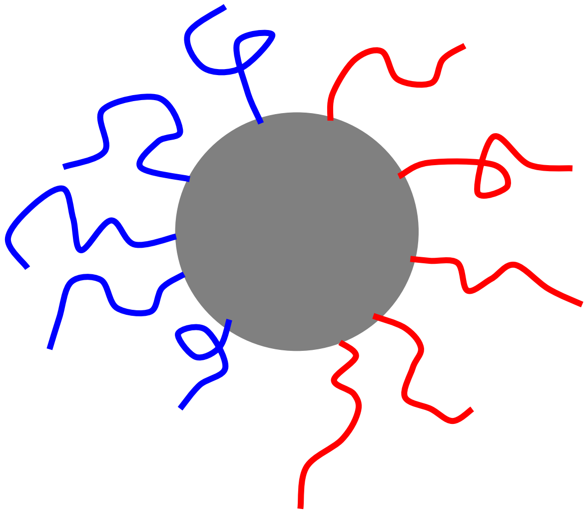




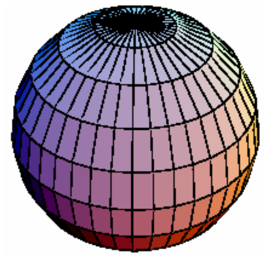
From A. W. Bosman *et al*., *Chem. Rev*. **99**, 1665 (1999).



From A. W. Bosman *et al*., *Chem. Rev.* **99**, 1665 (1999).



Effect of spherical geometry?



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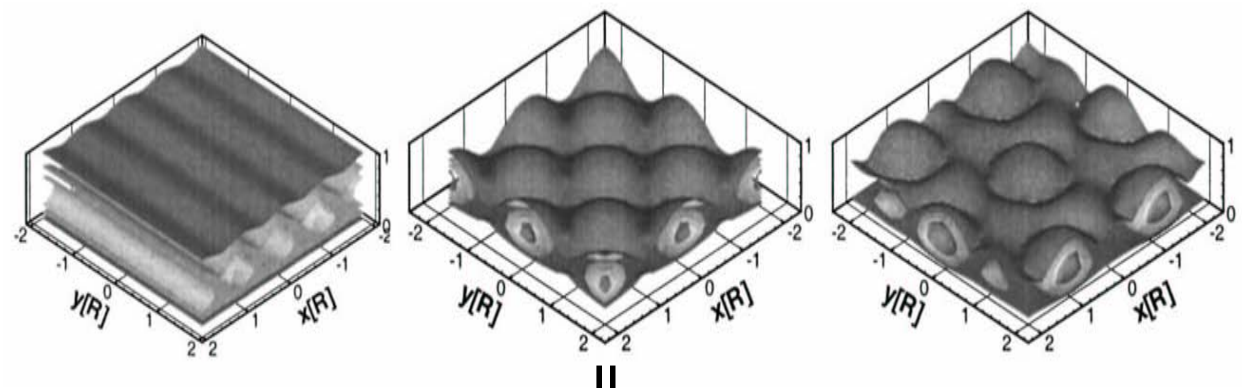

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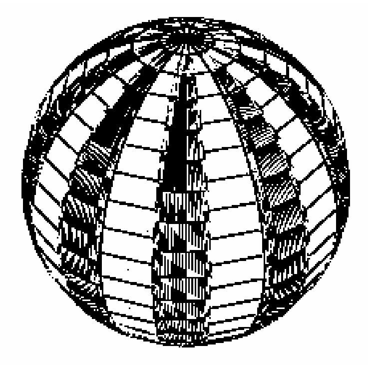
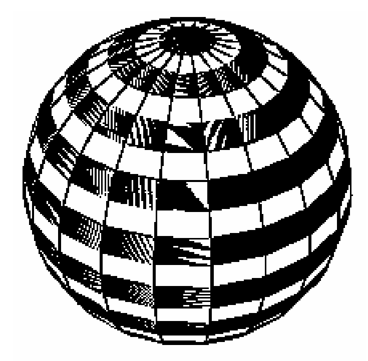


watermelon

or



hot air balloon

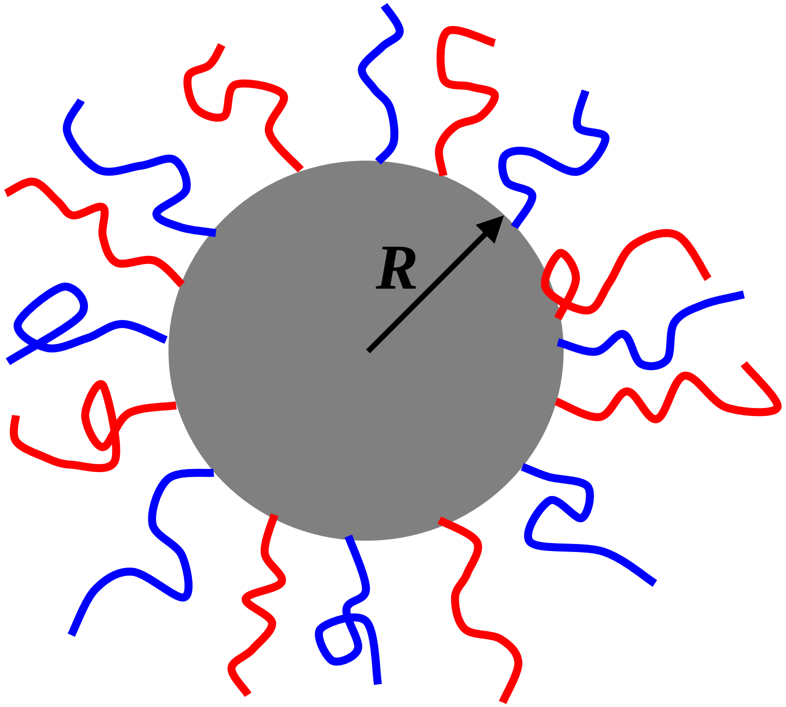
or something else?

Model

J.-R. Roan, *Int. J. Mod. Phys.* **18**, 2469 (2004), *Phys. Rev. Lett.* **96**, 248301 (2006).

f_A, N_A, b_A

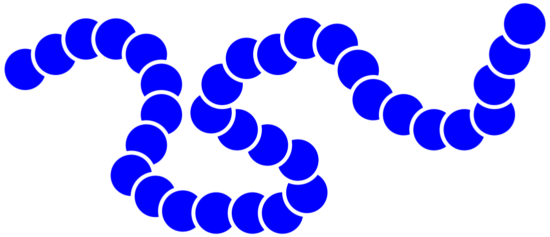
f_B, N_B, b_B



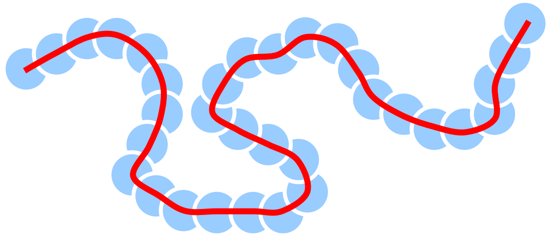
$$\nu_{AS}, \nu_{BS}, \nu_{AB} \begin{cases} \nu = 0, \text{ miscible} \\ \nu = 1, \text{ immiscible} \end{cases}$$

Edwards model for polymers

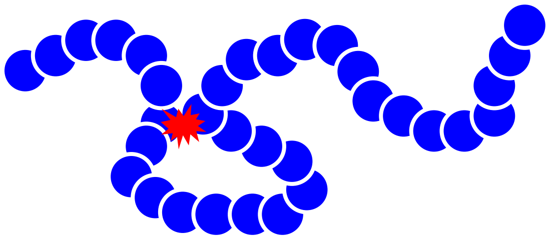
A polymer chain



A random walker



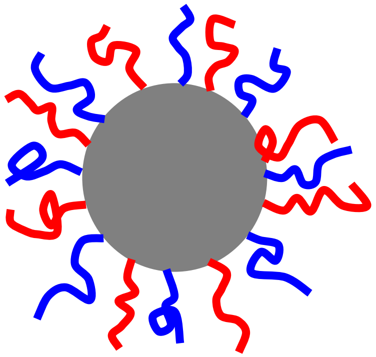
$$\frac{\partial}{\partial n} G(\boldsymbol{r}, n) = \frac{b^2}{6} \nabla^2 G(\boldsymbol{r}, n)$$



$$\frac{\partial}{\partial n} G(\boldsymbol{r}, n) = \left[\frac{b^2}{6} \nabla^2 - \omega(\boldsymbol{r}) \right] G(\boldsymbol{r}, n)$$

Self-consistent field
(SCF)

Binary spherical brush



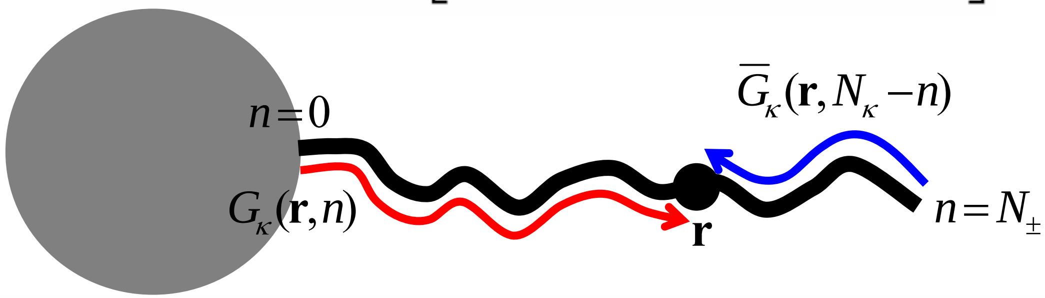
$$\phi_\kappa(\boldsymbol{r}) = \phi_\kappa^f(\boldsymbol{r}) + \phi_\kappa^0(\boldsymbol{r})$$

$$\phi_\kappa^0(\boldsymbol{r}) = \sigma_\kappa(\theta,\varphi)\delta(r-R)$$

$$\int \sigma_\kappa(\theta,\varphi)d\Omega = f_\kappa/R^2$$

$$\phi_\kappa^f(\boldsymbol{r}) = f_\kappa \int_{0^+}^{N_\kappa} \phi_\kappa^f(\boldsymbol{r},n)\,dn$$

$$\phi_s(\boldsymbol{r}) = \phi_{0s}\left[1 - \frac{\phi_A(\boldsymbol{r})}{\phi_{0A}} - \frac{\phi_B(\boldsymbol{r})}{\phi_{0B}}\right]$$



$$\phi_\kappa^f(\boldsymbol{r},n) = \frac{G_\kappa(\boldsymbol{r},n)\bar{G}_\kappa(\boldsymbol{r},N_\kappa-n)}{\int G_\kappa(\boldsymbol{r},n)\bar{G}_\kappa(\boldsymbol{r},N_\kappa-n)\,d\boldsymbol{r}}$$

Self-consistent-field equations

$$\frac{\partial}{\partial n}\bar{G}_\kappa(\boldsymbol{r},n) = \left[\frac{b_\kappa^2}{6}\nabla^2 - \omega_\kappa^f(\boldsymbol{r})\right]\bar{G}_\kappa(\boldsymbol{r},n)$$

$$\bar{G}_\kappa(\boldsymbol{r},0) = 1$$

$$\frac{\partial}{\partial n}G_\kappa(\boldsymbol{r},n) = \left[\frac{b_\kappa^2}{6}\nabla^2 - \omega_\kappa^f(\boldsymbol{r})\right]G_\kappa(\boldsymbol{r},n)$$

$$G_\kappa(\boldsymbol{r},0) = \frac{\sigma_\kappa(\theta,\varphi)\delta(r-R)}{\bar{G}_\kappa(\boldsymbol{r},N_\kappa)}$$

$$\omega_\kappa^f(\boldsymbol{r}) = v_{\kappa\kappa'}\phi_{\kappa'}(\boldsymbol{r}) - \frac{\phi_{0s}}{\phi_{0\kappa}}\ln\frac{\phi_s(\boldsymbol{r})}{\phi_{0s}}$$

Solving the (3+1)-D SCF equations

1. Discretization:

$$r_i = R + i\left(\frac{R_{max} - R}{N_r}\right), \quad i = 0, 1, \cdots, N_r$$

$$\theta_j = \frac{\pi}{N_\theta}\left(j + \frac{1}{2}\right), \quad j = 0, 1, \cdots, N_\theta - 1$$

$$\varphi_k = \frac{2\pi}{N_\varphi}k, \quad k = 0, 1, \cdots, N_\varphi - 1$$

2. Imposing periodicity:

$$\psi(r, -\theta, \varphi) = \psi(r, \theta, \varphi \pm \pi);$$

$$\psi(r, \pi + \theta, \varphi) = \psi(r, \pi - \theta, \varphi \pm \pi);$$

$$\psi(r, \theta, \pm\varphi) = \psi(r, \theta, 2\pi \pm \varphi);$$

Solving the (3+1)-D SCF equations

3. Modified alternating direction implicit method (ADI):

$$u_t = u_{xx} + u_{yy} + u_{zz}$$

$$\frac{1}{2}\delta_x^2\left(u^*_{n+1} + u_n\right) + \delta_y^2 u_n + \delta_z^2 u_n = \frac{u^*_{n+1} - u_n}{\Delta t}$$

$$\frac{1}{2}\delta_x^2\left(u^*_{n+1} + u_n\right) + \frac{1}{2}\delta_y^2\left(u^{**}_{n+1} u_n\right) + \delta_z^2 u_n = \frac{u^{**}_{n+1} - u_n}{\Delta t}$$

$$\frac{1}{2}\delta_x^2\left(u^*_{n+1} + u_n\right) + \frac{1}{2}\delta_y^2\left(u^{**}_{n+1} u_n\right) + \frac{1}{2}\delta_z^2\left(u_{n+1} + u_n\right) = \frac{u_{n+1} - u_n}{\Delta t}$$

- unconditionally stable
- locally second-order correct in space and time
- solvable tridiagonal algebraic systems

ADI $\xrightarrow{\textbf{nonlinearity}}$ modified ADI

4. Iteration until self-consistency is obtained

Parameters

System types:

- A-S system, $v_{AS} = 1$
- A-B-S system, $v_{AB} = 1$, $v_{AS} = 0$, $v_{BS} = 0$ (good solvent)
- A-B-S system, $v_{AB} = 1$, $v_{AS} = 0$, $v_{BS} = 1$ (selective solvent)

Grafting sites:

- uniform: $\sigma_\kappa(\theta, \varphi) \propto 1$
- gradient 1: $\sigma_\kappa(\theta, \varphi) \propto 1 + Y_{10}(\theta, \varphi)$
- gradient 2: $\sigma_\kappa(\theta, \varphi) \propto 3 + Y_{10}(\theta, \varphi)$
- step: $\sigma_\kappa(\theta, \varphi) \propto \text{step function}$

Discretization parameters:

- $N_r = 25\sim35$
- $N_\theta = 24\sim32$
- $N_\varphi = 48\sim64$

$\left.\right\}$ $N_r \times N_\theta \times N_\varphi \approx 30{,}000\sim70{,}000$

- $\Delta n = 0.1$, $N_\kappa = 10\sim30$; $N_n = 100\sim200$

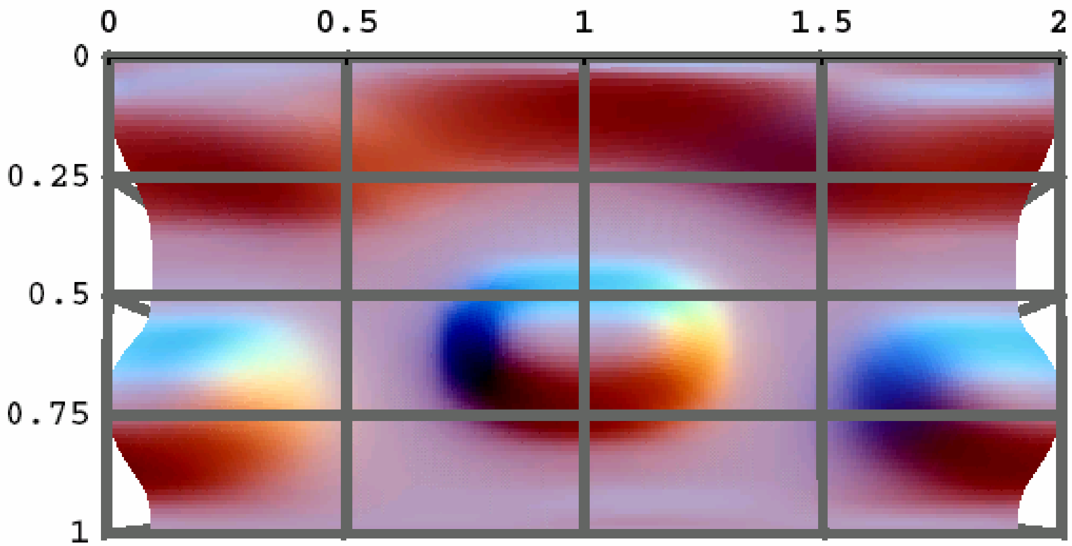
System parameters:

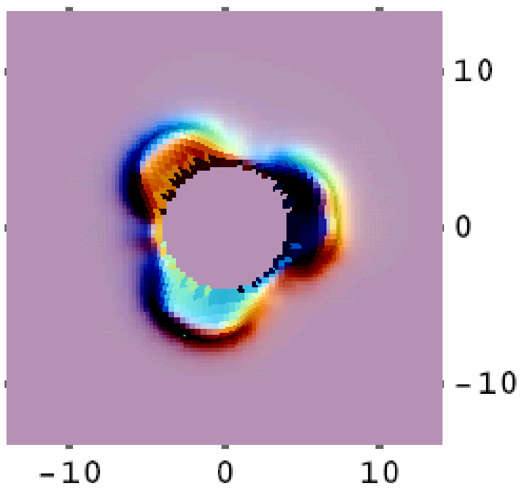
- $b_\kappa = 1$
- $R = 4$
- $N_\kappa = 10, 15, 20, 25, 30$
- f_A/f_B = 150/30, 120/60, 90/90, 60/120, 30/150;
  100/20, 80/40, 60/60, 40/80, 20/100;
  50/10, 40/20, 30/30, 20/40, 10/50

Results!

A-S system; uniform A

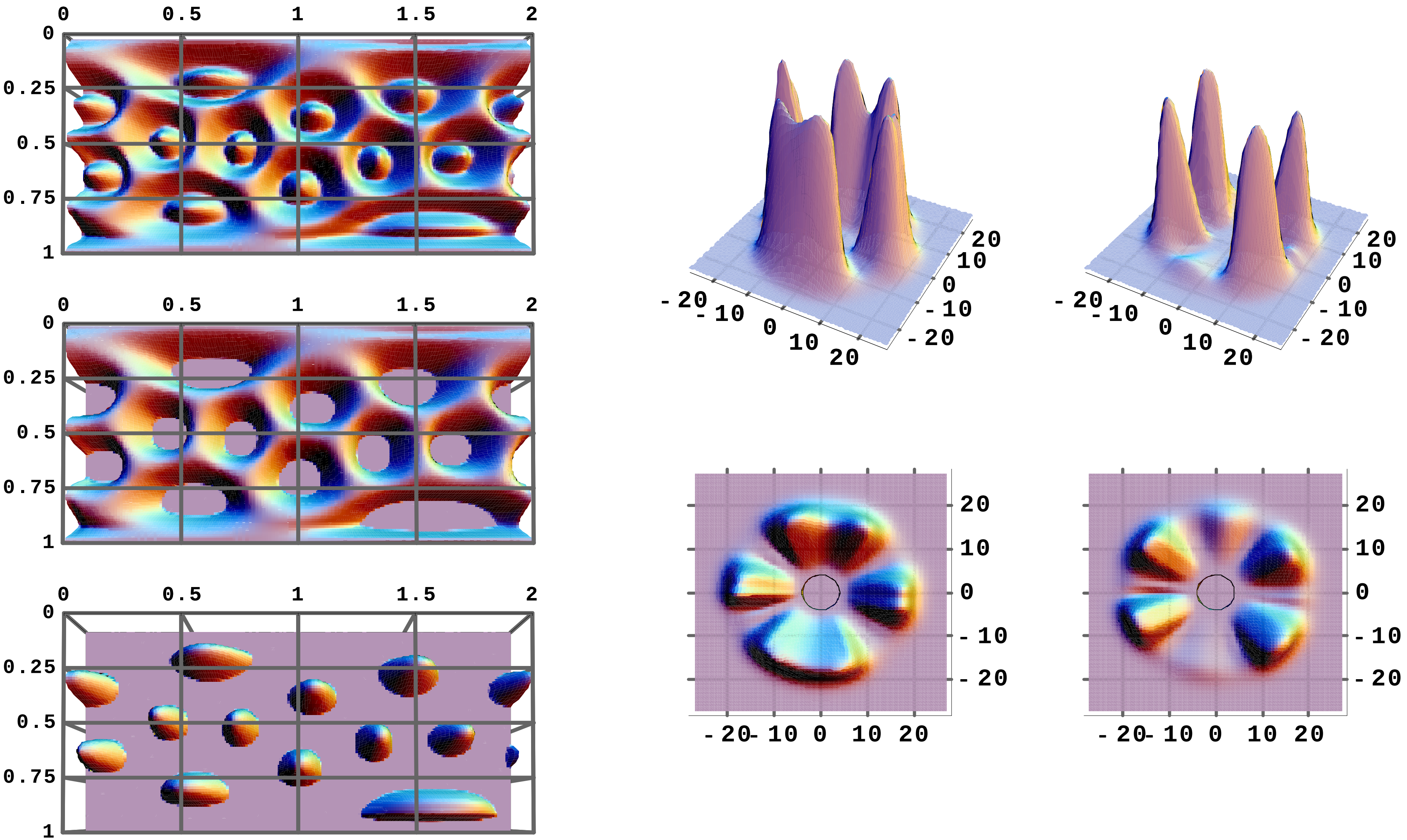
N_A=30, f_A=8 in a poor solvent

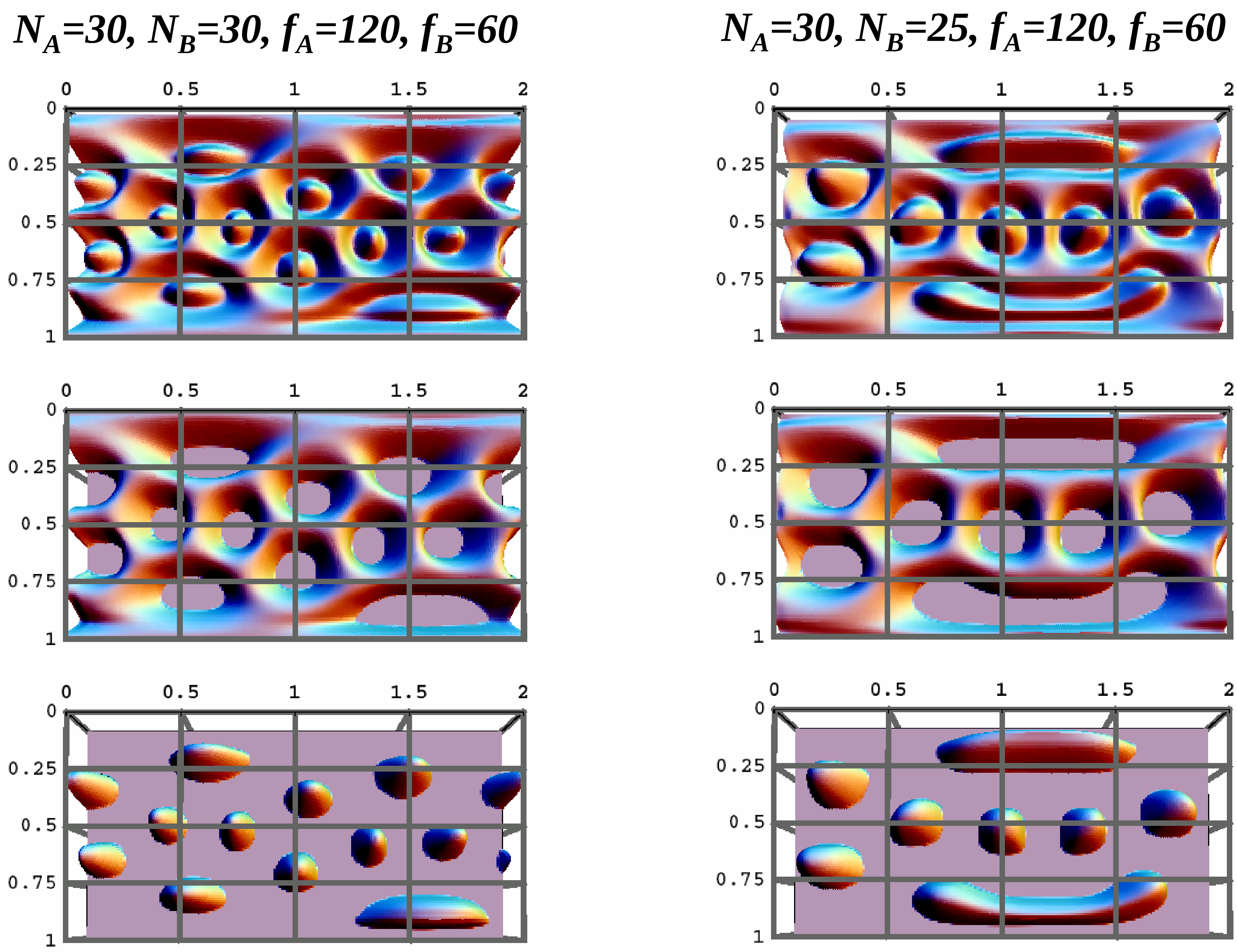




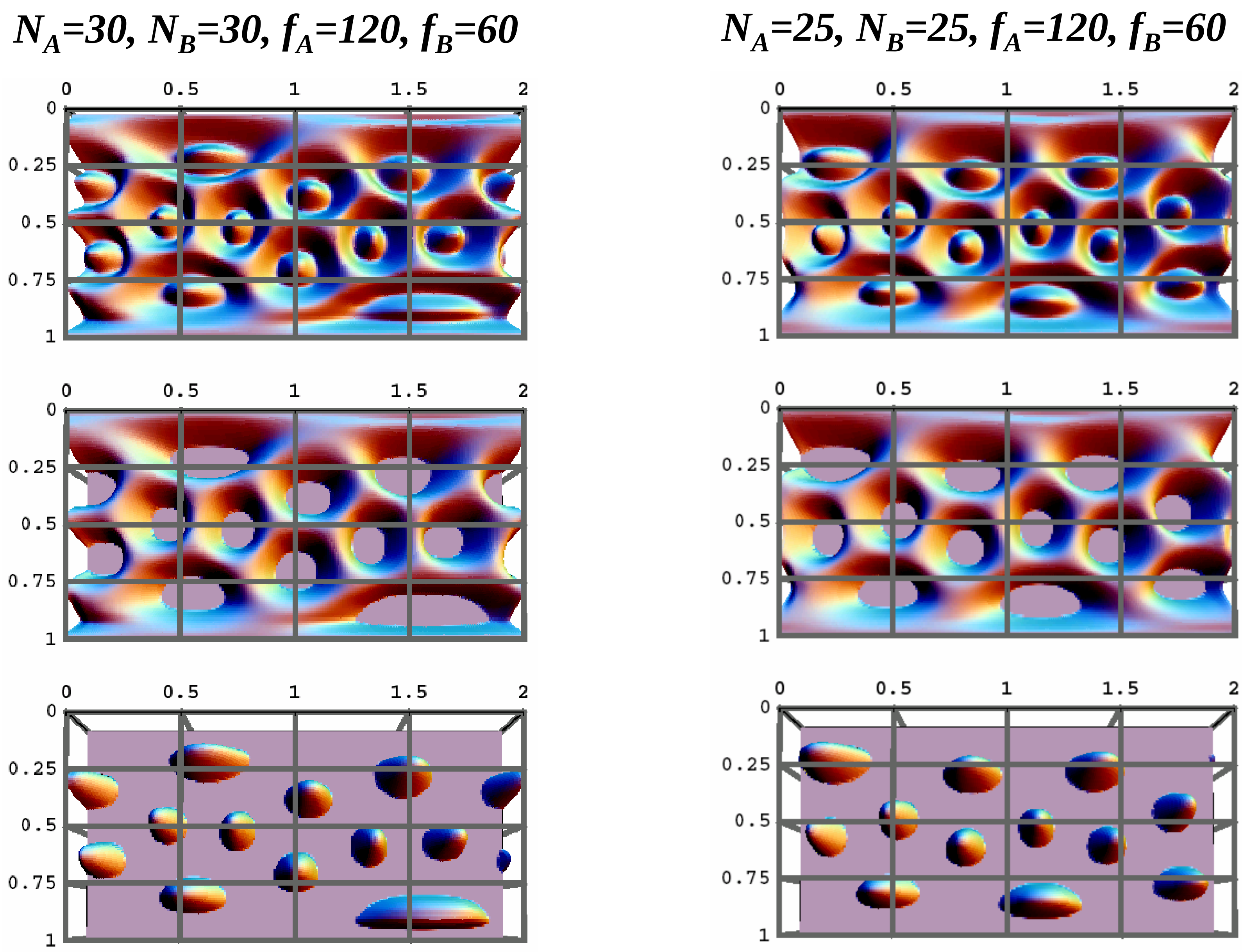
A-B-S system in a solvent good for A and B; uniform A and B

N_A=30, N_B=30, f_A=120, f_B=60

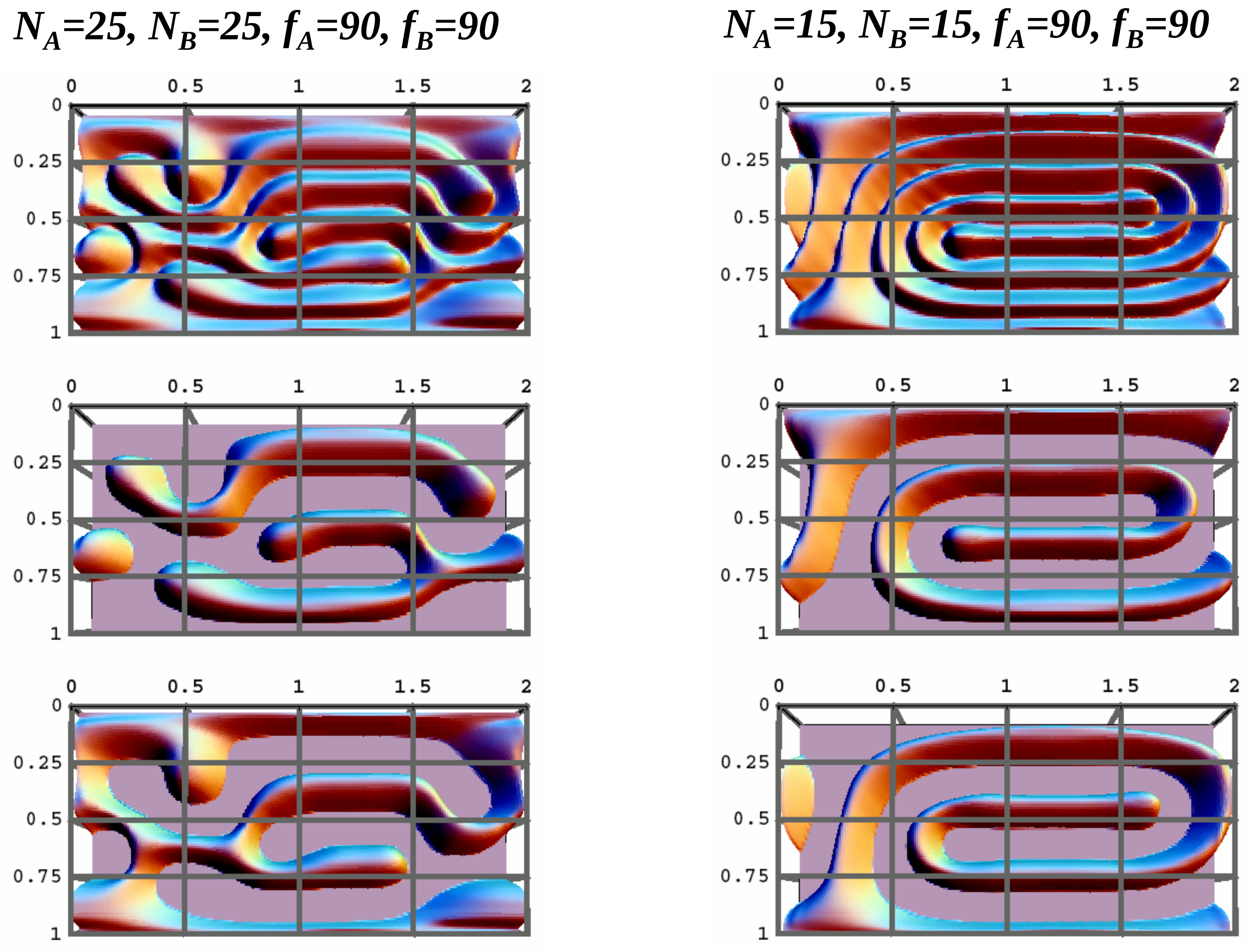




N_A=30, N_B=30, f_A=120, f_B=60
N_A=30, N_B=25, f_A=120, f_B=60
0
0.5
1
1.5
2
0
0.25
0.5
0.75
1

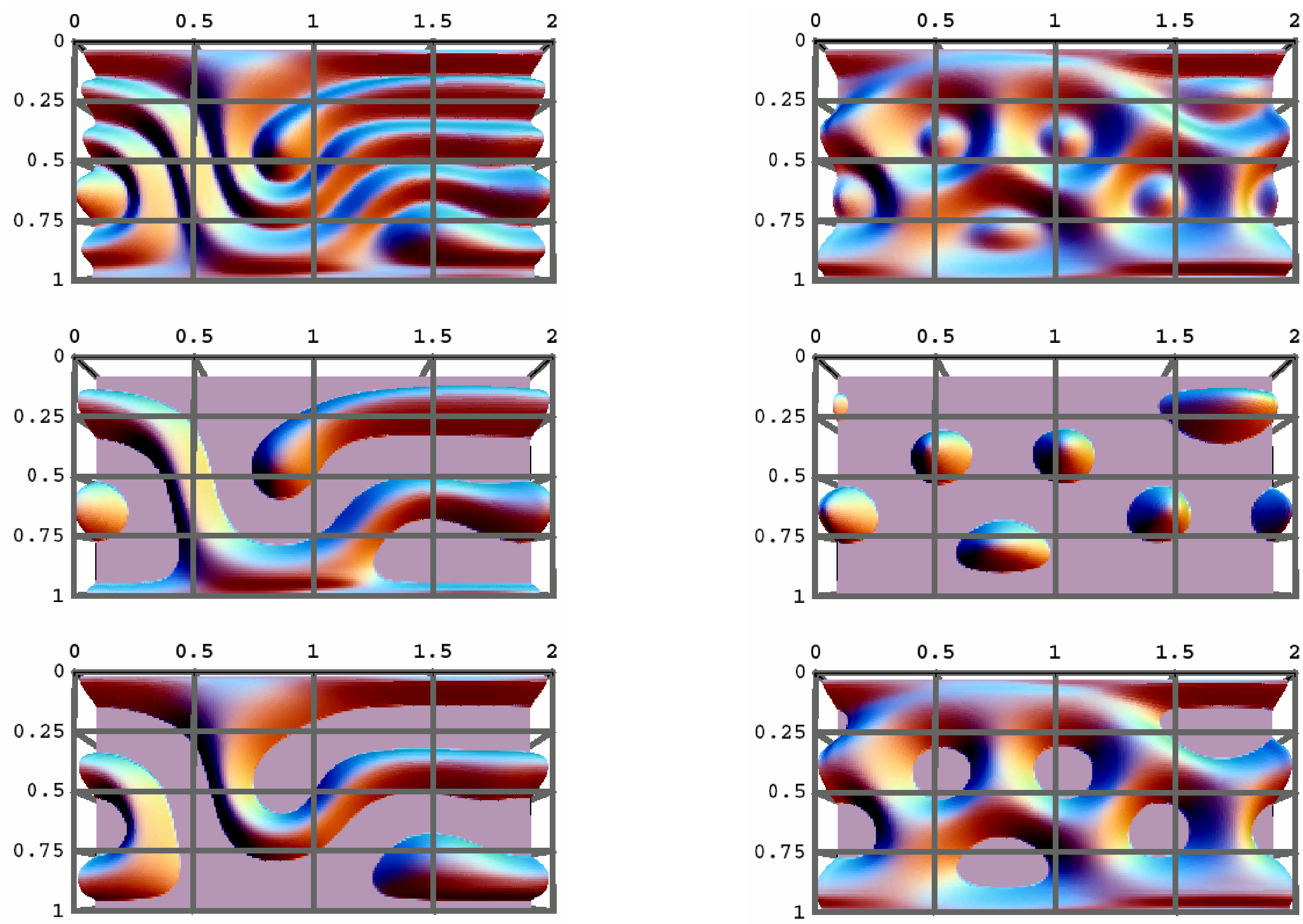


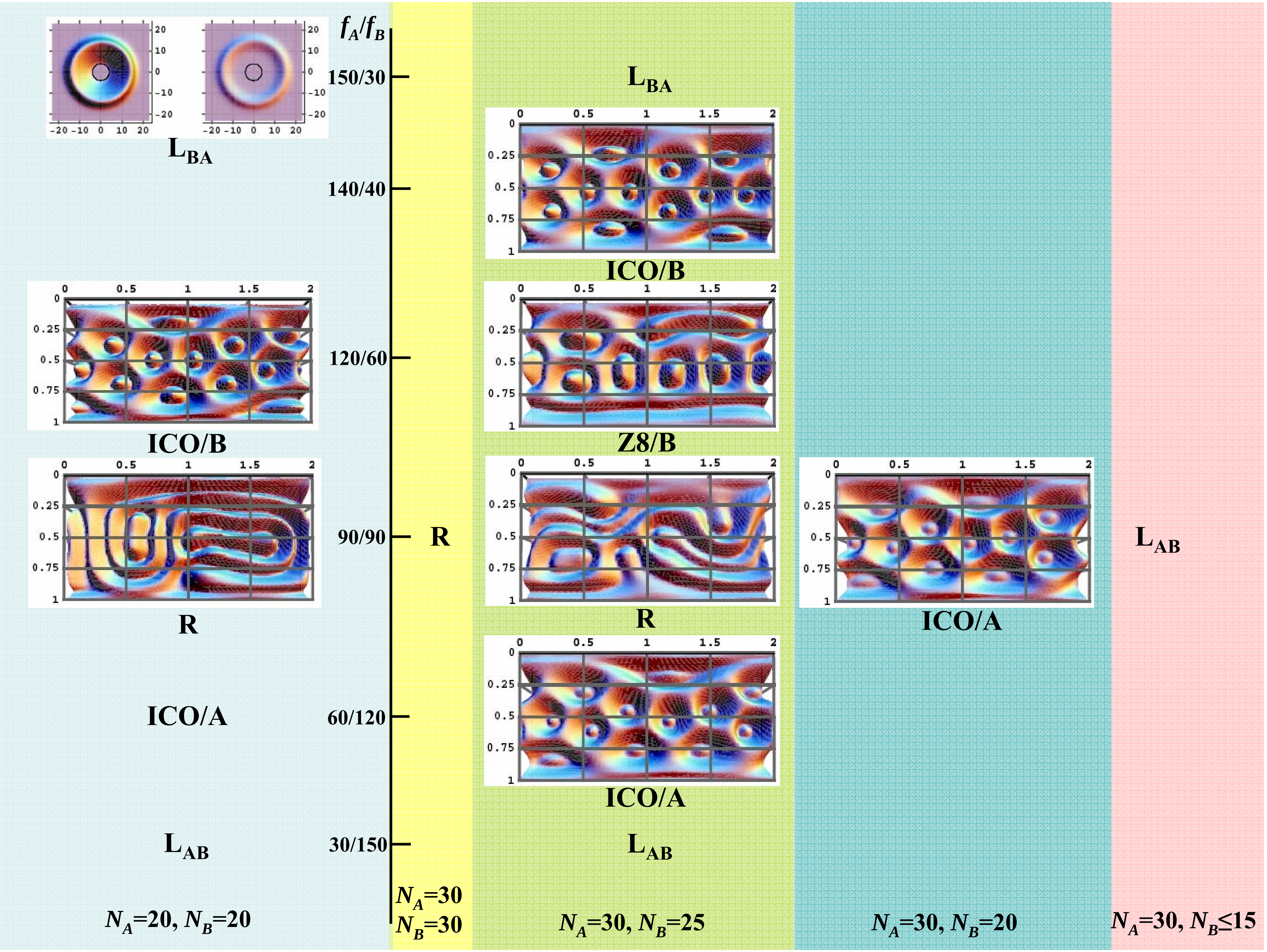
N_A=30, N_B=30, f_A=120, f_B=60
N_A=25, N_B=25, f_A=120, f_B=60
0
0.5
1
1.5
2
0
0.25
0.5
0.75
1



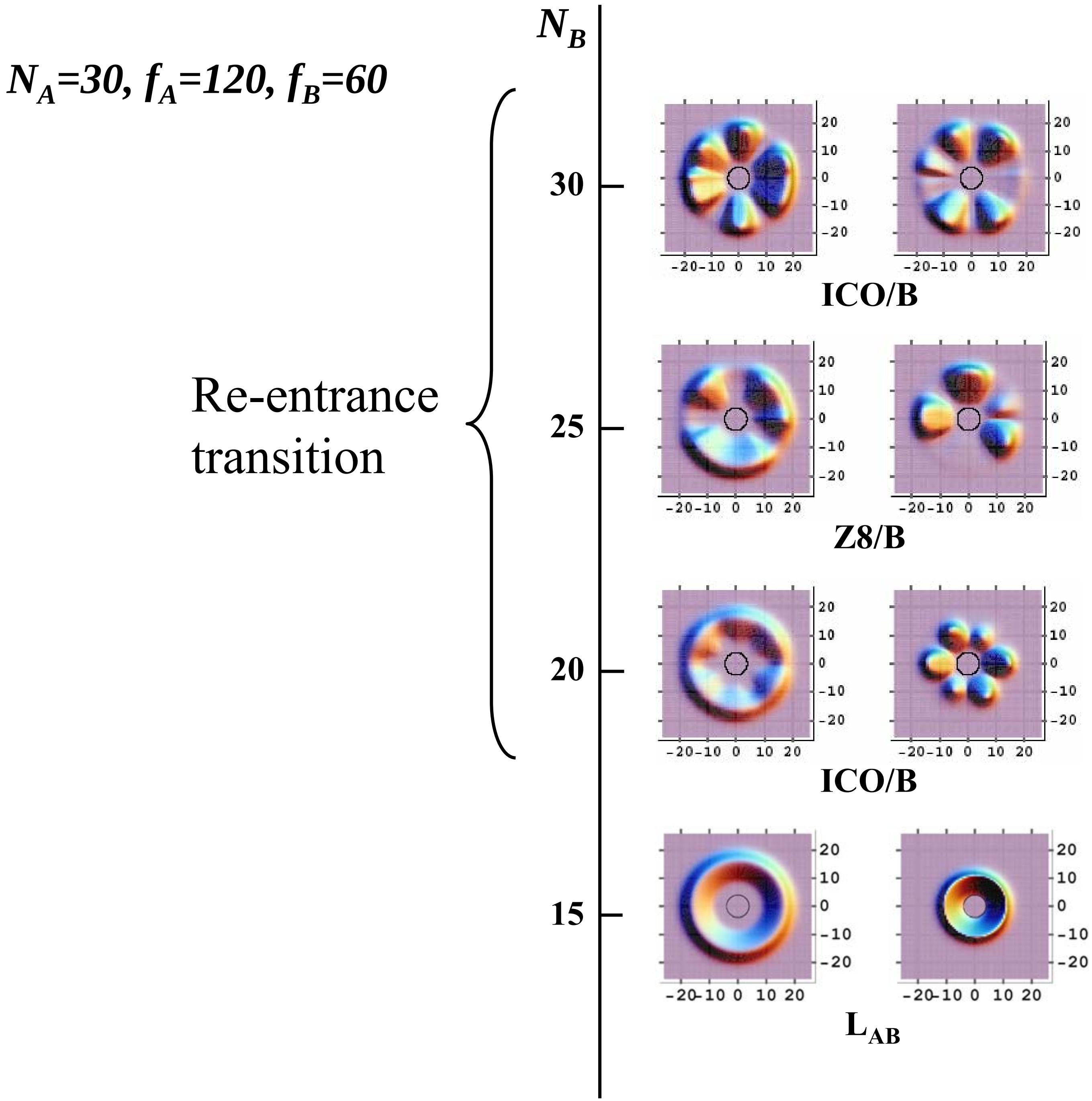
N_A=25, N_B=25, f_A=90, f_B=90
N_A=15, N_B=15, f_A=90, f_B=90
0
0.5
1
1.5
2
0
0.25
0.5
0.75
1

N_A=30, N_B=30, f_A=30, f_B=30 | N_A=30, N_B=25, f_A=30, f_B=30





f_A/f_B
150/30
140/40
120/60
90/90
60/120
30/150
L_{BA}
ICO/B
R
ICO/A
L_{AB}
N_A=20, N_B=20
R
N_A=30
N_B=30
L_{BA}
ICO/B
Z8/B
R
ICO/A
L_{AB}
N_A=30, N_B=25
ICO/A
N_A=30, N_B=20
L_{AB}
N_A=30, N_B≤15



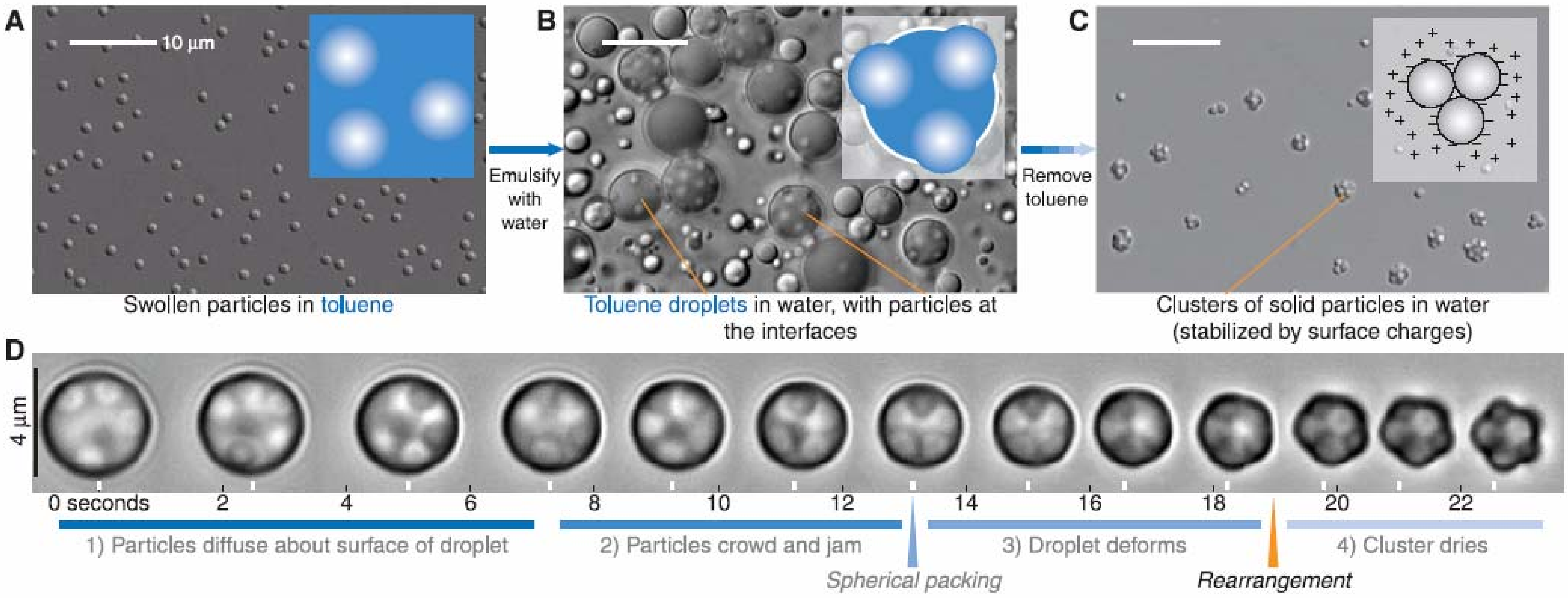
N_A=30, f_A=120, f_B=60
N_B
Re-entrance transition
30
25
20
15
ICO/B
Z8/B
ICO/B
L_{AB}

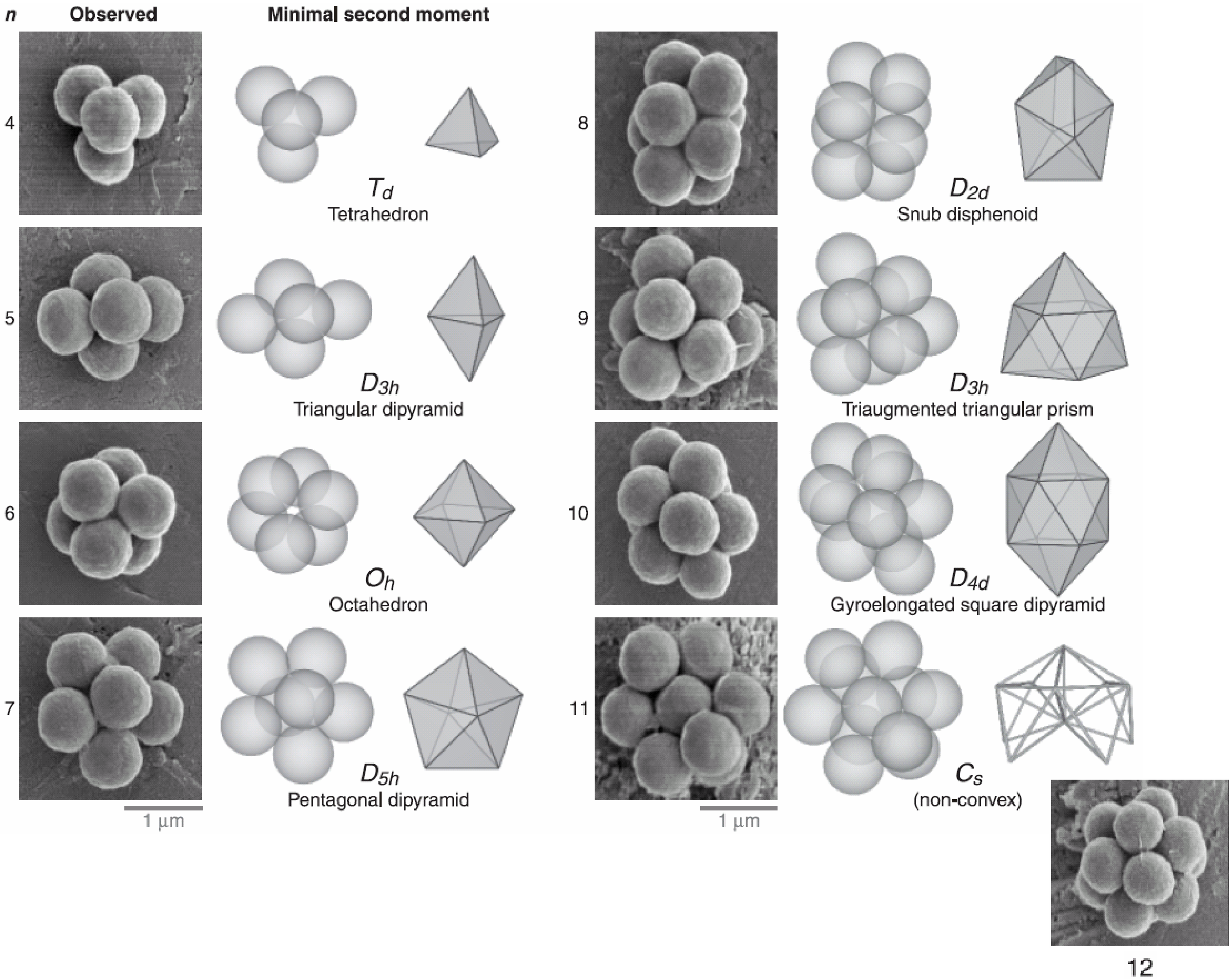
How are the islands arranged?

Dense Packing and Symmetry in Small Clusters of Microspheres

Vinothan N. Manoharan,[1] Mark T. Elsesser,[1] David J. Pine[1,2*]

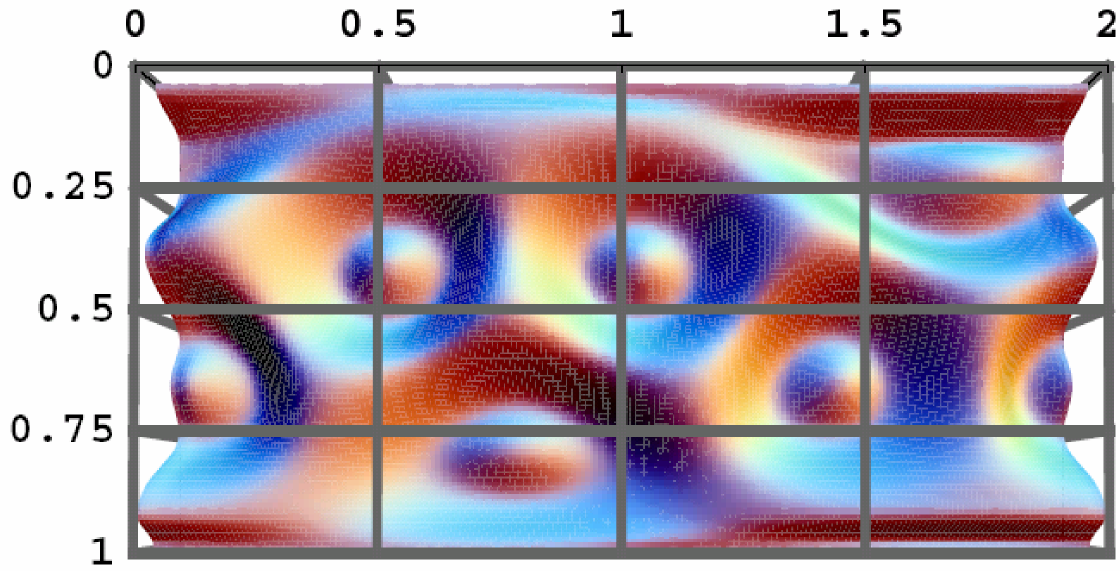
Science **301**, 483 (2003).

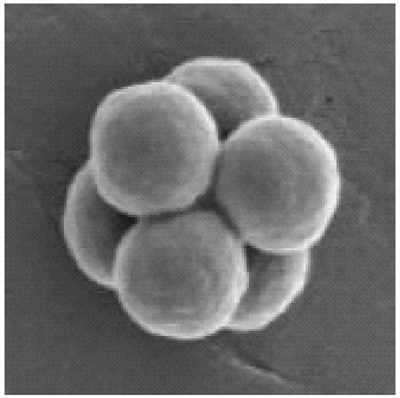


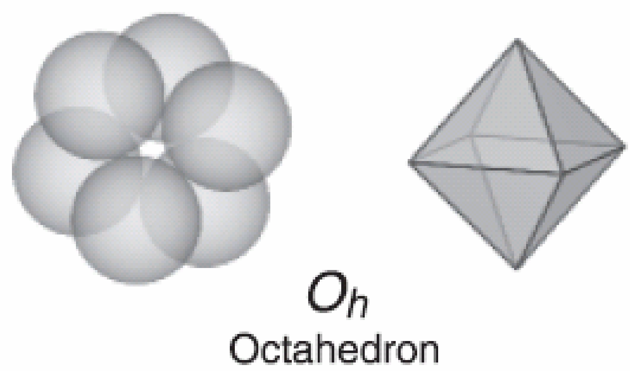


n
Observed
Minimal second moment
4
T_d
Tetrahedron
5
D_{3h}
Triangular dipyramid
6
O_h
Octahedron
7
D_{5h}
Pentagonal dipyramid
1 μm
8
D_{2d}
Snub disphenoid
9
D_{3h}
Triaugmented triangular prism
10
D_{4d}
Gyroelongated square dipyramid
11
C_s
(non-convex)
1 μm
12

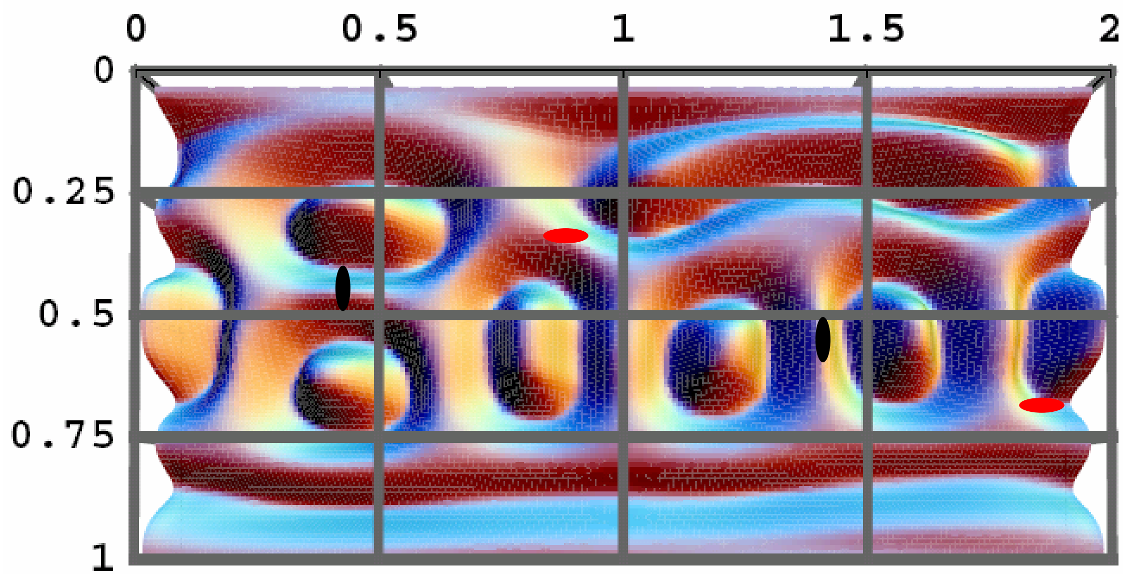
Z6: N_A=30, N_B=25, f_A=30, f_B=30

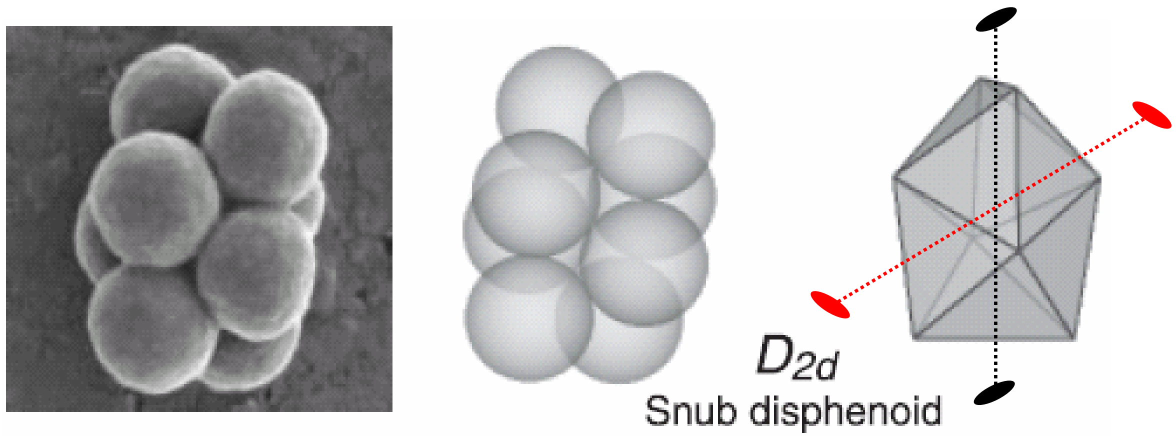




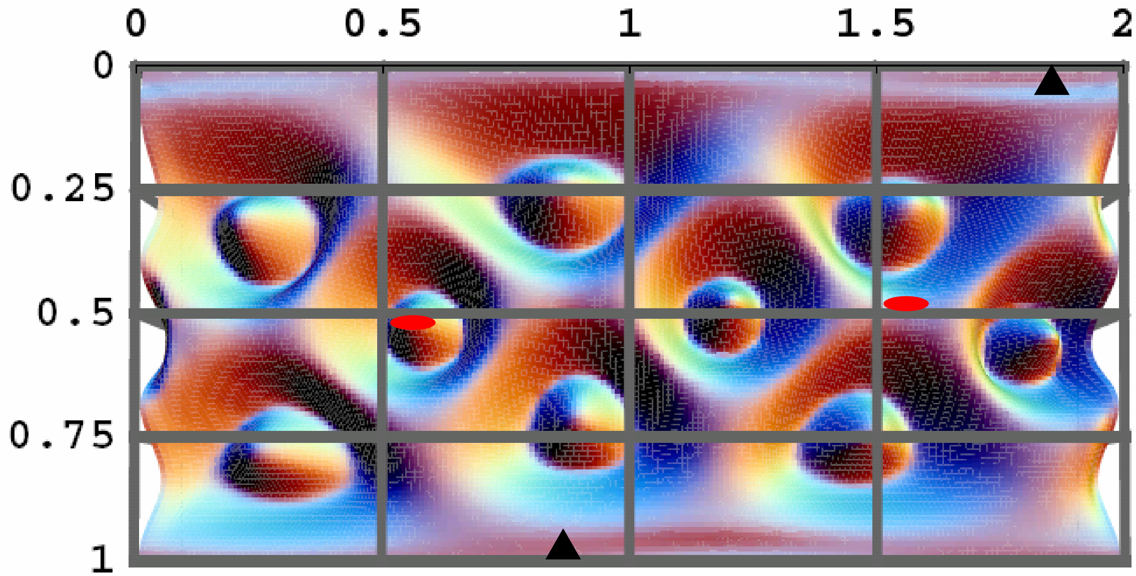


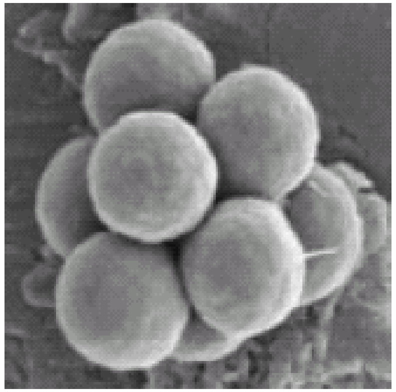
Z8: N_A=30, N_B=25, f_A=120, f_B=60

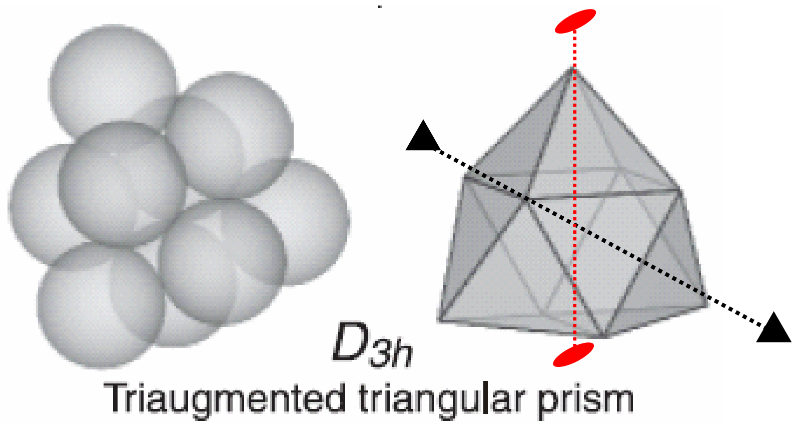




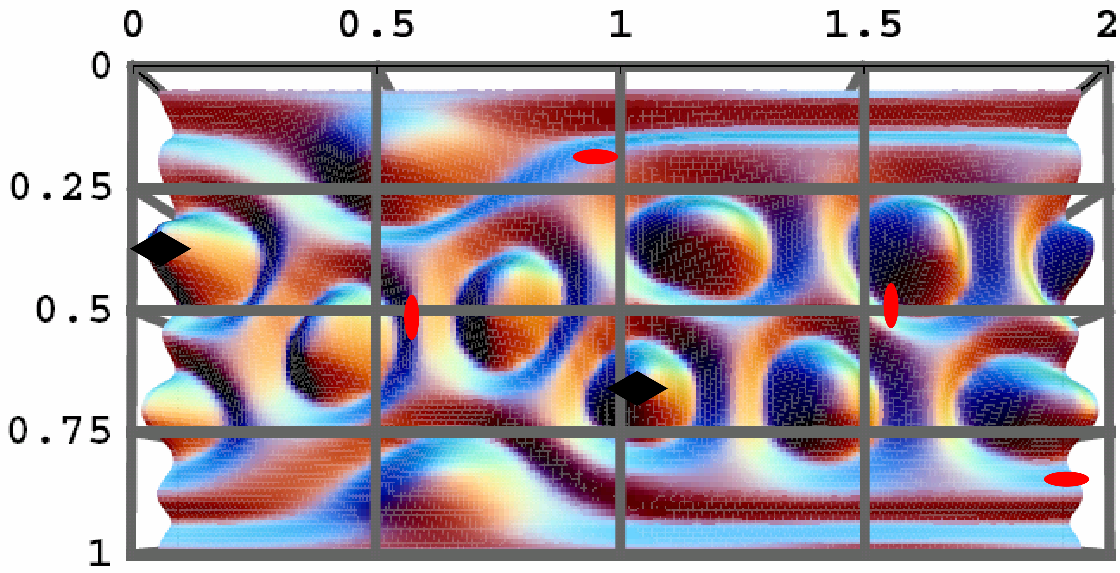
Z9: N_A=25, N_B=25, f_A=80, f_B=40

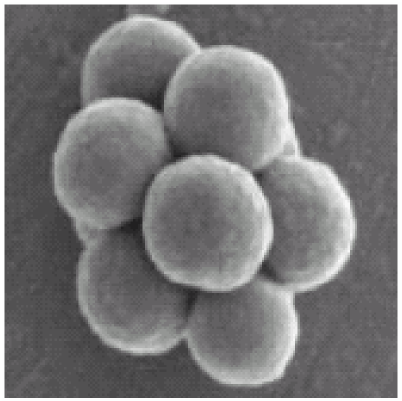


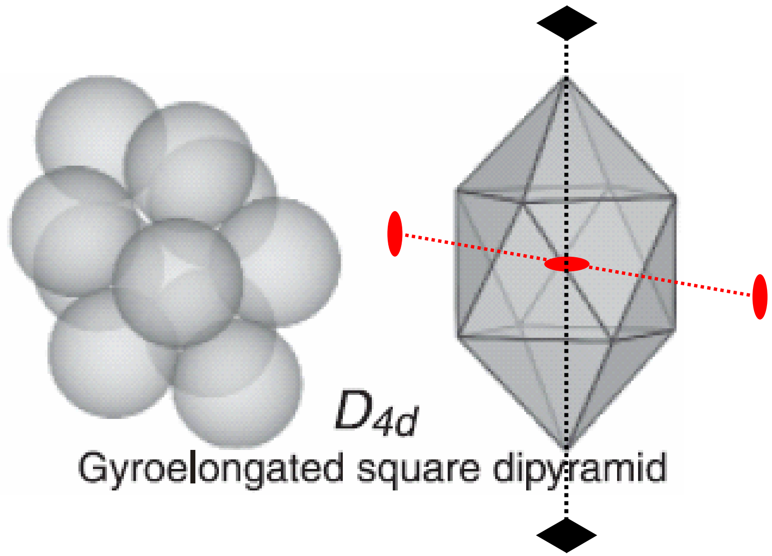




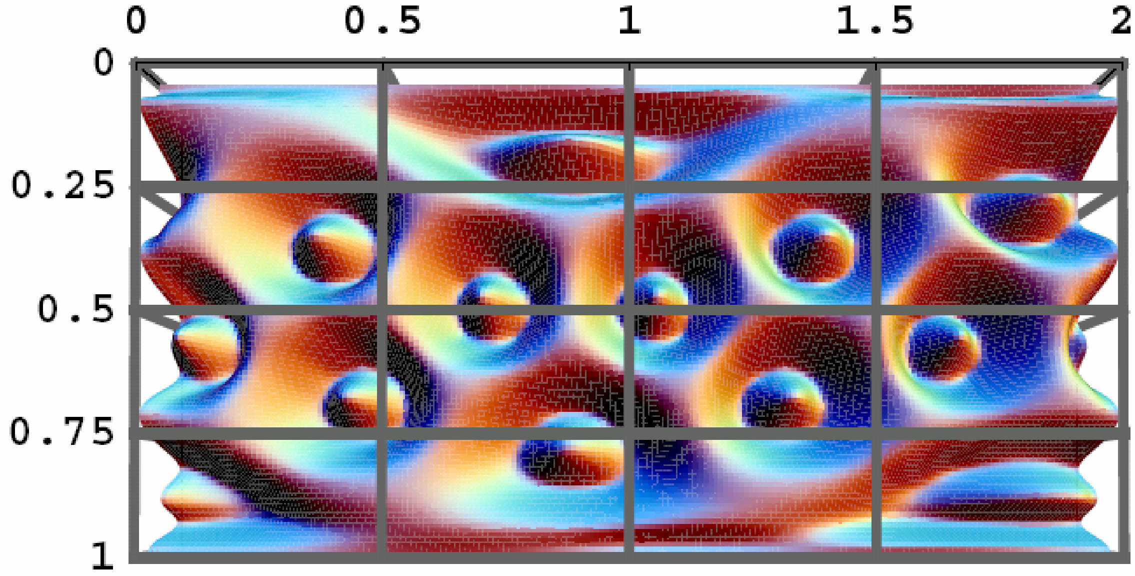
_Z10: N_A=25, N_B=20, f_A=120, f_B=60_

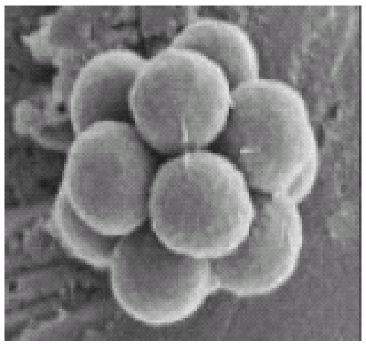




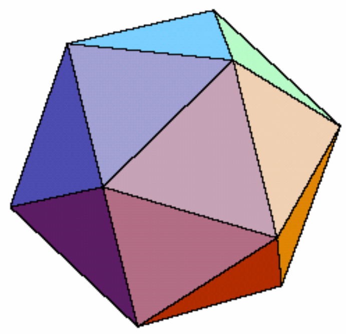


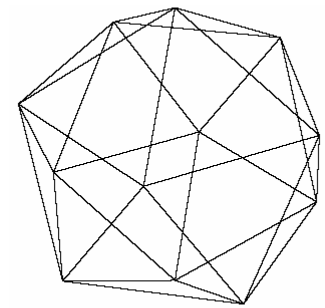
Z12(ICO): N_A=20, N_B=20, f_A=120, f_B=60





12

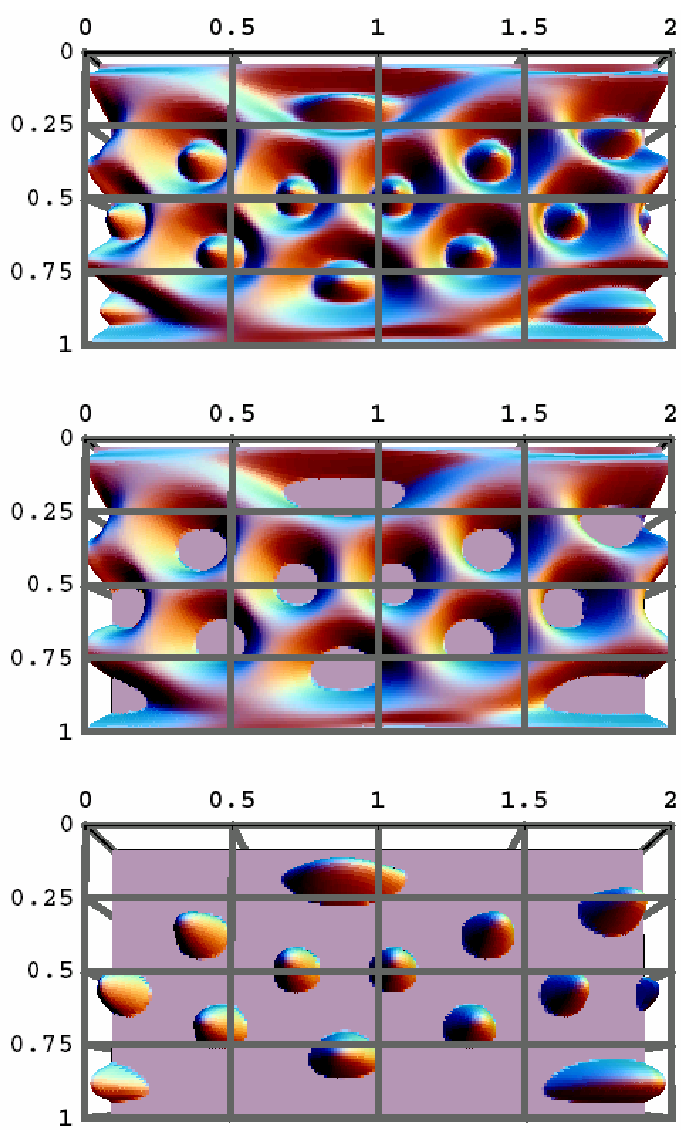




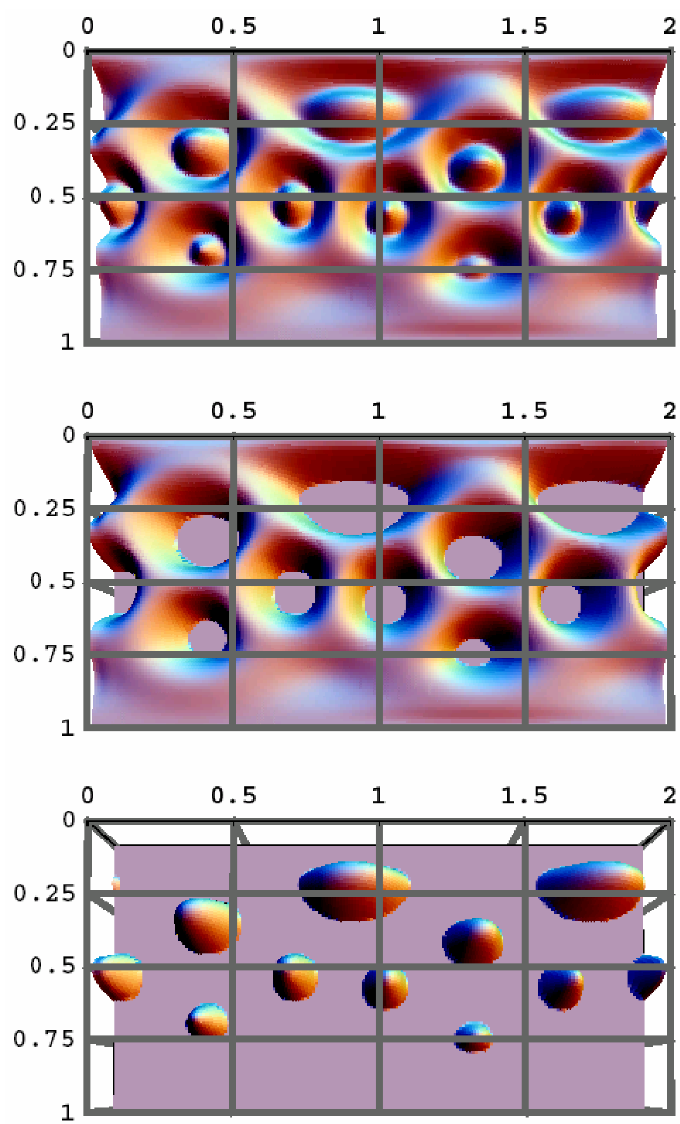
From: http://mathworld.wolfram.com/

A-B-S system in a solvent good for A and B; non-uniform A or B

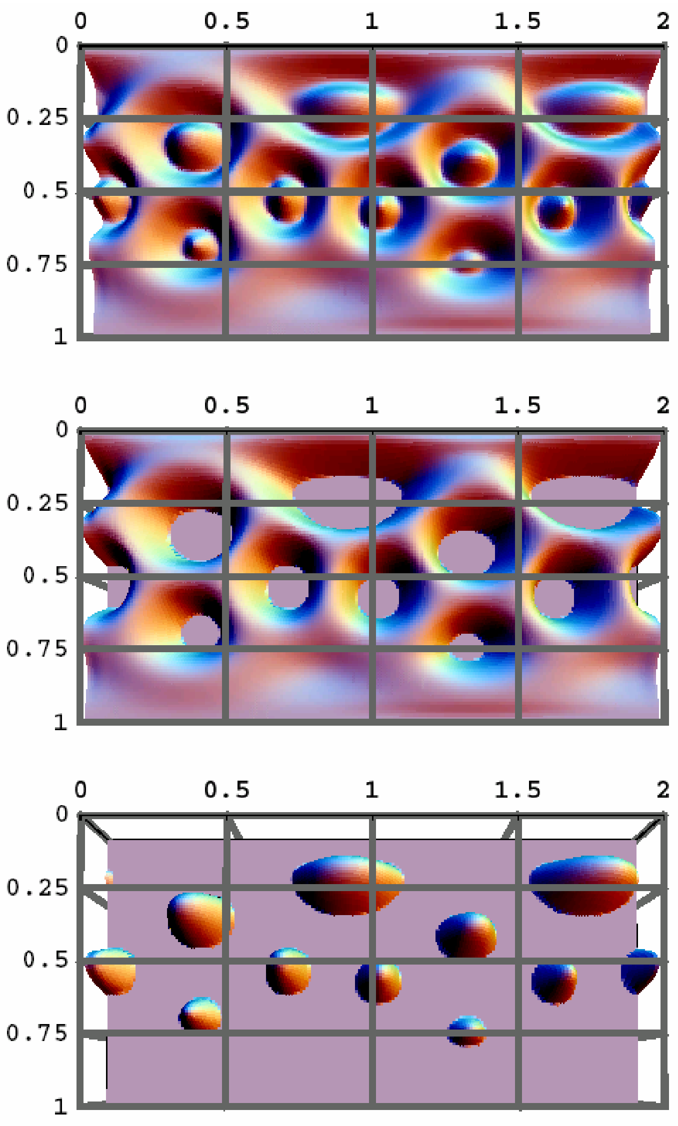
N_A=20, N_B=20, f_A=120, f_B=60
A: uniform; B: uniform



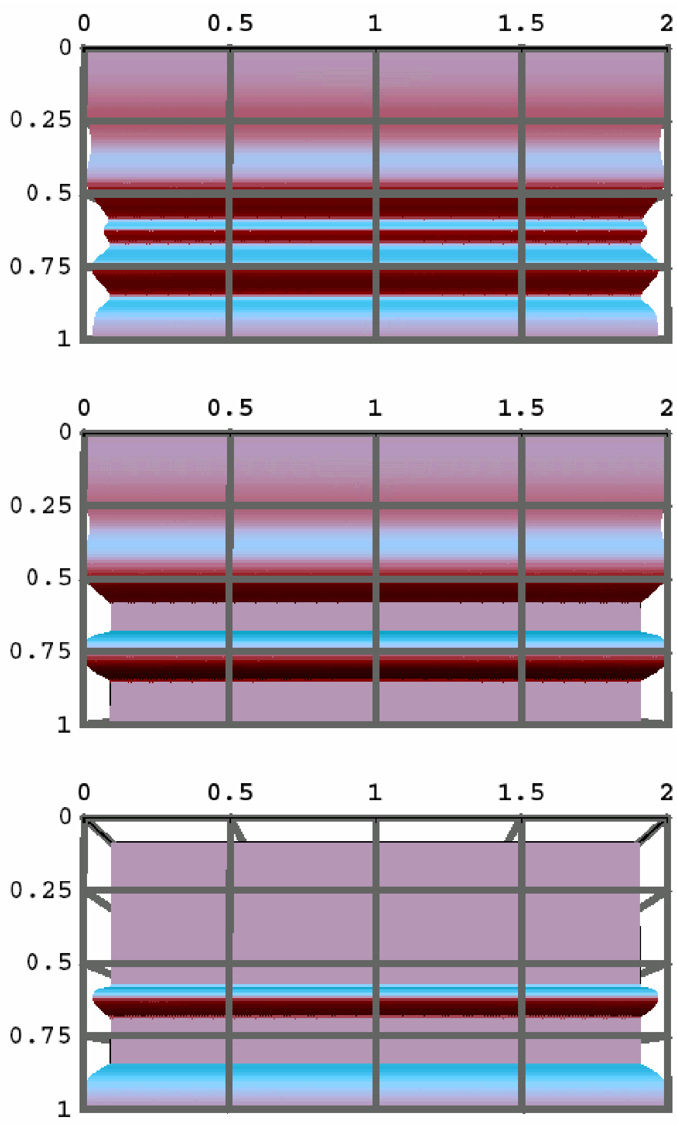
N_A=20, N_B=20, f_A=120, f_B=60
A: uniform; B: gradient 2



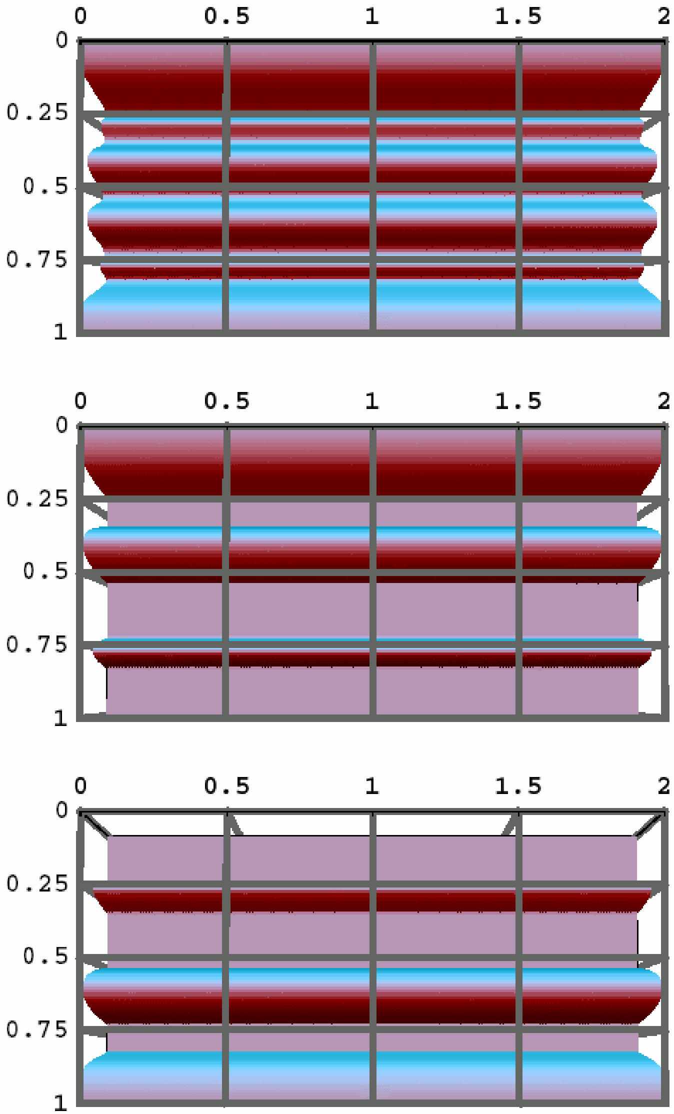
N_A=20, N_B=20, f_A=120, f_B=60
A: uniform; B: gradient 2



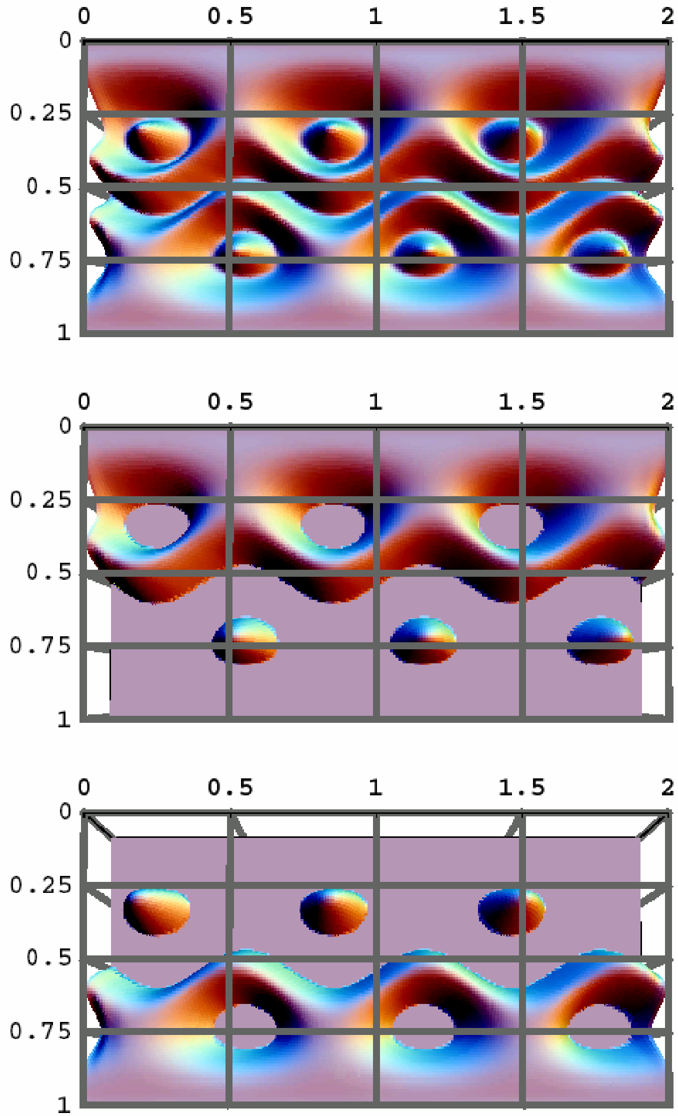
N_A=20, N_B=20, f_A=120, f_B=60
A & B: gradient 2



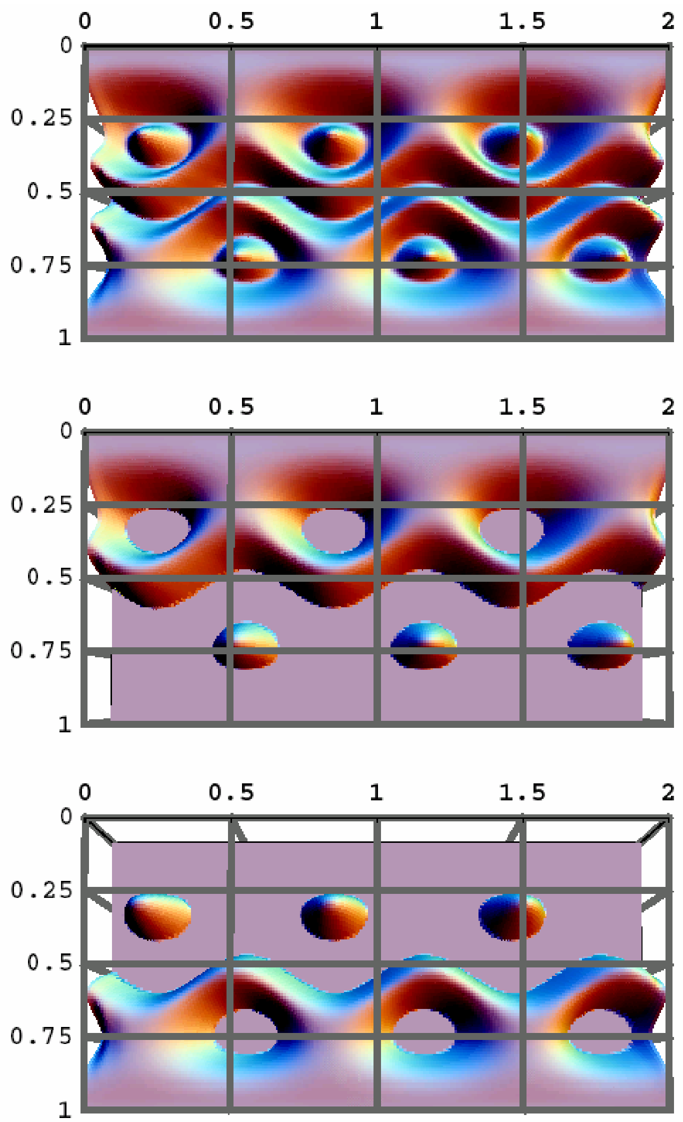
N_A=25, N_B=25, f_A=60, f_B=60
A & B: gradient 2



N_A=15, N_B=15, f_A=60, f_B=60
A & B: gradient 2



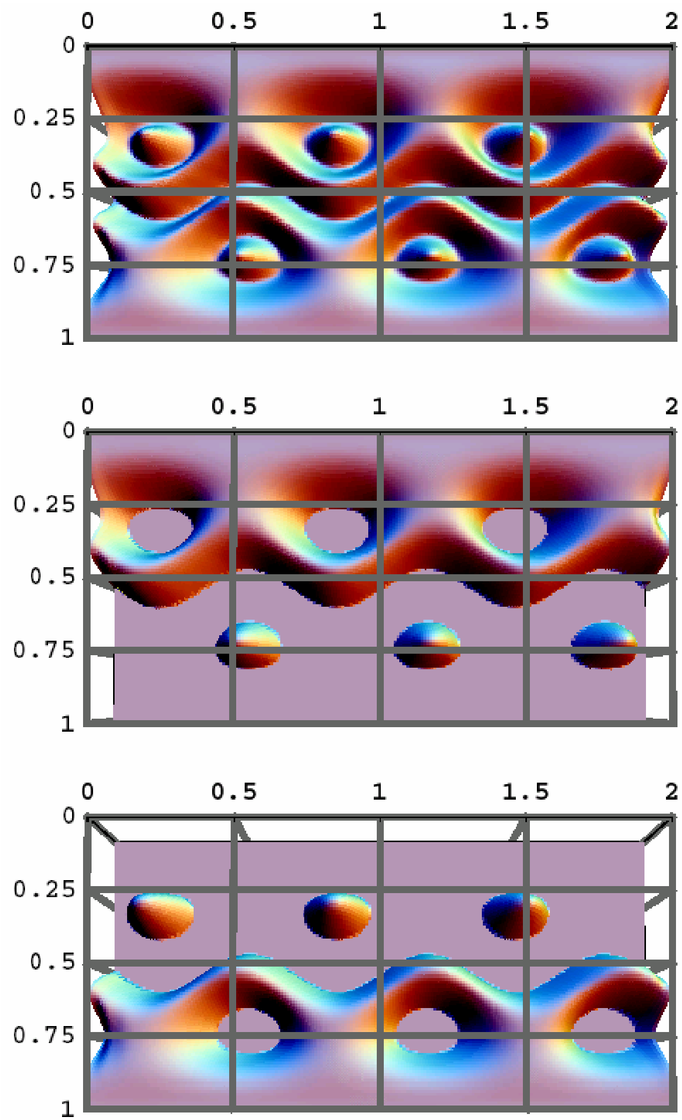
Giant-clam (GC) structure



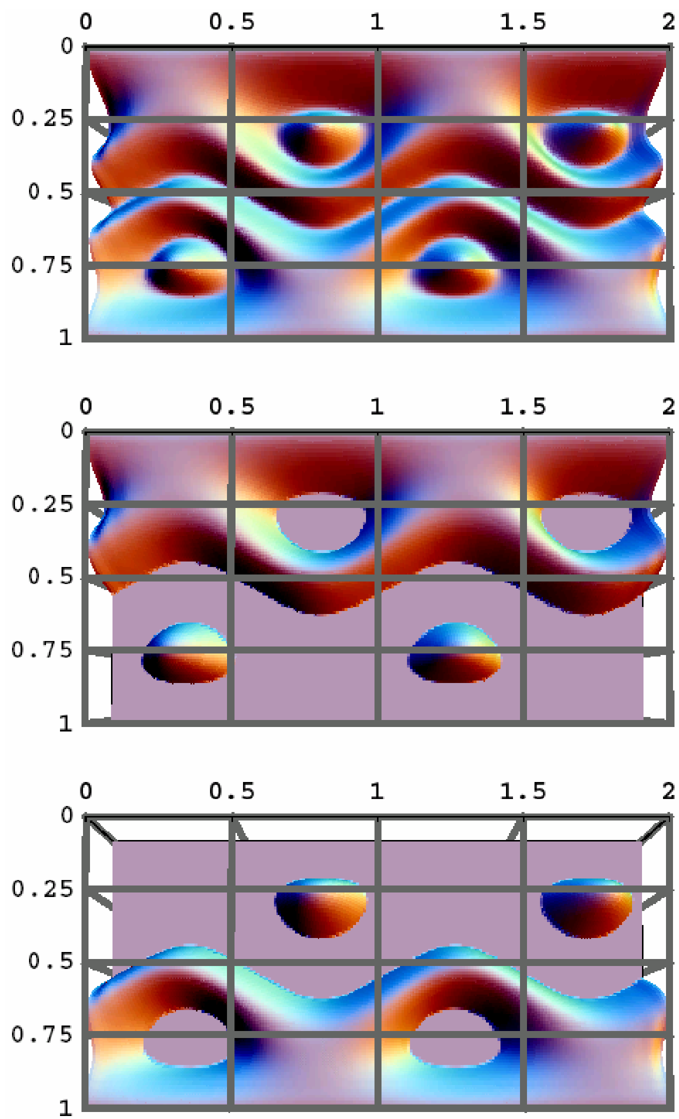
Credit: Lioneltimalistair/Science Photo Library

Credit: Georgette Douwma/Science Photo Library

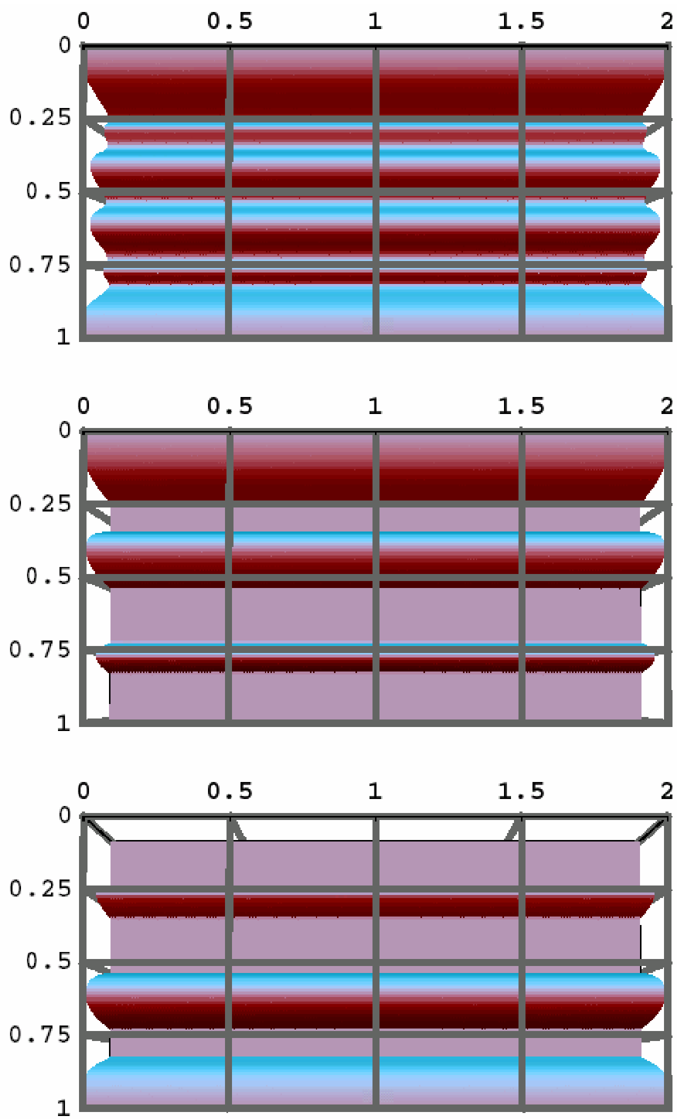
N_A=15, N_B=15, f_A=60, f_B=60
A & B: gradient 2



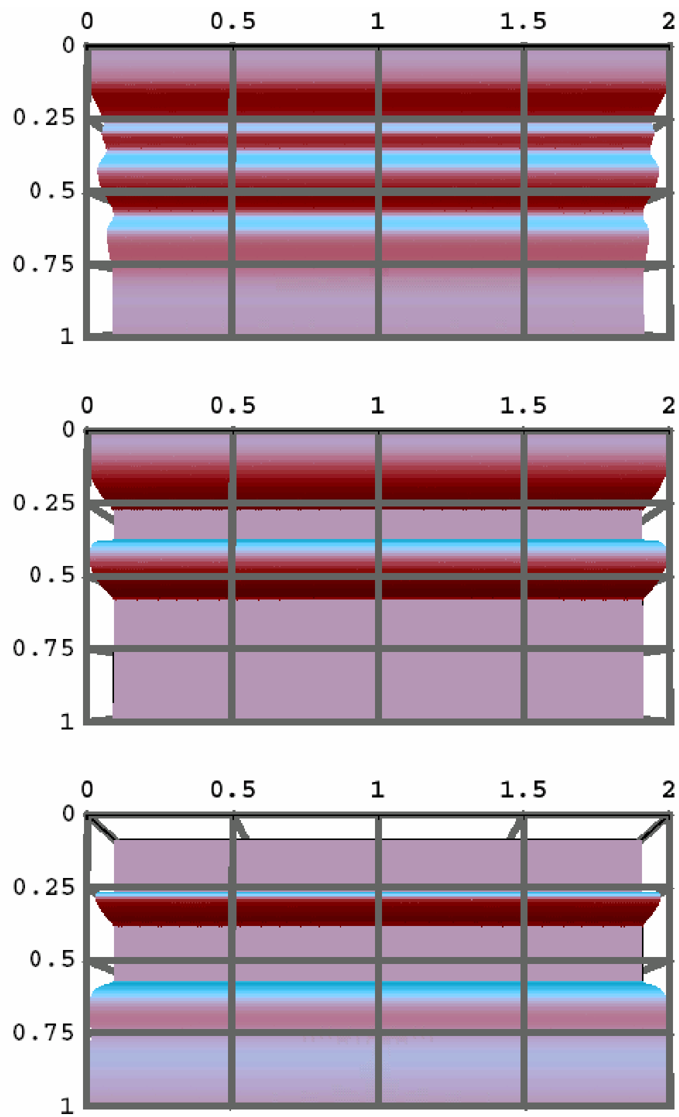
N_A=30, N_B=30, f_A=30, f_B=30
A & B: gradient 2



N_A=25, N_B=25, f_A=60, f_B=60
A & B: gradient 2

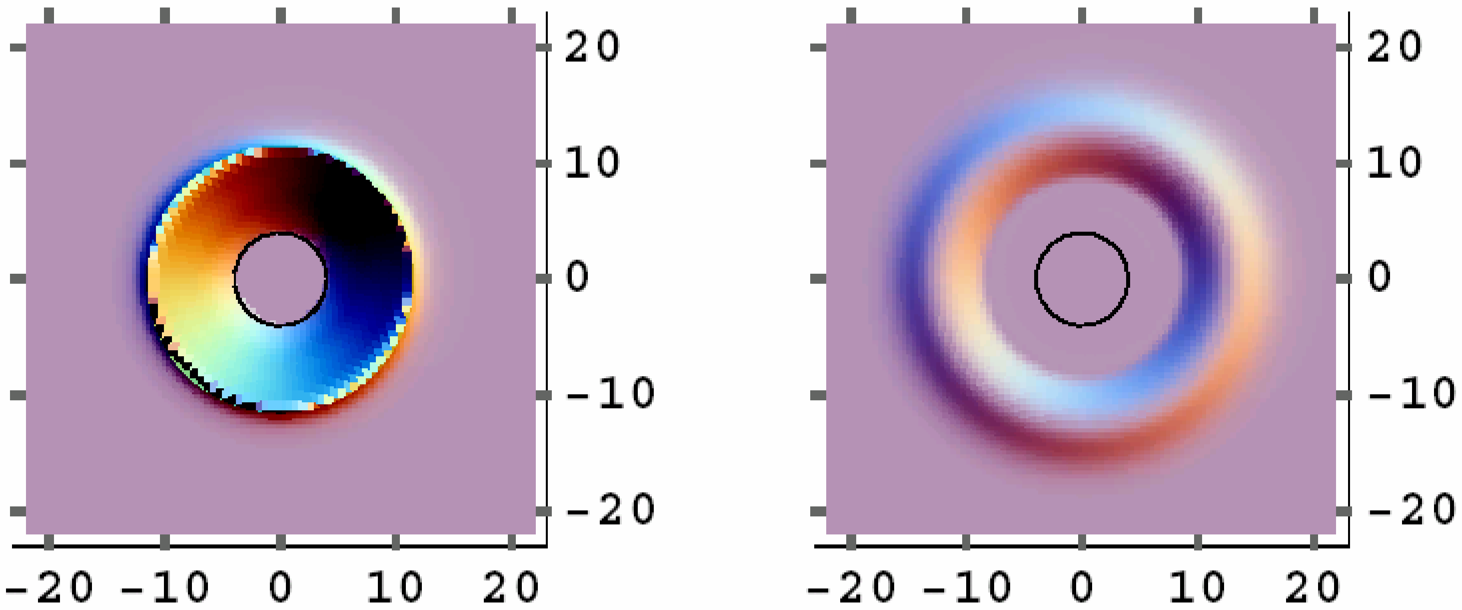


N_A=25, N_B=25, f_A=60, f_B=60
A: gradient 1; B: uniform

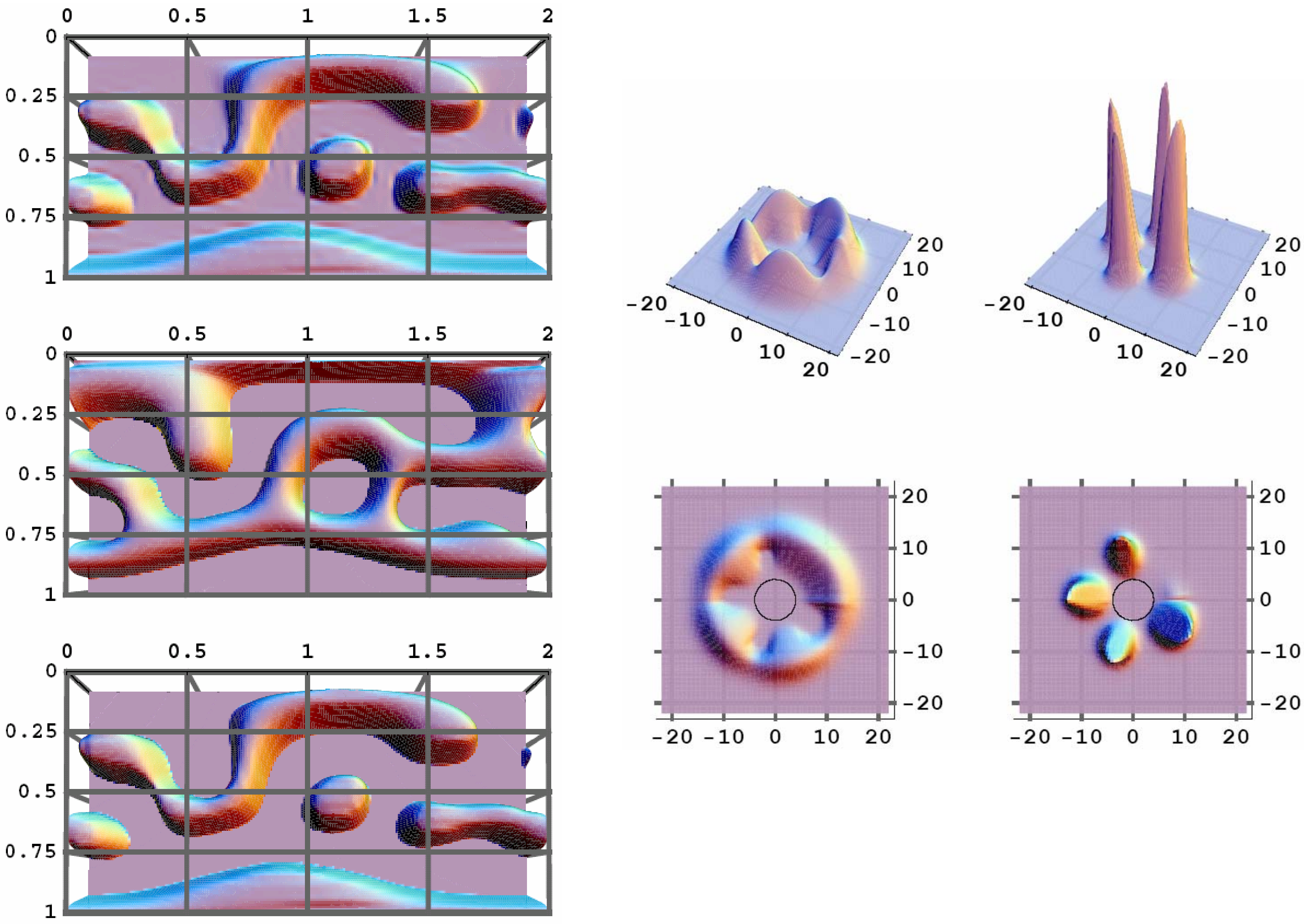


A-B-S system in a selective solvent; uniform A and B

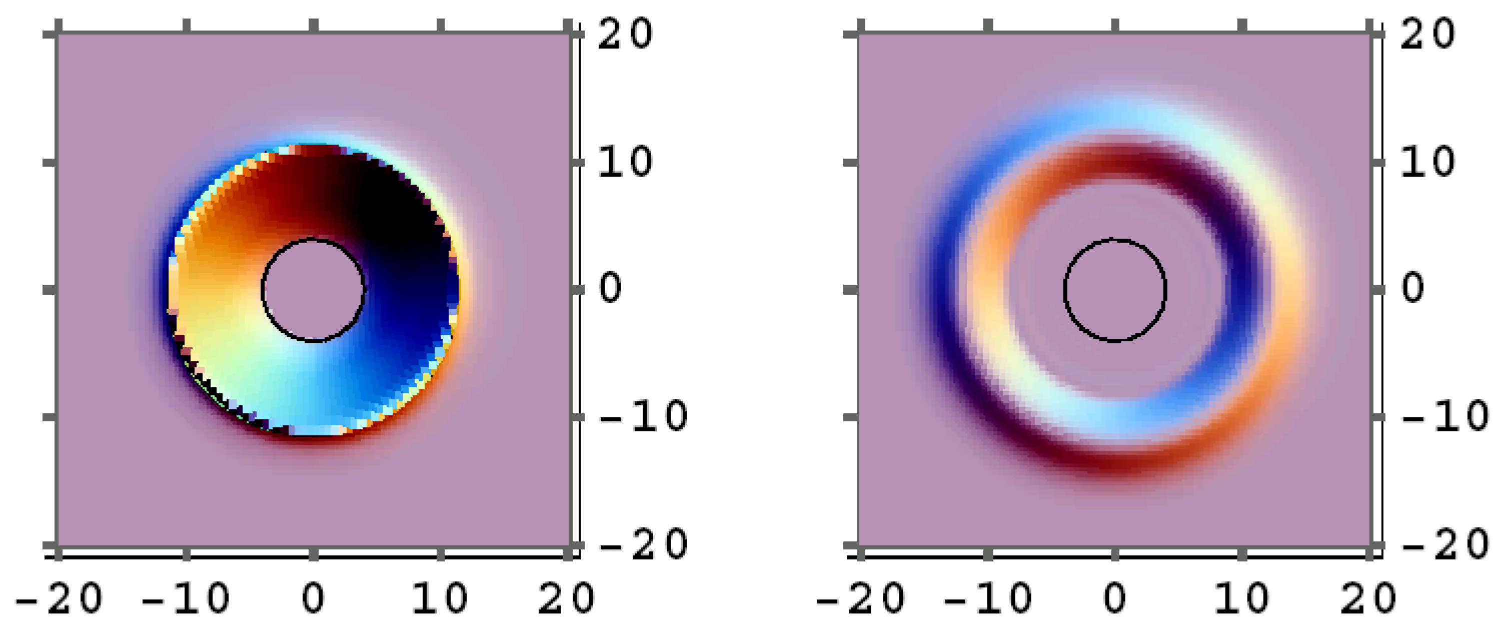
N_A=20, N_B=20, f_A=120, f_B=60 in a solvent poor for A but good for B



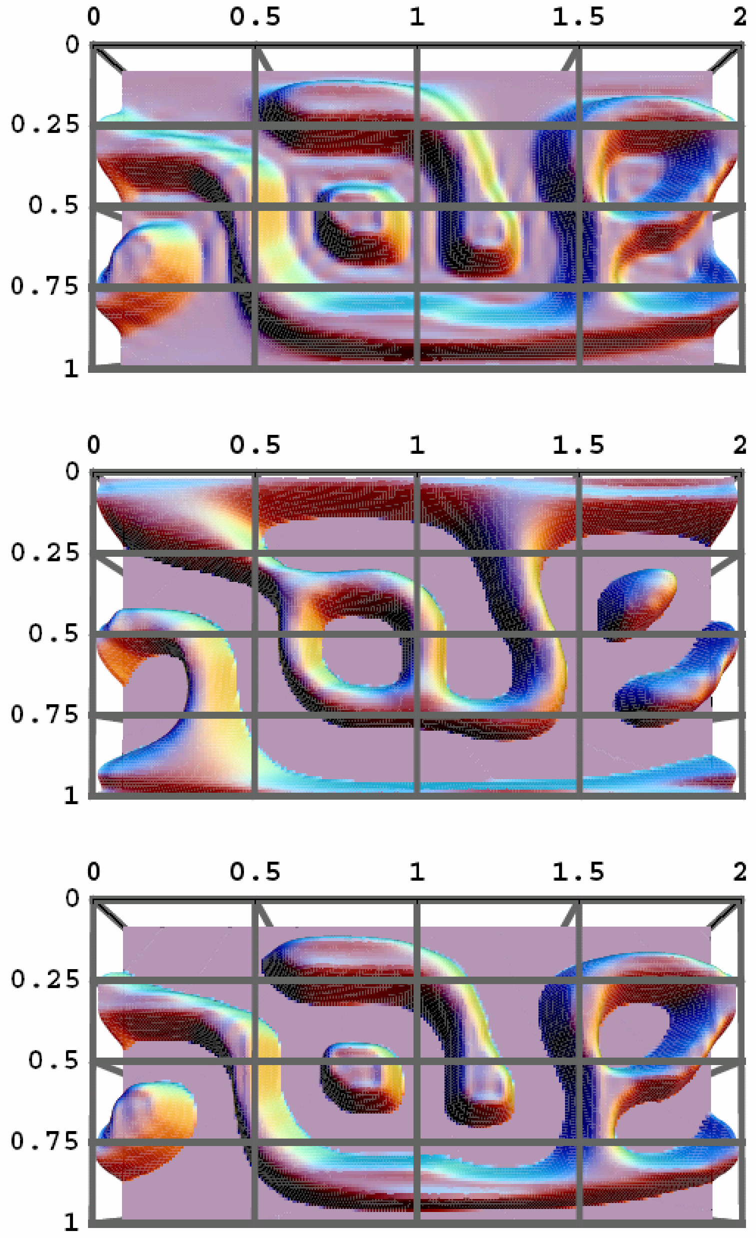
N_A=20, N_B=20, f_A=120, f_B=60 in a solvent good for A but poor for B

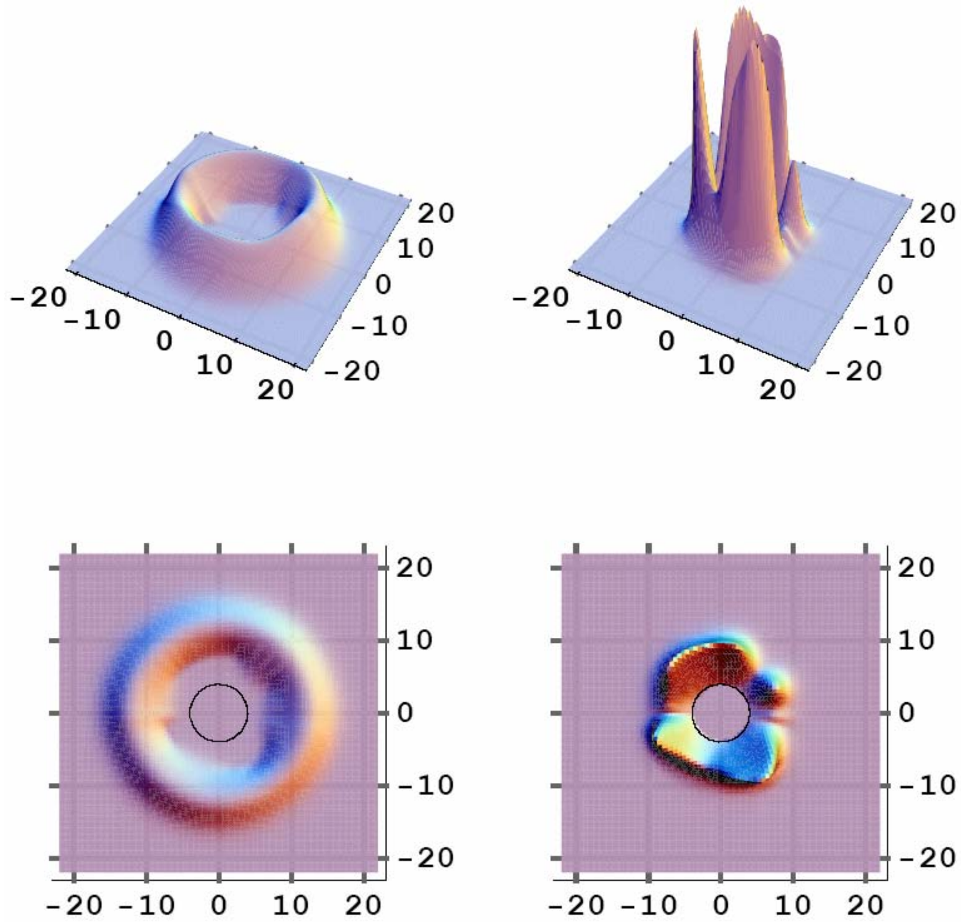


N_A=20, N_B=15, f_A=120, f_B=60 in a solvent poor for A but good for B

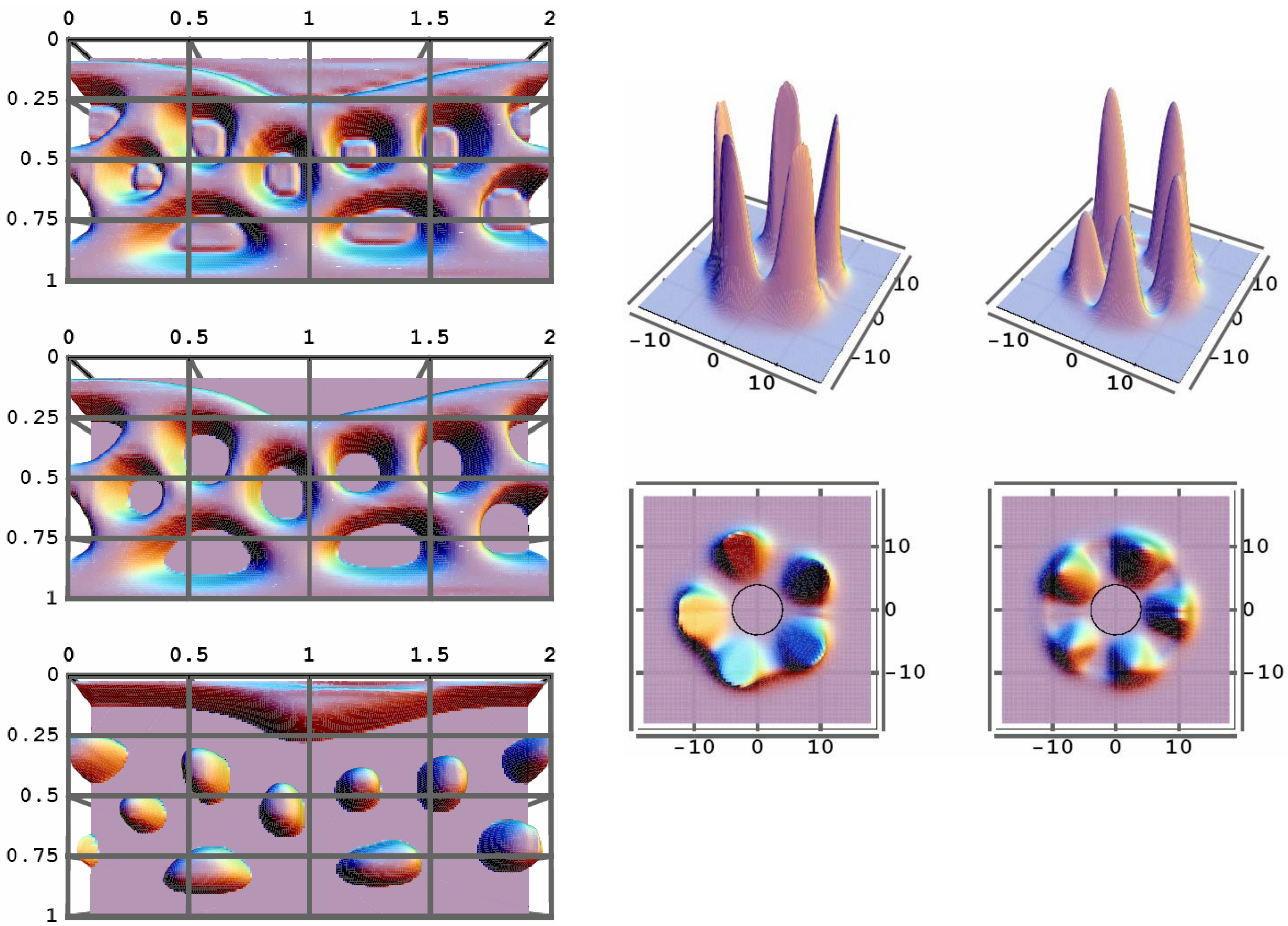


N_A=20, N_B=15, f_A=120, f_B=60 *in a solvent good for A but poor for B*

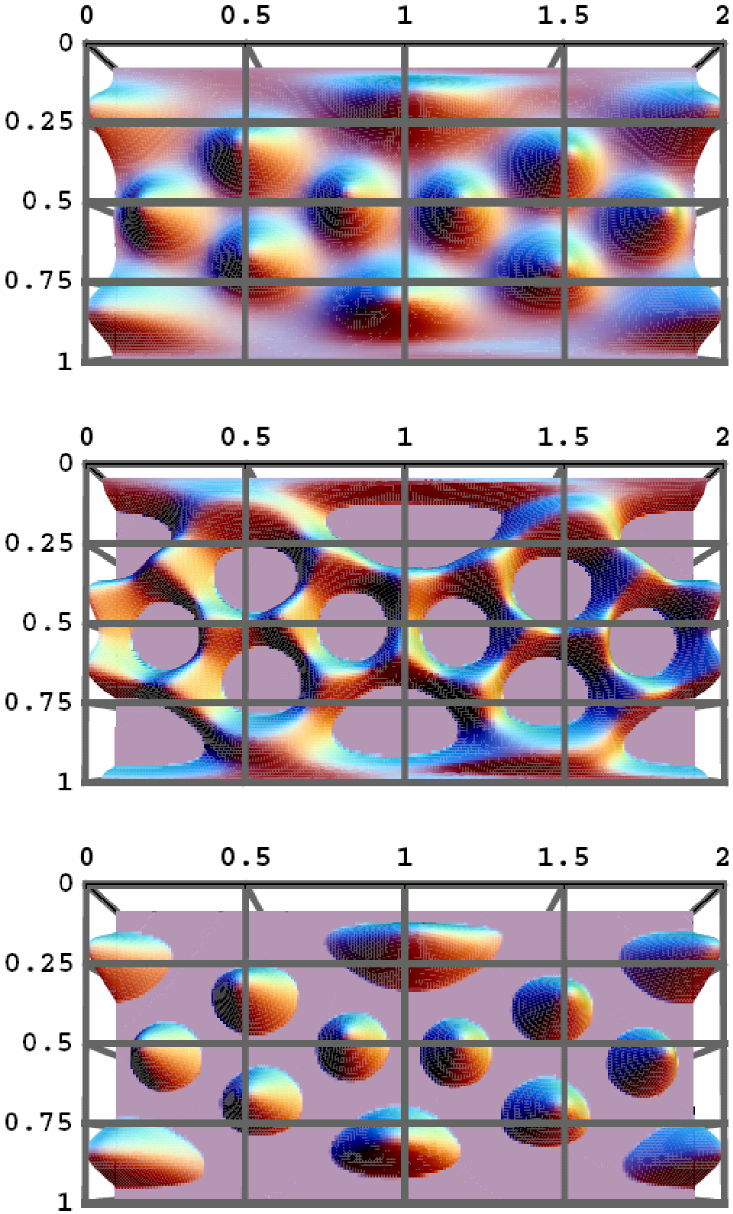


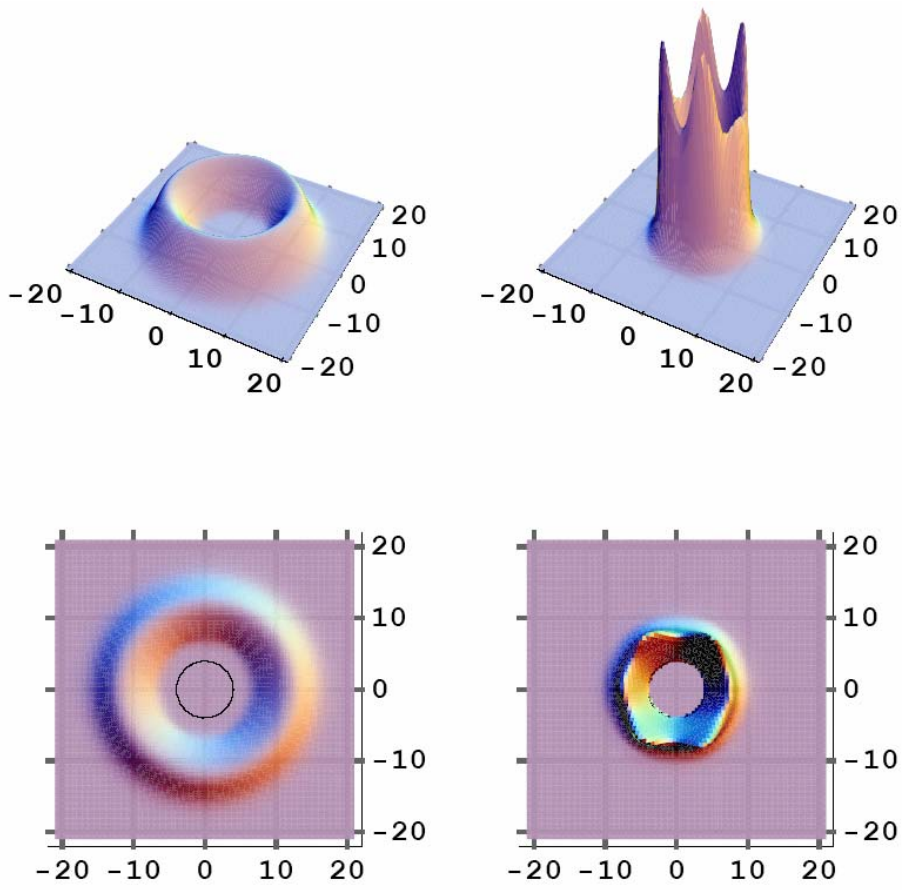


N_A=20, N_B=10, f_A=120, f_B=60 in a solvent poor for A but good for B



N_A=20, N_B=10, f_A=120, f_B=60 in a solvent good for A but poor for B





Applications?

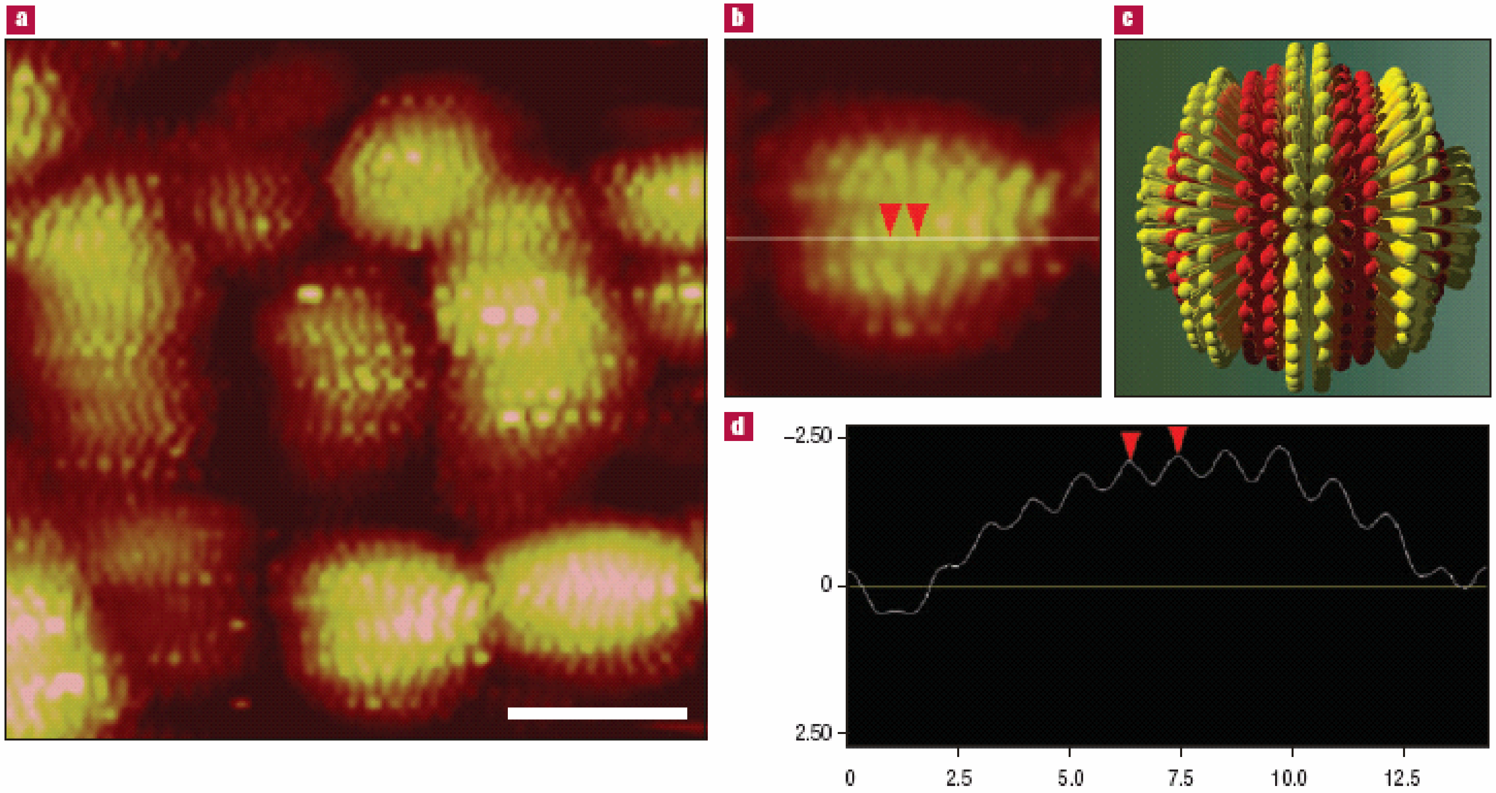
Nanostructured Nanoparticles

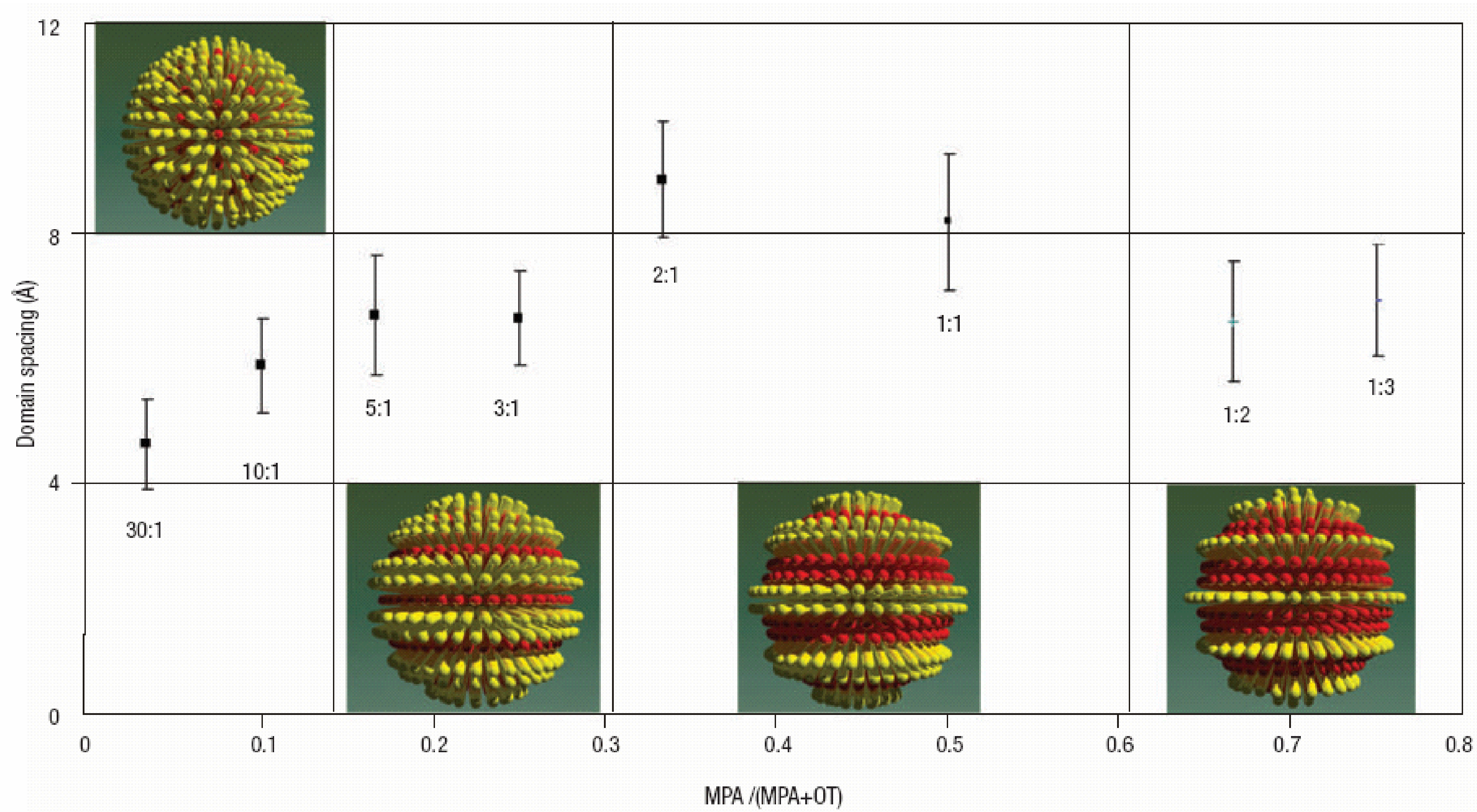
Spontaneous assembly of subnanometre-ordered domains in the ligand shell of monolayer-protected nanoparticles

ALICIA M. JACKSON, JACOB W. MYERSON AND FRANCESCO STELLACCI*

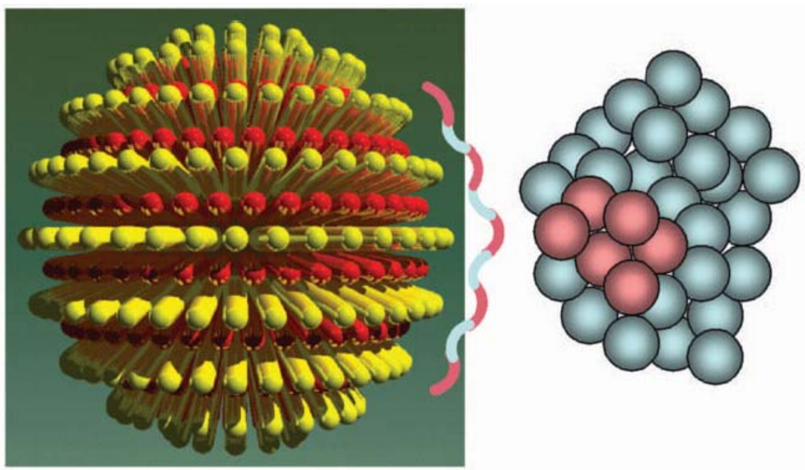
Nature Mater. **3**, 330 (2004).

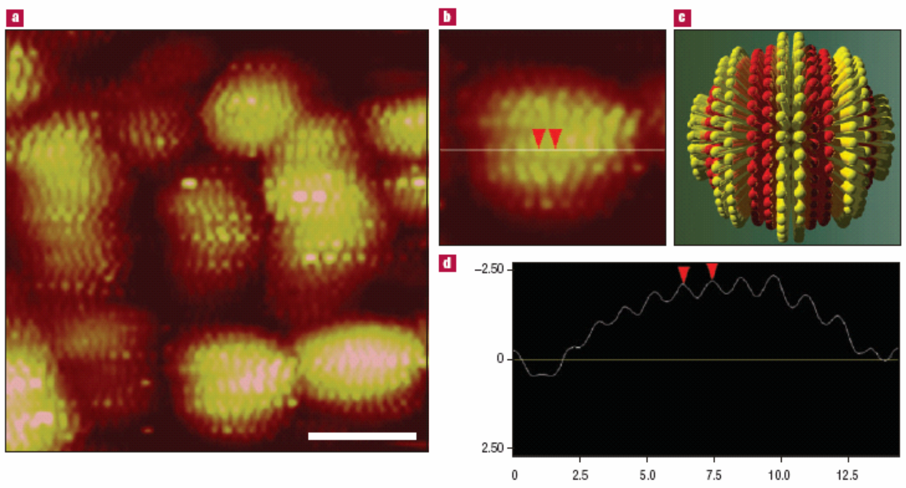
Binding of mercaptopropionic acid (MPA), HOOC–$(CH_2)_2$–SH and octanethiol (OT), CH_3–$(CH_2)_7$–SH on a gold nanoparticle.





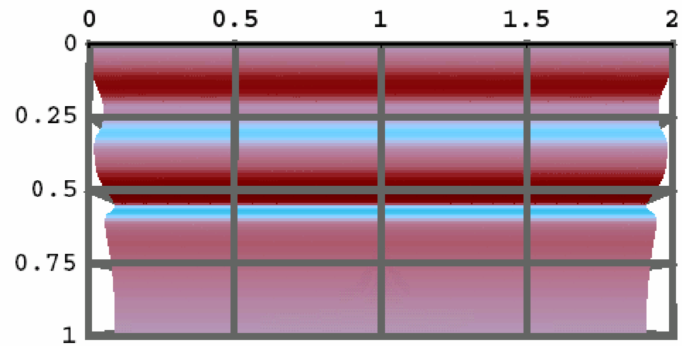
12
8
4
0
Domain spacing (Å)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
MPA /(MPA+OT)
30:1
10:1
5:1
3:1
2:1
1:1
1:2
1:3

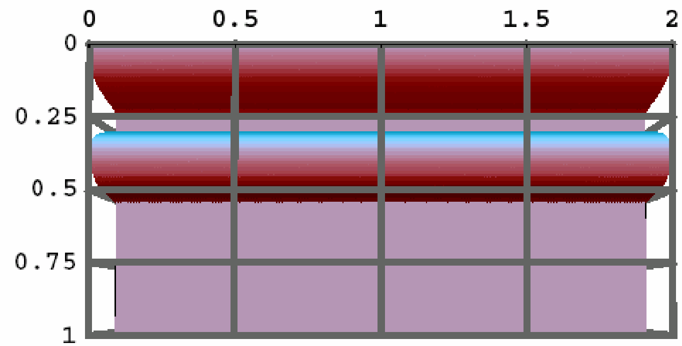


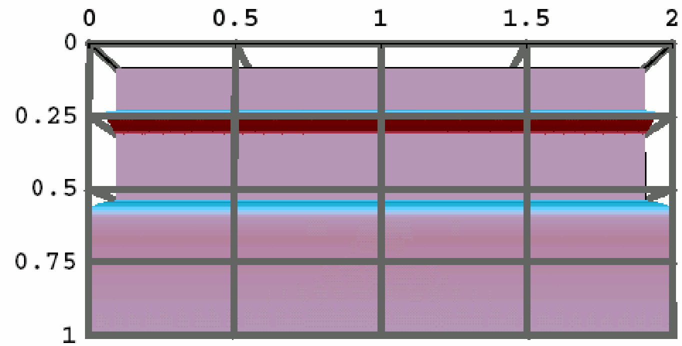


What might have happened...
surface-induced structures

N_A=25, N_B=25, f_A=60, f_B=60
A: southern hemisphere;
B: homogeneous





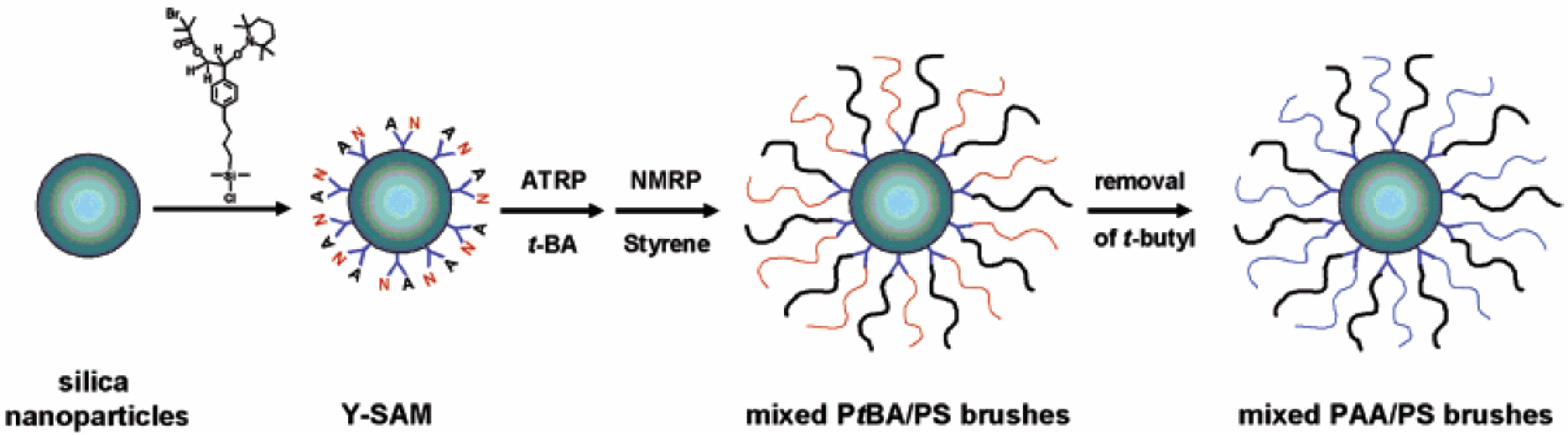


Smart Drug Carriers

Environmentally Responsive "Hairy" Nanoparticles: Mixed Homopolymer Brushes on Silica Nanoparticles Synthesized by Living Radical Polymerization Techniques

Dejin Li, Xia Sheng, and Bin Zhao*

J. Am. Chem. Soc. **127**, 6248 (2005).

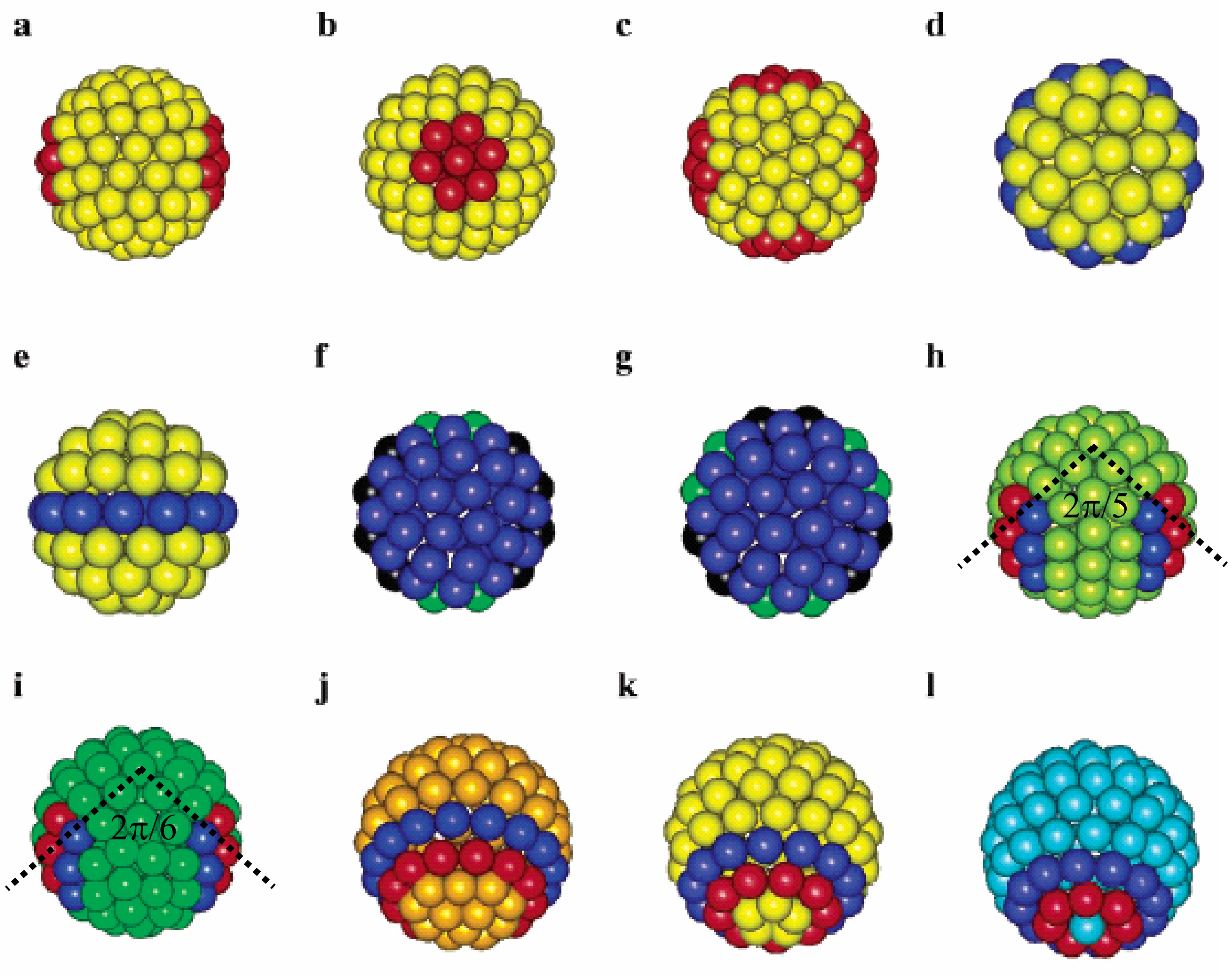


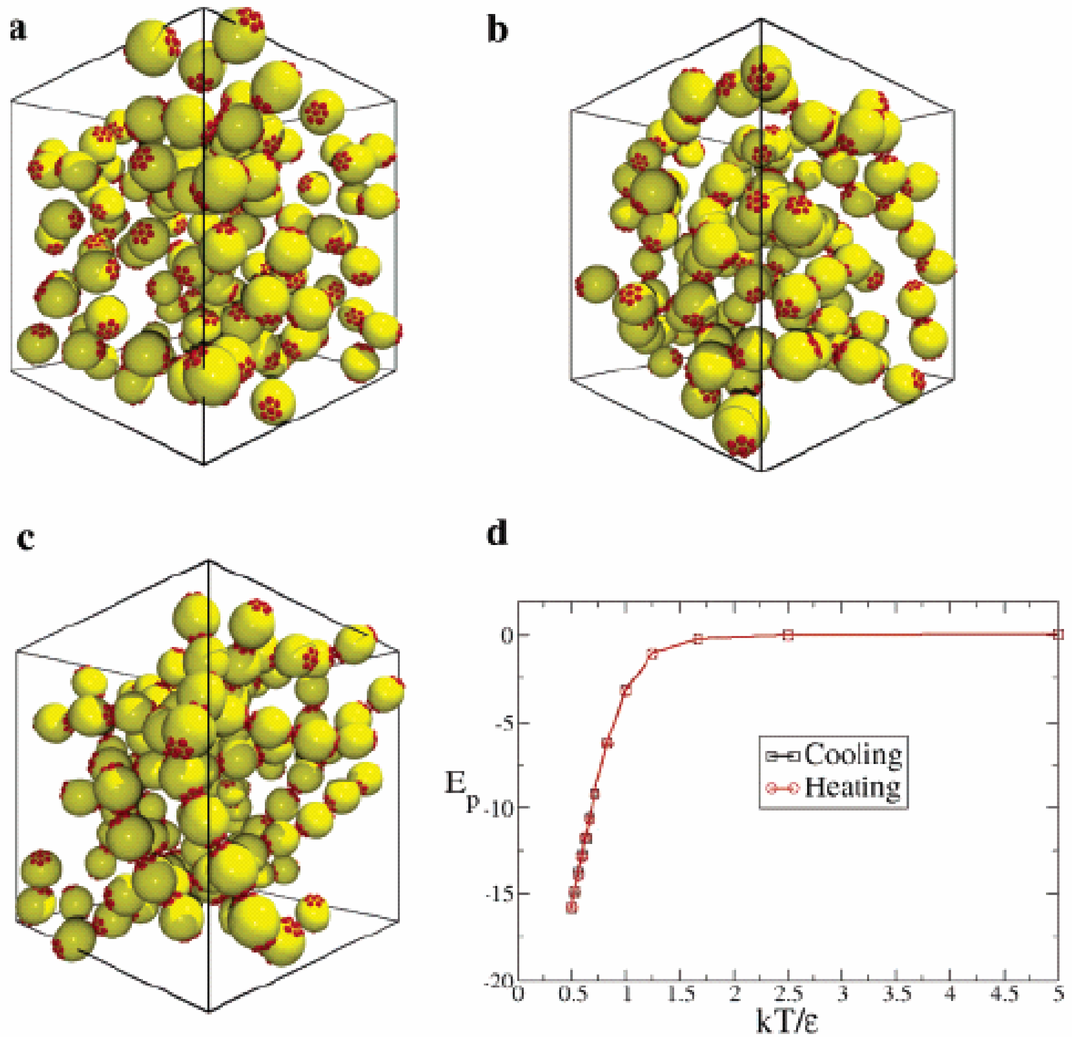
Self-assembly of Structured Particles
(Chemistry of "Colloid Molecules")

Self-Assembly of Patchy Particles

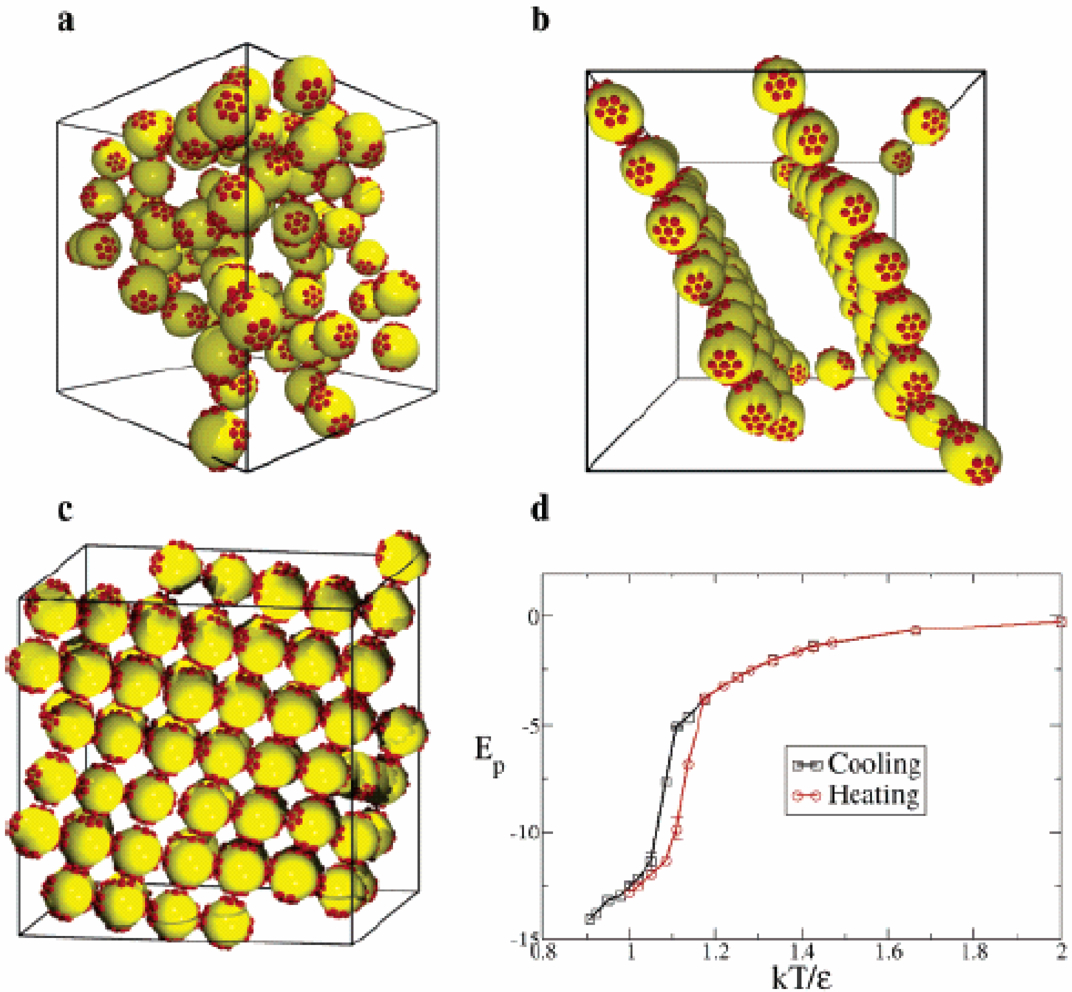
Zhenli Zhang[†] and Sharon C. Glotzer[*,†,‡]

Nano Lett. **4**, 1407 (2004).

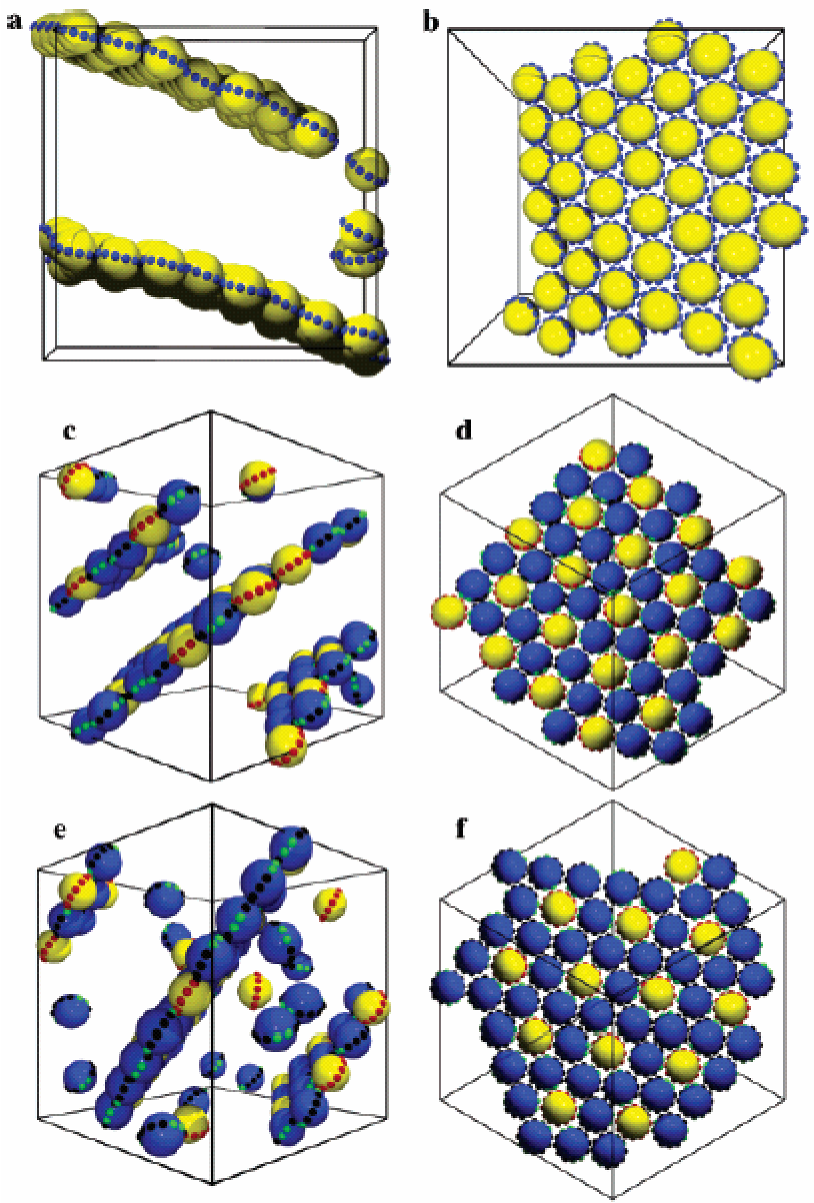




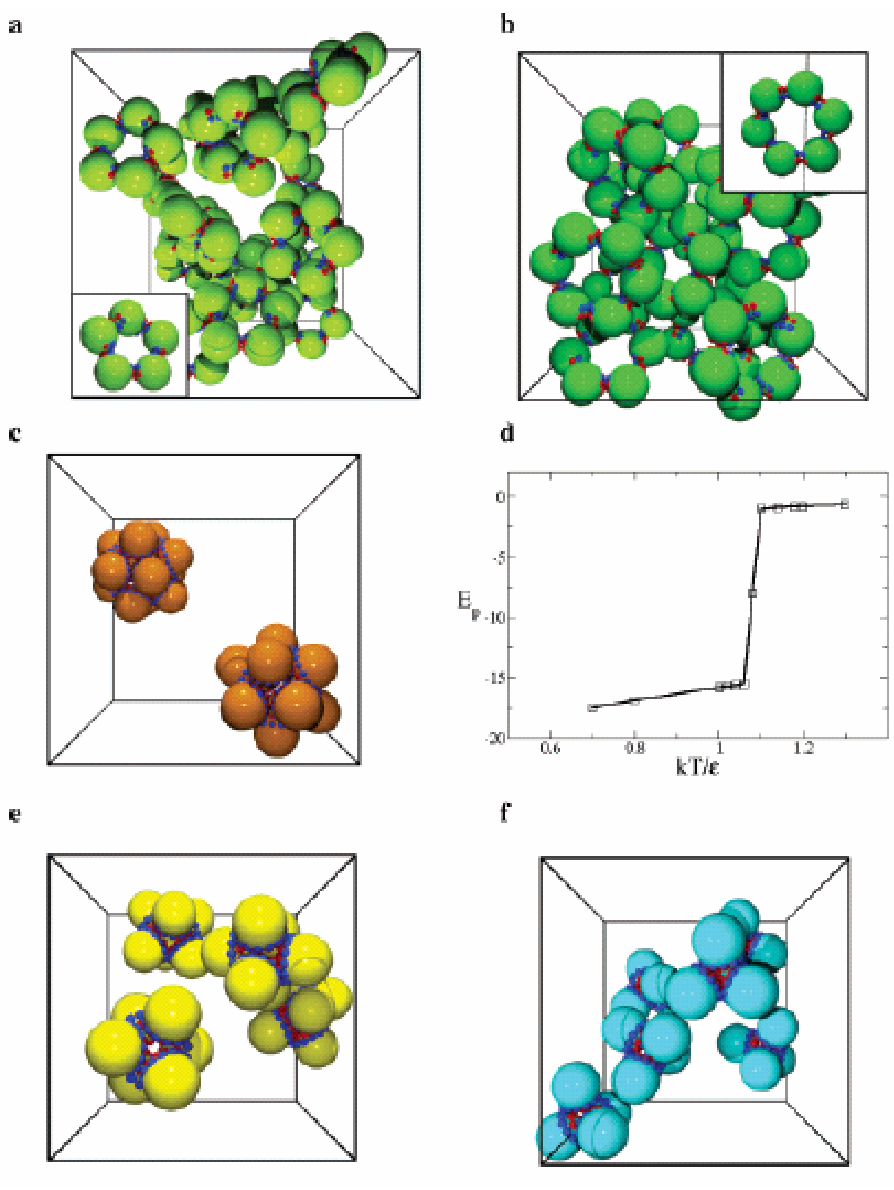
a
b
c
d
Cooling
Heating
E_p
kT/ε
0
-5
-10
-15
-20
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5



a
b
c
d
0
-5
-10
-15
0.8
1
1.2
1.4
1.6
1.8
2
E_p
kT/ε
Cooling
Heating



a
b
c
d
e
f



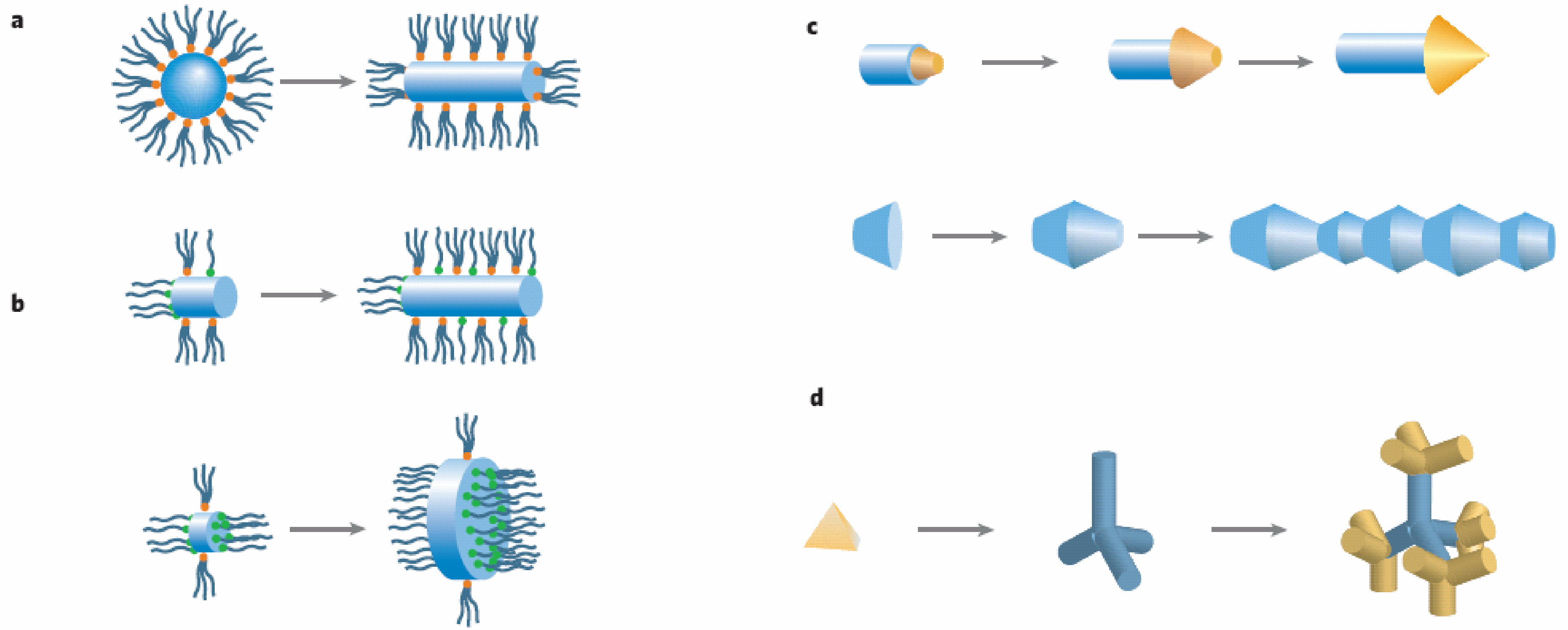
a
b
c
d
e
f
0
-5
-10
-15
-20
0.6
0.8
1
1.2
kT/ε
E_p

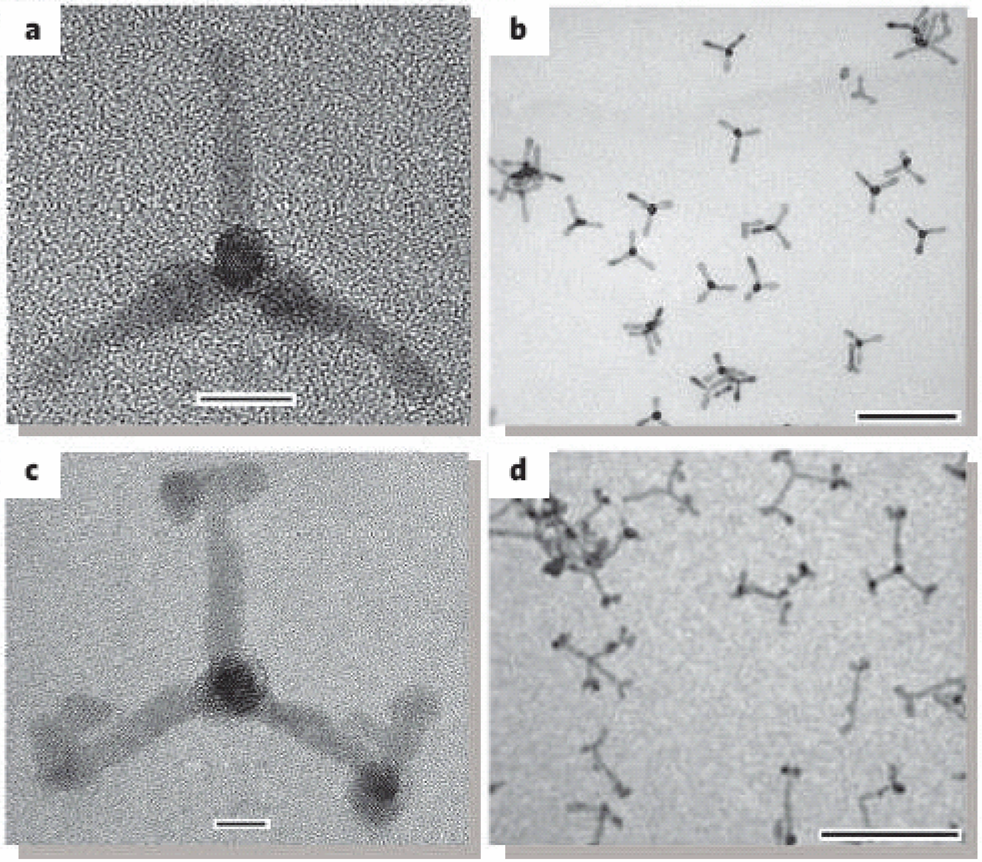
Fabrication of Multivalent Nanoparticles

Colloidal nanocrystal synthesis and the organic–inorganic interface

Yadong Yin[1] & A. Paul Alivisatos[1]

Nature **437**, 664 (2005).

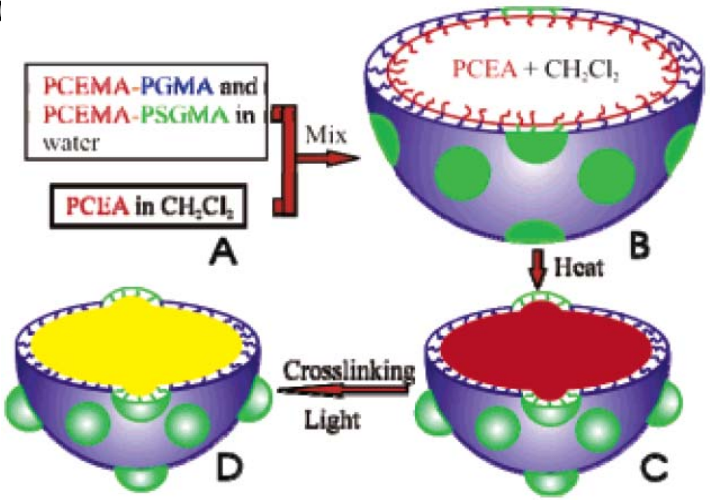


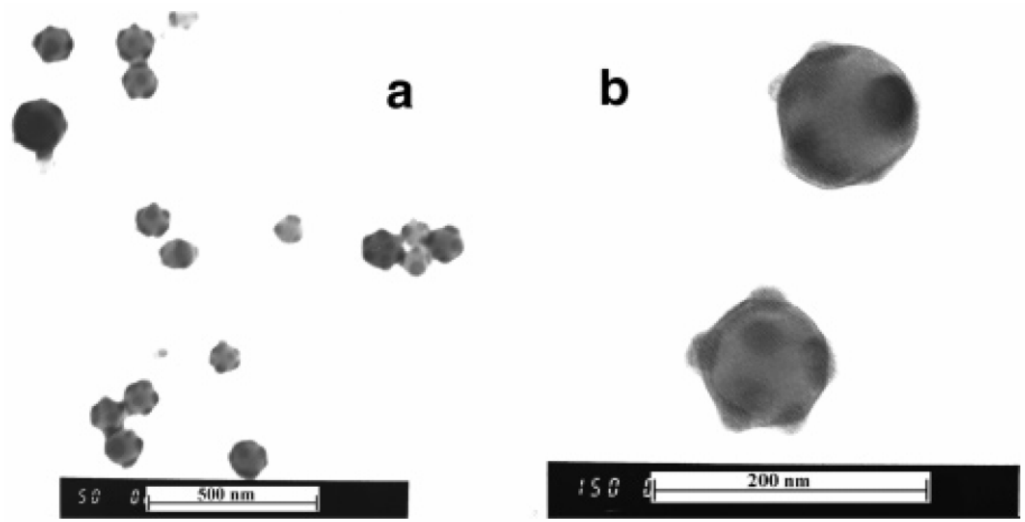

a
b
c
d

Polymer Nano- and Microspheres with Bumpy and Chain-Segregated Surfaces

Ronghua Zheng, Guojun Liu,* and Xiaohu Yan

JACS **127**, 15358 (2005)



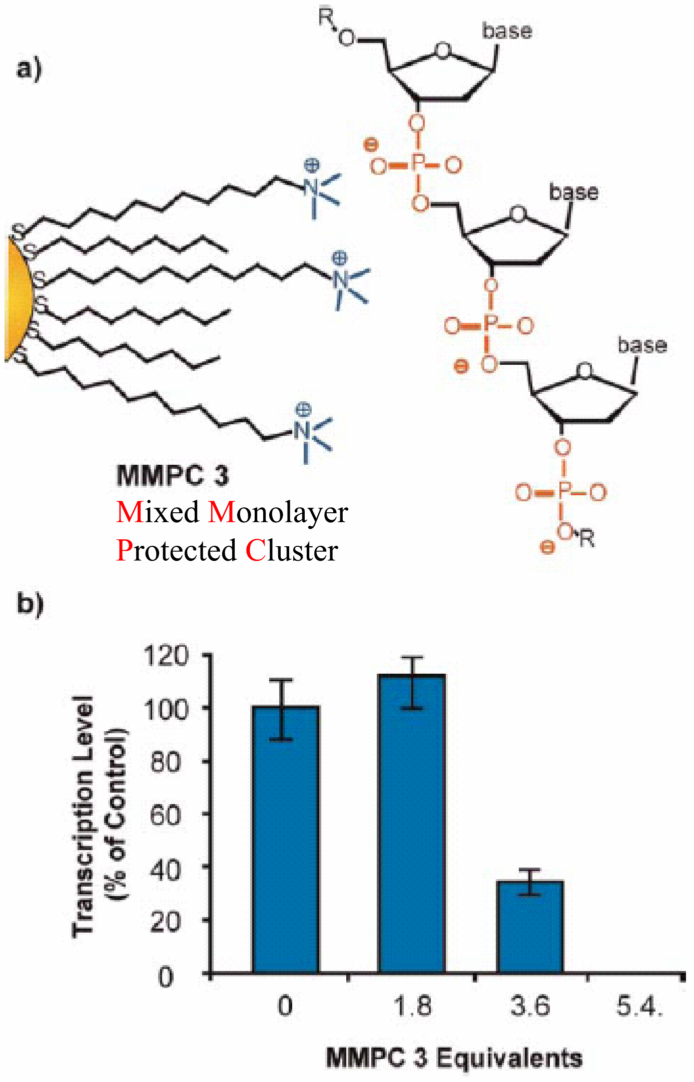


Biomolecular Recognition and Templation/Catalysis

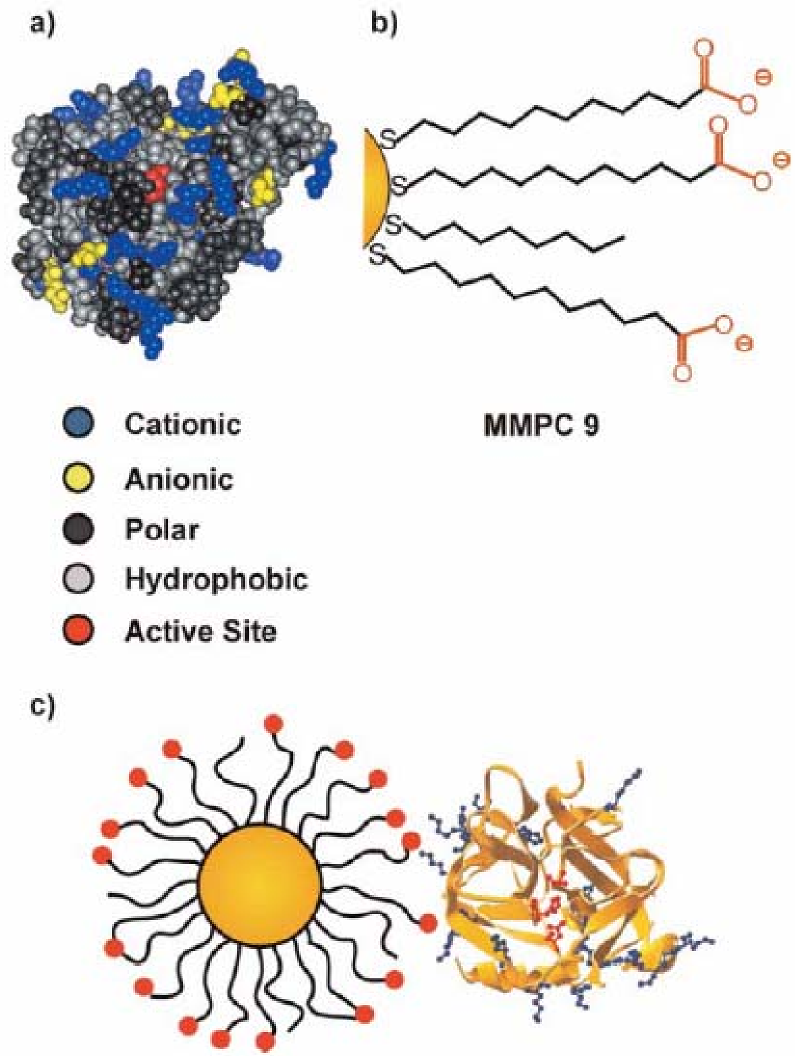
Surface recognition of biomacromolecules using nanoparticle receptors

Ayush Verma and Vincent M. Rotello*

Chem. Commun. **2005**, 303 (2005).

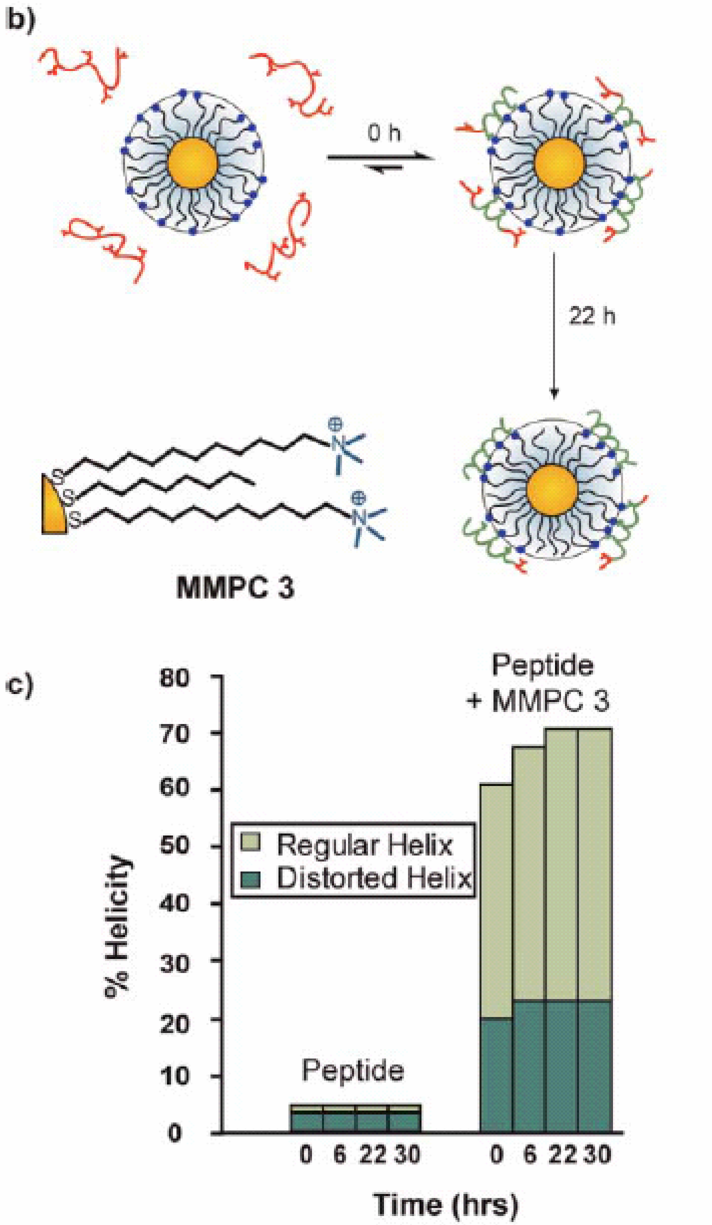


Mixed Monolayer
Protected Cluster



a) Ac-W-A-A-**D**-A-K-A-**D**-A-A-**D**-A-A-A-**D**-A-K-NH_2

Peptide 2



Discussion

- A pure mathematical problem: Packing on a sphere
  - Thomson's problem, Tammes' problem, VSEPR, etc.
- A practical technical problem: Nanostructured nanoparticle
  - "Atoms" for multivalent chemistry of colloids, templates for materials with hierarchical structure, etc.
- What do we need to know?
  - N_A, N_B, f_A, f_B, and interaction parameters v_{AB}, v_{AS}, v_{BS}.

Acknowledgment

- Prof. Toshihiro Kawakatsu (Tohoku University)
  川勝 年洋
- Dr. Hiroya Kodama (Mitsubishi Chemical Co. Ltd.)
  樹神 弘也
- Mr. Guo-Hau Huang (National Chung Hsing University)
  黃國豪
- National Science Council, Taiwan
- National Chung Hsing University, Taiwan