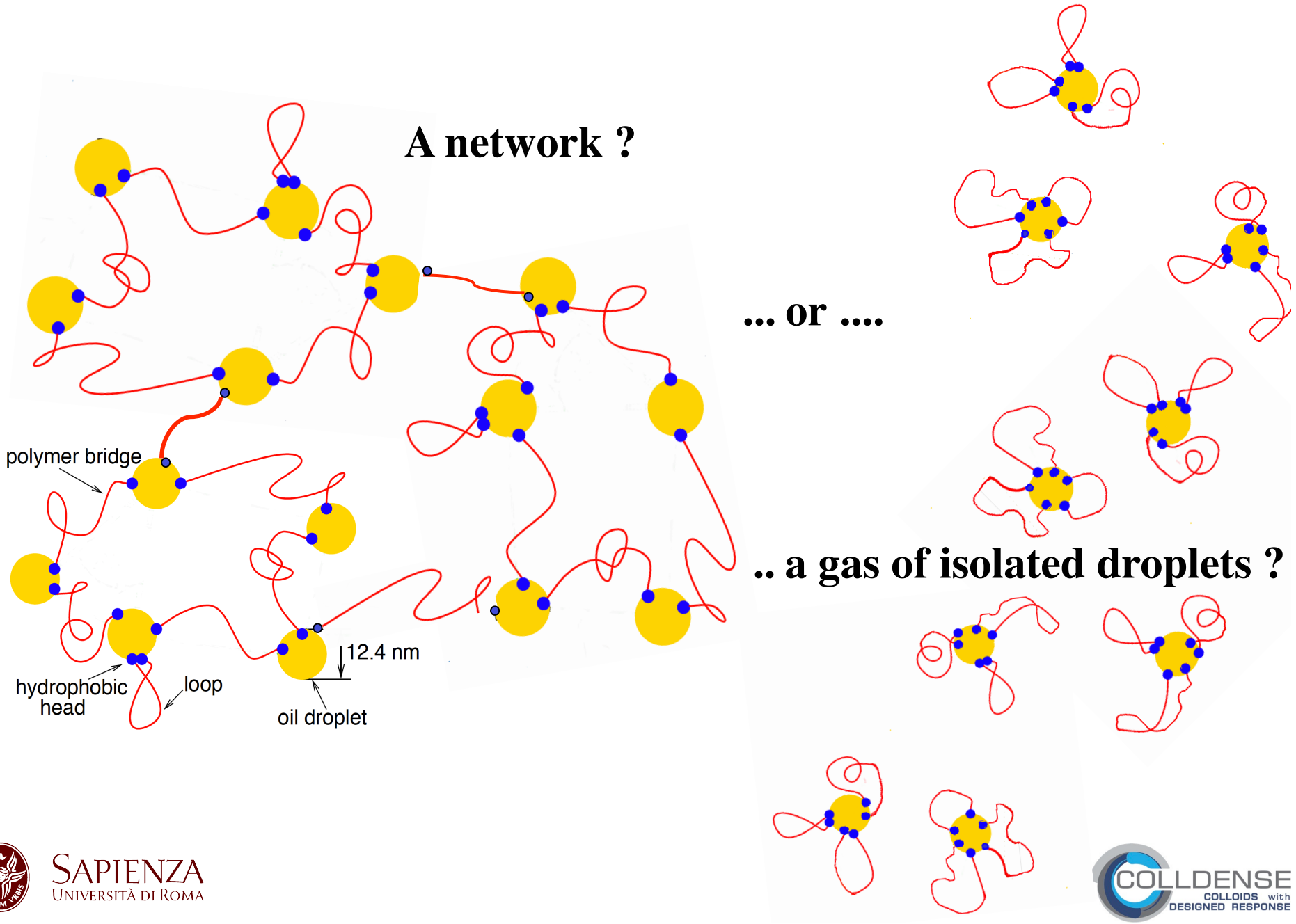
Safran's attraction

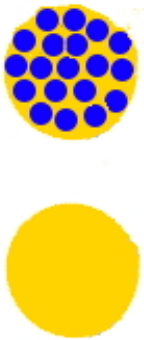


Two independent parameters: The droplet concentration $\rho_d = \frac{N}{V}$ and the polymer concentration $\rho_p = \frac{N_p}{V}$.

A very simplified free energy (which neglects many coupling ...) can be written as

$$\beta F = \beta F_{CS} + \beta F_{polymer}$$

$$\beta F_{polymer} = -N_p \ln Z_p \quad \text{with} \quad Z_p = N \frac{\Sigma_d}{\Sigma_p} \left(\frac{\Sigma_d}{\Sigma_p} + N_d^{accessible} \frac{\Sigma_d}{\Sigma_p} \right)$$



with $N_d^{accessible} \sim \rho_d$. Note that we have assumed that $\frac{\Sigma_d}{\Sigma_p}$ is the number of attachment points on a droplet (proportional to the surface area of the dropled divided by the surface area of the polymer head). Each polymer can then end with probability $\frac{\Sigma_d}{\Sigma_p}$ on the same droplet and with probability $N_d^{accessible} \frac{\Sigma_d}{\Sigma_p}$ on an accessible droplet.

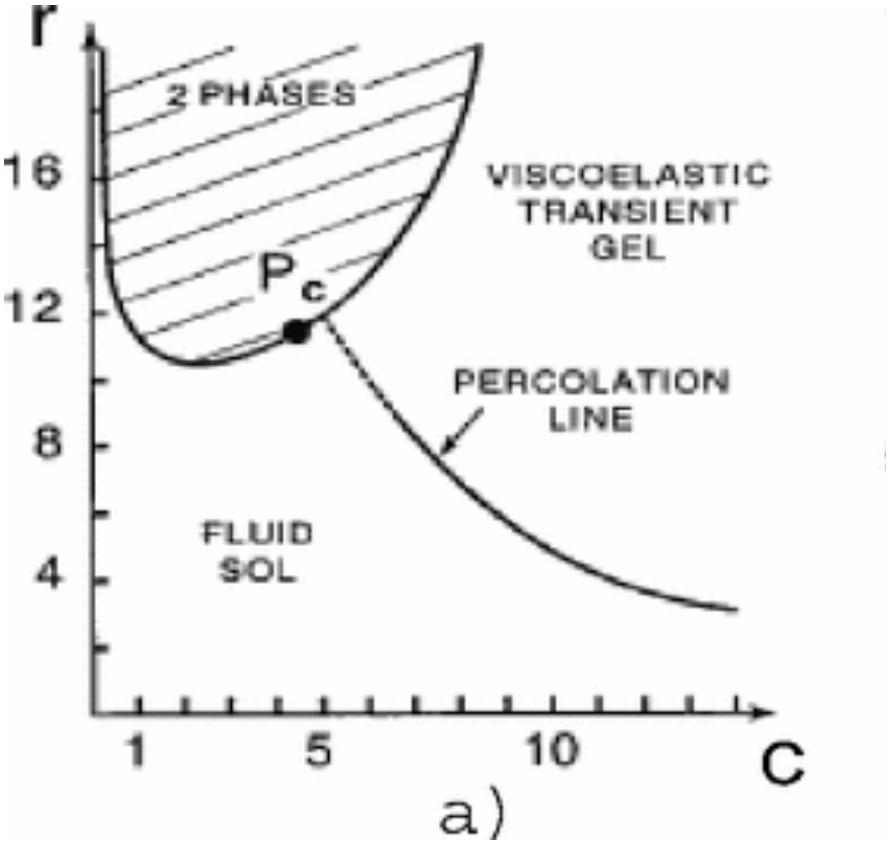
The system is thermodynamically stable if the free energy is a convex function of both ρ_p and ρ_d. This means that the second derivative of the free energy ($\delta^2 F = F_{\rho_d,\rho_d} \delta\rho_d^2 + 2F_{\rho_d,\rho_p} \delta\rho_d \delta\rho_p + F_{\rho_p,\rho_p} \delta\rho_p^2$) has to be positive or equivalently the matrix

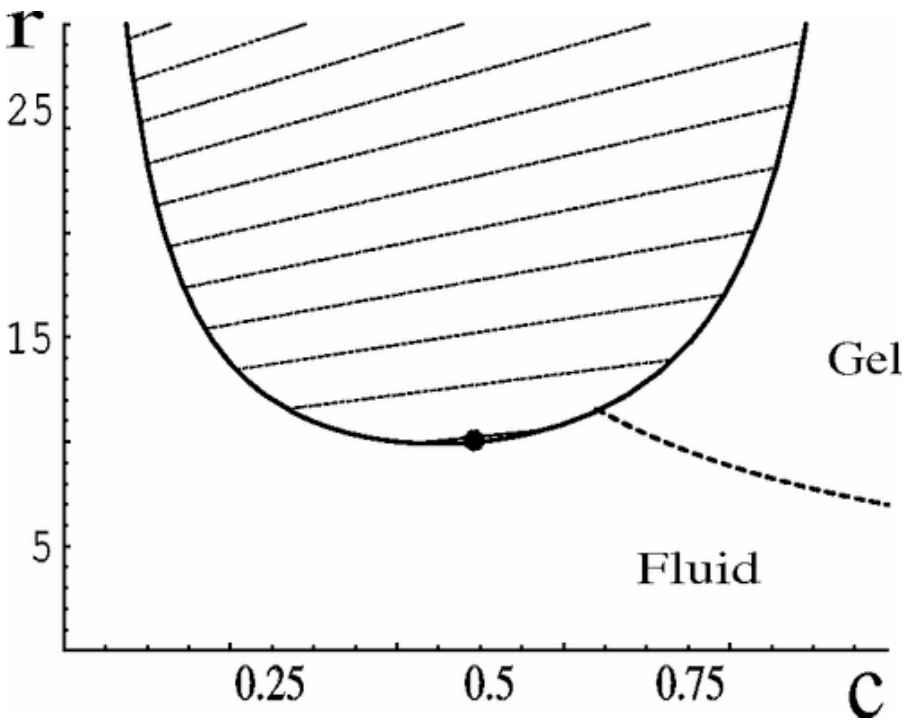
$$\begin{pmatrix} F_{\rho_d,\rho_d} & F_{\rho_d,\rho_p} \\ F_{\rho_d,\rho_p} & F_{\rho_p,\rho_p} \end{pmatrix}$$

posses two positive eigenvalues.

Entropic Phase Separation in Polymer-Microemulsion Networks

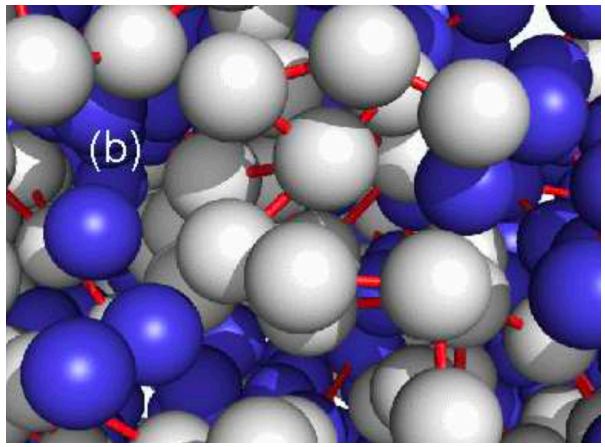
A. Zilman,[1] J. Kieffer,[2] F. Molino,[2] G. Porte,[2] and S. A. Safran[1]





Heterogeneous Diffusion in a Reversible Gel

Pablo I. Hurtado,[1,2] Ludovic Berthier,[1] and Walter Kob[1]



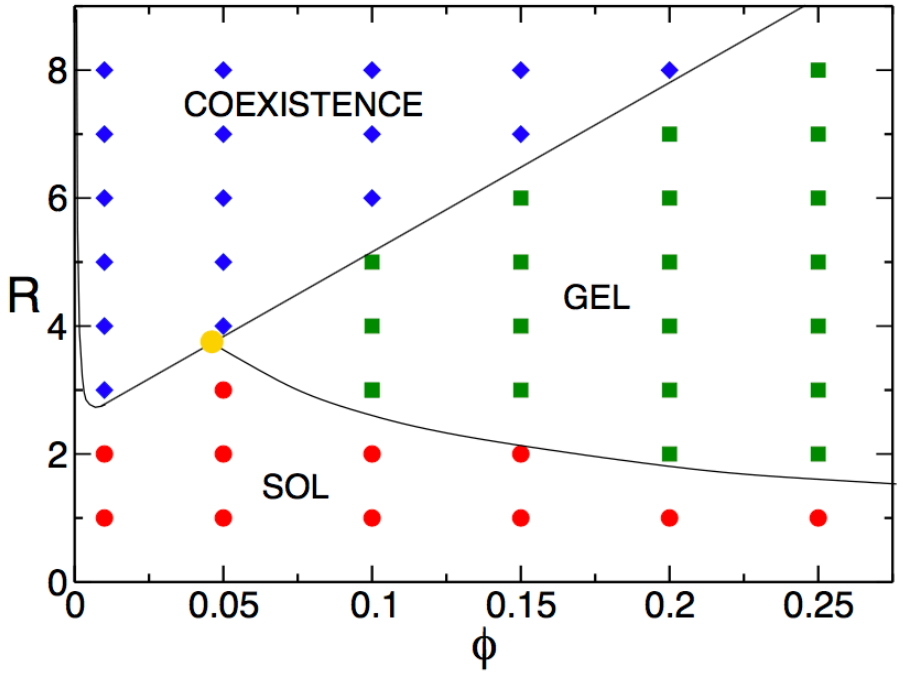
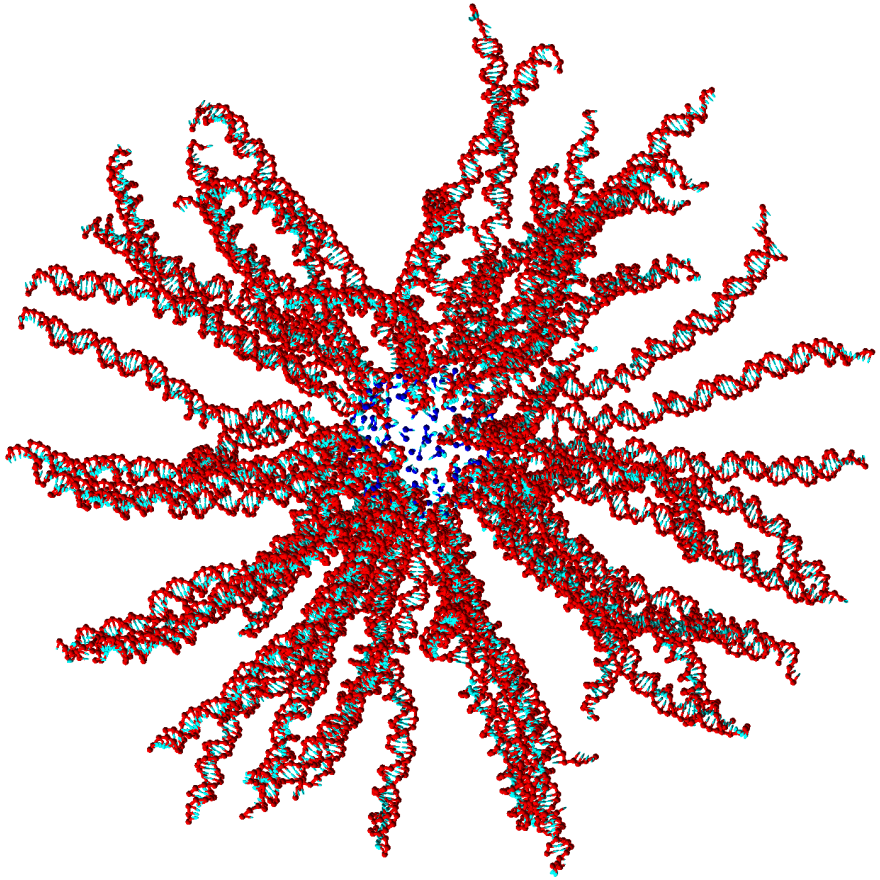


FIG. 2: Phase diagram for a wide range of volume fraction, ϕ, and number of polymer heads per droplet, R. Symbols are the investigated state points in the sol (◯), gel (□), and phase separated (◇) regions, the yellow point is the approximate location of the critical point. Transition lines are sketched.

Another interesting soft-matter case



DNA-grafted gold nanoparticles (palindromic sticky sequences)

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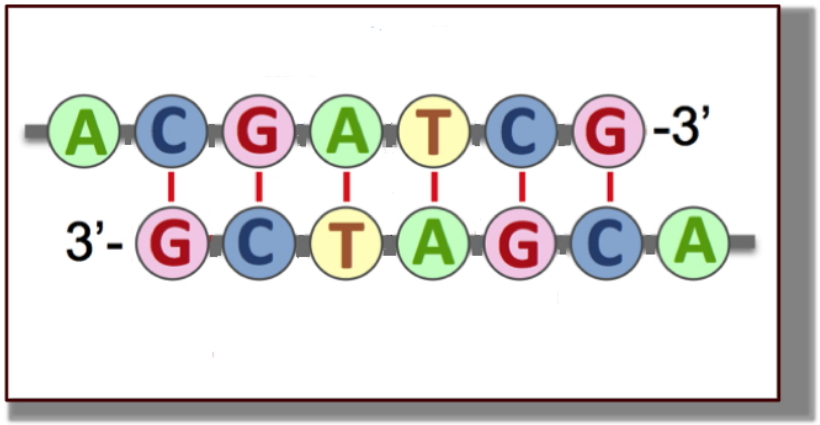
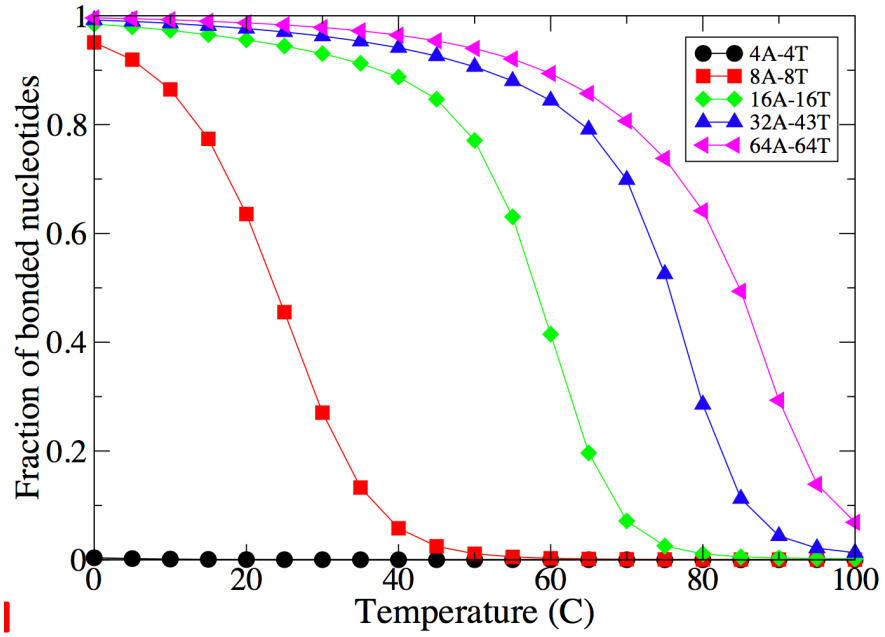
COLLDENSE
COLLOIDS with DESIGNED RESPONSE

Self complementary DNA sequences





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COLLDENSE
COLLOIDS with DESIGNED RESPONSE

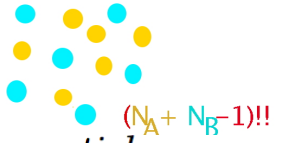
ACCAVALLAVACCA

The number of ways of forming pairs (bonds) only of AA and BB type (as we have when the particles are well separated) is

$$\Omega = (N_A - 1)!!(N_B - 1)!!$$

The number of ways of binding the $N_A + N_B$ sites in pairs allowing also for AB binding is instead

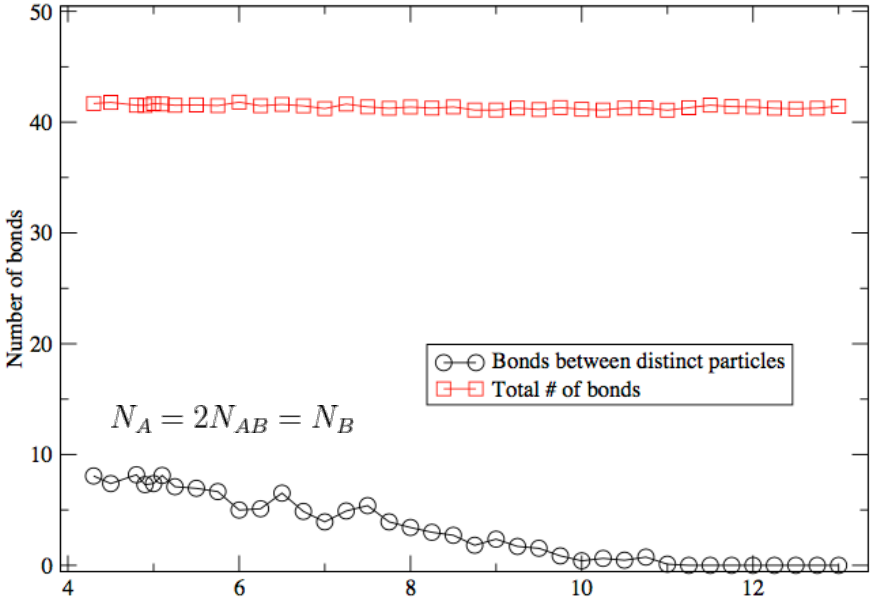
$$\Omega = (N_A + N_B - 1)!!$$

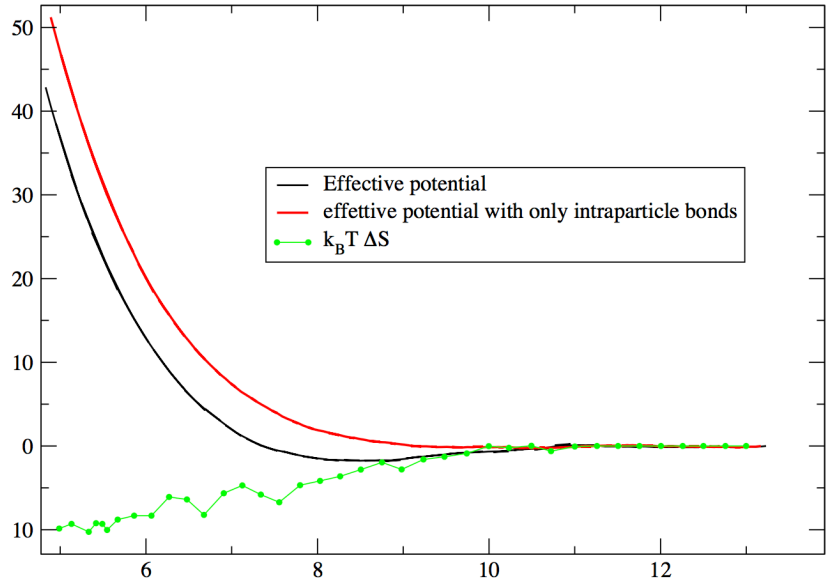


Then the change in entropy associated to converting *intraparticle* bonds with *interparticle* bonds is

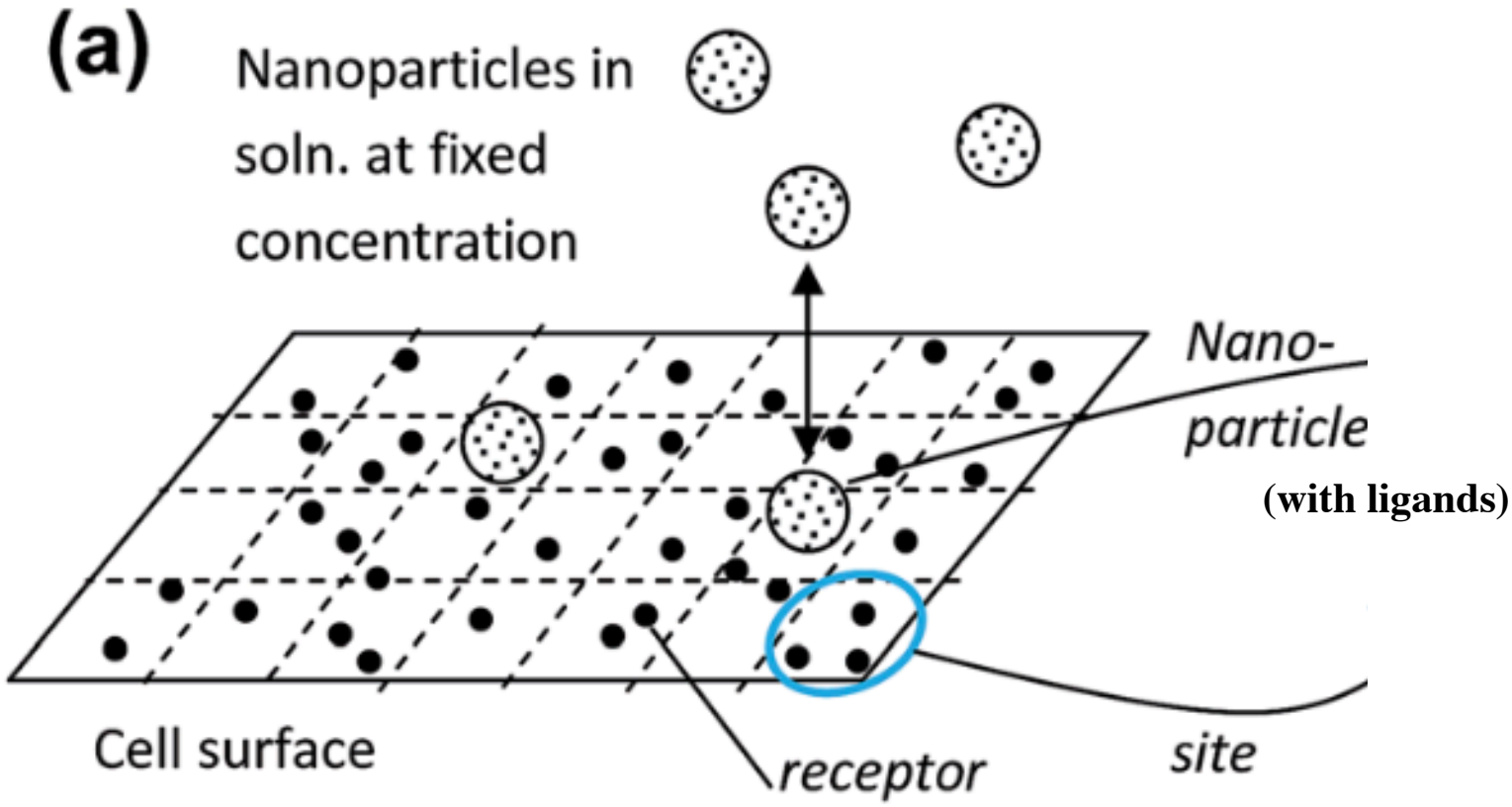
$$\frac{\Delta S}{k_B} = \ln[(N_A+N_B-1)!!] - \ln[(N_A-1)!!(N_B-1)!!] = \ln[(2N_A-1)!!] - 2\ln[(N_A-1)!!] \quad (1)$$

where we have used the fact that N_A=N_B.





Superselectivity



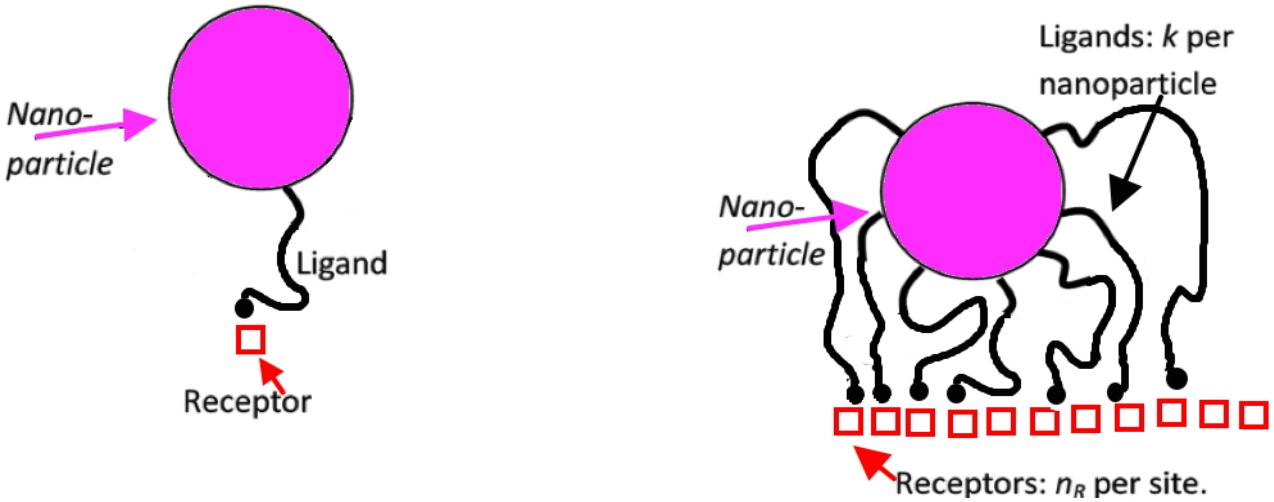
Designing super selectivity in multivalent nano-particle binding

Francisco J. Martinez-Veracoechea and Daan Frenkel[1]

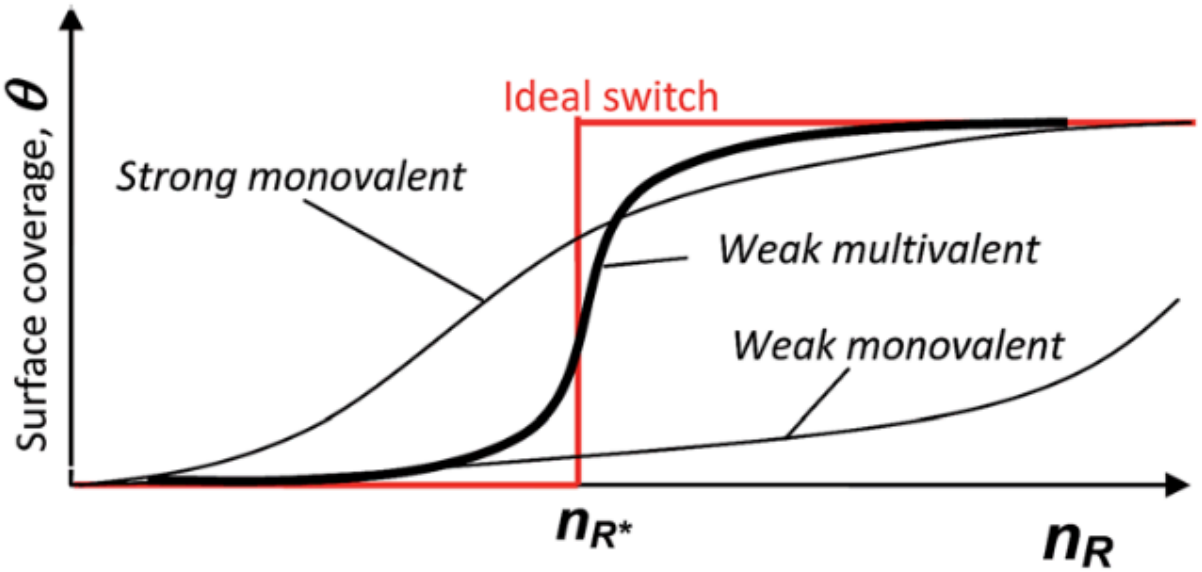
PNAS, 108 , 10963 (2011)

COLLDENSE COLLOIDS with DESIGNED RESPONSE

$$\mathcal{Z} = [Q_{unbound} + z \times Q_{bonded}]^{N_c}$$



(b)



$$\Omega(k, n_R, \#_b) = \frac{k!}{(k-\#_b)!(\#_b)!} \times \frac{n_R!}{(n_R-\#_b)!}$$

# of ways $\#_b$ element can be selected out of k

# of ways $\#_b$ bonds are distributed over n_R sites (first bond n_R ways, second bond n_R-1 ...)

$$Q(\#_b) = (e^{-\beta f_b})^{\#_b}\ \Omega(k, n_R, \#_b)$$

$$Q_{bonded} = \sum_{1}^{min(k,n_R)} Q_{\#_b} \qquad \text{if } n_R \gg k \quad Q_{bonded} = (1 + n_R e^{-\beta f_b})^k - 1$$

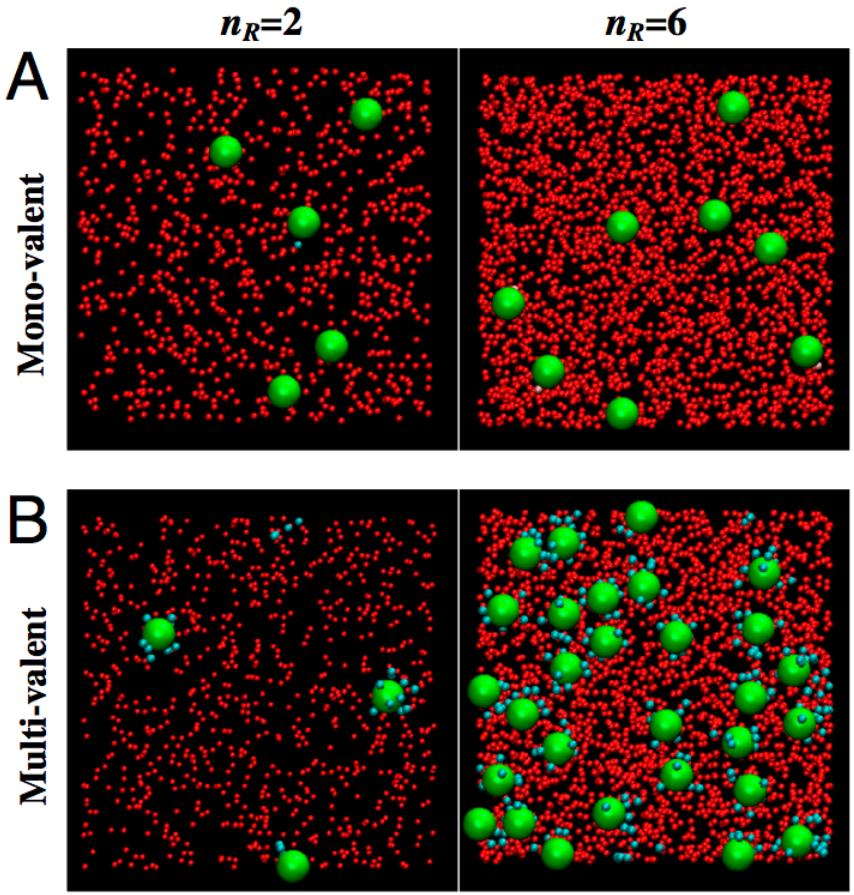


Fig. 1. Simulation snapshots comparing the targeting selectivity of monovalent and multivalent guest nano-particles. We compare the adsorption onto two host surfaces with receptor concentrations (n_R) that differ by a factor of three. (*A*) The monovalent guests provide little selectivity: increasing by three times the receptor coverage just increases the average number of bound guests by 1.8 (i.e., from 5.4 to 9.7 bound particles in average). (*B*) The multivalent nano-particles behave super selectively: an increase of three times in receptor coverage causes a 10-fold increase in the average number of adsorbed particles. (i.e., from 2.5 to 25.4 particles). The multivalent guests have ten ligands per particle. The individual bonds of the multivalent nano-particles are 5kT weaker than the monovalent ones.

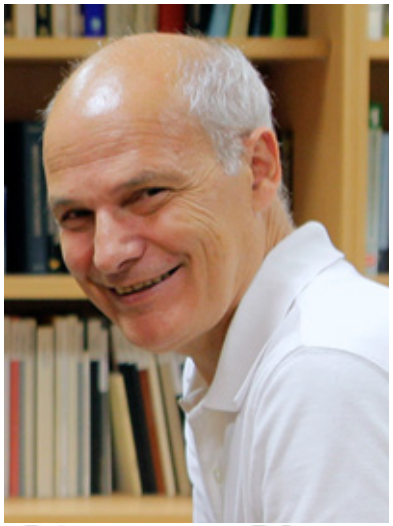
There is life in the ground state: vitrimers

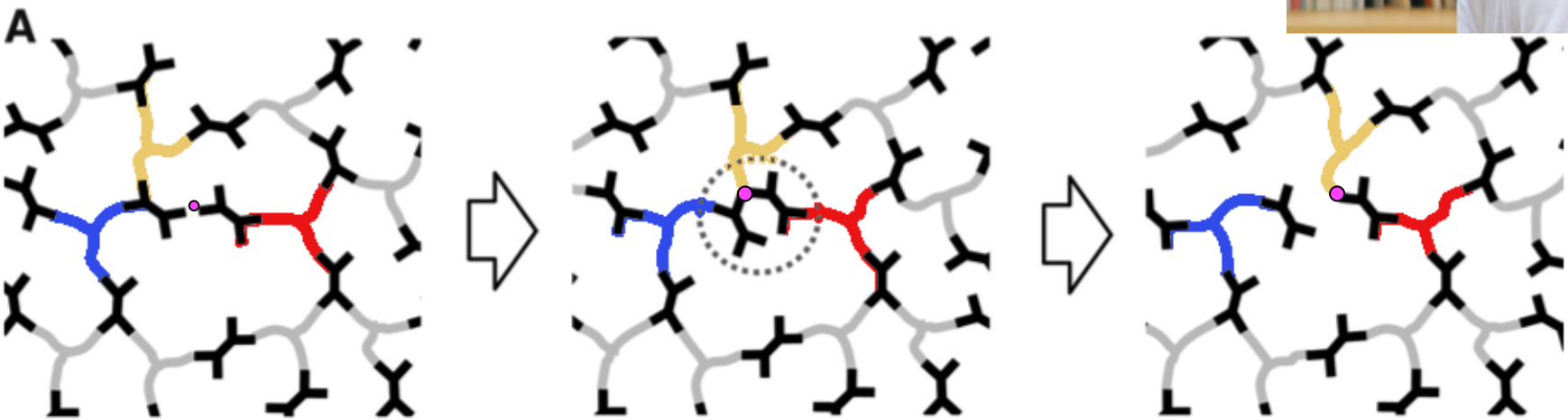
(entropy in action)

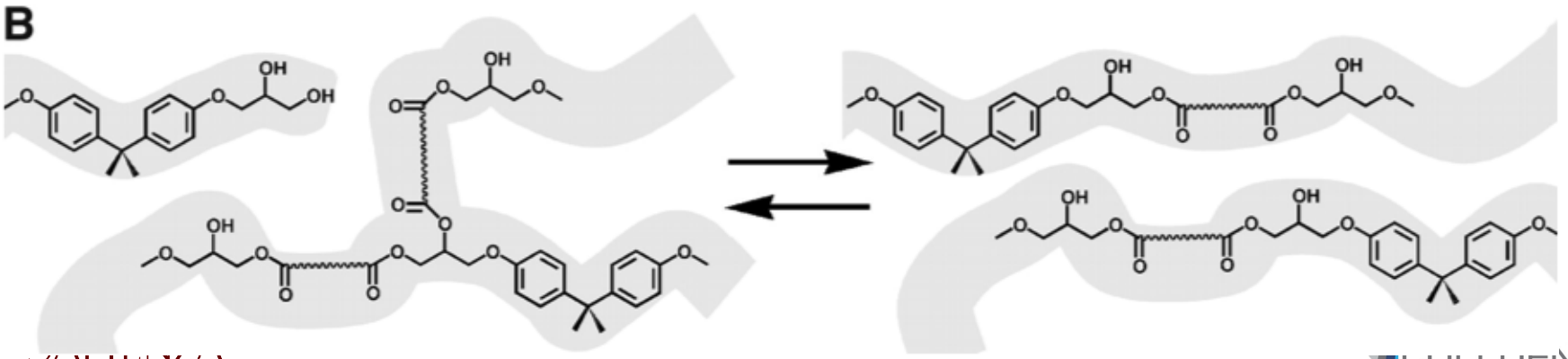
Science **334**, 965 (2011);
DOI: 10.1126/science.1212648

Silica-Like Malleable Materials from Permanent Organic Networks

Damien Montarnal, Mathieu Capelot, François Tournilhac, Ludwik Leibler*







Ludwik Leibler - Vitrimers – a new class of polymers - YouTube

https://www.youtube.com/watch?v=5tAOccD3o0I

Apr 21, 2015 - Uploaded by EPOfilms

More about exceptional inventors and the European Inventor Award here: http://buzz.mw/b1zgp_I European ...

From glass to vitrimers : a story of exchangeable links - YouTube

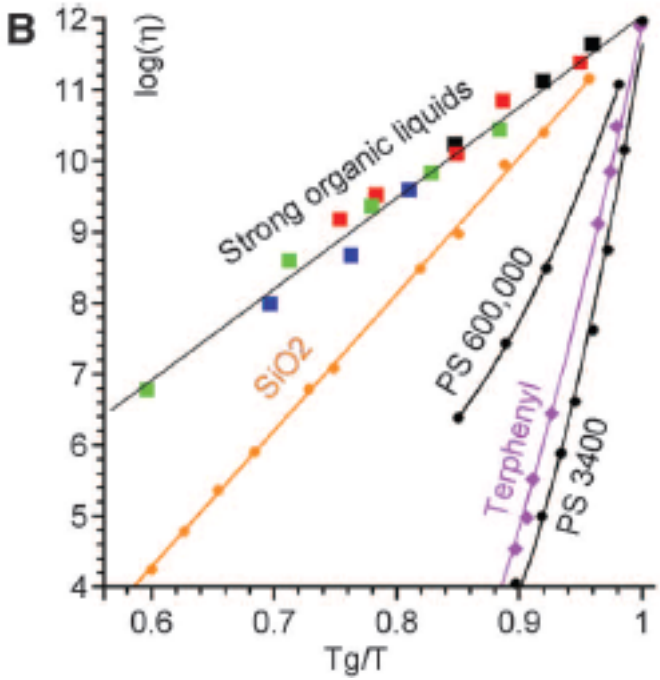
https://www.youtube.com/watch?v=cR_iiKrpCIQ

Nov 21, 2017 - Uploaded by Département de Physique de l'ENS

We use glass every day. But what is glass again? It is a solid phase... right? Ludwik Leibler (ESPCI) explains ...

Catalyst … Arrhenius Dynamics

“Strong glass former”



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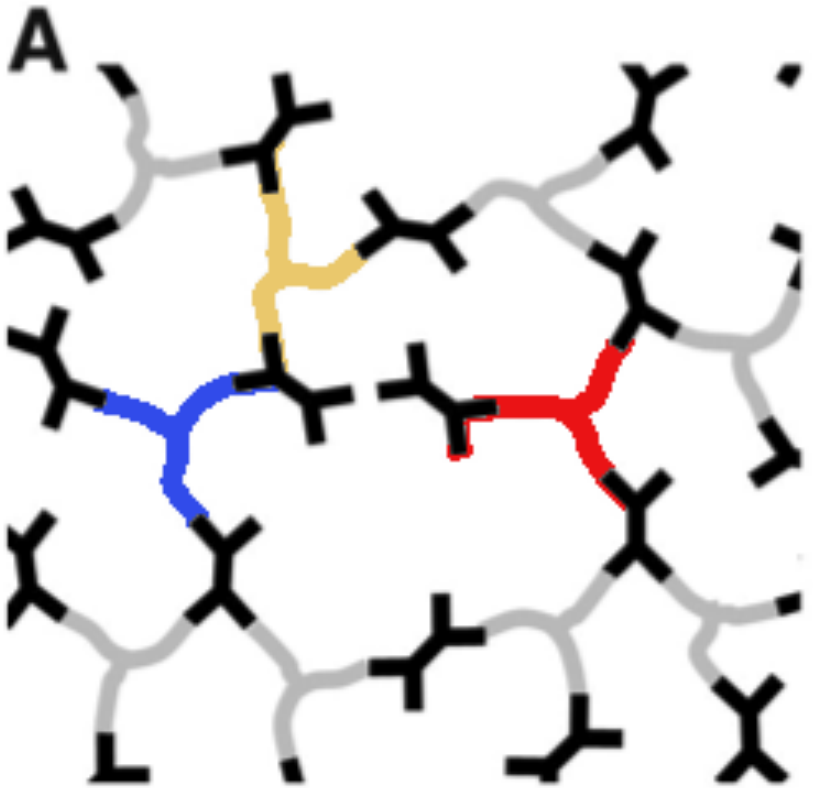
Connections to patchy particle

Network formed by a mixture of particles with valence f_1 and f_2 in non-stochiometric ratio in

which all possible bonds between particles of different type are present!

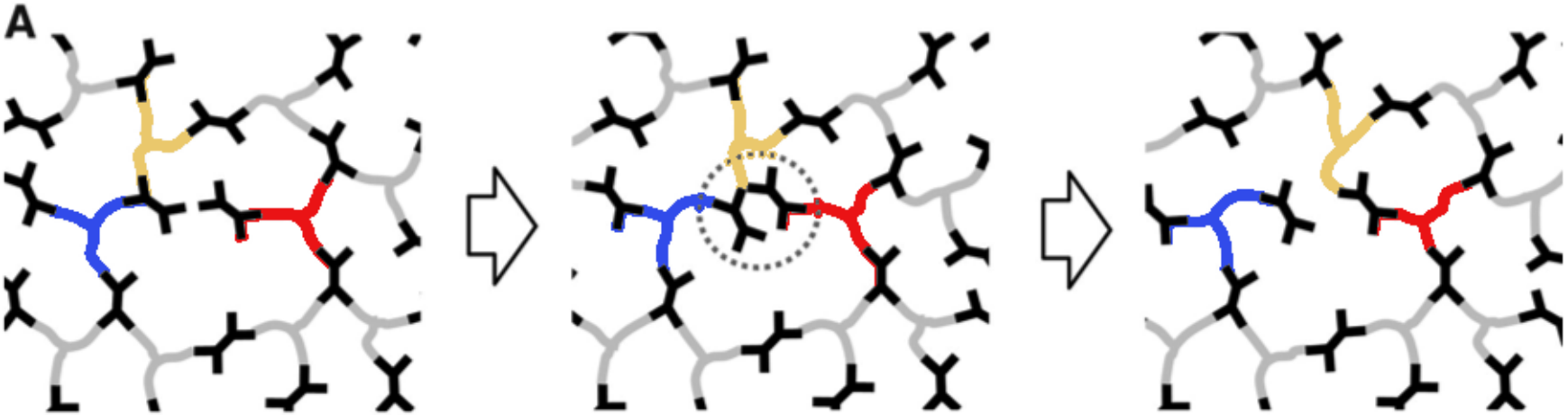


Where is T ? T=0 K !

What does it mean to switch ? Explore the different configurations of the ground state

There is life in the ground state !

The patchy model analog



Bonding volume and energy scale….

Wertheim theory: free energy

Using thermodynamic perturbation theory, we can approximate the (Helmholtz) free energy of the model system.

$$\beta F_{tot}/N = \beta f_{\text{bond}} + \beta f_{\text{HS}} + \beta f_{\text{mix}}$$

Free energy change as a result of forming bonds, in the limit of T going to zero (strong bonds):

$$f_{\text{bond}} = -\frac{T S_{\text{comb}}(4N_A, 2N_B)}{N} + \frac{n_b}{N}\left(-k_B T \log \frac{v_b(\rho)}{V} - \epsilon\right)$$

Combinatorial entropy term:

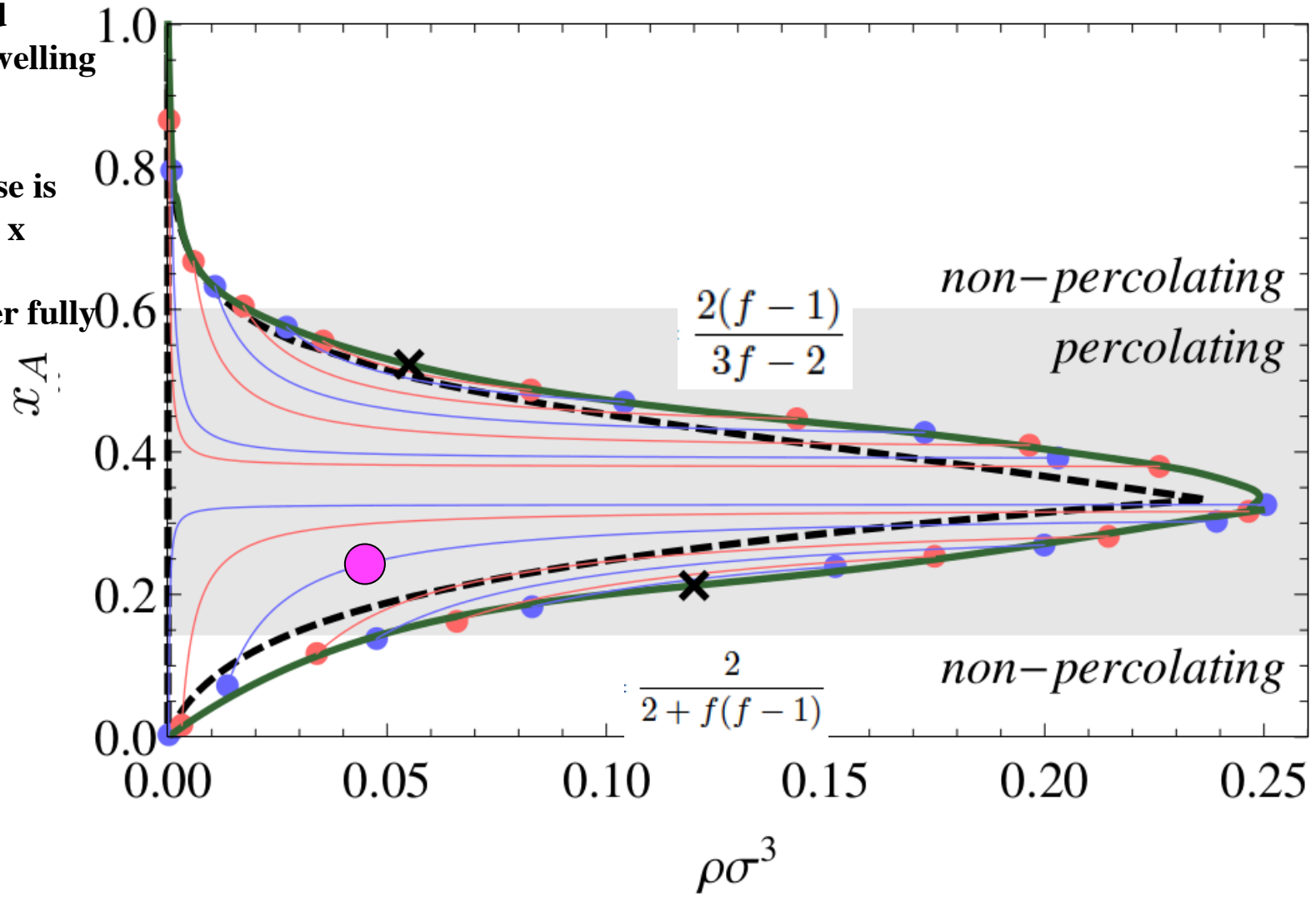
$$S_{\text{comb}}(n,m) = \begin{cases} k_B \log \frac{n!}{(n-m)!} & \text{if } n > m \\ k_B \log \frac{m!}{(m-n)!} & \text{otherwise} \end{cases}$$

T=0 K Equilibrium phase diagram (Entropy Only!)

Placing a vitrimer network in a good solvent leads to swelling

The network phase is closer to the ideal x

the network never fully dissolves



Theory: black dashed line
Simulations: points, solid line

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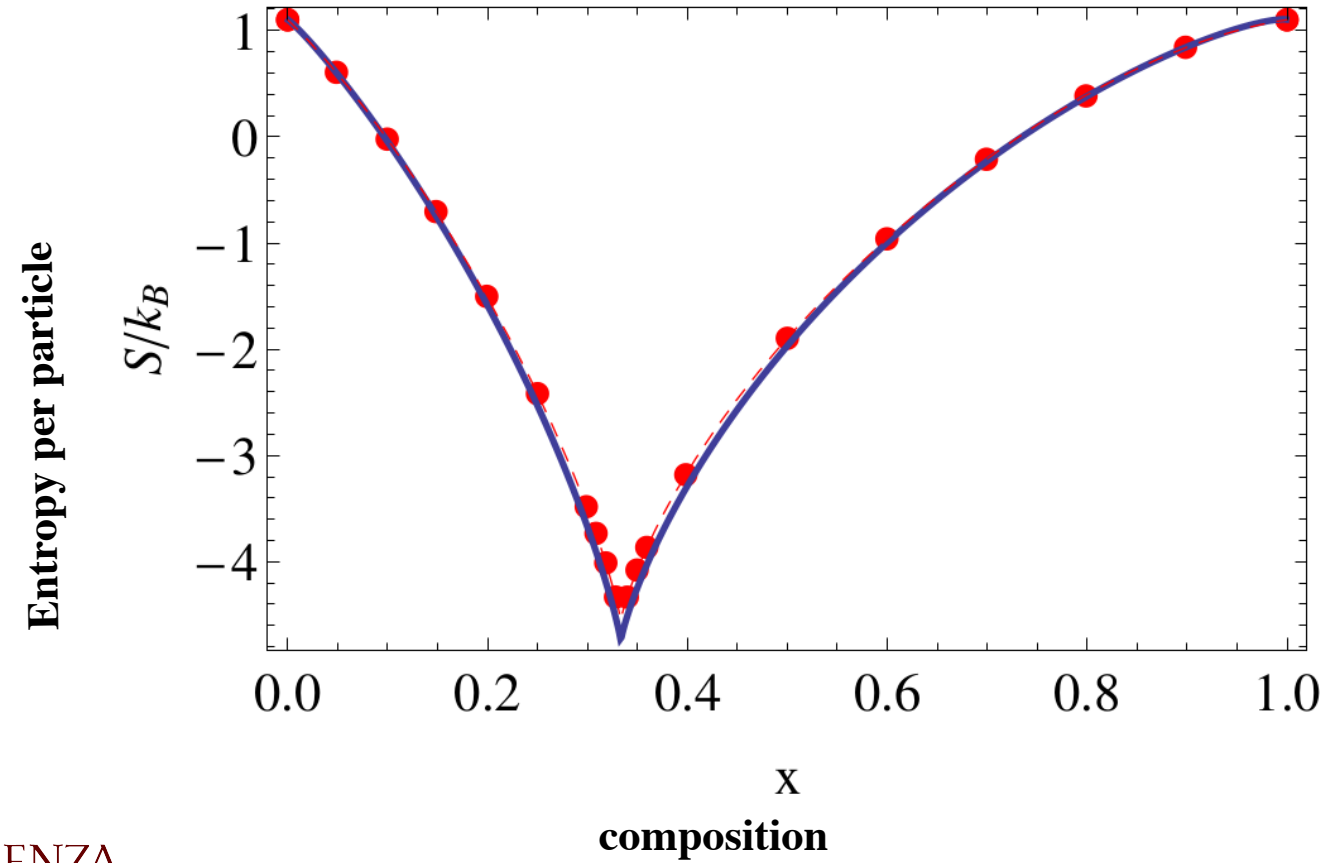
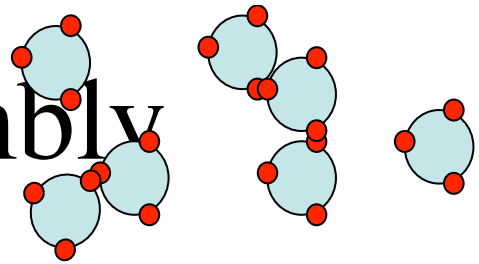
Entropy in Theory and Simulation: comparison

Comparison between the entropy from simulations (red) and theory (blue).

Number density $\rho\sigma^3 = 0.35$



Basic Concepts in Self Assembly



The canonical partition function a system composed by non-interacting clusters (ideal gas of cluster) composed each by n monomers, in the NVT ensemble (where N is the total number of monomers) is

$$Q = \prod_{n=1}^{\infty} \frac{Q_n^{N_n}}{N_n!} \tag{1}$$

where Q_n is the partition function of the n-cluster and N_n is the number of clusters of size n in the system. For spherical particles interacting with isotropic potentials

$$Q_n = \frac{1}{n!\lambda^{3n}} \int' d\vec{r}_1 .... d\vec{r}_N \exp\left[-\beta V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)\right] \tag{2}$$

where the $'$ sign in the integration limits indicates that only points in phase space $d\vec{r}_1 .... d\vec{r}_N$ for which the cluster does not break into disconnected smaller clusters should be considered.

Dimer partition function

$$Q_2 = \frac{1}{2!\Lambda^6} \int' d\mathbf{r_1} d\mathbf{r_2} d\Omega_1 d\Omega_2 e^{-\beta V(\mathbf{r_1},\mathbf{r_2},\Omega_1,\Omega_2)} / \int d\Omega_1 d\Omega_2$$

$$= V\ V_b\ e^{-\beta u_0}$$

For the monomer (assumed as a spherical rigid body, e.g. no internal fluctuations)

$$Q_1 = \frac{V}{\lambda^3}$$

The Helmholtz free energy F, the logarithm of the partition function Q, is given by

$$\beta F = -\ln Q = -\sum_{n=1}^{\infty}[N_n \ln Q_n - N_n \ln N_n + N_n] = \sum_{n=1}^{\infty} N_n[\ln Q_n - \ln N_n + 1] \tag{3}$$

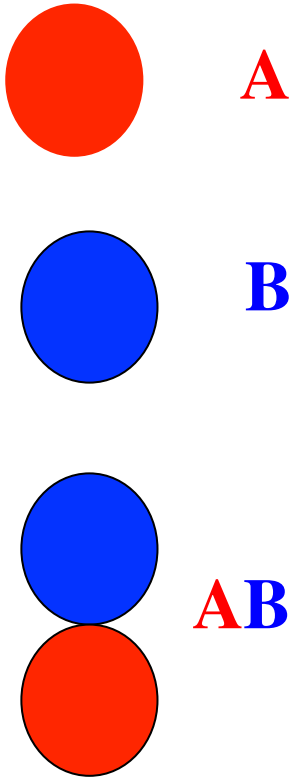
To evaluate the cluster size distribution N_n, we require F to be a minimum respect to all possible variation of N_n. Still, we must satisfy the constraint $\sum_n nN_n = N$. Introducing a Lagrange multiplier α

$$\frac{\partial(\beta F + \alpha \sum_k kN_k)}{\partial N_n} = 0 \qquad \ln \frac{N_n}{Q_n} - n\alpha = 0 \;\text{ or }\; N_n = Q_n(\exp\alpha)^n \tag{4}$$

Since $N_1 = Q_1 \exp\alpha$, the same expression can be written as

$$N_n = Q_n \frac{N_1^n}{Q_1^n} = Q_n \rho_1^n \quad (\Lambda^3 = 1) \tag{5}$$

1 A-B dimerization process



Three cluster types: A, B and AB. Assuming for simplicity $N_A^0 = N_B^0 = N^0/2$ and $Q_A = Q_B = V$ ($\lambda = 1$) the constraints are

$$N_A + N_{AB} = N_A^0 = \frac{N^0}{2} \qquad N_B + N_{AB} = N_B^0 = \frac{N^0}{2}$$

The total partition function Q is

$$Q = \frac{Q_A^{N_A}}{N_A!}\frac{Q_B^{N_B}}{N_B!}\frac{Q_{AB}^{N_{AB}}}{N_{AB}!}$$

Minimizing βF respect to N_A, N_B and N_{AB} (Lagrange multiplier α e β),

$$\ln Q_A - \ln N_A + \ln\alpha = 0 \quad \ln Q_B - \ln N_B + \ln\beta = 0 \quad \ln Q_{AB} - \ln N_{AB} + \ln\alpha + \ln\beta = 0$$

$$\text{or} \quad N_A = \alpha Q_A \qquad N_B = \beta Q_B \qquad N_{AB} = \alpha\beta Q_{AB}$$

Then

$$N_{AB} = \left(\frac{N_A}{Q_A}\right)^2 Q_{AB} \quad \text{or} \quad N_A = \sqrt{\frac{N_{AB}Q_A^2}{Q_{AB}}}$$

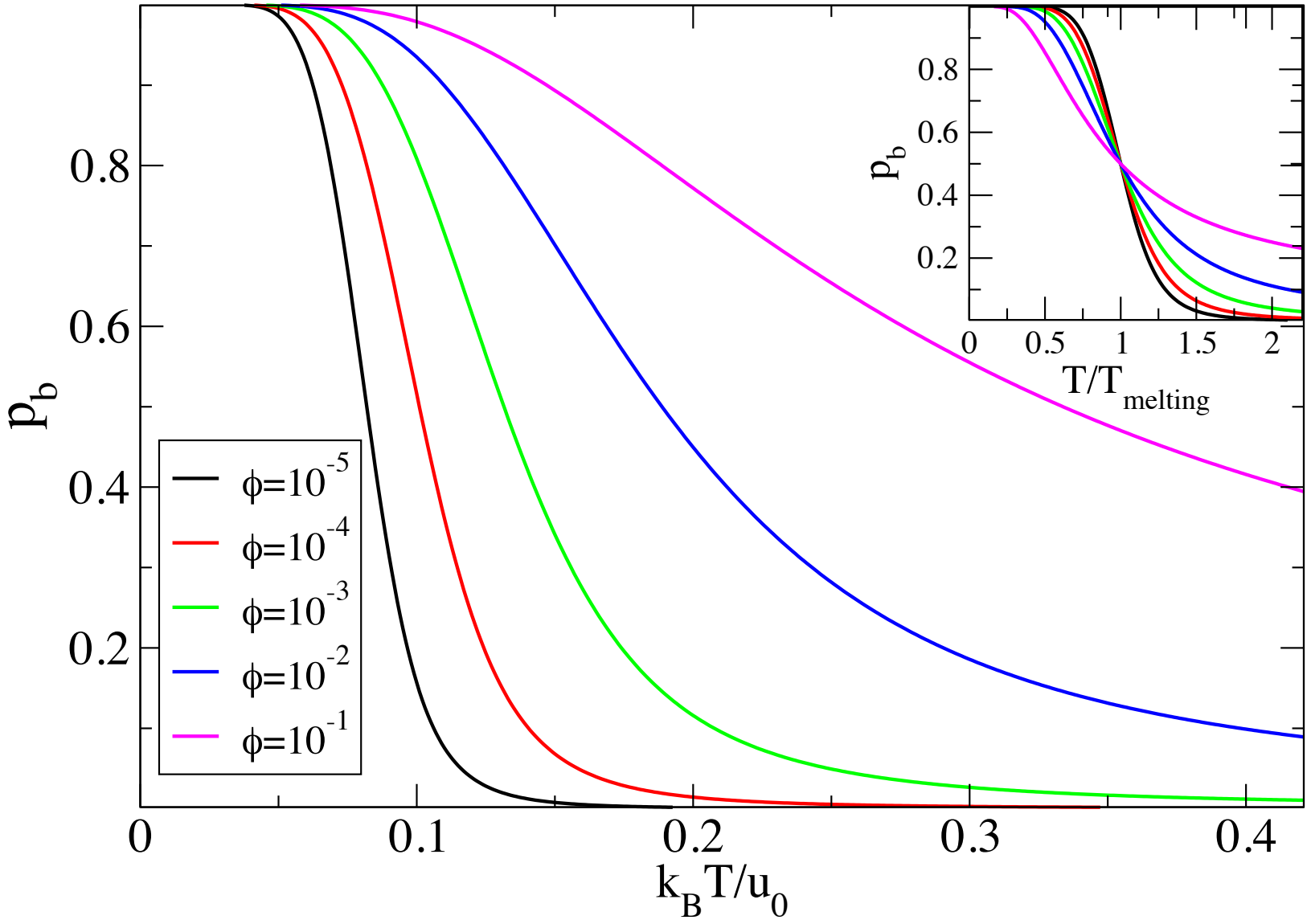
Defining the bond probability $p_B = \frac{N_{AB}}{N_0/2}$, the constraint expression

$$\sqrt{\frac{N_{AB}Q_A^2}{Q_{AB}}} + N_{AB} = \frac{N^0}{2} \quad \text{becomes} \quad \sqrt{\frac{2p_bQ_A^2}{N_0Q_{AB}}} = 1 - p_b \quad \text{or} \quad \frac{p_b}{(1-p_b)^2} = \frac{Q_{AB}}{Q_A^2}\frac{N_0}{2} =$$

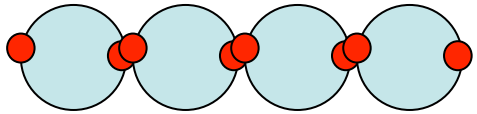
$$\text{with} \quad Q_{AB} = V\, V_b\, e^{-\beta u_0} \quad \rightarrow \quad \frac{p_b}{(1-p_b)^2} = \frac{N_0 V_b}{2V} e^{-\beta u_0}$$

Remember Pine's argument on the lock and key

$$\frac{p_b}{(1-p_b)^2} = \frac{N_0 V_b}{2V} e^{-\beta u_0} = \phi e^{-\beta u_0} = e^{\frac{\Delta S}{k_B}} e^{-\beta u_0}$$



One more example: equilibrium polymers



Let's assume we have N bifunctional particles which can form P bonds in a volume V. The particles will form chains of length n. We are interested in predicting the distribution N_n of chain lengths. There are two constraints to be satisfied by N_n:

$$\sum_{n=1}^{\infty} nN_n = N \qquad \sum_{n=1}^{\infty}(n-1)N_n = P = N - N_c \quad \text{where} \quad \sum_{n=1}^{\infty} N_n = N_c$$

In the approximation of an ideal gas of aggregates (e.g. neglecting aggregate-aggregate interactions) the free energy is the ideal gas entropy (with the thermal wavelength λ set to 1)

$$\beta F = -\frac{S}{k_B} = \sum_{n=1}^{\infty} N_n \left\{ \ln \frac{N_n}{V} - 1 \right\}$$

To calculate N_n we need to maximise S (but satisfying the constraints).

Defining α and β the Lagrange multiplier associated to the two constraints we have

$$\frac{dS}{dN_n} = \left(\ln \frac{N_n}{V} - 1\right) + 1 + \alpha n + \beta(n+1)$$

$$\frac{N_n}{V} = \exp[(\alpha+\beta)n + \beta] \qquad N_n = Ax^n$$

To calculate α and β (or equivalently A and x) we use the constraints

$$N = \sum_{n=1}^{\infty} nAx^n = A\frac{x}{(1-x)^2} \qquad N_c = \sum_{n=1}^{\infty} Ax^n = A\frac{x}{1-x}$$

providing

$$x = 1 - \frac{N_c}{N} \qquad A = N\frac{(\frac{N_c}{N})^2}{1-\frac{N_c}{N}}$$

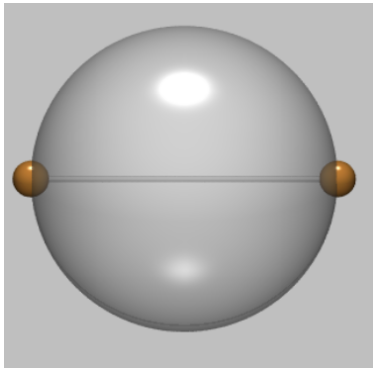
Defining

$$p_b = \frac{N_{bonds}}{N_{maxbonds}} = \frac{N - N_c}{N} = 1 - \frac{N_c}{N} \qquad < L >= \frac{N}{N_c} = \frac{1}{1-p_b}$$

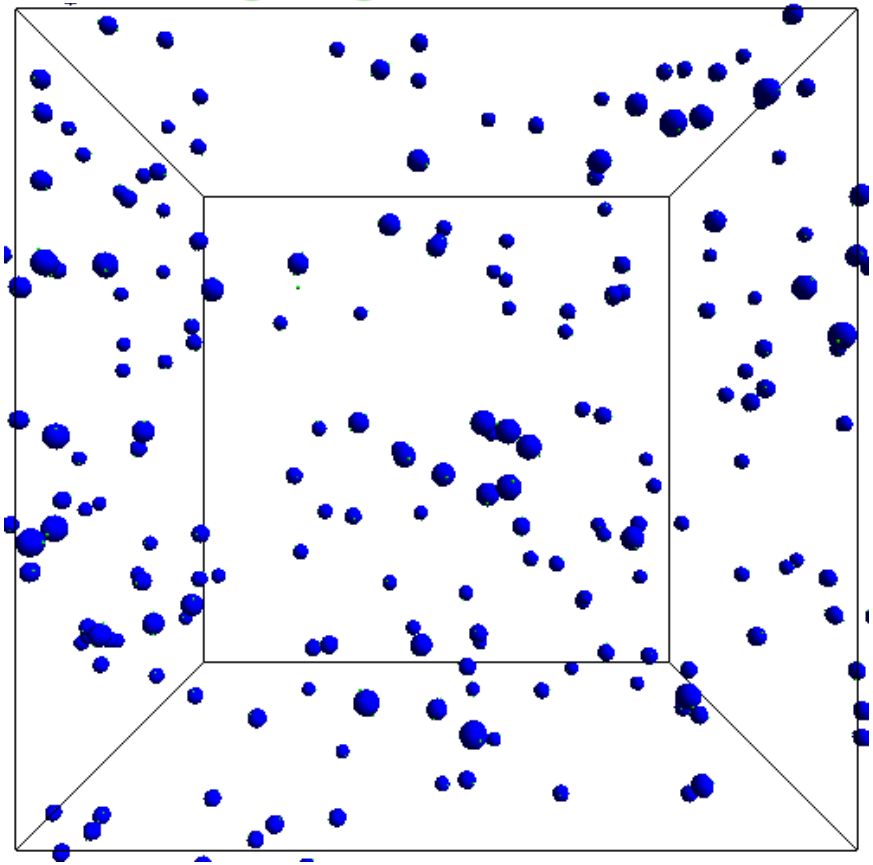
$$N_n = N(1-p_b)^2 p_b^{n-1}$$

Equilibrium chains

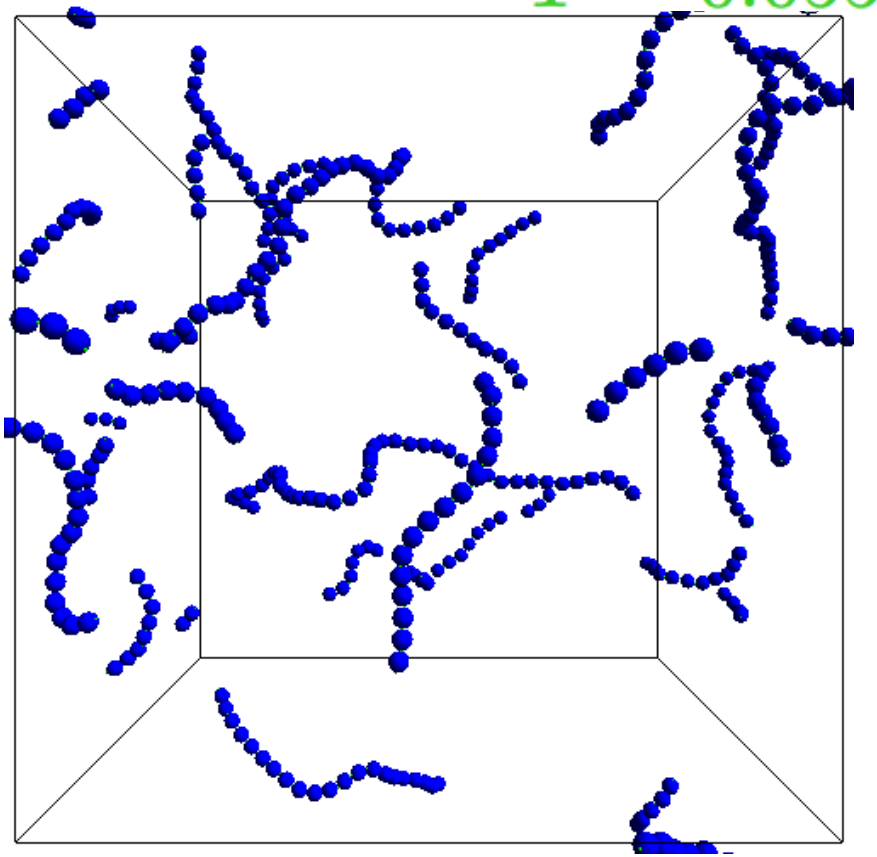
f=2



$T = 0.10$



$T = 0.055$



$\rho = 0.0035$

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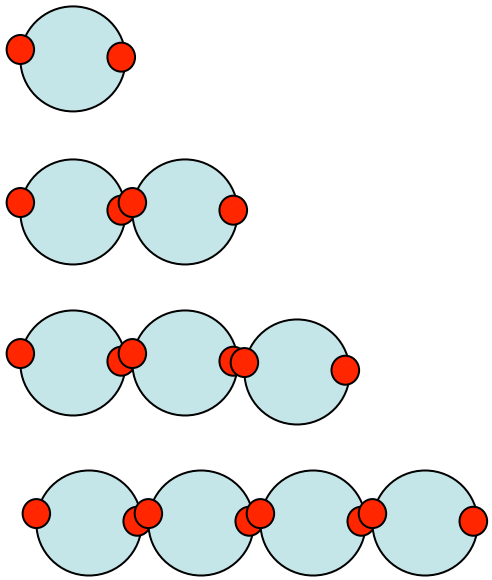
COLLDENSE
COLLOIDS with DESIGNED RESPONSE

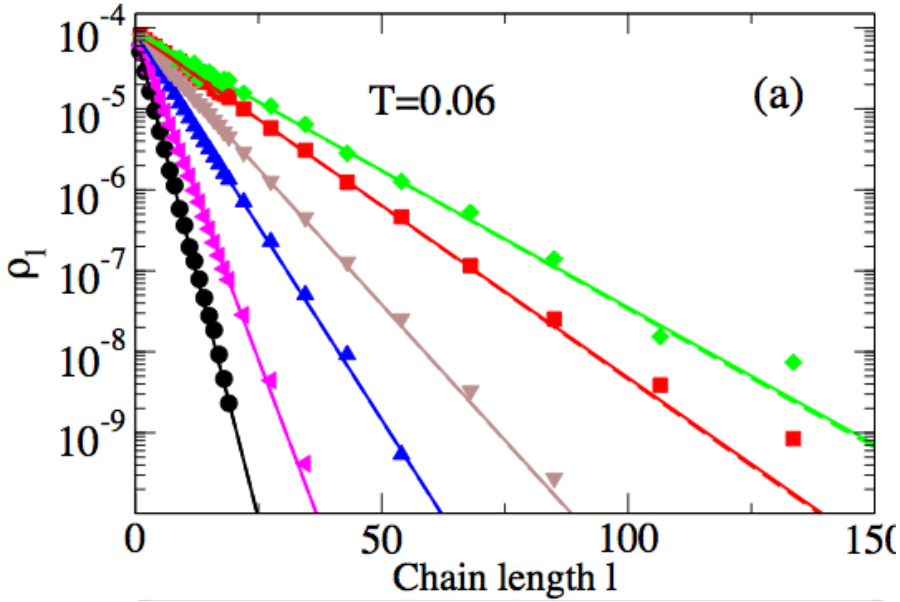


$$(1-p_b)^2$$

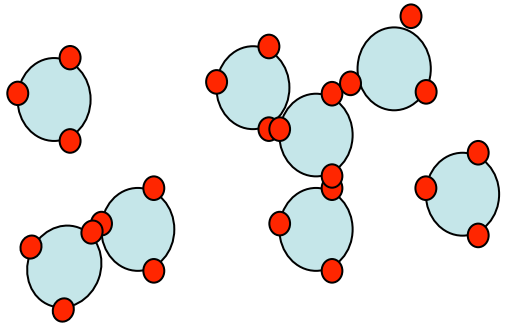
$$p_b(1-p_b)^2$$

$$p_b^2(1-p_b)^2$$

$$p_b^3(1-p_b)^2$$



Generalization to branching



$$p_b = \frac{N_b}{N_b^{max}}$$

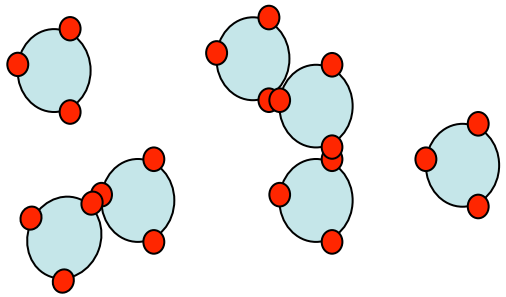
To "understand" self-assembly in these systems means:

A) To formulate a theory to calculate $p_b(\rho, T)$ **Thermodynamics**

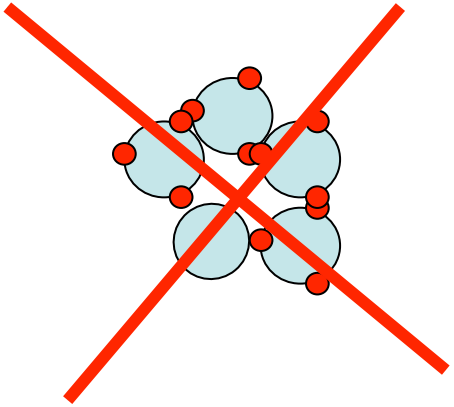
B) To formulate a theory to calculate the cluster size distribution N_n knowing p_b **Geometric properties**

Assume we have N particles with functionaly f

Assume there are N_b bonds between the particles



$$p_b = \frac{N_b}{(fN)/2}$$



What is the cluster size distribution ?

How do particle self − assemble into clusters ?

Solution exists for loop-less clusters (Stockmayer JCP 11, 45 1943)

Review of Stockmayer approach:

Let's call N_n the number of loopless clusters composed of n particles

$$\sum nN_n = N$$

The total number of clusters is $N_c = \sum N_n$

Fixing N and N_c (or equivalently N and p_b)

which is the MOST PROBABLE distribution N_n ?

We need to find the N_n which maximize the number of modes to connect with N_b bonds N $f-$functionalized particles

How to estimate the number of modes Ω

Let's call ω_n the number of modes of a cluster of size n

Since particles are identical we have to divide ω_n by $n!$

If there are N_n clusters of size n the number of modes becomes

$$\left(\frac{\omega_n}{n!}\right)^{N_n}$$

A further division by $N_n!$ accounts for permutations of clusters of the same size

As a result

$$\Omega = \prod_n \left(\frac{\omega_n}{n!}\right)^{N_n} \frac{1}{N_n!}$$

Find the cluster size distribution which maximize the **entropy** satisfying the two constraints:

$$\sum nN_n = N \qquad \sum N_n = N_c$$

$$y = \log(\Omega) + \log(A)\sum nN_n + \log(B)\sum N_n$$

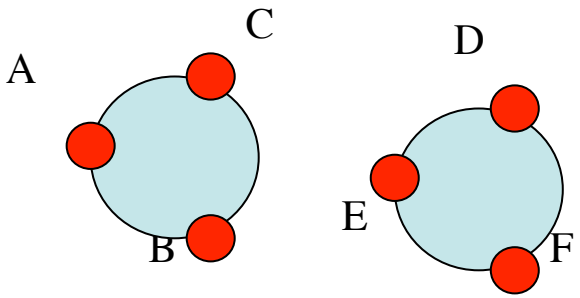
With A and B Lagrange multipliers

$$\frac{\partial y}{\partial N_n} = 0$$

$$\log\left(\frac{\omega_n}{n!}\right) + n\log(A) + \log(B) - \log(N_n) = 0$$

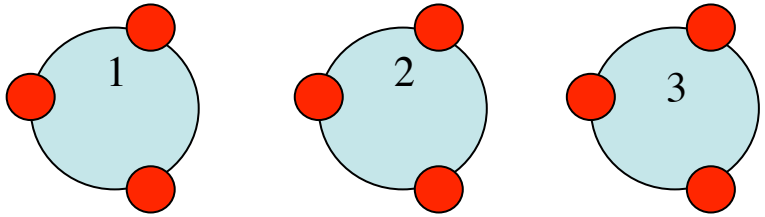
$$N_n = \frac{\omega_n}{n!}A^n B$$

$$f = 3, N = 2, \omega_2 = 9$$



AD,AE,AF, BD,BE,BF, CD,CE,CF

$$f = 3, N = 3, \omega_3 = 162$$



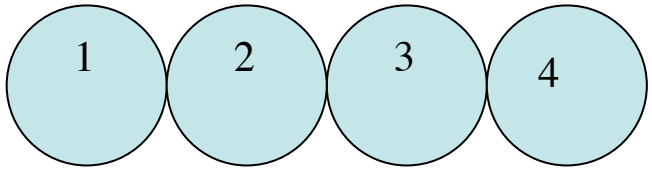
3 different dimers (12,13,23) each of them made in 9 ways, times 4x3 ways to mix a dimer with the remaining monomer, divided by two to avoid overcounting

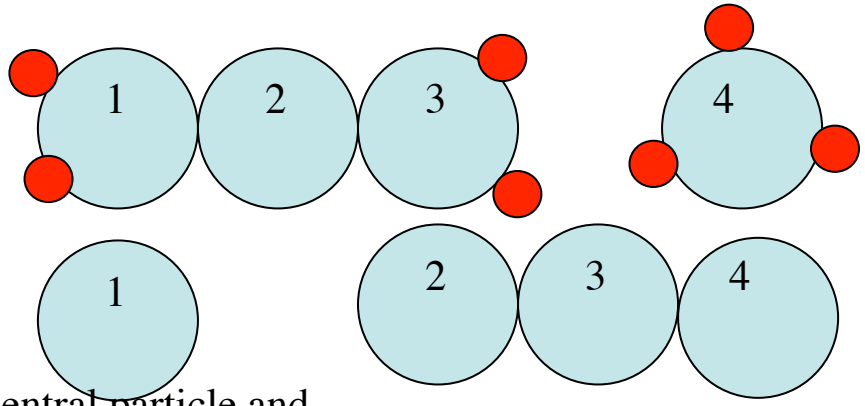
3x9x4x3/2=162

$f = 3, N = 4, \omega_4 = 4536$

4 different trimers (123,124,134,234),each of them made in 162 ways. Separating the linear and the star configurations one gets:

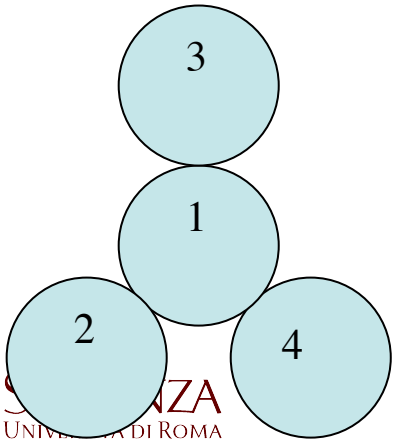
Linear configurations: times 4x3 (bonds, 4 on the trimer and 3 on the monomer) ways divided by two to avoid overcounting: 4 x 162 x 4 x 3 / 2 = 3888

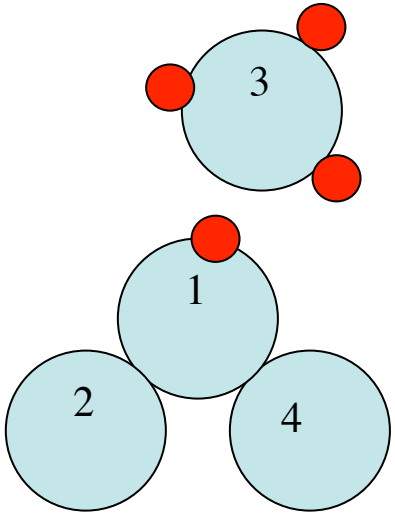


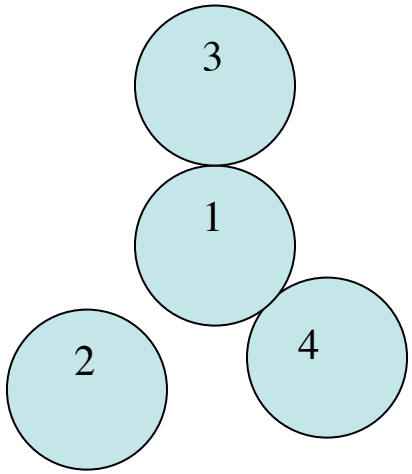


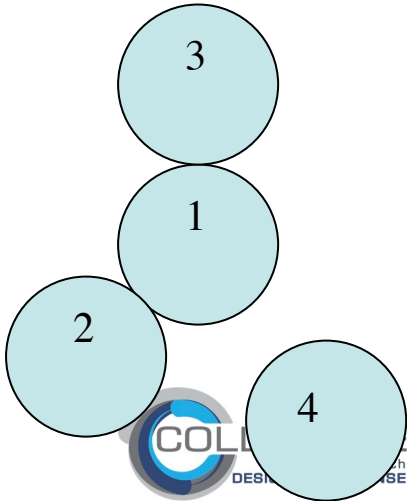
Star configuration: times 1x3 (bonds, 1 on the central particle and 3 on the monome) divided by three to avoid overcounting

4 x 162 x 1 x 3 / 3 = 648.









APPENDIX

A. Combinatory problems

1. We seek w_n, defined as the number of ways in which n distinguishable polyfunctional units, each bearing f distinguishable equivalent functional groups capable of reacting with each other, can be formed into a single polymeric molecule containing no cyclic structures.

To permit visualization, a unit can be represented as a mechanical frame containing f holes. We shall represent the polymeric molecule by introducing a number of indistinguishable bolts to connect the frames. Since an n-mer requires $(n-1)$ bonds, $(n-1)$ bolts are required to connect the frames, each bolt passing through a pair of holes belonging to different frames. In addition, we shall place bolts through each of the other holes, these not serving to connect different frames with each other. The total number of bolts required to accomplish this structure is, therefore,

$$fn-(n-1)=fn-n+1.$$

Now consider a particular bolted arrangement, corresponding to one of the w_n ways of forming an n-mer. We wish to dissociate it into n separate frames, each containing $(f-1)$ holes filled by bolts and one empty hole, with one free bolt left over. If the free bolt is chosen first, the empty hole in each of the n frames is thereby uniquely determined. Since any one of the $(fn-n+1)$ bolts may be chosen to be the free one, there are consequently $(fn-n+1)$ different dissociated arrangements of the required type corresponding to the same bolted arrangement. Therefore, if P is the number of different dissociated arrangements of this type which are possible, and if Q is the number of ways in which each such dissociated arrangement can be bolted together, the number of different bolted arrangements is

$$w_n=PQ/(fn-n+1). \tag{A1}$$

Now the number P is simply

$$P=f^n, \tag{A2}$$

since any one of the f holes on a frame may be chosen as the empty one, and since the bolts are indistinguishable. To find Q, we introduce the device of assigning a washer to each bolt which is ultimately to be used in forming a bond by passing through two holes. The washers are indistinguishable. The $(n-1)$ bolts which must receive washers may, therefore, be selected in

$$\frac{(fn-n+1)!}{(n-1)!(fn-2n+2)!} \text{ ways,}$$

How to calculate ω_n ? (Appendix A of JCP 11,45)

since each of the $(fn-n+1)$ bolts is now distinguishable by virtue of its having been assigned to a definite hole in forming a dissociated arrangement. The dissociated arrangement must now be bolted together. Washered bolts are chosen and placed through empty holes not on frames with which they are already connected, the free bolt always being kept for the last. Thus the first washered bolt can choose any of $(n-1)$ empty holes, for it must not pass through the empty hole on its own frame. Then there are still $(n-2)$ single frames and one "double frame," or altogether $(n-1)$ structures each still carrying one empty hole. Thus the second washered bolt can choose any of $(n-2)$ empty holes, the third can choose $(n-3)$, and so on. Finally, only the free bolt remains. If the free bolt has no washer, there remains just one empty hole into which it must go. If the free bolt has a washer, there remain two structures, each containing one empty hole, so that the free bolt serves to form the last bond. Hence for a given assignment of the washers the bolting process can be accomplished in $(n-1)!$ ways. Combining this result with the number of ways of assigning the washers, we find the number of ways of bolting together a given dissociated arrangement to be

$$Q=\frac{(fn-n+1)!}{(fn-2n+2)!}. \tag{A3}$$

Substitution of Eqs. (A2) and (A3) into (A1) then yields the desired result

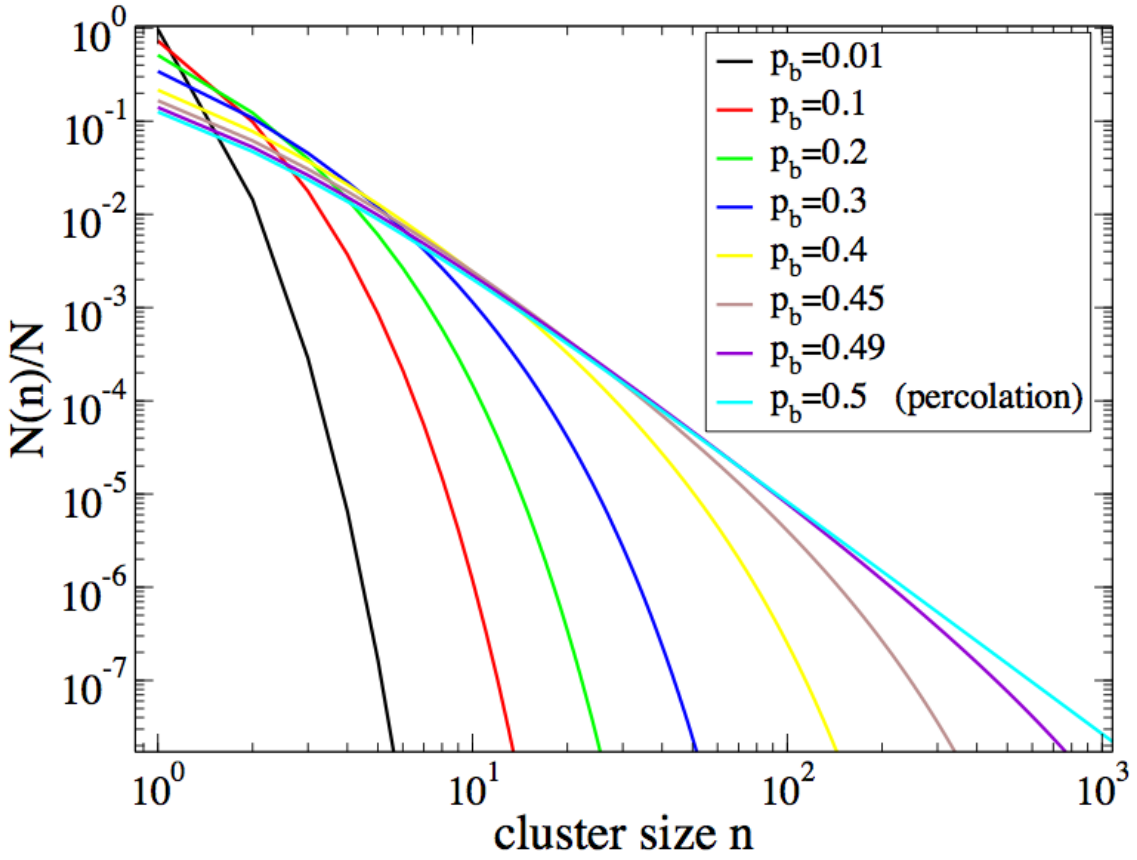
$$w_n=\frac{f^n(fn-n)!}{(fn-2n+2)!}. \tag{A4}$$

$$\omega_n = \frac{f^n(fn-n)!}{(fn-2n+2)!}$$

Performing the sums… one finds $0 < p_b < \frac{1}{f-1}$

$$N_n = N \frac{f(fn-n)!}{n!(fn-2n+2)!}(1-p_b)^f \left[p_b(1-p_b)^{f-2}\right]^{n-1}$$

f=3

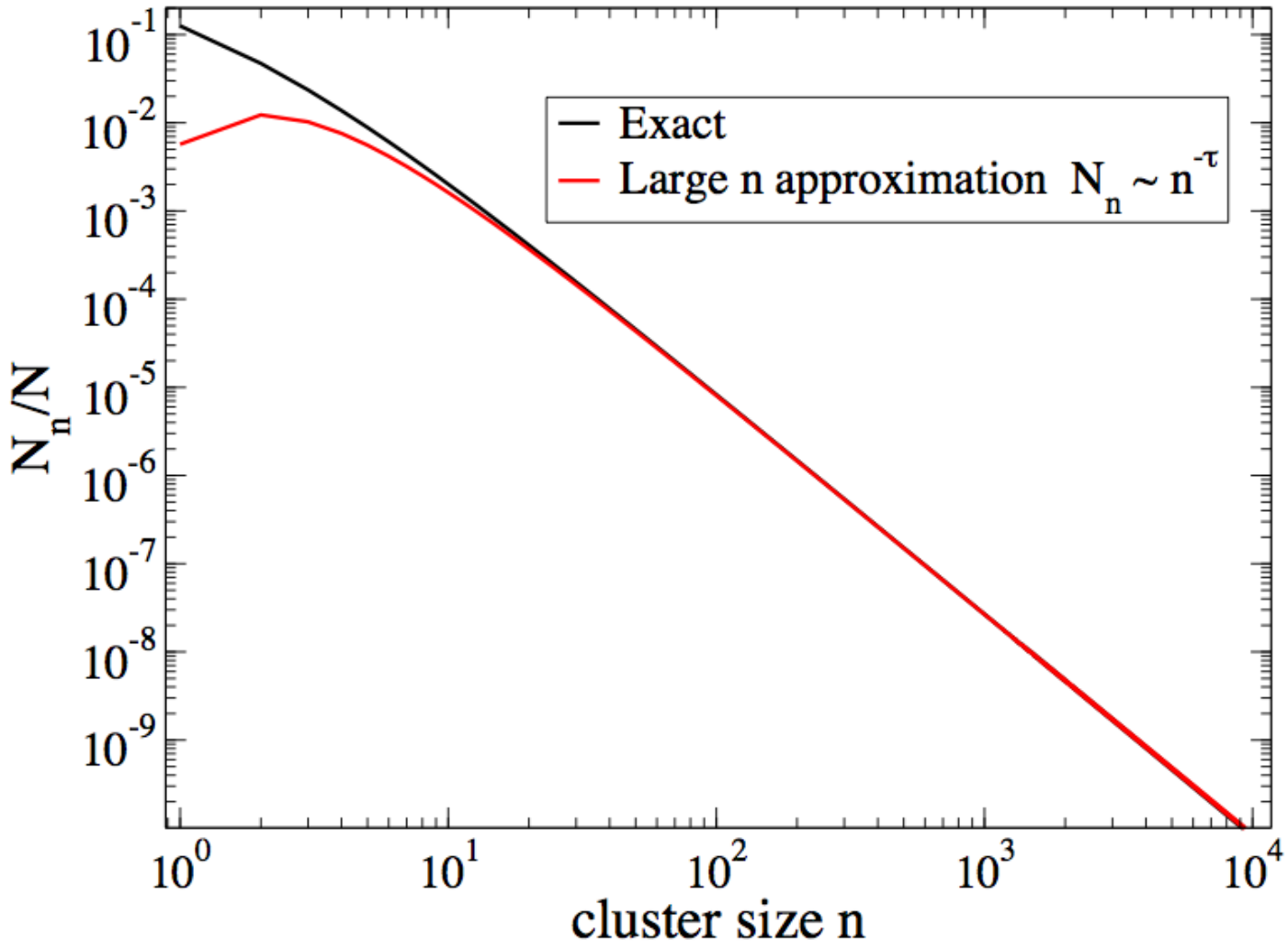


Increase of the polydispersity on increasing p_b

Cluster size distribution at percolation

$$N_n(p = p_b) \cong \frac{f}{\sqrt{2\pi(f-2)(f-1)}} e^{-5/[(f-2)n]} \quad n^{-2.5}$$

Critical behavior - power law dependence - critical exponent -2.5



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Absence of a characteristic size !!!

COLLDENSE
COLLOIDS with DESIGNED RESPONSE

When energy and entropy compete for self-assembly

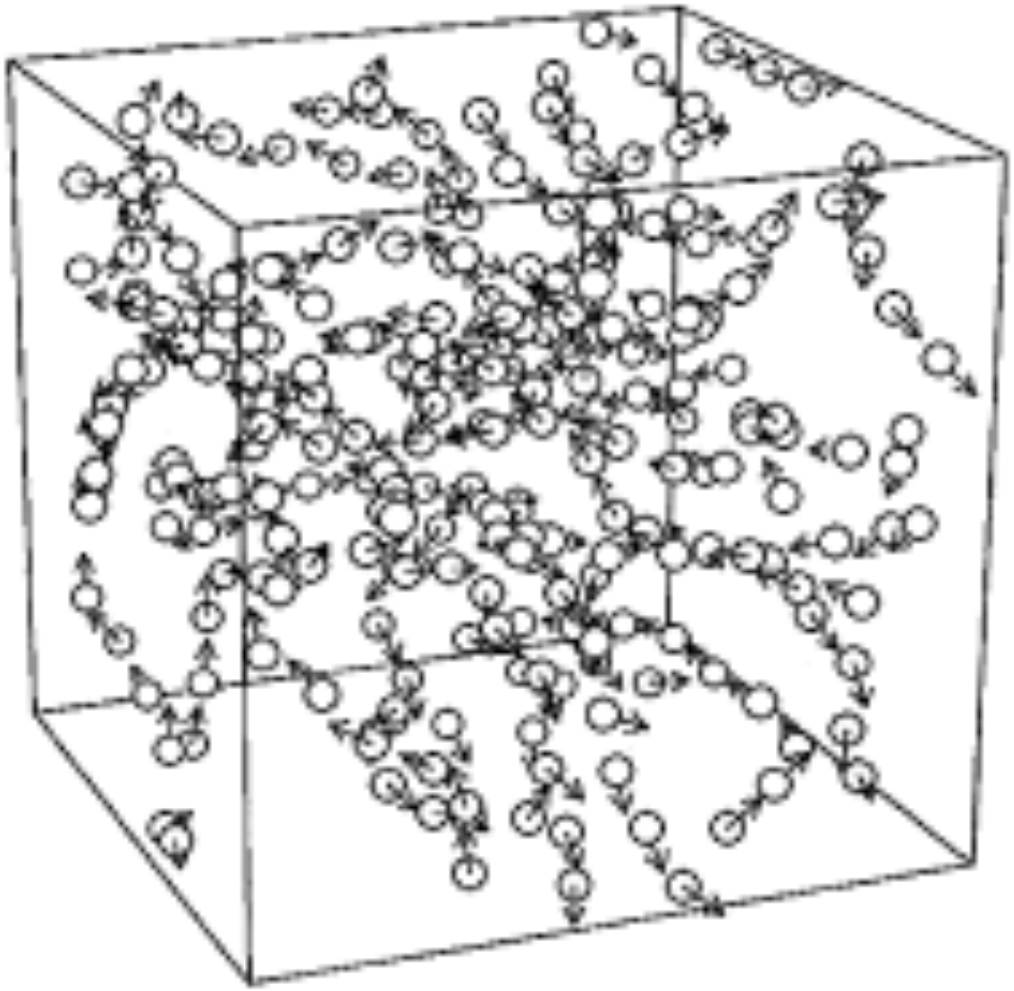
DHS+Patchy Colloids

Janus Particles

Gel on heating

Dipolar Hard Spheres…

Camp et al PRL (2000)



Tlusty-Safram, Science (2000)

We distinguish the particles in three groups: chains, chain ends, branching. Defining $\psi(\mathbf{r})$ the probability that there is an end in $\mathbf{r}$, then in mean field

$$\rho_{end} \sim \psi$$

$$\rho_{chain} \sim \phi \sim \psi^2$$

$$\rho_{branching} \sim \psi^3$$

Assuming that branching and ends are the key actors, whose concentration is fixed by the thermodynamic, one can assume that each of these defects contributes about $-k_BT$ to the free energy density.

Then

$$\beta f = \frac{\beta F}{V} = -(\rho_{end} + \rho_{branching}) + \frac{1}{2}\phi^2$$

where the last term account for the excluded volume at virial level.

The EOS is given by

$$\beta P = -\frac{\partial \beta F}{\partial V} = -\phi^2 \frac{\partial(\beta f/\phi)}{\partial \phi} = \frac{1}{2}(\rho_{end} - \rho_{branching}) + \frac{1}{2}\phi^2$$

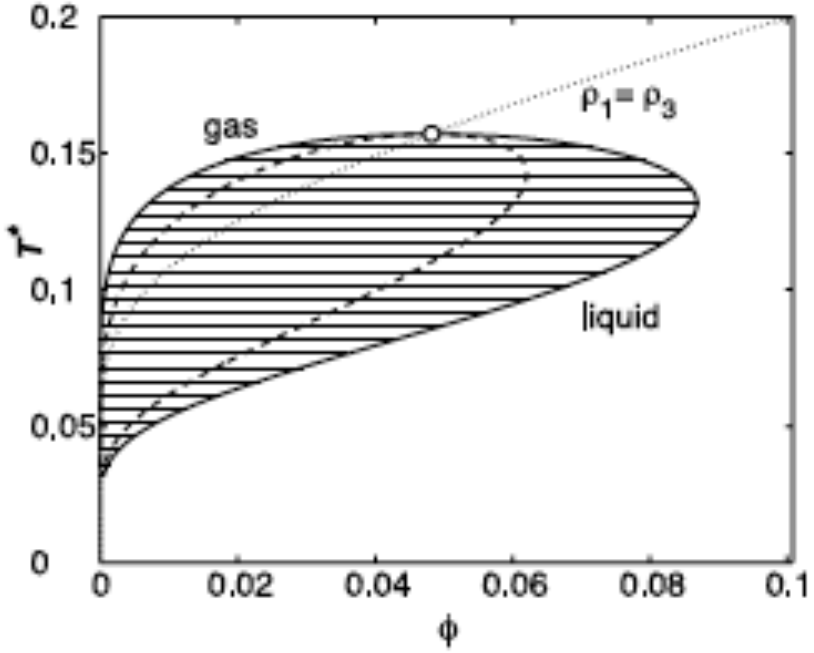
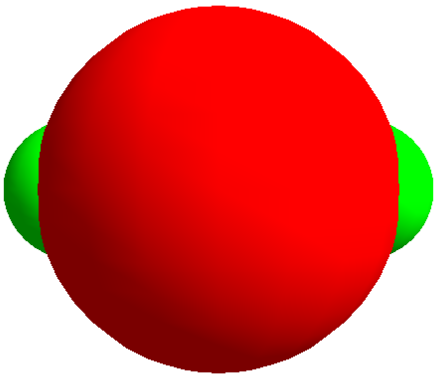


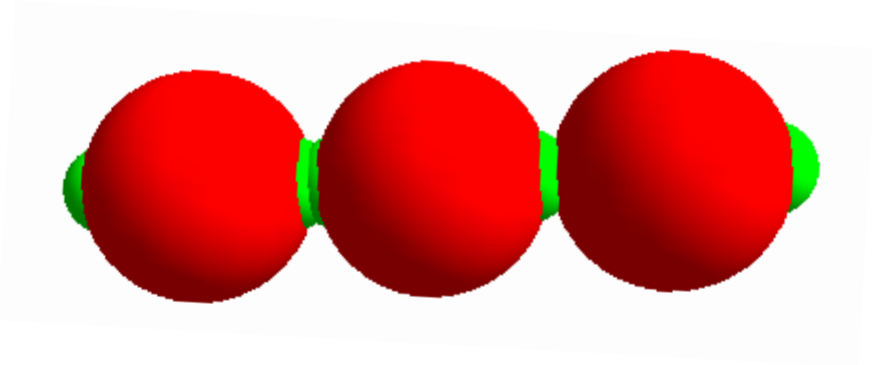
Fig. 2. The phase diagram of the dipolar network calculated for defect energies of $\varepsilon_1 = 0.67$ and $\varepsilon_3 = 0.12$. At the critical point (circle), the coexistence curve (thick solid line), the phase stability boundary (dashed line), and the connectivity transition (dotted line) meet. The lines denote the coexistence of the end-rich "gas" with the junction-rich "liquid." At low temperatures, the coexistence region narrows to very low densities.

A patchy particle models that behaves as Safran's DHS

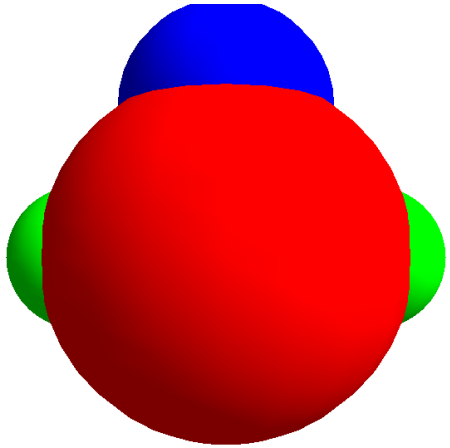
PATCHY PARTICLES THAT FORM CHAINS:



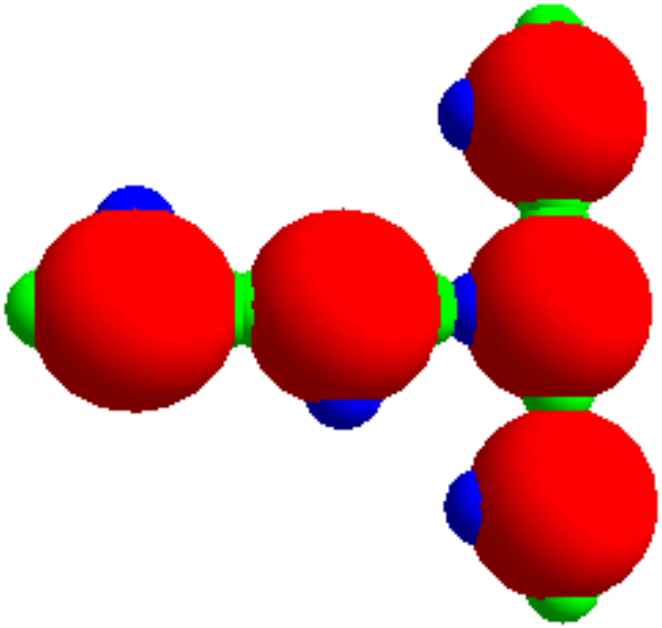
ε_{AA}



ADD BRANCHING POSSIBILITIES

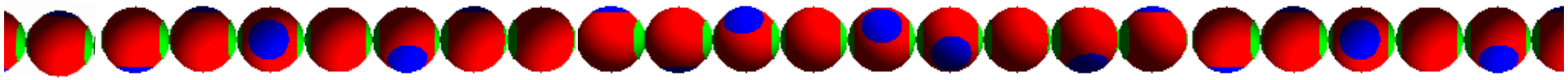


ε_{AB}



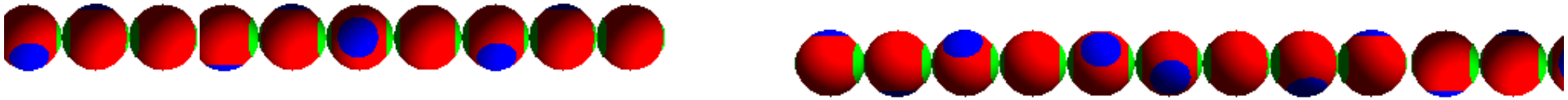
How the ground state looks like ?

Start from an infinite chain of AA bonds



Splitting the chain in two parts costs ε

AA



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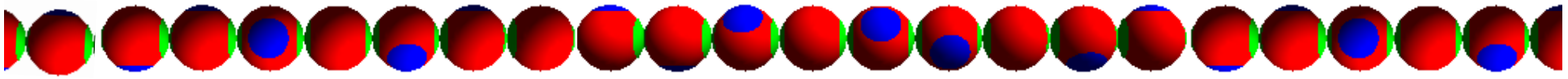
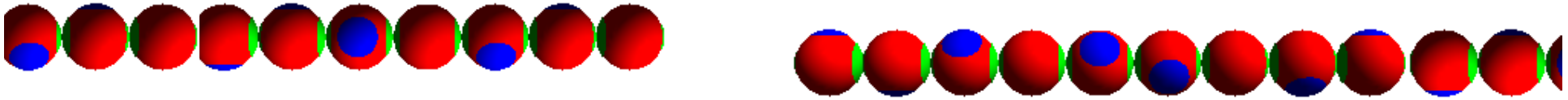
Start from an infinite chain of AA bonds



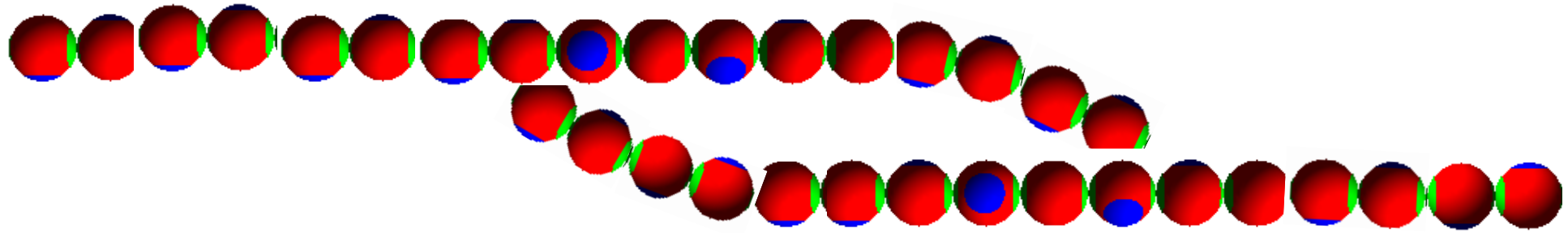
Splitting the chain in two parts costs ε

AA



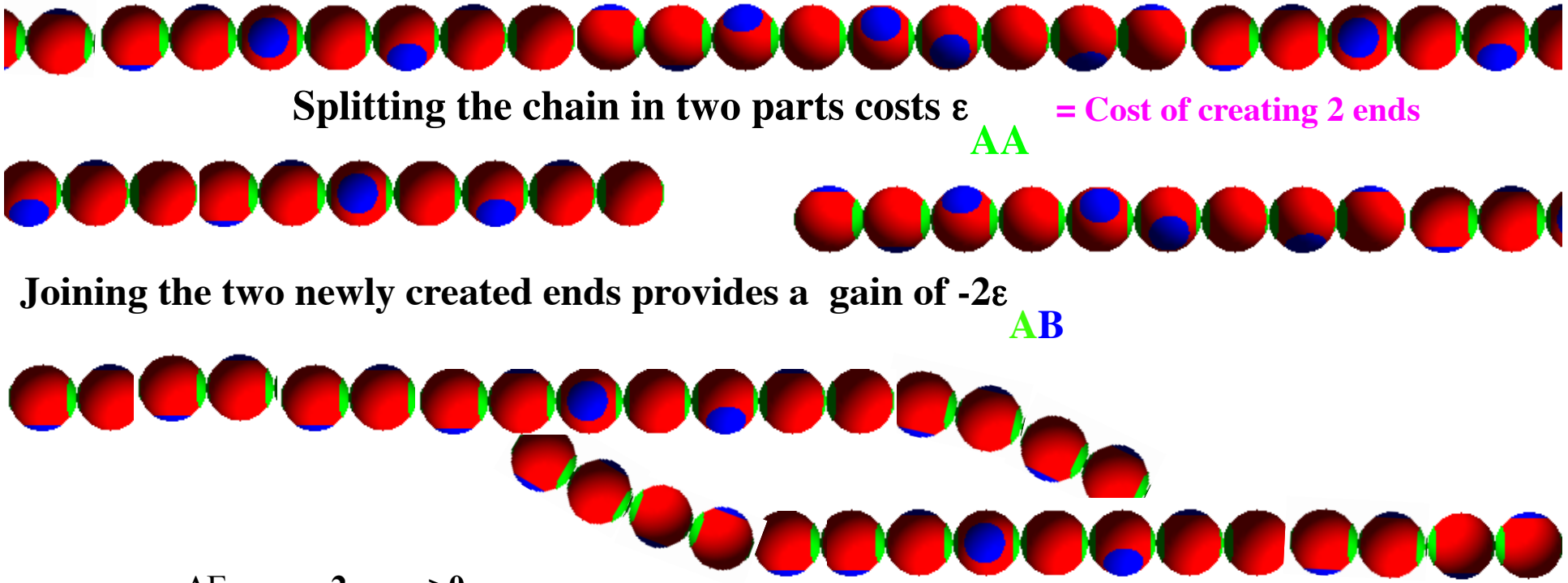
Joining the two newly created ends provides a gain of -2ε

AB



How the ground state looks like ?

Start from an infinite chain of AA bonds



Splitting the chain in two parts costs ε_{AA} = Cost of creating 2 ends

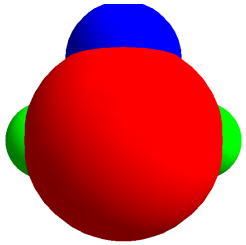
Joining the two newly created ends provides a gain of $-2\varepsilon_{AB}$

$\Delta E = \varepsilon_{AA} - 2\varepsilon_{AB} > 0$

= Cost of creating 2 branching points

Chaining wins at low T — $\varepsilon_{AB}/\varepsilon_{AA} = 0.5$ — **Branching wins even at low T**

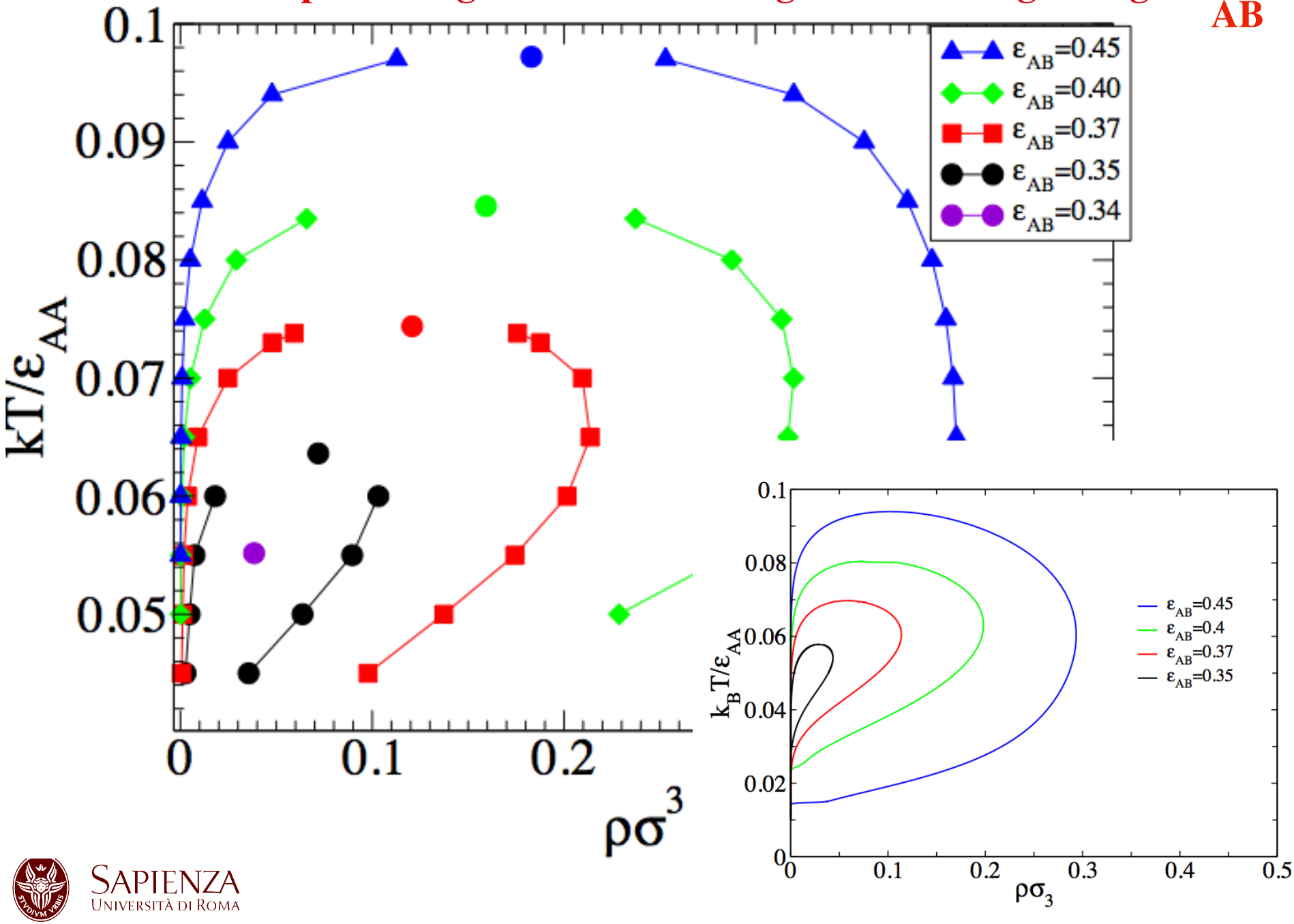
A patchy model with a "pinched" phase diagram



Russo et al PRL 106, 085703 (2011);

J. Russo, et al
Reentrant Phase Diagram of Network Fluids
Phys. Rev. Letts. 106, 085703 (2011)

Evolution of the phase diagram on modulating the branching strength ε_{AB}



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Re-entrant Phases: What is the physics of competitive interactions ?

the emergence of a structure controlled by energy (stable at low T) which competes with a structure stabilized by entropy at intermediate T.

entropy-energy balance to stabilize different local structures: