# Phase diagrams of self assembly patchy particles

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Theory: P.I.C. Teixeira, M.M. Telo da Gama (Lisbon) and D. de las Heras (Bayreuth);
Simulation (off lattice): F. Sciortino, L. Rovigatti (Rome) and J. Russo (Bristol);
Simulation (lattice): N. Almarza, E. Noya (Madrid);

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Portuguese Science Foundation

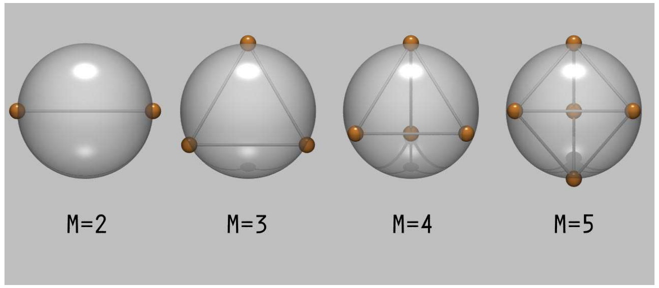
# Outline

1. Patchy particles. Empty and percolated liquid phase.

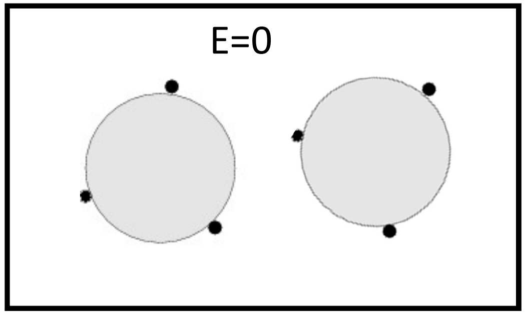
2. 2A+nB patchy particles:
    - Self assembly: chaining and branching.
    - Phase diagrams: none, one and two critical points.

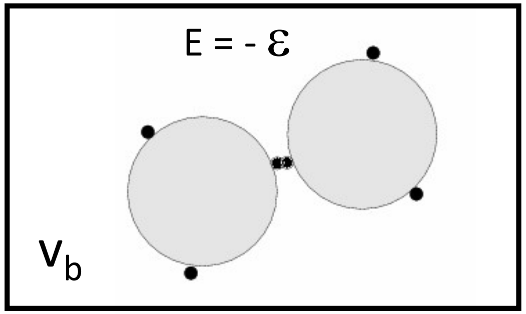
3. Binary mixtures of patchy particles: the role of the mixing entropy.

# 1. Patchy particles




Hard Spheres with M bonding sites or patches.




Two patches form a BOND when overlapped. Energy decreases by ε. Self-assembly in clusters at low temperatures.

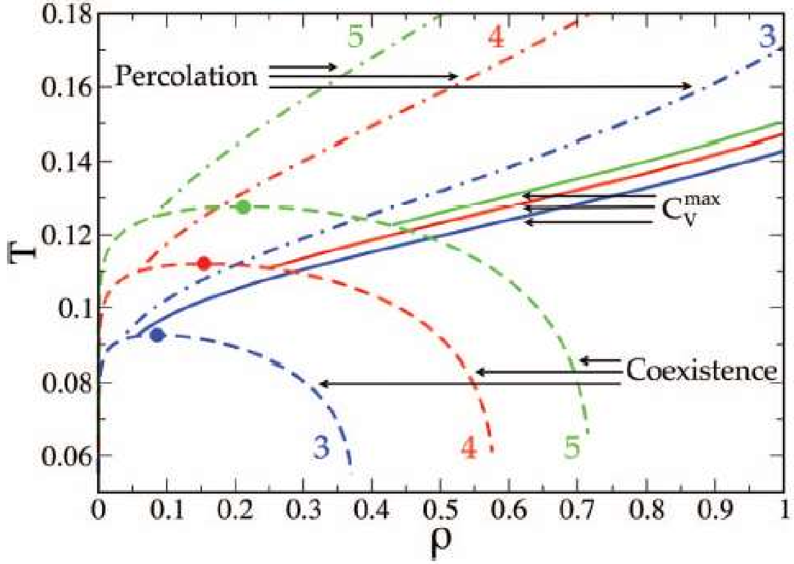
Imposed geometric restrictions:

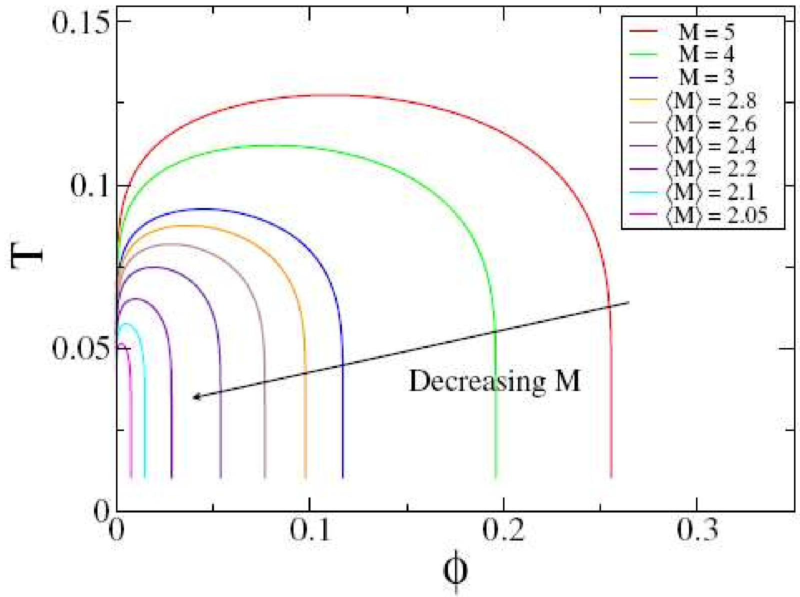
- A bond is formed by two patches only, that belong to different particles.
- Two particles can be connected by one bond only.

# 1. Patchy particles: phase diagram

Calculated using Monte Carlo Simulations and Wherteim's theory:

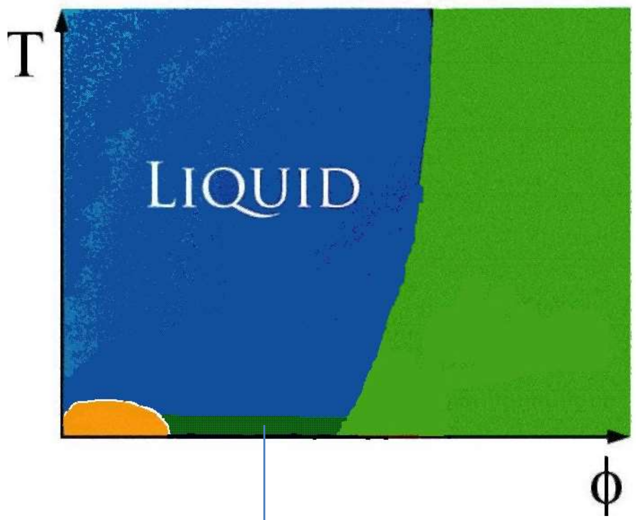
Phase diagrams for M=3 , 4, 5




Bianchi et al. : PRL **97**,168301(2006); JCP 128, 144504 (2008)

# 1. Patchy particles: phase diagram




Liquid
Percolated – gel.
EMPTY NETWORKED FLUID

- Low density equilibrium gels (empty networked liquids) are obtained in the limit M → 2 (chain limit).

- Reaching M → 2 continuously:

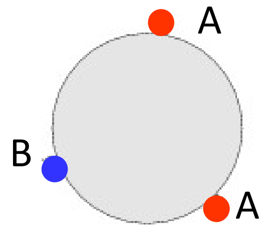
  - Particles with dissimilar patches

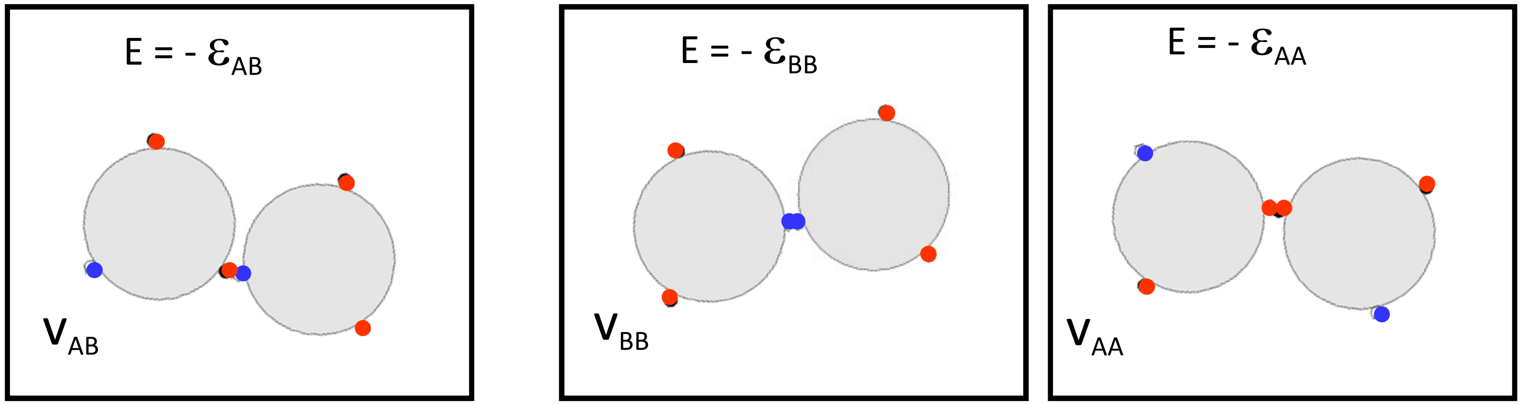
  - Binary mixtures of patchy particles (e.g. 3+2, 4+2...)

# 2. 2AnB patchy particles

2 patches of type A; n patches of type B

Example: 2A+1B



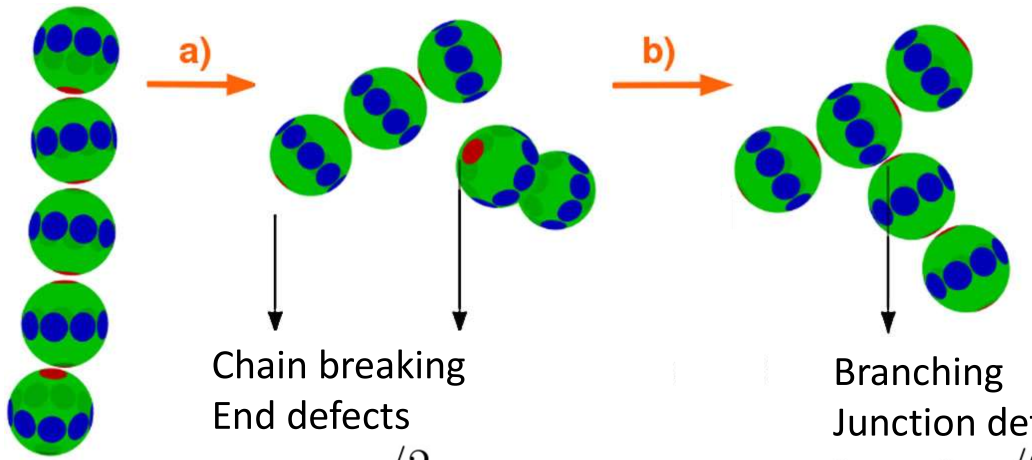

3 types of bonds: AA, AB, BB.

Tavares et al., Phys. Rev. E 80, 021506 (2009)
Tavares et al., Mol. Phys. 107, 453(2009)

# 2. 2AnB patchy particles

Choose the model parameters to reach the limit M → 2 (chain limit):

- $\varepsilon_{BB}=0$ ; $\varepsilon_{AB} < \varepsilon_{AA}/2$: ground state is infinitely long chains (or rings) AA




Chain breaking
End defects

$\epsilon_e = \epsilon_{AA}/2$

$s_e \simeq -1/2 \ln(2v_{AA}/v_{ref})$

Branching
Junction defects

$\epsilon_j = \epsilon_{AA}/2 - \epsilon_{AB}$

$s_j \simeq s_e + \ln(n v_{AB}/v_{ref})$

2 types of "thermal" or entropic defects: competition will set phase behavior

Tavares et al., J. Chem. Phys. 135, 034501 (2011)
Tavares et al., Phys. Rev. Lett. 106, 085703 (2011)

# 2. 2AnB patchy particles: Phase diagrams

Low density, low temperature (strong association) expansion:

$$\beta p = \frac{1}{2} v_{ref} \rho^2 + \phi_e - \phi_j$$

Excluded volume (excess)

density of end defects

density of junction defects

$$\phi_e = v_{ref}^{-\frac{1}{2}} \rho^{\frac{1}{2}} \exp(-\beta\epsilon_e + s_e) \qquad \phi_j = v_{ref}^{\frac{1}{2}} \rho^{\frac{3}{2}} \exp(-\beta\epsilon_j + s_j)$$

increase “effective” attractions:

- increase $nv_{AB}$ (decrease the entropic cost of junctions)
- increase $\varepsilon_{AB}/\varepsilon_{AA}$ (decrease the energetic cost of junctions)

# 2. 2AnB patchy particles: Phase diagrams

Low density, low temperature (strong association) expansion:

$$\beta p = B_2 v_s \rho^2 + \phi_e - \phi_j$$

Excluded volume (excess)

density of end defects

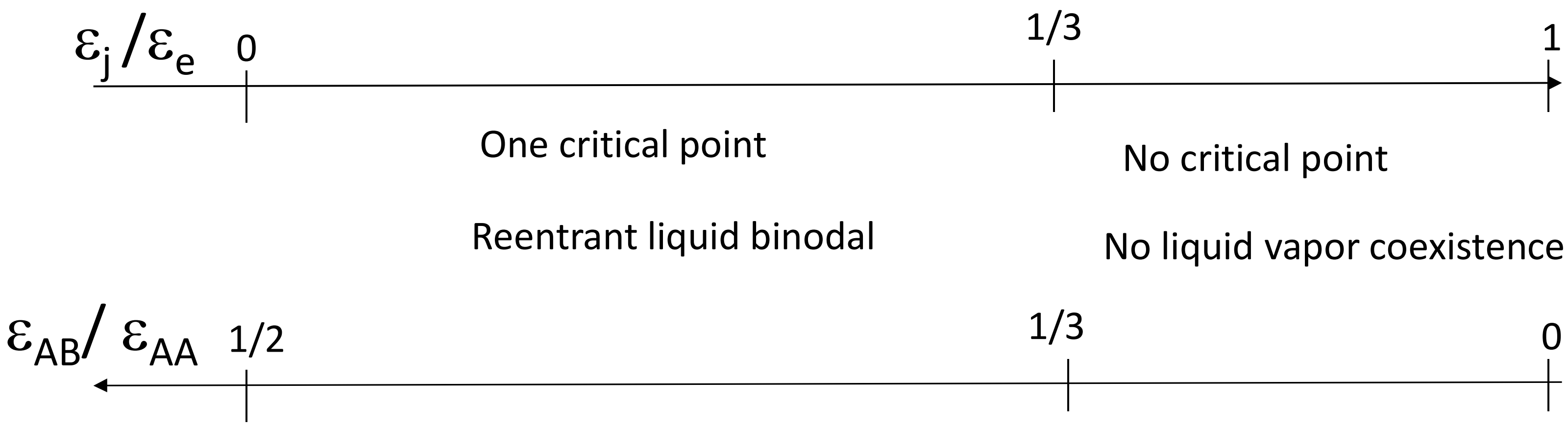
density of junction defects

$$\phi_e = \left( \frac{\rho \exp(-\beta \epsilon_{AA})}{2 v_{AA}} \right)^{\frac{1}{2}} \qquad \phi_j = \frac{n v_{AB}}{\sqrt{2 v_{AA}}} \exp(\beta(\epsilon_{AB} - \epsilon_{AA}/2)\rho^{\frac{3}{2}}$$

# 2. 2AnB patchy particles: Phase diagrams

PHASE DIAGRAMS for the different values of $\varepsilon_{\alpha\beta}$ and $v_{\alpha\beta}$

CASE 1: $s_e > 3s_j$

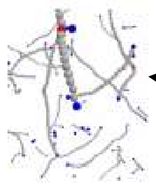


# 2. 2AnB patchy particles: Phase diagrams

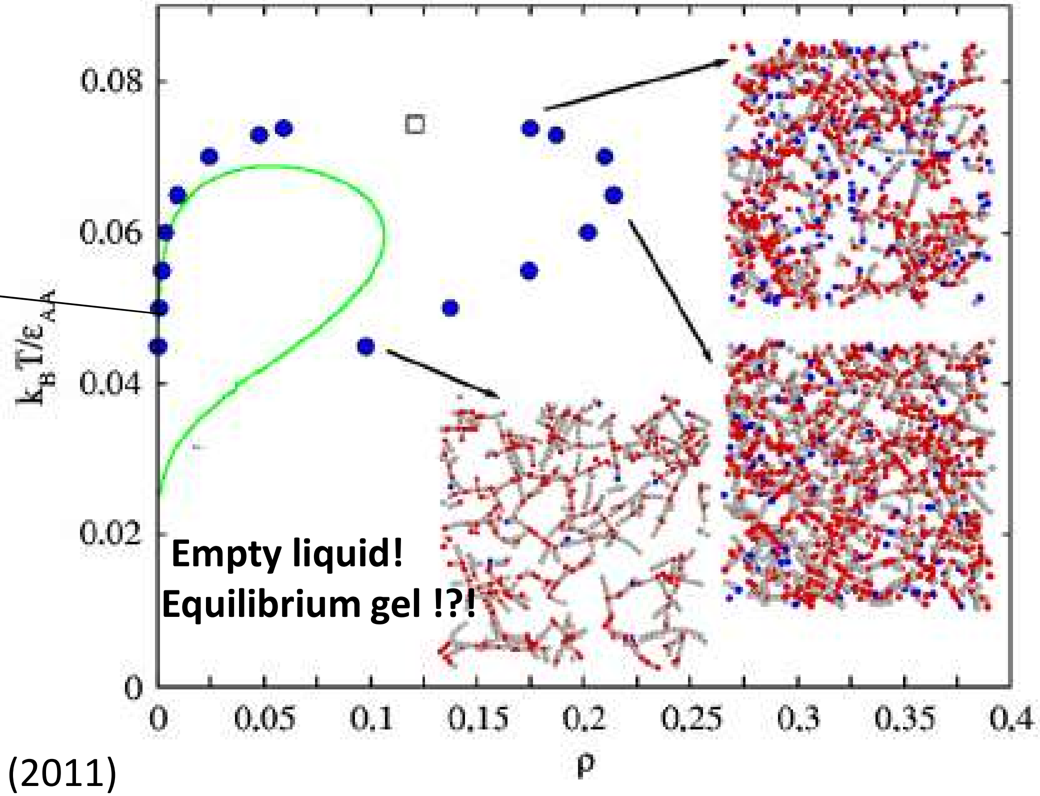
CASE 1: $s_e > 3s_j$

$\varepsilon_{AB} / \varepsilon_{AA} = 0.37$ or $\varepsilon_j / \varepsilon_e = 0.26$

2A + 9B



vapor



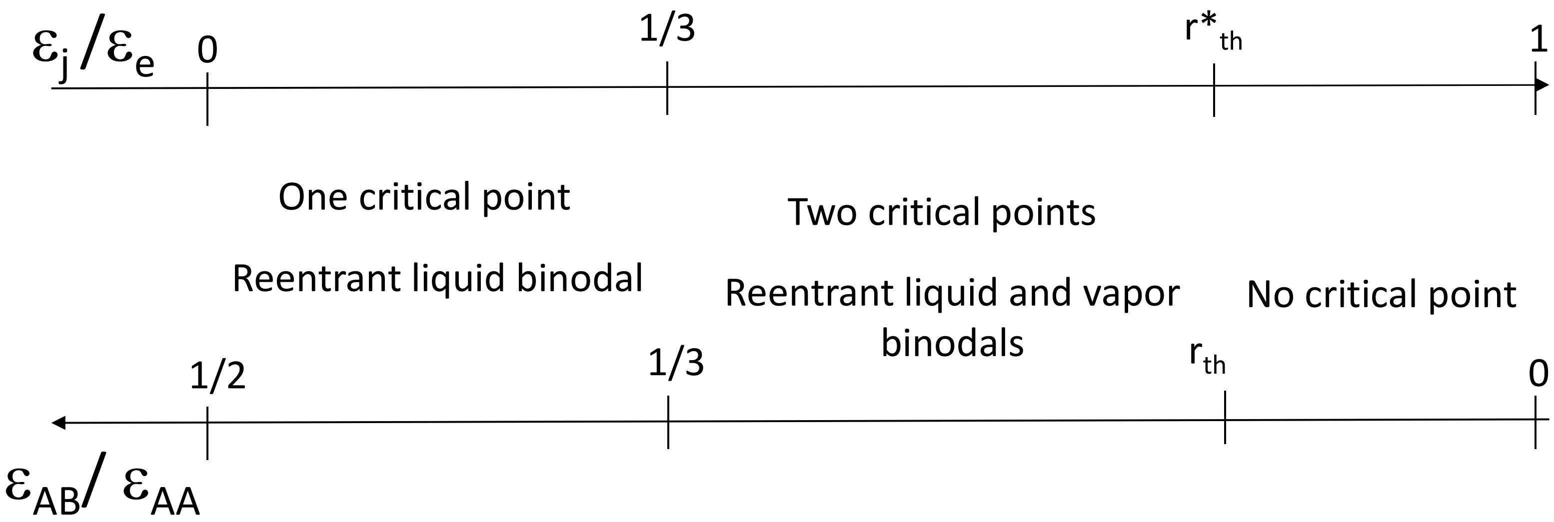

red: junctions

blue: chain ends

Tavares et al. ,
Phys. Rev. Lett. 106, 085703 (2011)

# 2. 2AnB patchy particles: Phase diagrams

CASE 2: $s_e < 3s_j$ (large n and $v_{AB}$)



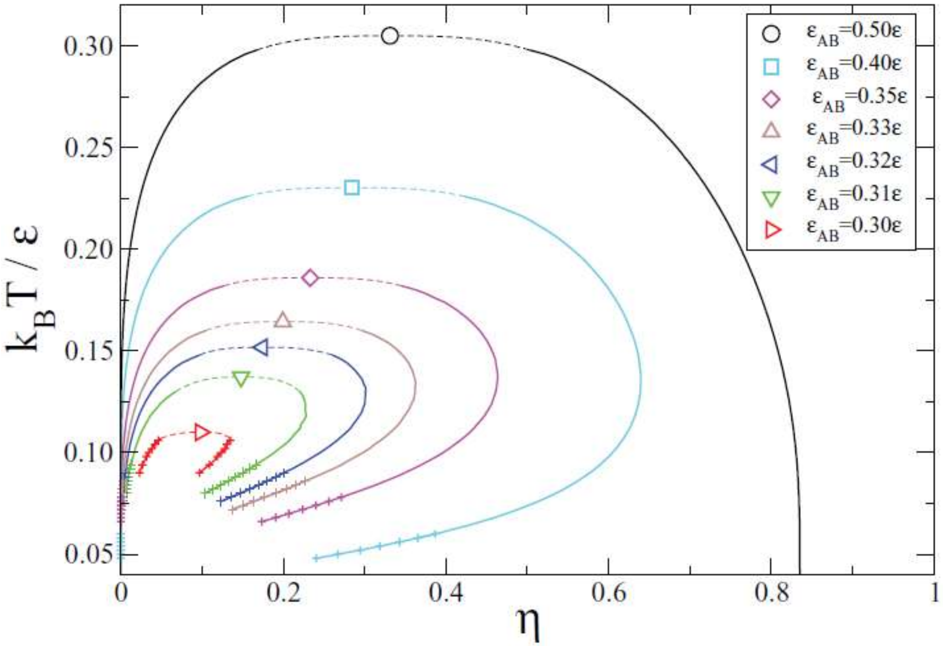

Tavares et al.,
J. Chem. Phys. 137, 244902 (2012)

# 2. 2AnB patchy particles: Phase diagrams

CASE 2: $s_e < 3s_j$

| $\varepsilon_{AB}/\varepsilon_{AA}$ | 1/2 | 1/3 | $r_{th}$ | 0 |
|---|---|---|---|---|
| | One critical point | Two critical points | No critical point | |
| | Reentrant liquid binodal | Reentrant liquid and vapor binodals | | |

fcc lattice model; n=10




Tavares et al.,
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# 2. 2AnB patchy particles: Phase diagrams

CASE 2: $s_e < 3s_j$

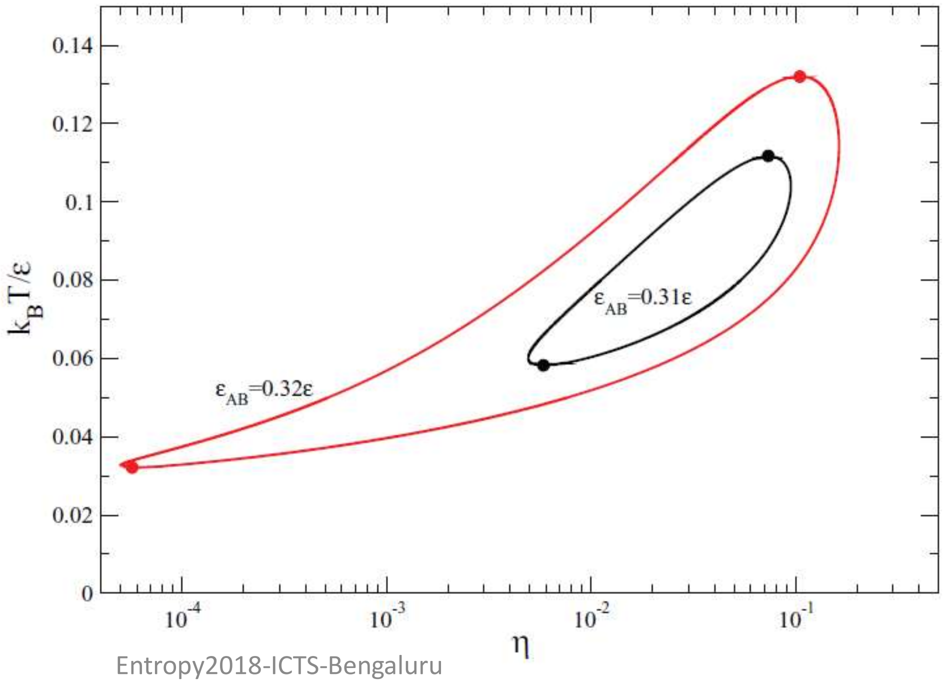
$\varepsilon_{AB}/\ \varepsilon_{AA}$

1/2 One critical point — 1/3 Two critical points — $r_{th}$ No critical point — 0

1/2 to 1/3: Reentrant liquid binodal

1/3 to $r_{th}$: Reentrant liquid and vapor binodals

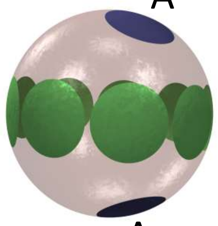
fcc lattice model; n=10

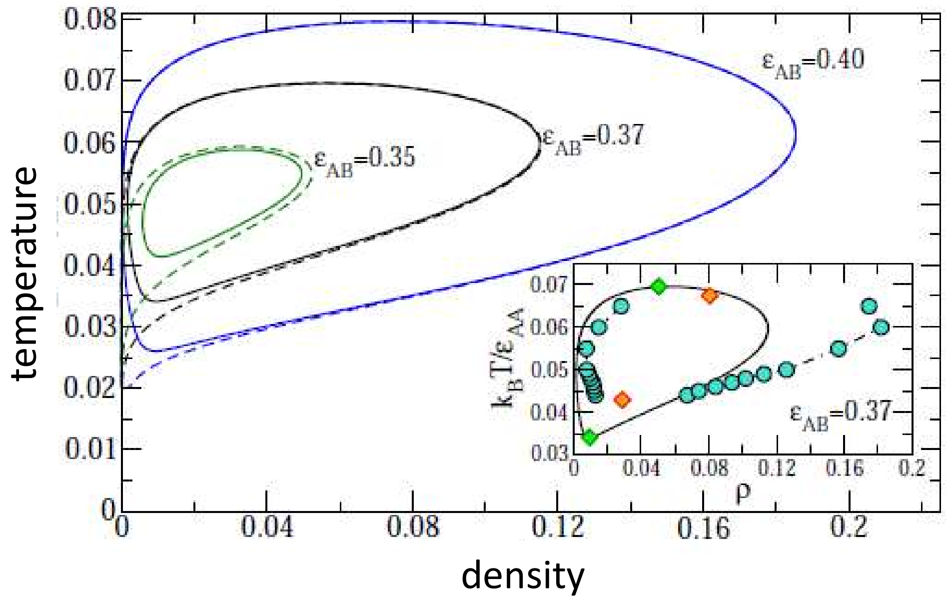



Tavares et al.,
J. Chem. Phys. 137, 244902 (2012)

# 2. 2AnB patchy particles: extensions

I. 2AnB patchy particles with enhanced RING FORMATION



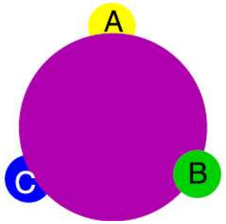

- Phase diagram: points (simulation); line (theory);

- Both liquid and vapour become reentrant on cooling.
- Single component system with 2 critical points!
- Phase diagram "shrinks" as the energy cost of junctions is increased.

Tavares et al. ,
Phys. Rev. Lett. 111, 168302 (2013)

# 2. 2AnB patchy particles: extensions

II. ABC particles (3 different types of patches) with three non-zero energy scales




Example: $\epsilon_{AC} > \epsilon_{AA}/2 + \epsilon_{BC}$ ; forms AC chains and BC junctions

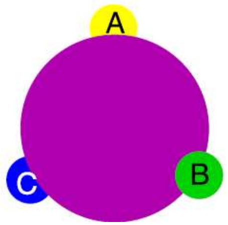
$$\beta p = \beta p_{HS} + \phi_{e,A} + \phi_{e,C} - \phi_{j,B}$$

$$\phi_{e,A} = v_b^{-\frac{1}{3}} \rho^{\frac{2}{3}} \exp(-\beta\epsilon_A) \qquad \phi_{e,C} = v_b^{-\frac{2}{3}} \rho^{\frac{1}{3}} \exp(-\beta\epsilon_C)$$

$$\phi_{j,B} = v_b^{\frac{1}{3}} \rho^{\frac{4}{3}} \exp(-\beta\epsilon_j)$$

Tavares et al. ,
Phys. Rev. E 95, 012612 (2017)

# 2. 2AnB patchy particles: extensions

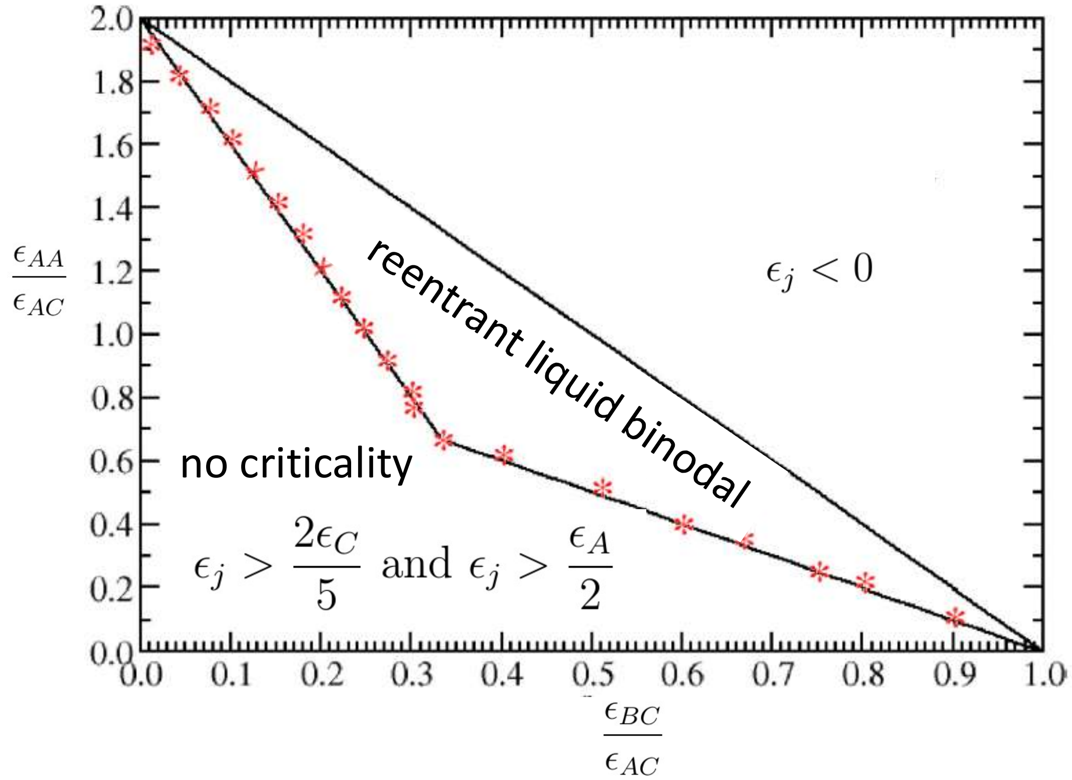



AC chains and BC junctions

$$\epsilon_j = \frac{2\epsilon_{AC} - \epsilon_{AA} - 2\epsilon_{BC}}{3}$$

$$\epsilon_A = \frac{\epsilon_{AC} + \epsilon_{AA} - \epsilon_{BC}}{3}$$

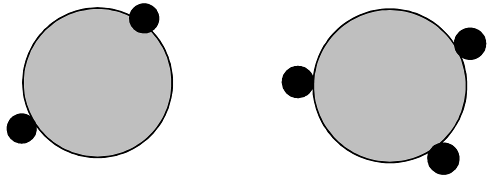
$$\epsilon_C = \frac{2\epsilon_{AC} - \epsilon_{AA} + \epsilon_{BC}}{3}$$



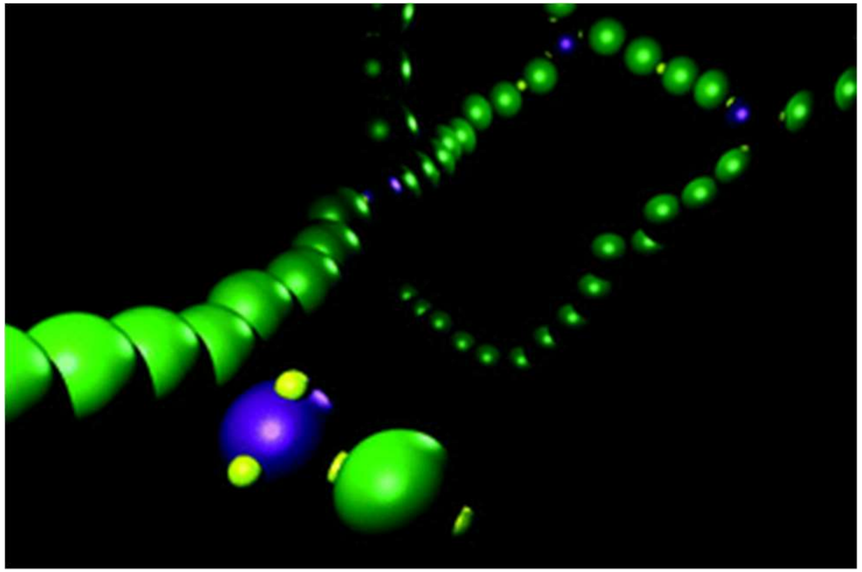

Tavares et al. ,
Phys. Rev. E 95, 012612 (2017)

# 3. Binary mixtures of patchy particles

2 species; same diameter; all patches (and bonds) are equal; species have different number of patches



$M_1=2$ $M_2=3$



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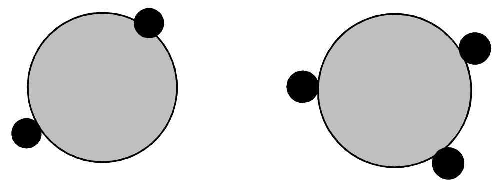
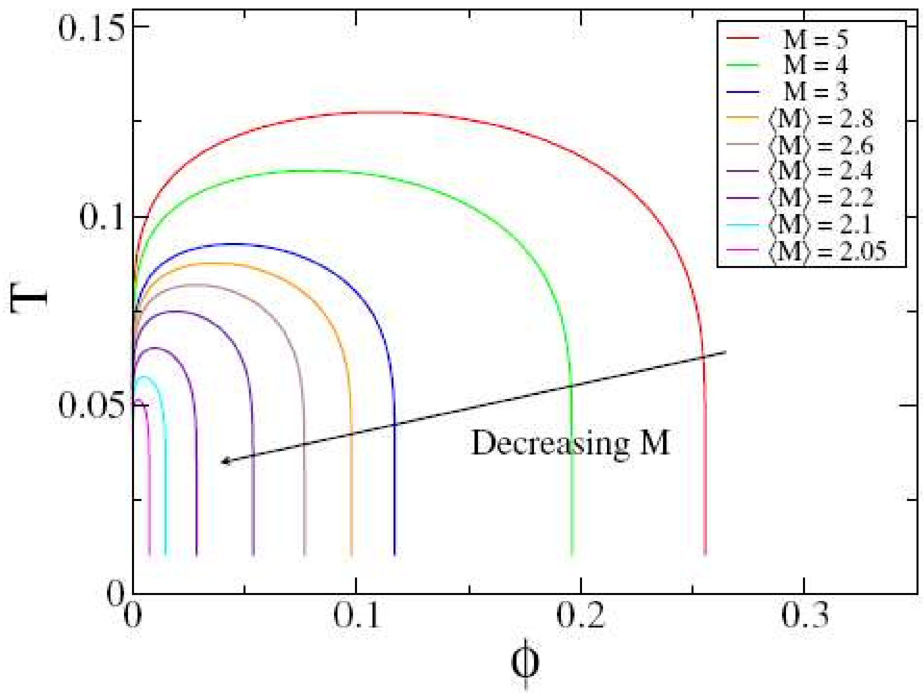


$M_1$=2 $M_2$=3

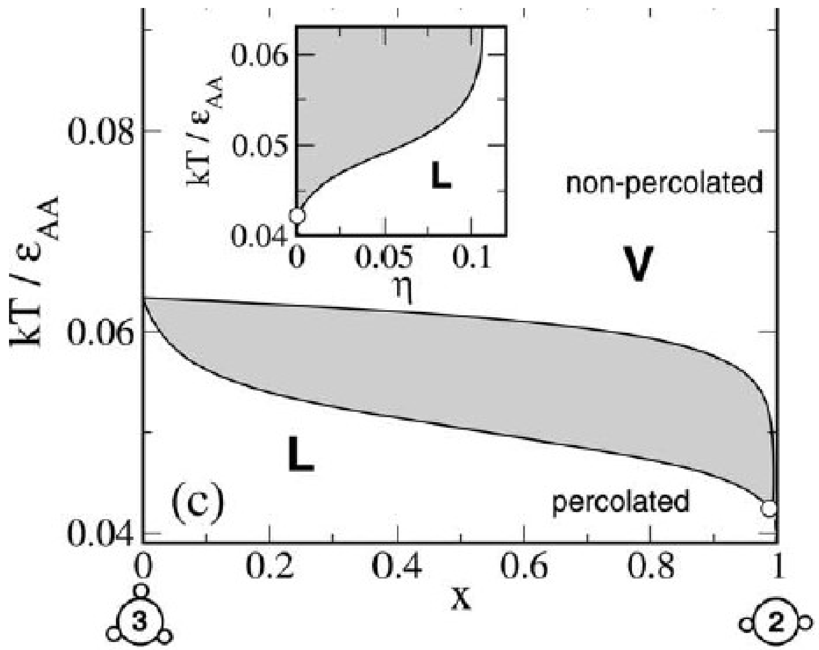


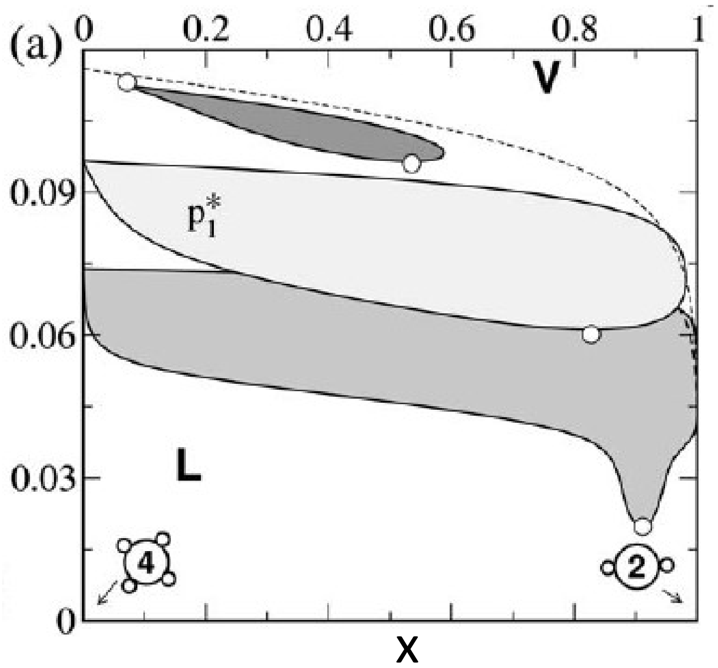

- Phase diagram neglecting entropy of mixing.
- As if all the particles have <M> patches.
- Empty network fluid

Bianchi et al. : PRL **97**,168301(2006); JCP 128, 144504 (2008)

# 3. Binary mixtures of patchy particles

Phase diagrams calculated using Wertheim's theory (including entropy of mixing)

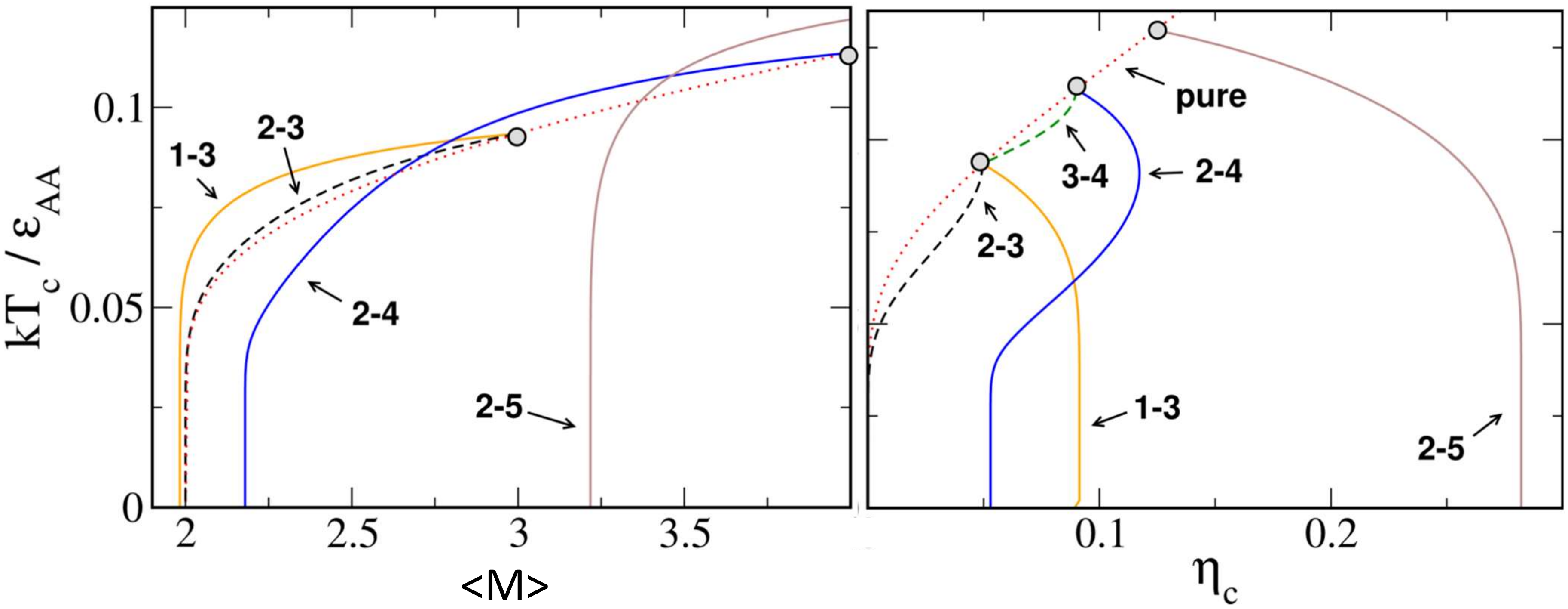



Tavares et al., Soft Matter **7**, 5615 (2011)

# 3. Binary mixtures of patchy particles

Critical properties




Entropy of mixing can only be neglected when $M_2$-$M_1$=1

Tavares et al., Soft Matter **7**, 5615 (2011)