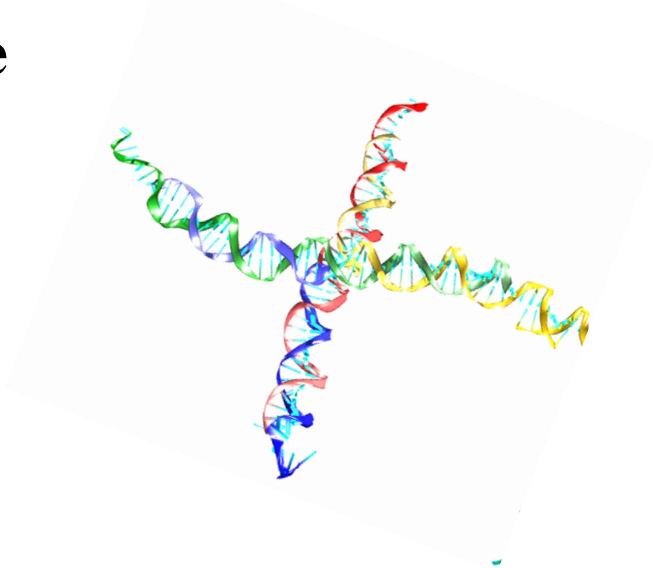
ISMC 2016, Grenoble



Unconventional collective behaviour of DNA-made nanoparticles

Francesco Sciortino

http://glass.phys.uniroma1.it/sciortino/

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COLLDENSE COLLOIDS with DESIGNED RESPONSE

Outline:

Why do we like DNA: bridging in-silico and in-charta intuitions into real experimental realizations

The limited-valence case. Equilibrium gels and q^0

The competing-interaction case "gelling on heating"

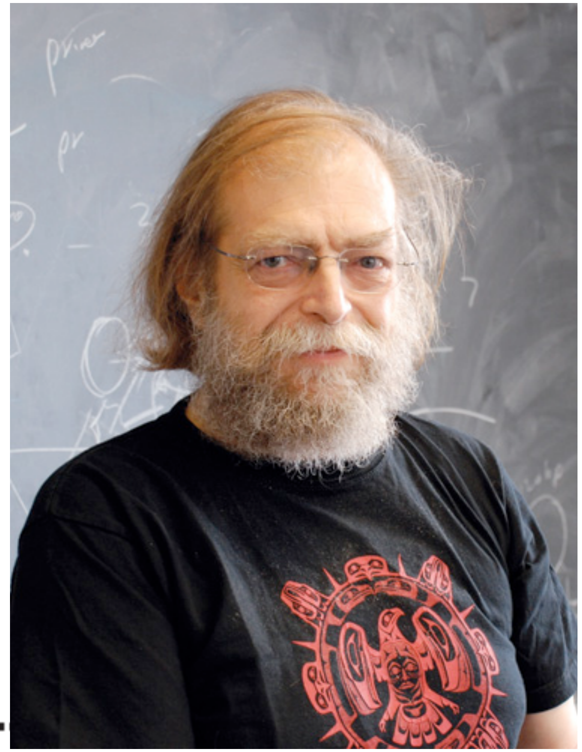
Vitrimers with DNA

DNA particles for LL transition ?

DNA in a material world

Nadrian C. Seeman

Department of Chemistry, New York University, New York 10003, USA (e-mail: ned.seeman@nyu.edu)

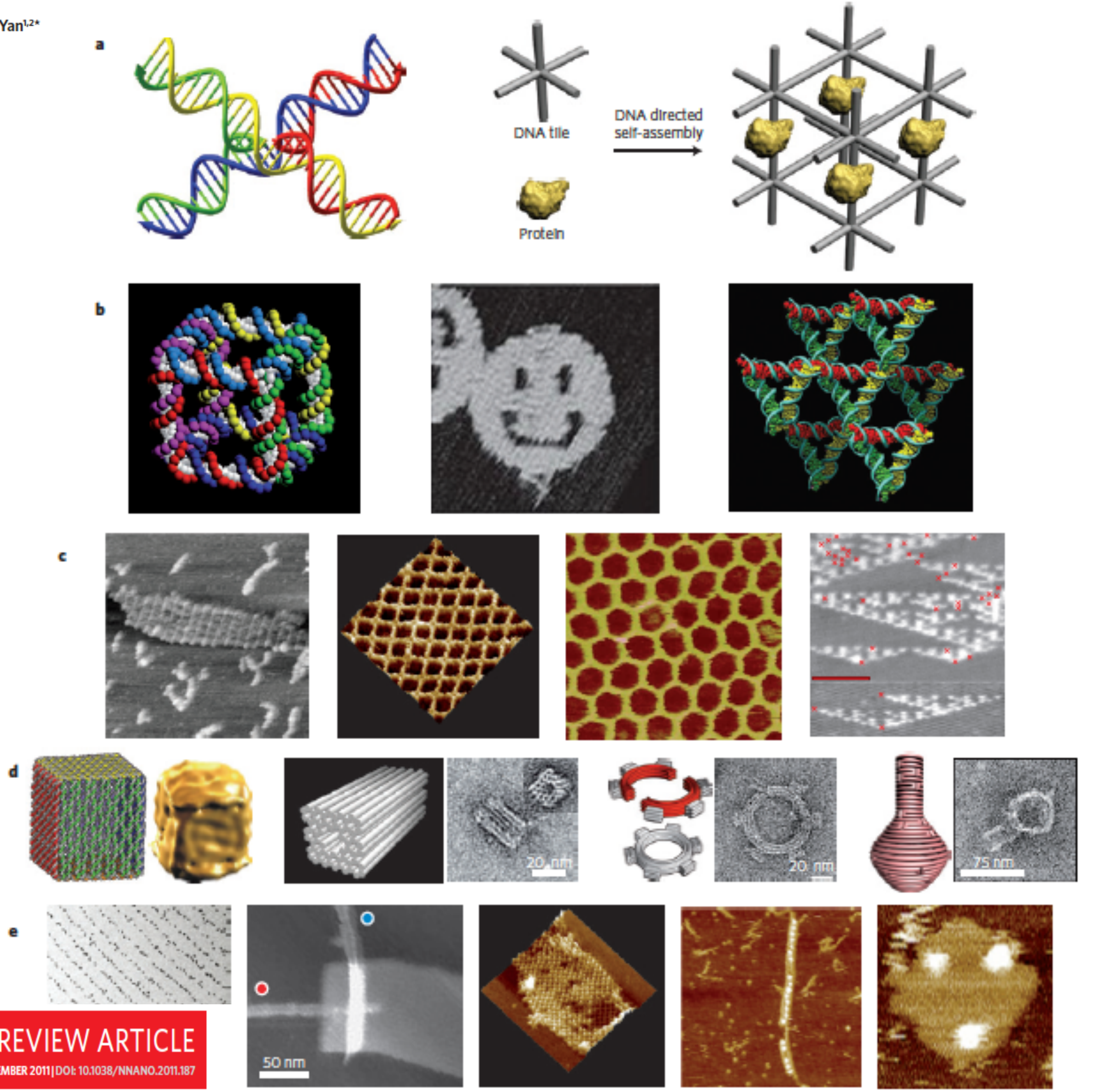


The specific bonding of DNA base pairs provides the chemical foundation for genetics. This powerful molecular recognition system can be used in nanotechnology to direct the assembly of highly structured materials with specific nanoscale features, as well as in DNA computation to process complex information. The exploitation of DNA for material purposes presents a new chapter in the history of the molecule.

Challenges and opportunities for structural DNA nanotechnology

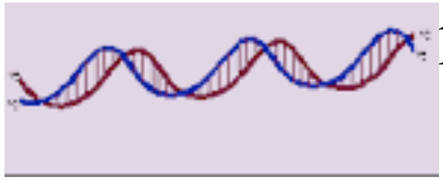
Andre V. Pinheiro[1], Dongran Han[1,2], William M. Shih[3,4,5]* and Hao Yan[1,2]*

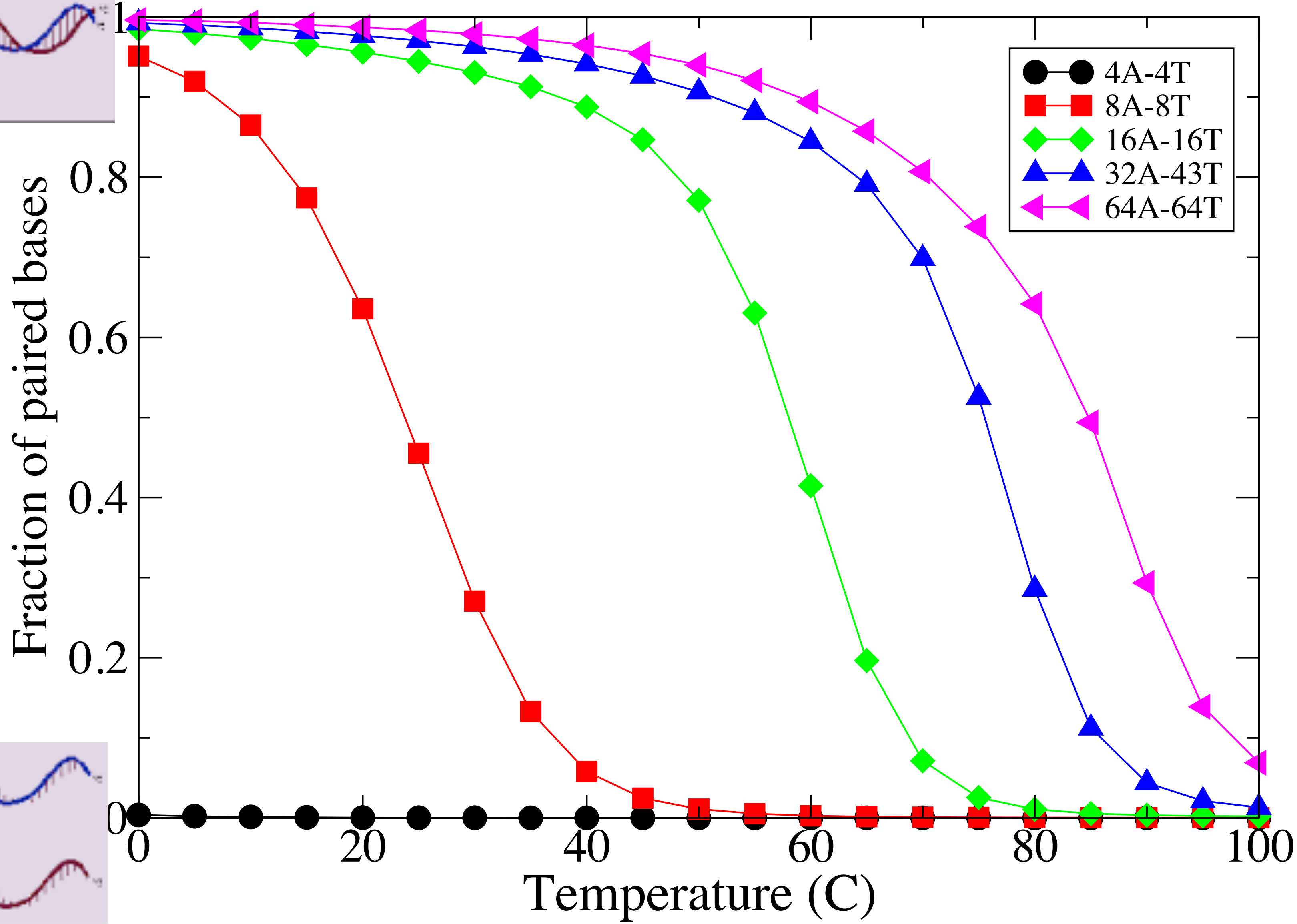
NATURE NANOTECHNOLOGY DOI: 10.1038/NNANO.2011.187

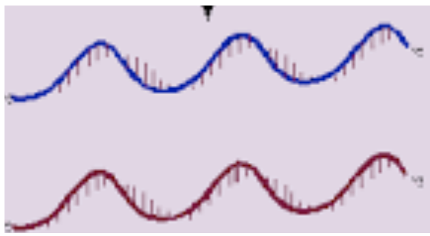


nature nanotechnology
REVIEW ARTICLE
PUBLISHED ONLINE: 6 NOVEMBER 2011 | DOI: 10.1038/NNANO.2011.187

What do we need to know 1 : single (high T) and double (low T) strands







What do we need to know 2: palindromes

saippuakivikauppias

detartrated

essayasse

ressasser

What do we need to know 2: palindromes

saippuakivikauppias

detartrated

ACCAVALLAVACCA

essayasse

ressasser

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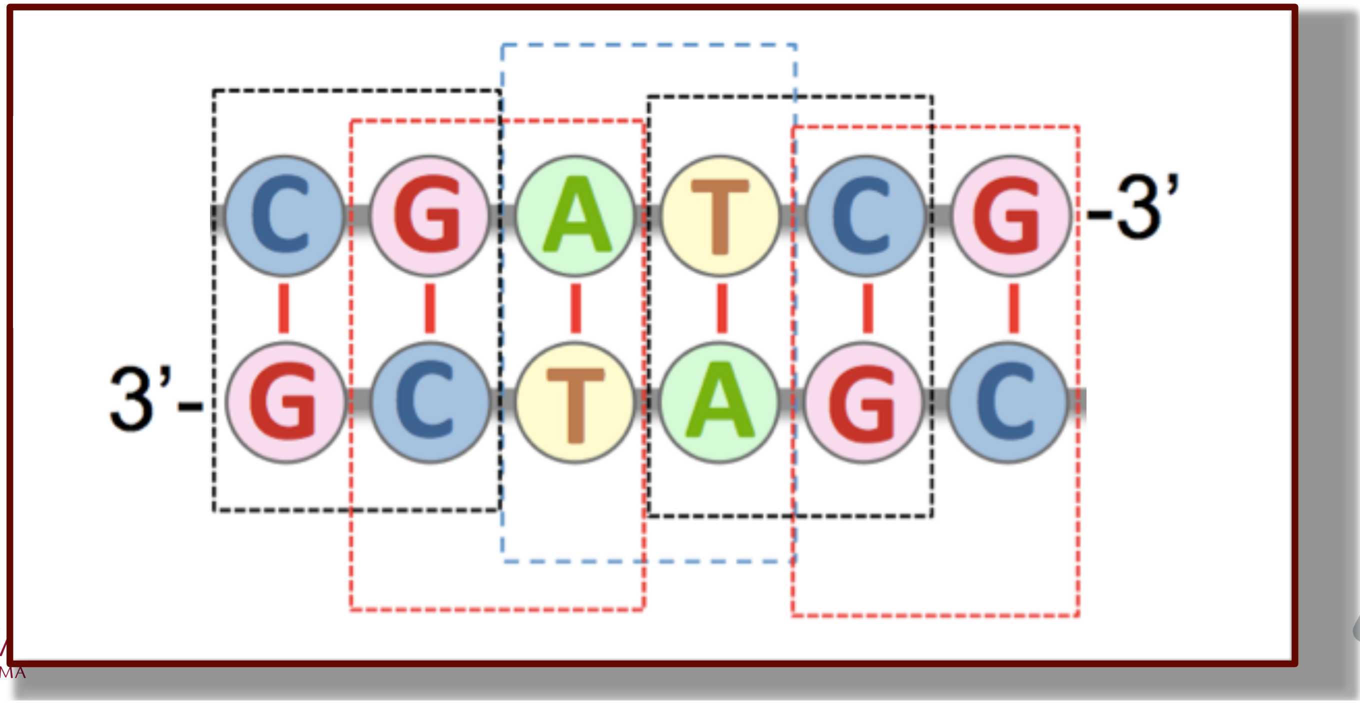
COLLDENSE COLLOIDS with DESIGNED RESPONSE

What do we need to know 2: self-complementary sequences can bind among themselves



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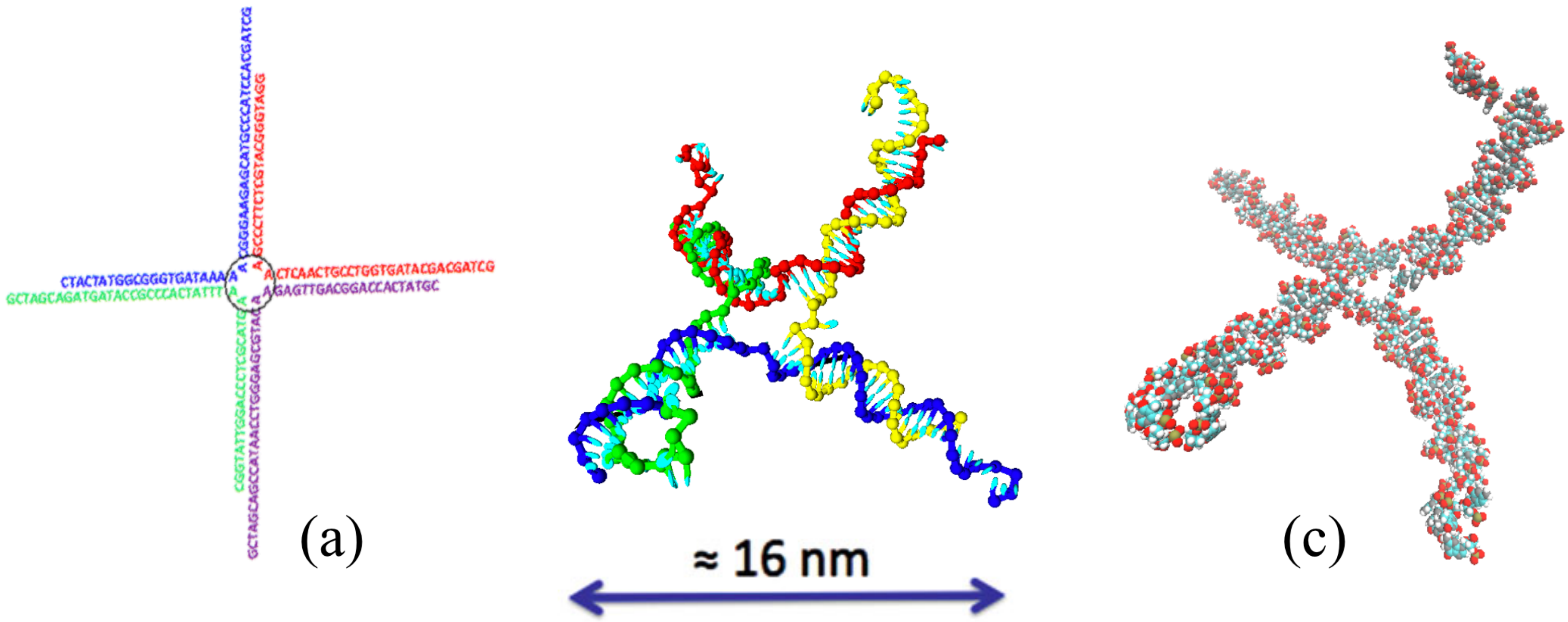
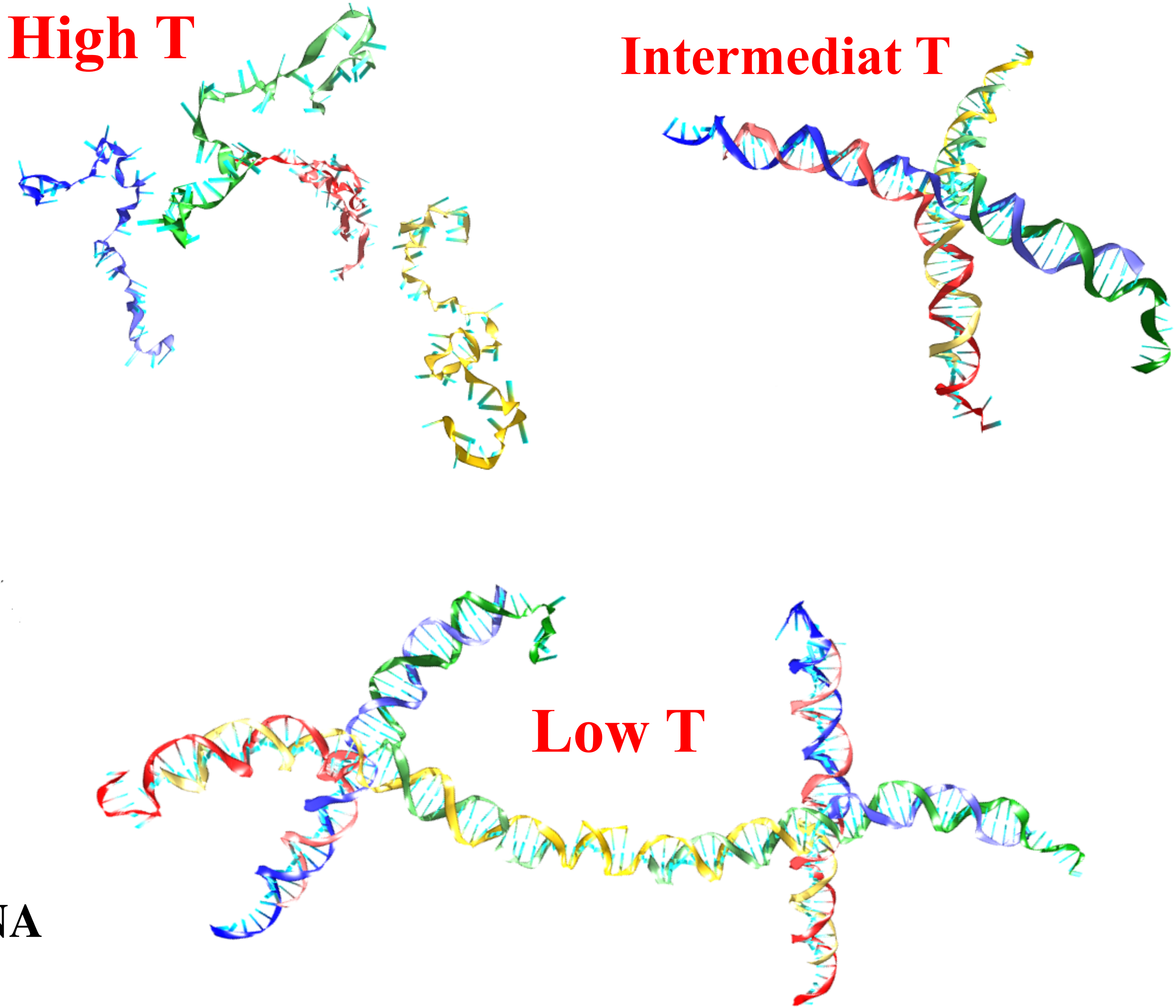
COLLOIDS with DESIGNED RESPONSE

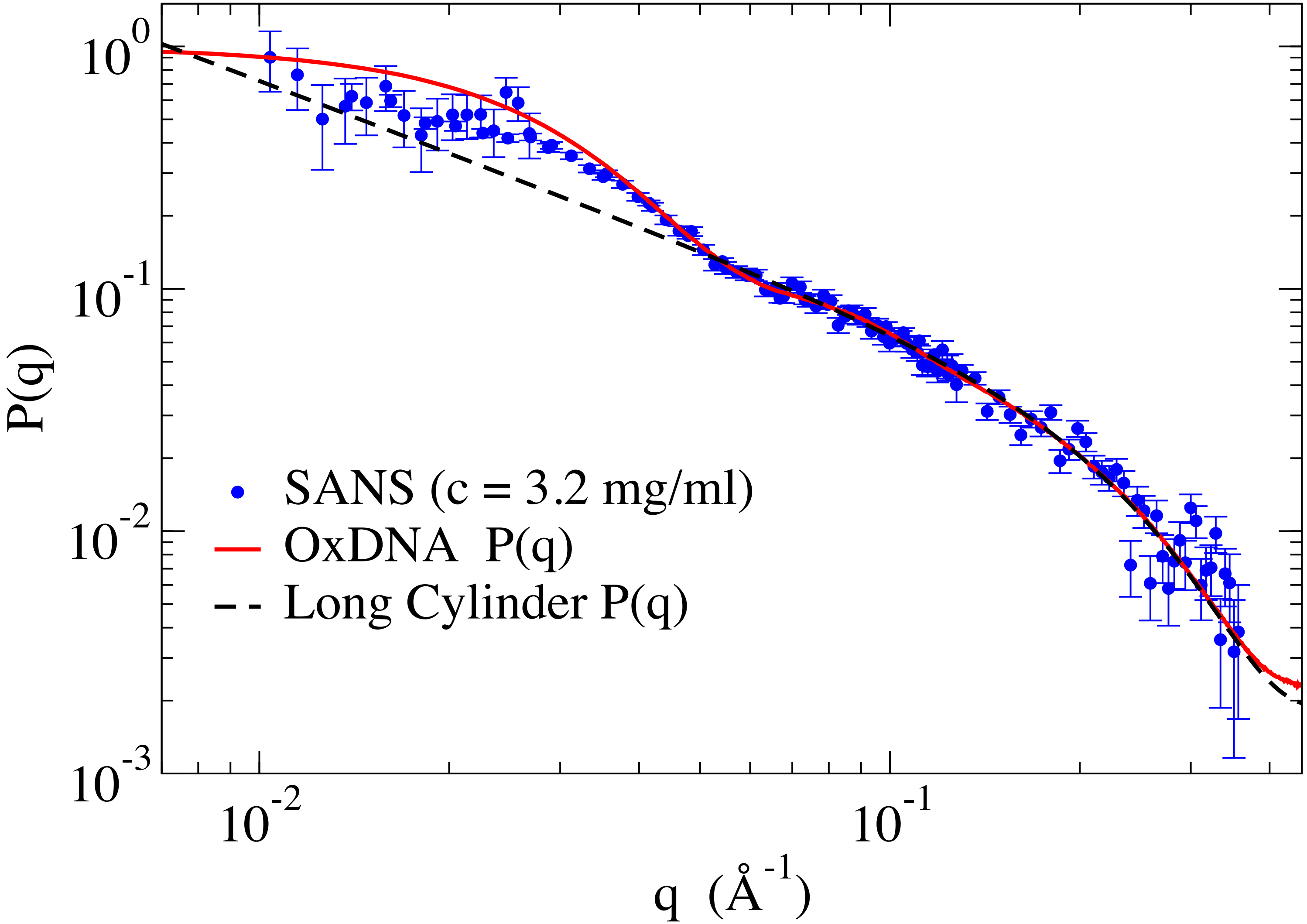
Our hero: The DNA nanostar





OxDNA

Test Simulation-Experiments and Test of NS formation



THE JOURNAL OF CHEMICAL PHYSICS **145**, 084910 (2016)

Small-angle neutron scattering and molecular dynamics structural study of gelling DNA nanostars

J. Fernandez-Castanon,[1] F. Bomboi,[1] L. Rovigatti,[2,3] M. Zanatta,[4,5] A. Paciaroni,[4]
L. Comez,[4,6] L. Porcar,[7] C. J. Jafta,[8] G. C. Fadda,[9] T. Bellini,[10] and F. Sciortino[1,5,a)]

COLLDENSE COLLOIDS with DESIGNED RESPONSE

Bridging *in-silico* and *in-charta* intuitions into real experimental realizations

Equilibrium gels:

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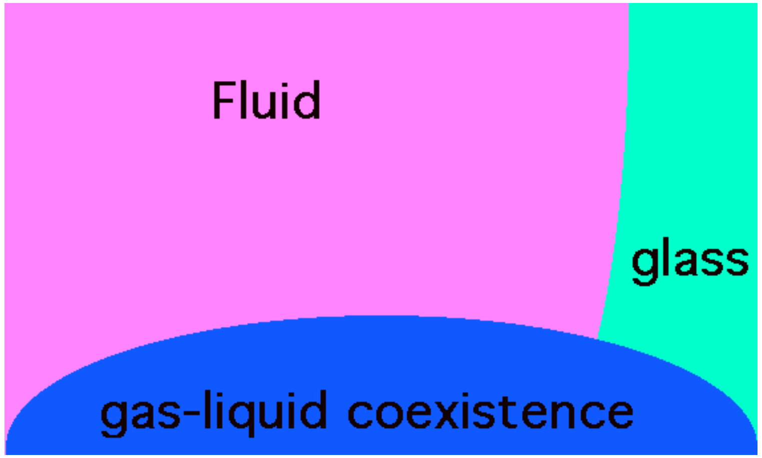
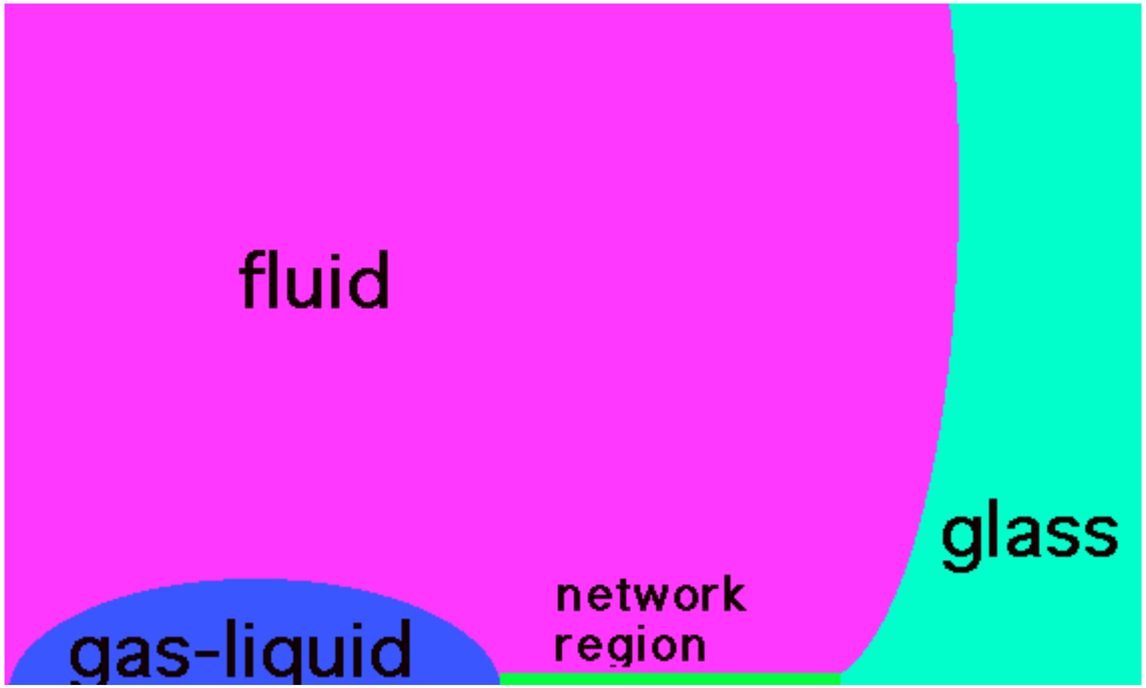
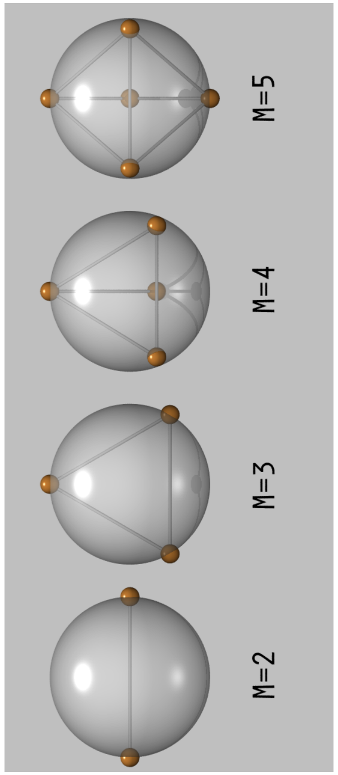
Evolution of the phase diagram

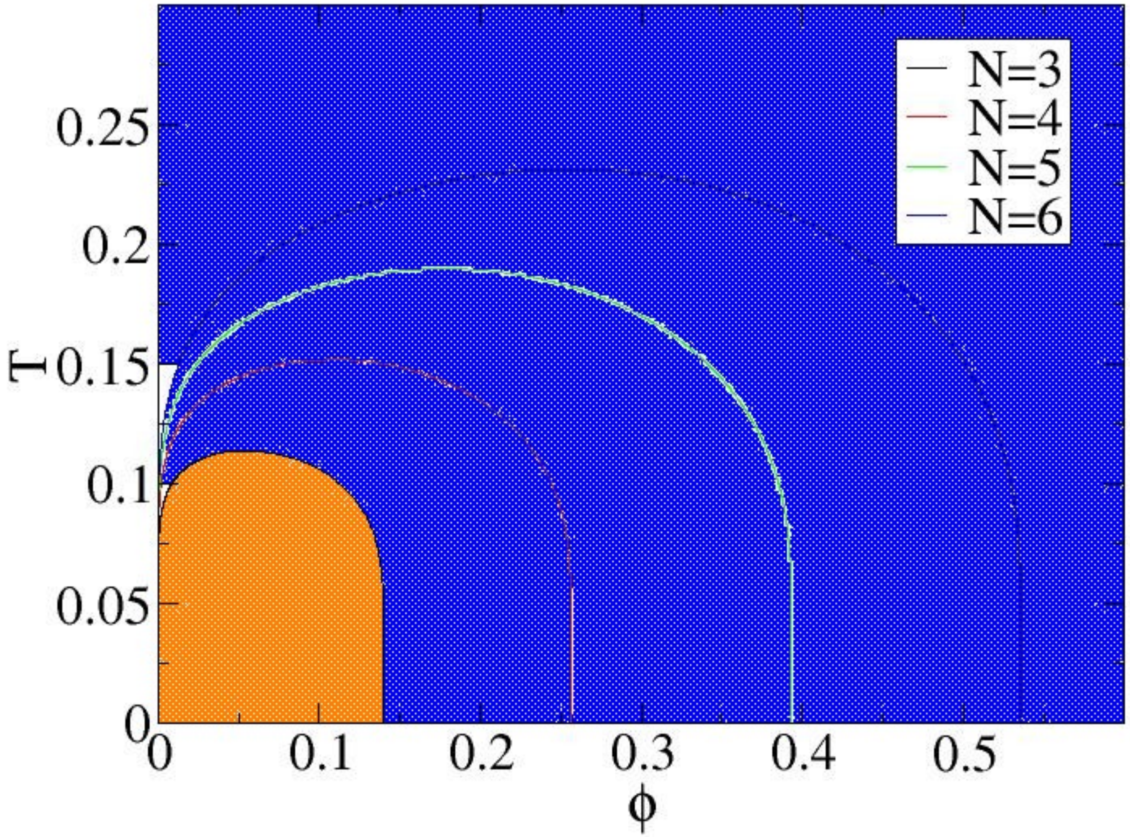


reducing "valence"



How does the valence affect the phase diagram?





Bianchi et al, PRL 97, 168301, 2006

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COLLDENSE COLLOIDS with DESIGNED RESPONSE

Phase behavior of DNA hydrogels

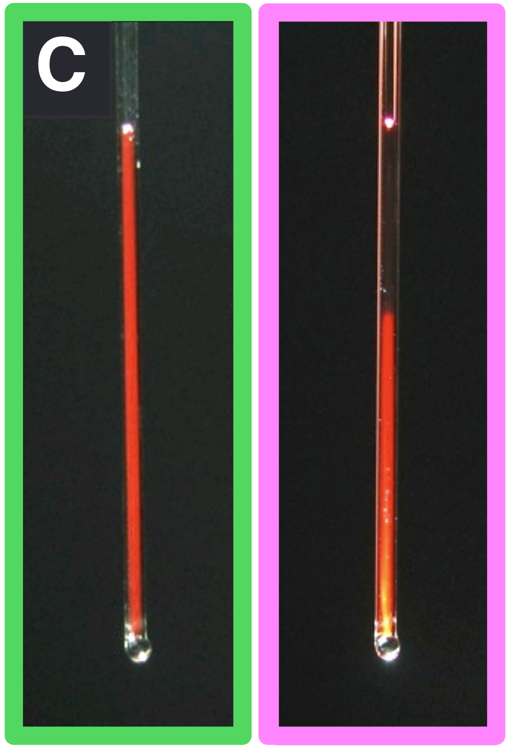
PNAS

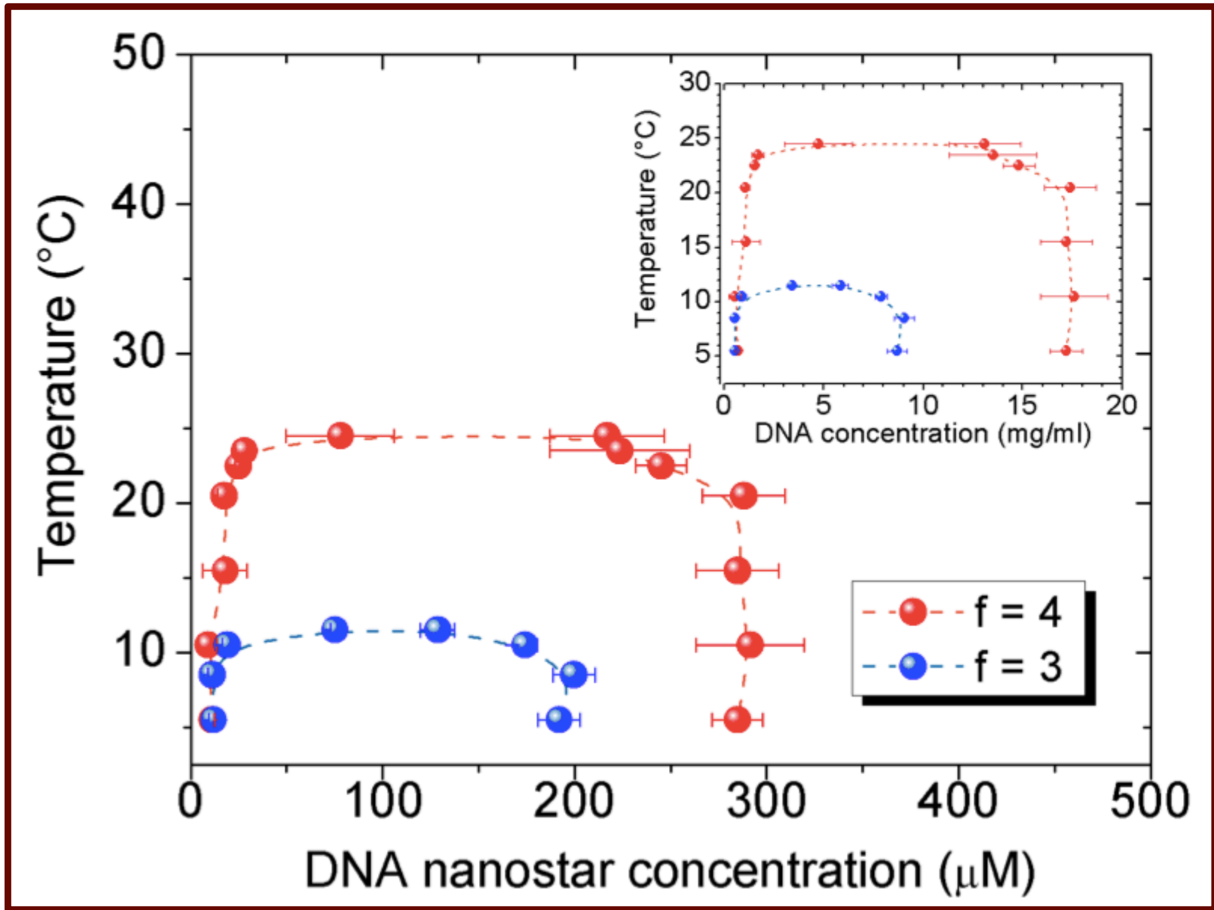
Phase behavior and critical activated dynamics of limited-valence DNA nanostars

Silvia Biffi[a], Roberto Cerbino[a], Francesca Bomboi[b,c], Elvezia Maria Paraboschi[a], Rosanna Asselta[a], Francesco Sciortino[b,1], and Tommaso Bellini[a,1]

[a]Department of Medical Biotechnology and Translational Medicine, Universitá degli Studi di Milano, I-20133 Milan, Italy; [b]Department of Physics, Sapienza, Universitá di Roma, I-00185 Rome, Italy; and [c]Department of Physics, Università degli Studi Roma Tre-Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia, I-00146 Rome, Italy

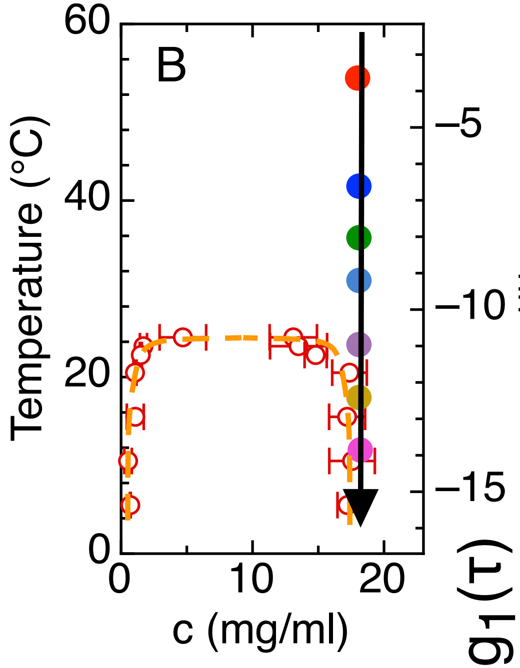
Edited by T. C. Lubensky, University of Pennsylvania, Philadelphia, PA, and approved August 6, 2013 (received for review March 14, 2013)





Dynamics of the DNA gel: Photon Correlation Spectroscopy

A truly equilibrium gel !



Langmuir, Vol. 16, No. 23, 2000 8707

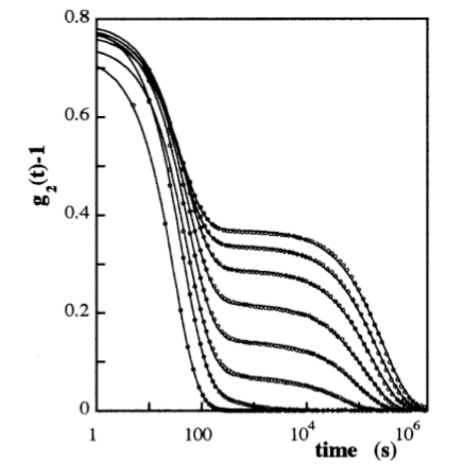
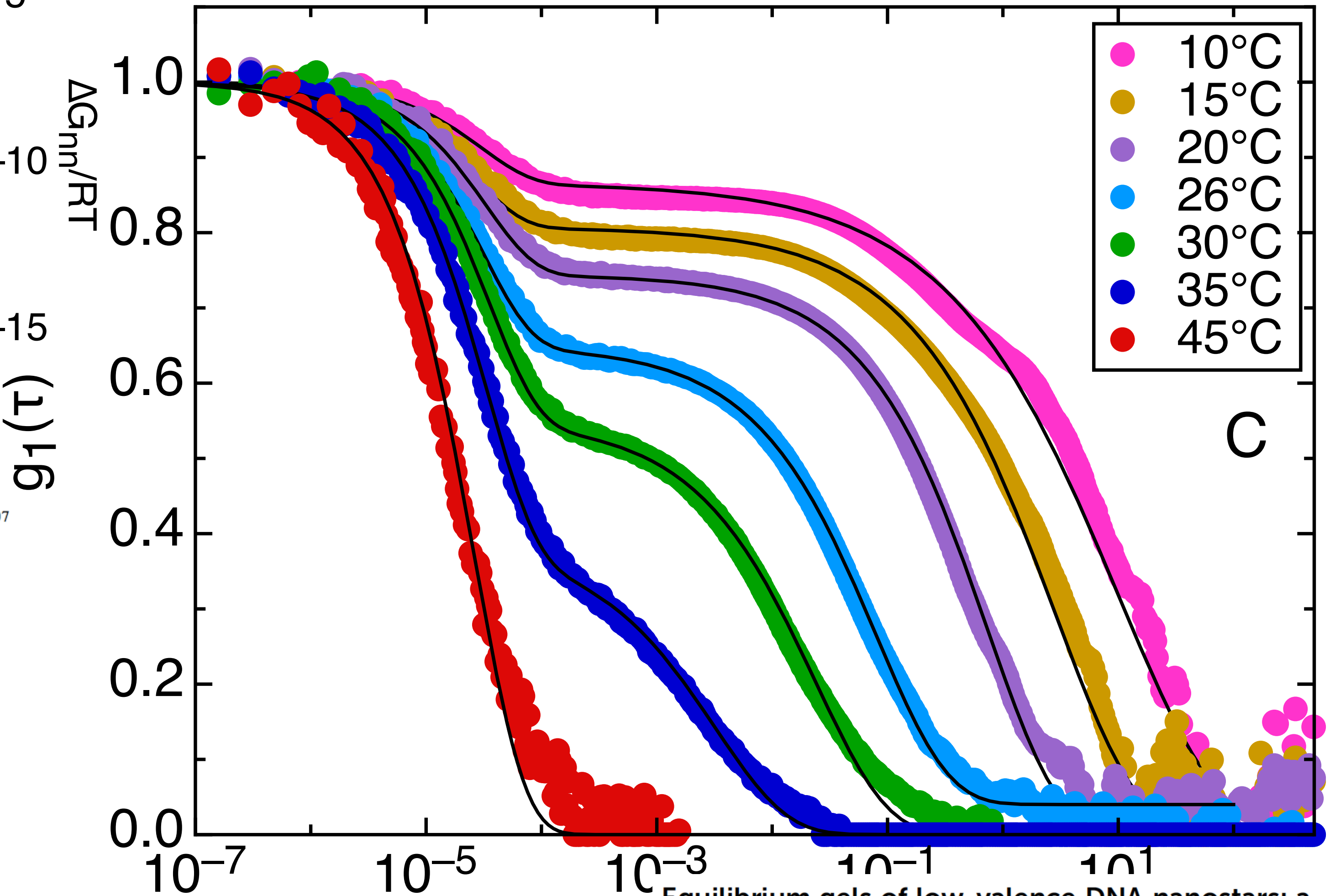


Figure 11. Normalized intensity autocorrelation curves measured at $\theta = 90°$ ($q = 2.3 \times 10^{-3}$ Å^{-1}) for samples with $\Phi = 12.4\%$ and $r = 0, 3, 6, 9, 12, 15, 18,$ and 21 for the curves

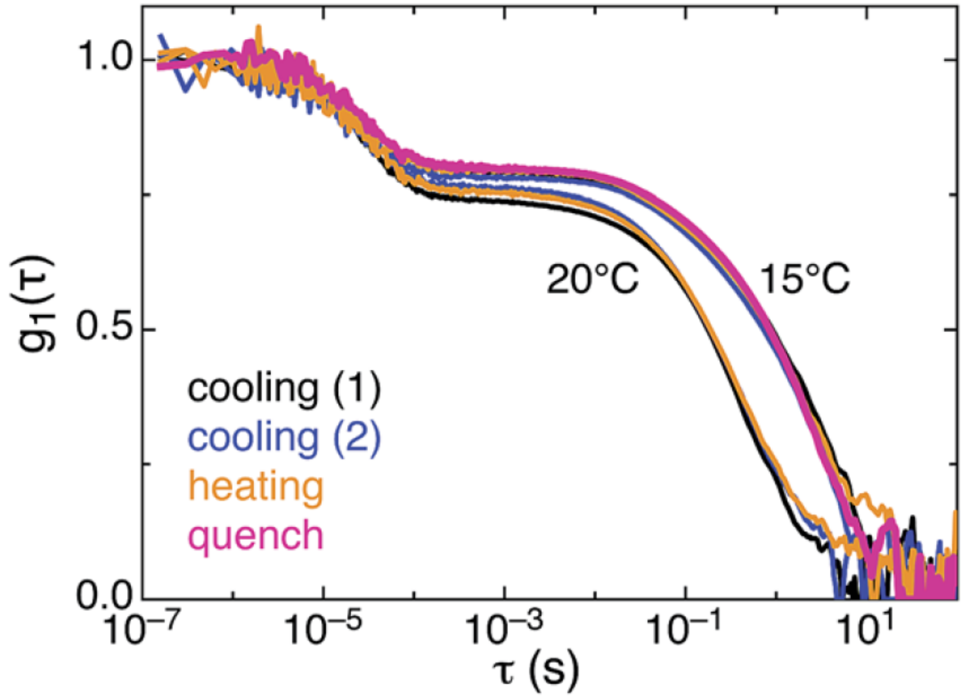


Equilibrium gels of low-valence DNA nanostars: a colloidal model for strong glass formers†

Silvia Biffi,[ab] Roberto Cerbino,[a] Giovanni Nava,[a] Francesca Bomboi,[b] Francesco Sciortino[bc] and Tommaso Bellini*[a]

Gel reversibility

Light Scattering



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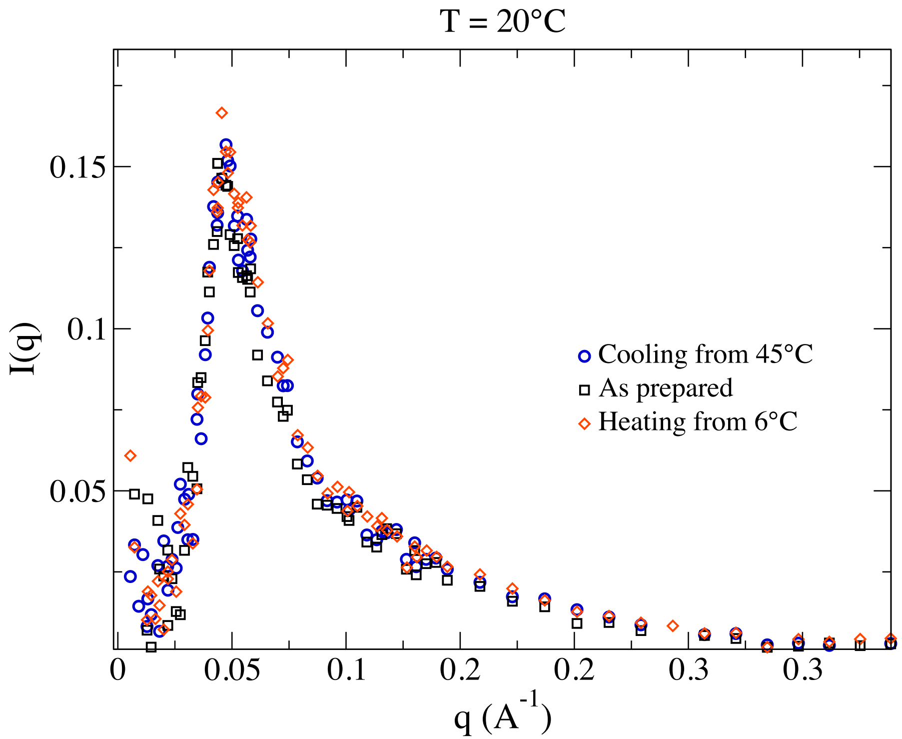
Neutrons



THE JOURNAL OF CHEMICAL PHYSICS **145**, 084910 (2016)

Small-angle neutron scattering and molecular dynamics structural study of gelling DNA nanostars

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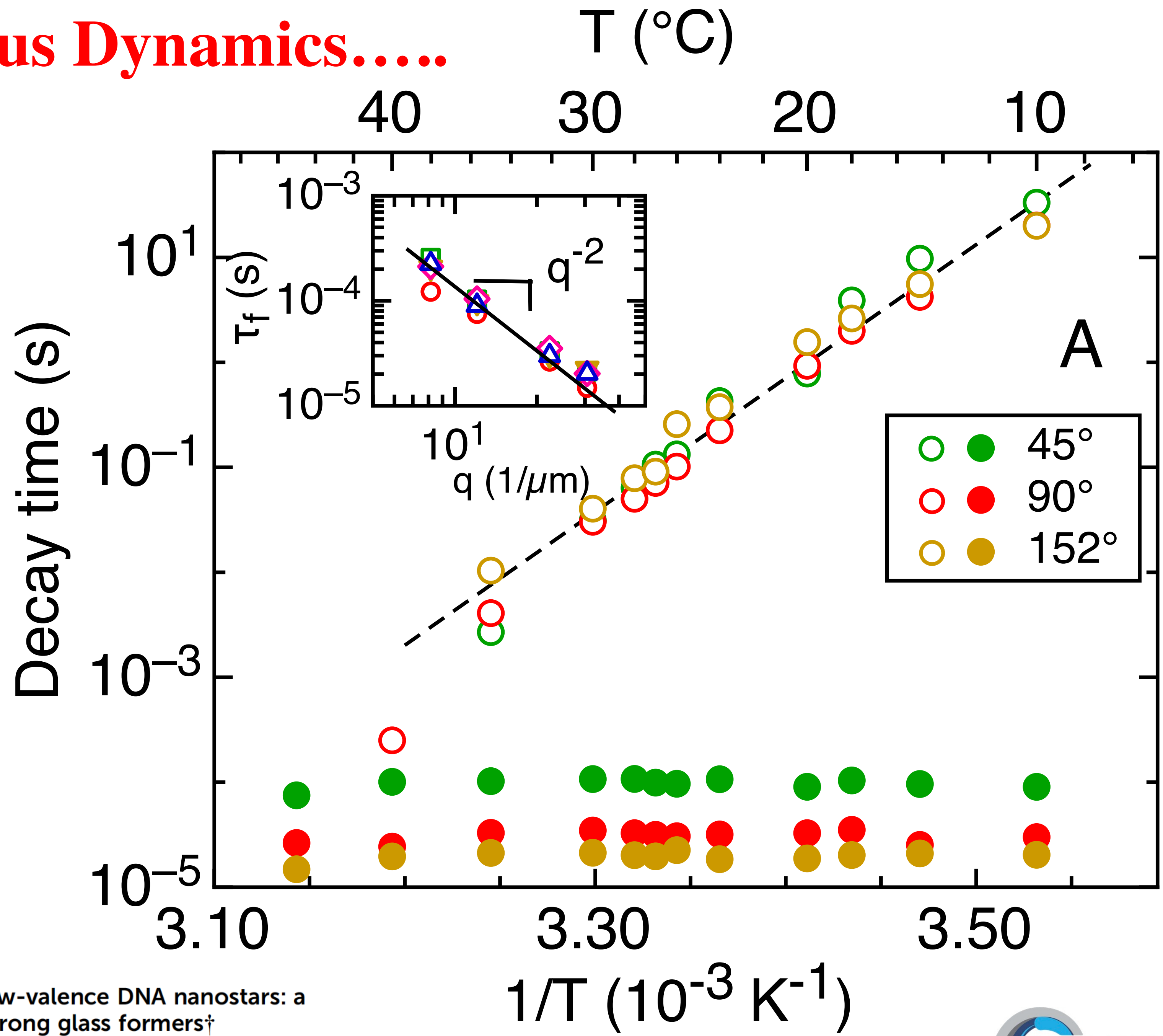
COLLDENSE
COLLOIDS with DESIGNED RESPONSE

Arrhenius Dynamics…..

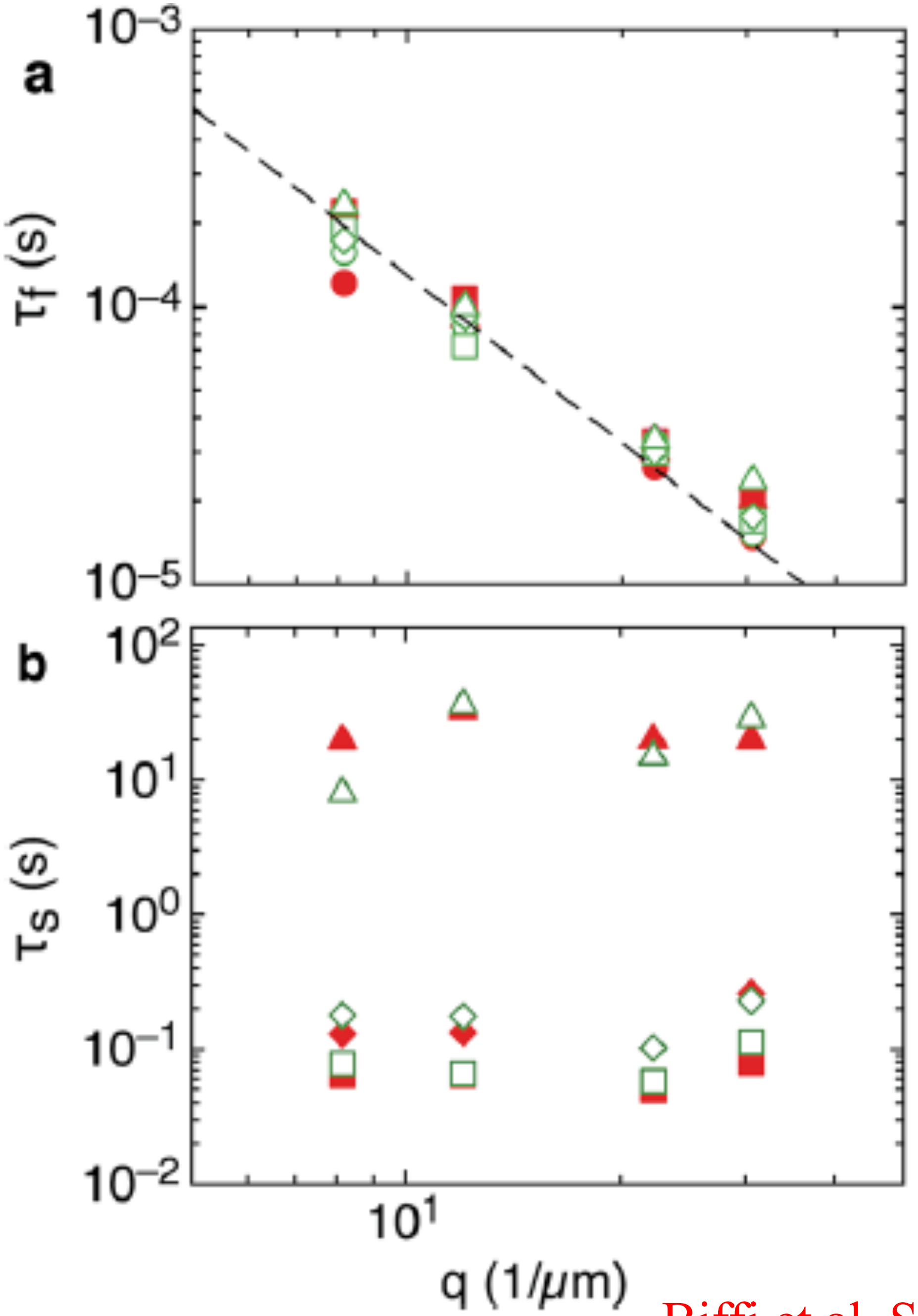


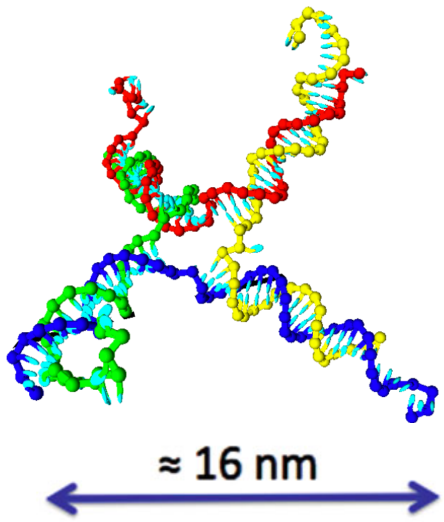
Equilibrium gels of low-valence DNA nanostars: a colloidal model for strong glass formers†

Silvia Biffi,[ab] Roberto Cerbino,[a] Giovanni Nava,[a] Francesca Bomboi,[b] Francesco Sciortino[bc] and Tommaso Bellini[*a]

COLLDENSE COLLOIDS with DESIGNED RESPONSE

An unexpected feature: a q^0 mode



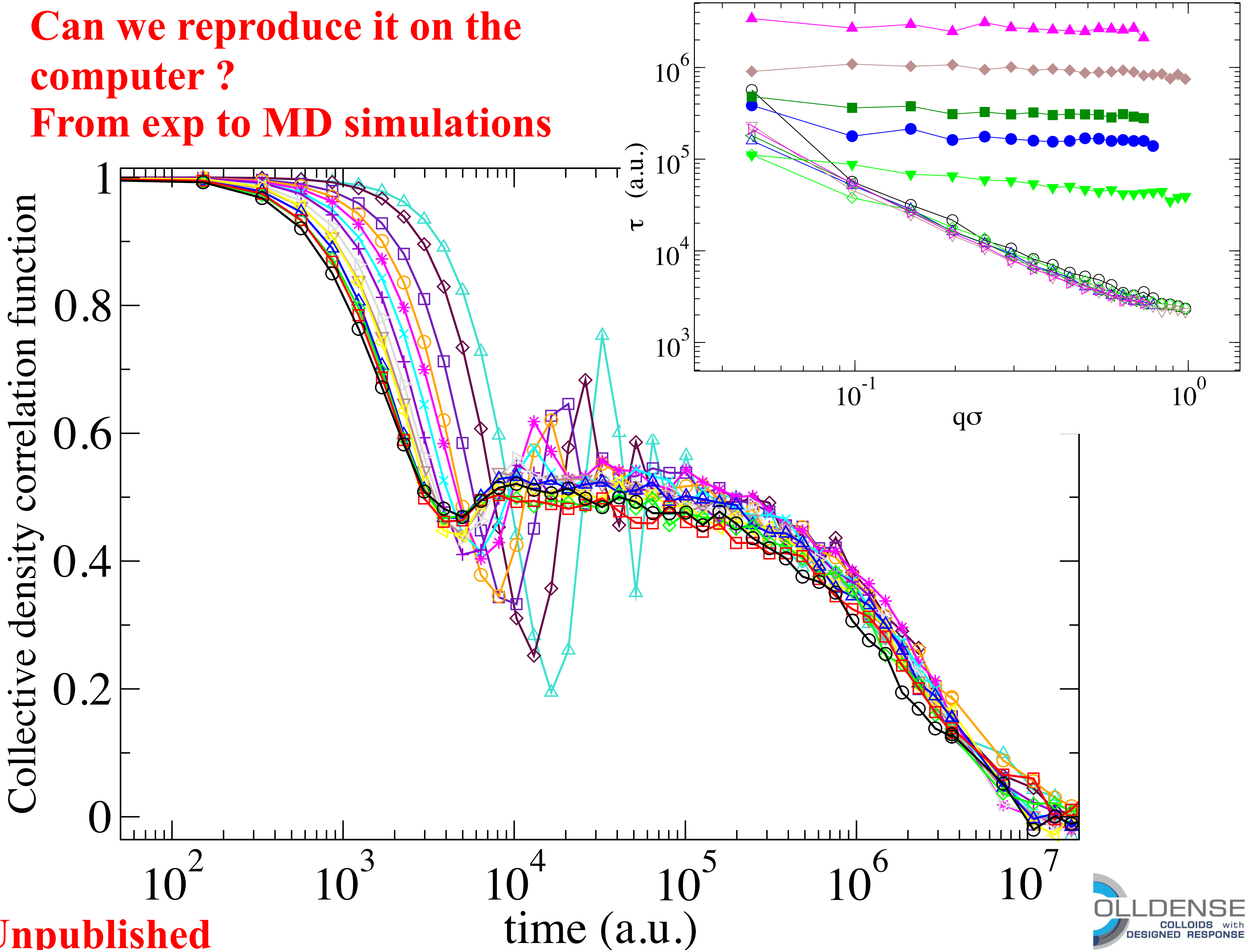


$200 < \lambda < 750$ nm

$12 < \lambda < 50$ NS size

Biffi et al, Soft Matter, 2015, 11, 3132

Can we reproduce it on the computer ?
From exp to MD simulations



Unpublished

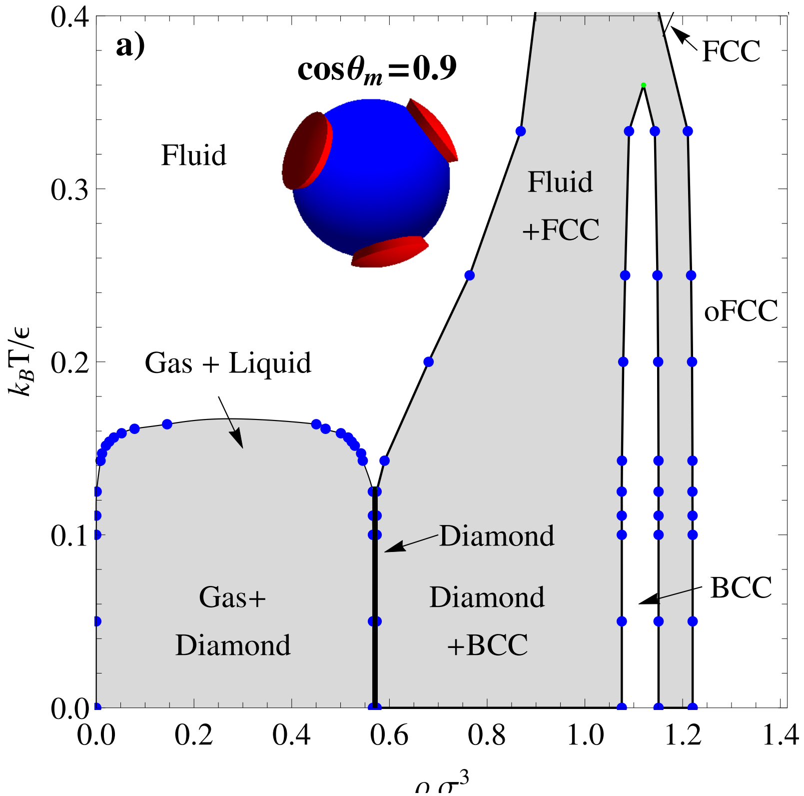
nature physics

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



nature physics

LETTERS

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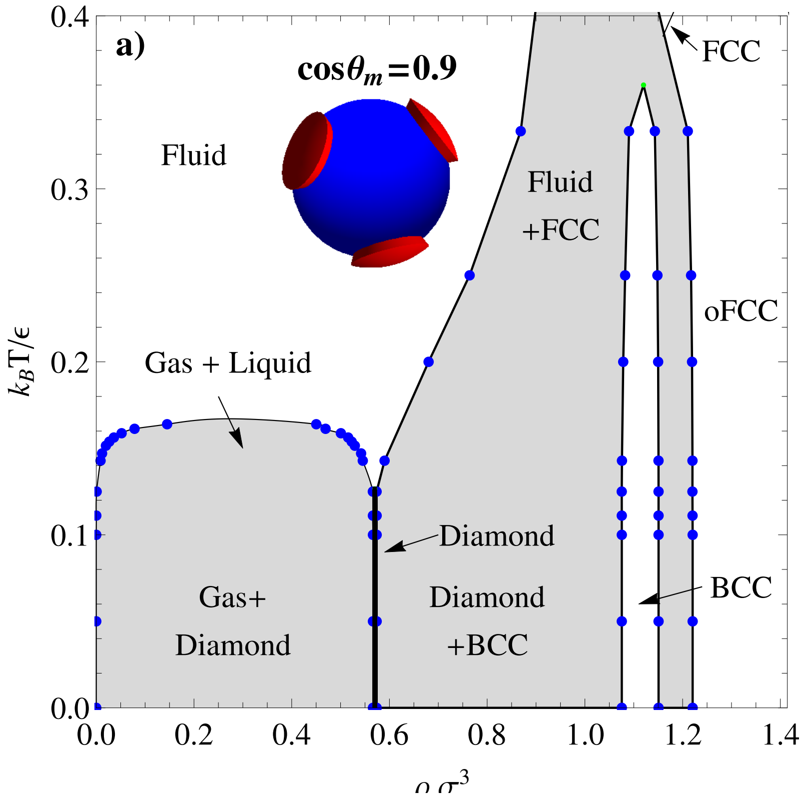
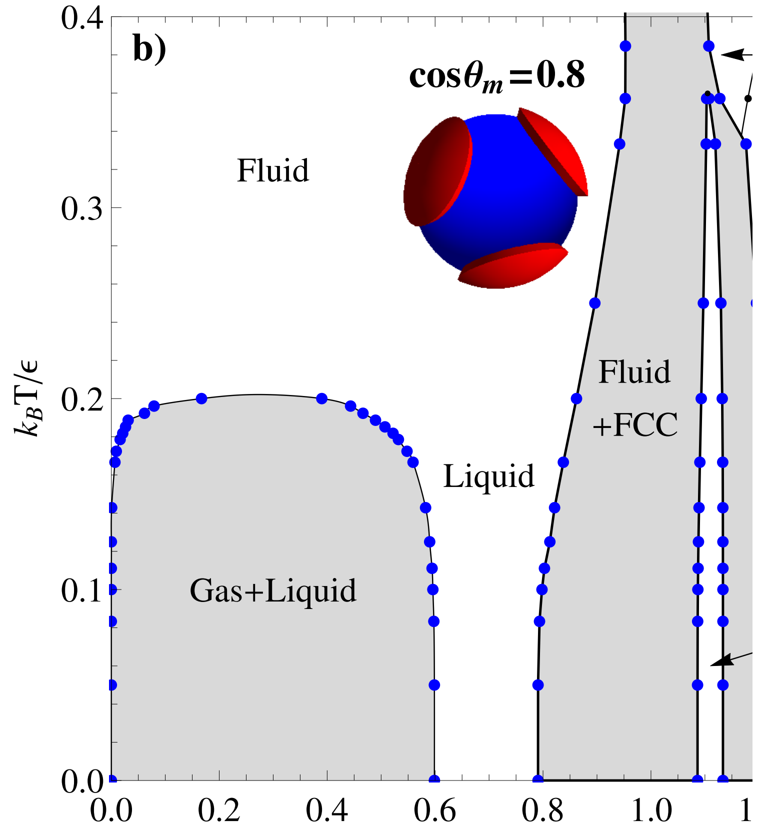
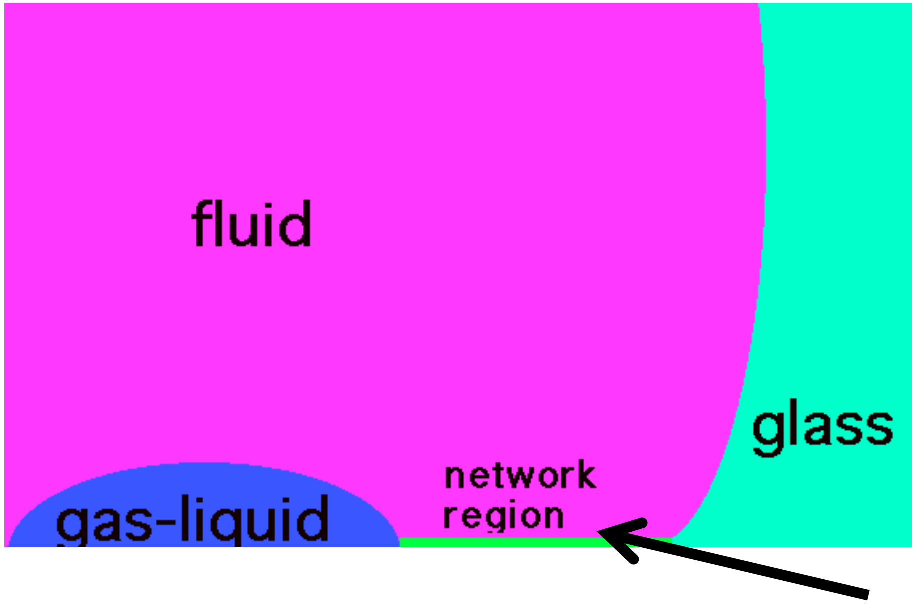




Key elements for liquid stability at T=0 K:
(ultrastable liquids !)



Thermodynamically stable !

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

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

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COLLOIDS with DESIGNED RESPONSE

Gels of DNA Nanostars Never Crystallize

Lorenzo Rovigatti,[†,*] Frank Smallenburg,[†] Flavio Romano,[‡] and Francesco Sciortino[†]

[†]Dipartimento di Fisica, Sapienza Università di Roma, Piazzale A. Moro 2, 00185 Roma, Italy and [‡]Physical & Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

ACS Nano, 8, 3567-3574, 2014

Bridging *in-silico* and *in-charta* intuitions into real experimental realizations

Gelling by heating:

a patchy-particle gel that forms both on cooling AND on heating *(a topic close to the Chairman's heart)*

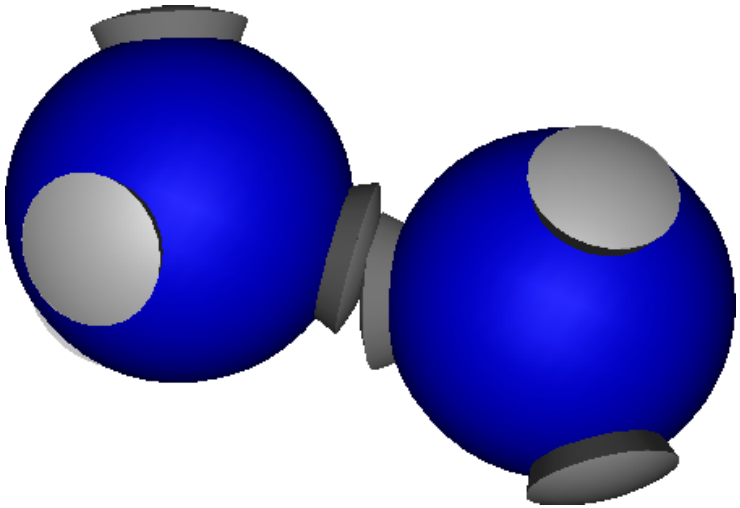
Gelling by Heating

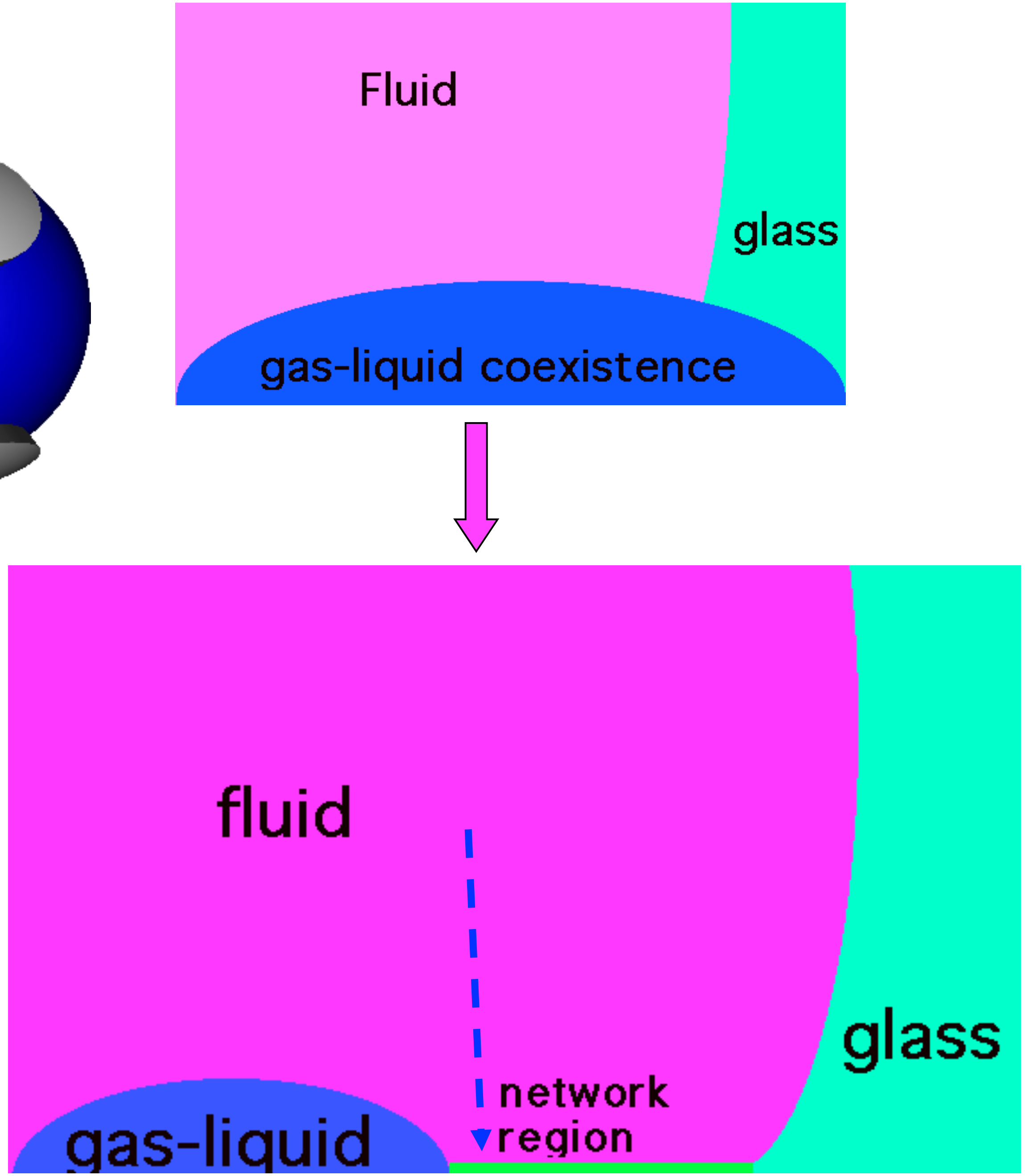
Sándalo Roldán-Vargas[1], Frank Smallenburg[1], Walter Kob[2] & Francesco Sciortino[1]

SCIENTIFIC REPORTS | 3 : 2451 | DOI: 10.1038/srep02451

COLLDENSE COLLOIDS with DESIGNED RESPONSE

How do we form an equilibrium gel ?





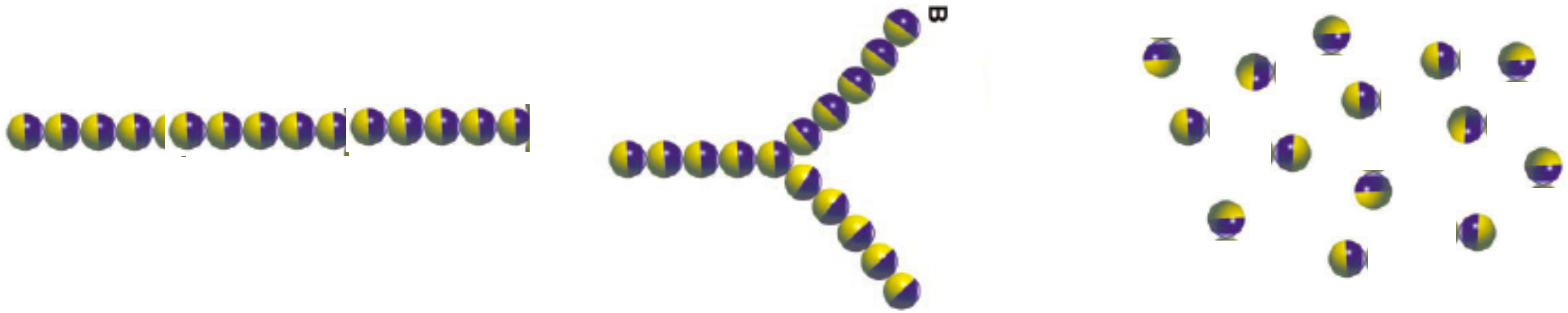
How do we break a gel ?

Competitive interactions

How do we break a gel ?

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.



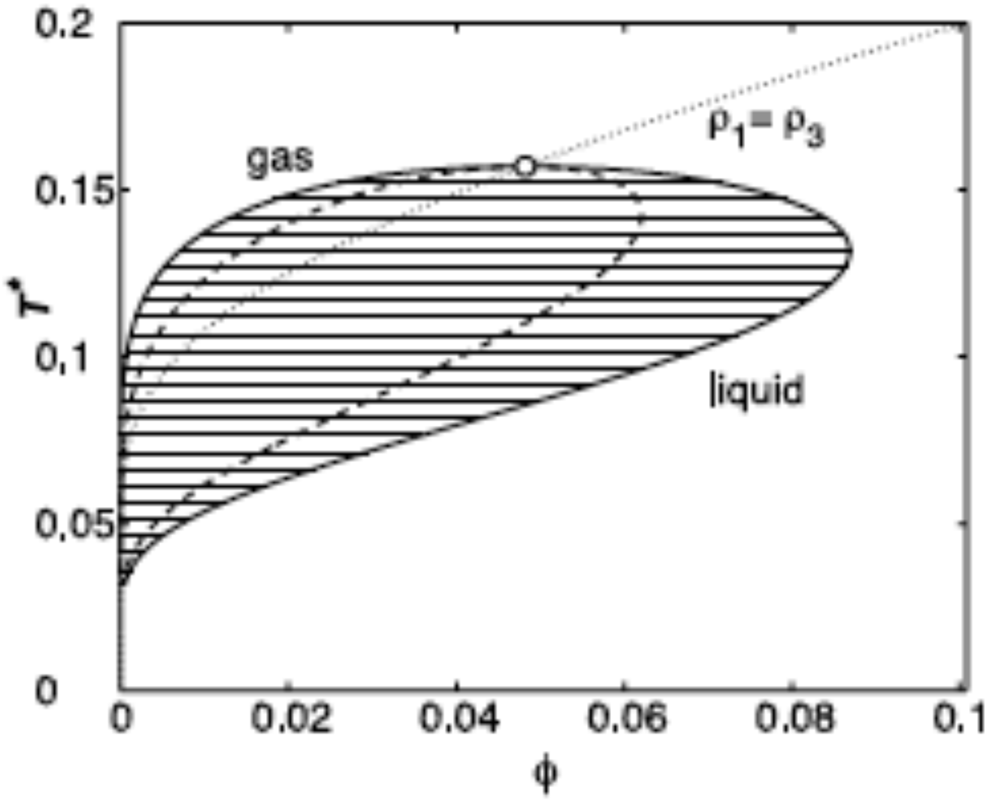
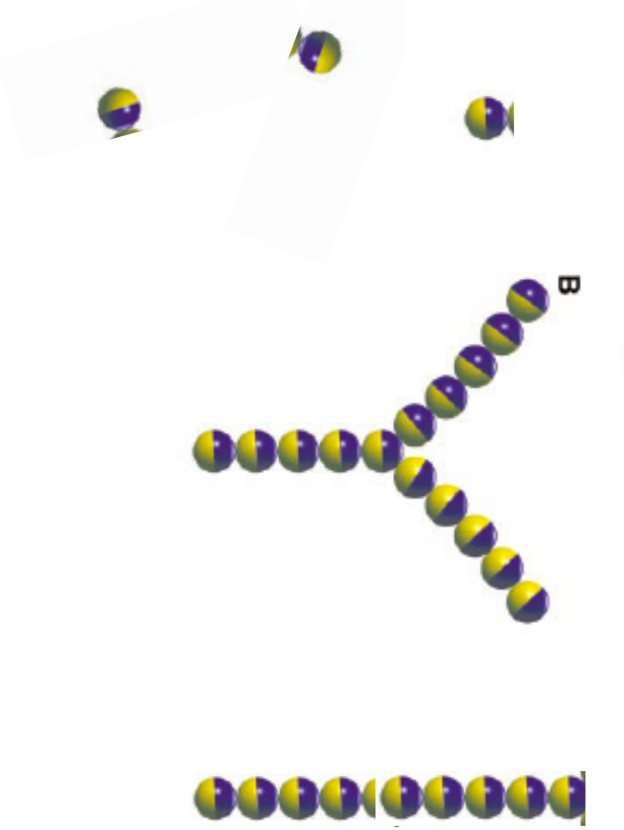


Fig. 2. The phase diagram of the dipolar network calculated for defect energies of $\varepsilon_1 = 0.67$ and $\varepsilon_3 = 0.12$. At the critical point (circle), the coexistence curve (thick solid line), the phase stability boundary (dashed line), and the connectivity transition (dotted line) meet. 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.



Tlusty-Safran, Science (2000)

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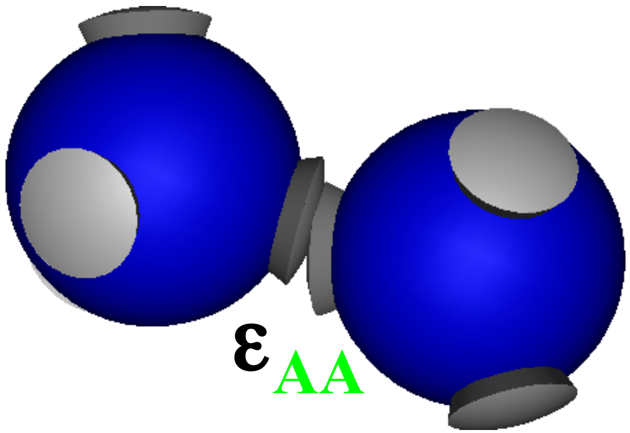
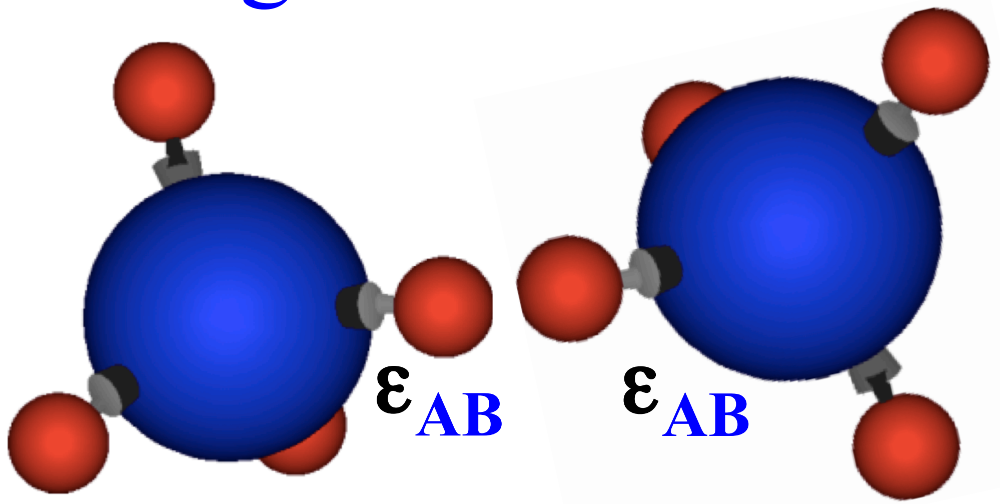
How do we break a gel ?

Add a competitor blocking the AA bonds !





Network

Blocked particle

$$2\,\varepsilon_{AB} < \varepsilon_{AA}$$

THE JOURNAL OF CHEMICAL PHYSICS **127**, 114706 (2007)

Temperature dependence of the colloidal agglomeration inhibition: Computer simulation study

Mariana Barcenas
Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central 152, 07730 México DF, Mexico

Janna Douda
UPITA-IPN, 07340 México DF, Mexico

Yurko Duda[a)]
Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central 152, 07730 México DF, Mexico

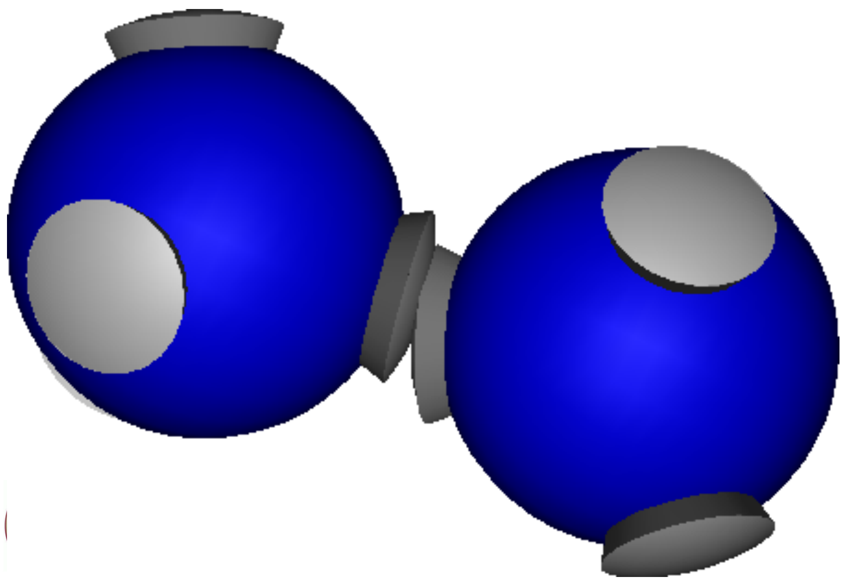
Gelling by Heating

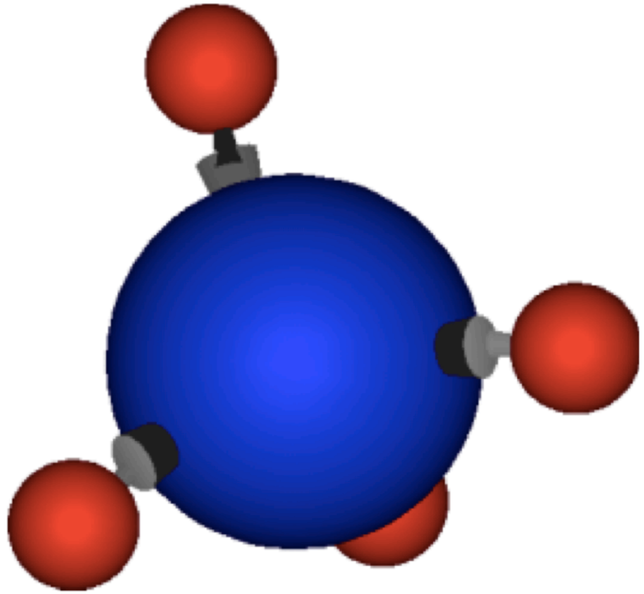
Sándalo Roldán-Vargas[1], Frank Smallenburg[1], Walter Kob[2] & Francesco Sciortino[1]

SCIENTIFIC REPORTS | 3 : 2451 | DOI: 10.1038/srep02451

How to stabilize the network: Bonding entropy !

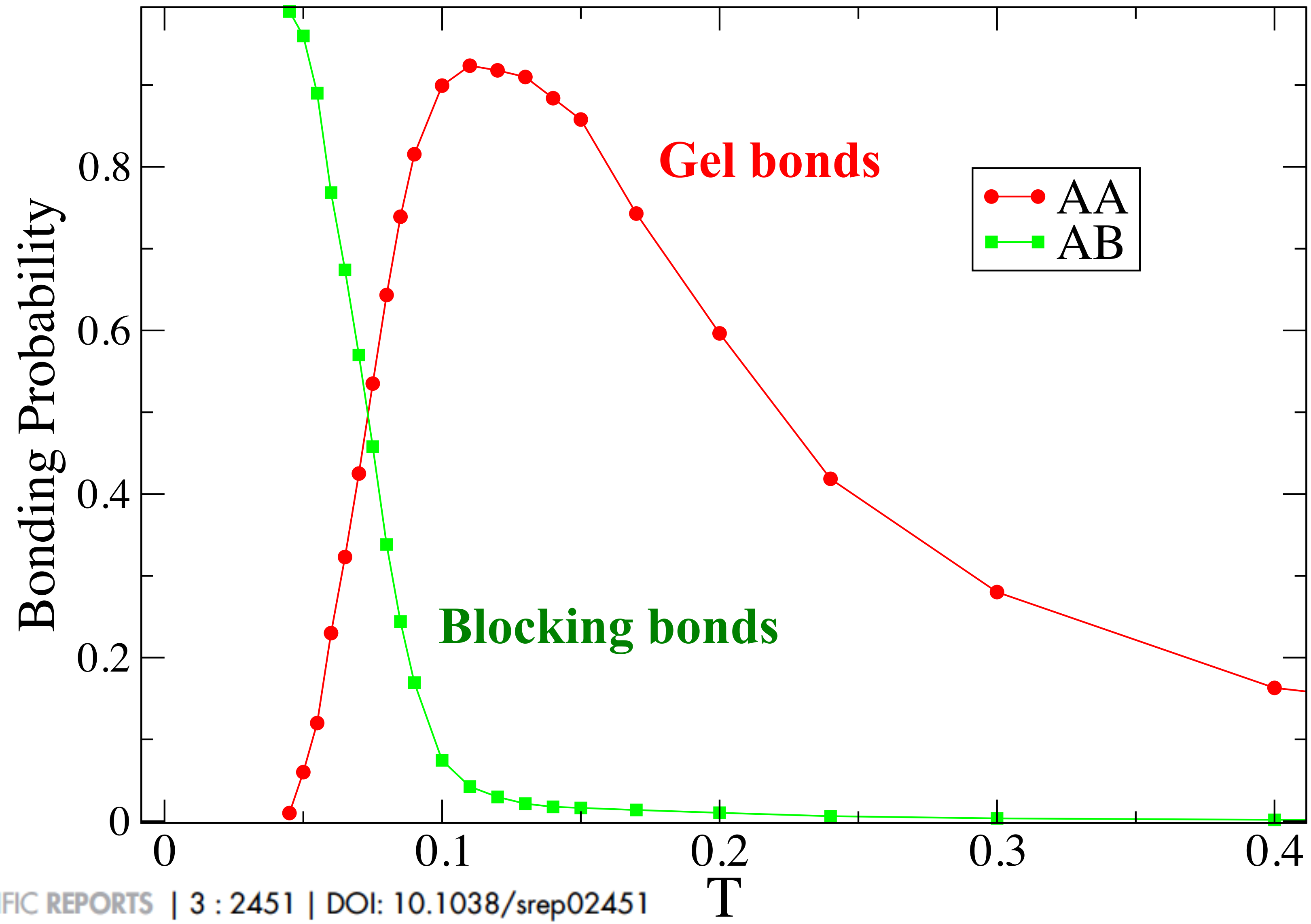
Bonding volume AA >> Bonding volume AB





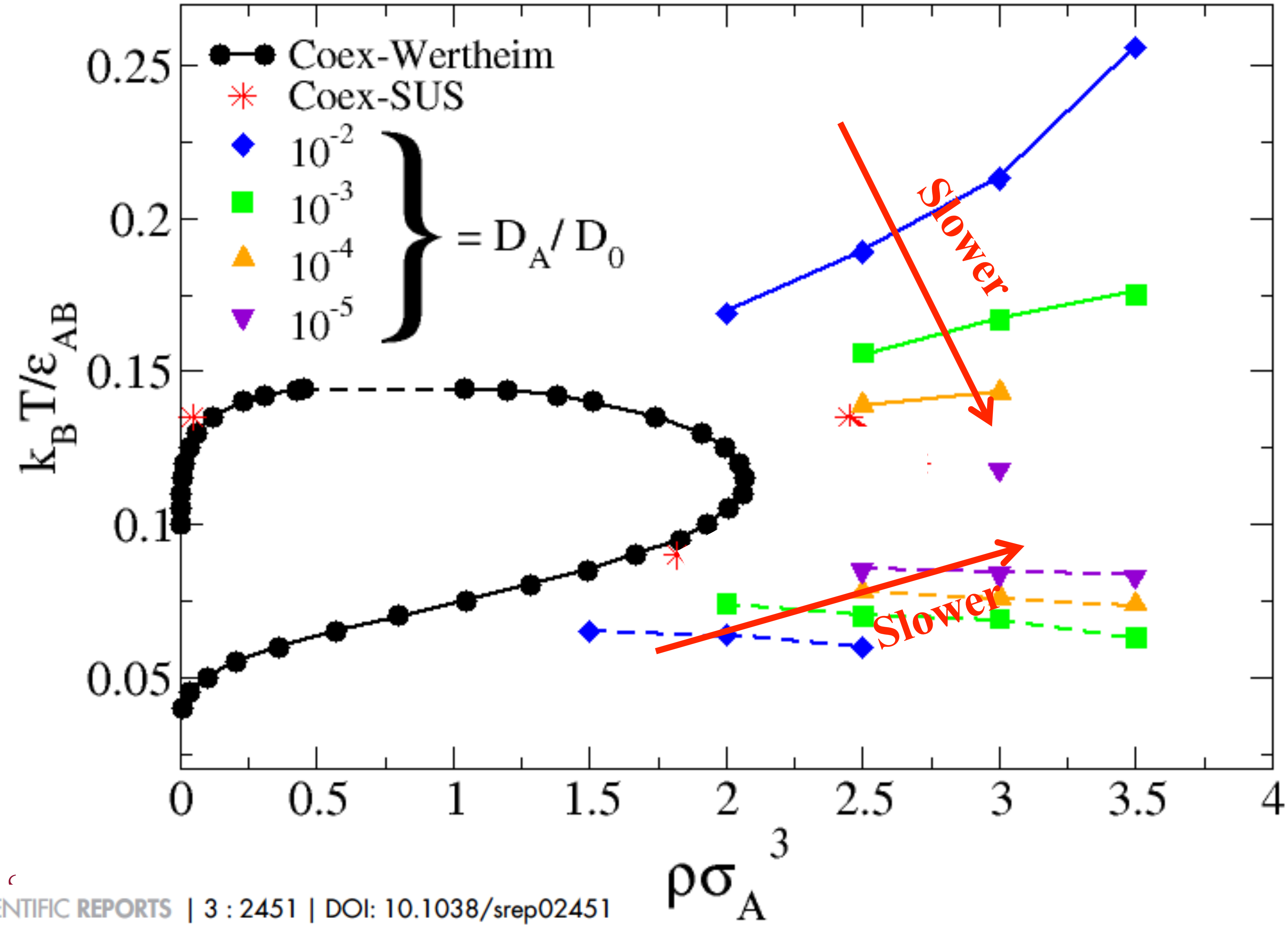
Forming and melting the gel

Wertheim theory

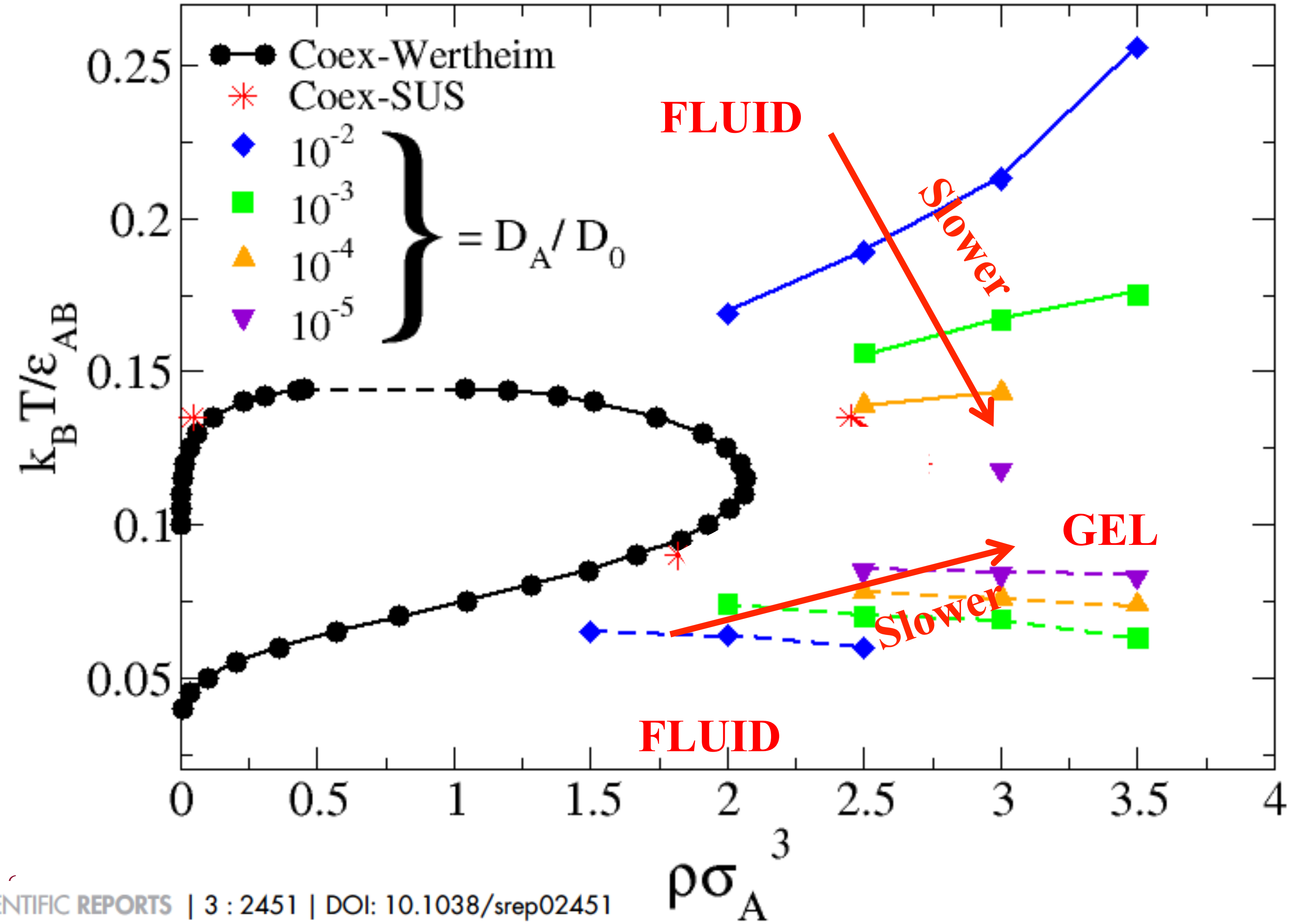


SCIENTIFIC REPORTS | 3 : 2451 | DOI: 10.1038/srep02451

Simulations (stochiometric)



Simulations (stochiometric)



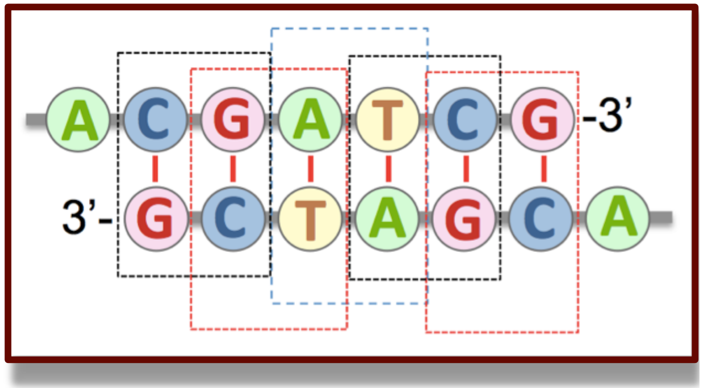
SCIENTIFIC REPORTS | 3 : 2451 | DOI: 10.1038/srep02451

Can we design a system that does it in the laboratory ?

With DNA particles:
Control on the valence
Bulk quantities
Reasonable T intervals

The competitor….. (B particle)

(“palindromic”)



Two serious problems to solve:

1) **How to avoid BB pairing ?**
2) **How to increase the entropy cost of bonding ?**

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The proposed solution:

AA bonding

***NANOSTAR-ARM*-3'(TGA)GCGTACGC(AAT)-5'**

3'-ATTGCG-5' **3'-CGCTCA-5'**

B- particle (competitor)

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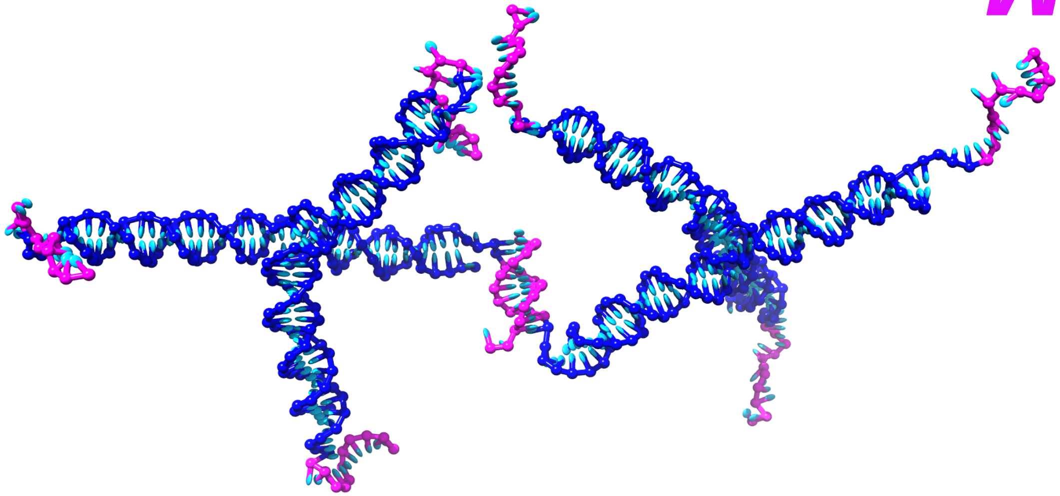
AA-bonding: 8 bases paired

STAR-ARM-3'(TGA)GCGTACGC(AAT)-5'

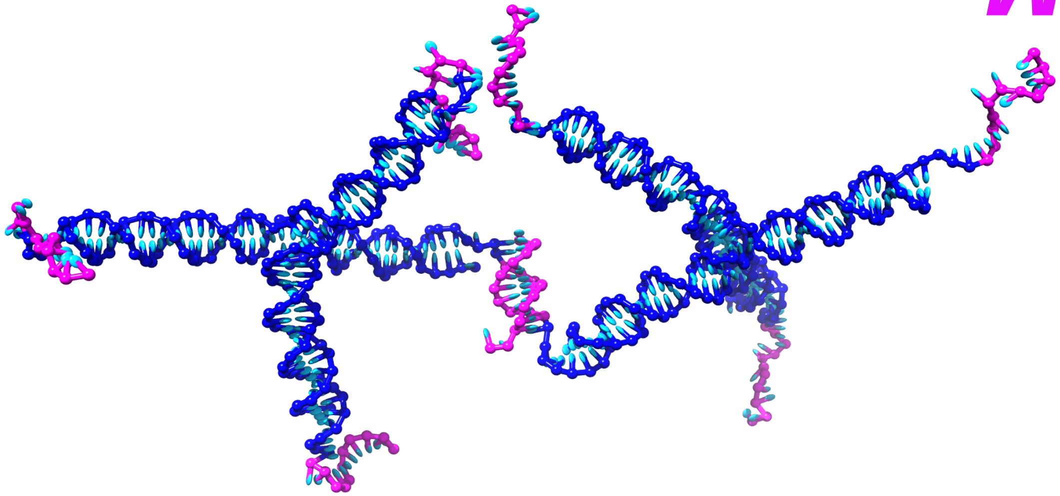
STAR-ARM-3'(TGA)GCGTACGC(AAT)-5'



AA-bonding: 8 bases paired

STAR-ARM-3'(TGA)GCGTACGC(AAT)-5'

STAR-ARM-3'(TGA)GCGTACGC(AAT)-5'

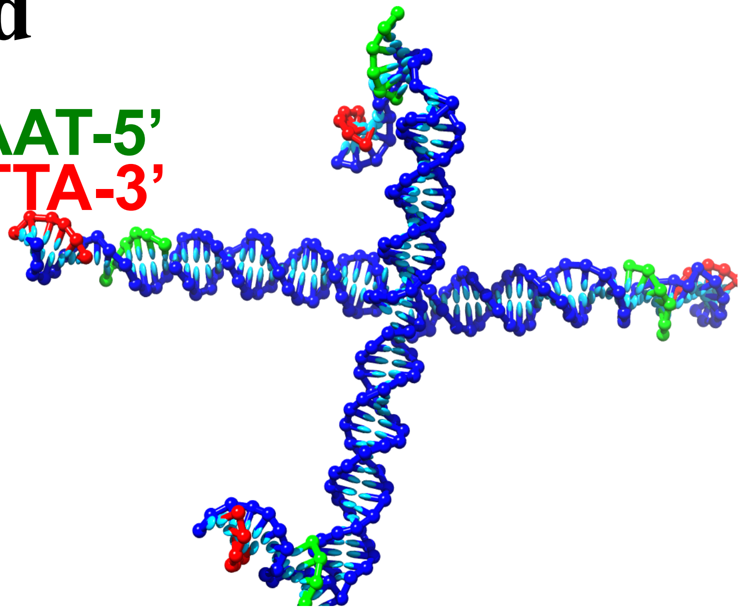


AB-bonding: 12 bases paired

5'-ACTCGC-3'

STAR-ARM-3'-TGAGCGTACGCAAT-5'

5'-GCGTTA-3'



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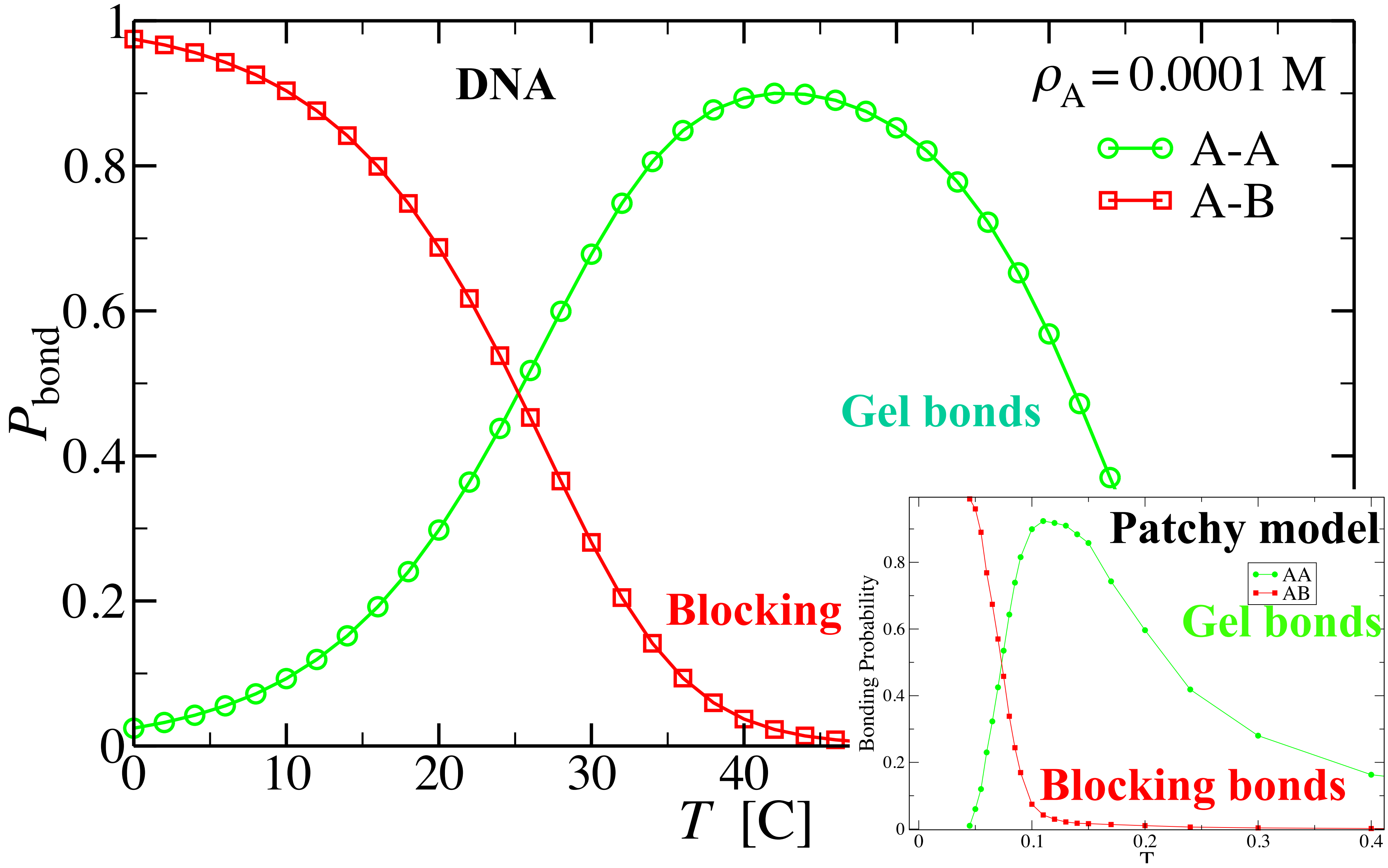
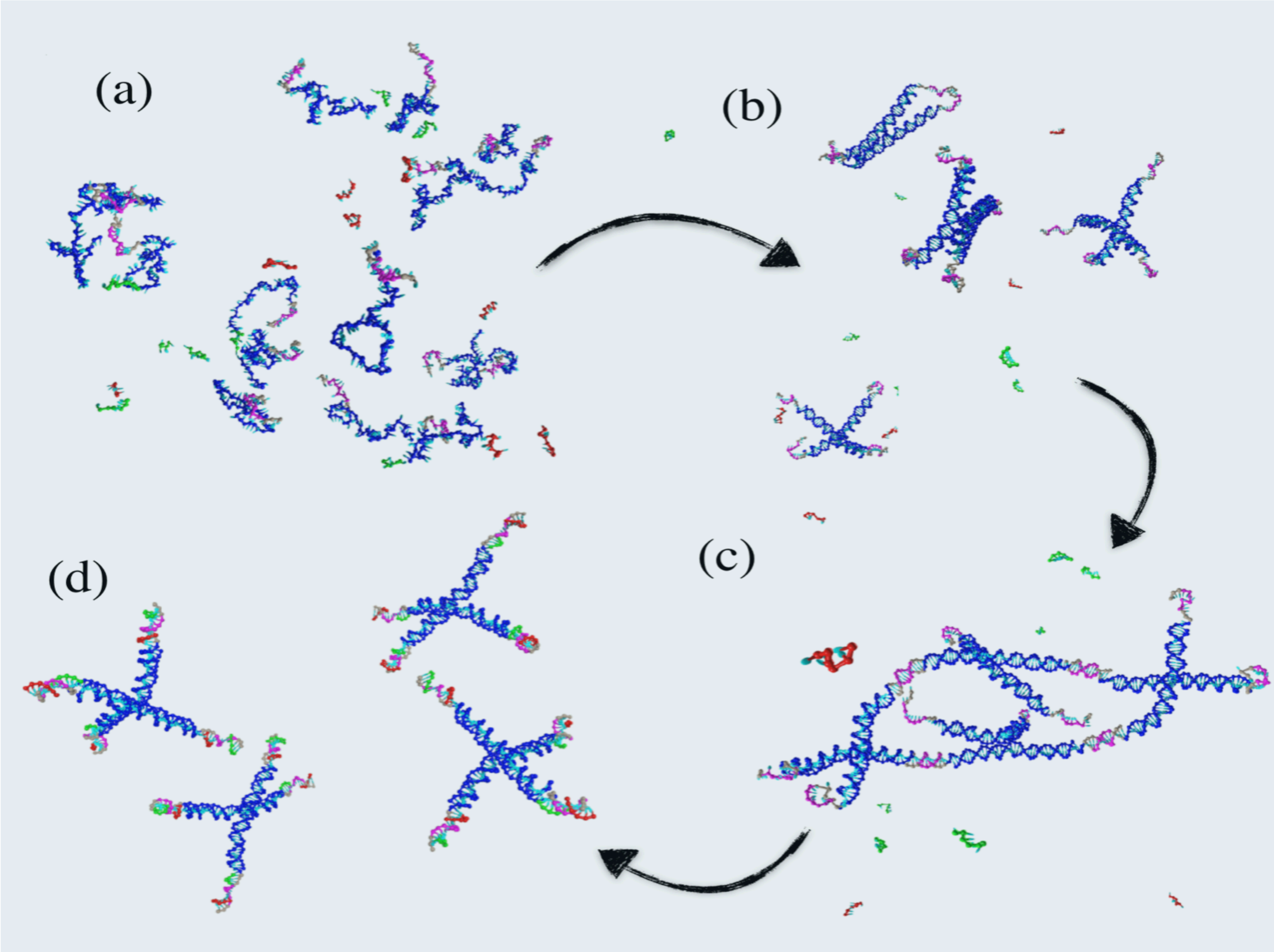
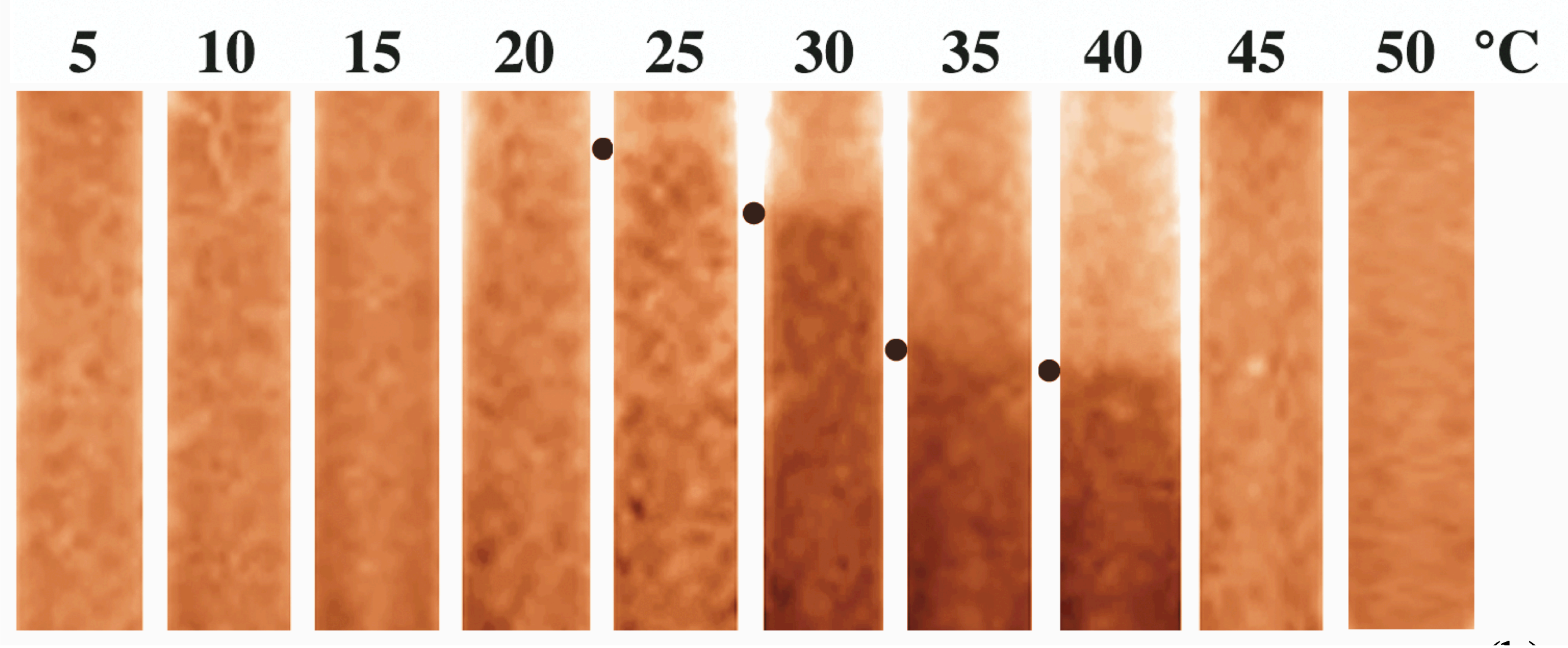
Nupack Evaluations: www.nupack.org




(a)
(b)
(c)
(d)

Now… experiments:
The phase diagram



(ethidium bromide)

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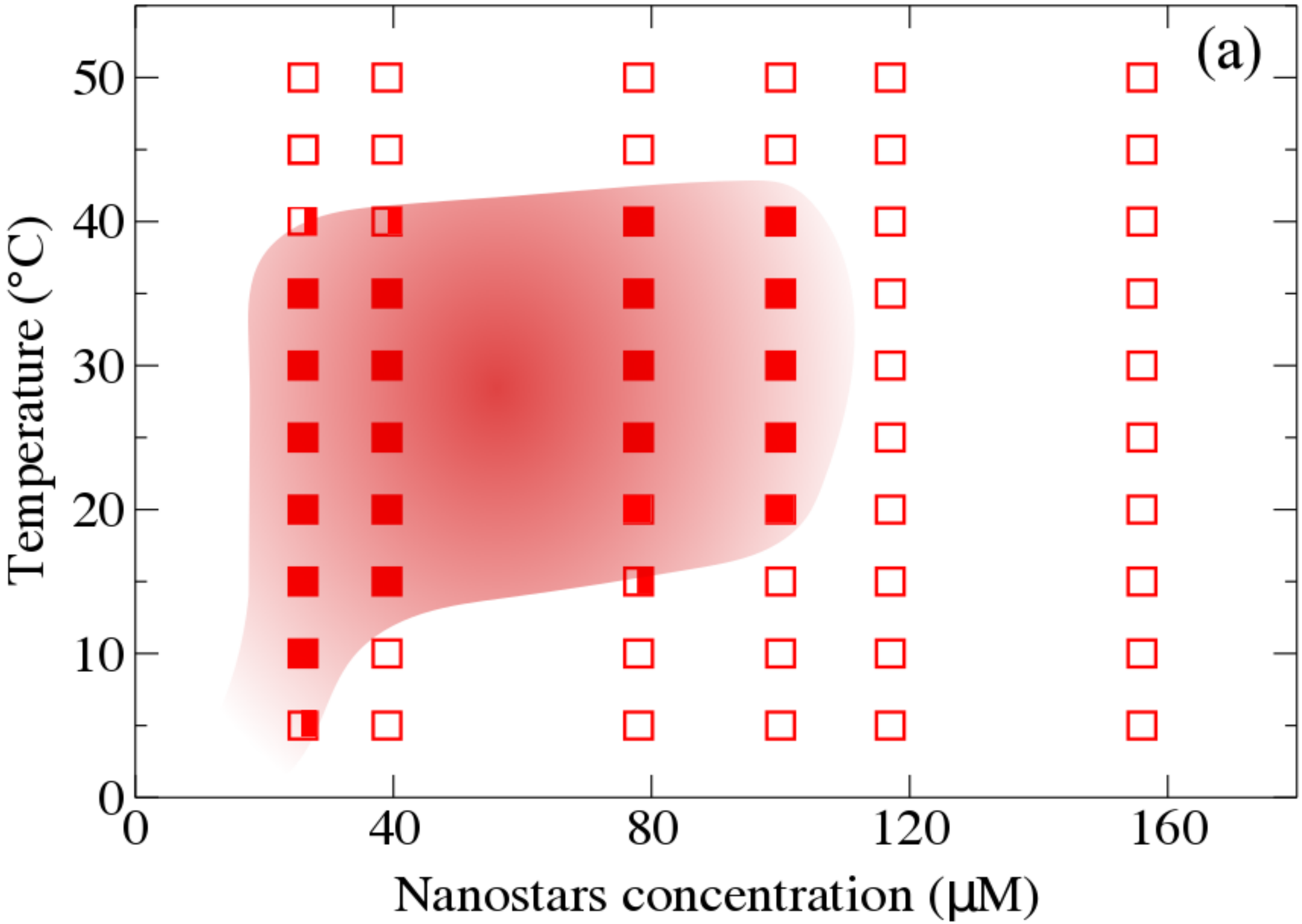
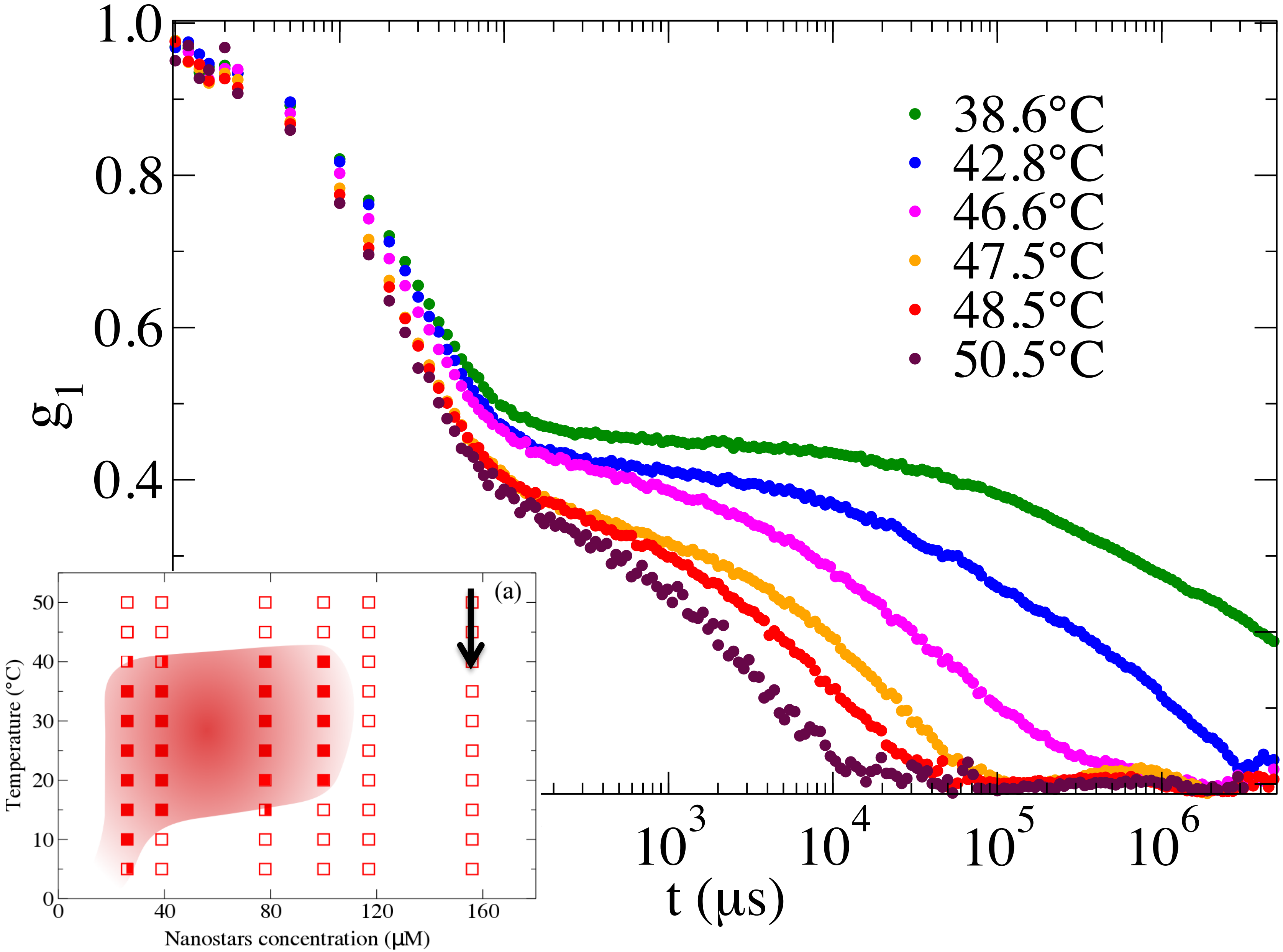
Bomboi et al, Nat Comm. In press

COLLDENSE
COLLOIDS with
DESIGNED RESPONSE

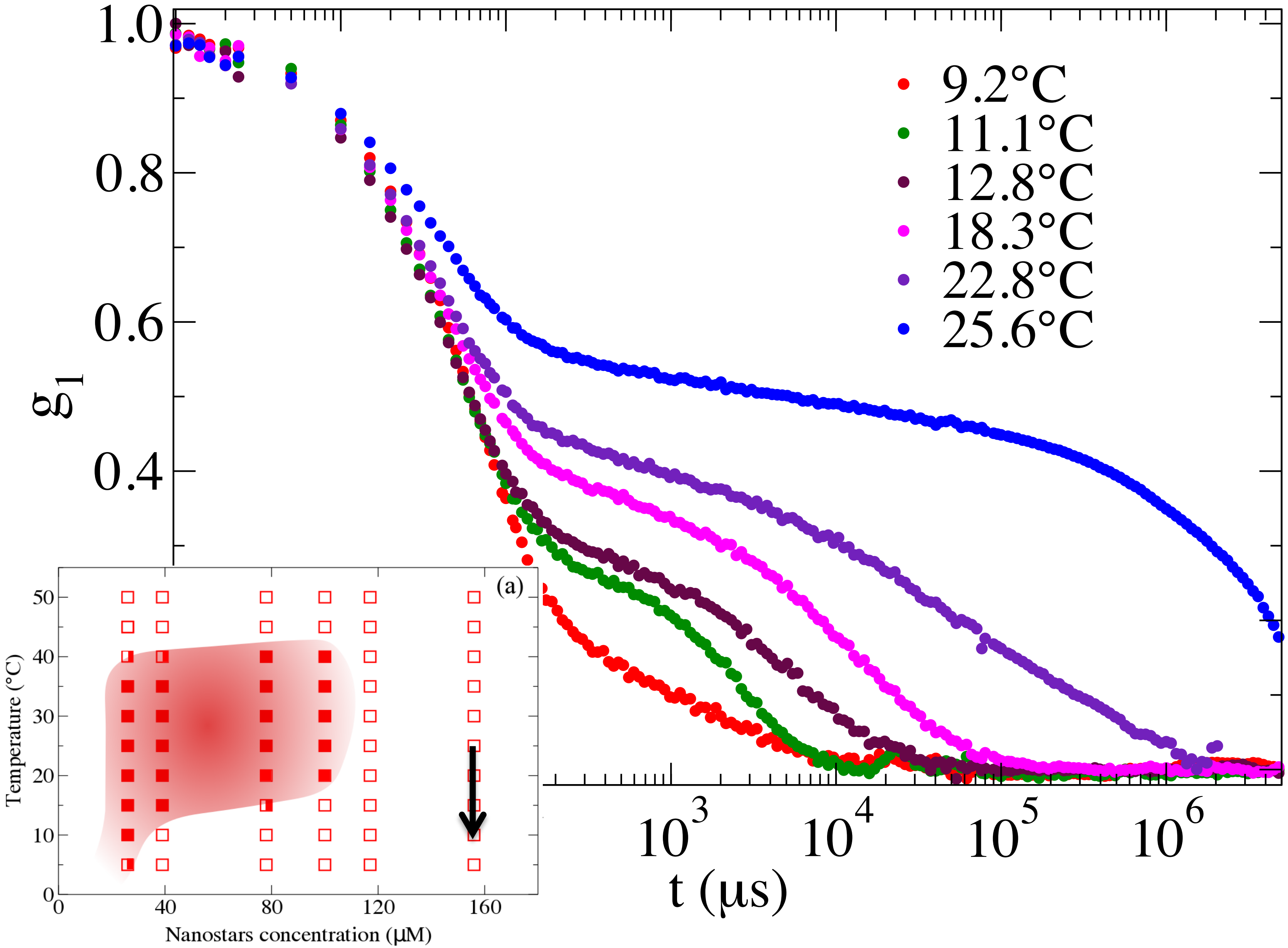
The phase diagram:



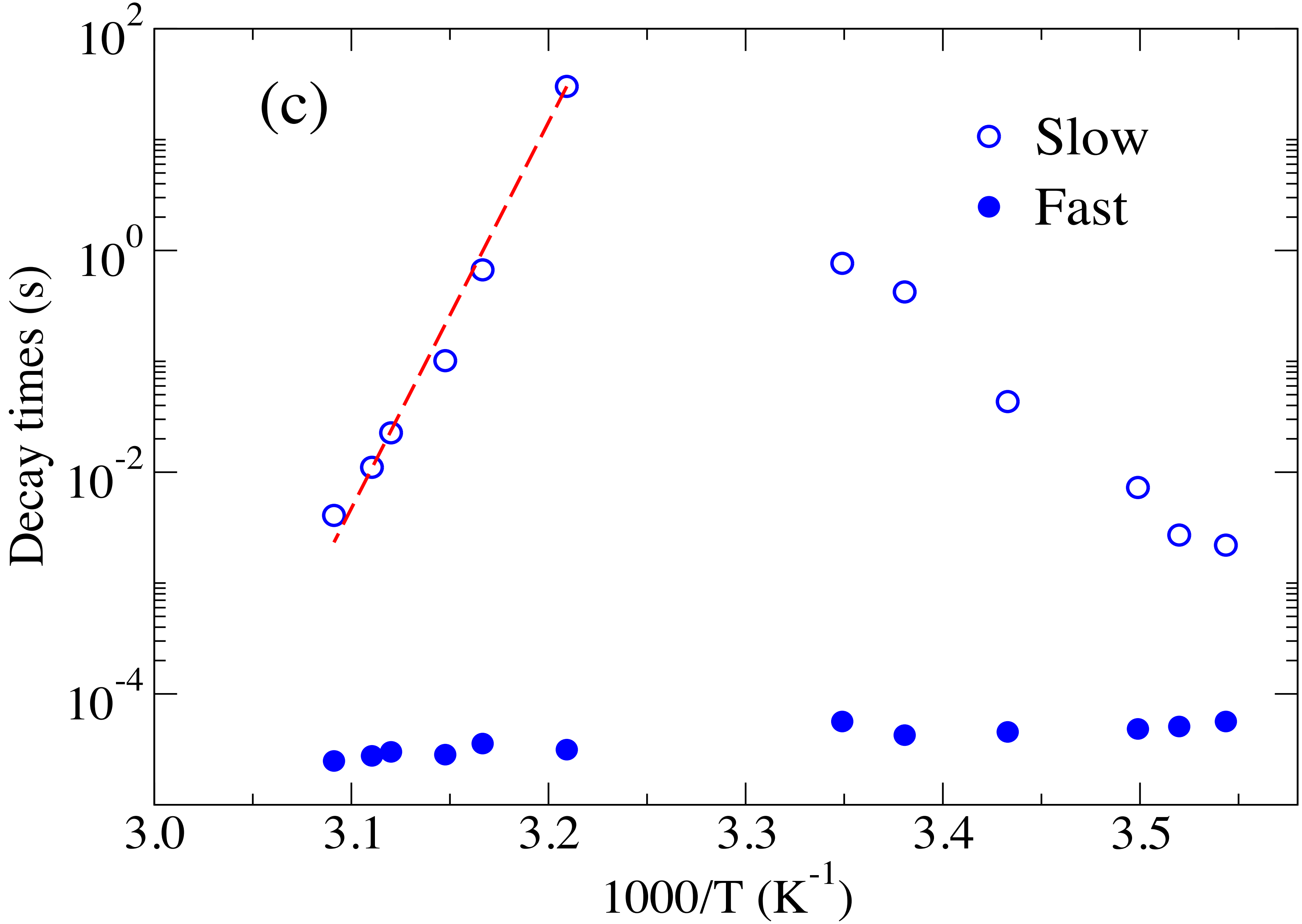
The T-region where the gel forms



The T-region where the gel breaks



The characteristic time



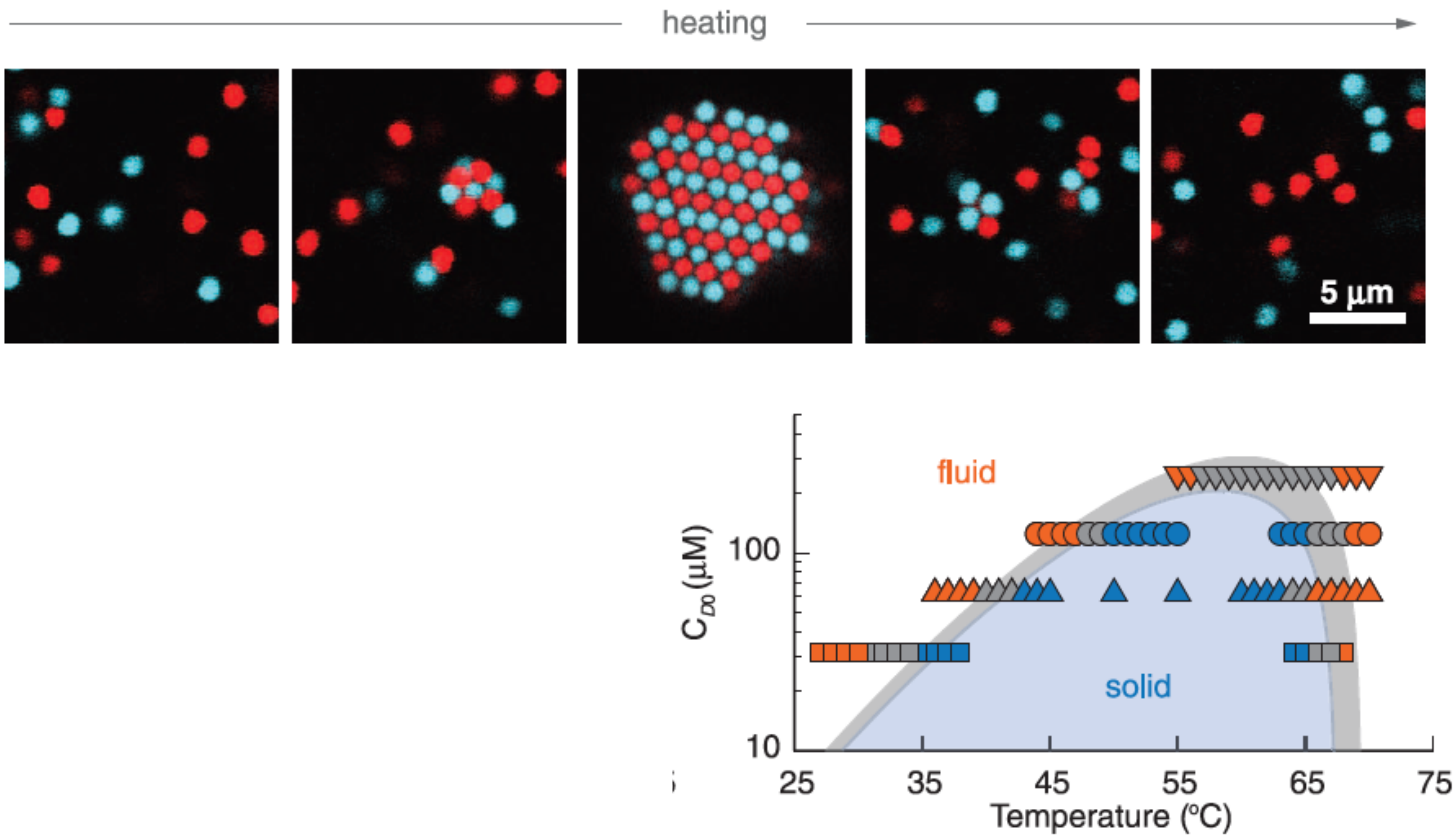
Bomboi et al, Nat Comm. in press

Science AAAS

Programming colloidal phase transitions with DNA strand displacement

W. Benjamin Rogers and Vinothan N. Manoharan

Science **347**, 639 (2015);
DOI: 10.1126/science.1259762



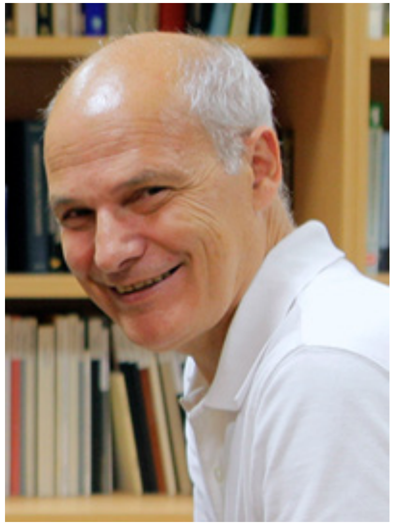
Bridging *in-silico* and *in-charta* intuitions into real experimental realizations

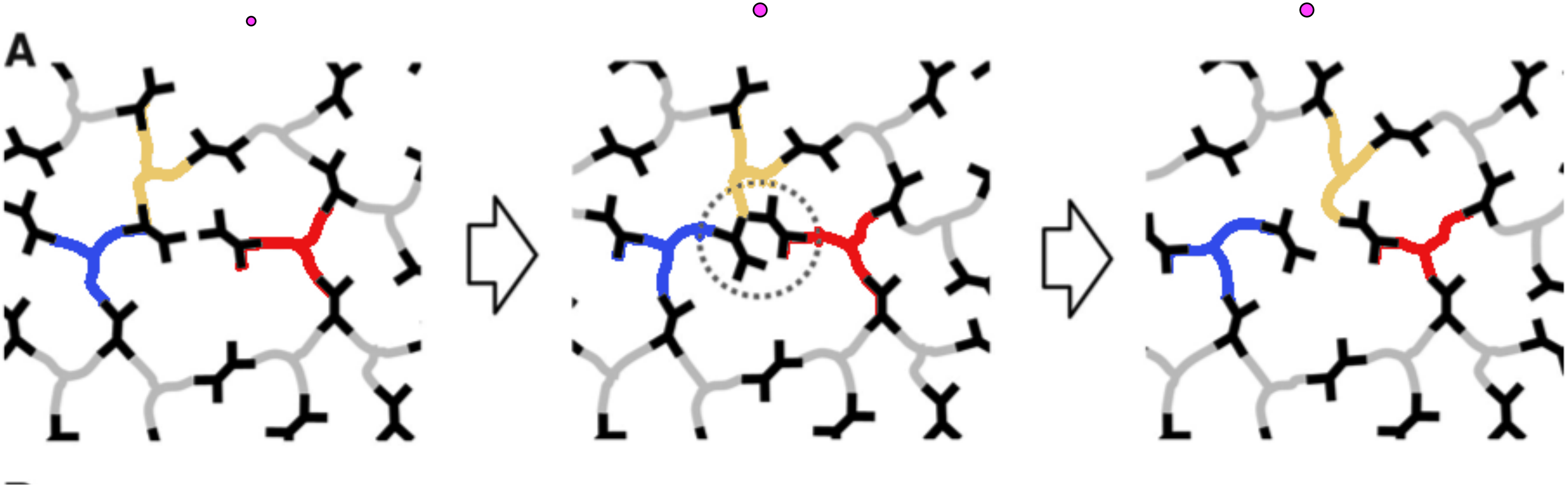
Vitrimers:

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*





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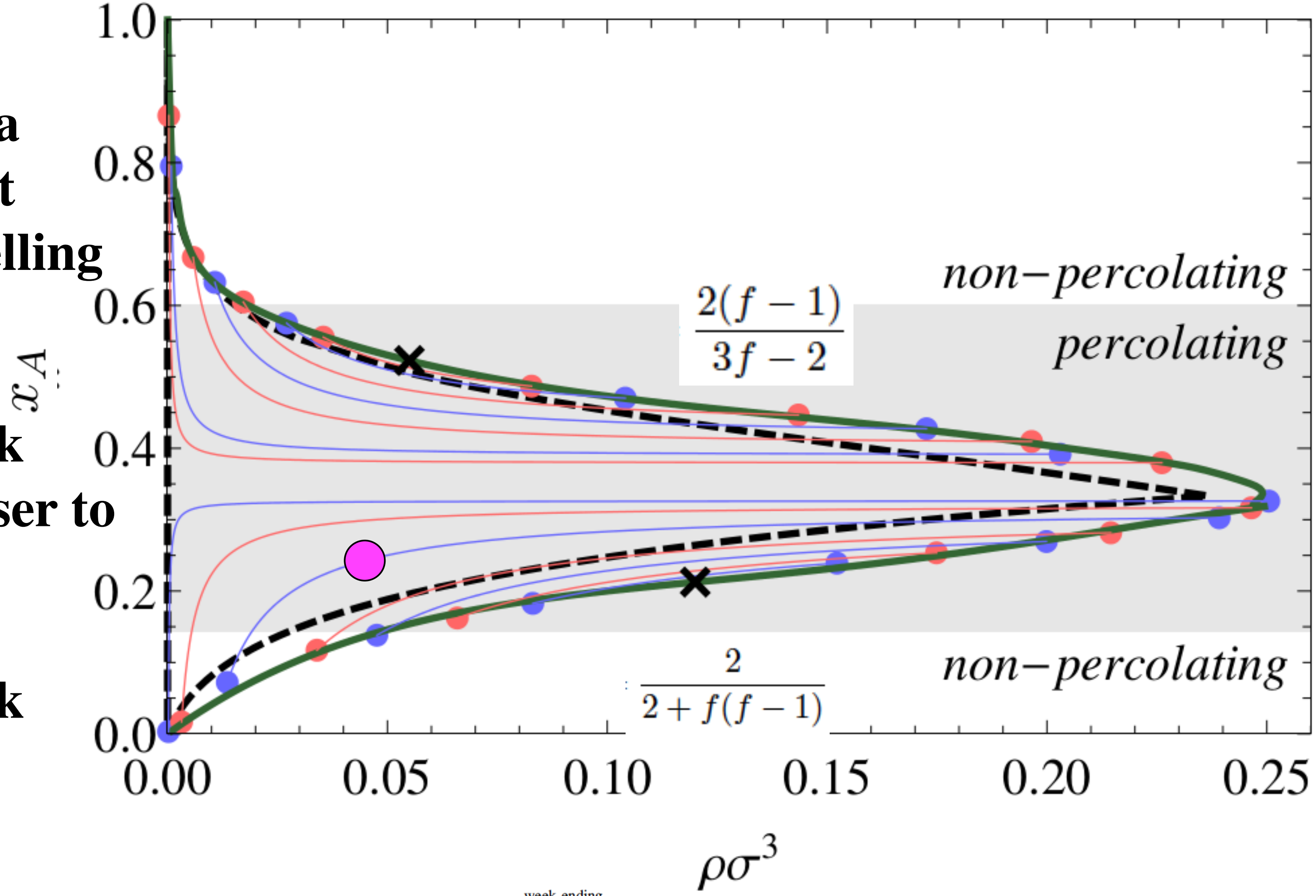
T=0 K Equilibrium phase diagram (Entropy Only!)

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



PRL **111**, 188002 (2013) PHYSICAL REVIEW LETTERS week ending 1 NOVEMBER 2013

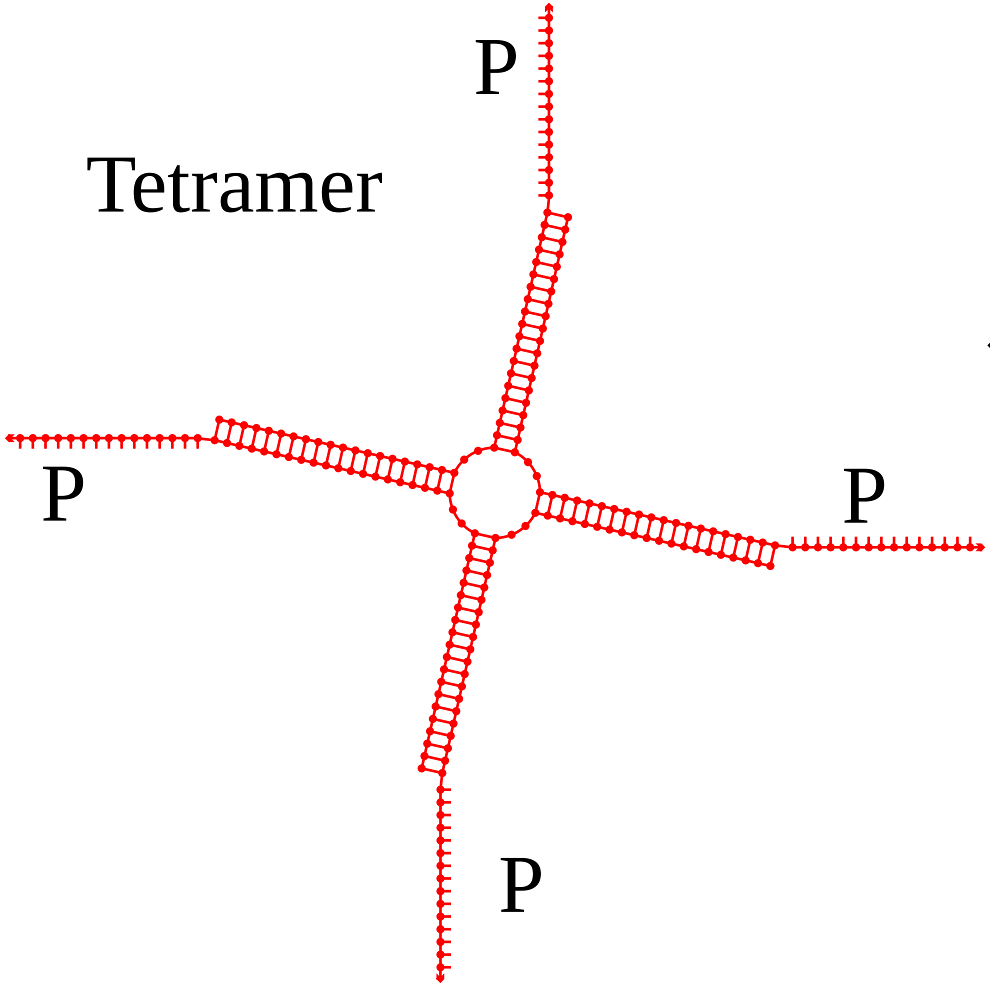
Patchy Particle Model for Vitrimers

Frank Smallenburg,[1,*] Ludwik Leibler,[2] and Francesco Sciortino[1]

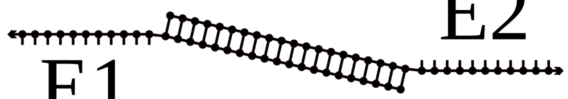
Theory: black dashed line
Simulations: points, solid line

An all DNA vitrimer !

Tetramer



Bridge



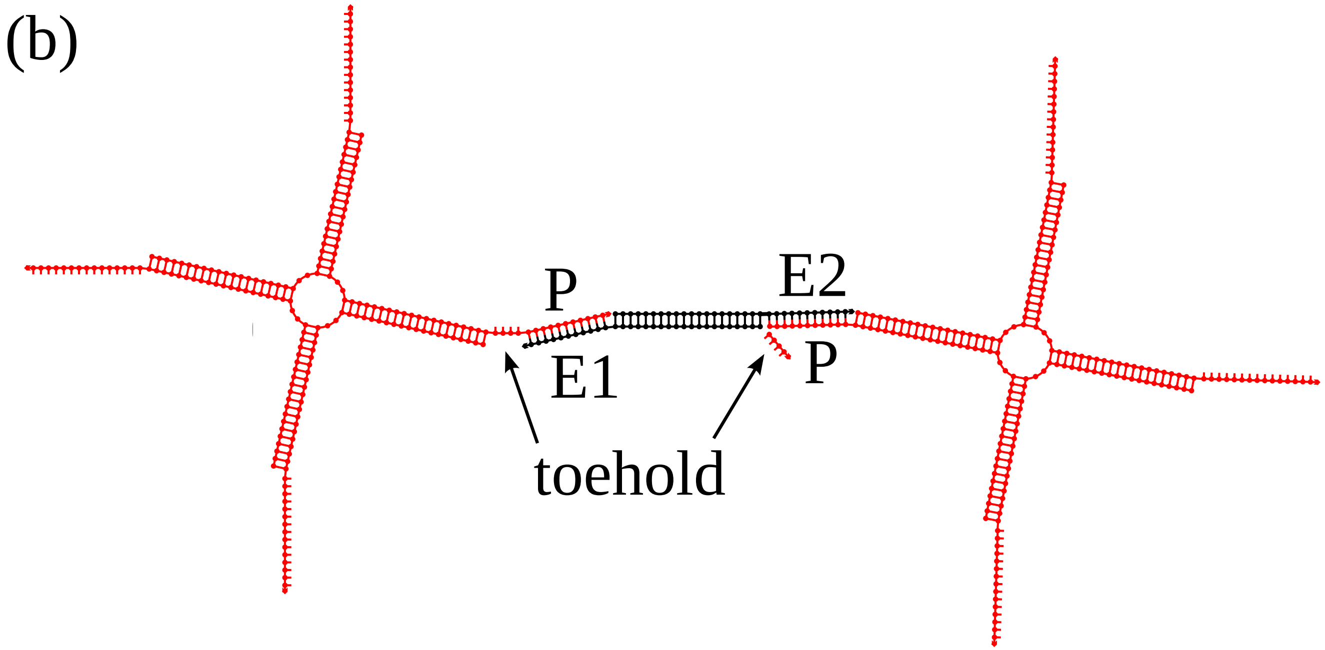
114, 078104 (2015) PHYSICAL REVIEW LETTERS

Switching Bonds in a DNA Gel: An All-DNA Vitrimer

Flavio Romano[1] and Francesco Sciortino[2]

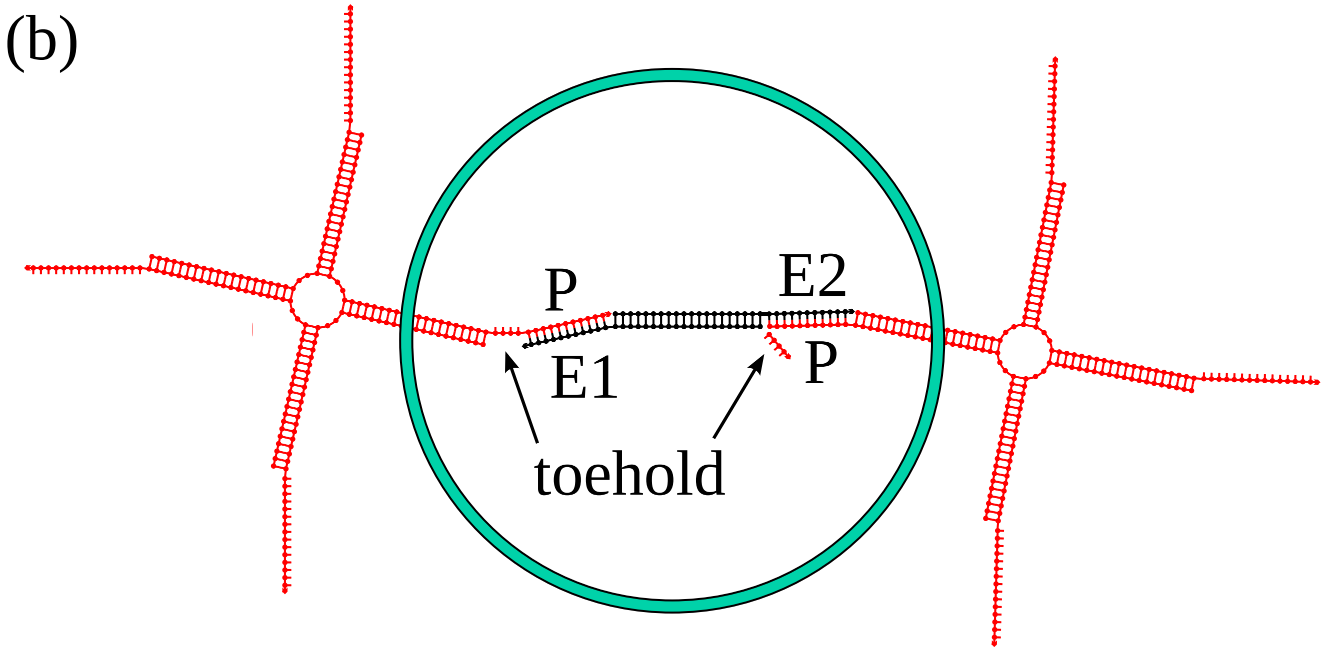
$E1$	5′-GGTTCGACACG-3′
P	3′-CCAAGCTGTGCTCAC-5′
$E2$	5′-CGACACGAGTG-3′

An all DNA vitrimer !



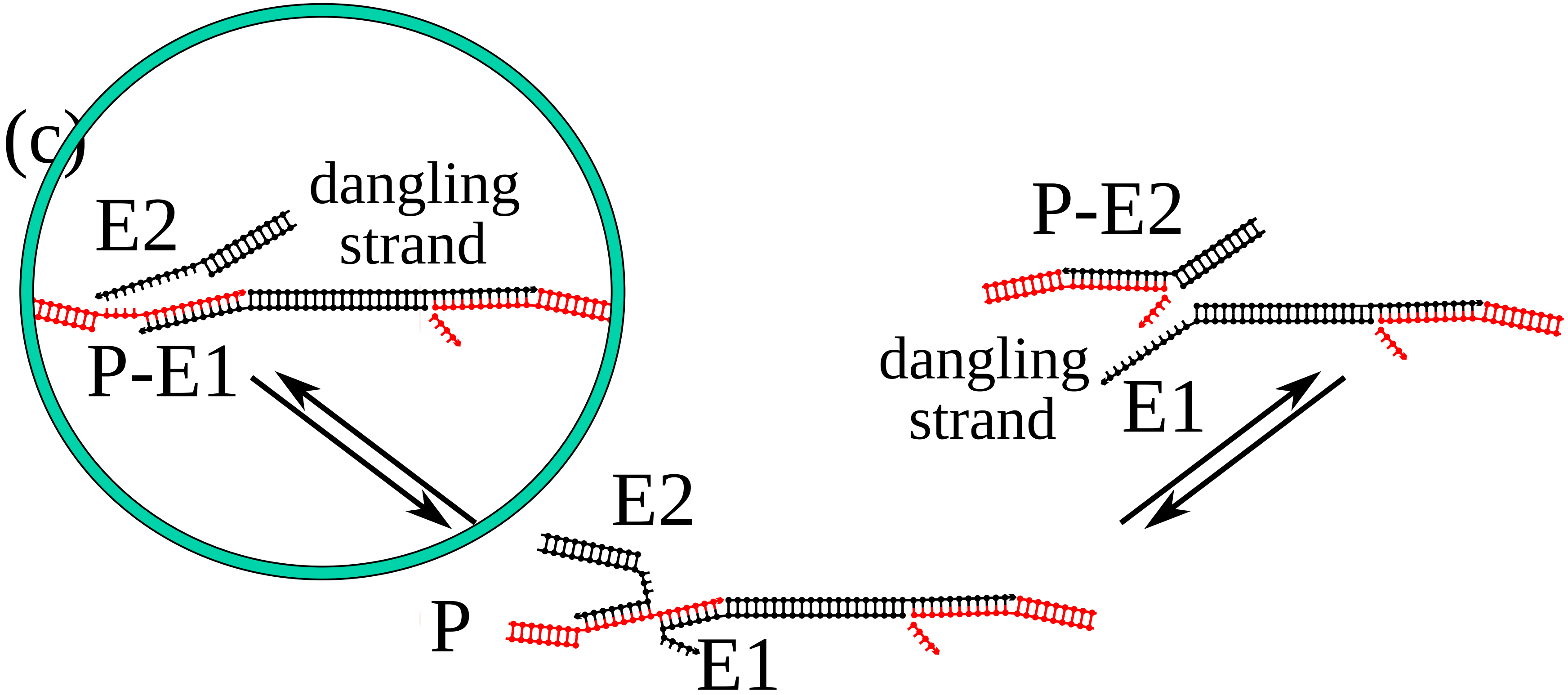
Toehold mediated strand displacement

An all DNA vitrimer !



Toehold mediated strand displacement

An all DNA vitrimer !



$E1$		5′-GGTTCGACACG-3′
P		3′-CCAAGCTGTGCTCAC-5′
$E2$		5′-CGACACGAGTG-3′

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Conclusions

Beside their nanotech applications DNA-made particles can be exploited to bring *in-silico* and *in-charta* intuitions into real experimental realizations.

We have seen applications to:

Equilibrium gels
Ultrastable liquids
Unconventional dynamics
Re-entrant gel
Vitrimers (undergoing)

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COLLDENSE COLLOIDS with DESIGNED RESPONSE

Who did the work

Lorenzo Rovigatti, Simon Ramirez - DNA simulations

Walter Kob, Sandalo Roldan, Frank Smallenburg - Gel on heating (in silico)

Tommaso Bellini, Roberto Cerbino, Silvia Biffi, Francesca Bomboi, Javier Castanon, Patriza Filetici, Manuela Leo, Federico Bordi – Gel on heating (experiments)

Flavio Romano - Gel on heating and vitrimers (design)

Animation by L. Rovigatti

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COLLDENSE