Surprises in patchy colloids

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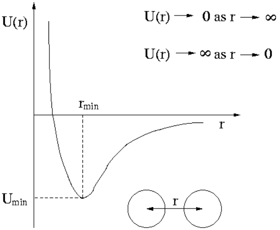
Phases and phase transitions

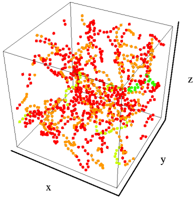
- In general, interactions between atoms, molecules or ions comprise a short-range repulsion and a longer-ranged attraction.



- In the Van der Waals picture, the interplay of interaction energy and entropy – expressed as free energy – determines which phases are realised.
  - At low temperatures/high densities energy wins and we have a condensed phase – a liquid or a solid.
  - At high temperatures/low densities entropy wins and we have a dilute phase – a gas.

Motivation

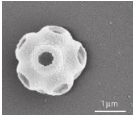
- Most molecular species have permanent dipoles.
- Criticality of strongly dipolar fluids is still unsolved problem (image by J.-J. Weis).

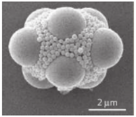


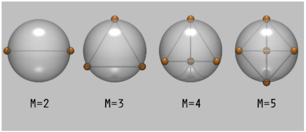
- A related, more general issue is interplay between condensation and association.
- We want to study a model that retains the essential symmetry of dipolar forces leading to association, but leaves out apparently inessential features (long range and complex angular dependence).

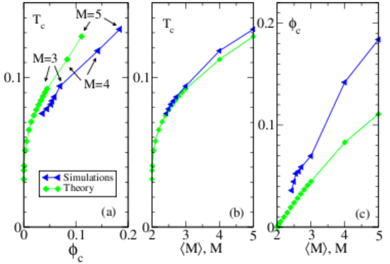
Patchy colloids

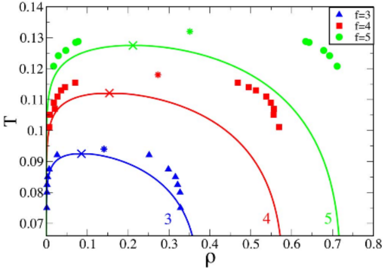
- Patchy colloids are custom-fabricated matter that exhibits both self-assembly and the usual phase transitions (condensation, freezing, etc) (images by Y. S. Cho *et al.*).
- Sciortino *et al.* [Phys. Rev. Lett. **97**, 168301 (2006); J. Chem. Phys. **128**, 144504 (2008)] simulated patchy particles with M identical sites: $\rho_c \to 0$ and $T_c \to 0$ as $M \to 2$.





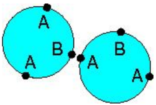






Theory and model

- Hard spheres of diameter σ and volume v_s, each decorated with $2 + m_B$ sticky spots: two A's and m_B B's. AA, BB or AB bonds may form.



- Bonding free energy from Wertheim's theory:

$$\beta f_b \equiv \frac{\beta F_b}{N} = 2 \ln X_A + m_B \ln X_B - X_A - \frac{m_B X_B}{2} + \frac{2 + m_B}{2}$$

X_i is the probability of having a sticky spot of type i not bonded.

- Law of mass action yields:

$$\begin{aligned} X_A + 2\eta\Delta_{AA}X_A^2 + m_B\eta\Delta_{AB}X_AX_B &= 1 \\ X_B + m_B\eta\Delta_{BB}X_B^2 + 2\eta\Delta_{AB}X_AX_B &= 1, \end{aligned}$$

where $\eta \equiv (N/V)v_s$ is the packing fraction, and

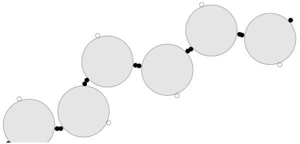
$$\Delta_{ij} = \frac{1}{v_s^{ij}} \int_{v_{ij}} g_{ref}(\mathbf{r}) \left[\exp(-\beta\epsilon_{ij}) - 1\right] d\mathbf{r}$$

- Free energy per particle is a function of (η, T) only:

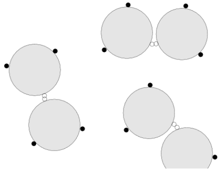
$$\beta f = \beta f_{HS} + \beta f_b$$

Ground states (without loops)

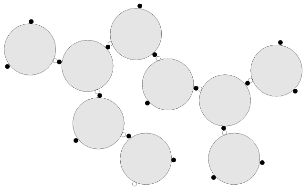
Linear chains
($\epsilon_{AB} = \epsilon_{BB} = 0$, $\epsilon_{AA} \neq 0$)



Dimers ($m_B = 1$ only!)
$\epsilon_{AA} = \epsilon_{AB} = 0$, $\epsilon_{BB} \neq 0$

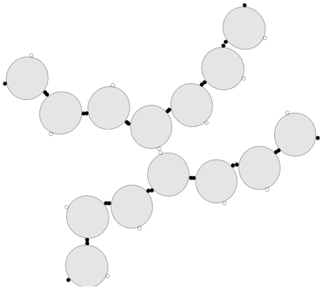


Hyperbranched polymers
($\epsilon_{AA} = \epsilon_{BB} = 0$, $\epsilon_{AB} \neq 0$)

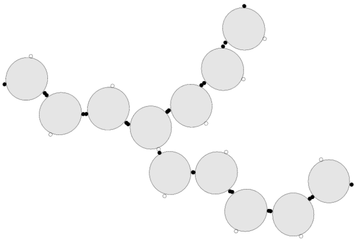


Elementary excitations

X-junction is always favourable:
$\epsilon_j = -\epsilon_{BB} < 0$



Y-junction is favourable only if
$\epsilon_j = -\epsilon_{AB} + \epsilon_{AA}/2 < 0$
$\Leftrightarrow \epsilon_{AB}/\epsilon_{AA} > 1/2$



Asymptotic behaviour

- X-junction driven criticality: $\epsilon_{AB} = 0$, $\epsilon_{BB} \to 0$

$$T_c = \frac{\epsilon_{BB}}{\ln b},$$
$$\eta_c = \left[\frac{9v_b}{8v_s(B_3 + 6B_2^2)^2}\right]^{\frac{1}{5}} \exp\left[-\frac{\ln b}{5(\epsilon_{BB}/\epsilon_{AA})}\right].$$

A critical point is always present, with lower and lower critical density and temperature.

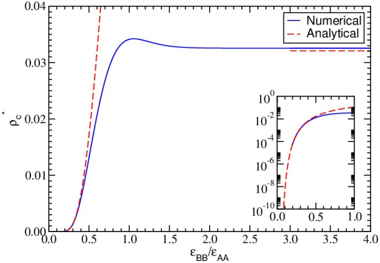
- Y-junction driven criticality: $\epsilon_{BB} = 0$, $\epsilon_{AB} \to 0$

$$T_c = \frac{\epsilon_{AB} - \frac{1}{3}\epsilon_{AA}}{b},$$
$$\eta_c = \frac{v_b}{v_s} \exp\left(-\frac{b\epsilon_{AB}}{3\epsilon_{AB} - \epsilon_{AA}}\right).$$

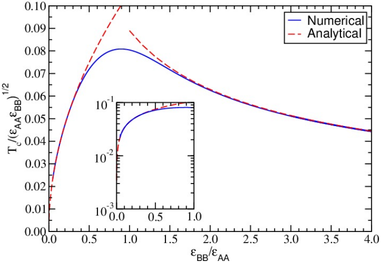
On decreasing ϵ_{AB} a critical point of vanishingly small density and temperature is obtained only up to $\epsilon_{AB}/\epsilon_{AA} = \frac{1}{3}$.

X and Y criticality

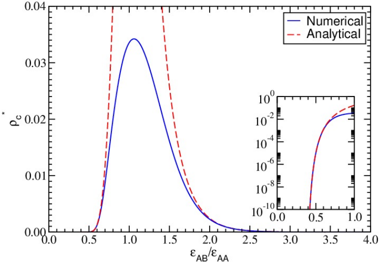
(a)



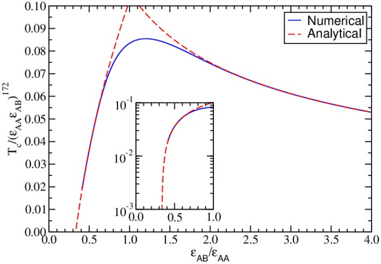
(b)



(a)



(b)

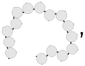
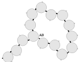


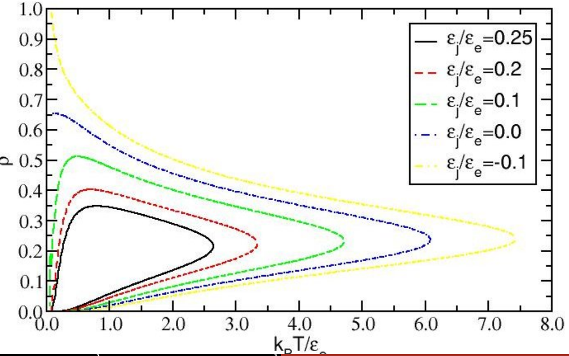
Summary of results so far

- If $\epsilon_{AA} = 0$ there is no critical point.
- If $\epsilon_{AA} \neq 0$:
  - If $\epsilon_{AB} = 0$, the critical point exists all the way to $\epsilon_{BB}/\epsilon_{AA} = 0$. This corresponds to X-junction condensation.
  - If $\epsilon_{BB} = 0$, there is no critical point for $\epsilon_{AB}/\epsilon_{AA} < 1/3$. This corresponds to Y-junction condensation.
- By changing the ratio of interaction strengths, we are able to engineer very low density liquid phases: 'empty liquids'.
- Likewise, different cluster structures may result, which may or may not lead to percolation.
- But wait... What happens if $1/3 < \epsilon_{AB}/\epsilon_{AA} < 1/2$?

Diversion: Tlusty and Safran's theory

- At low T (large μ), dipolar fluid consists mostly of long chains.
- Treated as a perturbation of a ground state of infinitely long chains.
- Perturbation consists of two types of thermally-excited defects:

  chain ends , of energy ϵ_e and Y-junctions  of energy ϵ_j.
- There is a critical point if $\epsilon_j/\epsilon_e < 3$. Coexistence is between a lower-density phase rich in ends and a higher-density phase rich in junctions. Phase diagram pinches (is re-entrant) at low T.



Issues to be addressed ($\epsilon_{BB} = 0$)

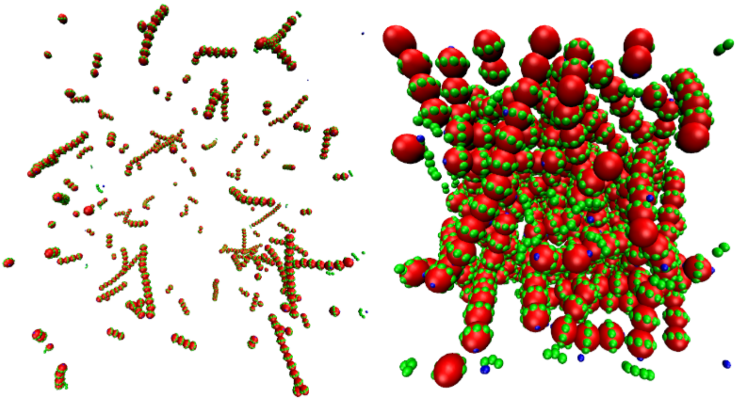
1. Can we also find pinching in our theory?
   - TS theory coincides with ours in limit $\epsilon_{AB}/\epsilon_{AA} << 1$. It affords greater insight into our own theory, BUT:
     - TS theory is lattice-based $\Rightarrow$ not-so-good entropy.
     - ϵ_e and ϵ_j are not related to interparticle potentials.
   - BUT we need to be able to approach limit where critical point disappears, where vapour densities are extremely low.

     Solution: Artificially increase AB-bond volume by choosing $m_B = 9$: not one larger patch, but many small ones.
2. How do we go from 'pinched' to 'normal' phase behaviour?

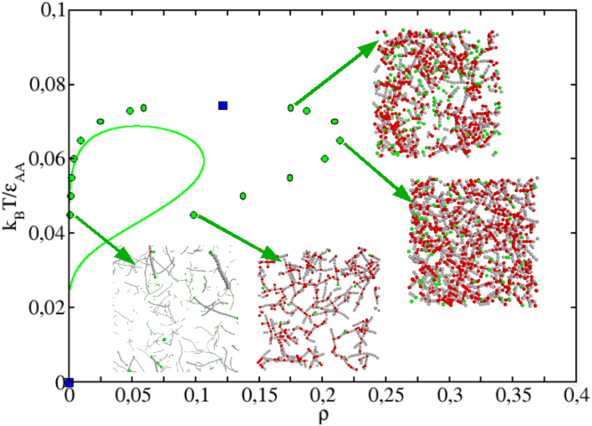
   Solution: Switch on ϵ_{BB} at fixed $1/3 < \epsilon_{AB}/\epsilon_{AA} < 1/2$.

Results for $2A + 9B$ model, $\epsilon_{BB} = 0$, $\epsilon_{AB} = 0.37\epsilon_{AA}$

Snapshot of vapour and liquid phases

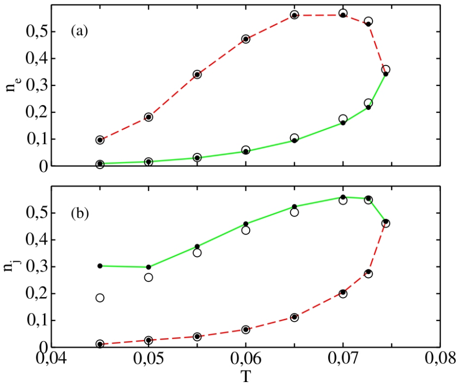


Phase diagram



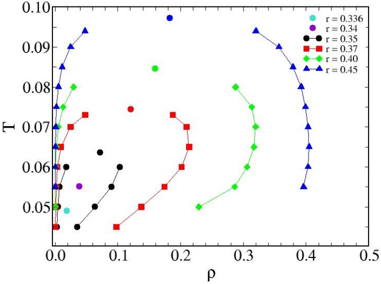
- T_c^* well predicted, ρ_c^* less so.
- Vapour phase rich in ends, liquid phase rich in junctions.

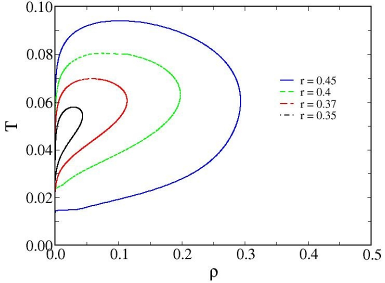
Fractions of chain ends and junctions along coexistence line



- Excellent agreement between theory and simulation (using simulation input).
- Vapour phase rich in ends, liquid phase rich in junctions.

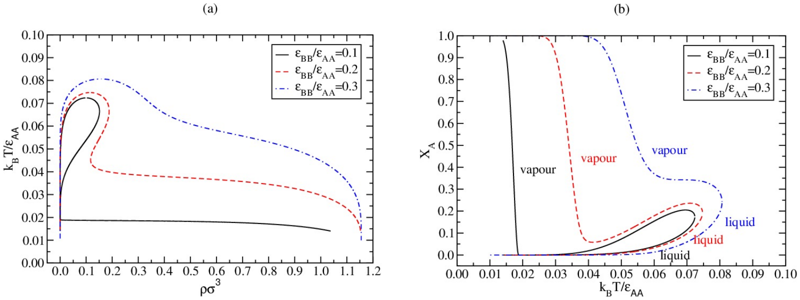
Phase diagram





- For all $\epsilon_{AB}/\epsilon_{AA}$ a clear pinching is observed, which becomes more pronounced as $\epsilon_{AB}/\epsilon_{AA} \to 1/3$.
- On decreasing $\epsilon_{AB}/\epsilon_{AA}$, both T_c and ρ_c decrease.
- Theory correctly predicts the temperature range of condensation, but significantly underestimates ρ_c and the density of the liquid-branch of the binodal.

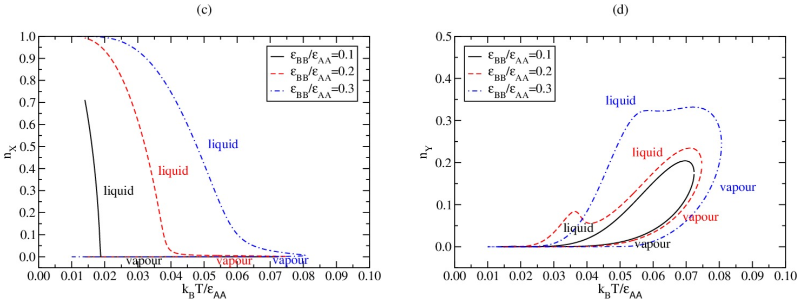
Phase diagram and fraction of unbonded A's



- Phase diagram gradually un-pinches as $\epsilon_{BB}/\epsilon_{AA}$ increases.
- In the re-entrant region for small $\epsilon_{BB}/\epsilon_{AA}$, both phases consists almost exclusively of extremely long chains ($X_A \approx 0$).

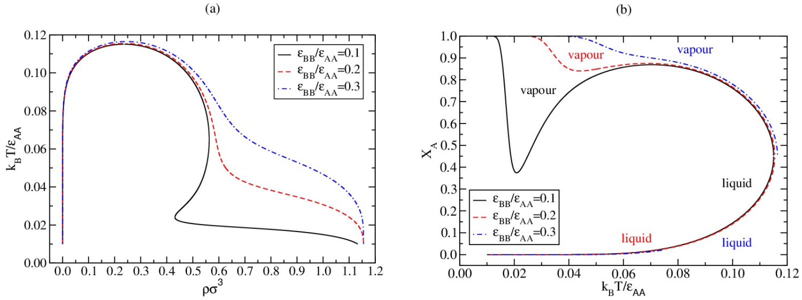
Results for $2A + 9B$ model, $\epsilon_{AB} = 0.35\epsilon_{AA}$, variable ϵ_{BB} II

Fractions of X- and Y-junctions



- Close to T_c, coexistence is between a liquid of long chains and rich in Y-junctions, and a vapour of shorter chains with fewer Y-junctions, both with practically no X-junctions
- As $T \to 0$, the liquid has many X-junctions and no Y-junctions, the vapour is an ideal gas of monomers.
- At intermediate T, coexistence is between a gas of short chains and a liquid of very long chains with X- and, in some cases, Y-junctions.

Phase diagram and fraction of unbonded A's



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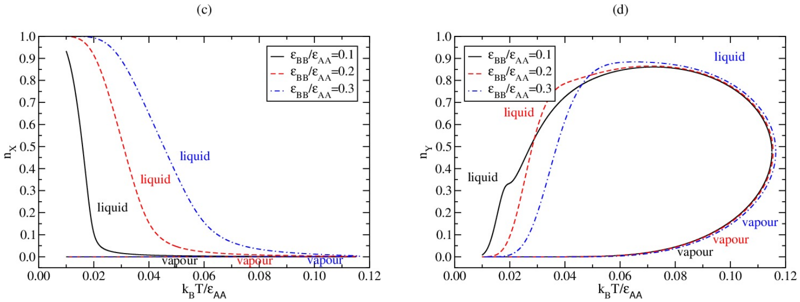
Fractions of X- and Y-junctions



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Summary and conclusions

- We have applied Wertheim's theory of association to patchy colloids with two A sites and m_B B sites.
- For $\epsilon_{BB} \to 0$ or $\epsilon_{AB} \to 0$, long AA chains form with either AB or BB branches. These are relevant to strong-dipolar-fluid criticality.
- When $\epsilon_{BB} = \epsilon_{AB} = 0$ we recover the non-trivial limit of two A's:
  - If $\epsilon_{AB} = 0$, the critical point exists all the way to $\epsilon_{BB}/\epsilon_{AA} = 0$. This corresponds to X-junction condensation.
  - If $\epsilon_{BB} = 0$, there is no critical point for $\epsilon_{AB}/\epsilon_{AA} < 1/3$. This corresponds to Y-junction condensation.
- We have been able to reproduce the pinched phase diagram of Tlusty-Safran theory using our patchy particles and Wertheim's theory of association.
- This re-entrance can be understood a temperature controlled effective valence: the number of bonded sites per particle goes down with decreasing T.
- The structure of the coexisting phases can be understood simply by noting that Y-junctions are favoured at high temperatures, whereas X-junctions dominate at low temperatures.

Outlook

BUT this version of the theory ignores completely:

- higher densities;
- rings;
- patch positions on the hard core $\Rightarrow$ orientational correlations.

References

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