Challenges and opportunities in non-equilibrium soft matter

September 24, 2023 - September 27, 2023

Registration deadline: September 1, 2023

Location: Mont Sant Benet, Spain

Multinodal event: CECAM-UK-JCMAXWELL, CECAM-FR-MOSER, CECAM-FR-RA, CECAM-FR-GSO, CECAM-DE-JUELICH, CECAM-DE-MMS, CECAM-DE-SMSM, CECAM-IT-SISSA-SNS, CECAM-IT-SIMUL, CECAM-NL, CECAM-UK-DARESBURY, CECAM-AT

Daanentropy:
A disease spreading within the Computational Soft Matter Community

Dedicated to Daan

Daanentropy

From Wikipedia, the free encyclopedia

Not to be confused with Entropy

Daanentropy is a sickness that is most commonly associated with the interest in states of disorder, randomness, or uncertainty. It has been observed in scientists working in diverse fields, from classical thermodynamics, where it was first recognized, to the microscopic description of nature in statistical physics, and to the principles of information theory. It has found far-ranging spreading in chemistry and physics, in biological systems and their relation to life, in cosmology, economics, sociology, weather science, climate change, and information systems.

Can you explain me what Daanentropy is ?

Free Research Preview. ChatGPT may produce inaccurate information about people, places, or facts. ChatGPT August 3 Version

- I have specific information about a sickness called "Daanentropy" that affects computational scientists. It appears that it spreads among scientists working in soft condensed matter associated with the repeated reading of some selected Daan Frenkel's articles. At an early stage it generates an incontrollable need to calculate entropic phase diagram. At a later stage an urge to develop novel computational methods appears. The late stage involves a continuous mumbling of what entropy-driven attraction can do. Daanentropy has been first identified in Europe, but there are now propositions to consider it a pandemic infection.

A case study of a patient (FS) affected by Daanentropy

Let’s examin the different stages

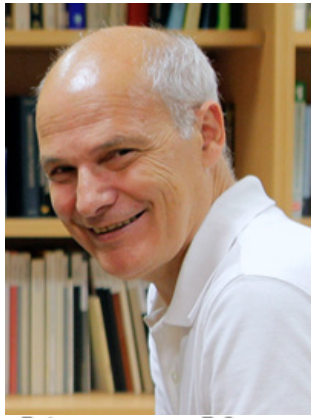
A case study of a patient (FS) affected by Daanentropy

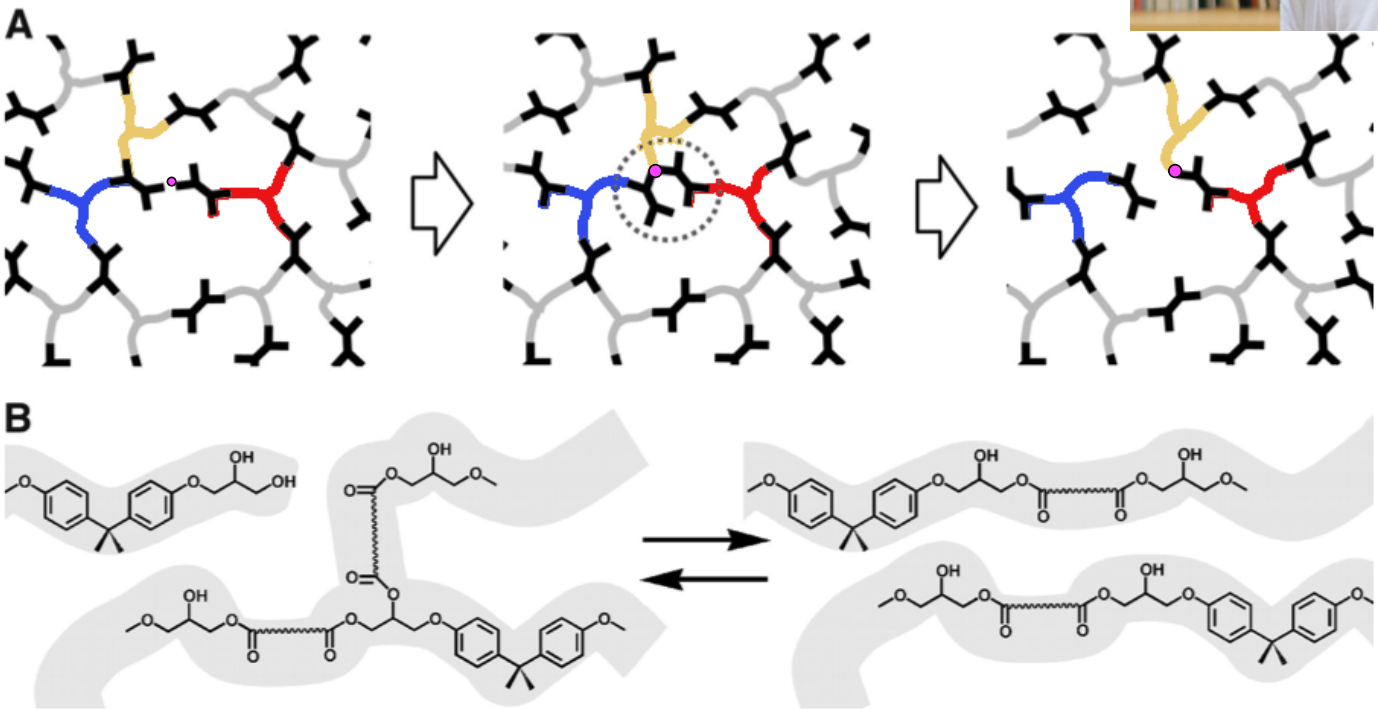
Early stage: calculation of entropic phase diagram

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*





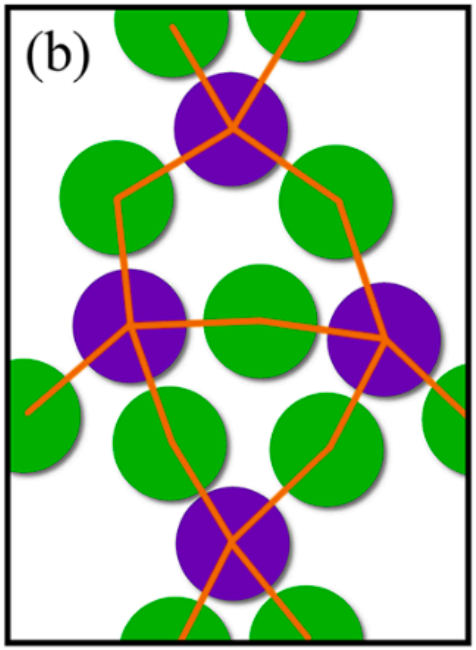
Non stochiometric mixture of 4- and 3-functional Molecules

Always same number of

A simple (patchy particle-like) idea.

bifunctional

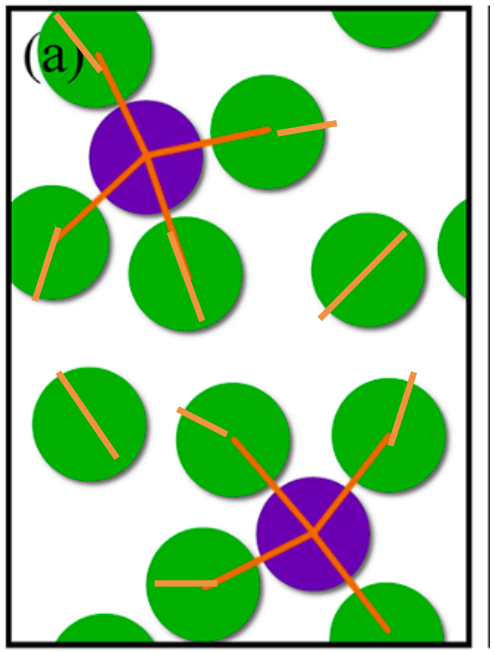
tetrafunctional



Stochiometric mixture of bifunctional and tetrafunctional in the ground state ($kT \ll \varepsilon$)

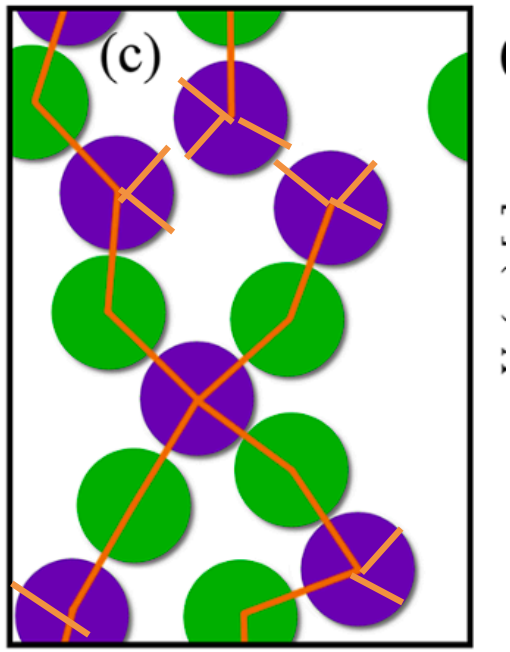
A simple idea. Non-stochiometric binary mixtures a T=0 K

Excess of bivalent



All tetravalent are coordinated

Excess of tetravalent



All bivalent are coordinated

It is possible to control the number of saturated and non-saturated bonds !

Wertheim free energy

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

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

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

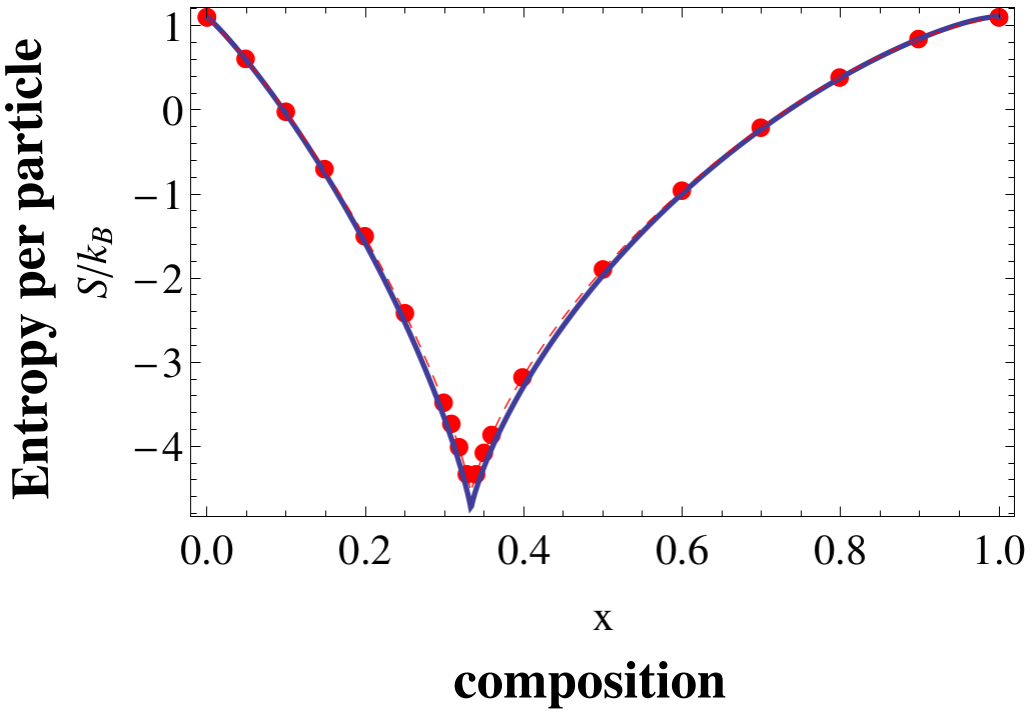
Combinatorial entropy term:

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

Testing the theory

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

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

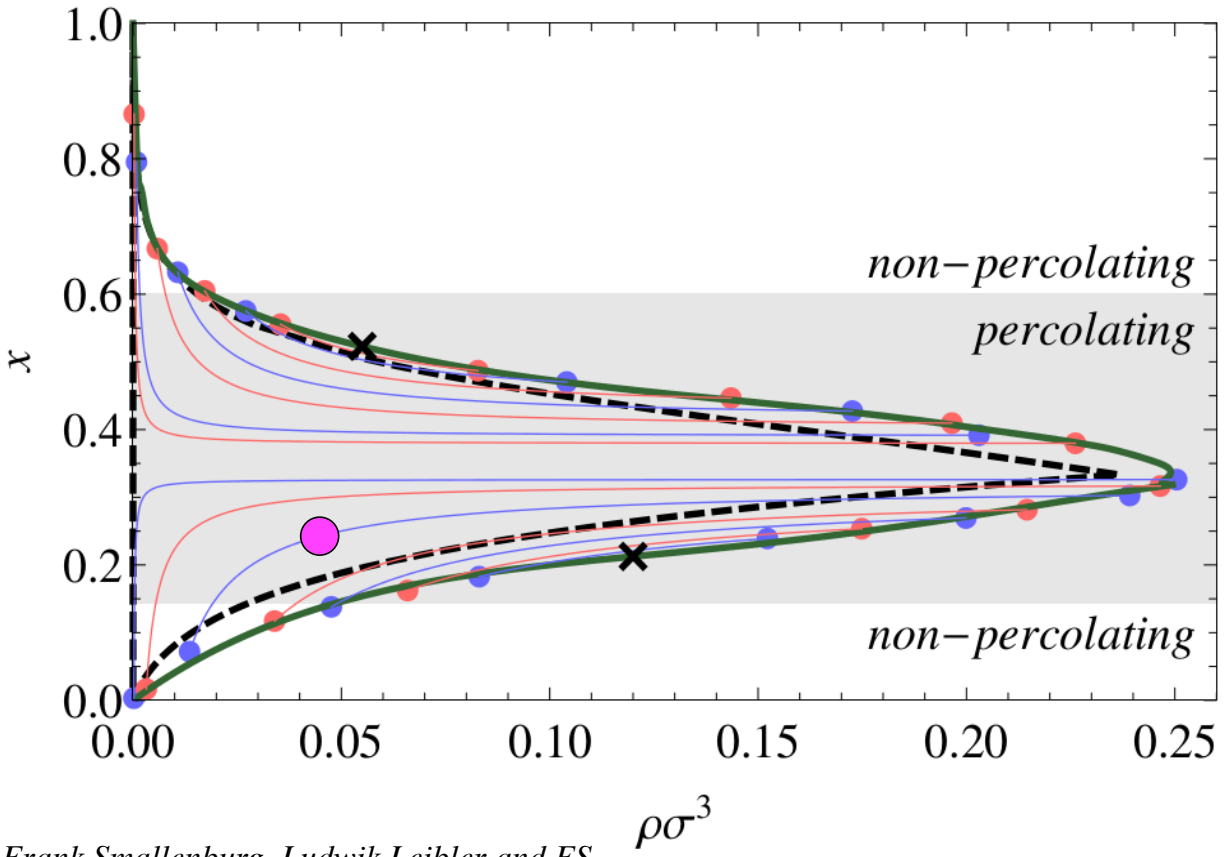


T=0 K Equilibrium phase diagram (Entropy Only!)

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



Frank Smallenburg, Ludwik Leibler and FS
Patchy Particle Model for Vitrimers
Phys. Rev. Lett. 111, 188002 (2013)

Simulation: black dashed line
Theory: points, solid line

Merging two distinct pieces….

Early stage: calculation of entropic phase diagram

Another example of the early stage……

If (a limited valence [patchy]) liquid reaches a fully bonded state, then it has the same energy of the fully bonded crystal !

(effectively an a-thermal system !)

Entropy decides the most stable phase (exactly as in HS!)

Competition between:

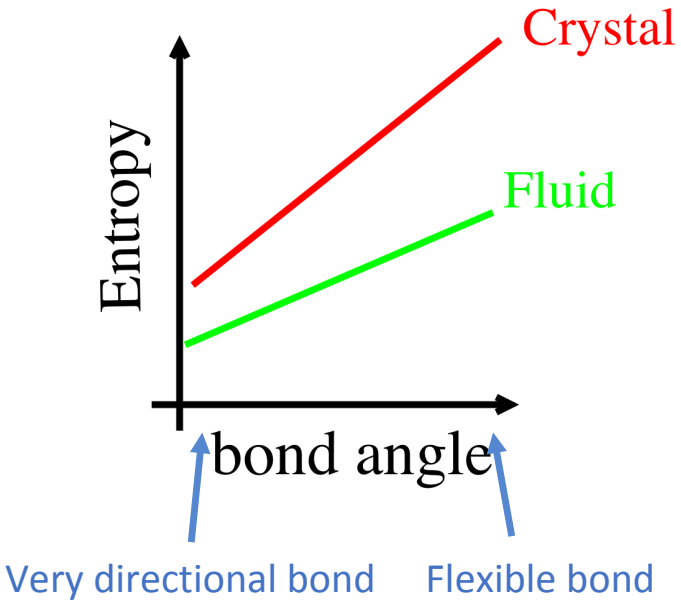
- Number of microstates accessed at "fixed bonding" (vibrational entropy) (both crystal and fully bonded liquid)

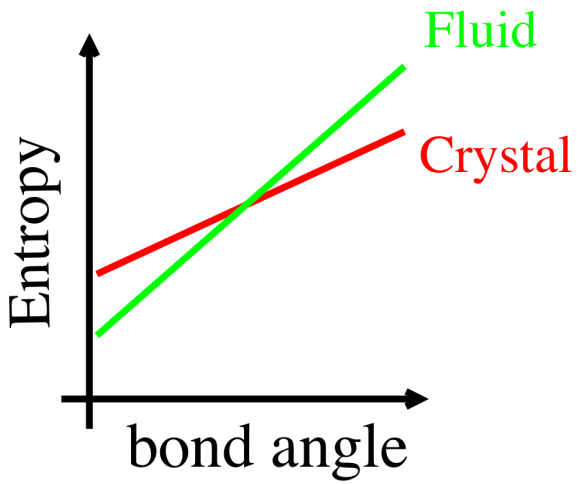
- **Number of different bonding topologies (configurational entropy) (only fully bonded liquid)**

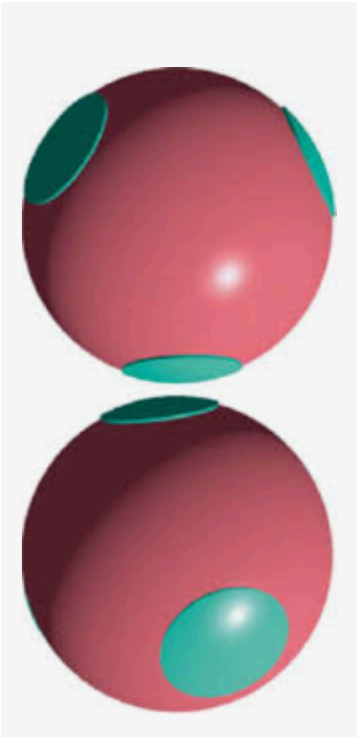
Like in HS, the crystal (diamond for tetrahedral particles) is stable because

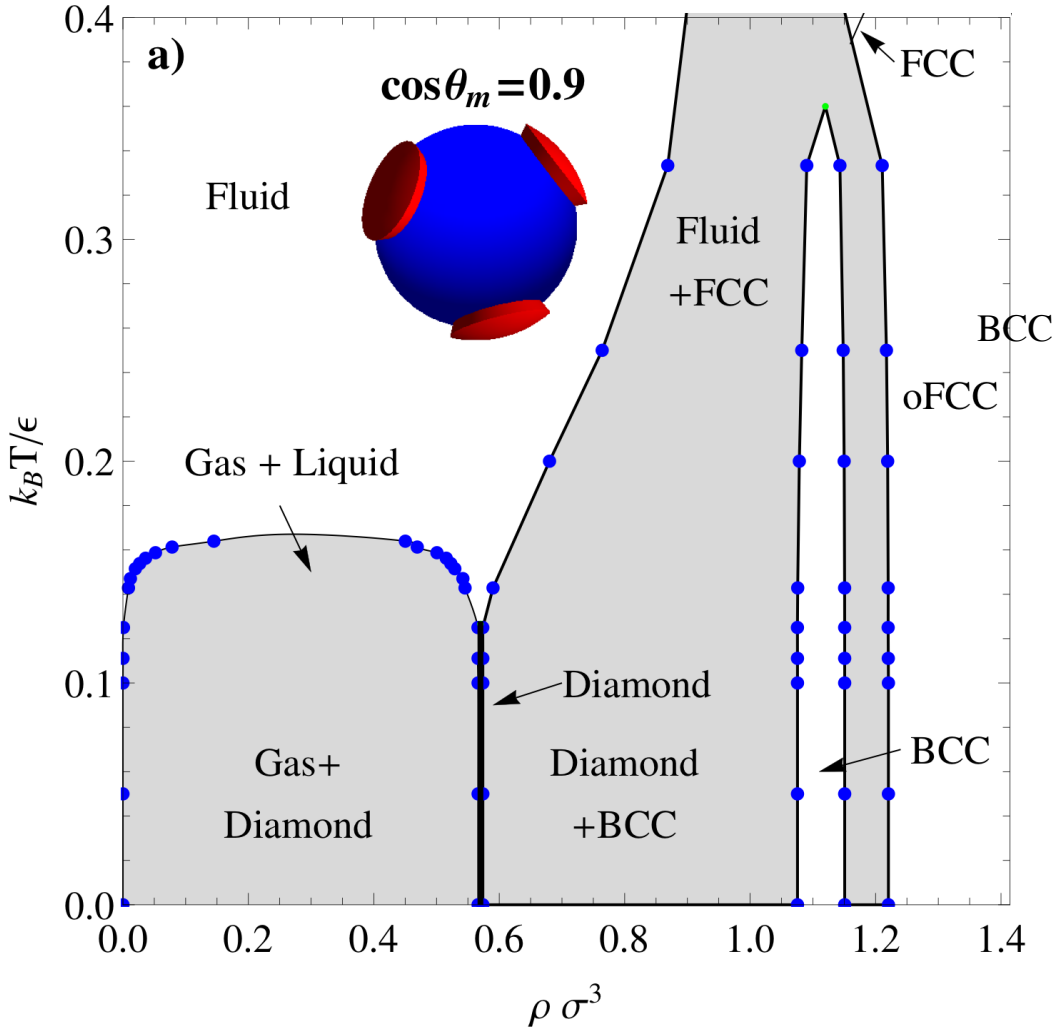
$$S_{vib\ crystal} > (S_{vib} + S_{conf})_{liquid}$$

What happen when the angular width of the patch increases (but single bond per patch) ?





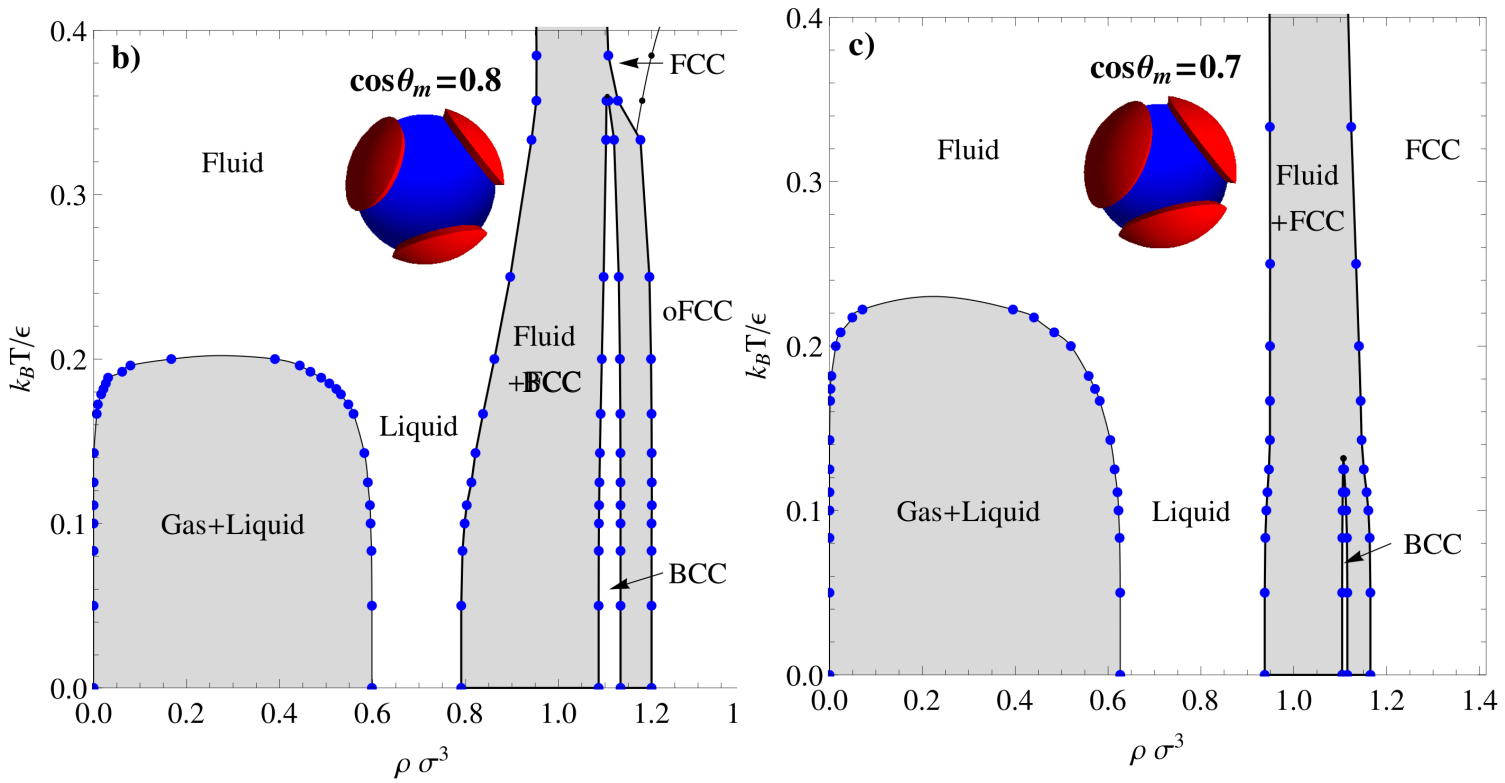




nature physics
LETTERS
PUBLISHED ONLINE: 4 AUGUST 2013 | DOI: 10.1038/NPHYS2693

Liquids more stable than crystals in particles with limited valence and flexible bonds

Frank Smallenburg* and Francesco Sciortino



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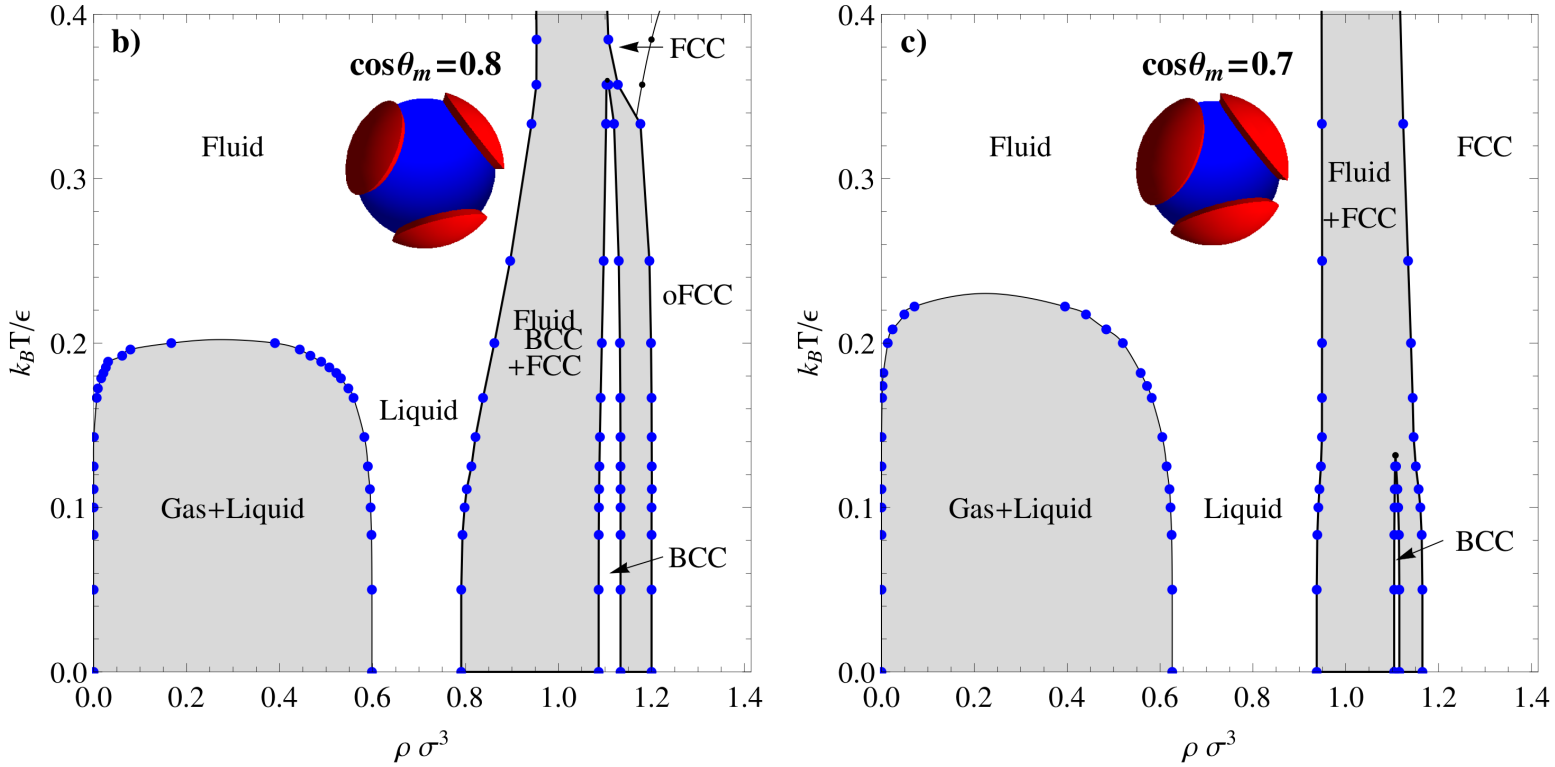
Liquids more stable than crystals in particles with limited valence and flexible bonds

Frank Smallenburg* and Francesco Sciortino

Ultrastable liquids !



Also 3 patches

Martinez-Veracoechea, F. J., Mladek, B. M., Tkachenko,A. V. & Frenkel, D. Design rule for colloidal crystals of dna-functionalized particles. Phys. Rev. Lett. 107, 045902 (2011).

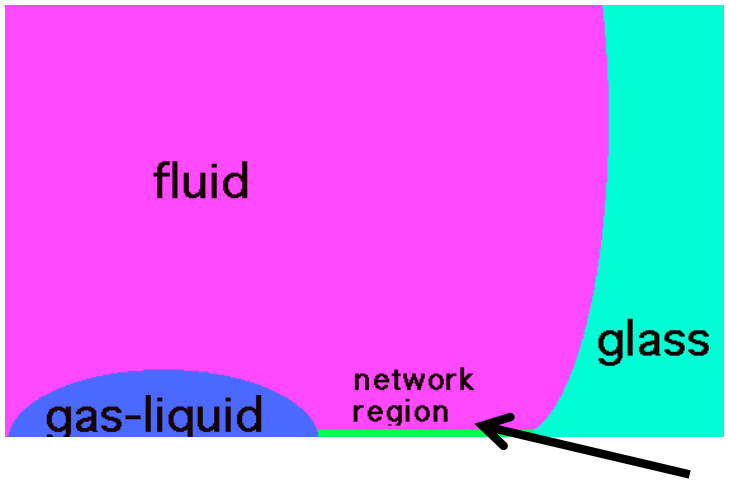
nature physics — LETTERS

PUBLISHED ONLINE: 4 AUGUST 2013 | DOI: 10.1038/NPHYS2693

Liquids more stable than crystals in particles with limited valence and flexible bonds

Frank Smallenburg* and Francesco Sciortino

Key elements for liquid stability at T=0 K: (ultrastable liquids !)



Thermodynamically stable !

*** Patchness - Low valence. Small density of the coexisting liquid phase**

*** Large flexibility of the angular interactions: (wide variety of networks, increasing S_{conf})**

Intermediate stage in Daanentropy:

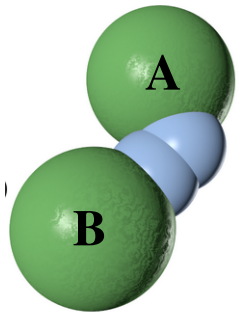
(urge to develop smart equilibration methods)

How to equilibrate networks at low temperature

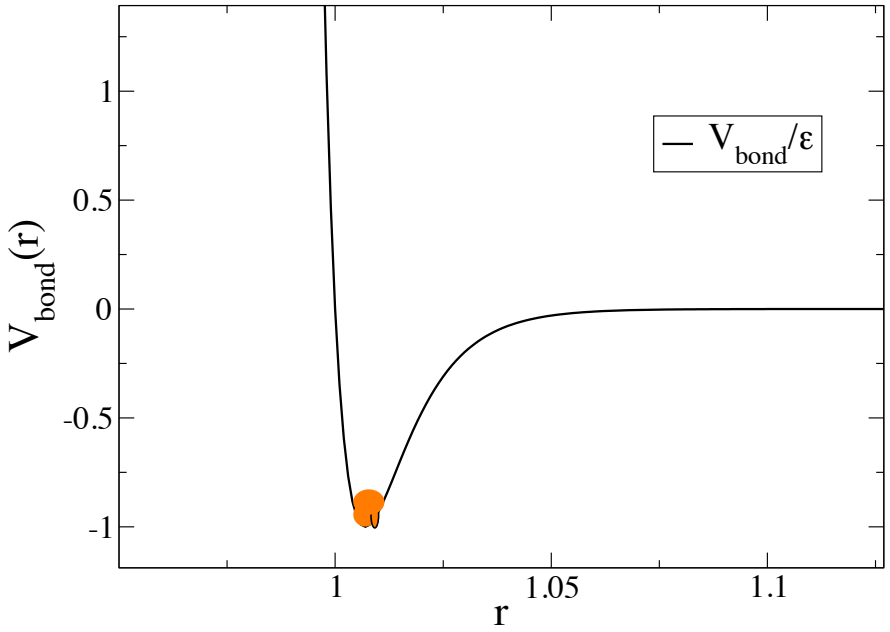
Swapping instead of breaking

See Bortolo Mognetti work for MC methods

Molecular Dynamics of Swap Events



Short-range with clear minimum and cut-off

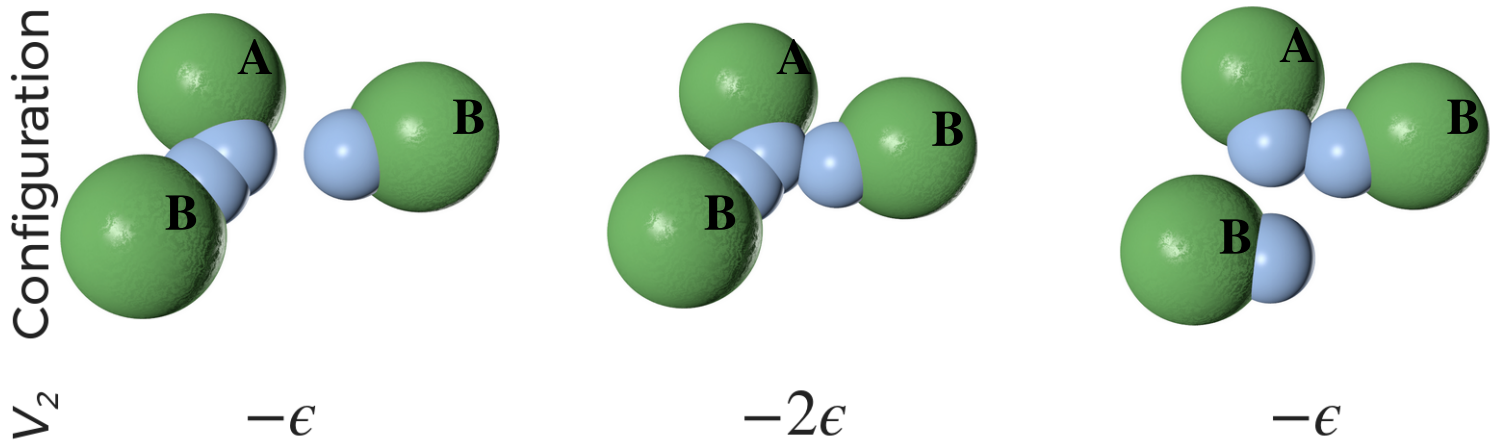


Three-body potential for simulating bond swaps in molecular dynamics

Eur. Phys. J. E (2017) **40**: 3

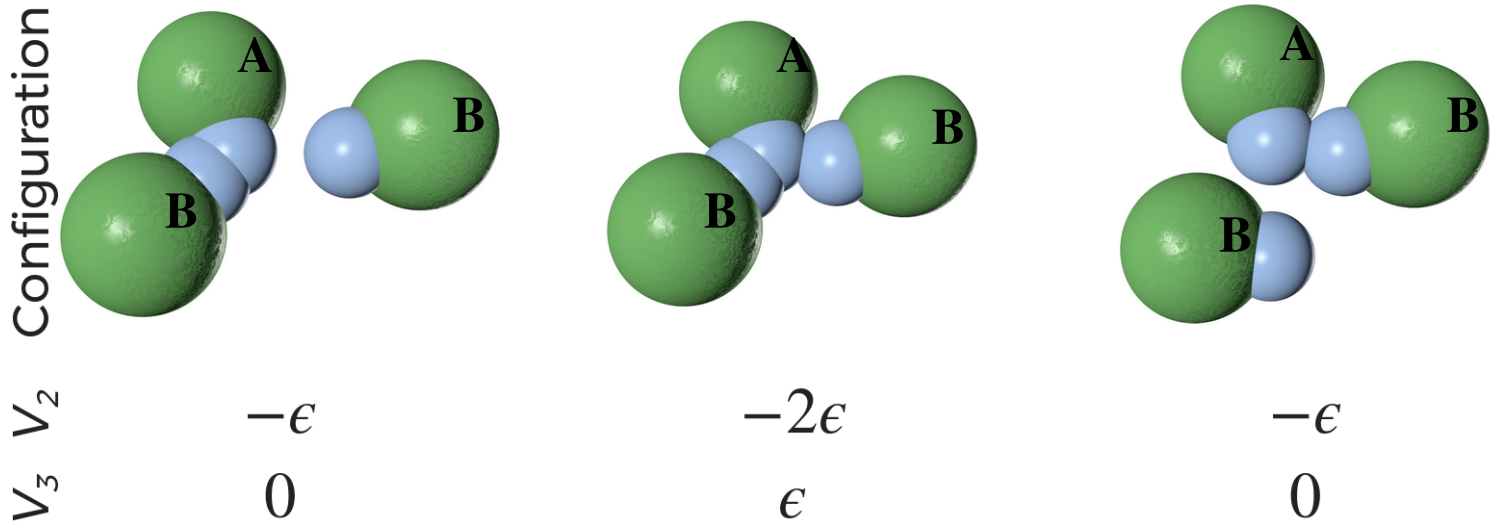
kT<ε

Molecular Dynamics of Swap Events



We need a flat energy surface for swap

Molecular Dynamics of Swap Events



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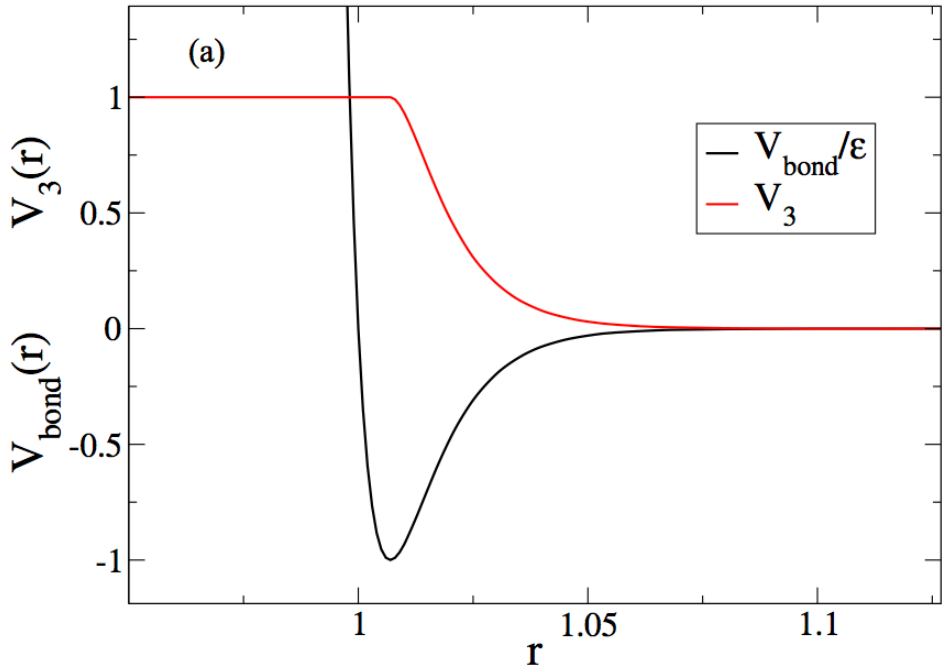
Molecular Dynamics of Swap Events



$$V_3(r) = \begin{cases} 1, & r \le r_{\min}, \\ \dfrac{-V_{\text{bond}}(r)}{\epsilon}, & r_{\min} \le r \le r_{\text{cutoff}} \end{cases}$$

Eur. Phys. J. E (2017) **40**: 3
DOI 10.1140/epje/i2017-11496-5

THE EUROPEAN PHYSICAL JOURNAL E

Tips and Tricks

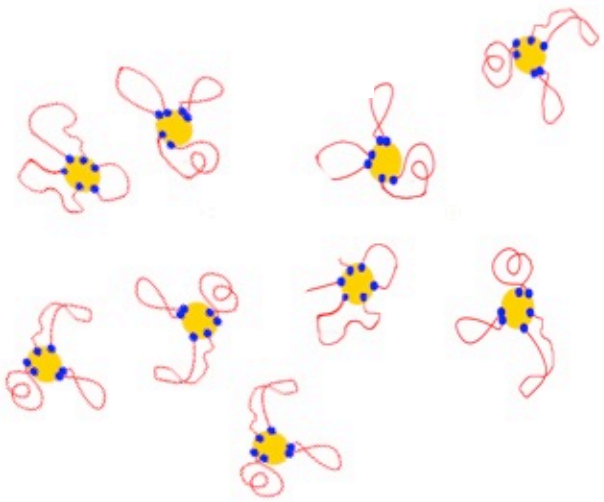
Three-body potential for simulating bond swaps in molecular dynamics

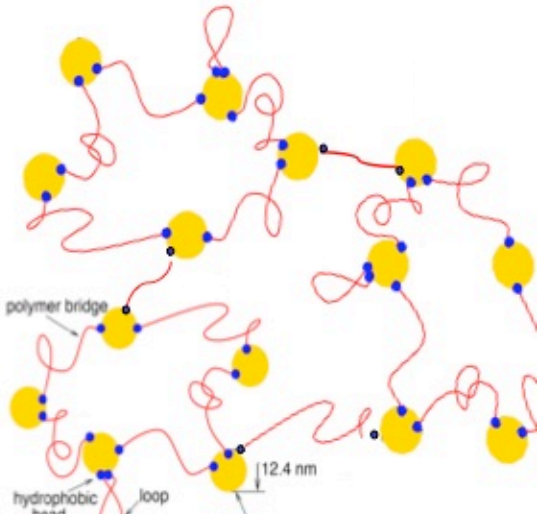
Francesco Sciortino[a]

$$V_{\text{threebody}} = \lambda \sum_{ijk} \epsilon V_3(r_{ij}) V_3(r_{ik})$$ **(always positive)**

The late stage: Entropy Attracts !

Useful for students:
Francesco Sciortino
Entropy in self assembly
Riv. Nuovo Cimento, Vol. 42 (2019) 511, DOI: 10.1393/ncr/i2019-10165-1




polymer bridge
12.4 nm
hydrophobic
loop

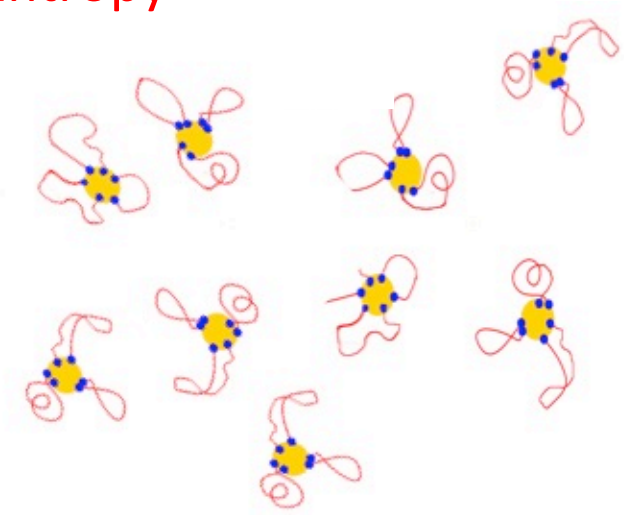
Another important source of entropy:

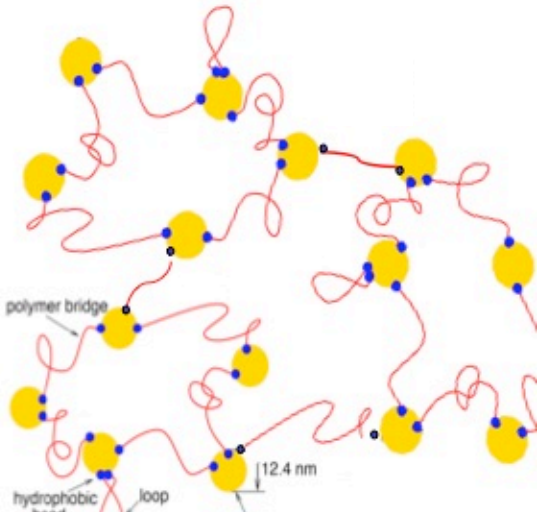
Combinatorial Entropy

VOLUME 91, NUMBER 1 PHYSICAL REVIEW LETTERS week ending 4 JULY 2003

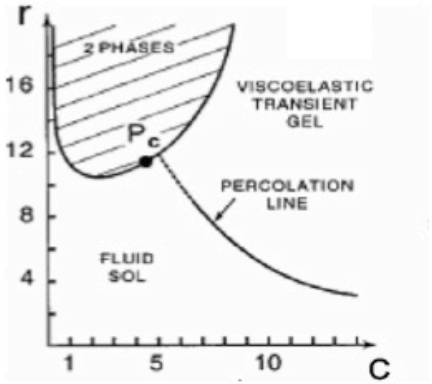
Entropic Phase Separation in Polymer-Microemulsion Networks

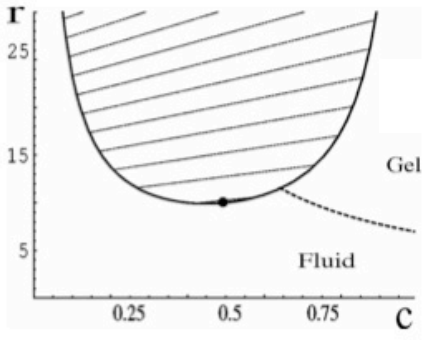
A. Zilman,[1] J. Kieffer,[2] F. Molino,[2] G. Porte,[2] and S. A. Safran[1]
[1]*Department of Materials and Interfaces, Weizmann Institute of Science, 76100 Rehovot, Israel*
[2]*Groupe de Dynamique des Phasees Condensees, Universite de Montpellier II, 34095 Montpellier Cedex 05, France*
(Received 27 January 2003; published 3 July 2003)



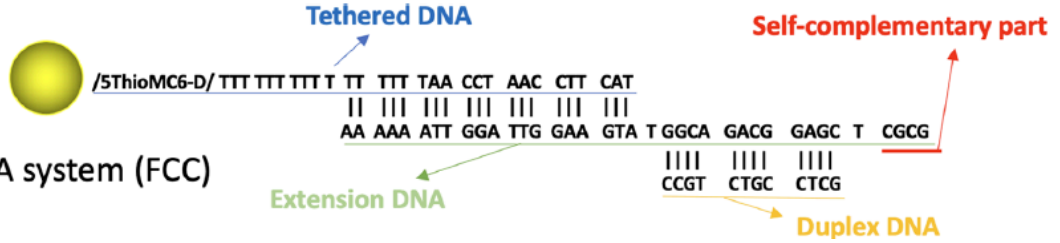


(Exp)

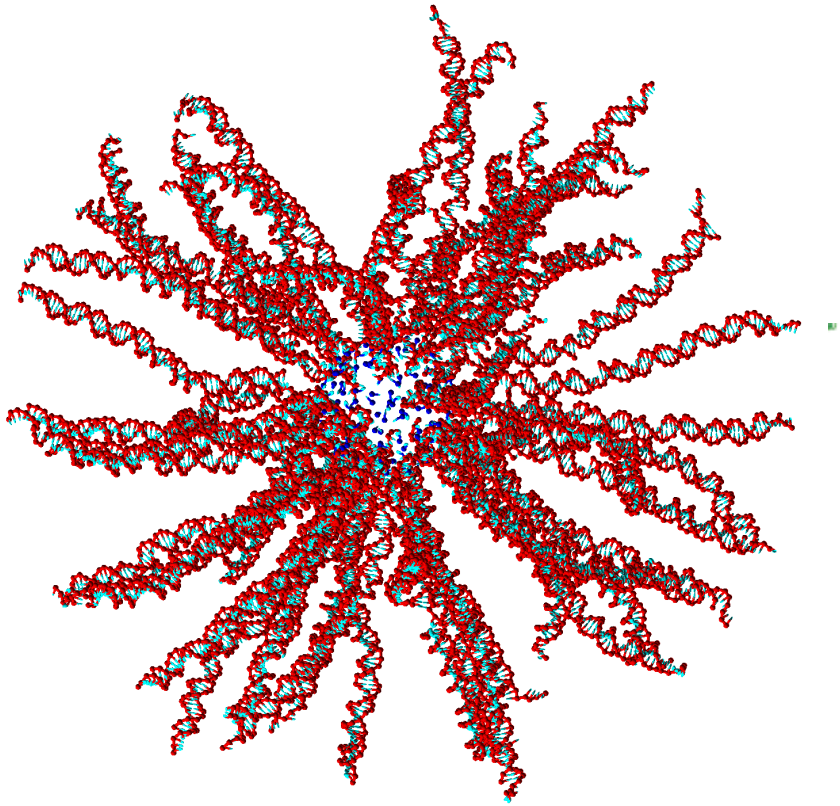


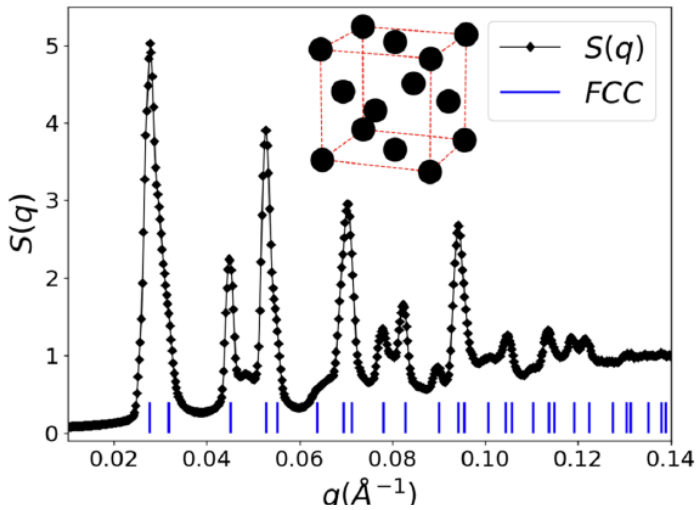


(Teo)



AA system (FCC)





Oleg Gang (Brookhaven and Columbia)

------CGCG
GCGC------

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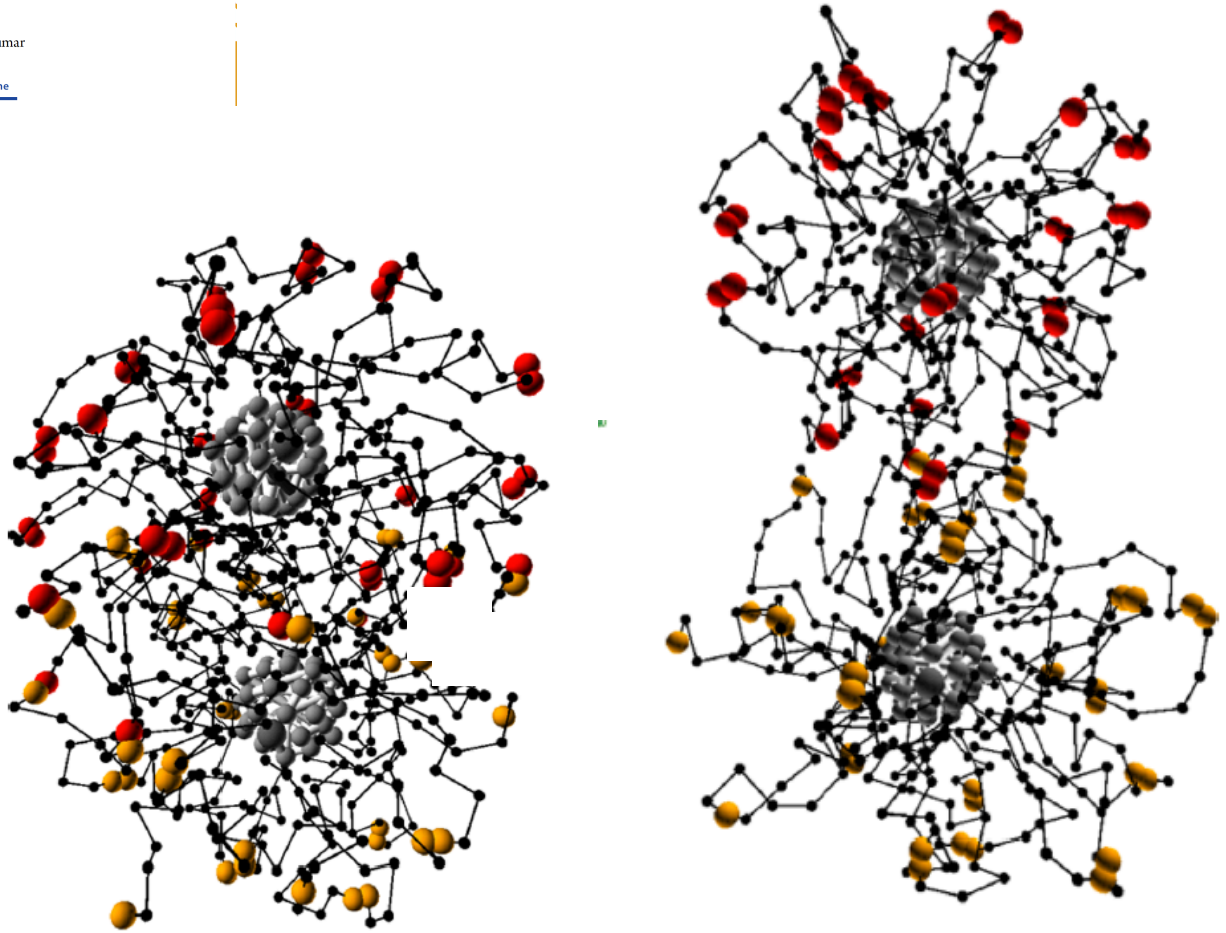
www.acsnano.org

Combinatorial-Entropy-Driven Aggregation in DNA-Grafted Nanoparticles

Francesco Sciortino,* Yugang Zhang, Oleg Gang, and Sanat K. Kumar

Cite This: *ACS Nano* 2020, 14, 5628−5635 Read Online

A coarse-grained version of the DNA-decorated gold nanoparticle



Can we quantify the entropic gain ?

$\Omega=(N-1)!!$

$\Omega=(N-1)!!$

$\Omega=(2N-1)!!$

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Combinatorial-Entropy-Driven Aggregation in DNA-Grafted Nanoparticles

Francesco Sciortino,* Yugang Zhang, Oleg Gang, and Sanat K. Kumar

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$$\frac{\Delta S^{\mathrm{comb}}(d)}{k_{\mathrm{B}}} = \ln\left[\frac{(2N(d)-1)!!}{[(N(d)-1)!!]^2}\right]$$

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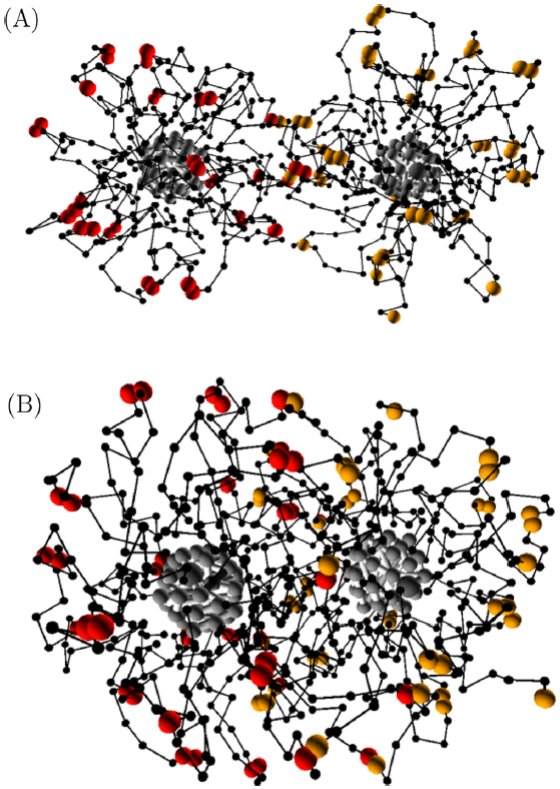
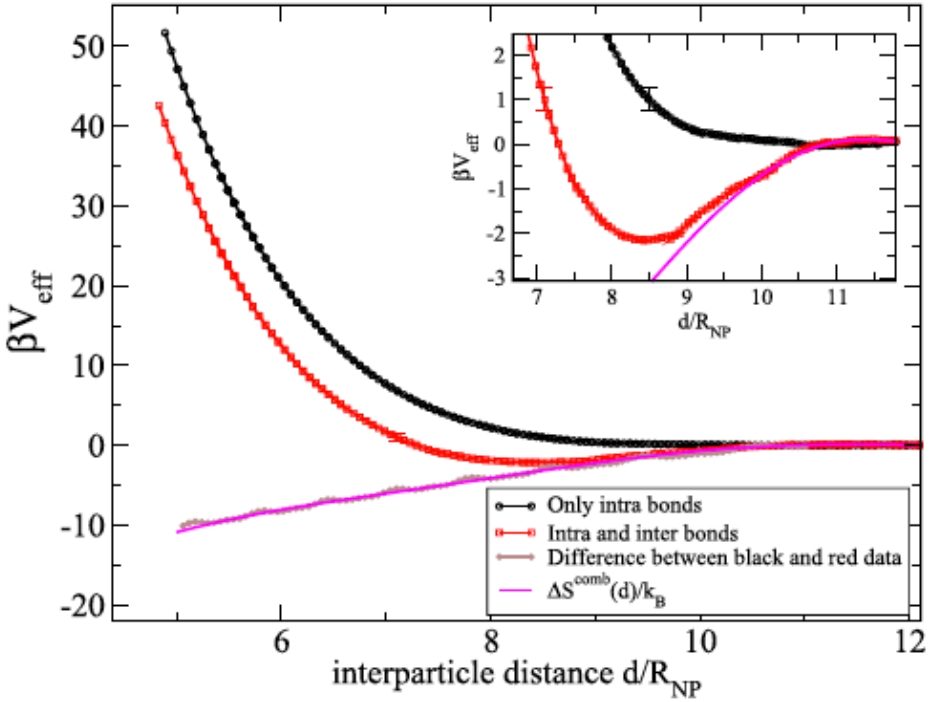


Umbrella sampling (+swap) evaluation of the effective potential

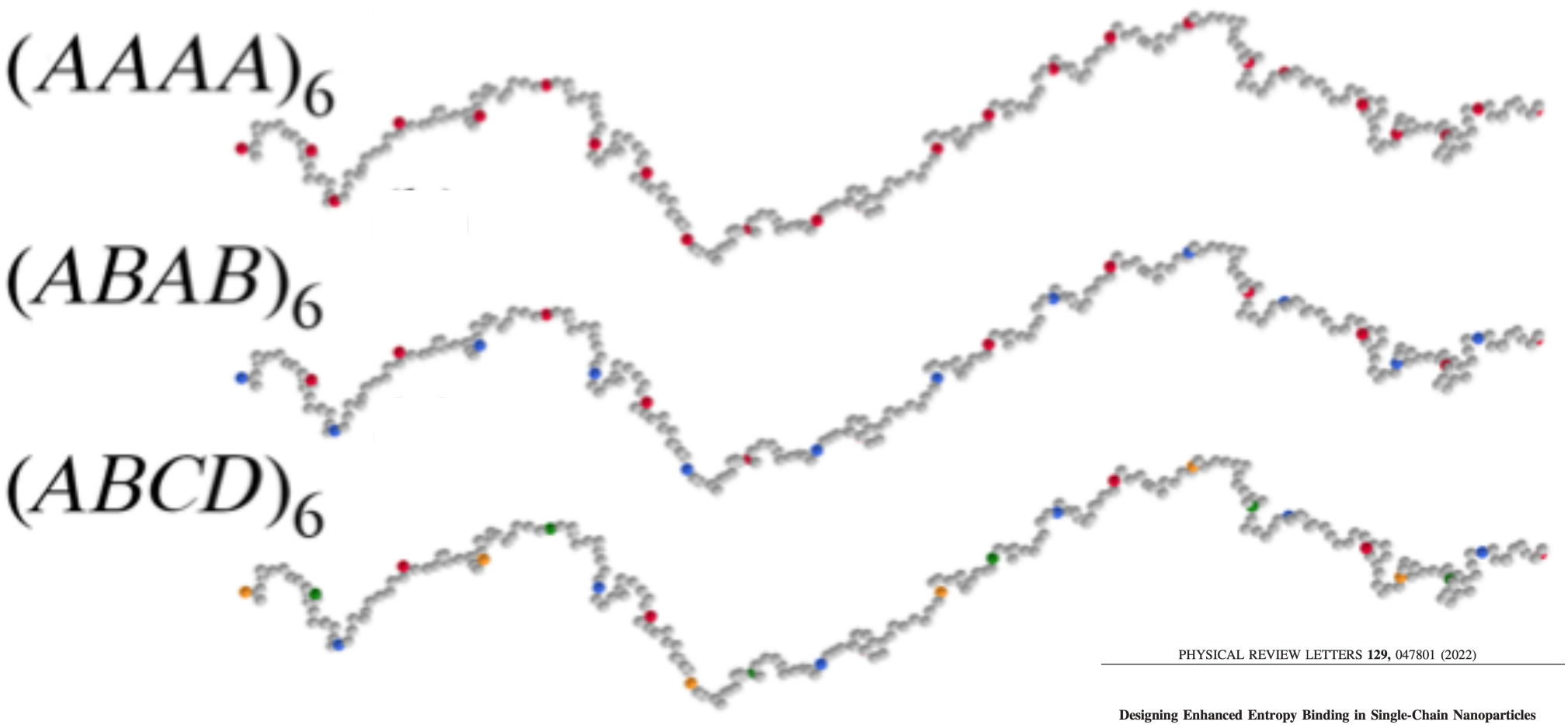


$$\frac{\Delta S^{\mathrm{comb}}(d)}{k_{\mathrm{B}}} = \ln\left[\frac{(2N(d)-1)!!}{[(N(d)-1)!!]^2}\right]$$

The late stage: mumbling Entropy Attracts !

“Patchy” polymers

Useful for students:
FS
Entropy in self assembly
Riv. Nuovo Cimento, Vol. 42 (2019) 511, DOI: 10.1393/ncr/i2019-10165-1



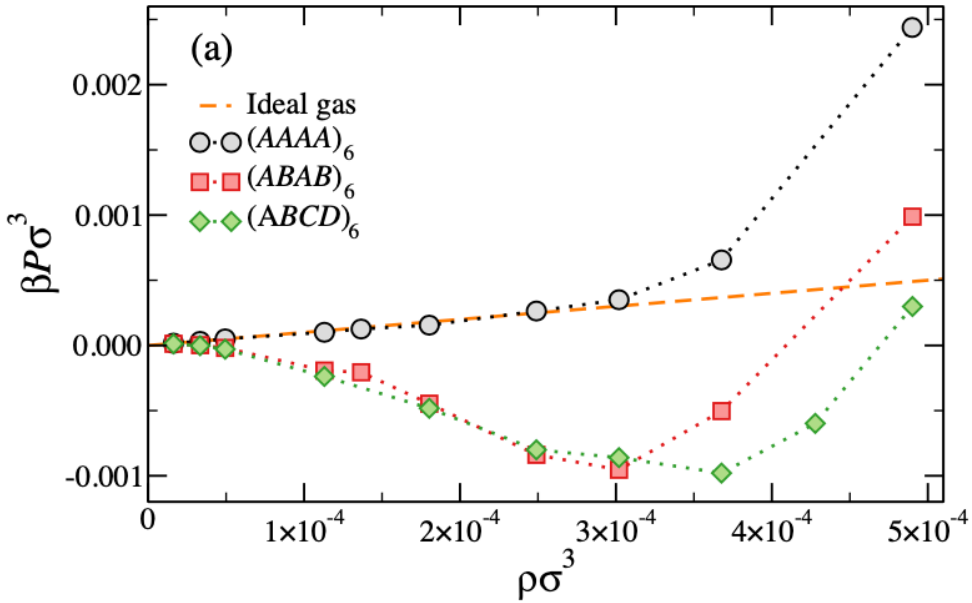
PHYSICAL REVIEW LETTERS **129,** 047801 (2022)

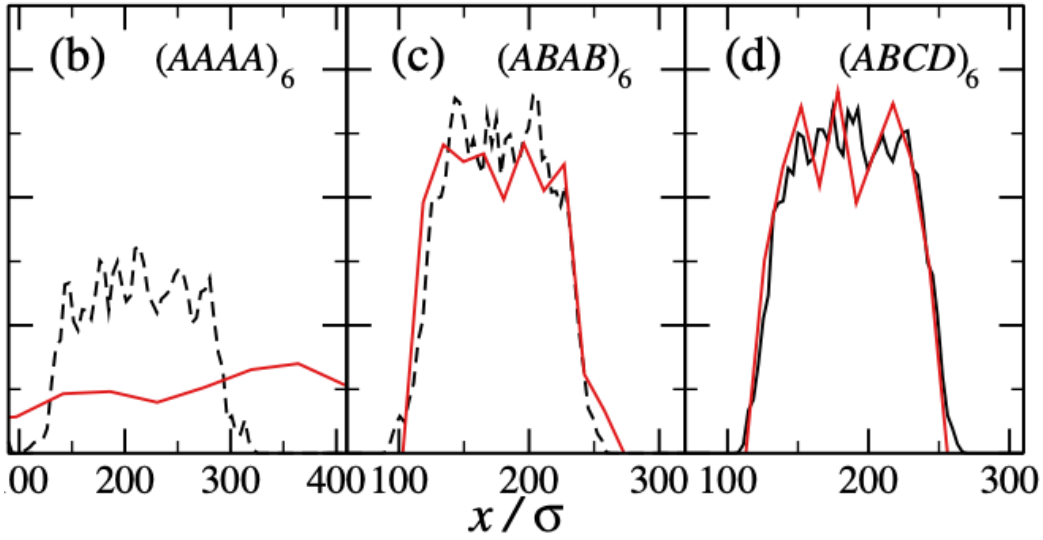
Designing Enhanced Entropy Binding in Single-Chain Nanoparticles

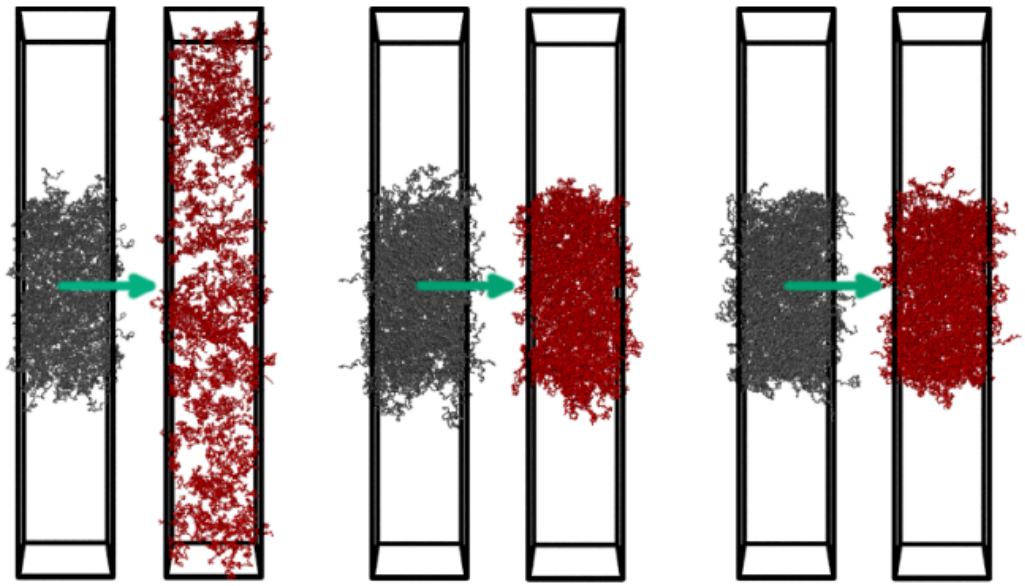
Lorenzo Rovigatti
Department of Physics, Sapienza Università di Roma, Piazzale A. Moro 2, IT-00185 Roma, Italy and CNR-ISC Uos Sapienza, Piazzale A. Moro 2, IT-00185 Roma, Italy

Francesco Sciortino
Department of Physics, Sapienza Università di Roma, Piazzale A. Moro 2, IT-00185 Roma, Italy









Phase behavior

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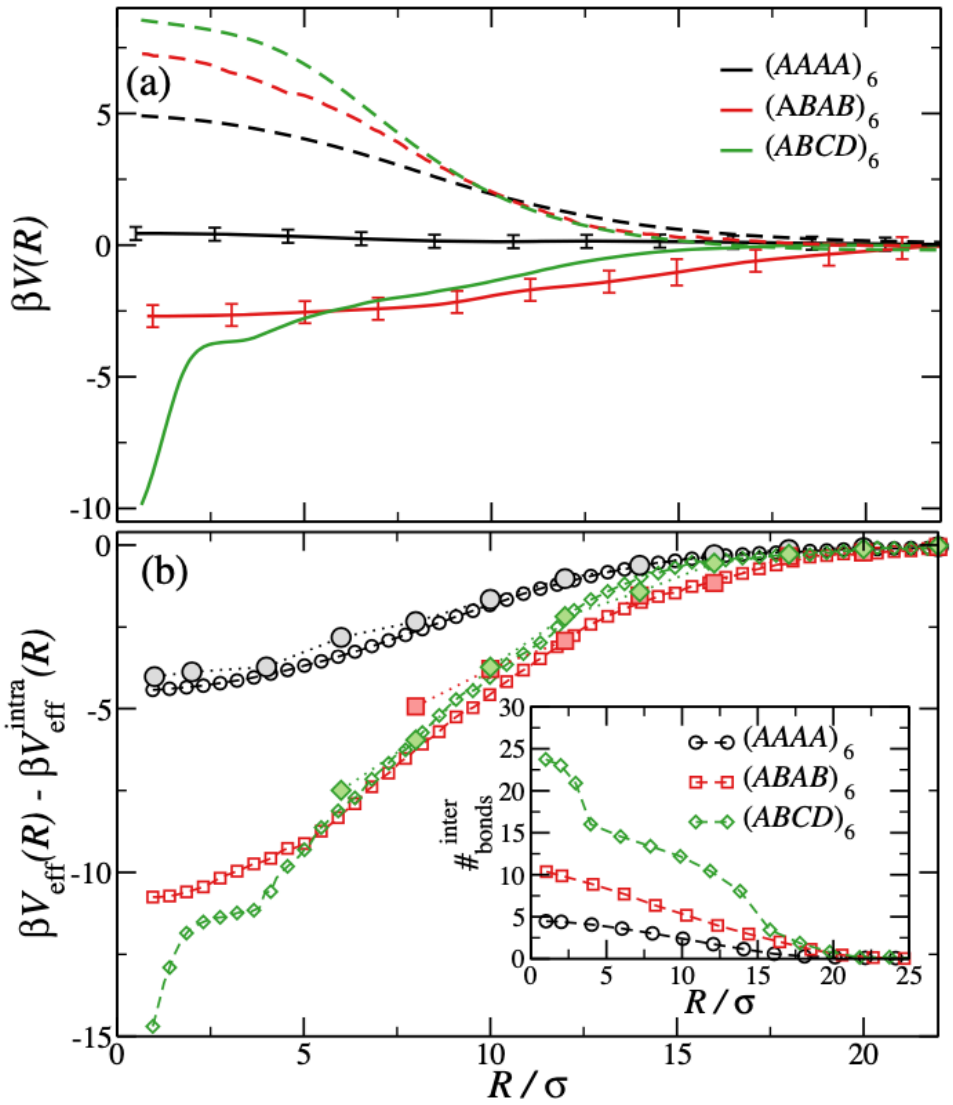
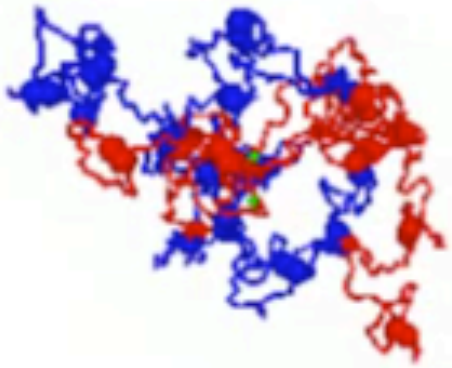

(a)
$(AAAA)_6$
$(ABAB)_6$
$(ABCD)_6$
$\beta V(R)$
5
0
-5
-10
(b)
$\beta V_{eff}(R) - \beta V_{eff}^{intra}(R)$
0
-5
-10
-15
0
5
10
15
20
R / σ
$\#_{bonds}^{inter}$
30
25
20
15
10
5
0
$(AAAA)_6$
$(ABAB)_6$
$(ABCD)_6$
R / σ



Thank you Daan for infecting me (and many others)!