Glass formation, gelation and colloidal aggregation

17-21 August 2008, Smögen, Sweden.

Aggregation of patchy colloidal particles: The role of the valence

Francesco Sciortino

La Sapienza
Università degli Studi di Roma

soft INFM
Complex Dynamics in Structured Systems

Phase behavior of functionalized (patchy) particles
(a well defined system to study self-assembly and formation of physical-gel)

Geometric Properties (percolation ideas)

Thermodynamic Properties (phase diagram)

Gel Dynamics

nature materials | VOL 6 | AUGUST 2007 |

SHARON C. GLOTZER[1,2]*
AND MICHAEL J. SOLOMON[1]*

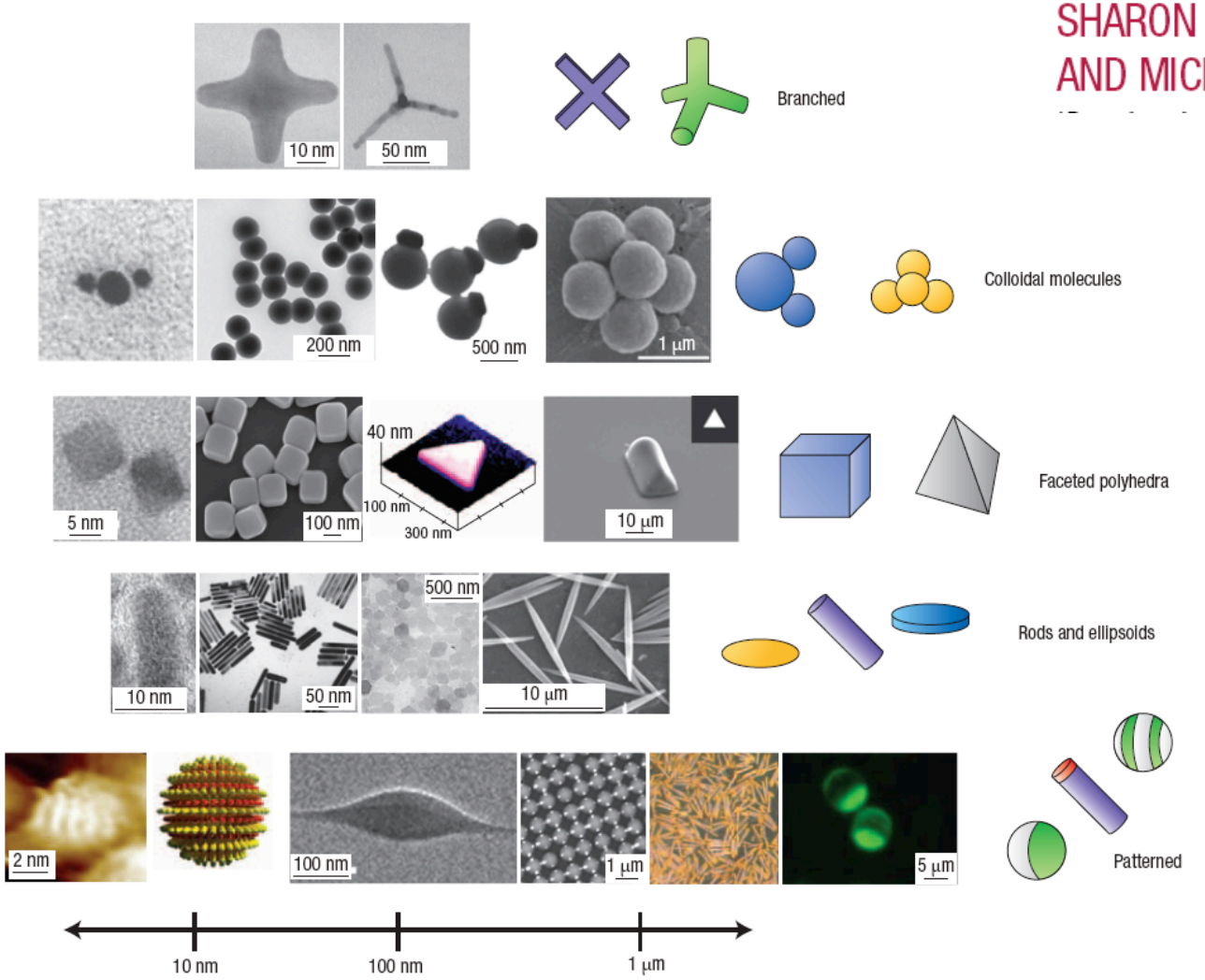
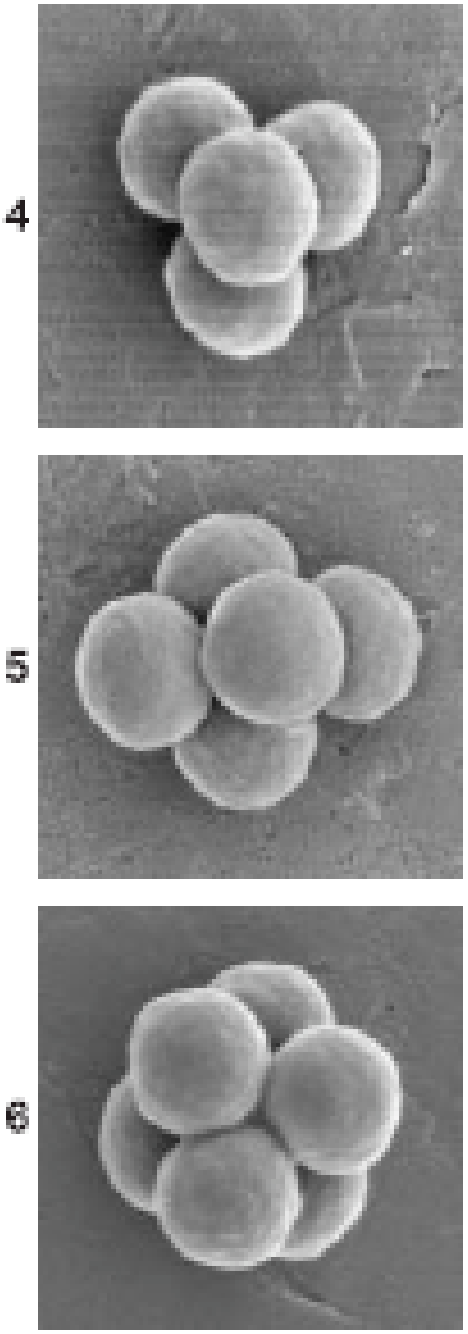
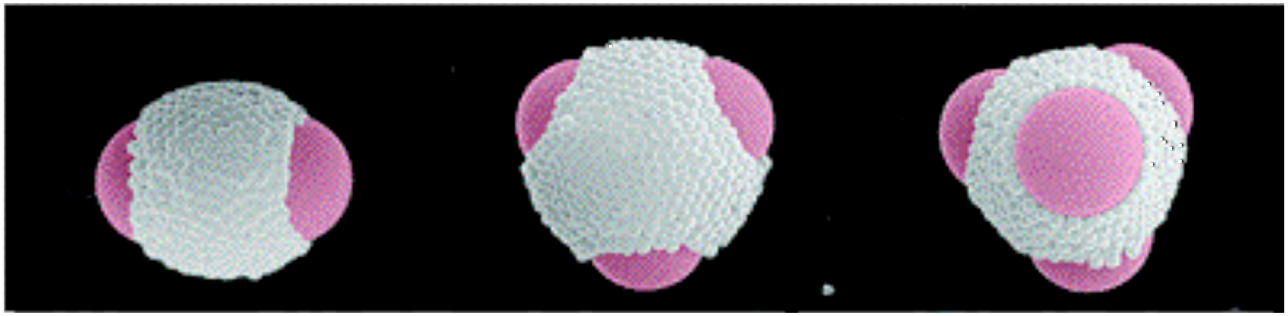


Figure 1 Representative examples of recently synthesized anisotropic particle building blocks. The particles are classified in rows by anisotropy type and increase in size from left to right according to the approximate scale at the bottom. From left to right, top to bottom: branched particles include gold[31] and CdTe[71] tetrapods. DNA-linked gold nanocrystals[50] (the small and large nanocrystals are 5 nm and 10 nm respectively), silica dumb-bells[72], asymmetric dimers[73] and fused clusters[17] form colloidal molecules. PbSe[74] and silver cubes[10] as well as gold[26] and polymer triangular prisms[15] are examples of faceted particles. Rods and ellipsoids of composition CdSe[75], gold[76], gibbsite[4] and polymer latex[60] are shown. Examples of patterned particles include striped spheres[77], biphasic rods[14], patchy spheres with 'valence'[34], Au–Pt nanorods[78] (the rod diameters are of the order of 200–300 nm) and Janus spheres[13]. Images reprinted with permission from the references as indicated. Copyright, as appropriate, AAAS, ACS, RSC, Wiley-VCH.

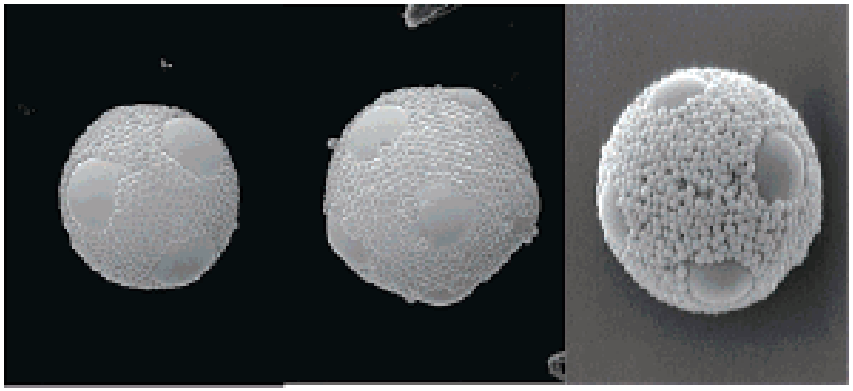
Directional Interactions

(Pine's particles)

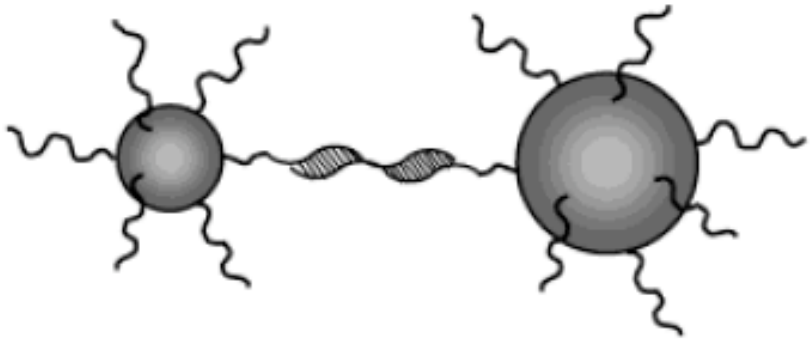




Self-Organization of Bidisperse Colloids in Water Droplets
Young-Sang Cho, Gi-Ra Yi, Jong-Min Lim, Shin-Hyun Kim, Vinothan N. Manoharan,, David J. Pine, and Seung-Man Yang J. Am. Chem. Soc.; **2005**; *127*(45) pp 15968 - 15975;



DNA functionalized particles



1.10μm fluorescent **1.87μm nonfluorescent**

TACATAGTTCCATTTTTT-B = ***b18***
a18 = B-TTTTTTATGTATCAAGGT

ACATAGTTCCATTTTTT-B = ***b17***
a17 = B-TTTTTTATGTATCAAGG

CATAGTTCCATTTTTT-B = ***b16***
a16 = B-TTTTTTATGTATCAAG

Cy5-a12 = ATGTATCAAGGT-Cy5
Cy5-b12 = Cy5-TACATAGTTCCA

Langmuir **2003**, *19*, 10317−10323

DNA-Driven Assembly of Bidisperse, Micron-Sized Colloids

Valeria T. Milam,[†,‡] Amy L. Hiddessen,[†,‡] John C. Crocker,[†,‡]
David J. Graves,[†] and Daniel A. Hammer*[,†,‡,§]

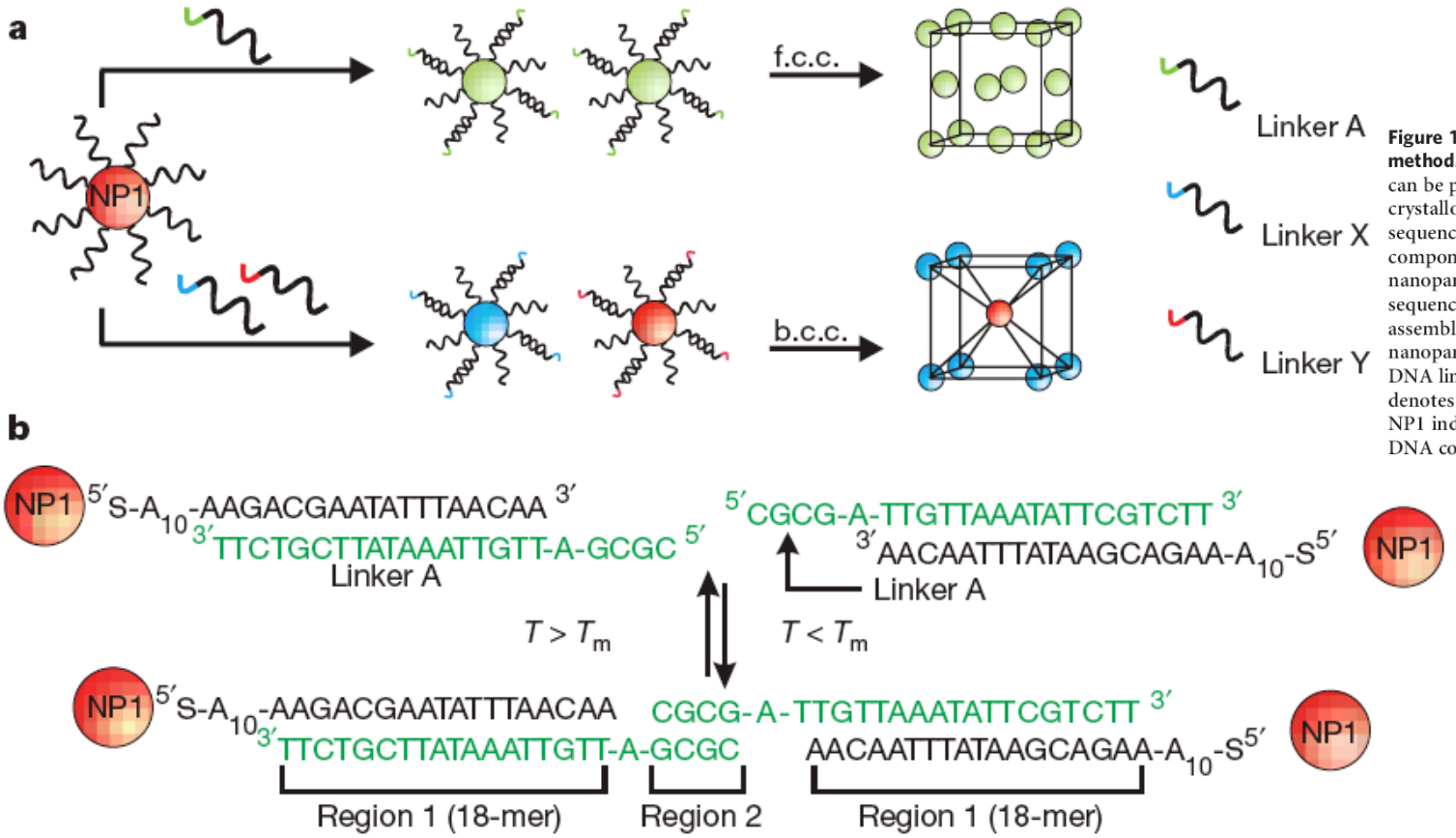


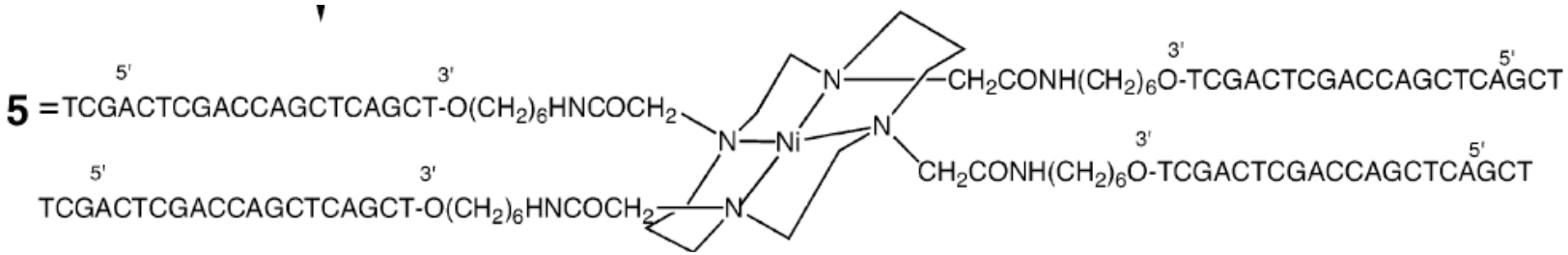
Figure 1 | Scheme of gold nanoparticle assembly method. **a**, Gold nanoparticle–DNA conjugates can be programmed to assemble into different crystallographic arrangements by changing the sequence of the DNA linkers. **b**, Single-component assembly system (f.c.c.) where gold nanoparticles are assembled using one DNA sequence, linker-A. **c**, Binary-component assembly system (b.c.c.) in which gold nanoparticles are assembled using two different DNA linkers -X and -Y. X in the DNA sequence denotes the flexor region: A, PEG_6 or no base. NP1 indicates that the same gold nanoparticle-DNA conjugates were used in all experiments.

Vol 451|31 January 2008

DNA-programmable nanoparticle crystallization

Sung Yong Park[1]*†, Abigail K. R. Lytton-Jean[1]*, Byeongdu Lee[2], Steven Weigand[3], George C. Schatz[1] & Chad A. Mirkin[1]

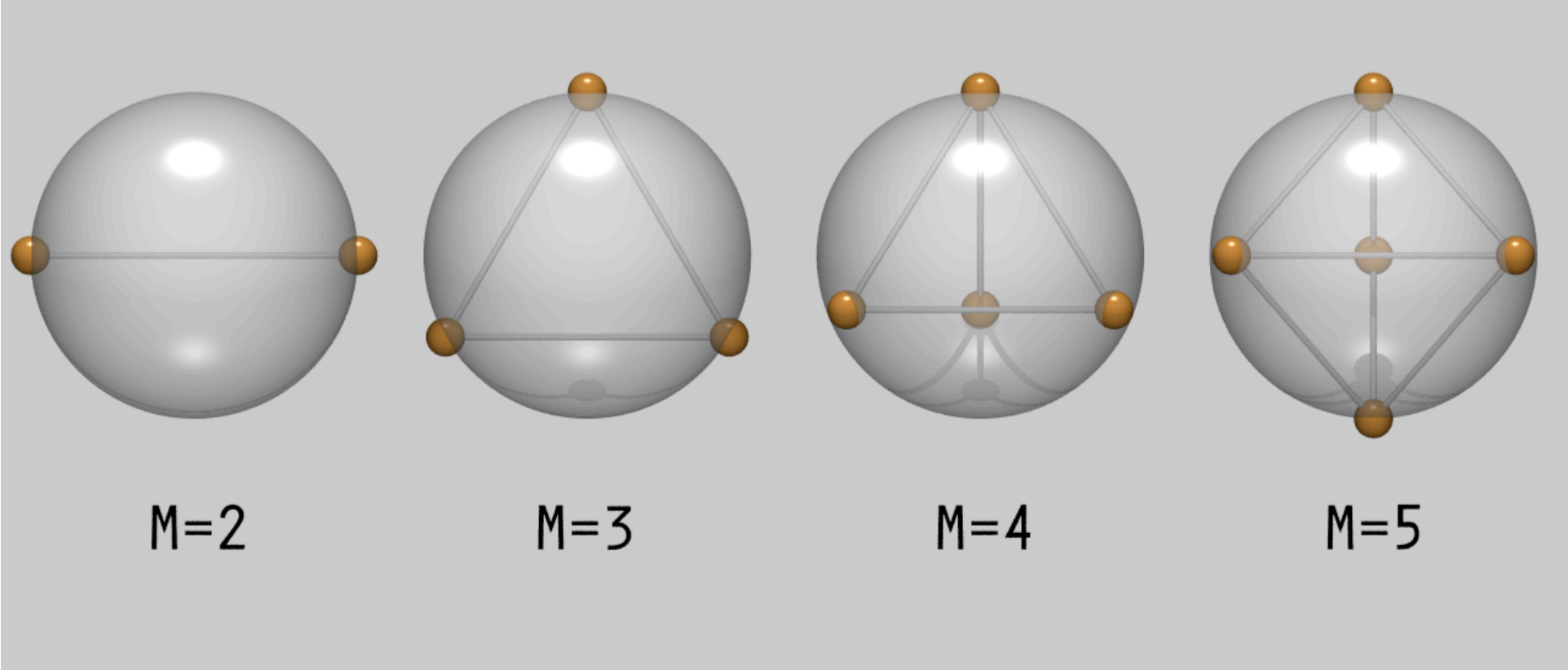
DNA-dendrimers



Kristen M. Stewart and Larry W. McLaughlin*

Four Arm Ologonucleotide Complexes as precursors for the generation of supramolecular periodic assemblies
JACS 126, 2050 2004

The class of particles I will focus on includes particles with controlled valence (functionality), i.e. with a well defined maximum number f of bonded neighbors.



TACATAGTTCCATTTTTT-B = ***b18***

a18 = B-TTTTTTATGTATCAAGGT

The “number of bonds” is properly defined

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

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**

Let's start with the "geometry"

Assume we have N particles with functionaly f

Assume there are N_b bonds between the particles

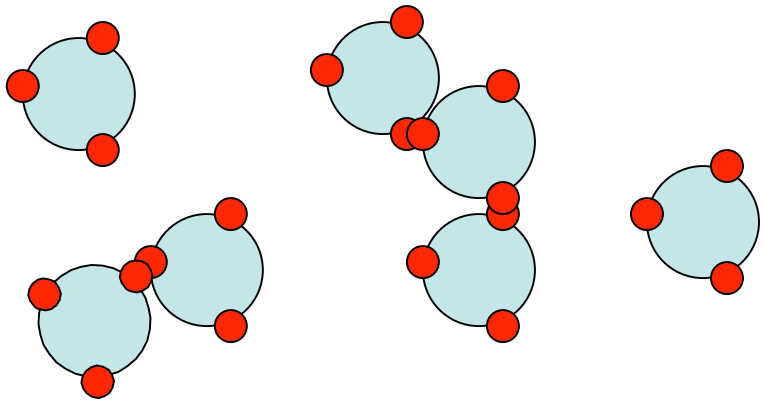
$$p_b = \frac{N_b}{(fN)/2}$$

What is the cluster size distribution ?

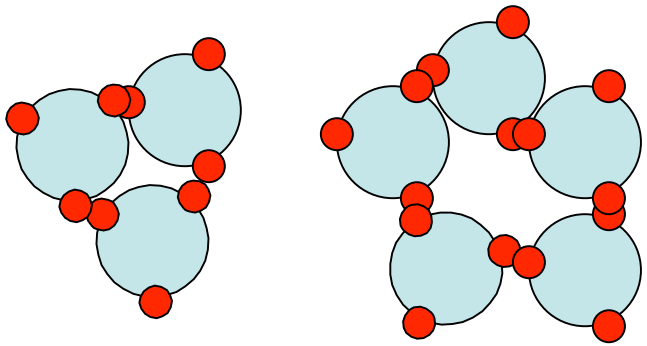
How do particle self − assemble into clusters ?

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

Bond loop-less clusters

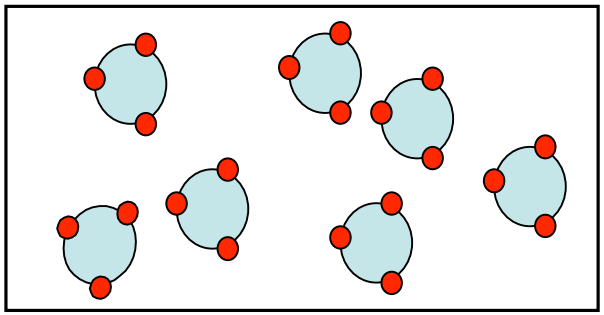


Cluster with bond loops

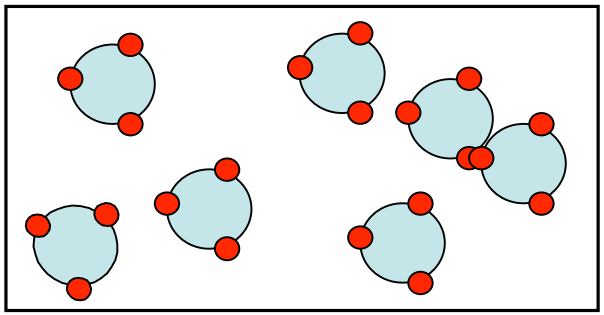


Why theoreticians like loop-less clusters ?
Simple relation between Number of clusters and Number of bonds

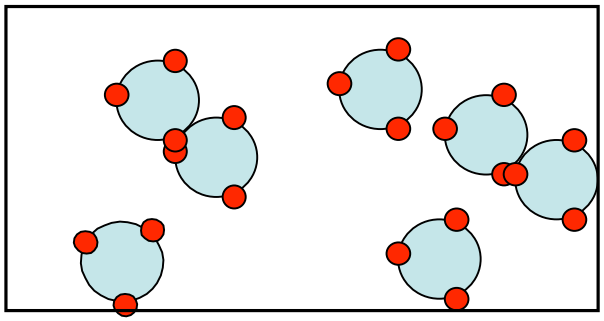
Each bond decreases by one the number of cluster !!!



7 clusters - 0 bonds



6 clusters - 1 bonds



5 clusters - 2 bonds

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 $N_c = \sum N_n$

$$N_b = N - N_c \Longrightarrow p_b = \frac{2(N - N_c)}{Nf}$$

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

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

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

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

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

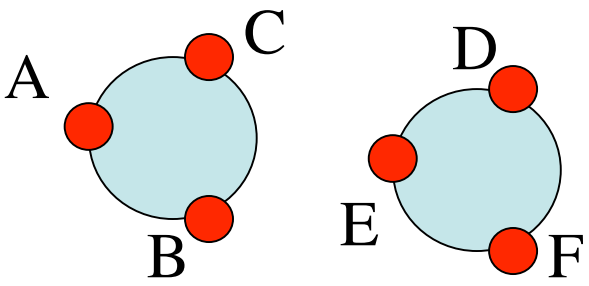
With A and B Lagrange multipliers

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

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

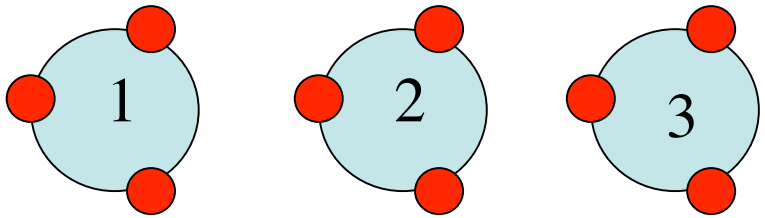
$$N_n = \frac{\omega_n}{n!}A^n B$$

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



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

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

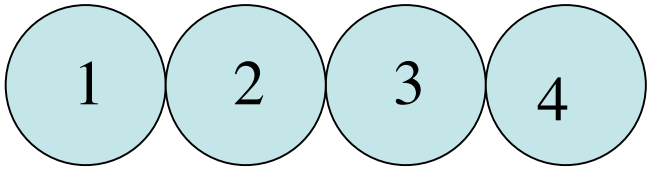


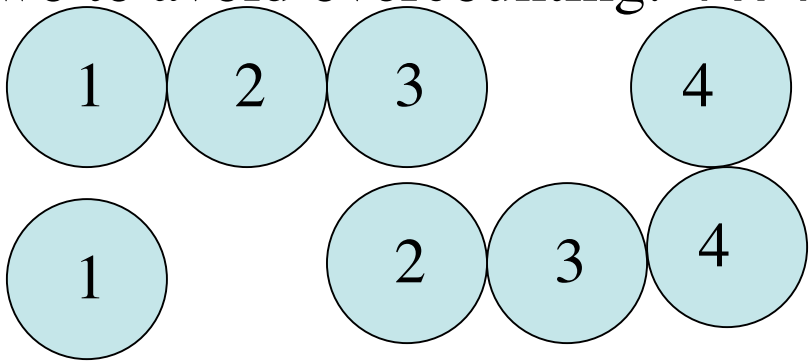
3 different dimers (12,13,23) each of them made in 9 ways, times 4x3 ways to mix a dimer with the remaining monomer, divided by two to avoid overcounting

3x9x4x3/2=162

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

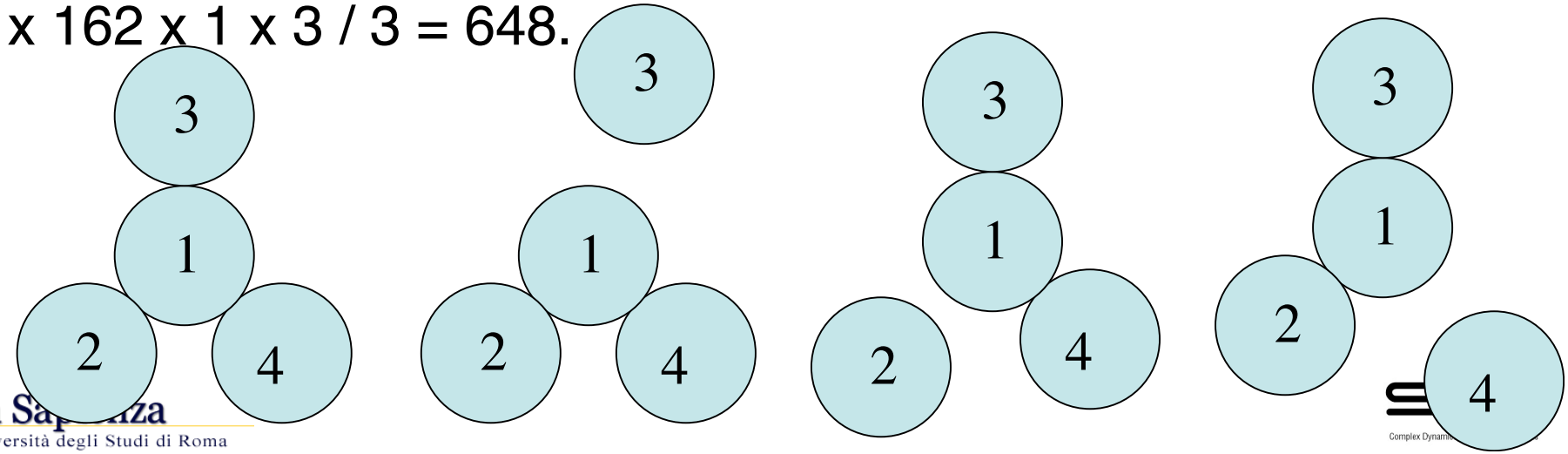
4 different trimers (123,124,134,234),each of them made in 162 ways. Separating the linear and the star configurations one gets: Linear configurations: times 4x3 (bonds, 4 on the trimer and 3 on the monomer) ways divided by two to avoid overcounting: 4 x 162 x 4 x 3 / 2 = 3888





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

$$0 < p_b < \frac{1}{f-1}$$

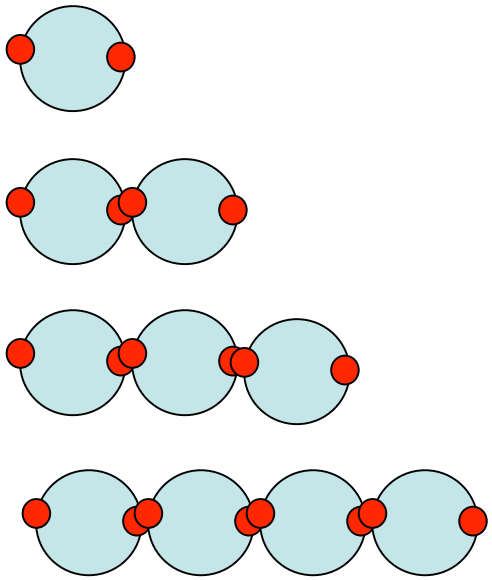
$$N_n = N \frac{f(fn-n)!}{n!(fn-2n+2)!}(1-p_b)^f \left[p_b(1-p_b)^{f-2}\right]^{n-1}$$

$$N_c = N(1 - p_b \frac{f}{2})$$

Simple case: f=2 (chains) (see JCP 126, 194903 2007)

$$0 < p_b < 1$$

$$N_n = N(1-p_b)^2 p_b^{n-1} = N\frac{(1-p_b)^2}{p_b}\exp(n\log(p_b))$$

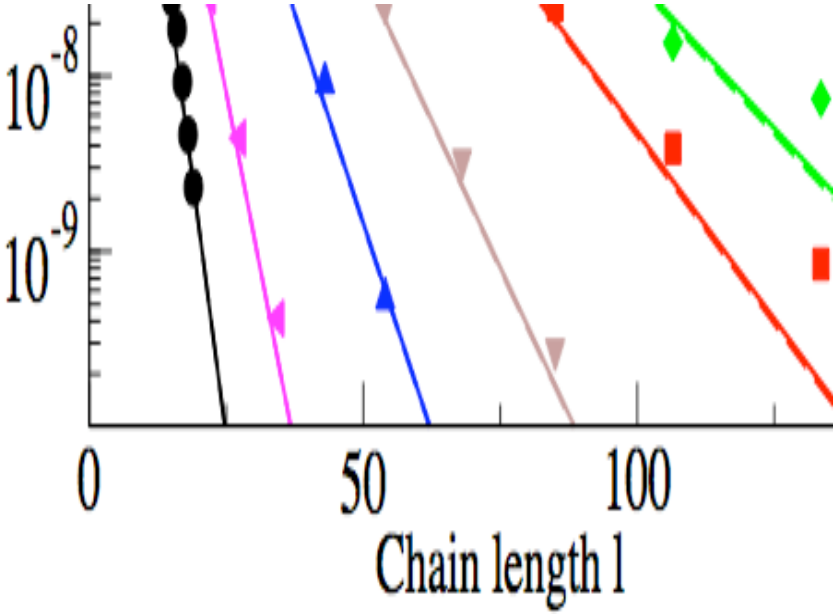


$$(1-p_b)^2$$

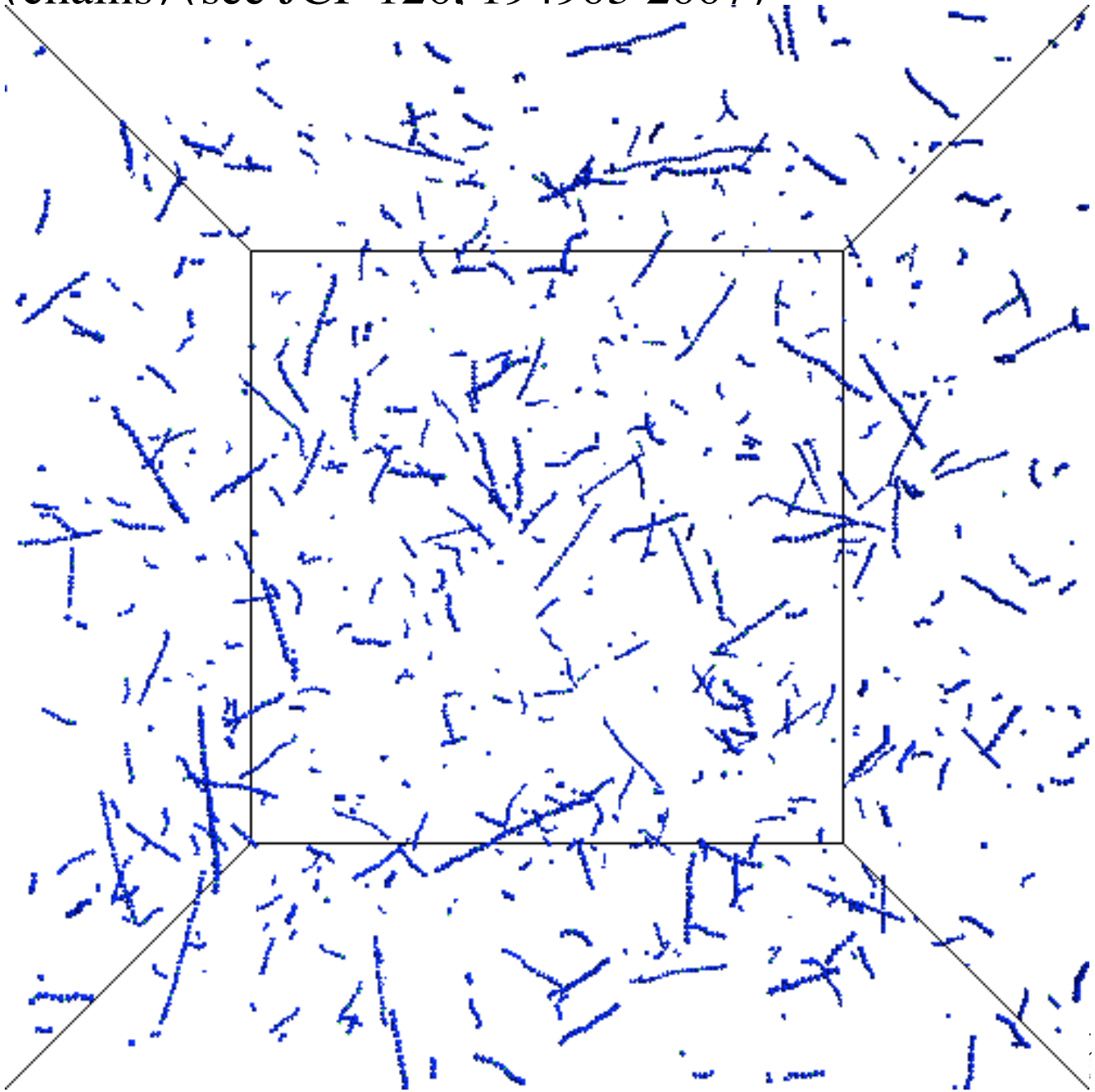
$$p_b(1-p_b)^2$$

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

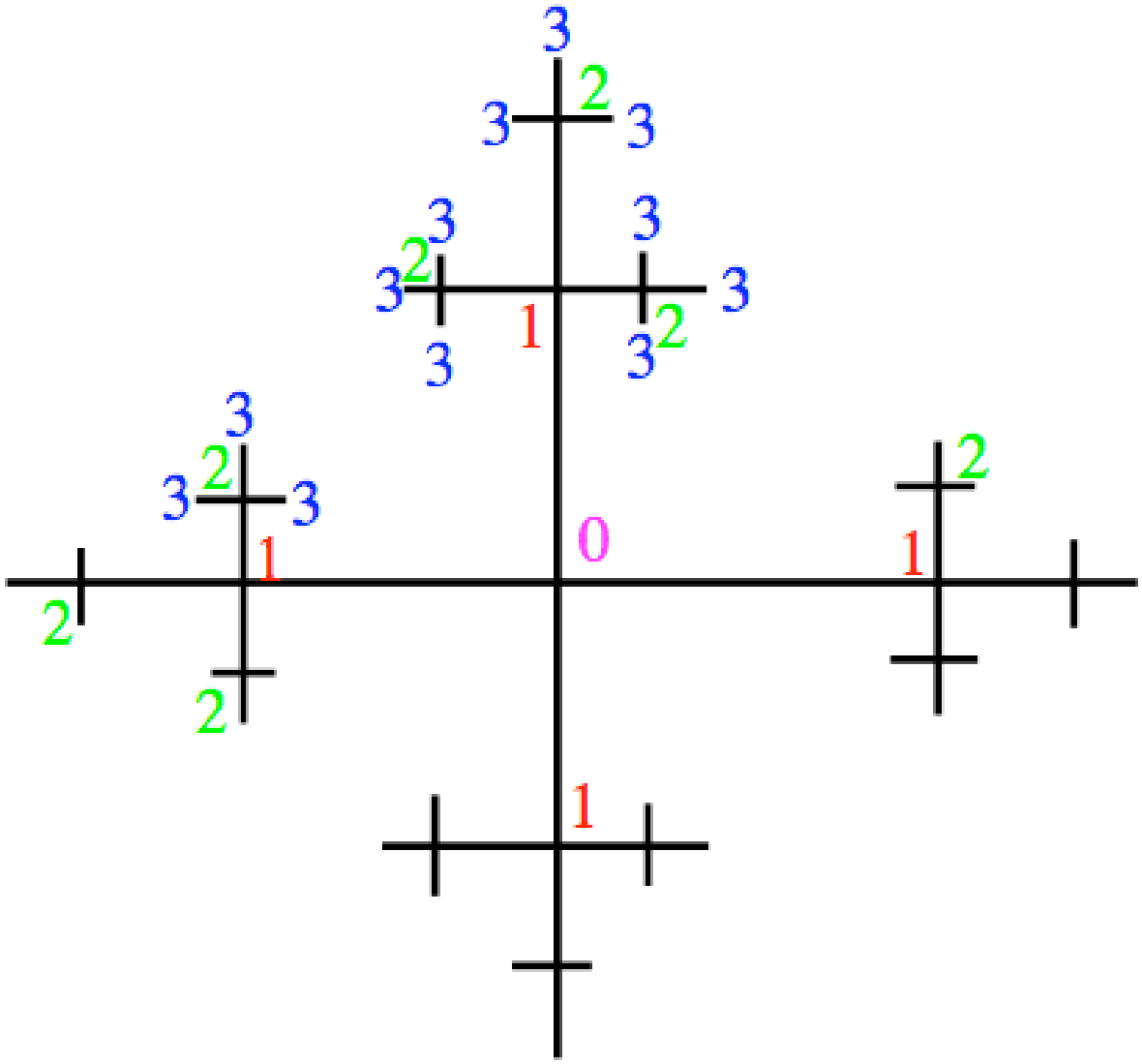
$$p_b^3(1-p_b)^2$$



Simple case: f=2 (chains) (see JCP 126, 194903 2007)



Now… f>2 (branching). Where does the system percolate ?



Bond probability=p

$C_1 = f\,p$

$C_2 = (f-1)\,p\,C_1$

$C_3 = (f-1)\,p\,C_2$

……

$C_N = [(f-1)\,p]^{N-1}\,C_1$

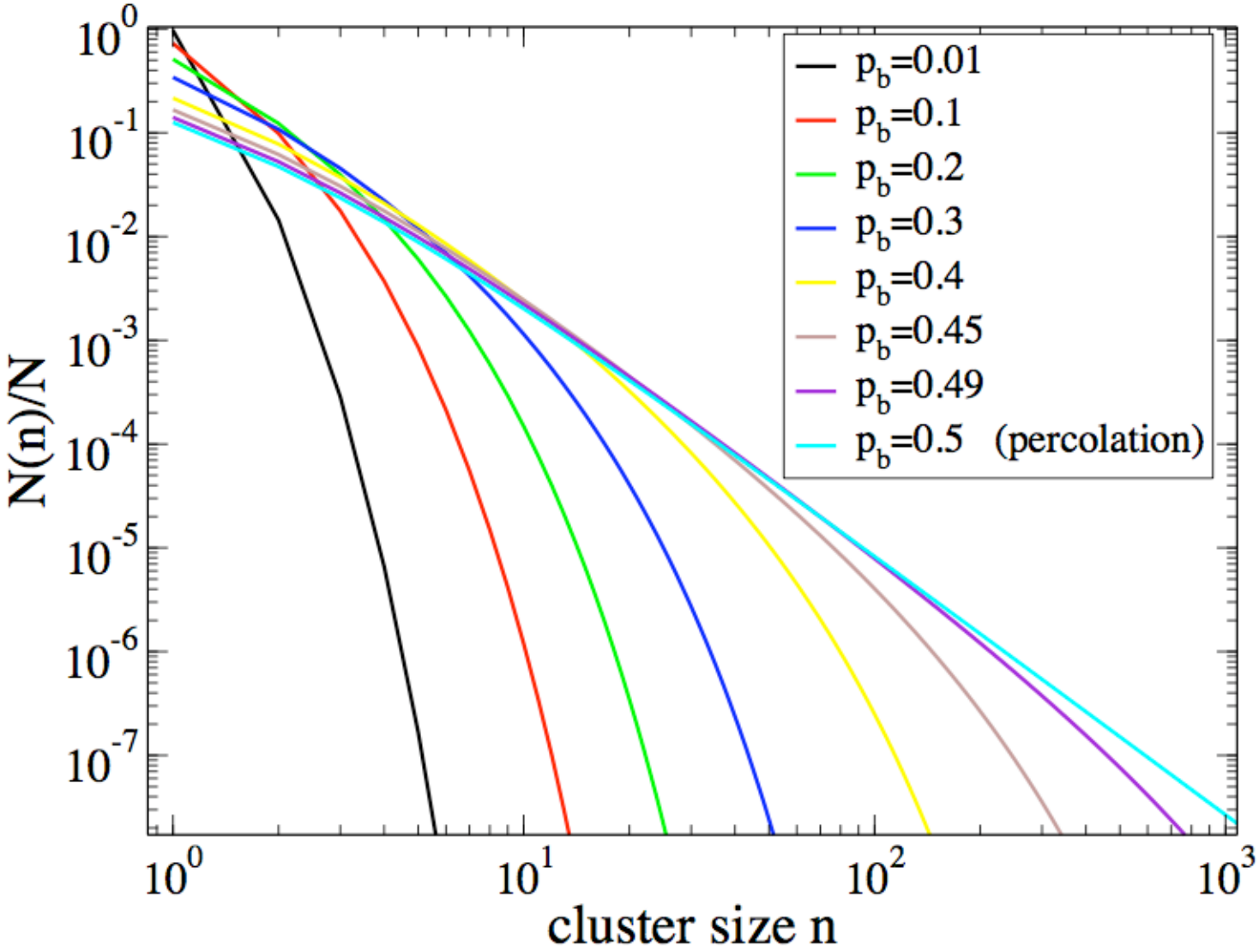
Critical Value !!!

$(f-1)\,p_c = 1$

$$p_c = 1/(f-1)$$

Complex Dynamics in Structured Systems

Let’s go back to the cluster size distribution…. (f=3)



Increase of the polydispersity on increasing pb

Cluster size distribution at percolation

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

$$substitute\ p_b = \frac{1}{f-1}$$

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

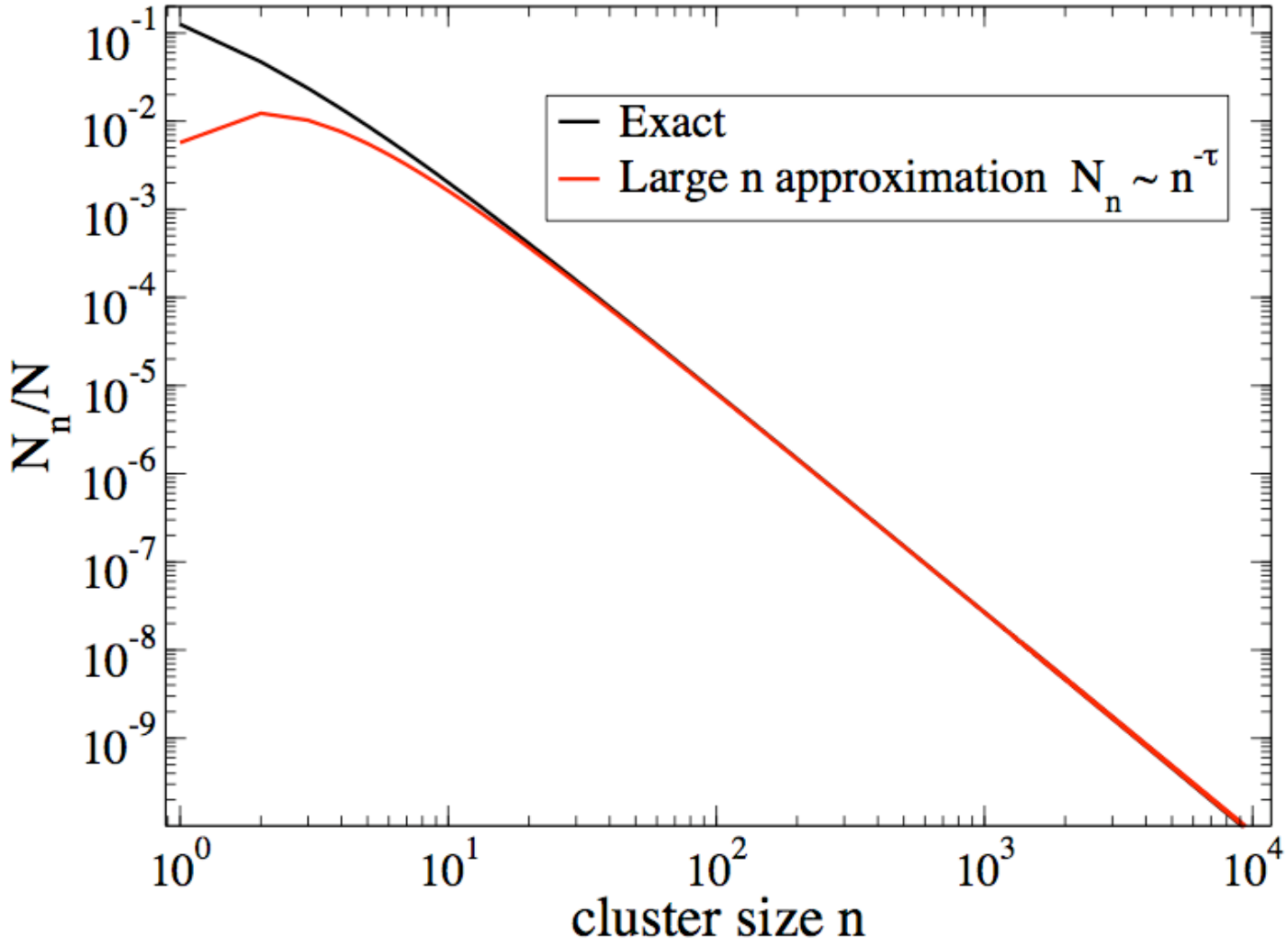
Using Stirling's approximation $\ln(n!) = n\ln(n) - n + \frac{1}{2}\ln(2\pi n)$

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

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



Absence of a characteristic size

Cluster size distribution close to percolation p_c…..

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

Expanding $\left[p_b(1-p_b)^{f-2}\right]$ around percolation, one finds

$$N_n(p_b) \sim n^{-2.5} e^{-\mathcal{K} n \Delta p^2}$$

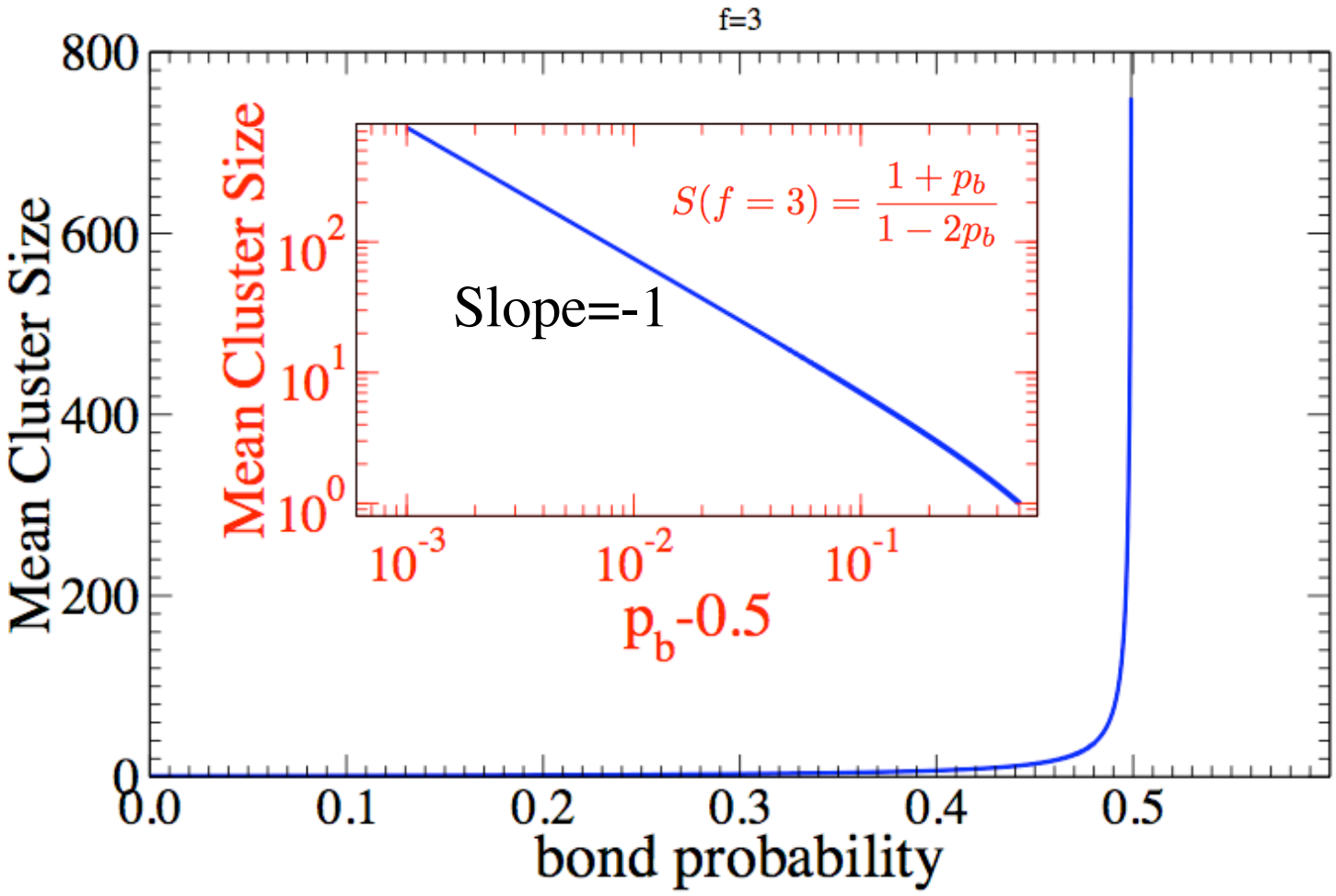
$$N_n(p_b) \sim n^{-\tau} f(n^{\sigma} \Delta p)$$

$$\tau = 2.5 \qquad \sigma = 0.5$$

Mean Cluster Size S

Diverges at percolation with critical exponent -1

$$S = \frac{\sum_n n^2 N_n}{\sum_n n N_n}$$

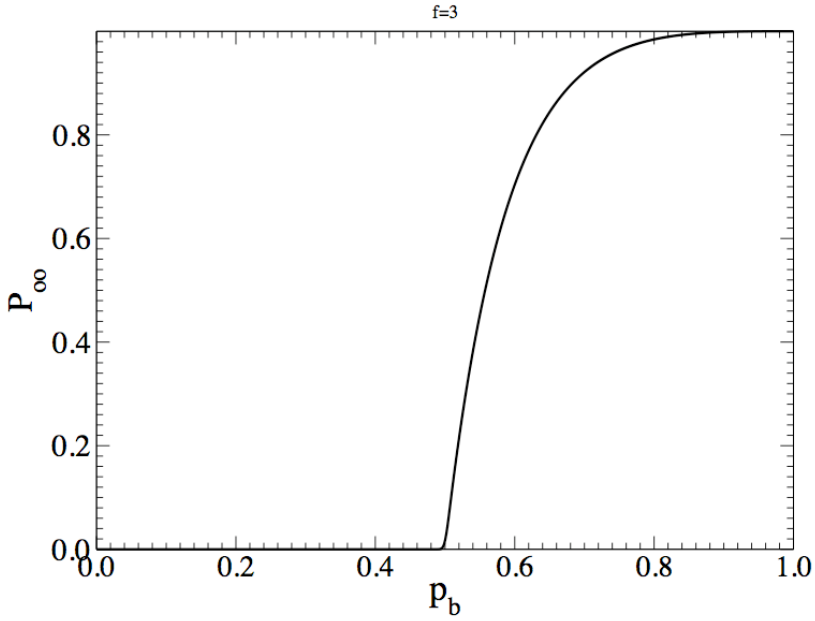


Fraction of particles in the infinite cluster:

$$P_\infty = 1 - \frac{\sum_n n N_n}{N}$$

$$P_\infty(f=3) = 0, \qquad p_b < 0.5$$

$$P_\infty(f=3) = 1 - \frac{(1-p_b)^3}{p_b^3}, \qquad p > 0.5$$



Critical exponent
Beta=1

$$P_\infty \sim (p_b - p_b^{percolation})$$

Predictions (close to p_c) :

$$n_s \sim s^{-\tau} f[s^{\sigma}(p - p_c)]$$

No loops: τ=2.5, σ=0.5 (d_f=4)
3d (approx): τ=2.18, σ=0.45, d_f=2.53

$$S = \int s^2 n_s \sim |p - p_c|^{\frac{-(3-\tau)}{\sigma}} \qquad \gamma$$

suscettibility

$$P_\infty \sim |p - p_c|^{\frac{(\tau-2)}{\sigma}} \qquad \beta$$

magnetization
(order parameter)

$$\xi_c \sim |p - p_c|^{-\frac{1}{d_f \sigma}} \qquad \nu$$

Stauffer Phys. Rep. 1979

Little break

Percolation: what does it means for reversible bonds ?

Thermodynamics $p_b(\rho, T)$

(in the "ideal gas" limit)

$$\beta PV = N_c$$

$$N_c = N - N_b = N\left(1 - \frac{f}{2}p_b\right)$$

$$\beta P = \rho\left(1 - \frac{f}{2}p_b\right)$$

Since it is a system in dynamic equilibrium ….

$$z \equiv \frac{1}{\Lambda^3}\exp(\beta\mu) \qquad z = \rho_1 = \rho(1 - p_b)^f$$

$$\frac{\beta F}{V} = \rho\beta\mu - \beta P = \rho \ln\left[\rho\Lambda^3(1 - p_b)^f\right] - \rho\left(1 - \frac{f}{2}p_b\right)$$

$$\frac{\beta F}{V} = \rho\beta\mu - \beta P = \rho \ln\left[\rho\Lambda^3(1-p_b)^f\right] - \rho\left(1 - \frac{f}{2}p_b\right)$$

$$\beta F(p_b = 0) = \beta F_{ig} = \rho \ln\left[\rho\Lambda^3\right] - \rho$$

$$\frac{\beta F_{bonding}}{V} = \frac{\beta F - \beta F_{ig}}{V} = \rho \ln\left[(1-p_b)^f\right] + \rho\frac{f}{2}p_b$$

To improve substitute F_{ig} with F_{HS}

keeping the same $F_{bonding}$

An alternative route to the ideal gas of clusters free energy

$$\rho_n = \frac{N_n}{V}$$

$$\frac{\beta F}{V} = \sum_i \left(\rho_i \ln[\Lambda^3 \rho_i] - \rho_i\right) + \sum_i \beta \mathcal{F}_b (i-1)\rho_i$$

$$\mathcal{F}_b \approx u_0 - k_B T \ln \frac{V_b}{\Lambda^3}$$

Substituting the known cluster size distributions

$$\frac{p_b}{(1-p_b)^2} = \Lambda^3 \rho e^{-\beta \mathcal{F}_b}$$

$$\frac{p_b}{(1-p_b)^2} = \frac{f N V_b e^{-\beta u_0}}{V}$$

$$p_b(\rho, T) \quad !!!!!!$$

Some additional (potentially useful) relations

$$\frac{\beta F}{V} = \sum_i \left(\rho_i \ln[\Lambda^3 \rho_i] - \rho_i\right) + \sum_i \mathcal{F}_i \rho_i$$

$$\beta\mu_i = \frac{\partial \beta F}{\partial N_i} = \frac{\partial(\beta F/V)}{\partial \rho_i} = \ln(\Lambda^3 \rho_i) + \beta \mathcal{F}_i$$

$$\beta\mu_i = i\beta\mu_1$$

$$\ln(\Lambda^3 \rho_i) + \beta \mathcal{F}_i = \ln(\Lambda^3 \rho_1)^i + i\beta \mathcal{F}_1$$

$$\rho_i = \rho_1^i \; e^{\beta(i\mathcal{F}_1 - \mathcal{F}_i)} \; \frac{\Lambda^{3i}}{\Lambda^3}$$

$$(i\mathcal{F}_1 - \mathcal{F}_i) = k_B T \ln\left(\frac{\rho_i \Lambda^3}{\rho_1^i \Lambda^{3i}}\right)$$

Case f=2

$$\frac{\beta F}{V} = \sum_i \left(\rho_i \ln[\sigma^3 \rho_i] - \rho_i\right) + \sum_i \mathcal{F}_b (i-1)\rho_i$$

$$\rho_i = \rho(1-p_b)^2 p_b^{i-1} \qquad \frac{N_c}{N} = \frac{\rho_c}{\rho} = (1-p_b)$$

$$\frac{\beta F}{V} = \sum \left(\rho_i \ln[\sigma^3 \rho (1-p_b)^2 p_b^{i-1}] - \rho_i\right) + \sum \mathcal{F}_b (i-1)\rho_i \qquad \frac{\beta F}{V} = \sum_i \left(\rho_i \ln[\sigma^3 \rho (1-p_b)^2] + (i-1)\rho_i \ln p_b] - \rho_i\right) + \sum_i \mathcal{F}_b (i-1)\rho_i$$

$$\frac{\beta F}{V} = \sum_i \rho_i \left(\ln[\sigma^3 \rho (1-p_b)^2] - 1\right) + \sum_i [\mathcal{F}_b + \ln p_b](i-1)\rho_i$$

$$\frac{\beta F}{V} = \left(\ln[\sigma^3 \rho (1-p_b)^2] - 1 - \mathcal{F}_b - \ln p_b\right) \sum_i \rho_i + [\mathcal{F}_b + \ln p_b] \sum_i i\rho_i$$

$$\frac{\beta F}{V} = \left(\ln[\sigma^3 \rho (1-p_b)^2] - 1 - \mathcal{F}_b - \ln p_b\right) \rho_c + [\mathcal{F}_b + \ln p_b]\rho$$

$$\frac{\beta F}{V} = -\rho p_b \left(\ln[\sigma^3 \rho (1-p_b)^2 e^{-\beta \mathcal{F}}/p_b] - 1\right) + \rho \left(\ln[\sigma^3 \rho (1-p_b)^2] - 1\right)$$

$$\frac{\beta F}{V} = -\rho p_b \left(\ln[\sigma^3 \rho (1-p_b)^2 e^{-\beta \mathcal{F}}/p_b]\right) + \frac{\beta F_{ig}}{V} + \rho \ln[(1-p_b)^2] - \rho p_b$$

$$\frac{p_b}{(1-p_b)^2} = \sigma^3 \rho e^{-\beta \mathcal{F}_b}$$

A chemical reaction approach: Focus on the reactive site

O + O <=> C

$$F = N_O\mu_O + N_C\mu_C$$

$$dF = 0 = dN_O\mu_O + dN_C\mu_C = dN_C(-2\mu_O + \mu_C)$$

Ideal gas

$$\beta\mu = \frac{\partial\beta F}{\partial N} = -\ln\frac{Q}{N} \qquad \frac{N_C}{N_O^2} = \frac{Q_C}{Q_O^2}$$

$$Q_O = V \qquad Q_C = \frac{1}{2!}V_b V e^{-\beta u_0}$$

$$\frac{N_C}{N_O^2} = \frac{\frac{fN}{2}p_b}{[fN(1-p_b)]^2} \qquad \frac{p_b}{(1-p_b)^2} = \frac{fNV_b e^{-\beta u_0}}{V}$$

$$p_b(\rho, T)$$

$$\frac{p_b}{(1-p_b)^2} = \frac{f N V_b e^{-\beta u_0}}{V}$$

Wertheim TPT for associated liquids

(particles with f identical sticky sites)

$$\frac{\beta F_{bond}}{N} = f \ln(1 - p_b) - \frac{f}{2} p_b$$

$$\frac{p_b}{(1 - p_b)^2} = f \rho \Delta$$

$$\Delta = 4\pi \int g_{HS}(r_{12}) \langle f(12) \rangle_{\omega_1, \omega_2} r_{12}^2 dr_{12}$$

At low densities and low T (for SW)…..

$$g_{HS}(r) \approx 1$$

$$f(r) \approx e^{\beta u_0} \quad (bond\ volume) \ V_b$$

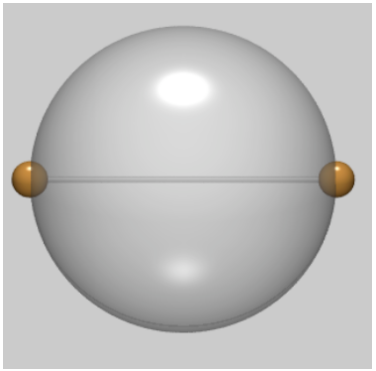
$$0 \quad (otherwise)$$

$$\Delta = V_b \exp[\beta u_0]$$

Wertheim in a nut-shell
Appendix A: Bianchi et al
J. Chem. Phys. 128, 144504 (2008)

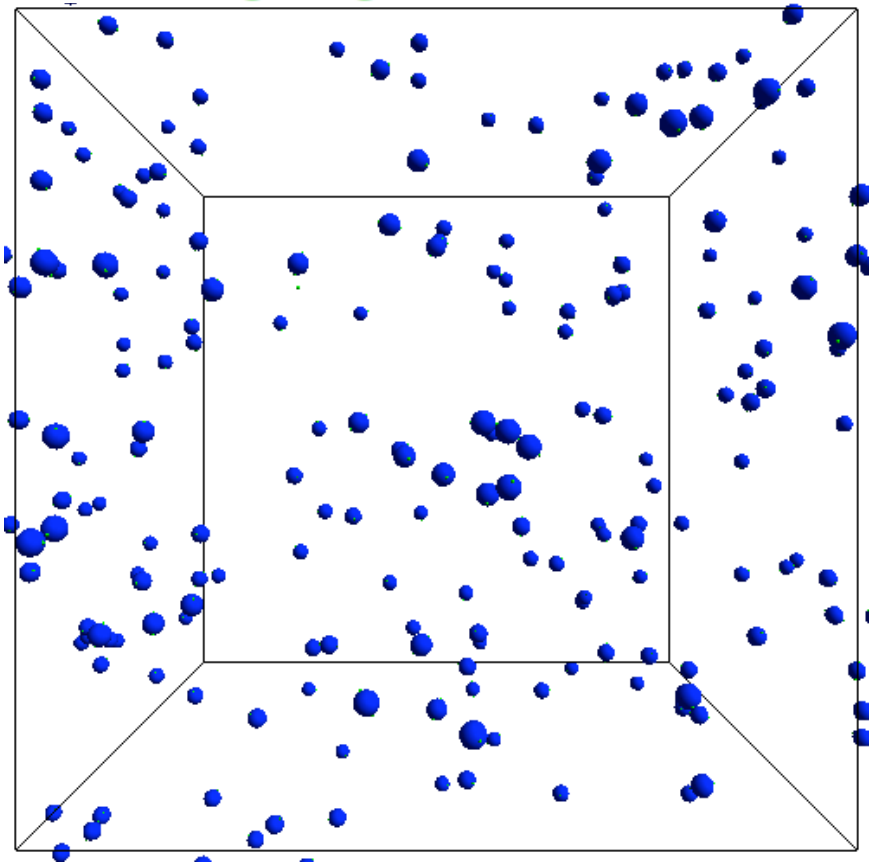
Equilibrium chains

f=2

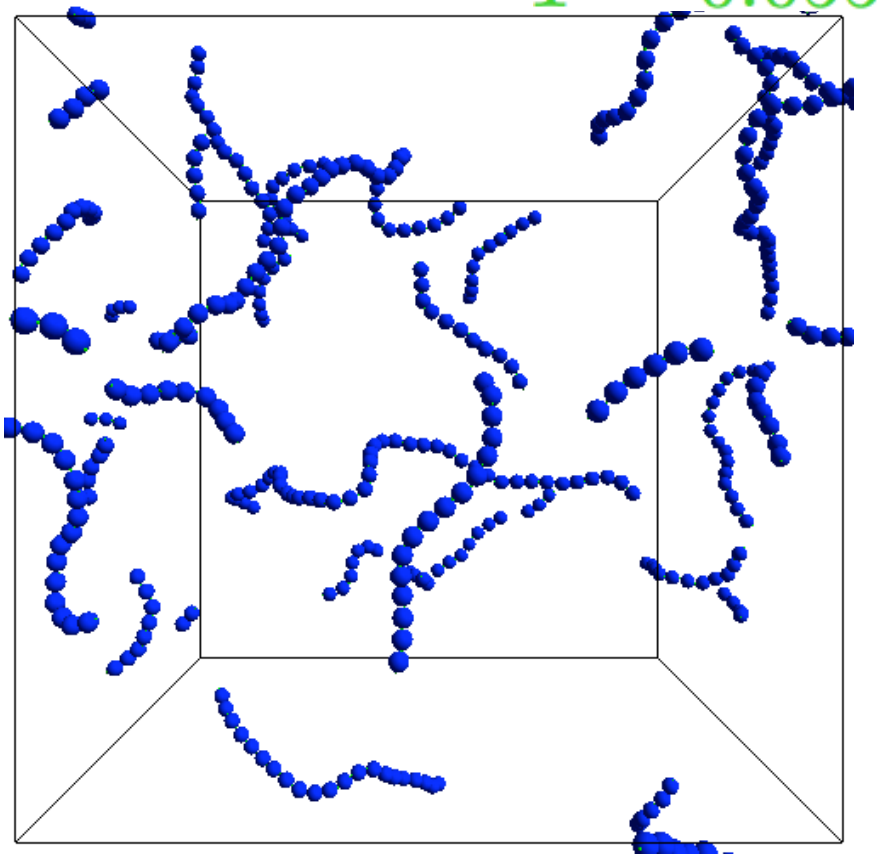


JCP

$T = 0.10$



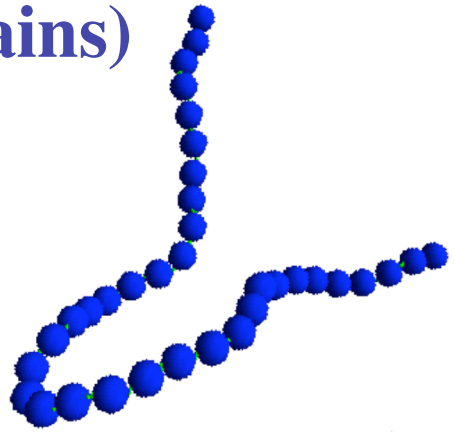
$T = 0.055$



$\rho = 0.0035$

f=2 (Chains)

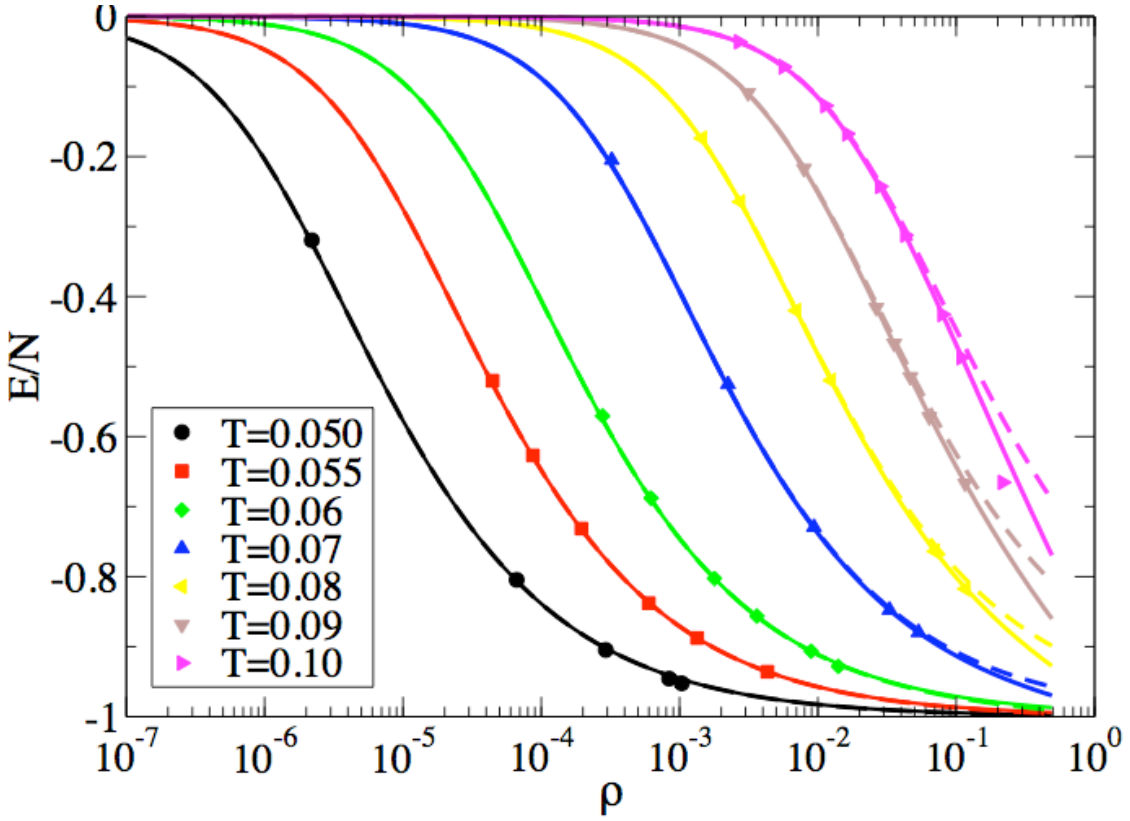
JCP



$$\frac{p_b}{(1-p_b)^2} = \frac{fNV_b e^{-\beta u_0}}{V}$$

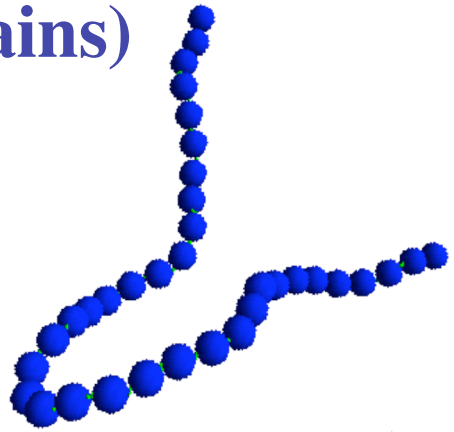
$$\frac{E}{N} = -u_0 \frac{N_b}{N} = -u_0 p_b \frac{f}{2}$$

Energy per particle



f=2 (Chains)

JCP



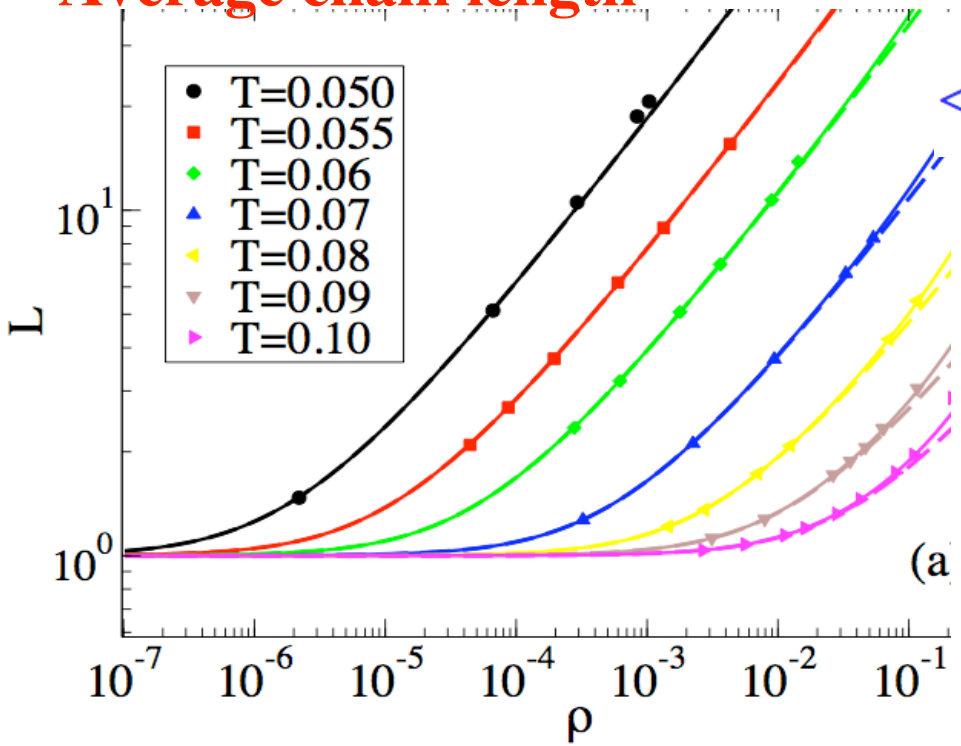
$$N_c = N - N_b = N\left(1 - \frac{f}{2}p_b\right)$$

$$< L >= \frac{N}{N_c} = \frac{1}{1 - p_b}$$

$$\frac{p_b}{(1-p_b)^2} = \frac{fNV_b e^{-\beta u_0}}{V}$$

$$\frac{1}{(1-p_b)^2}(1 - p_b + 1) = \frac{1}{1-p_b} + \frac{1}{(1-p_b)^2} = -\frac{fNV_b e^{-\beta u_0}}{V}$$

Average chain length



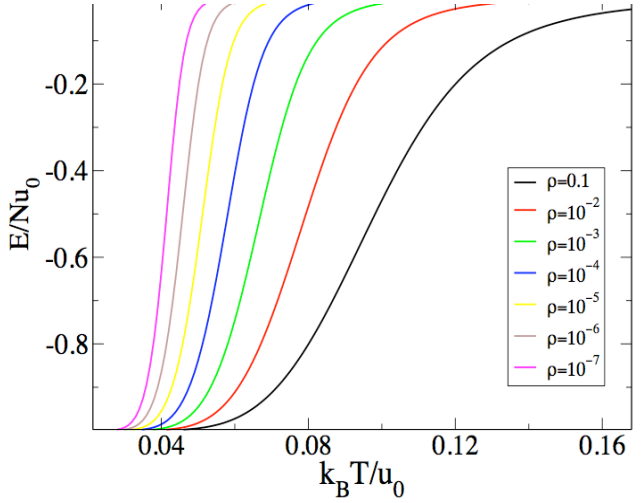
$$< L >= \frac{1 + \sqrt{1 + 8\rho V_b e^{-\beta u_0}}}{2}$$

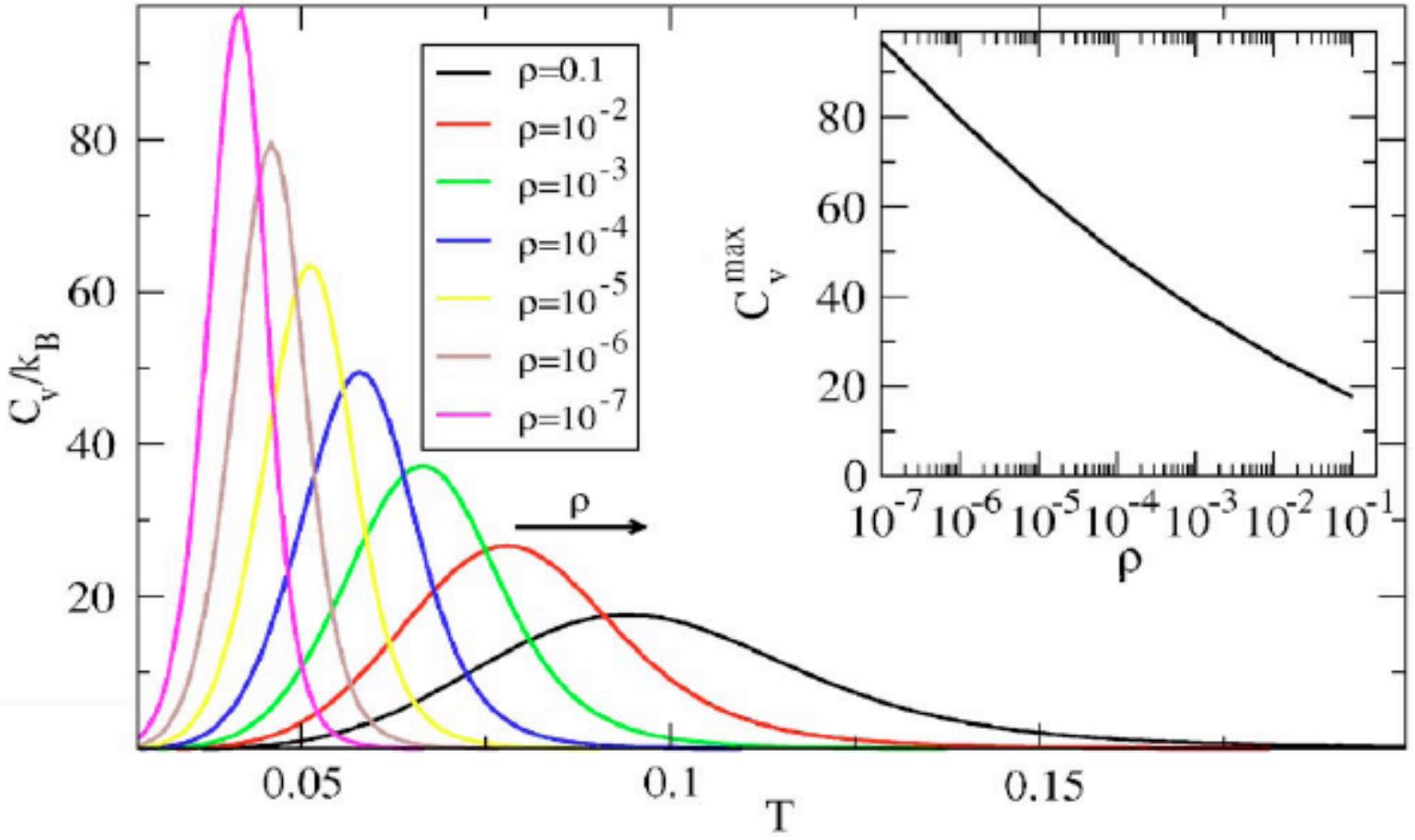
scaling behaviors

$$< L > \sim e^{-\beta u_0/2}$$

$$< L > \sim \sqrt{\rho}$$

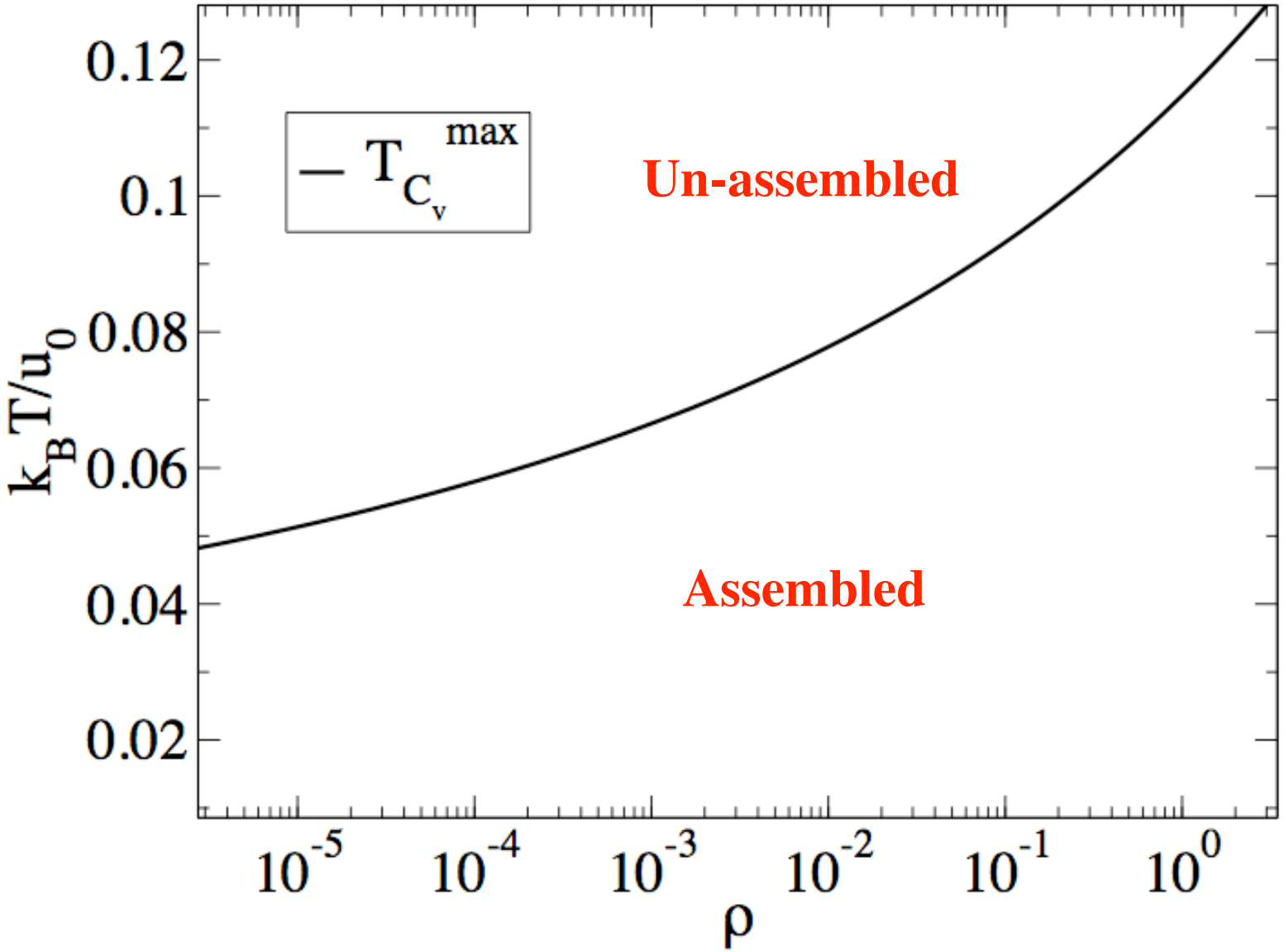
Specific Heat Maxima…..





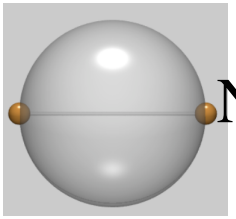
Complex Dynamics in Structured Systems

A line in the phase diagram…….

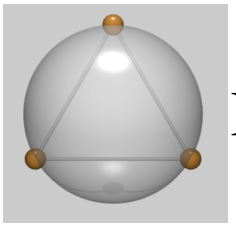


Branching: Mixtures of two and three….

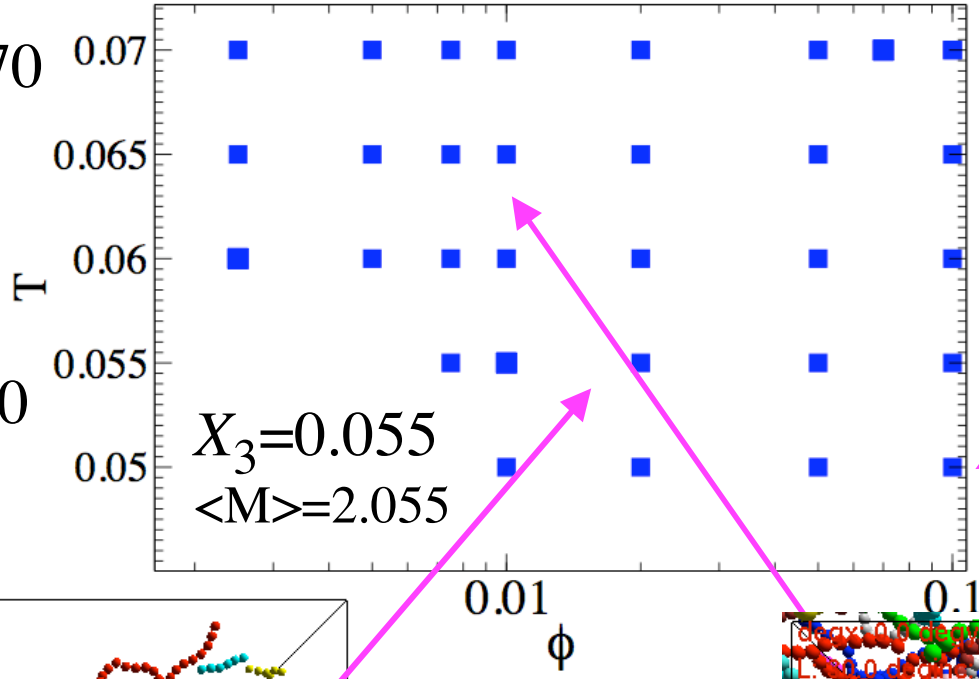
Binary Mixture of f=2 and 3

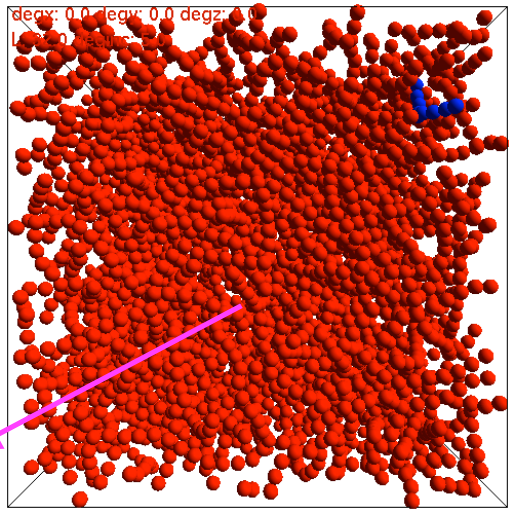


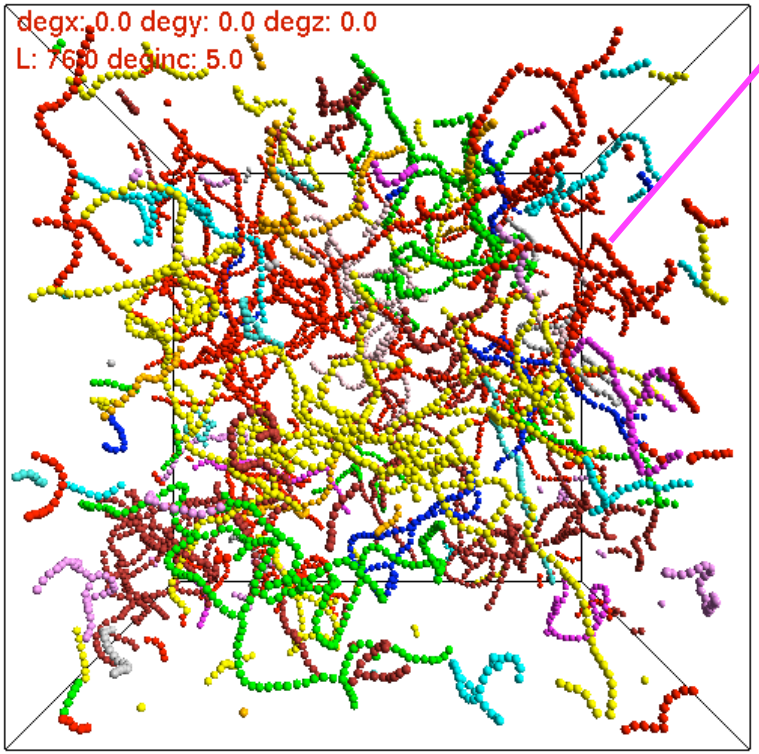
N_2=5670



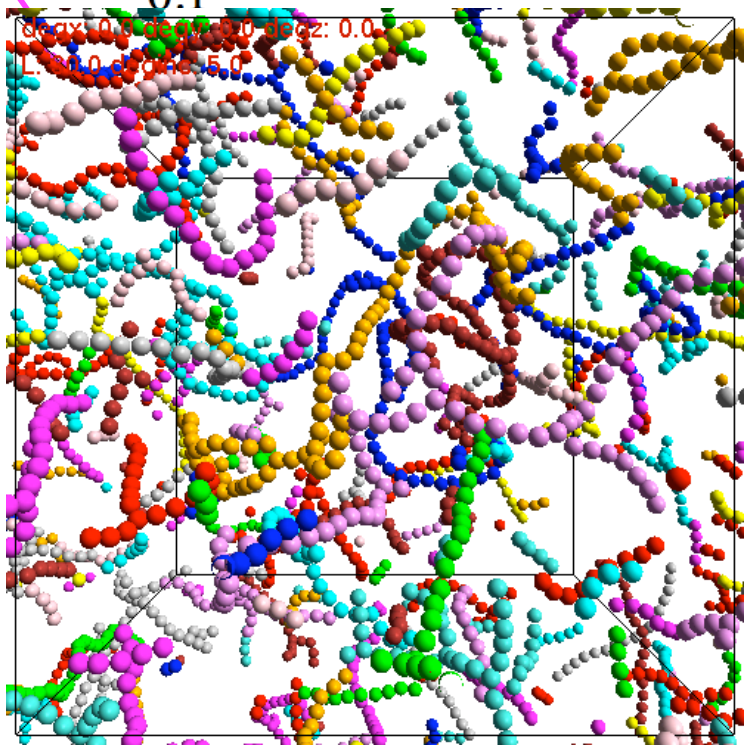
N_3=330



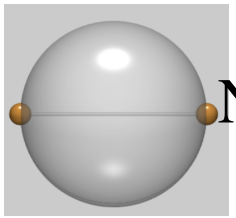




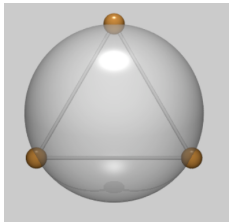
Each color labels a different cluster



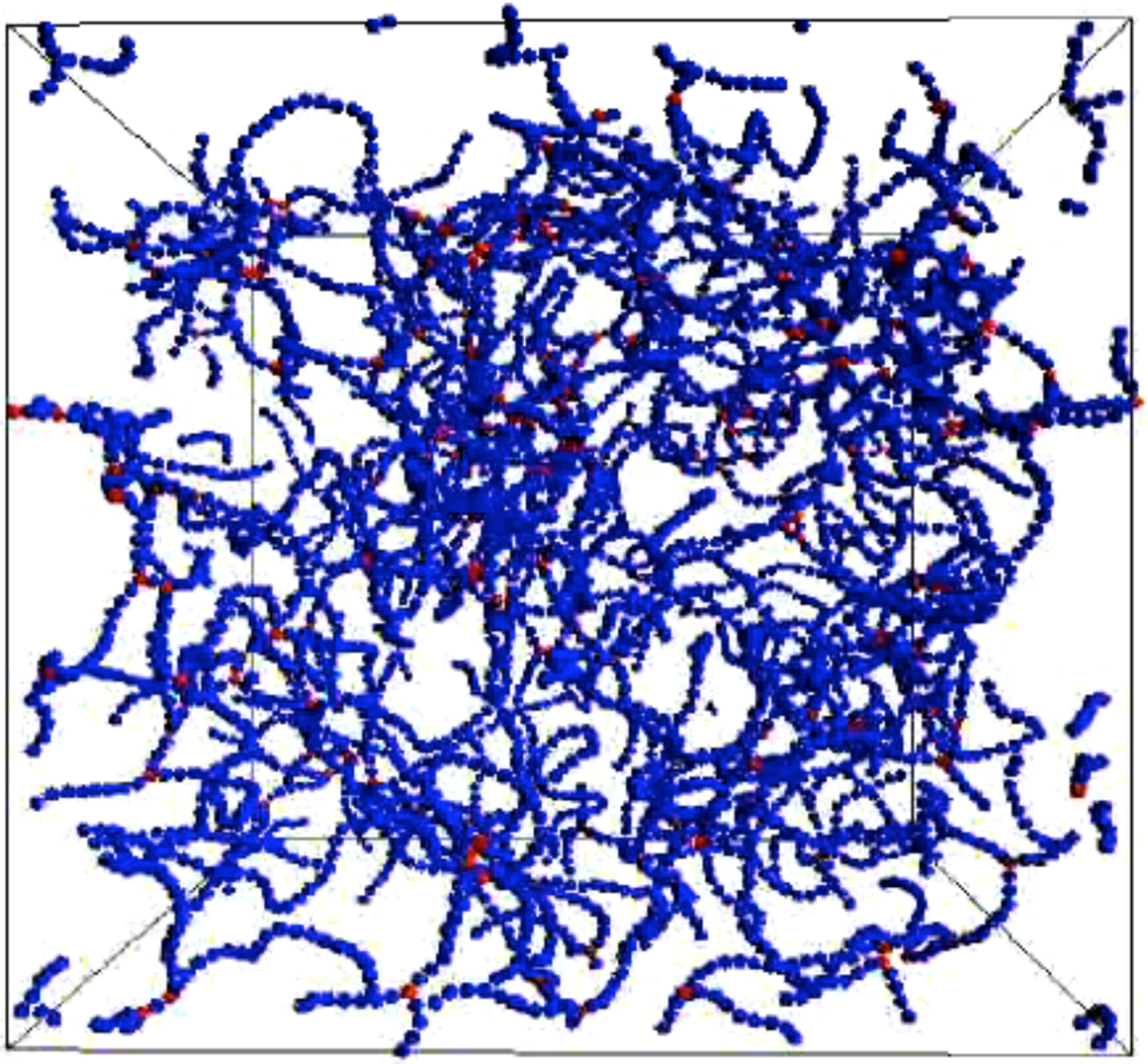
A snapshot of <f>=2.025



N_2=5670



N_3=330



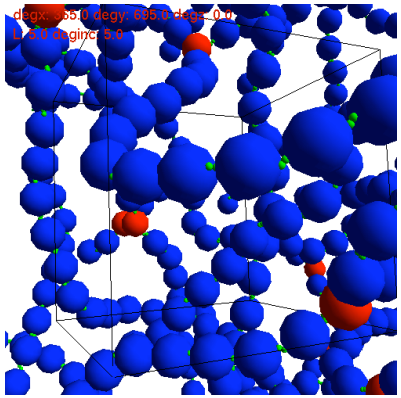
T=0.05, ϕ=0.01

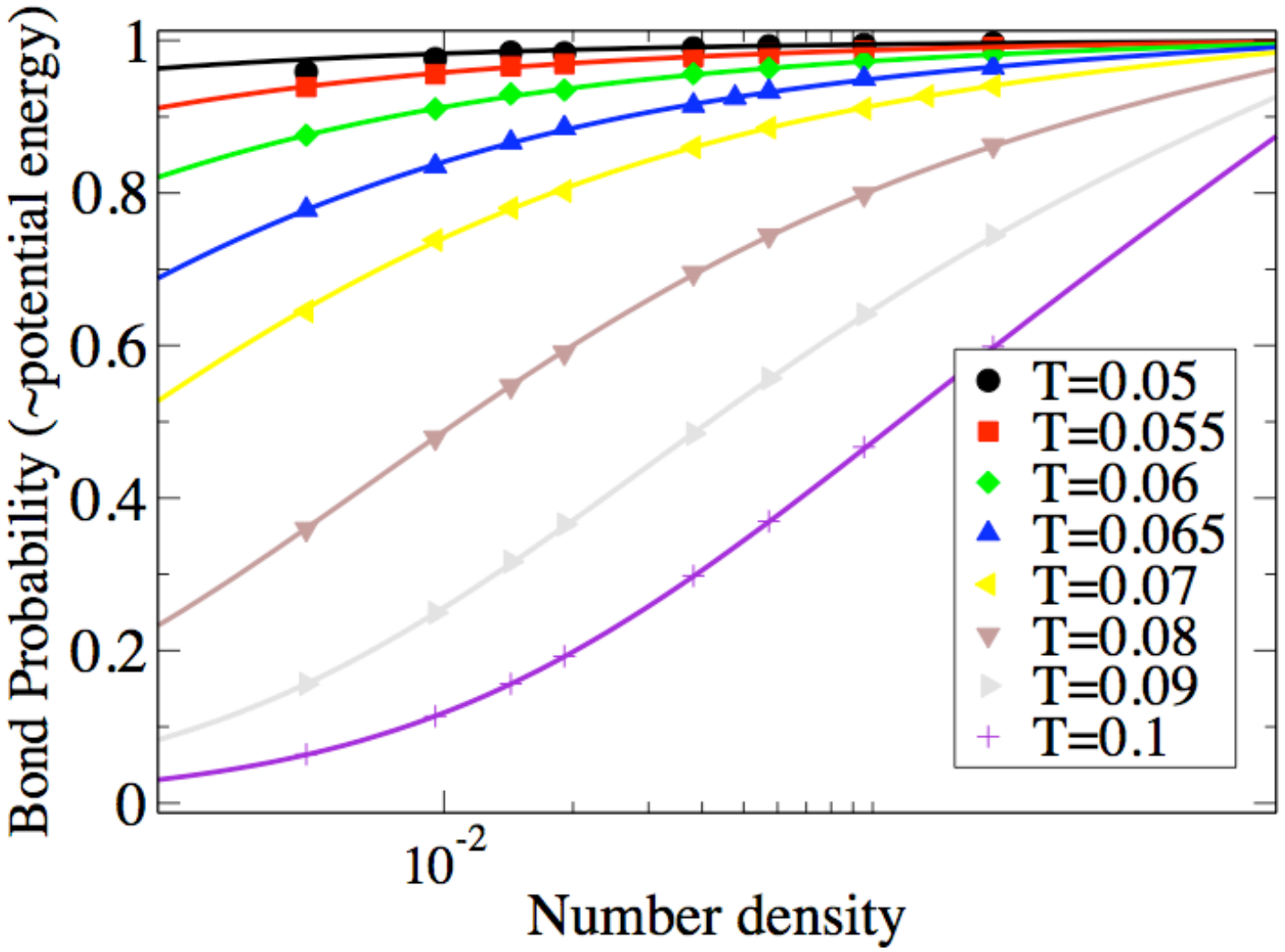
La Sapienza
Università degli Studi di Roma

Soft INFM
Complex Dynamics in Structured Systems

p_b predicted extremely well (in this model) !

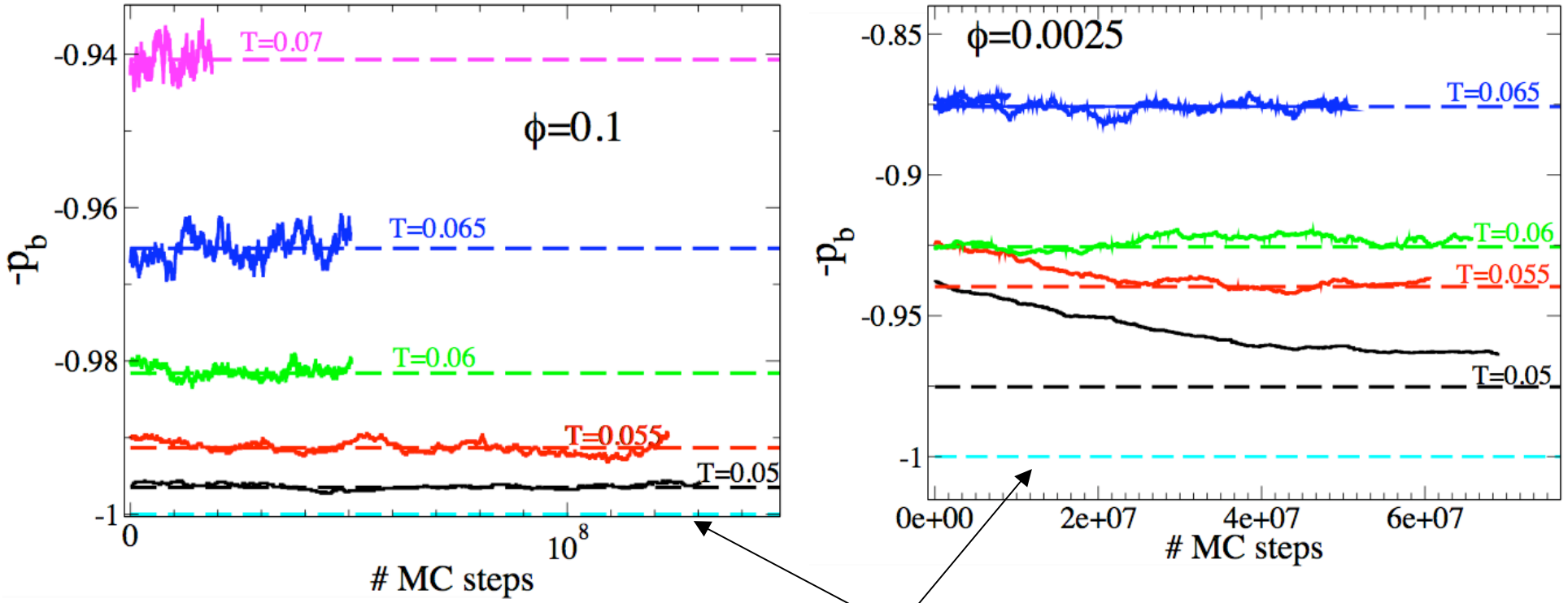
<M>=2.055



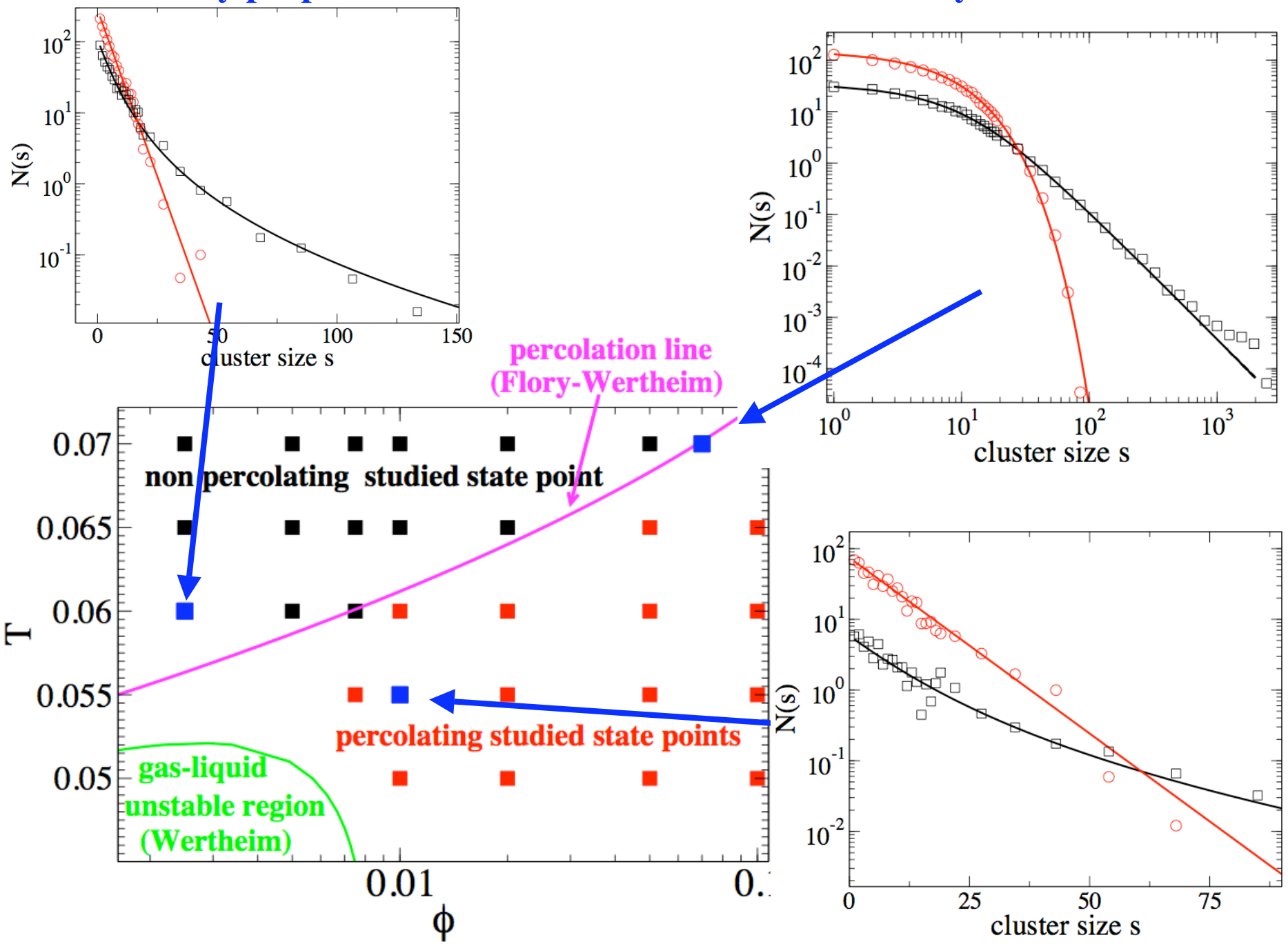


(ground state accessed in equilibrium)

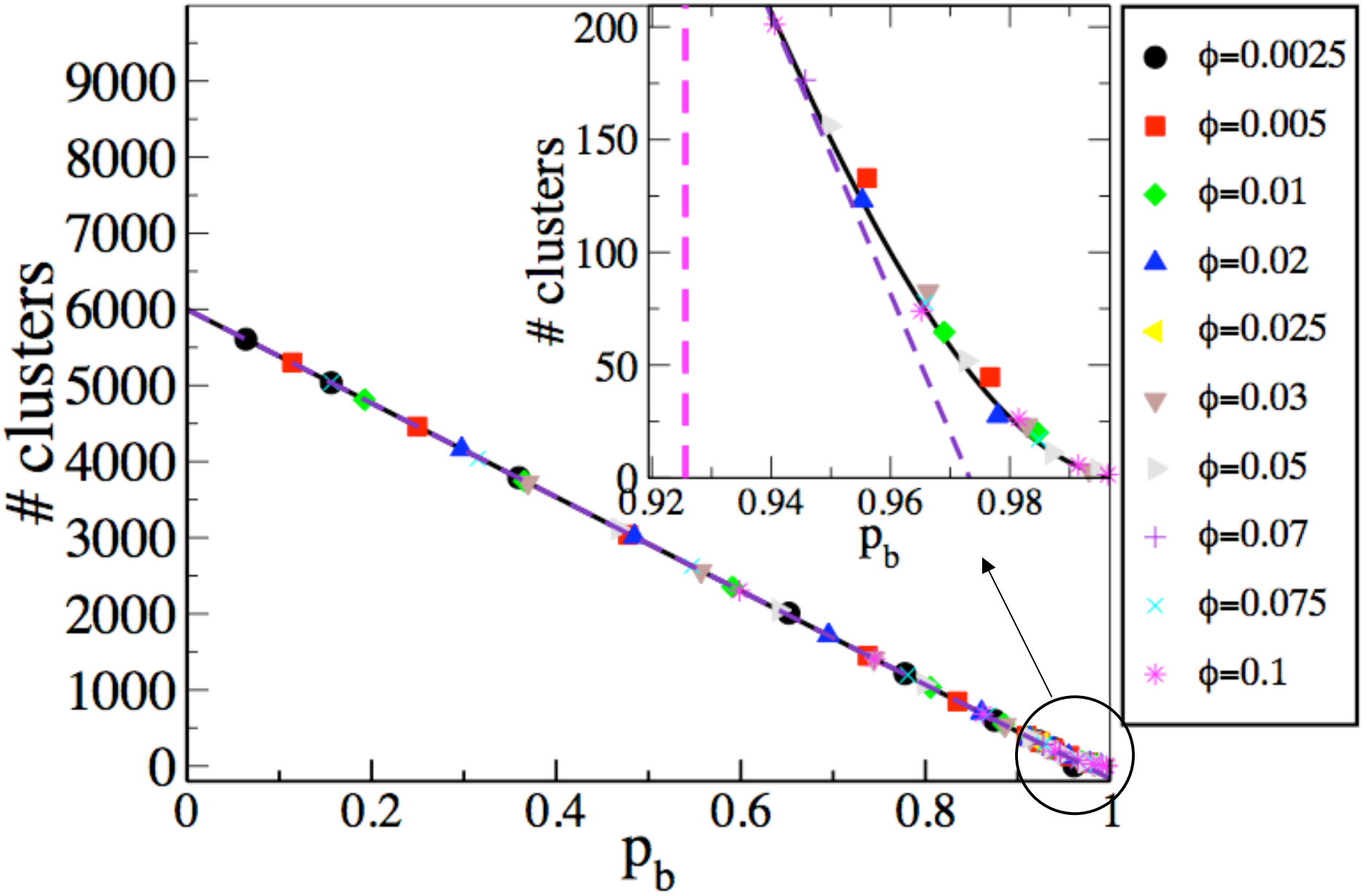
"Time" dependence of the potential energy ($\sim p_b$) around the predicted Wertheim value



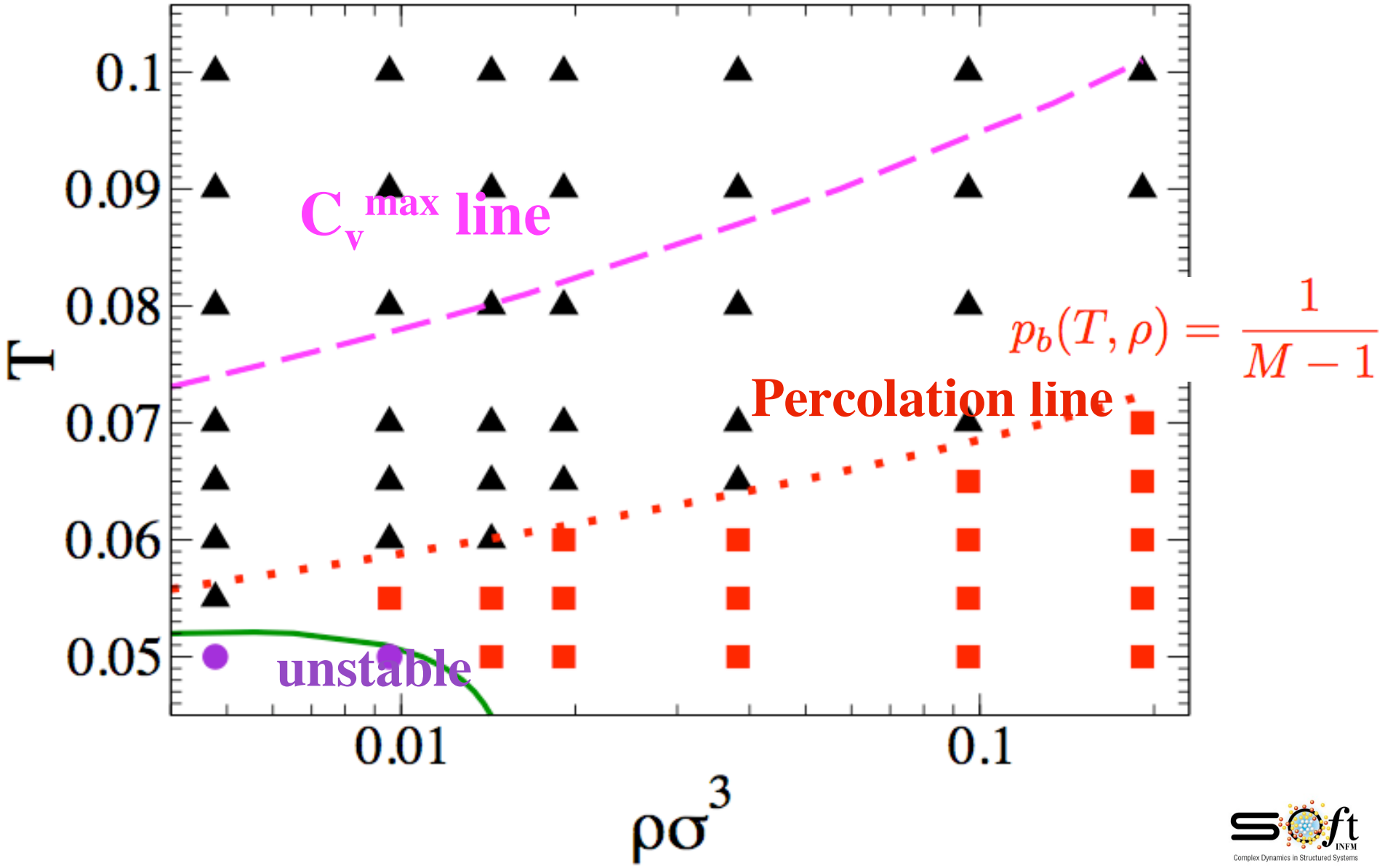
Connectivity properties and cluster size distributions: Flory and Wertheim



No bond-loops in finite clusters !



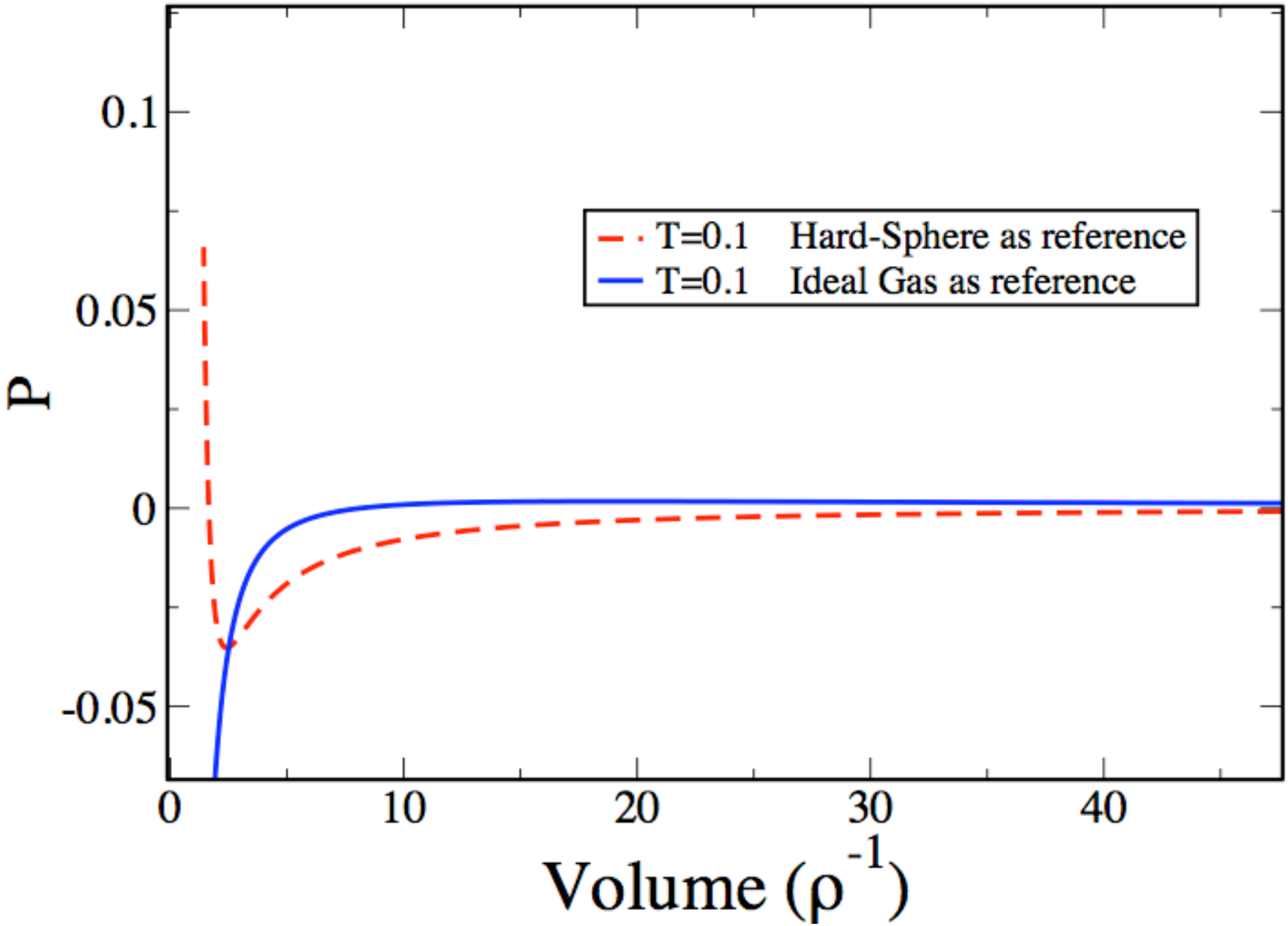
Generic features of the phase diagram
Branching introduces percolation and phase-separation!



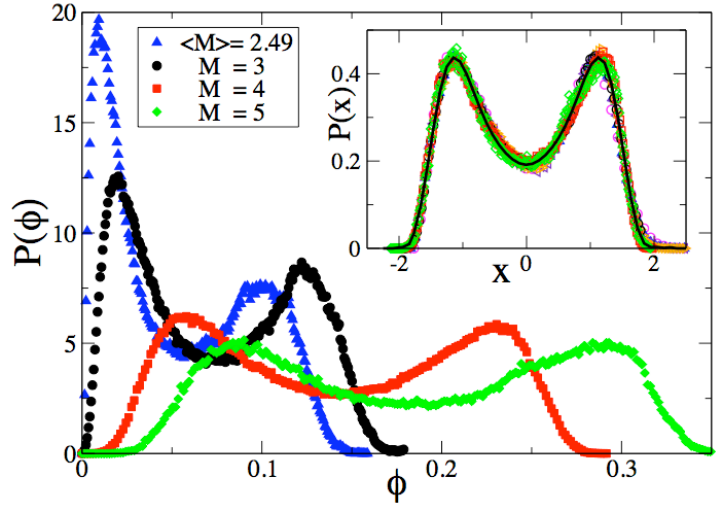
Complex Dynamics in Structured Systems

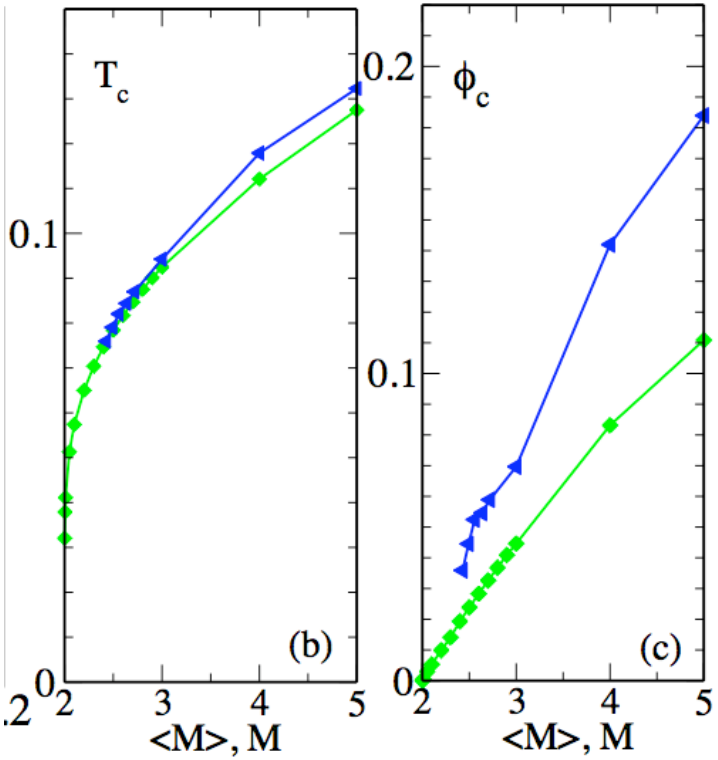
Why is there a phase separation ?

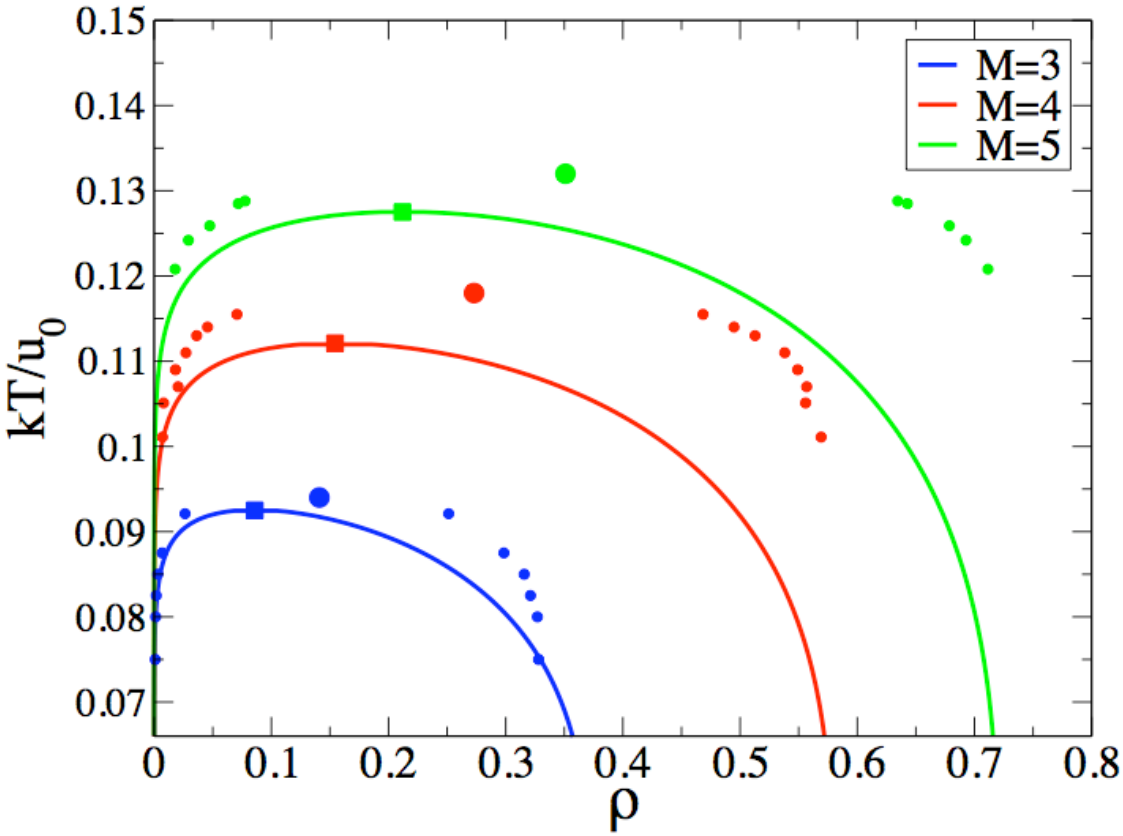
$$\beta P = \rho \left(1 - \frac{f}{2} p_b \right)$$



Phase Diagram - Theory and Simulations



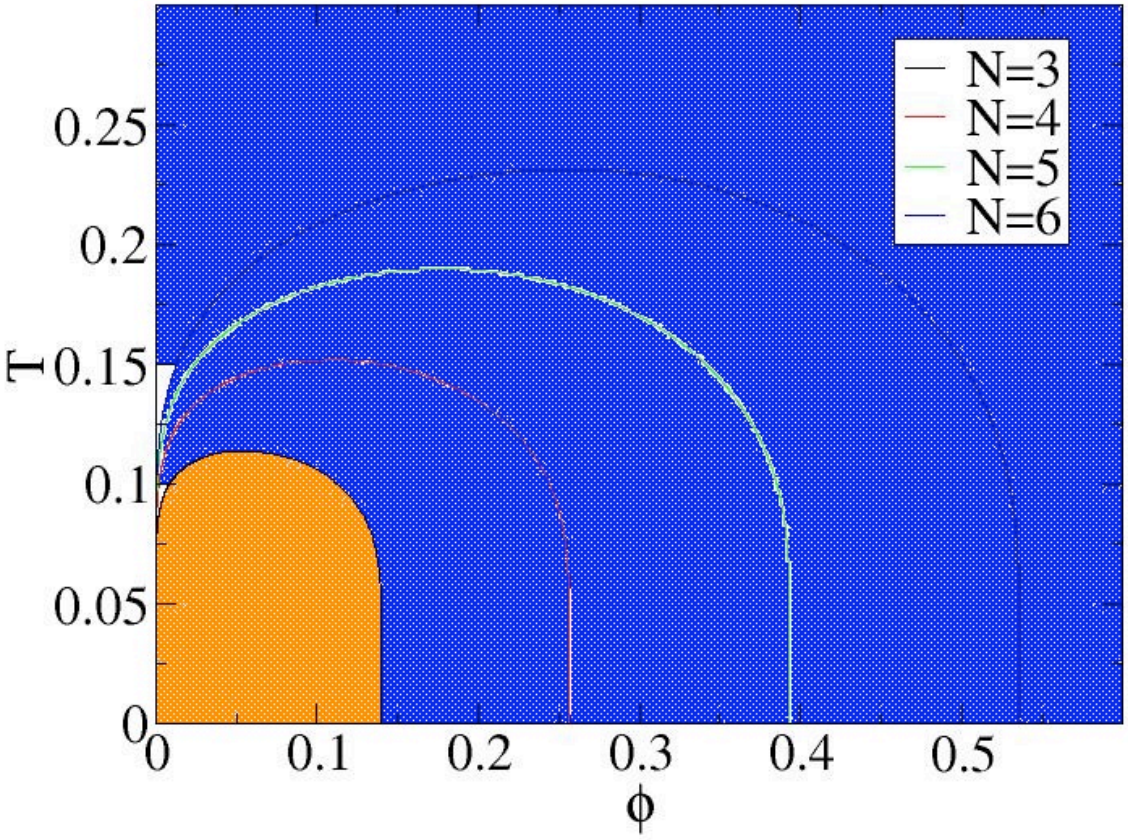




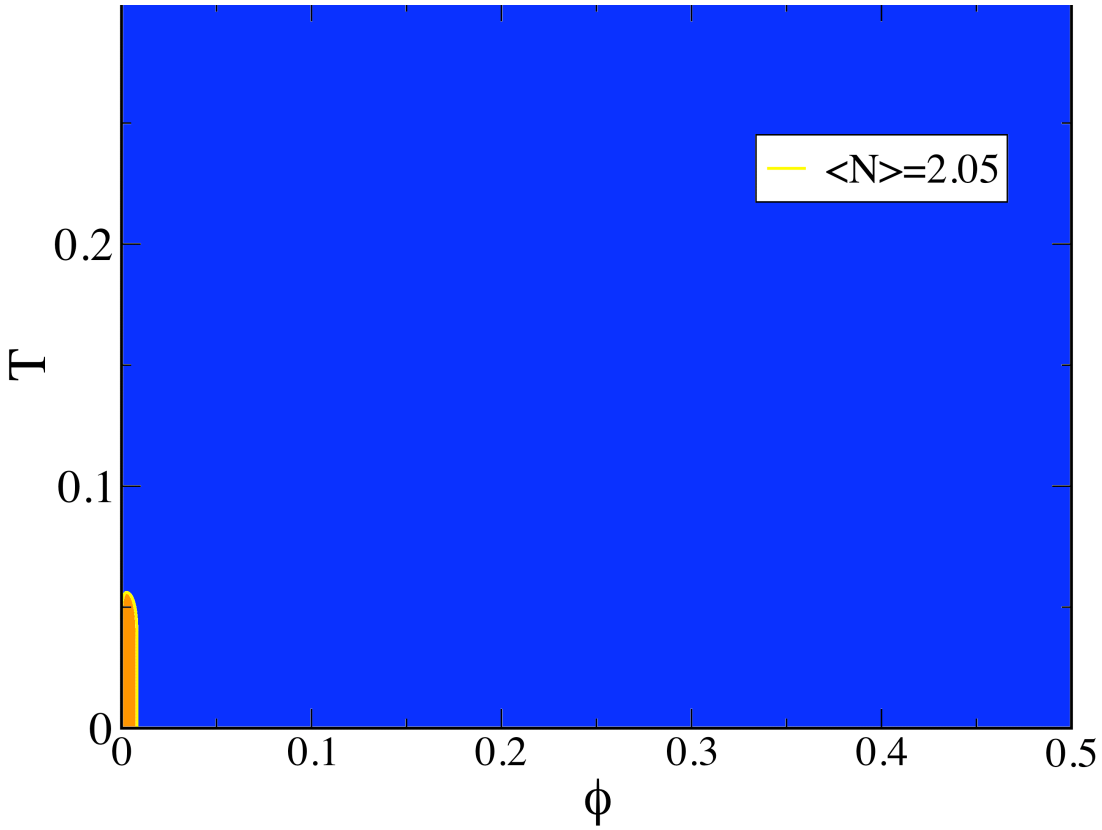
E. Bianchi, J. Largo, P. Tartaglia,
E. Zaccarelli, FS
Phase diagram of patchy colloids:
towards empty liquids
Phys. Rev. Lett. 97, 168301, 2006

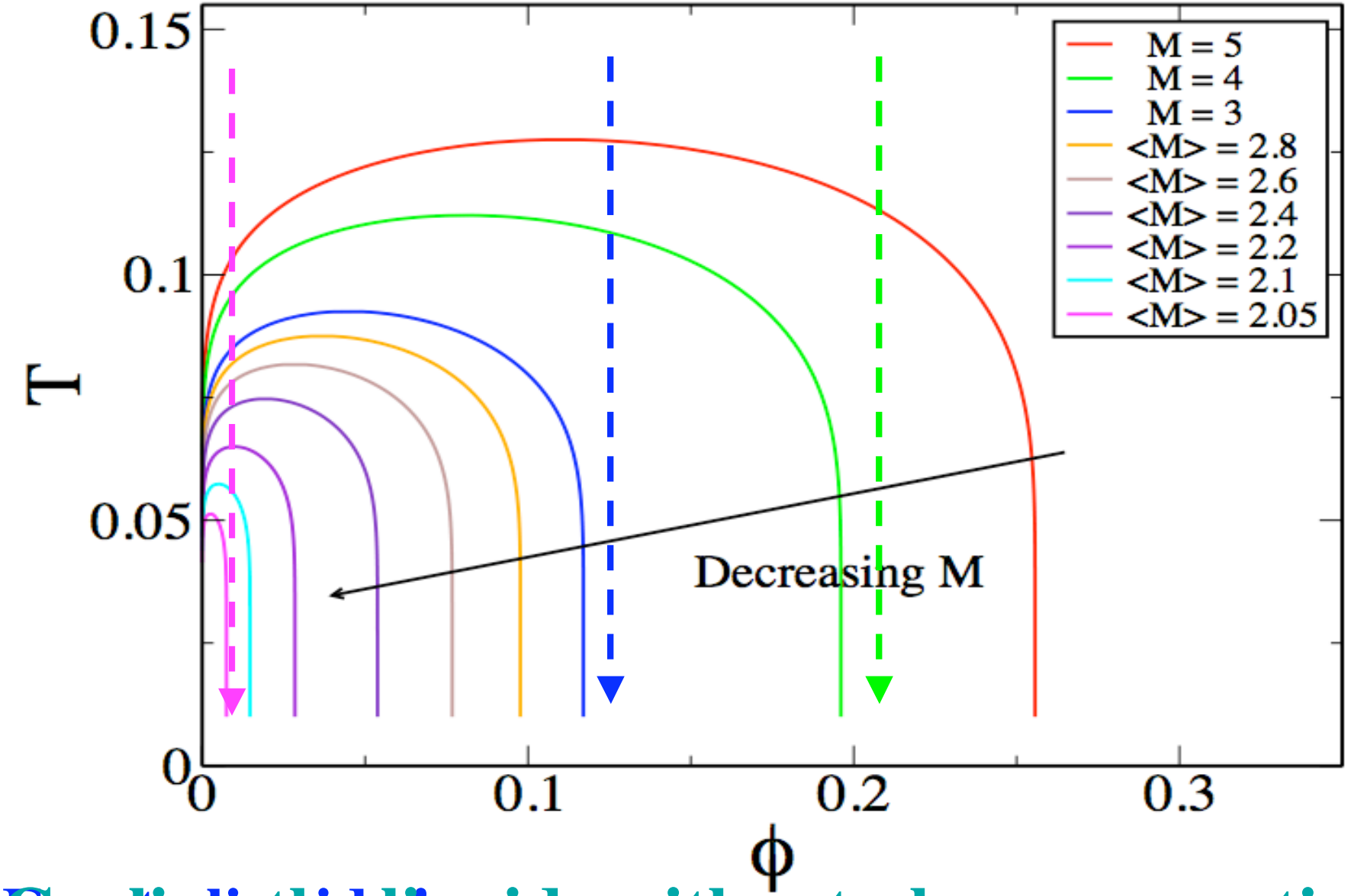
SOft INFM
Complex Dynamics in Structured Systems

How does the valence affect the phase diagram?



Further reduction with f<3 (mixtures)





Coupling the liquids!

Coupling the liquids without phase separating!

Message:

Possibility to reach (in homogeneous conditions) states where βu>>1 and the bond lifetime is large

A DIFFERENT final fate to the liquid state. Arrested states at low ϕ !!!

In the newly available density region (whose with is controlled by the valence), at low T the system forms a "equilibrium" gel