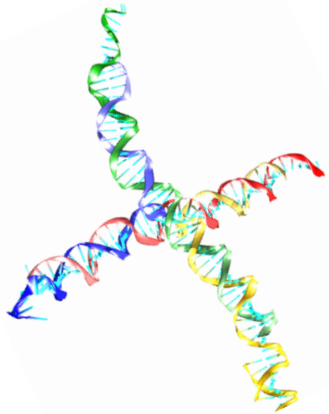
ICTS | INTERNATIONAL CENTRE for THEORETICAL SCIENCES

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

ENTROPY, INFORMATION & ORDER IN SOFT MATTER



Francesco Sciortino

http:www.roma1.infn.it/~sciortif

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COLLDENSE COLLOIDS with DESIGNED RESPONSE

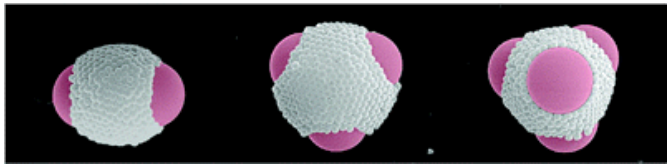
Use DNA-made particles to investigate….

- Limited valence and equilibrium gels
- Gelling on heating
- Swapping gels

First part : simulation and theory

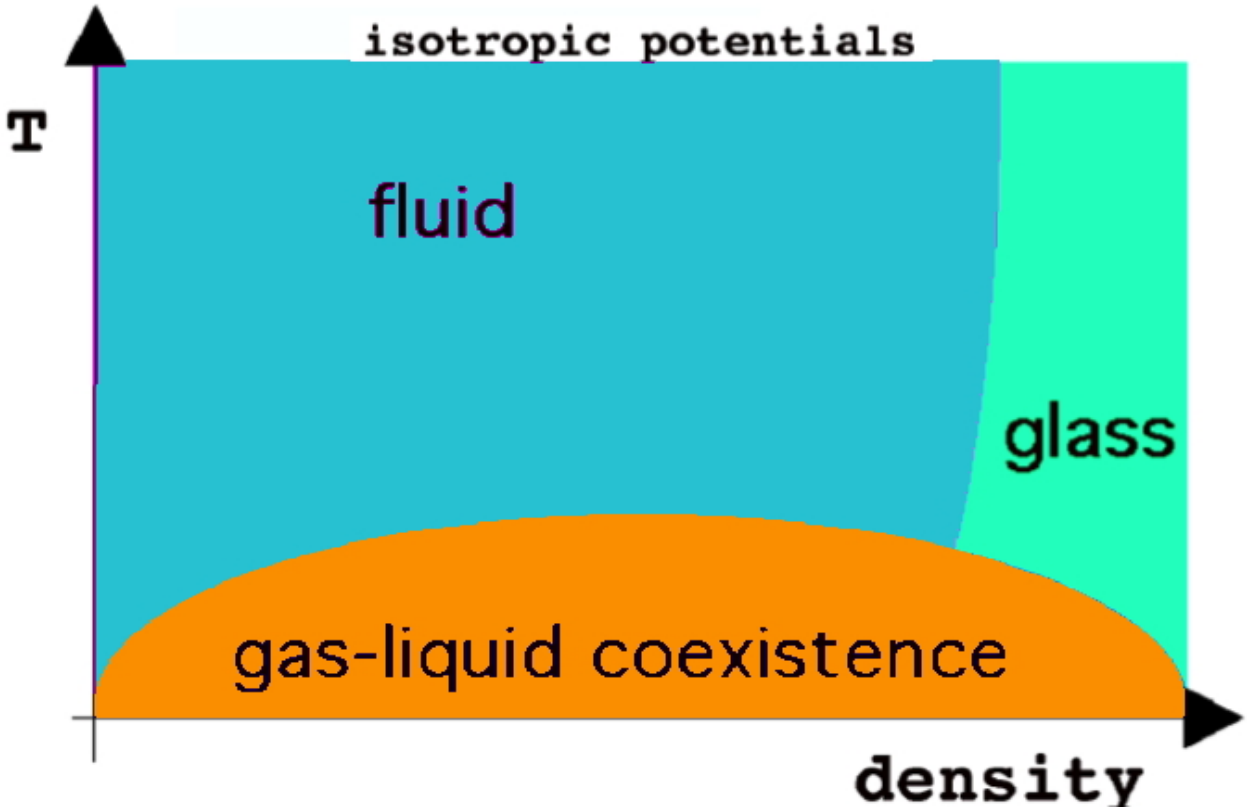
Second part : experiments with DNA

How does the valence affect the phase diagram?

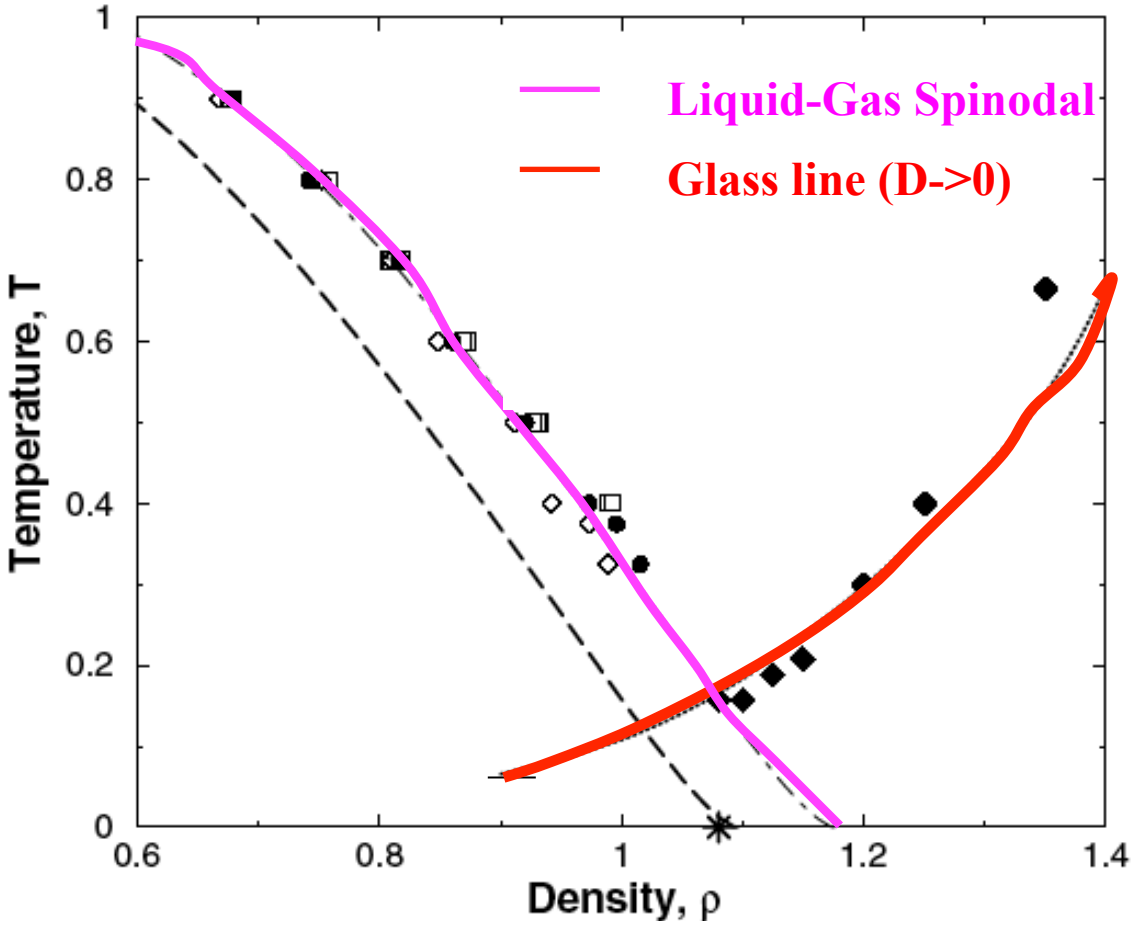


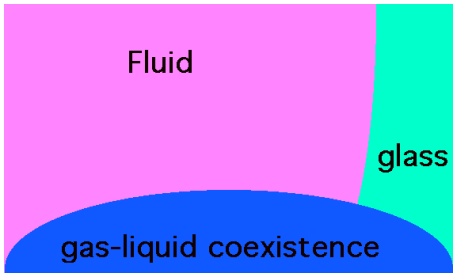
The (conventional) phase diagram of spherical potentials*

(excluding crystals)



***One component, "Hard-Core" plus attraction**





Binary mixture LJ particles

"homogeneous" arrested states only for large packing fraction

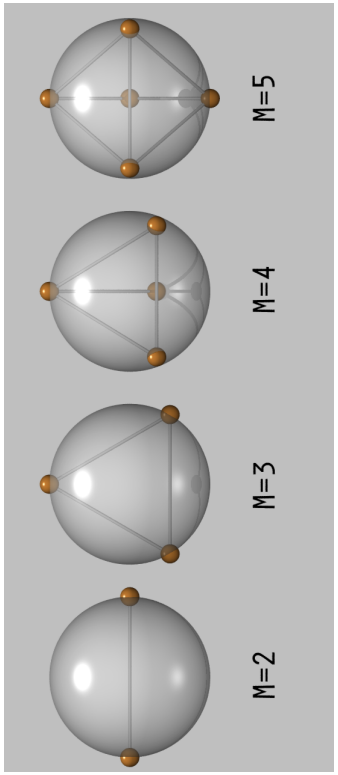
VOLUME 85, NUMBER 3 PHYSICAL REVIEW LETTERS 17 JULY 200

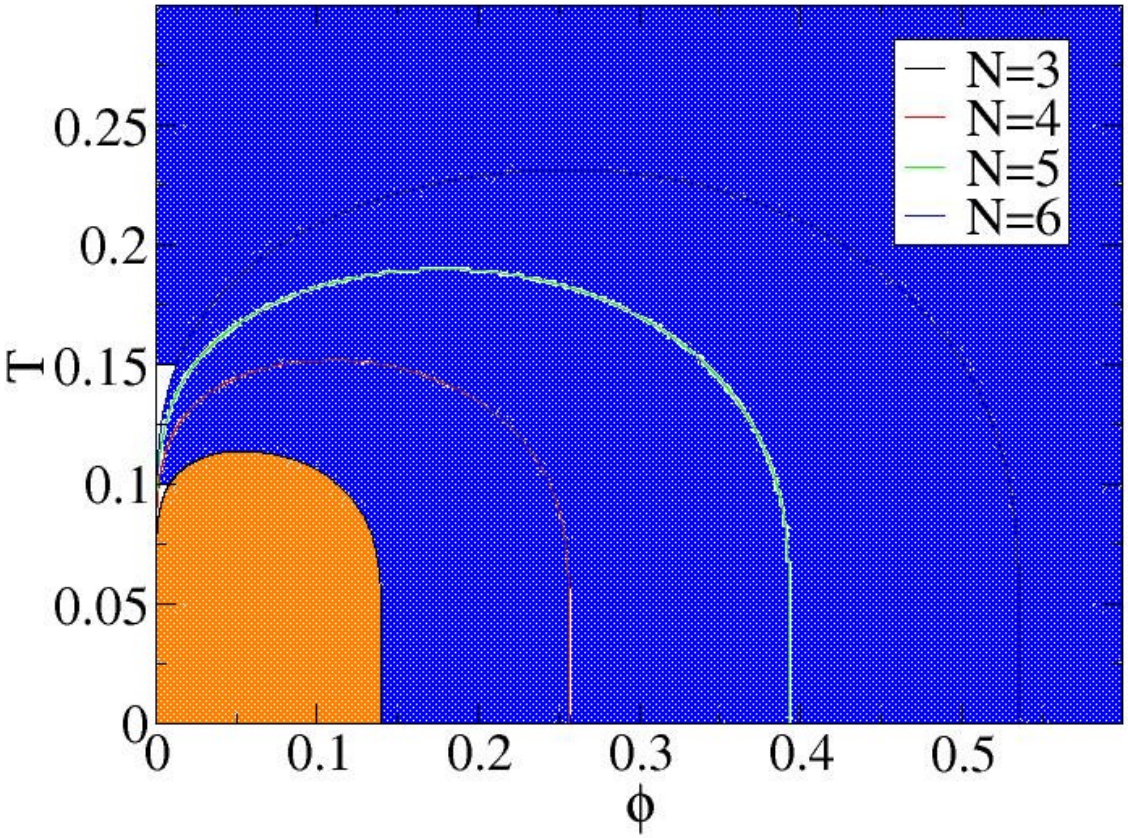
Liquid Limits: Glass Transition and Liquid-Gas Spinodal Boundaries of Metastable Liquids

Srikanth Sastry*
Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560064, India
(Received 15 November 1999)

COLLDENSE
COLLOIDS with DESIGNED RESPONSE

How does the valence affect the phase diagram?





Bianchi et al, PRL 97, 168301, 2006

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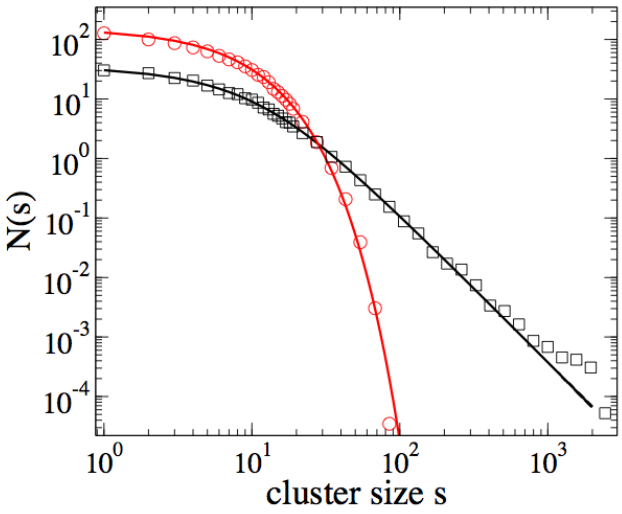
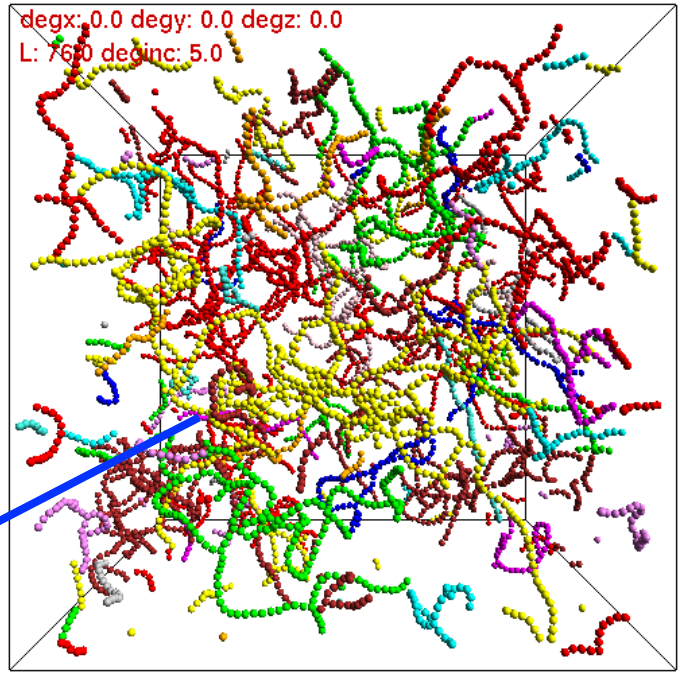
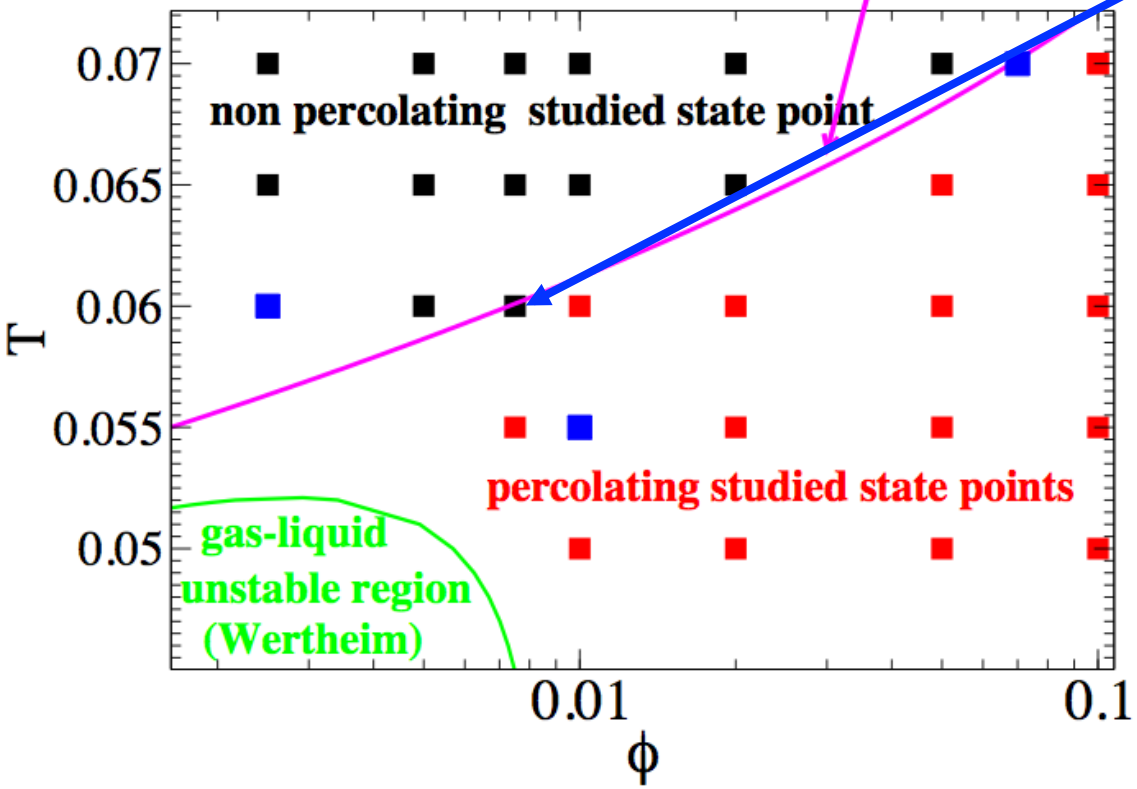
COLLDENSE
COLLOIDS with DESIGNED RESPONSE

Connectivity properties and cluster size distributions: Flory and Wertheim







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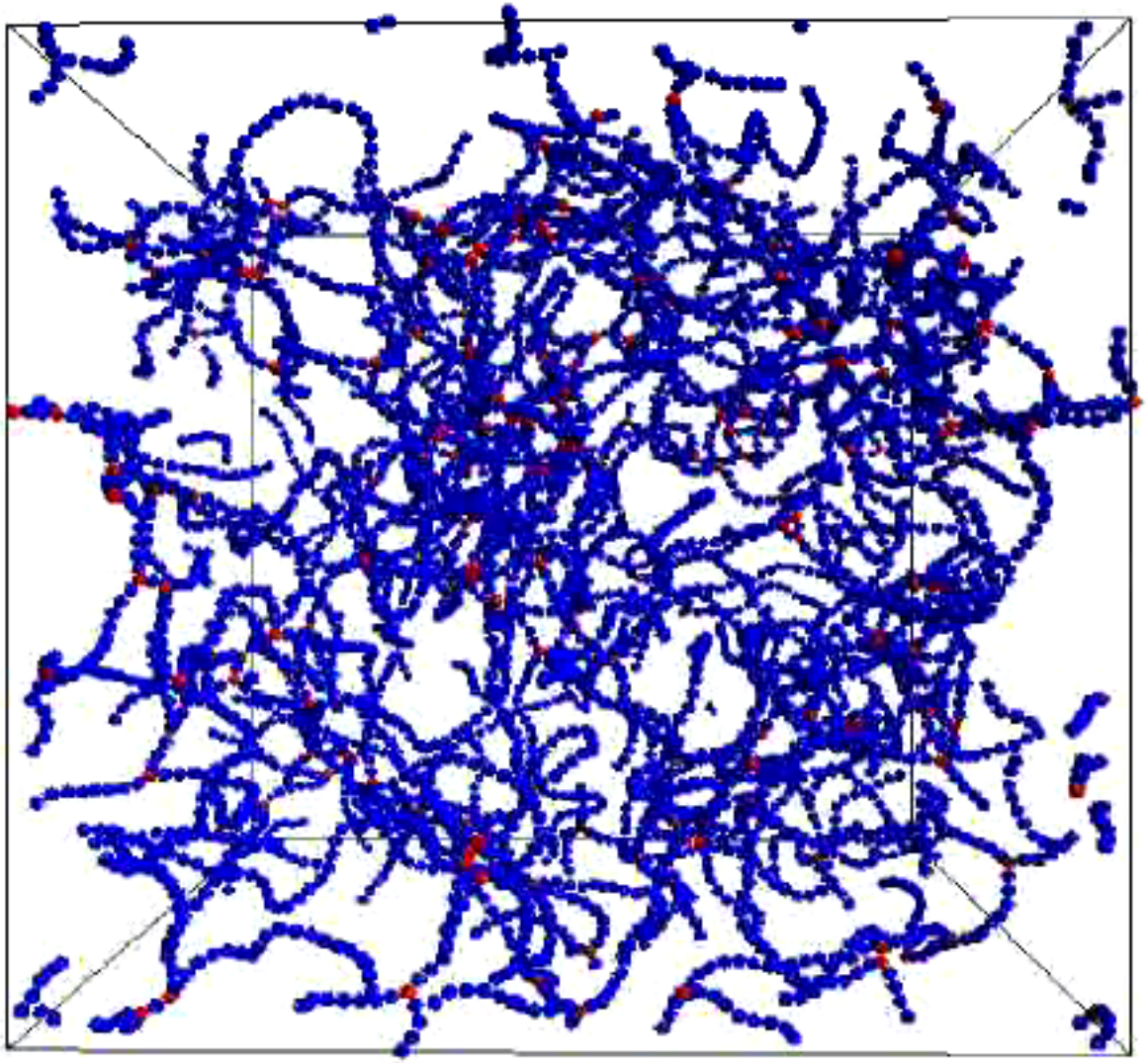
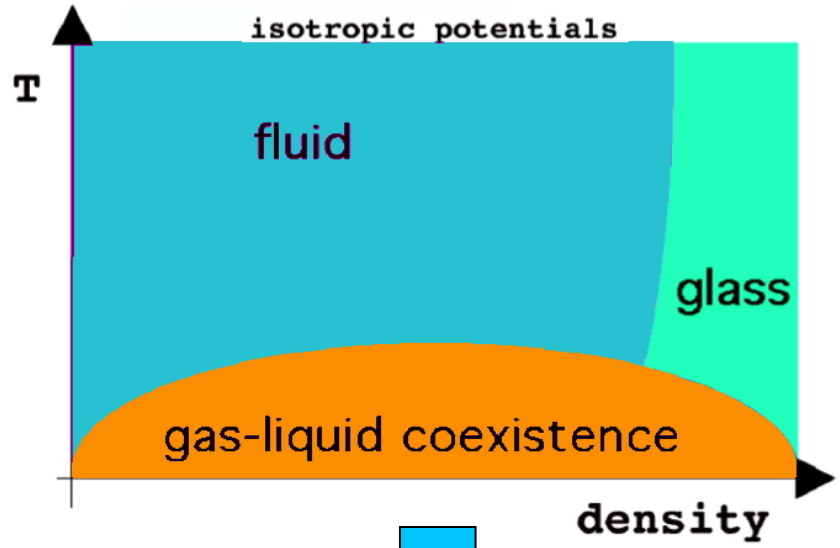
COLLOIDS with DESIGNED RESPONSE

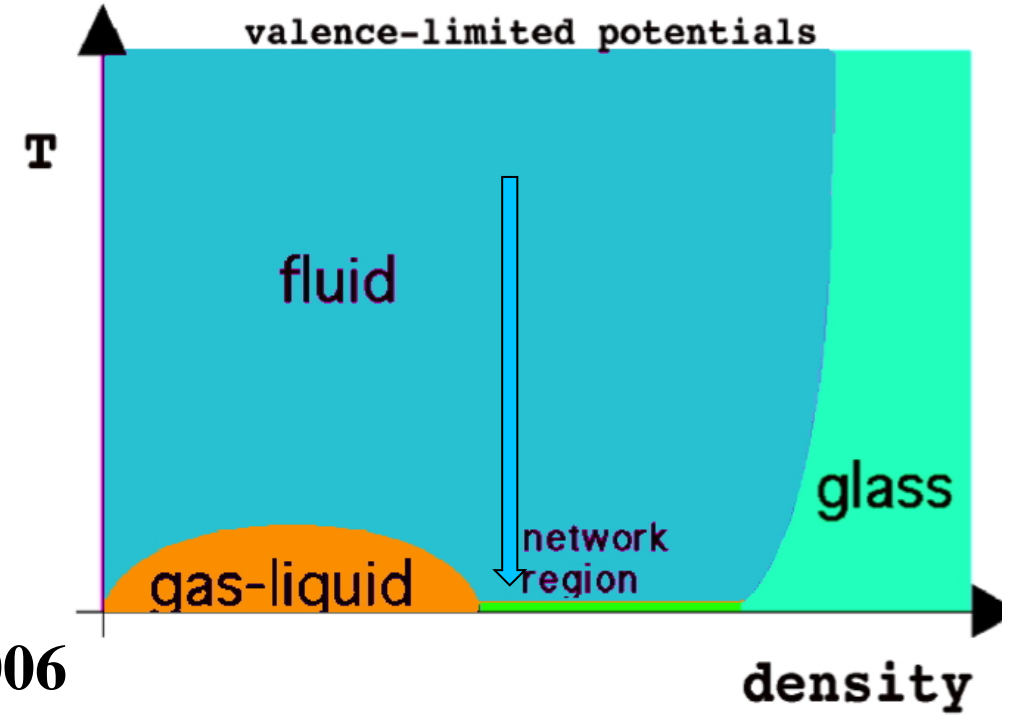


A DIFFERENT final fate to the liquid state. Arrested states at low ϕ !!!



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

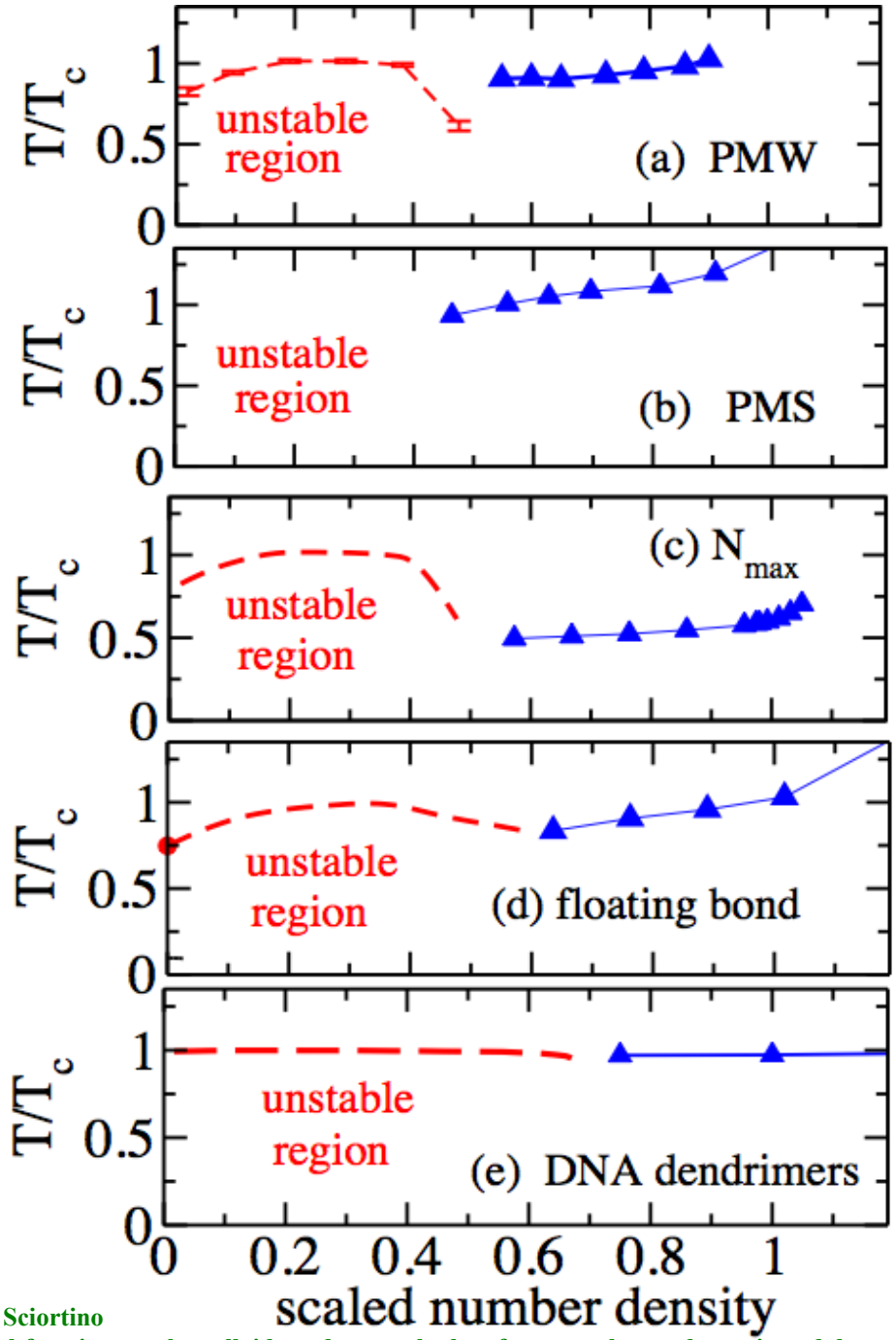
(a network of long-living bonds)

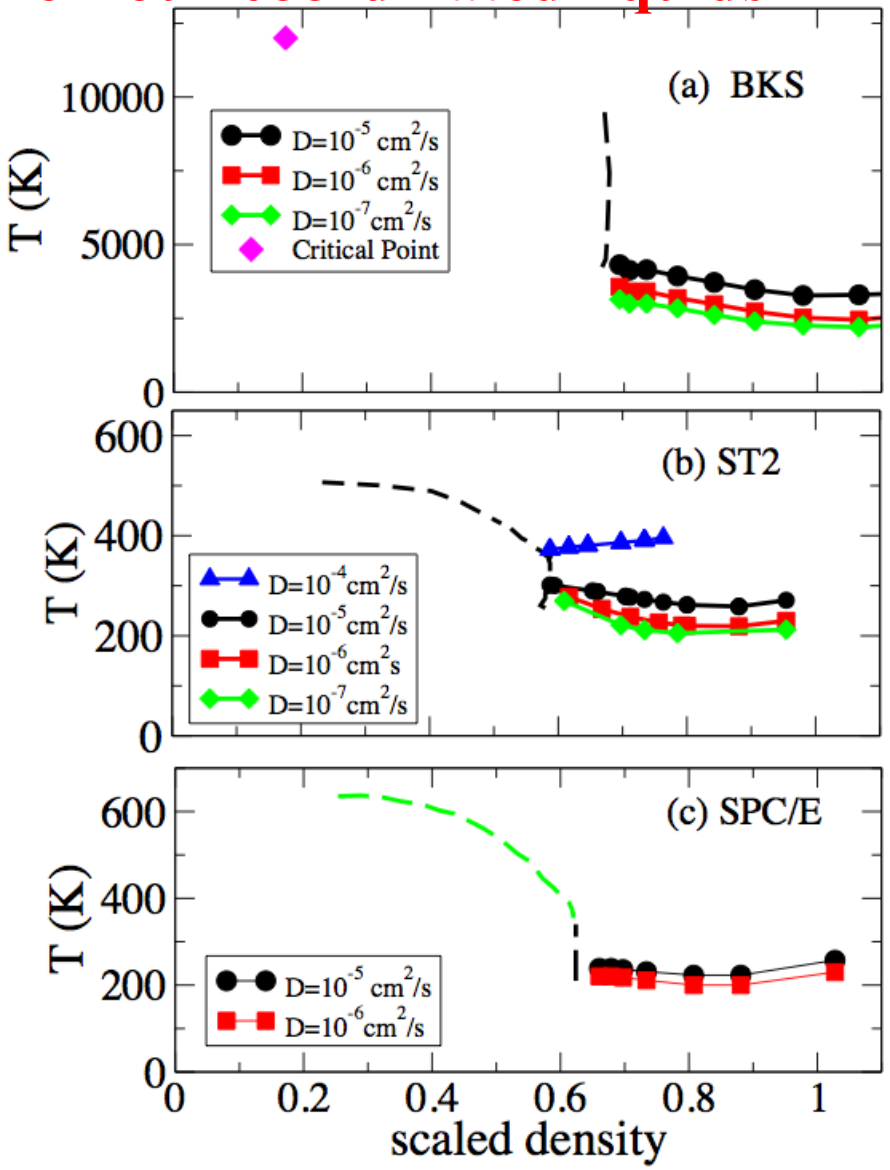


Bianchi et al, PRL 97, 168301, 2006

Universality in the valence:

A collection of phase diagrams of four-coordinated liquids

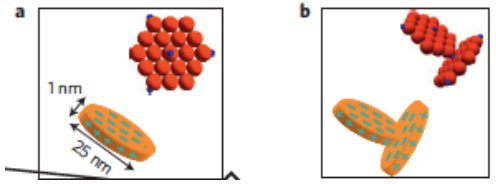




F. Sciortino
Gel-forming patchy colloids and network glass formers: thermodynamic and dynamic analogies
Eur. Phys. J. B 64, 505-509, (2008)

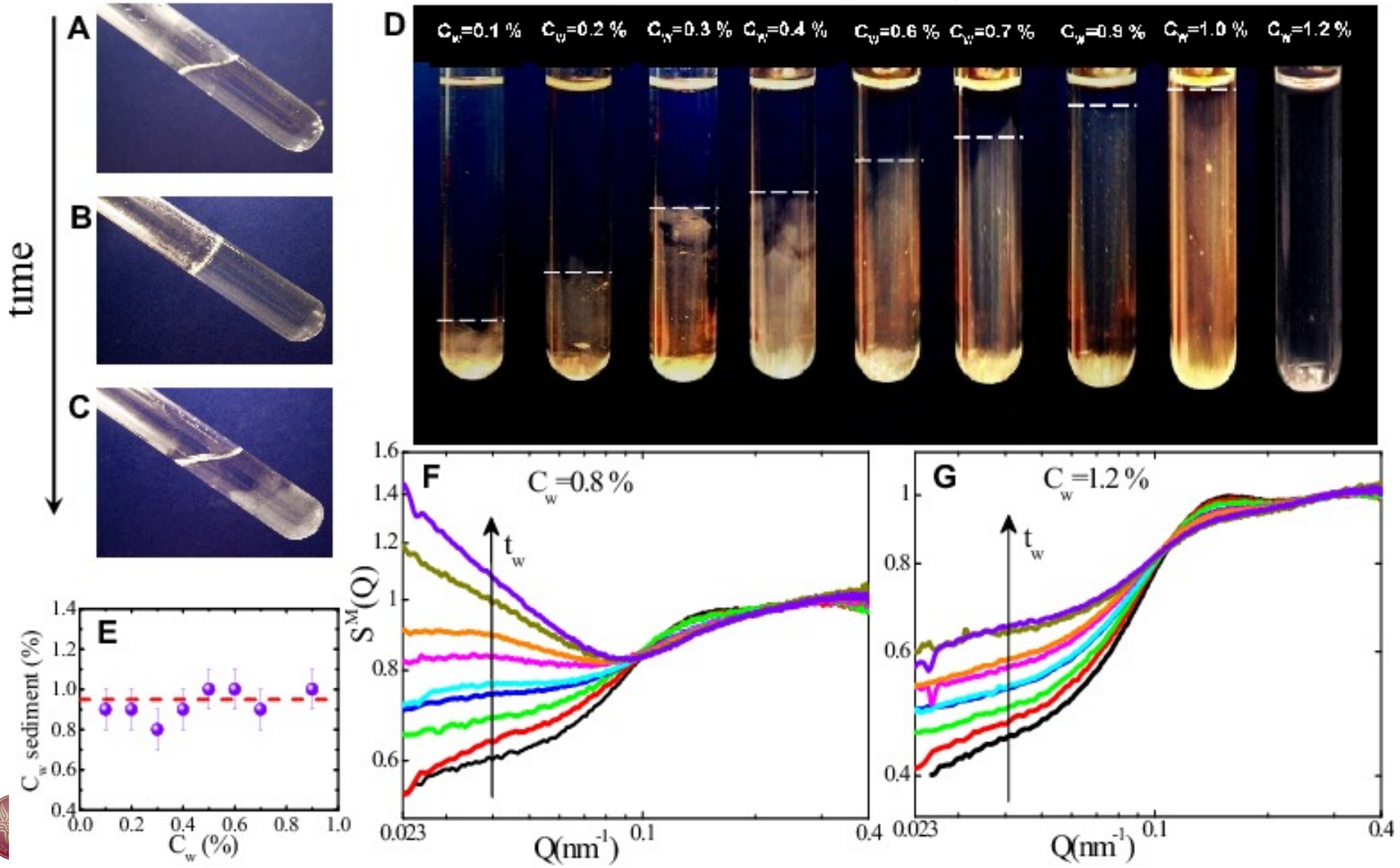
Physical Gels <===> Network forming liquids

nature materials
DOI: 10.1038/NMAT2921 LETTERS
PUBLISHED ONLINE: 12 DECEMBER 2010 | DOI: 10.1038/NMAT2921



Observation of empty liquids and equilibrium gels in a colloidal clay

Barbara Ruzicka[1]*, Emanuela Zaccarelli[2]*, Laura Zulian[3], Roberta Angelini[1], Michael Sztucki[4], Abdellatif Moussaïd[4], Theyencheri Narayanan[4] and Francesco Sciortino[2]



RESEARCH ARTICLES

SCIENCE

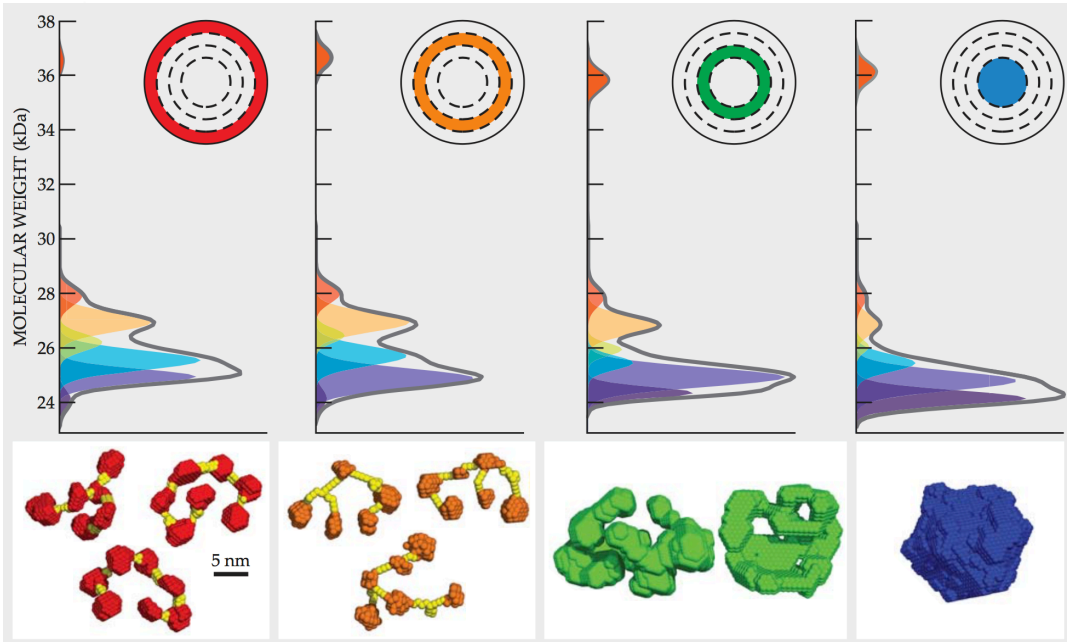
BIOMATERIALS

11 AUGUST 2017 • VOL 357 ISSUE 6351 565

Eye patches: Protein assembly of index-gradient squid lenses

J. Cai,[1] J. P. Townsend,[2] T. C. Dodson,[1] P. A. Heiney,[1] A. M. Sweeney[1]*

A parabolic relationship between lens radius and refractive index allows spherical lenses to avoid spherical aberration. We show that in squid, patchy colloidal physics resulted from an evolutionary radiation of globular S-crystallin proteins. Small-angle x-ray scattering experiments on lens tissue show colloidal gels of S-crystallins at all radial positions. Sparse lens materials form via low-valence linkages between disordered loops protruding from the protein surface. The loops are polydisperse and bind via a set of hydrogen bonds between disordered side chains. Peripheral lens regions with low particle valence form stable, volume-spanning gels at low density, whereas central regions with higher average valence gel at higher densities. The proteins demonstrate an evolved set of linkers for self-assembly of nanoparticles into volumetric materials.



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COLLDENSE COLLOIDS with DESIGNED RESPONSE

ACS central science

ACS AuthorChoice

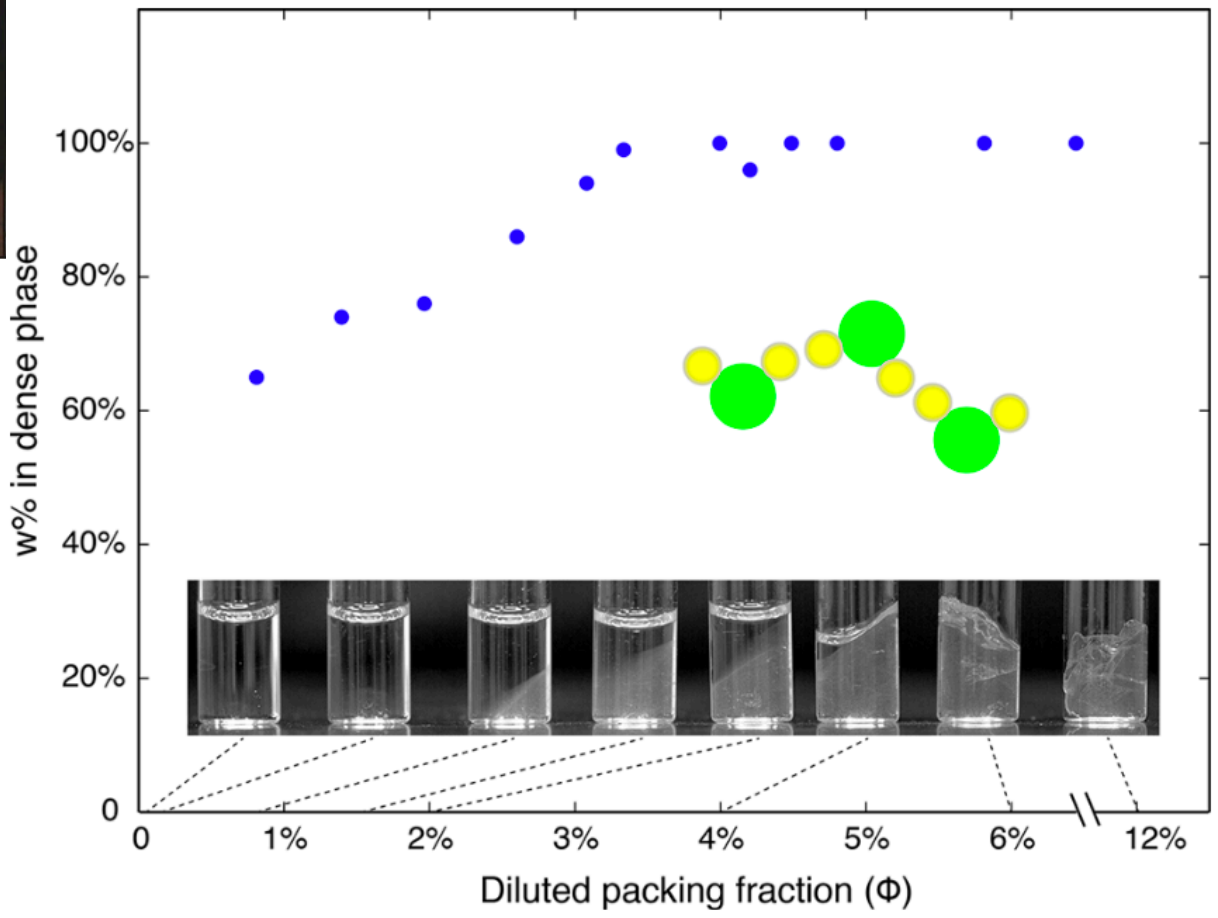
Research Article

Cite This: ACS Cent. Sci. 2018, 4, 840–853

The Proof Is in the *Pidan*: Generalizing Proteins as Patchy Particles

Jing Cai and Alison M. Sweeney*

Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States



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- Limited valence and equilibrium gels
- Liquids more stable than crystals
- Gelling on heating
- Vitrimers (in progress)

Gelling by Heating

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

Scientific Report 3, 2451 (2013)

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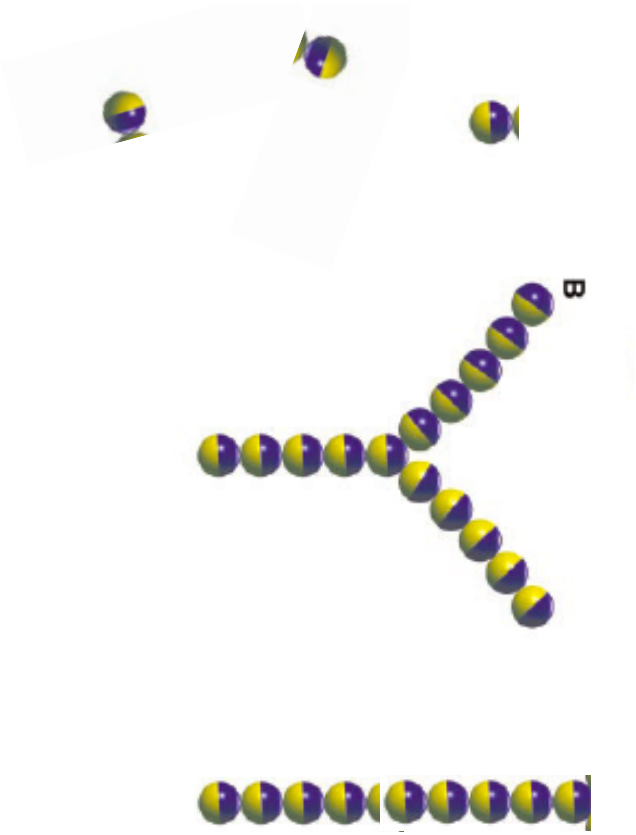
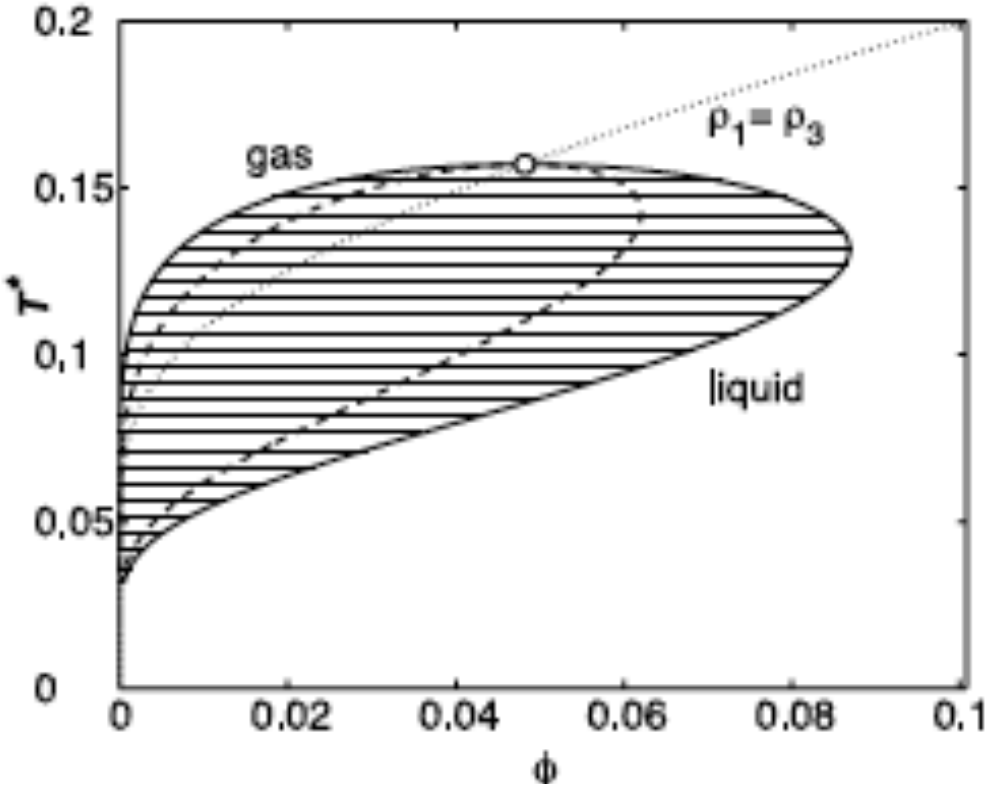
COLLOIDS with DESIGNED RESPONSE

Competing Interactions:

The Dipolar Hard Sphere Case





Tlusty-Safran, Science (2000)

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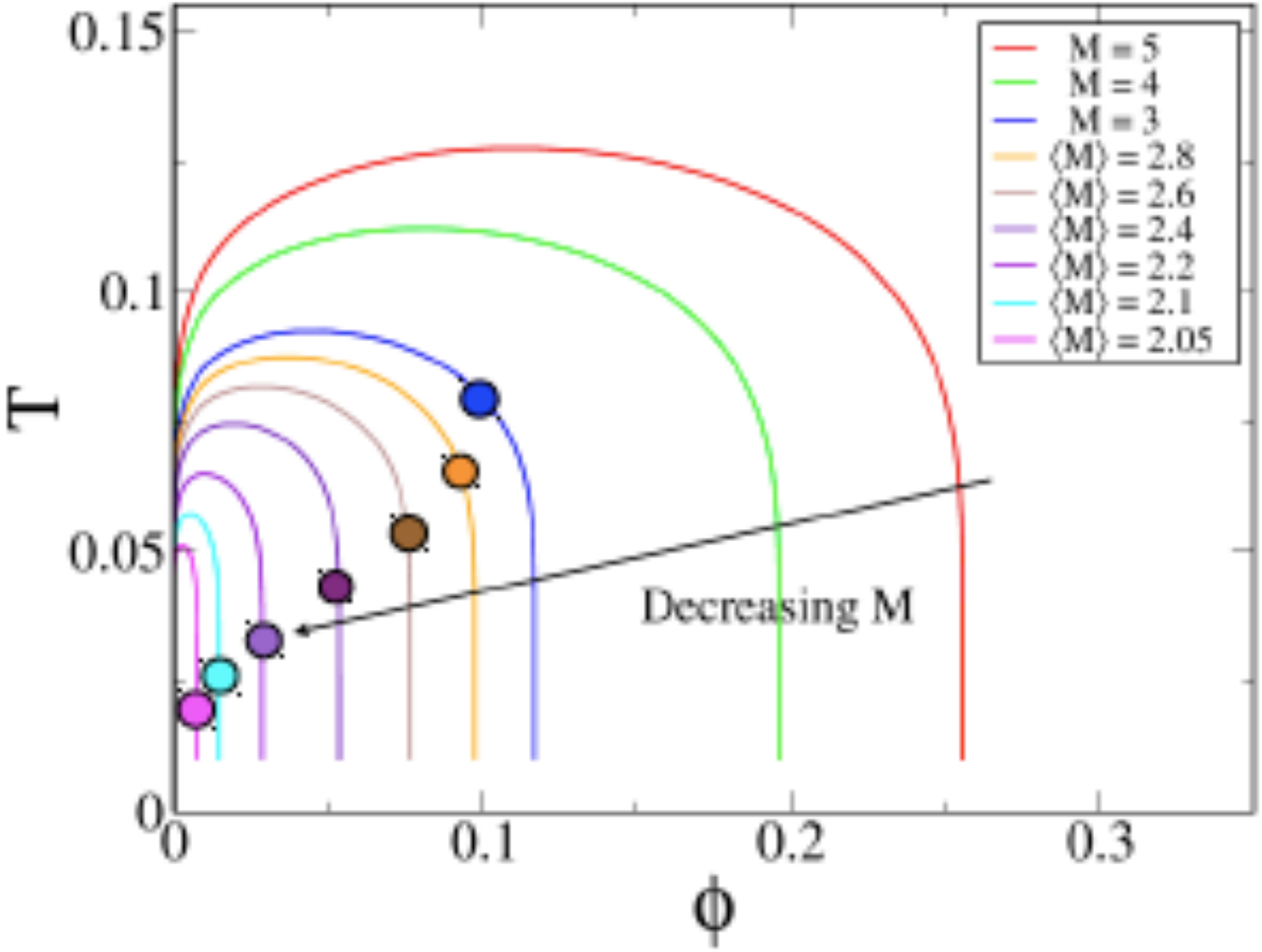
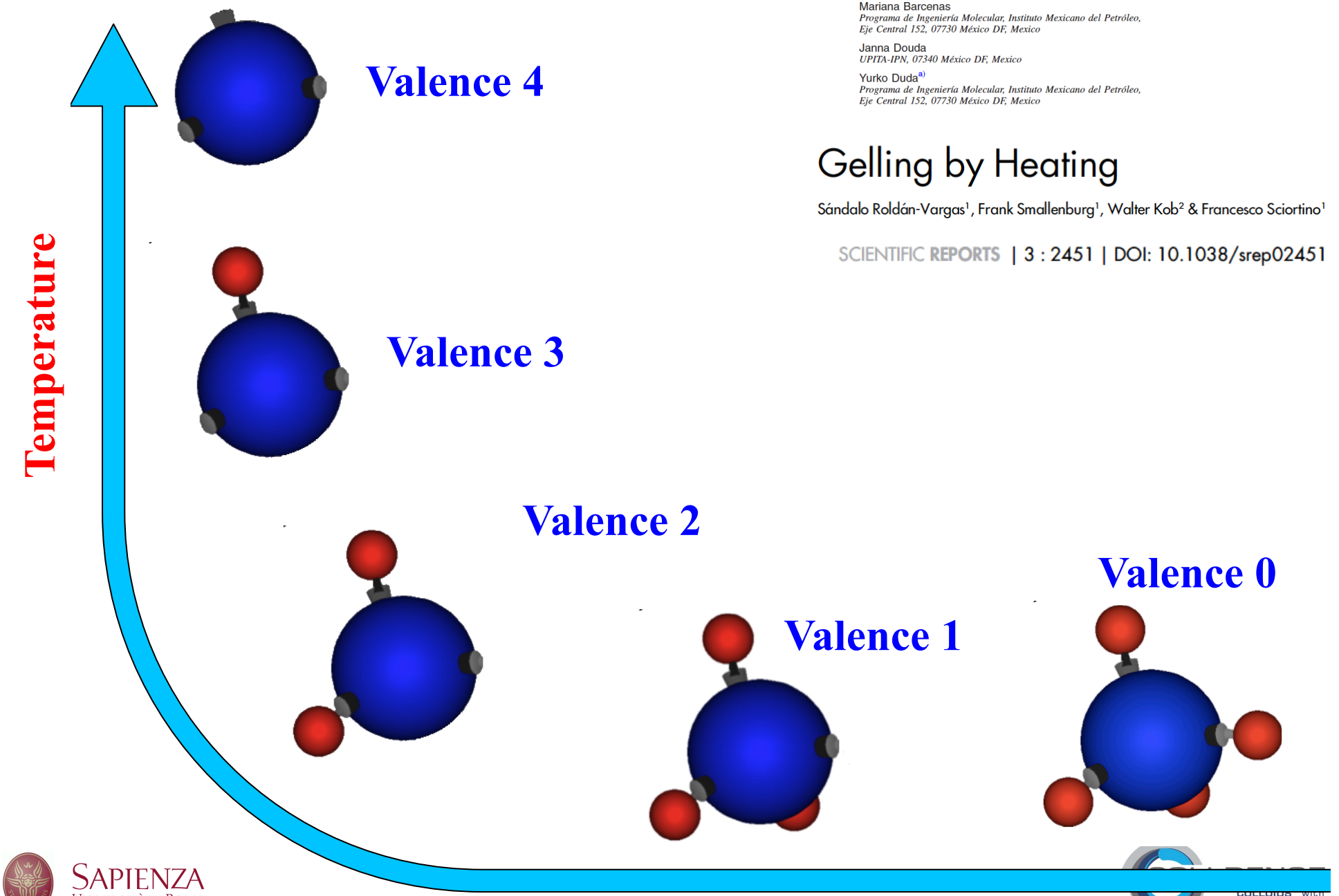
COLLOIDS with DESIGNED RESPONSE

Effective temperature valence



E. Bianchi et al., PRL **97**, 168301 (2006)



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

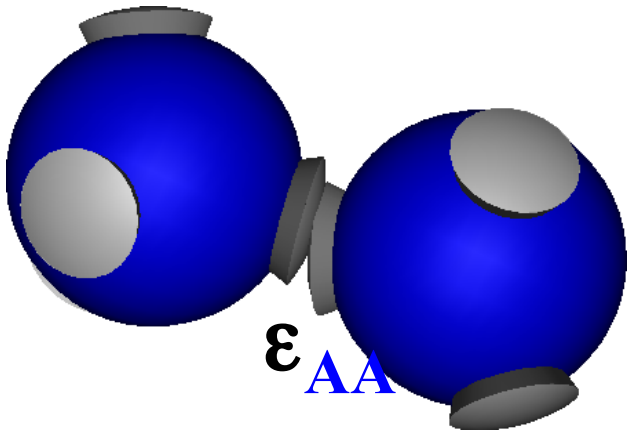
Yurko Duda[a)]
Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central 152, 07730 México DF, Mexico

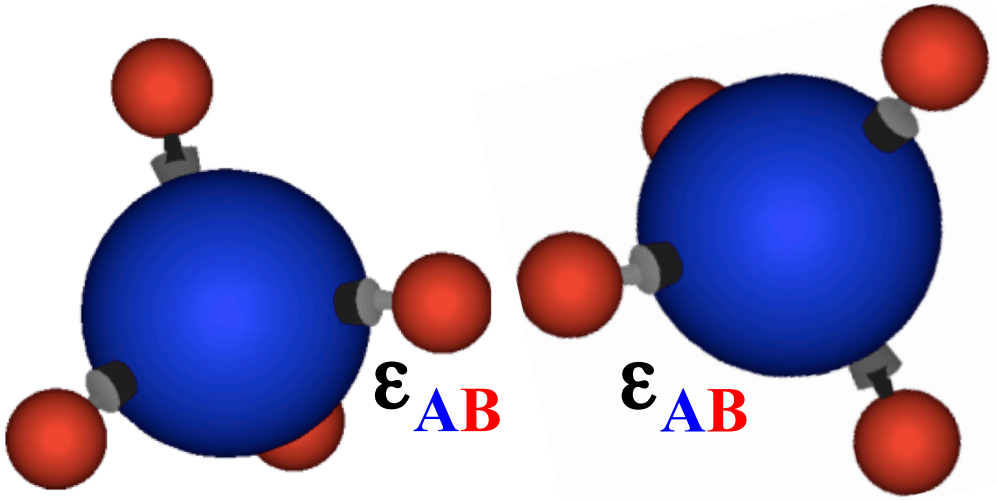
Gelling by Heating

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

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

Selecting the energy: Ground state estimates





Network

Blocked particle

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

$$\varepsilon_{BB}=0 \text{ !!!!}$$

THE JOURNAL OF CHEMICAL PHYSICS 127, 114706 (2007)

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Mariana Barcenas
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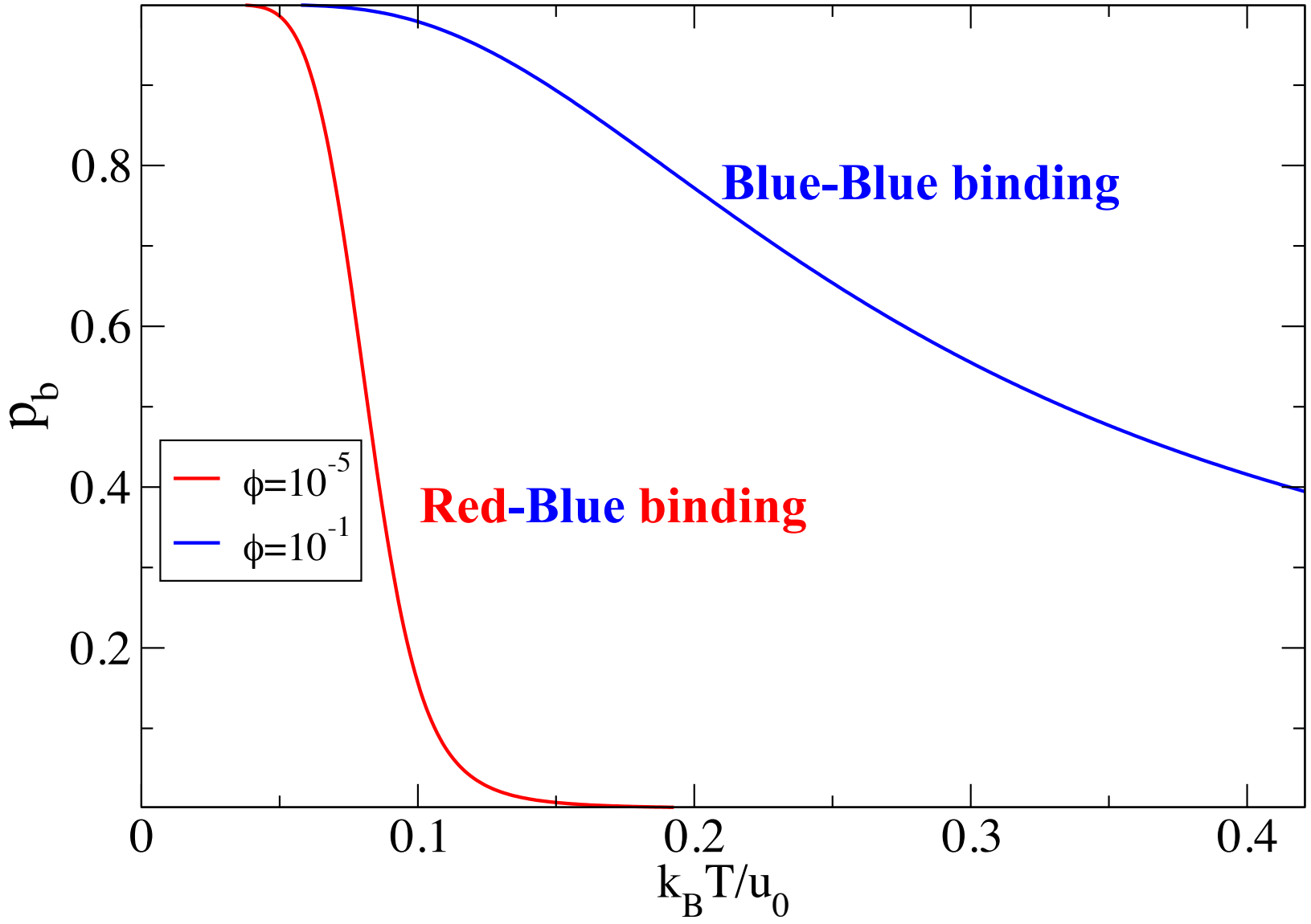
Gelling by Heating

Sándalo Roldán-Varaas[1], Frank Smallenbura[1], Walter Kob[2] & Francesco Sciortino[1]

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

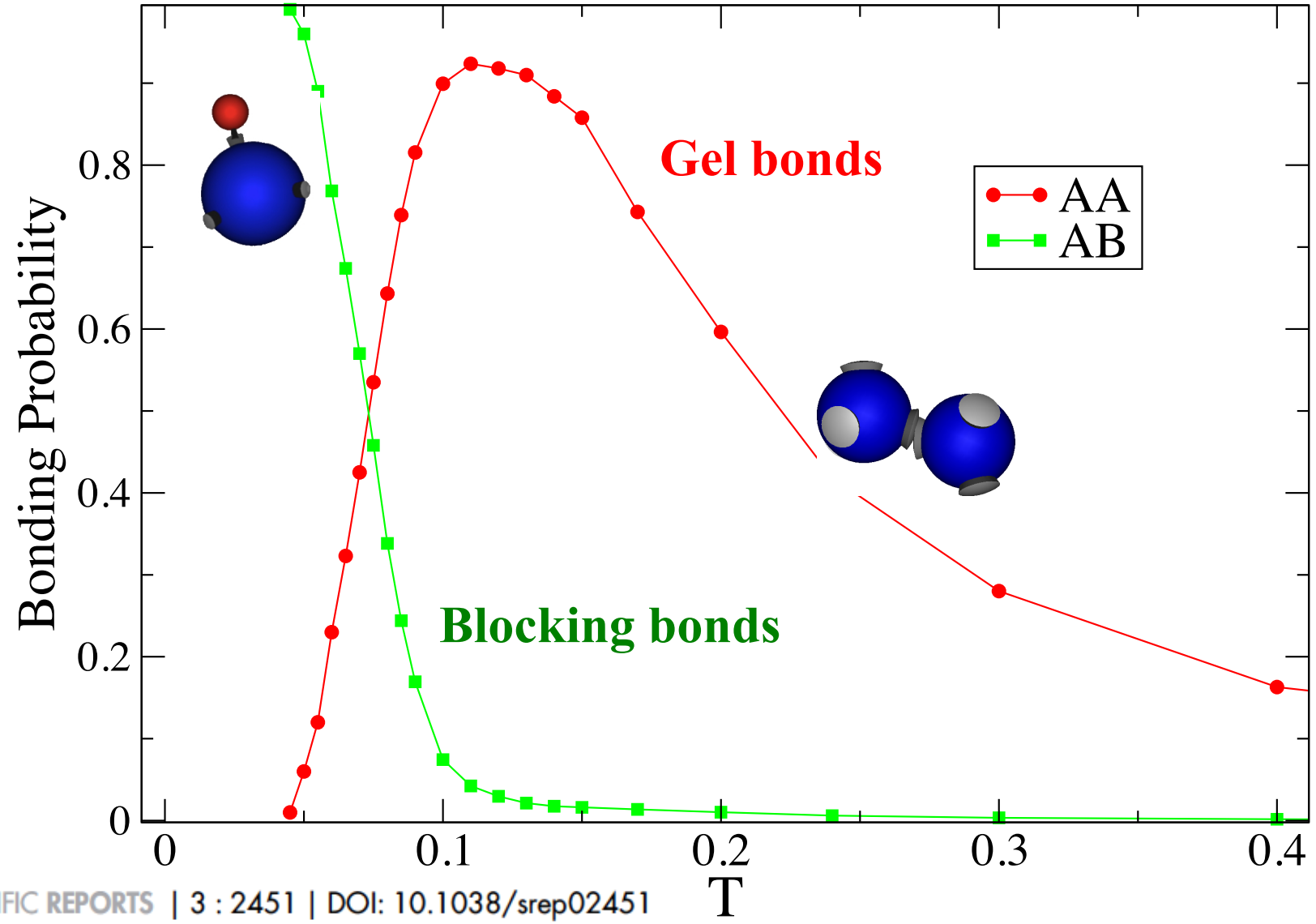
Selecting the entropy:

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



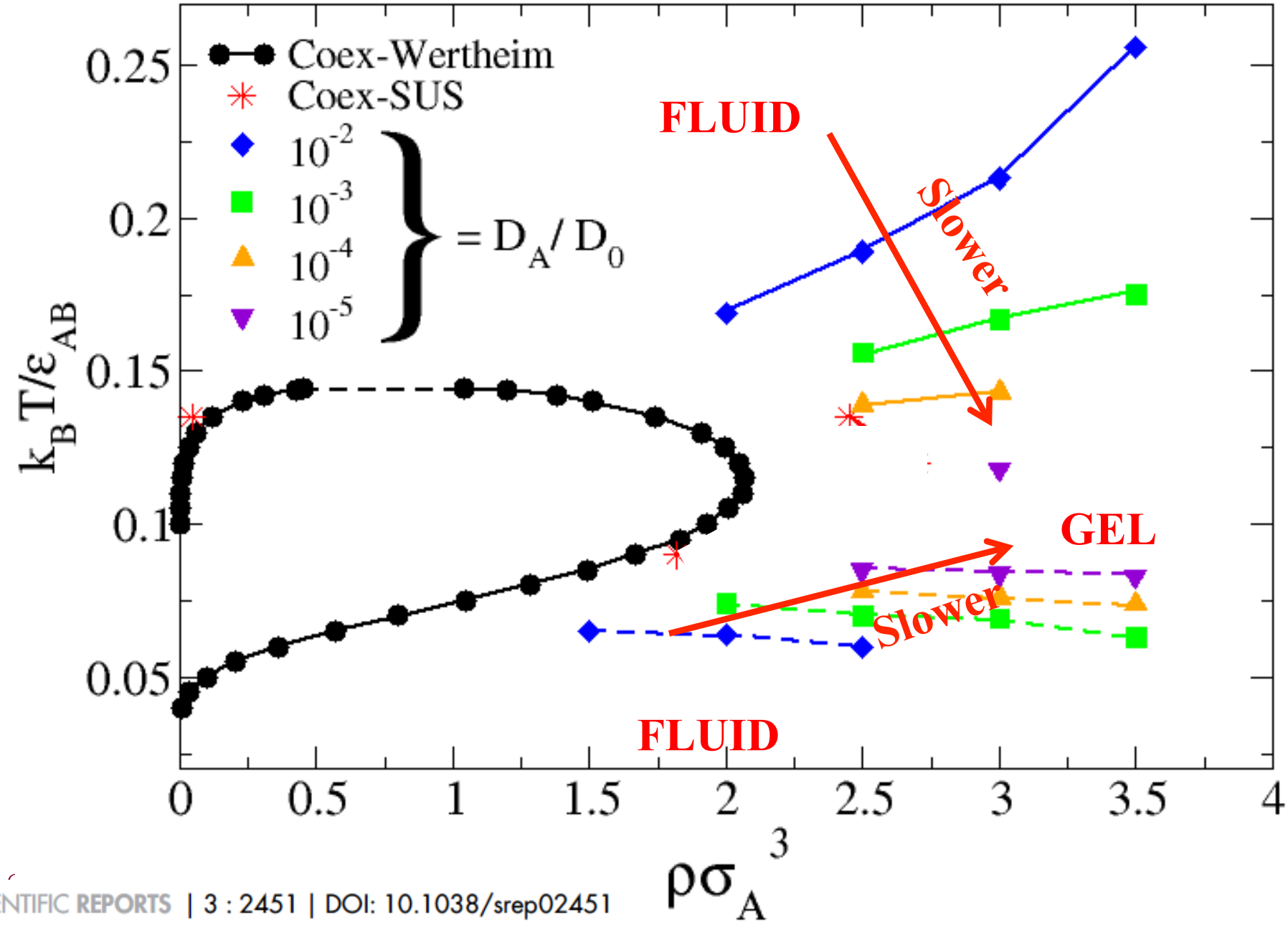
Forming and melting the gel

Wertheim theory

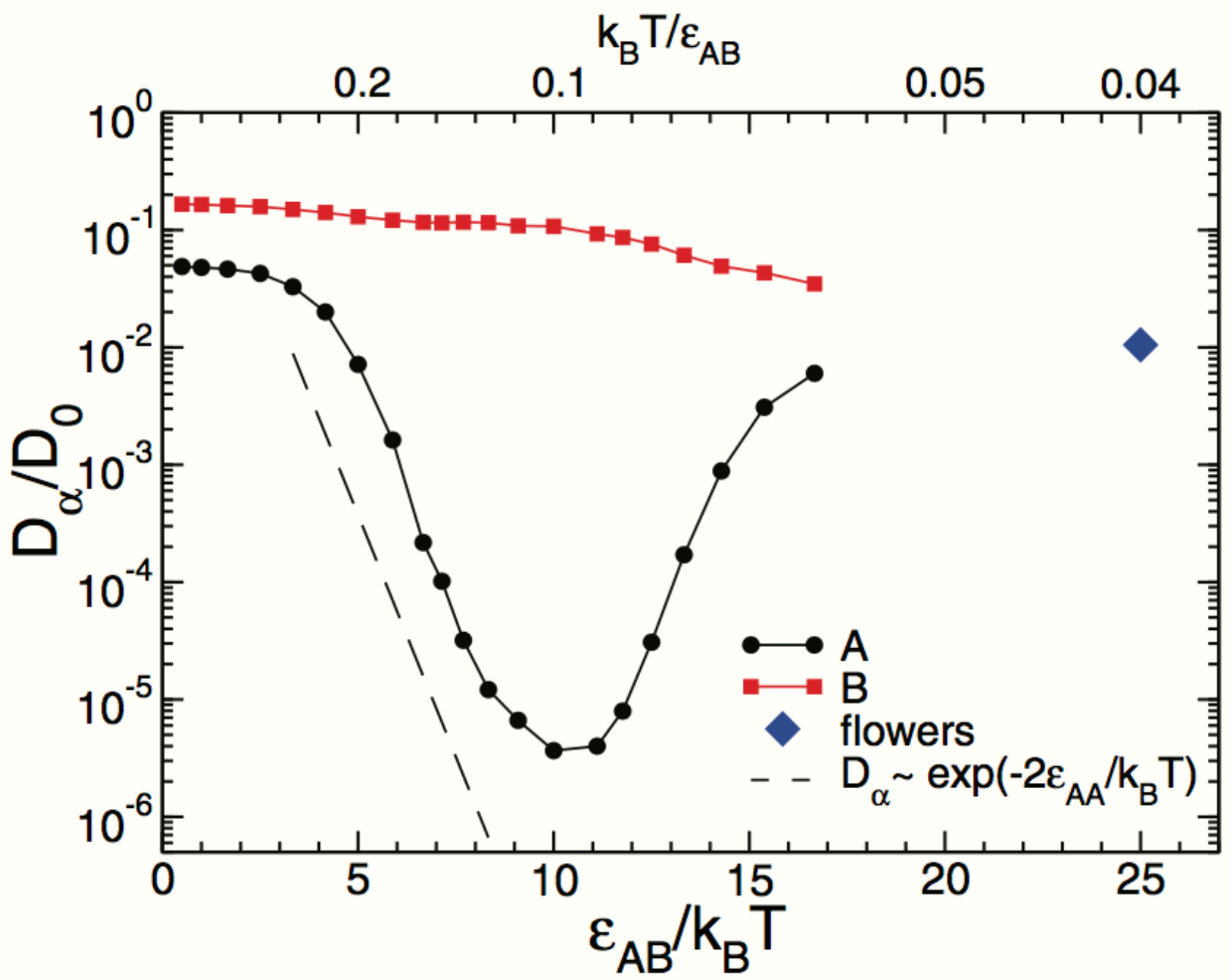


SCIENTIFIC REPORTS | 3 : 2451 | DOI: 10.1038/srep02451

Simulations (stochiometric)



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

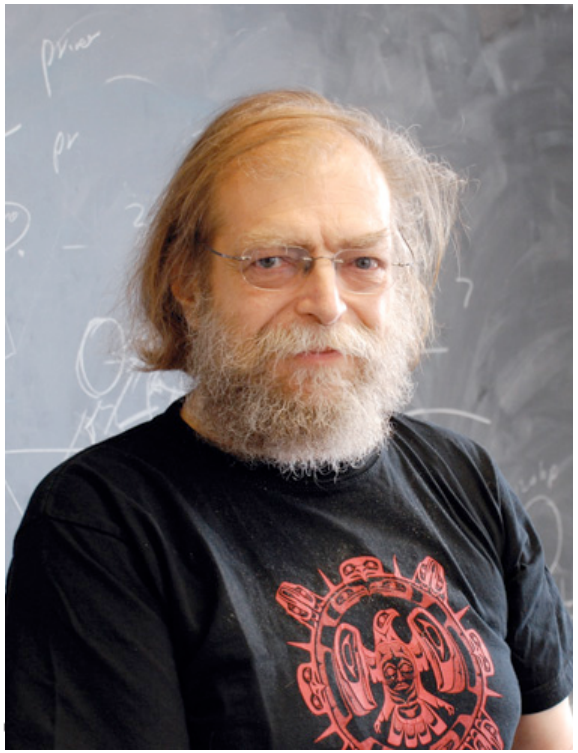

k_BT/ε_{AB}
0.2
0.1
0.05
0.04
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
D_α/D_0
0
5
10
15
20
25
ε_{AB}/k_BT
A
B
flowers
$D_\alpha \sim \exp(-2\varepsilon_{AA}/k_BT)$

Do it with DNA made particles

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.

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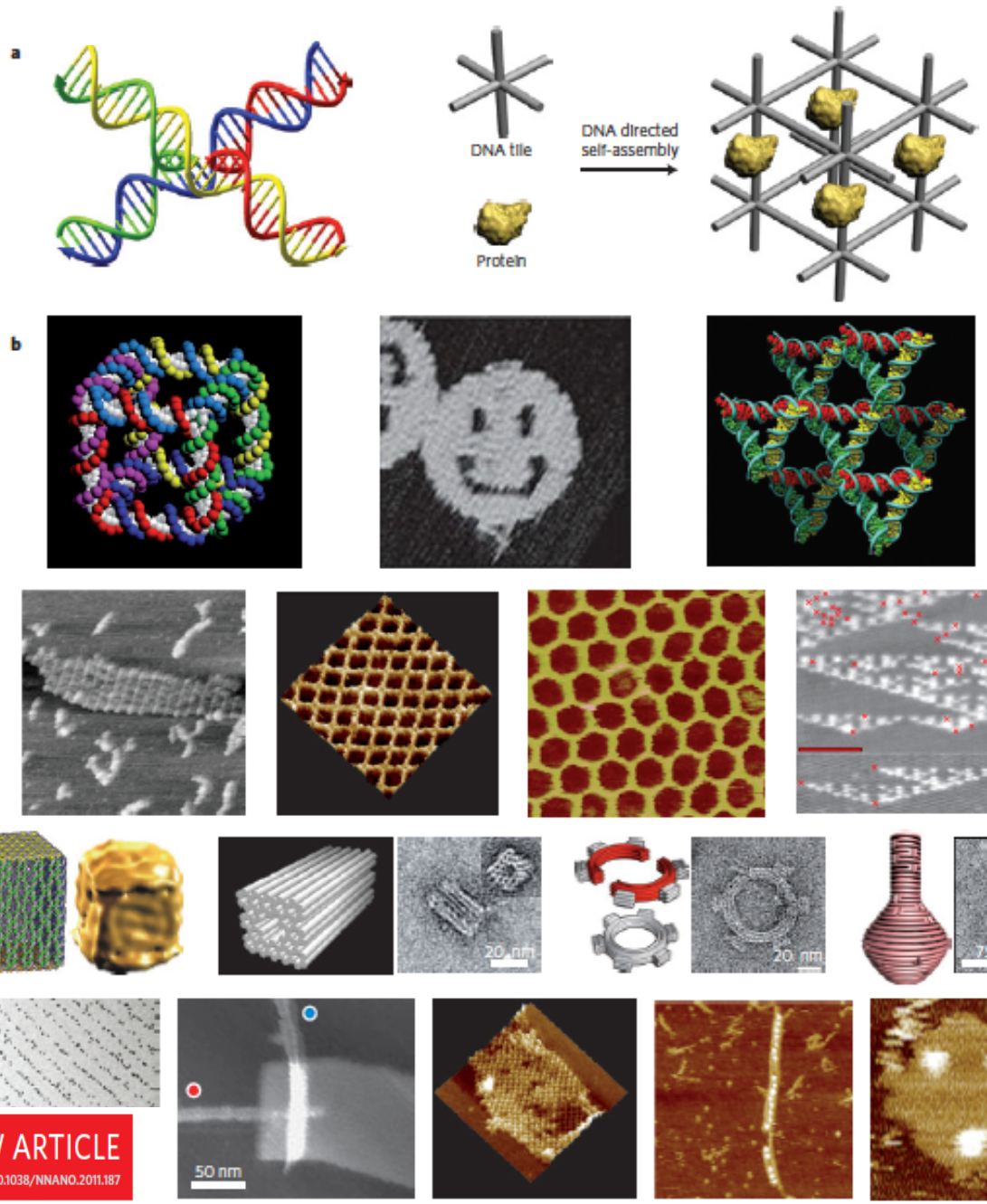
COLLDENSE
COLLOIDS with DESIGNED RESPONSE

Challenges and opportunities for structural DNA nanotechnology

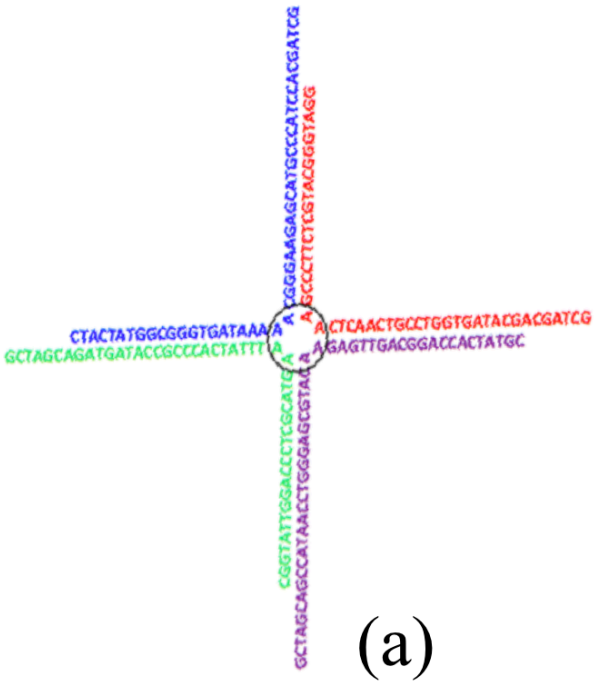
Andre V. Pinheiro[1], Dongran Han[1,2], William M. Shih[3,4,5]* and Hao Yan[1,2]*

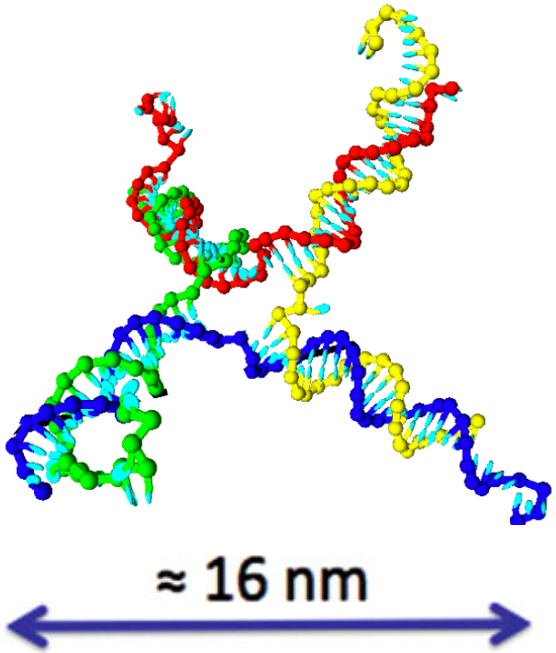
NATURE NANOTECHNOLOGY DOI: 10.1038/NNANO.2011.187

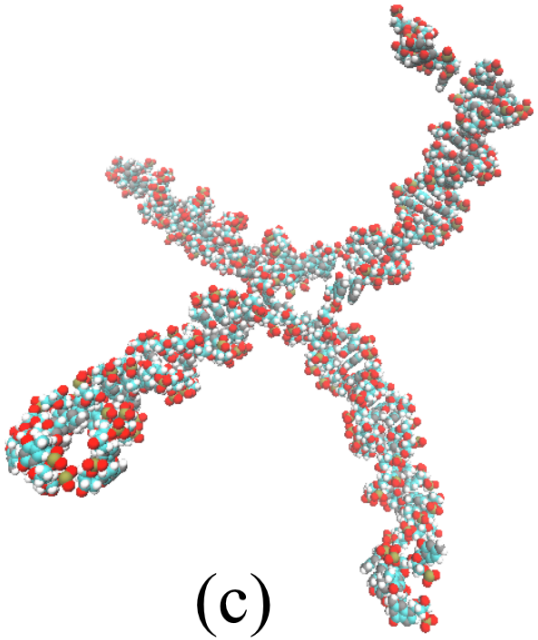


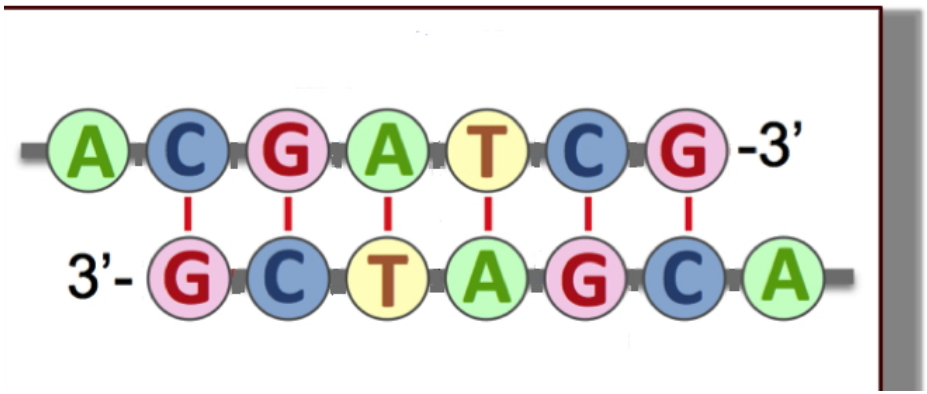
nature nanotechnology
REVIEW ARTICLE
PUBLISHED ONLINE: 6 NOVEMBER 2011 | DOI: 10.1038/NNANO.2011.187

A limited valence colloid: The DNA nanostar



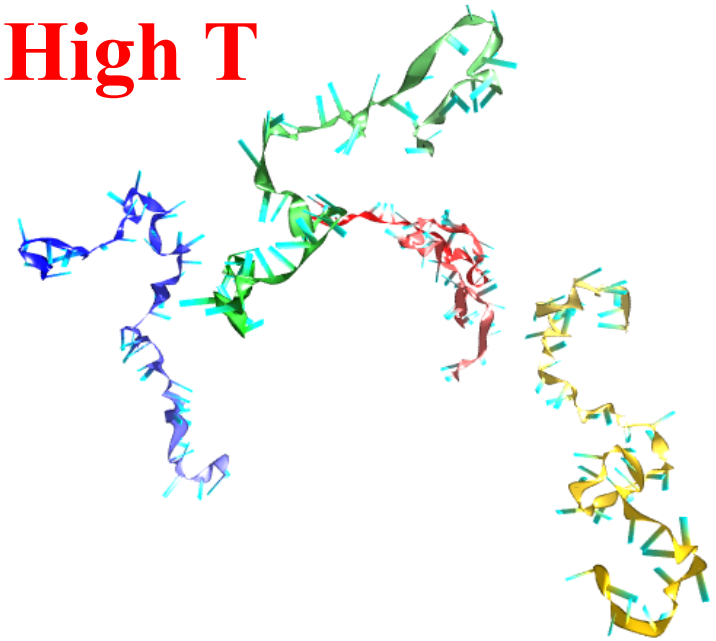




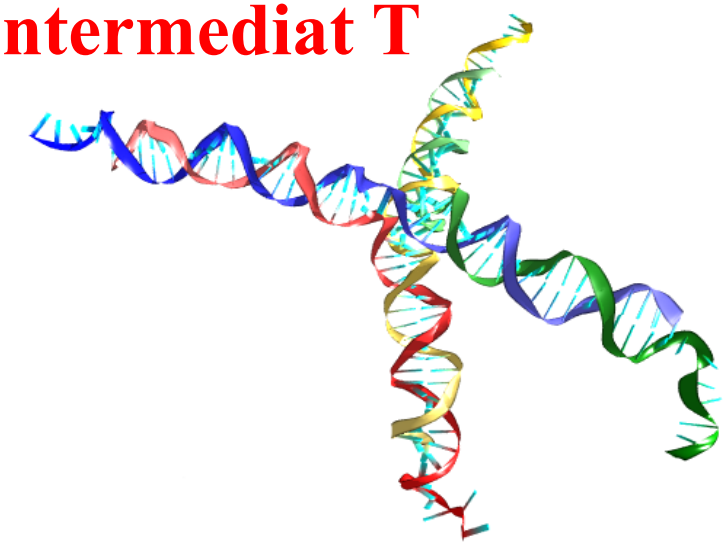


COLLDENSE
COLLOIDS with DESIGNED RESPONSE

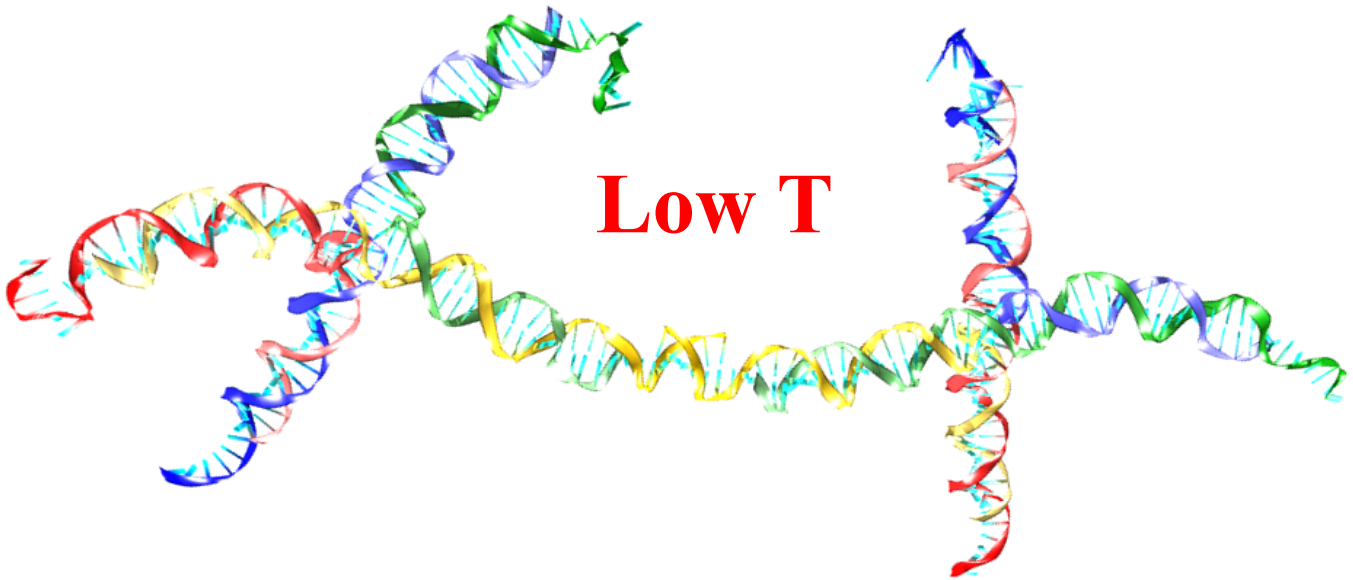
High T



Intermediat T

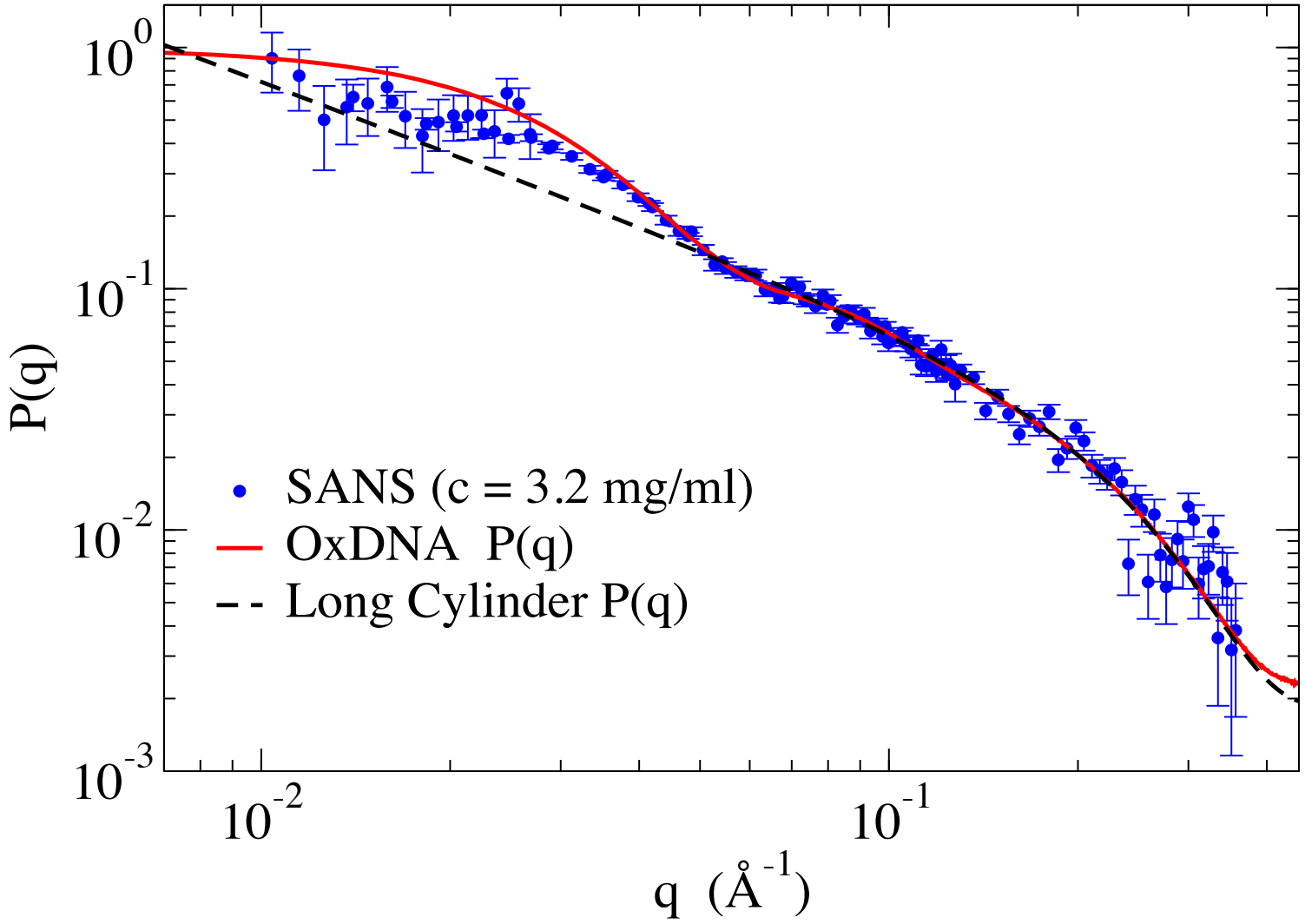


Low T



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

- Limited valence and equilibrium gels
- Gelling on heating
- Swapping gels

Phase behavior of DNA hydrogels

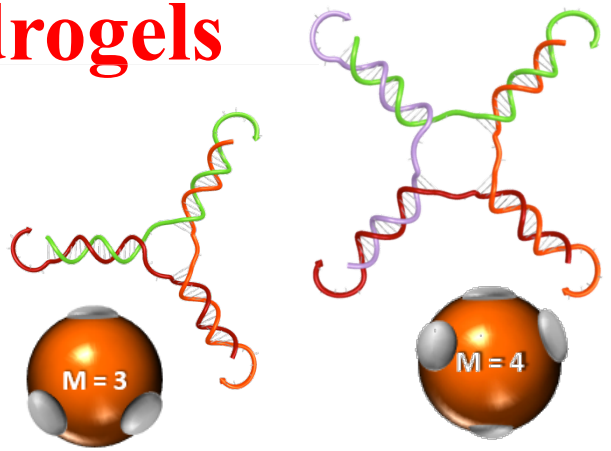
PNAS

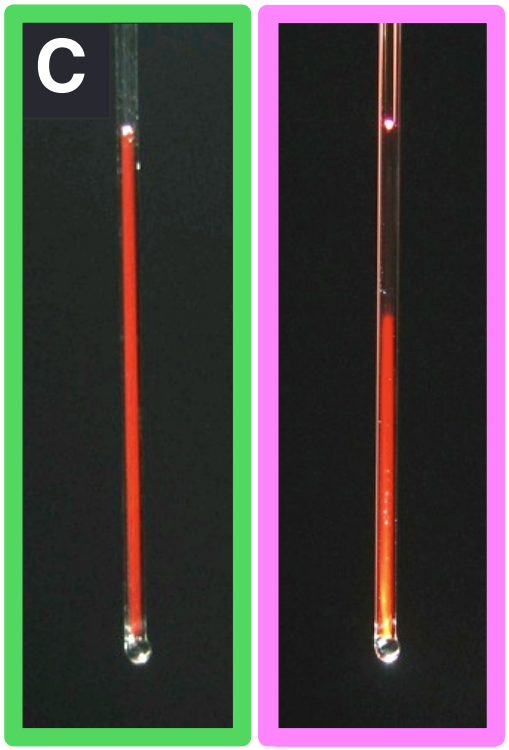
Phase behavior and critical activated dynamics of limited-valence DNA nanostars

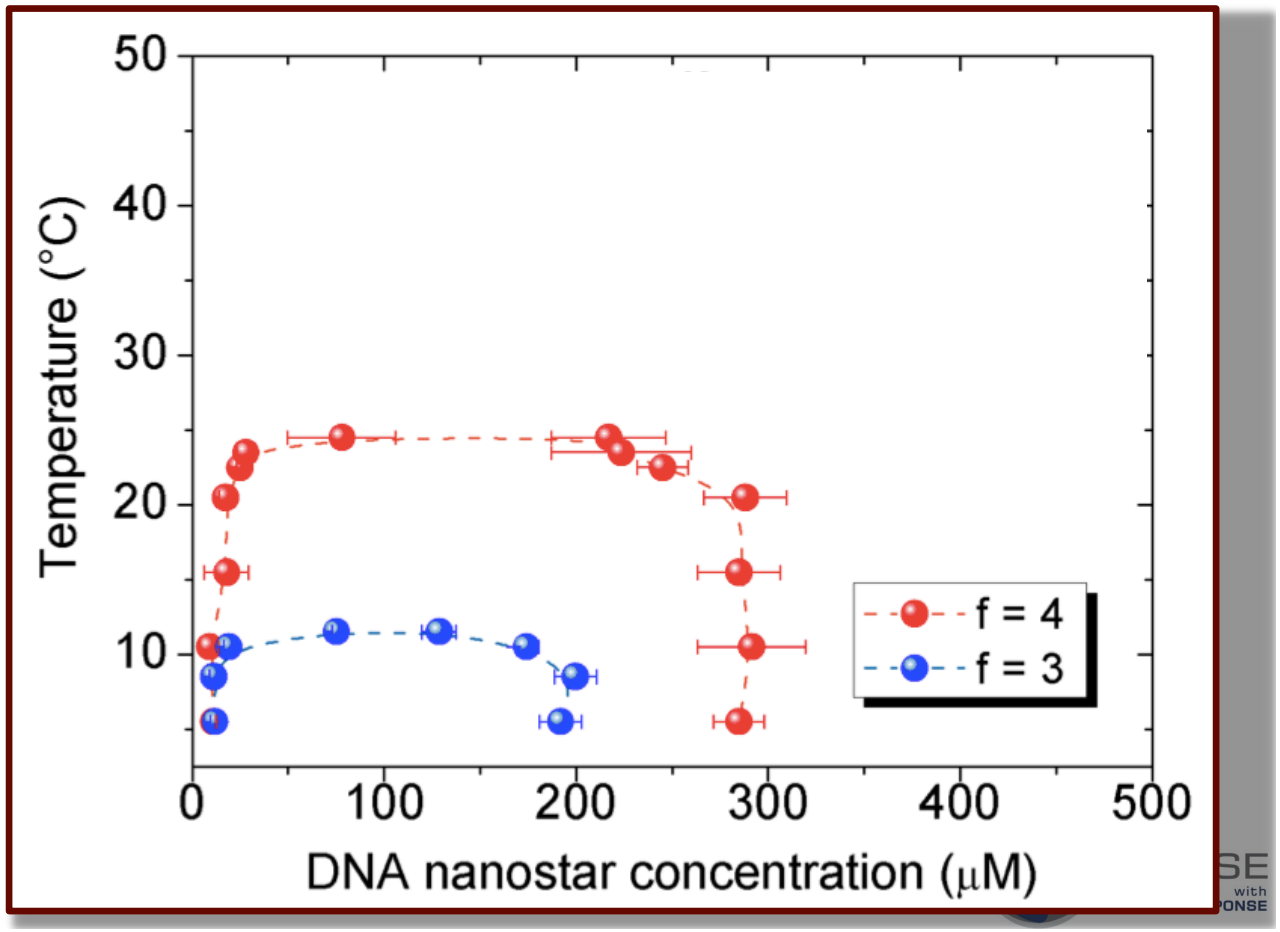
Silvia Biffi[a], Roberto Cerbino[a], Francesca Bomboi[b,c], Elvezia Maria Paraboschi[a], Rosanna Asselta[a], Francesco Sciortino[b,1], and Tommaso Bellini[a,1]

[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

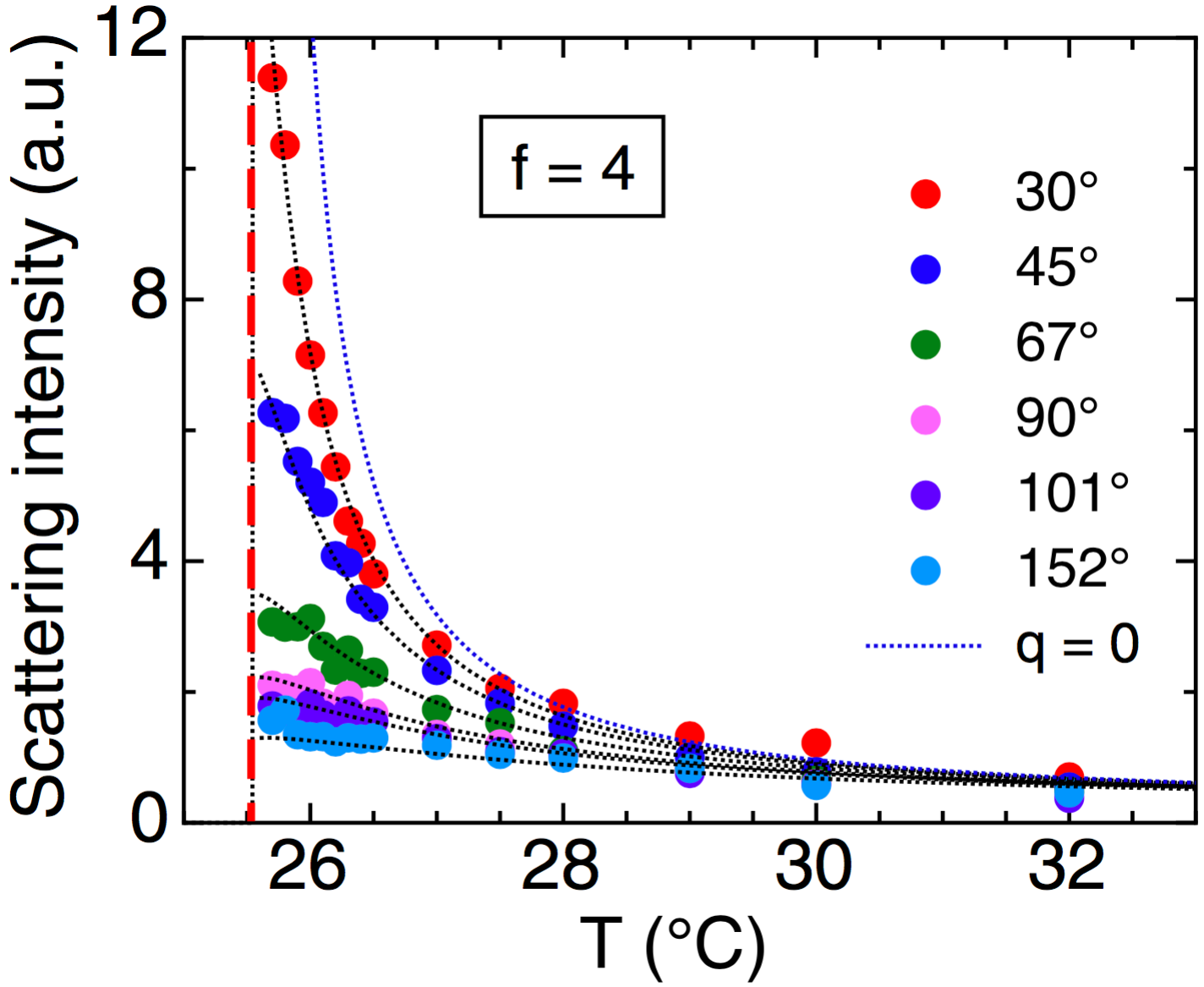
Edited by T. C. Lubensky, University of Pennsylvania, Philadelphia, PA, and approved August 6, 2013 (received for review March 14, 2013)





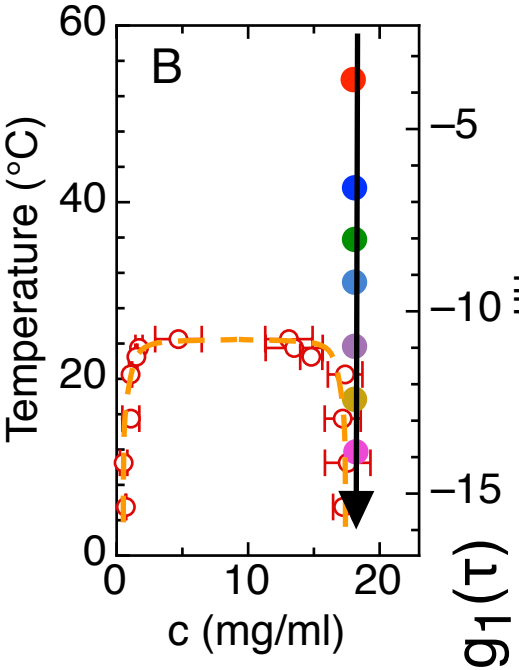


Critical Scattering



Dynamics of the DNA gel: Photon Correlation Spectroscopy

A truly equilibrium gel !



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

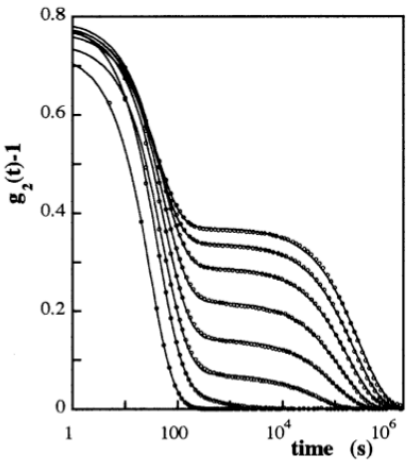
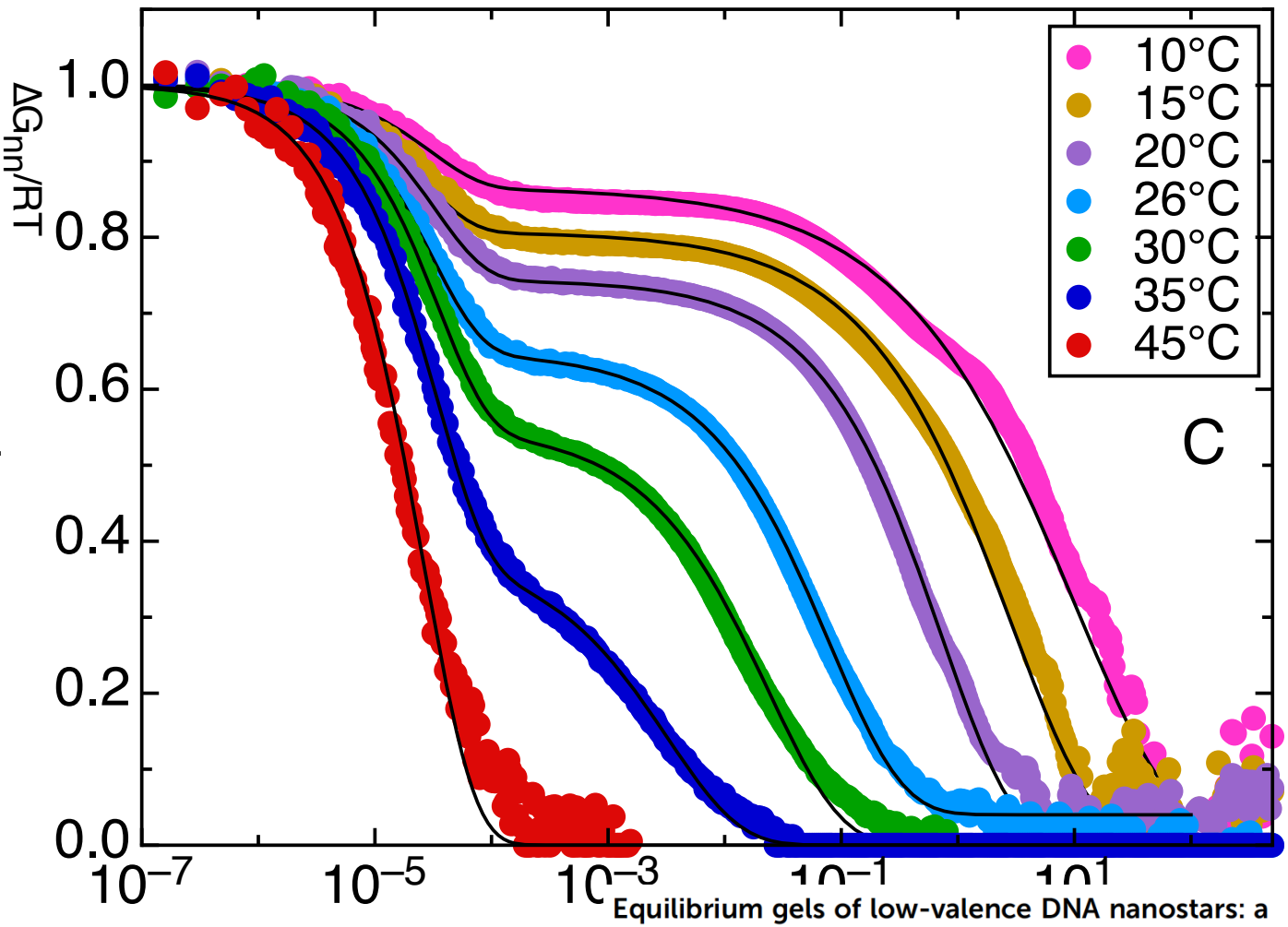


Figure 11. Normalized intensity autocorrelation curves measured at $\theta = 90°$ ($q = 2.3 \times 10^{-3}$ Å^{-1}) for samples with $\Phi = 12.4\%$ and $r = 0, 3, 6, 9, 12, 15, 18$, and 21 for the curves

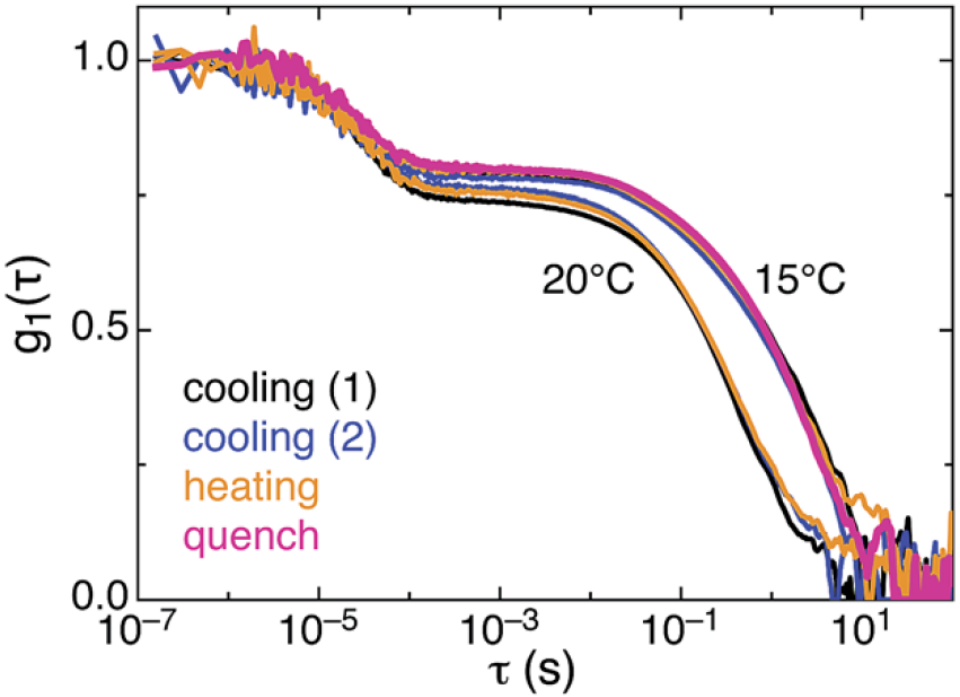


Equilibrium gels of low-valence DNA nanostars: a colloidal model for strong glass formers†

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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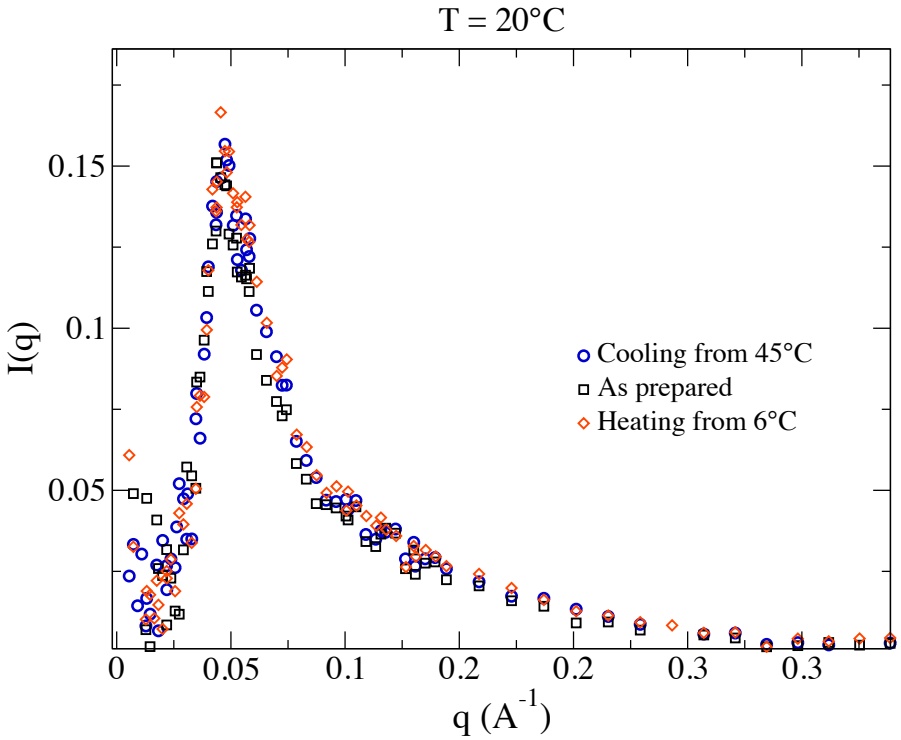
Neutrons



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

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

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)]

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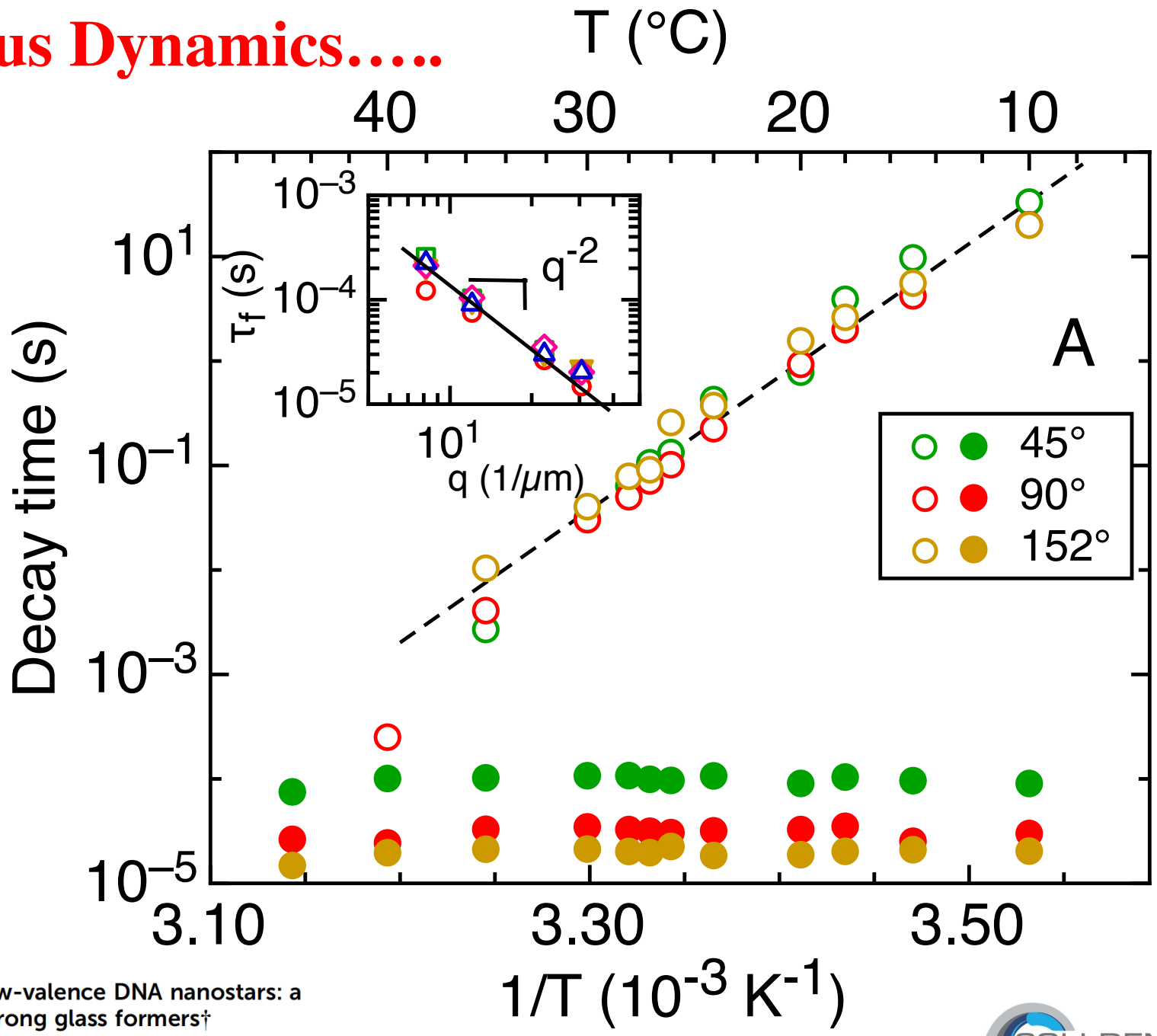
COLLDENSE COLLOIDS with DESIGNED RESPONSE

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]

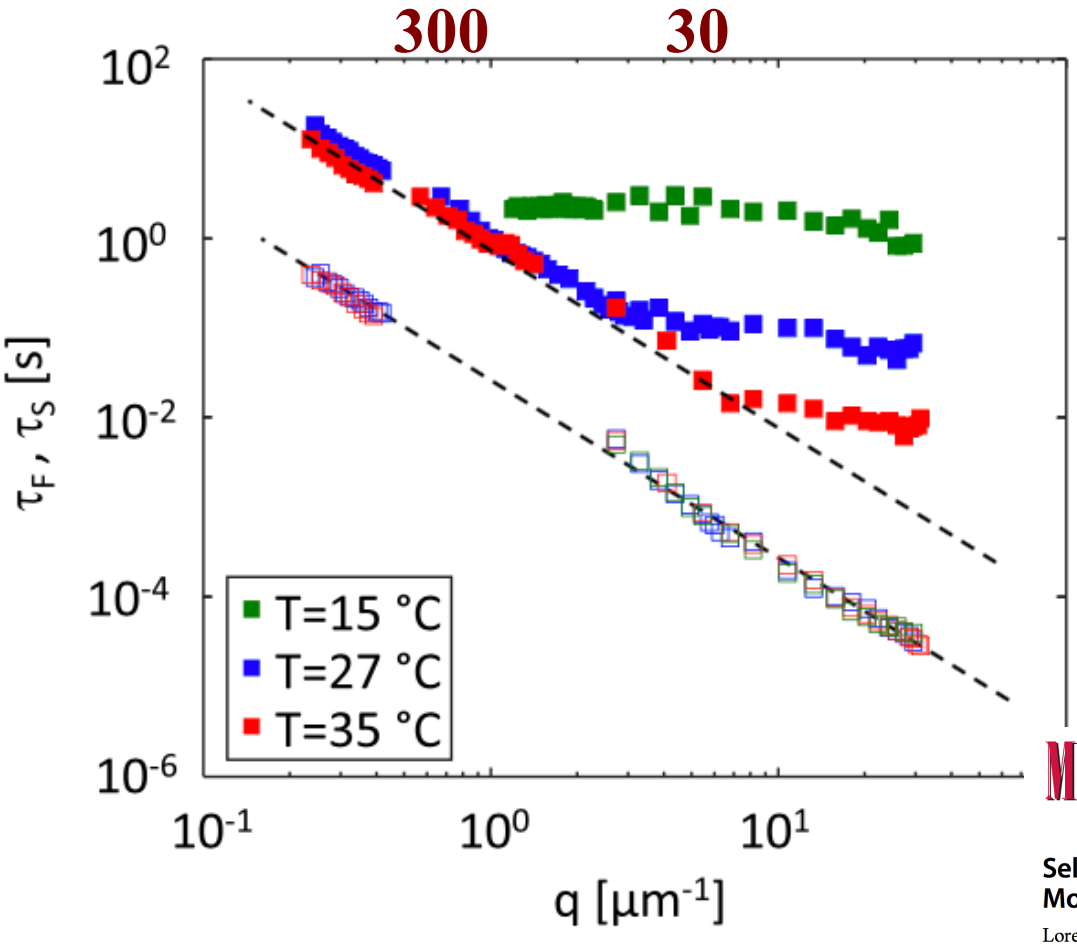
COLLDENSE
COLLOIDS with DESIGNED RESPONSE

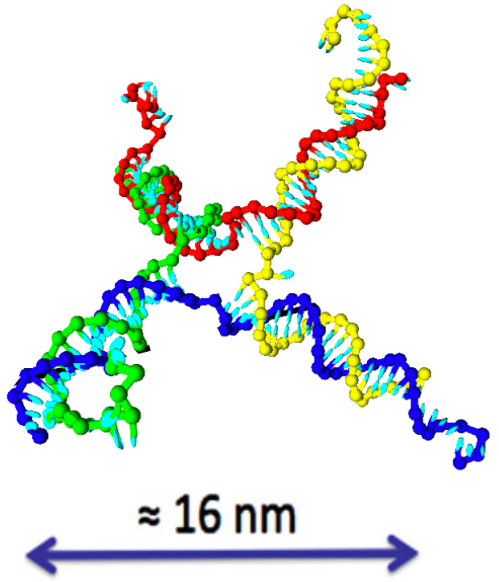
An unexpected feature: a q^0 mode

PRL 119, 078002 (2017) PHYSICAL REVIEW LETTERS week ending 18 AUGUST 2017

Fluctuating Elasticity Mode in Transient Molecular Networks

Giovanni Nava,[1] Marina Rossi,[1] Silvia Biffi,[1] Francesco Sciortino,[2] and Tommaso Bellini[1,*]
[1]Department of Medical Biotechnology and Translational Medicine, Università degli Studi di Milano, via Fratelli Cervi 93, I-20090 Segrate, Milano, Italy
[2]Department of Physics and CNR-ISC, Sapienza Università di Roma, Piazzale Aldo Moro 2, I-00185 Roma, Italy
(Received 19 April 2017; published 16 August 2017)





Macromolecules Article
Cite This: Macromolecules 2018, 51, 1232–1241

Self-Dynamics and Collective Swap-Driven Dynamics in a Particle Model for Vitrimers

Lorenzo Rovigatti,*[,†,‡] Giovanni Nava,[§] Tommaso Bellini,[§] and Francesco Sciortino[‡]

Water (TIP4P-2005)

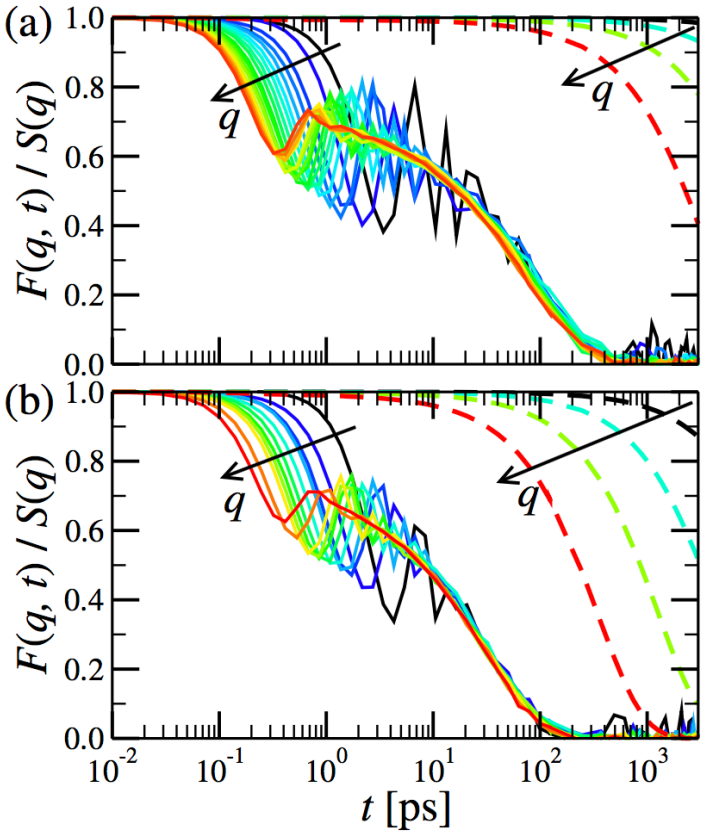


FIG. 1. Decay of the (full lines) collective and (dashed lines) self density fluctuations at (a) $T = 240$ K $\rho = 0.9$ g/cm^3 and (b) $T = 250$ K $\rho = 1.0$ g/cm^3. In both panels q varies between 0.3 (black lines) and 3.0 (red lines) nm^{-1}.

Silica (BKS)

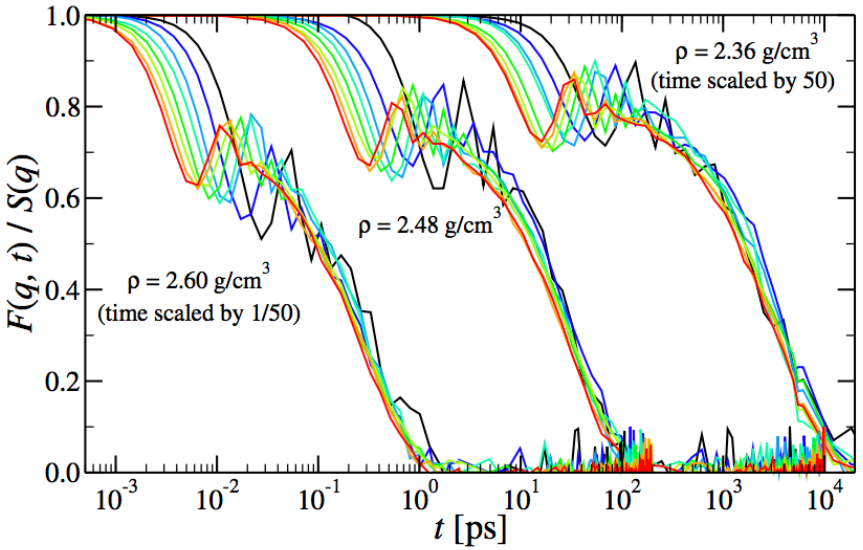
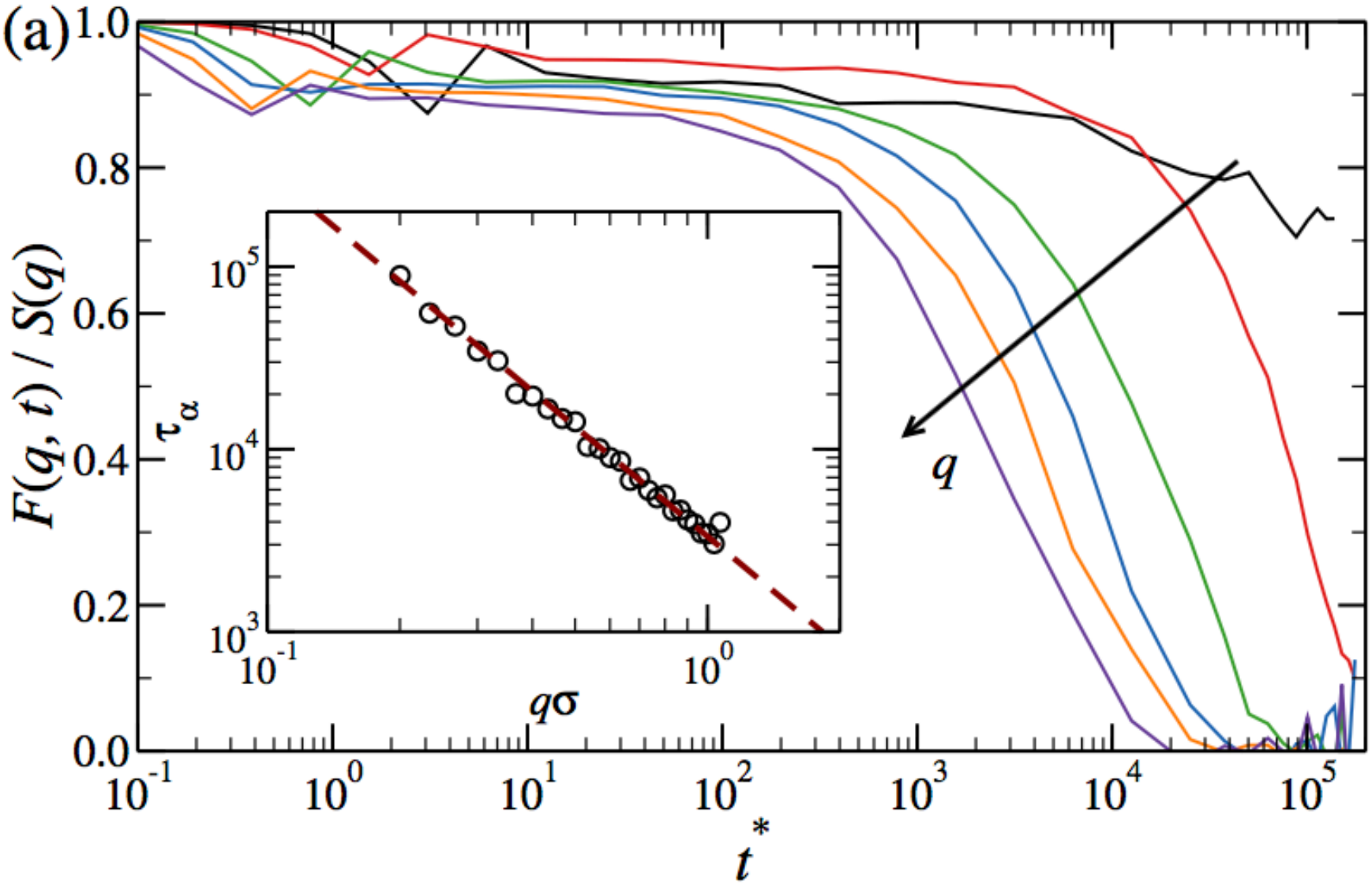


FIG. 3. Decay of the collective number density fluctuations in BKS silica at $T = 3500$ K for different densities. In all plots, $0.4 < q < 2$ nm^{-1} (from black to red). Note that, for the sake of clarity, the time associated to the $\rho = 2.60$ g/cm^3 and $\rho = 2.63$ g/cm^3 data has been multiplied by a factor 1/50 and 50, respectively. As a reference, the Si-Si distance is ≈ 0.31 nm.

Our beloved Kob-Anderson



Philip H. Handle, Lorenzo Rovigatti and FS unpublished

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

- Limited valence and equilibrium gels
- Liquids more stable than crystals
- Gelling on heating
- Swapping gels

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

DNA nanostars:

Highly flexible patchy particles

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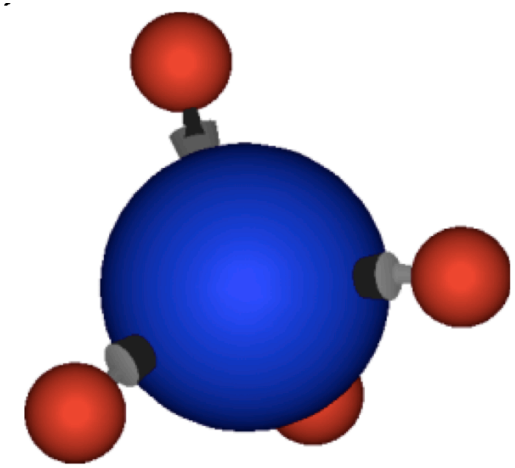
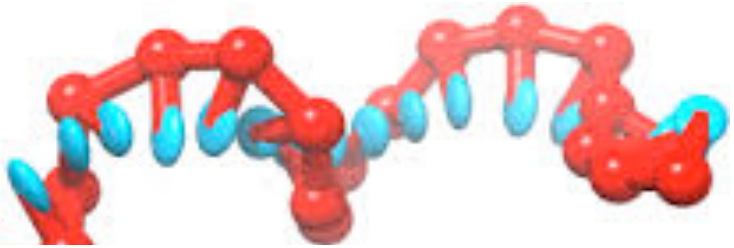
COLLDENSE COLLOIDS with DESIGNED RESPONSE

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

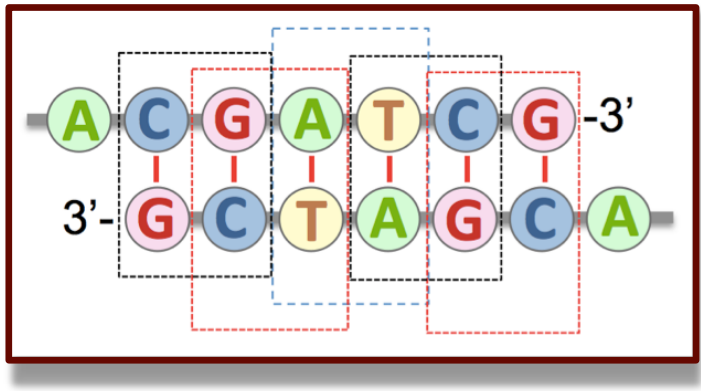
- Limited valence and equilibrium gels
- Liquids more stable than crystals
- Gelling on heating
- Swapping gels

The competitor….. (B particle)





("palindromic")



Two serious problems to solve:

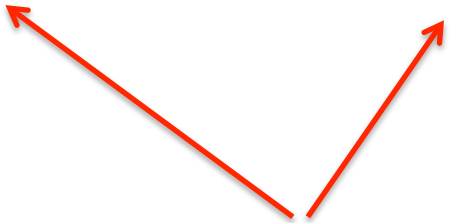
1) **How to avoid BB pairing ?**
2) **How to increase the entropy cost of bonding ?**

The proposed solution:

AA bonding

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

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



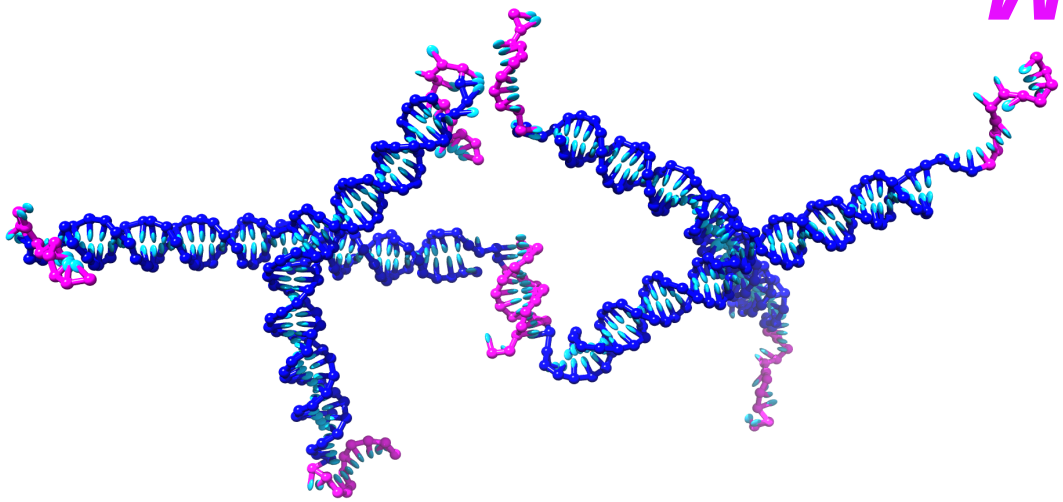
B- particle (competitor)

The proposed solution:

AA-bonding: 8 bases paired

STAR-ARM-3’(TGA)GCGTACGC(AAT)-5’

5’-(AAT)CGCATGCG(AGT)-3’-*MRA-RATS*

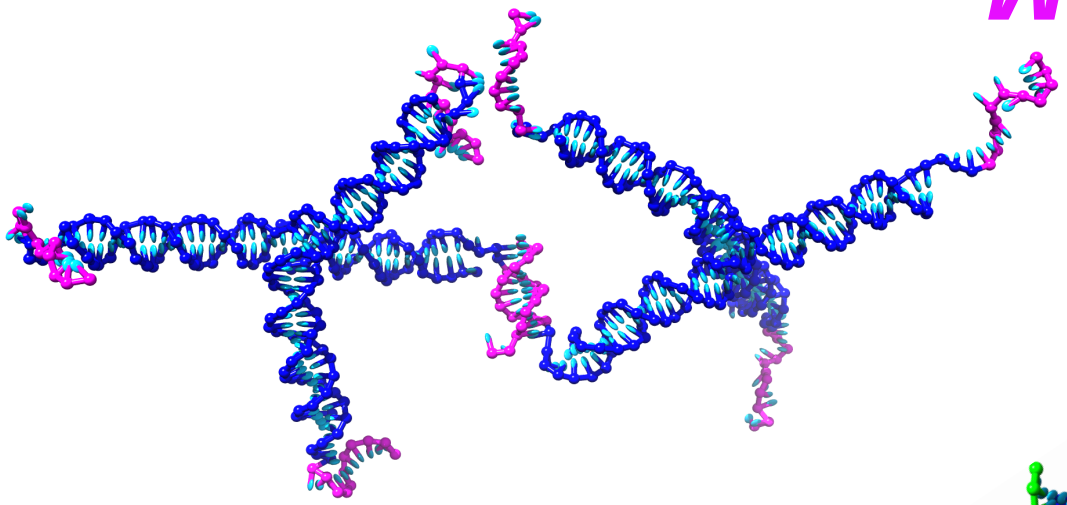


The proposed solution:

AA-bonding: 8 bases paired

STAR-ARM-3’(TGA)GCGTACGC(AAT)-5’

STAR-ARM-3’(TGA)GCGTACGC(AAT)-5’

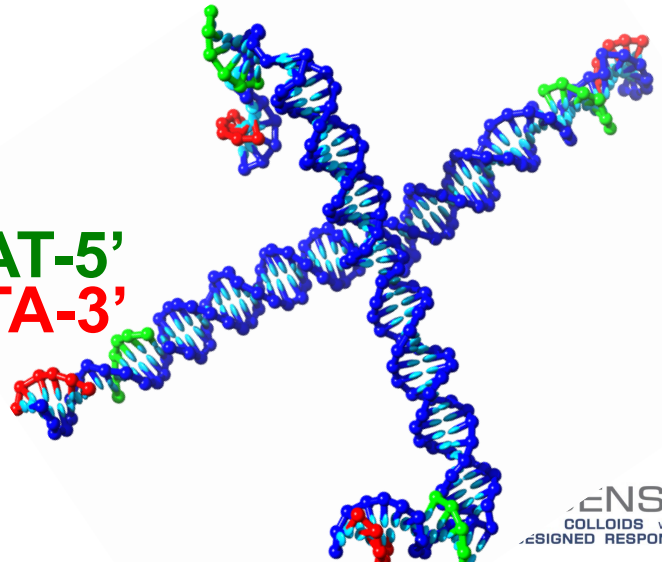


AB-bonding: 12 bases paired

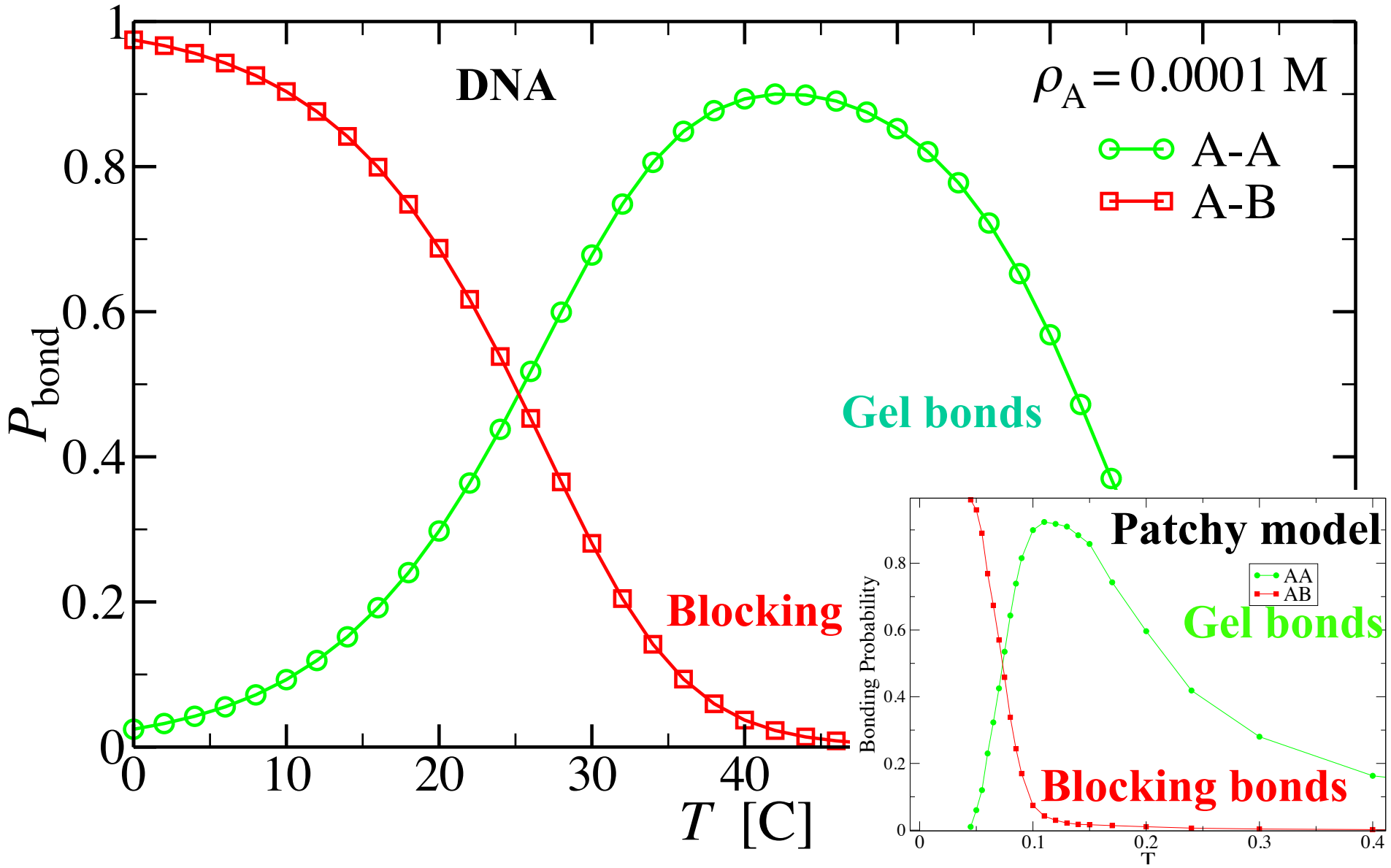
5’-ACTCGC-3’

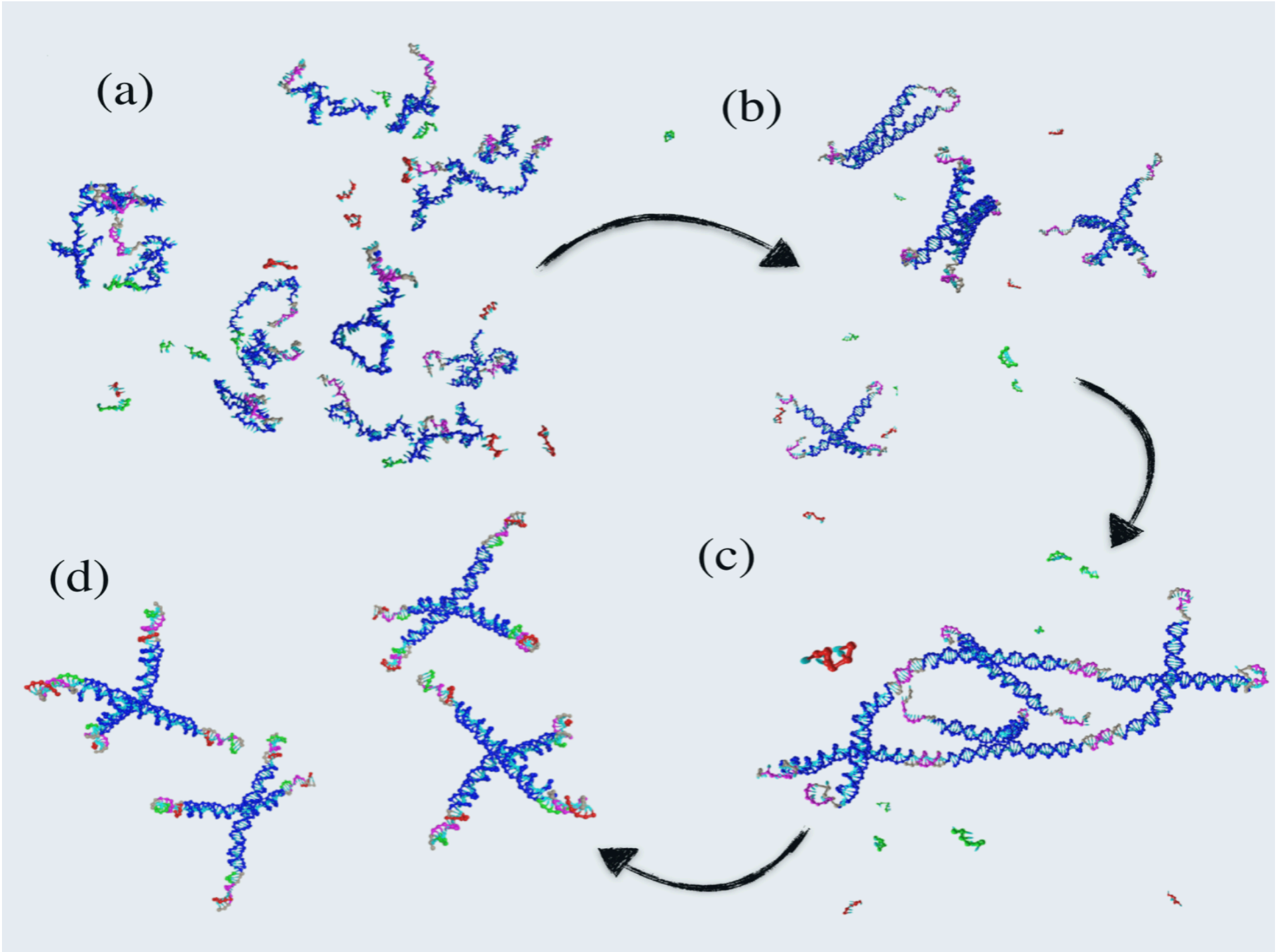
STAR-ARM-3’-TGAGCGTACGCAAT-5’

5’-GCGTTA-3’

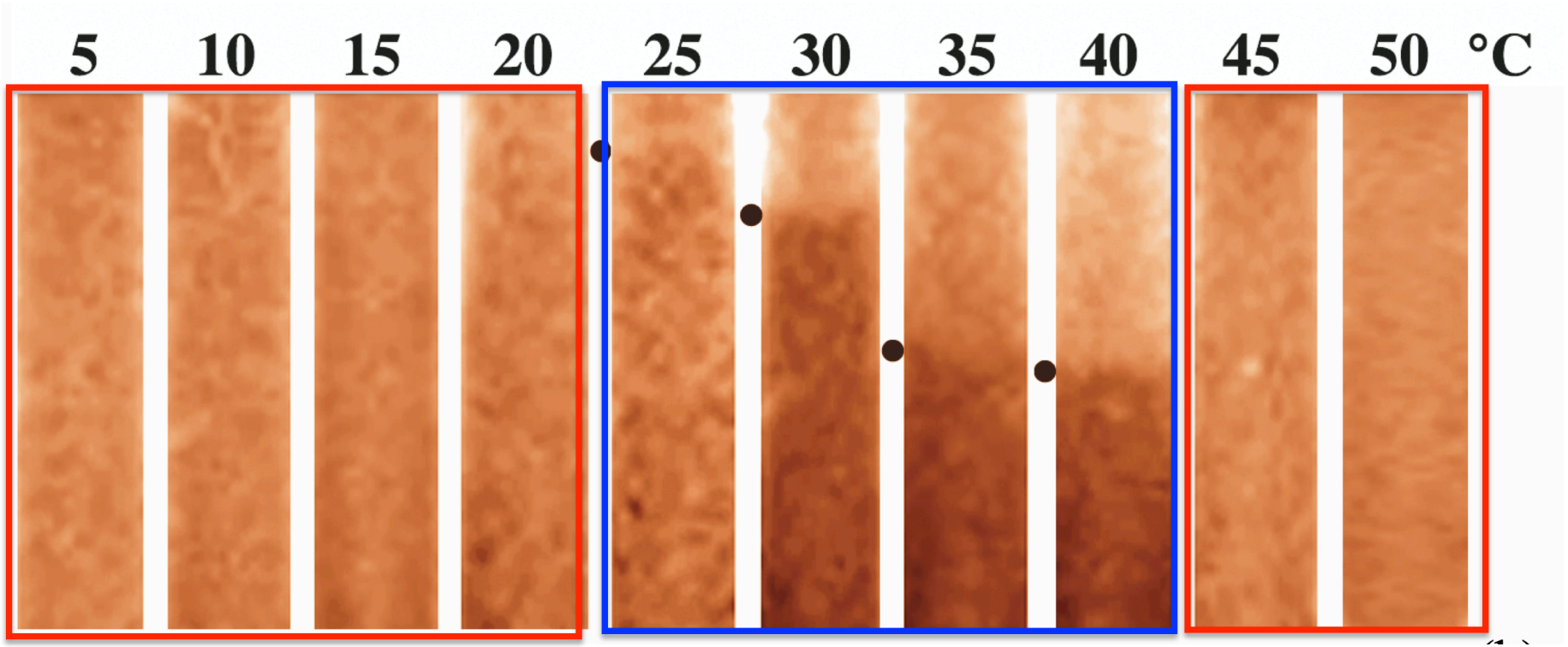


Nupack Evaluations: www.nupack.org



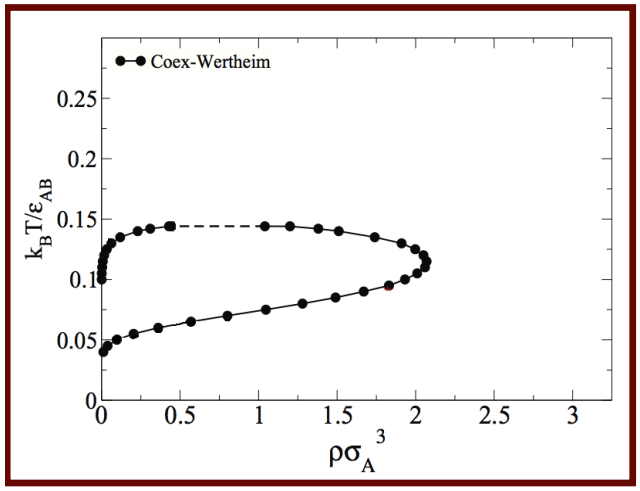

(a)
(b)
(c)
(d)

Now… experiments: The phase diagram



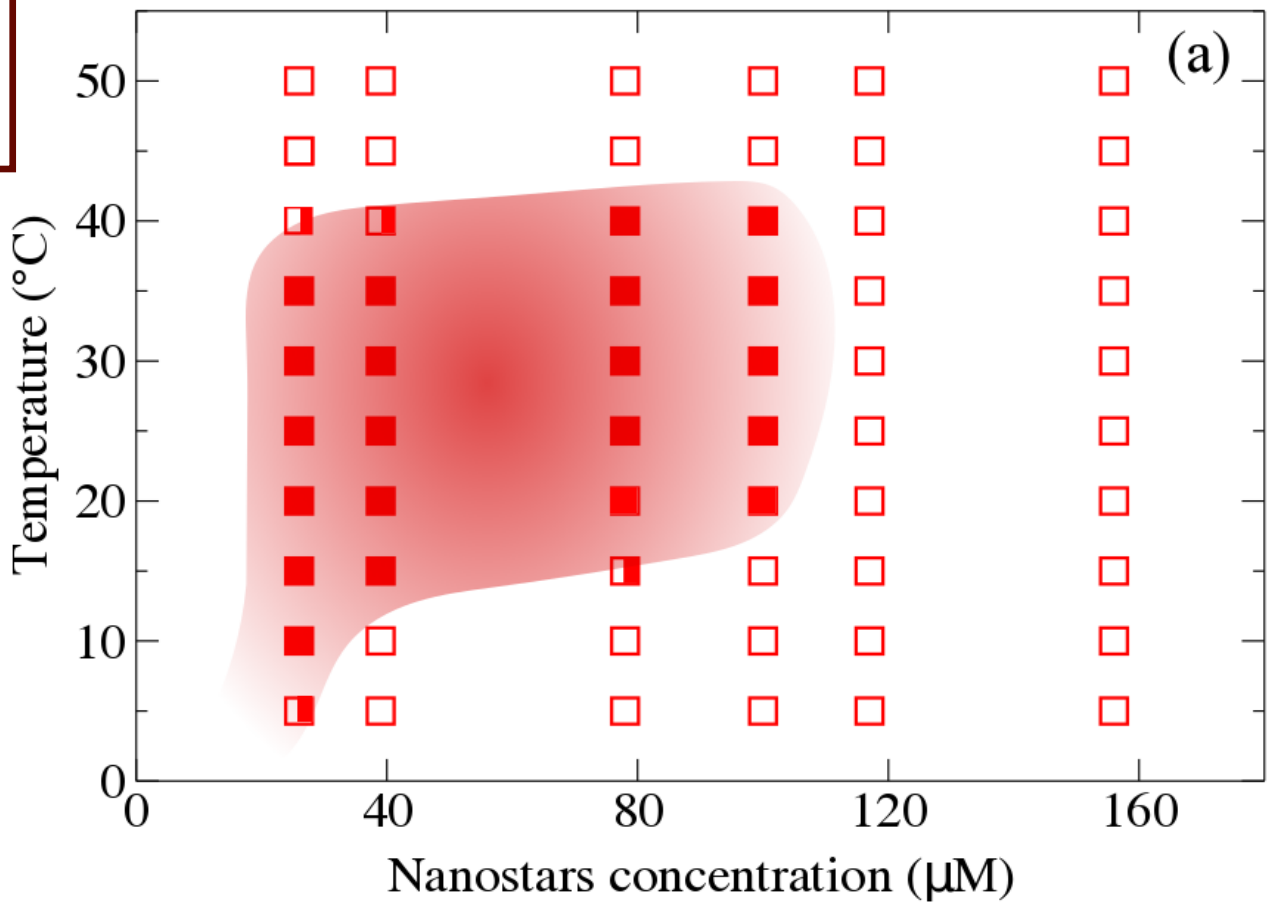
(ethidium bromide)

F. Bomboi et al., Nature Commun. 7, 13191 (2016)



S. Roldán-Vargas,et al., J. Chem. Phys. 139, (2013)

The phase diagram:



F. Bomboi et al., Nature Commun. 7, 13191 (2016)

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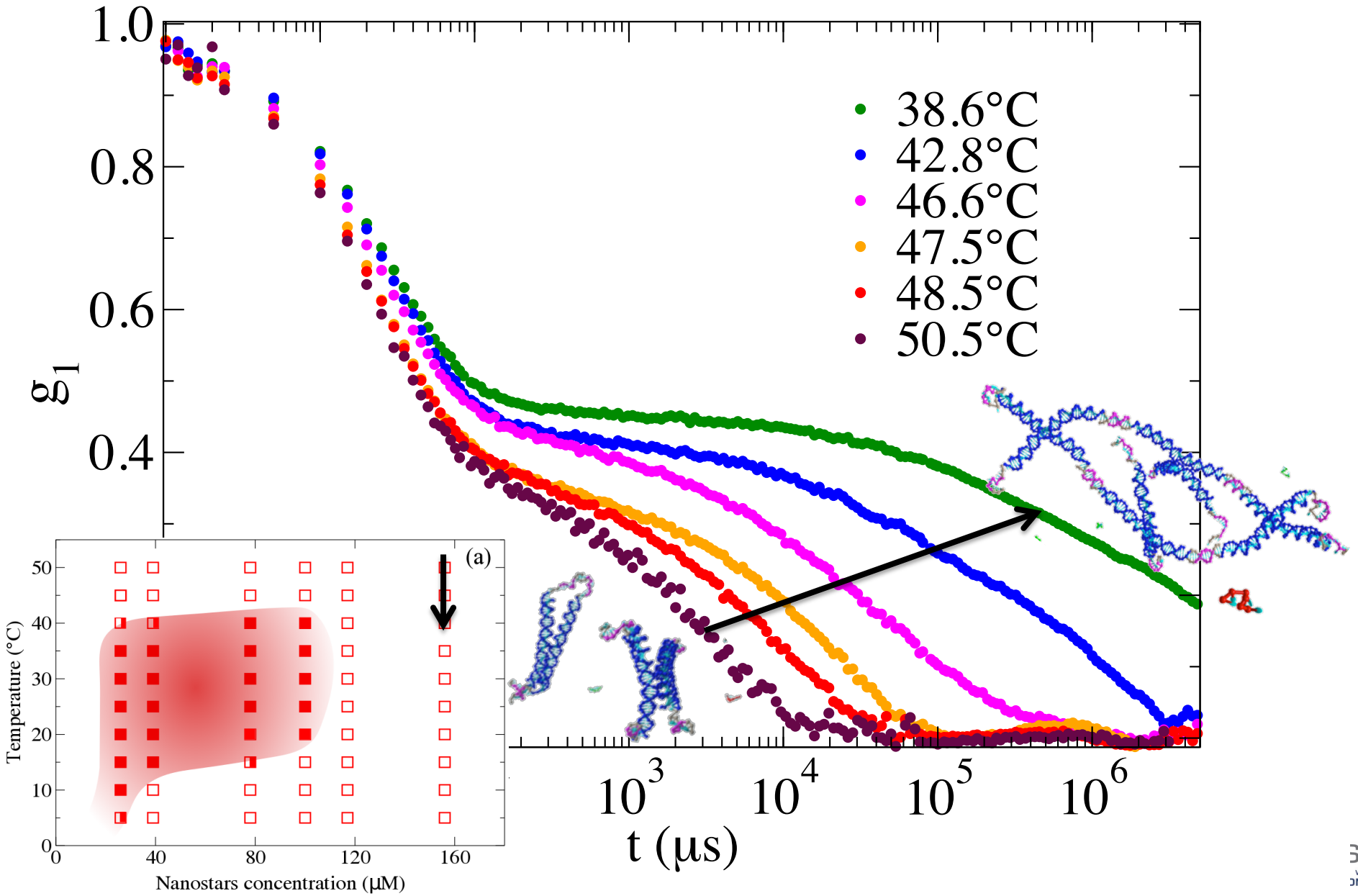
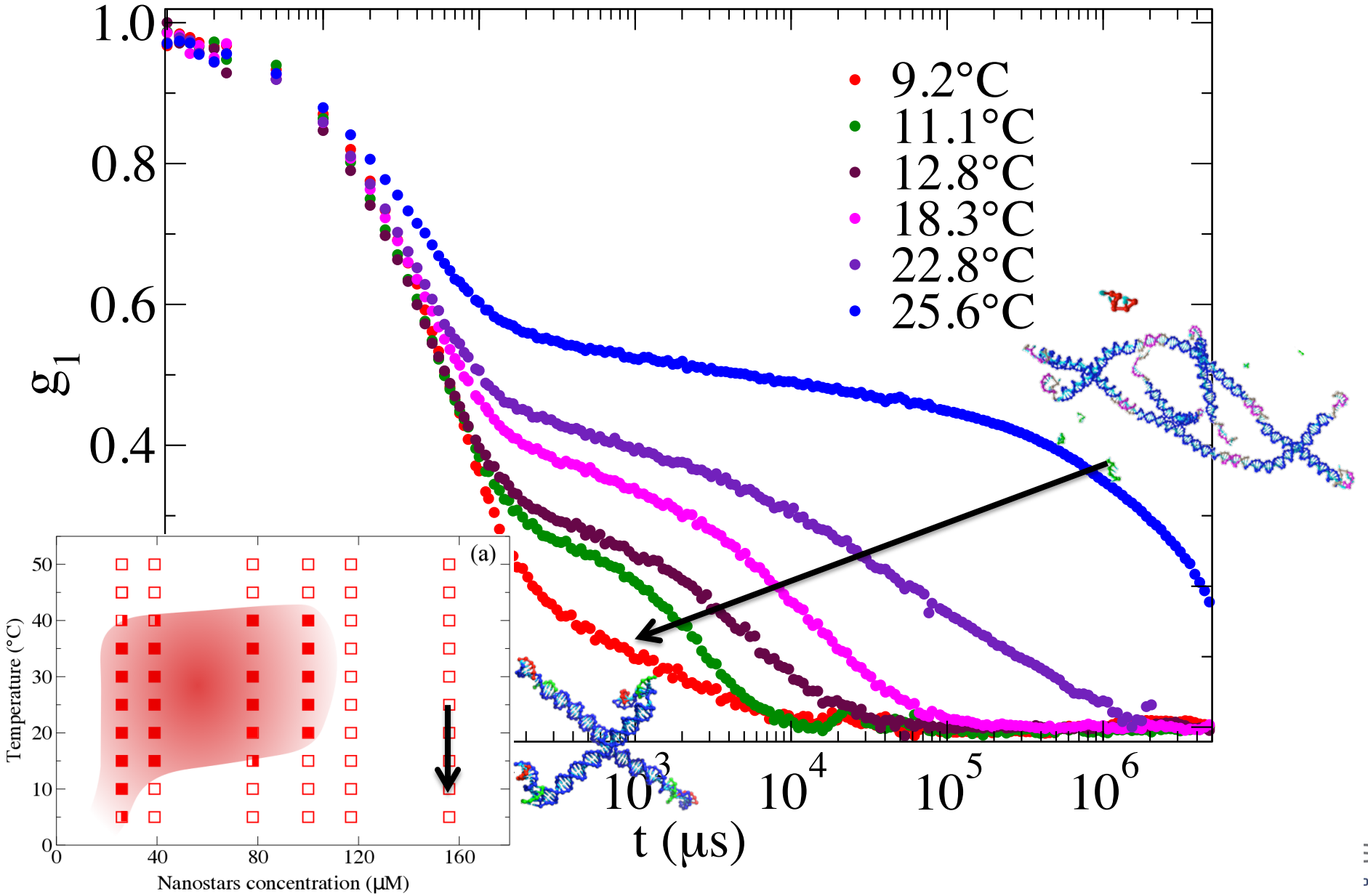
COLLDENSE COLLOIDS with DESIGNED RESPONSE

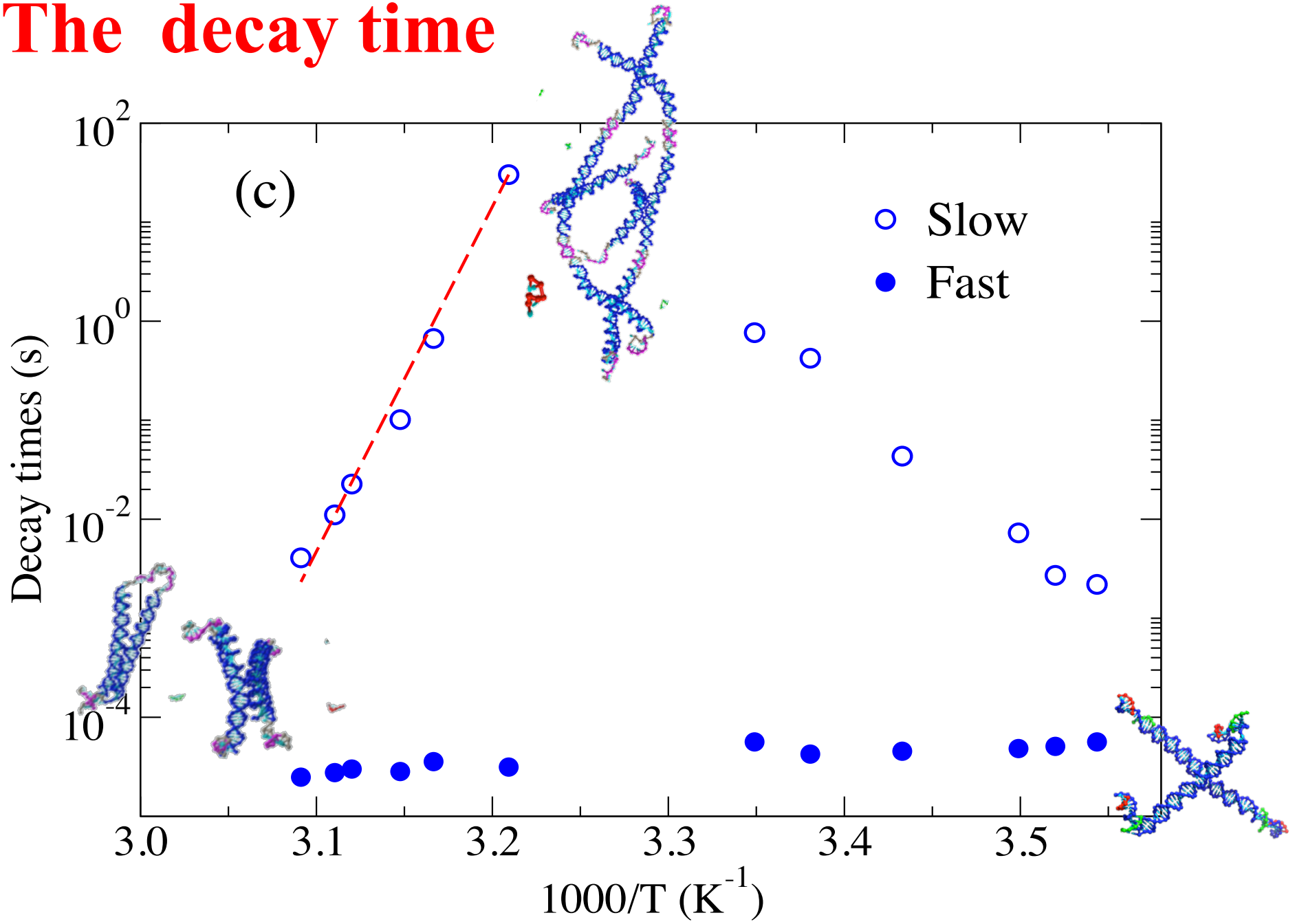
The T-region where the gel forms



The T-region where the gel breaks

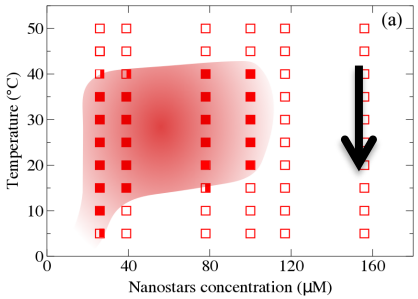


The decay time

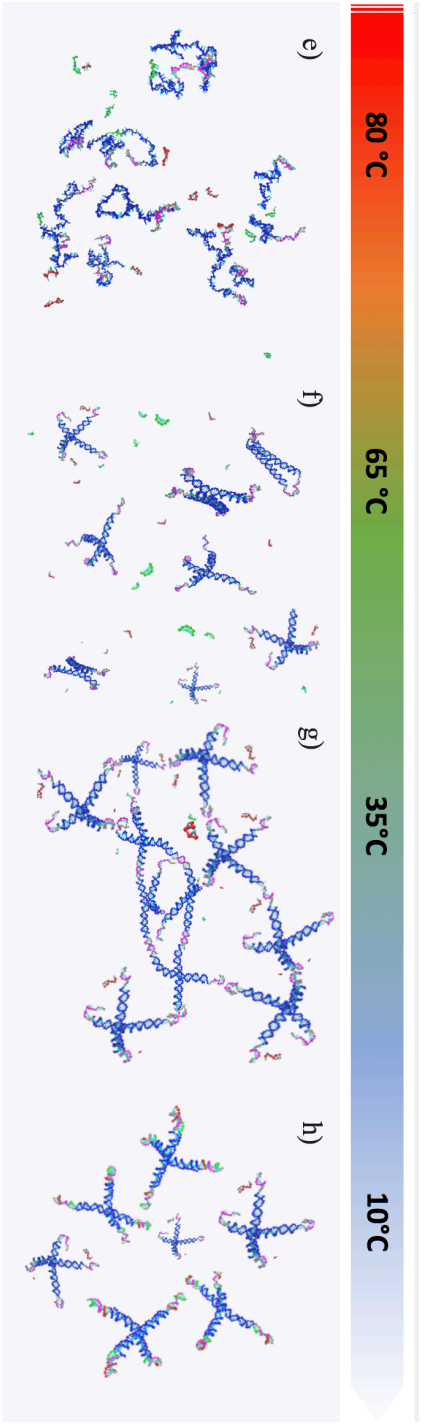


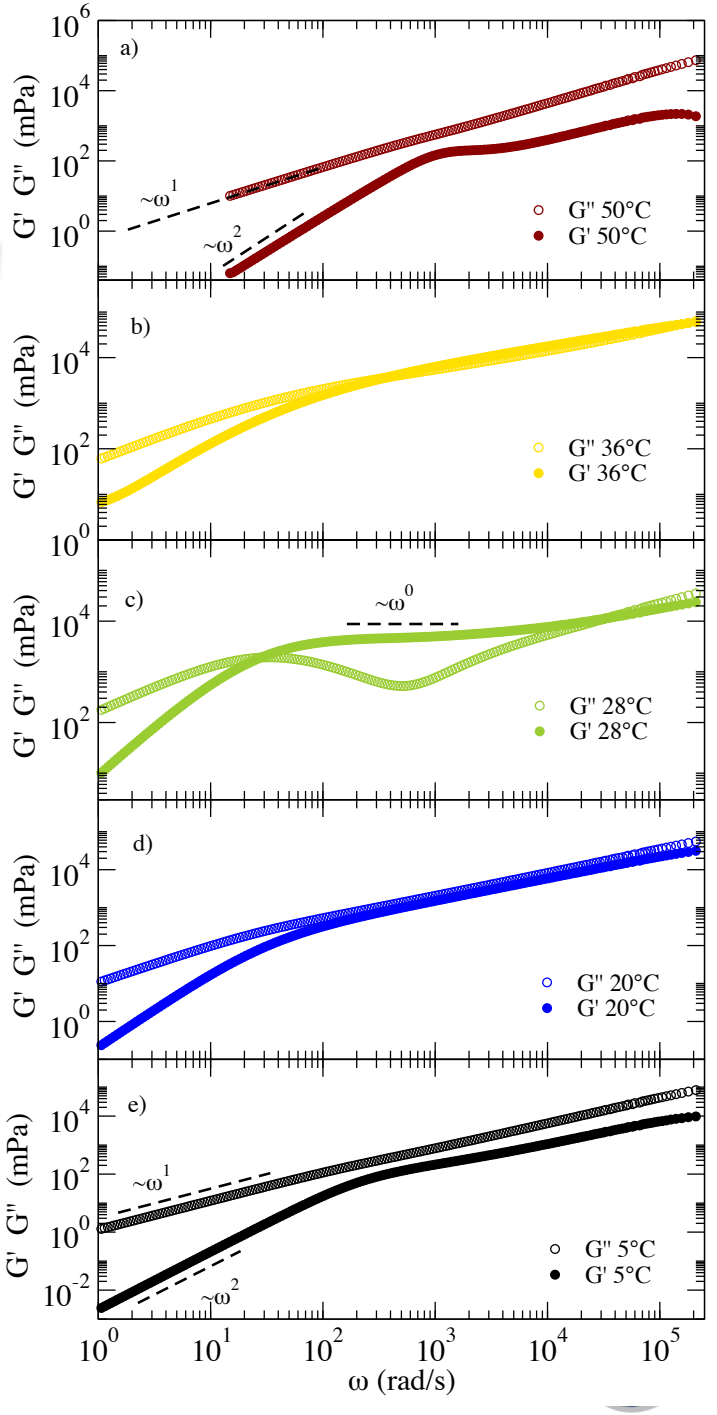
Passive microrheology

DLS with probes



Castanon et l,
Soft Matter 2018





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A swappable DNA gel

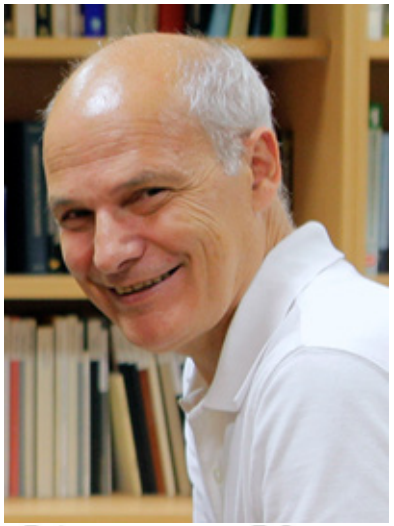
PRL 114, 078104 (2015) PHYSICAL REVIEW LETTERS

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

Flavio Romano[1] and Francesco Sciortino[2]

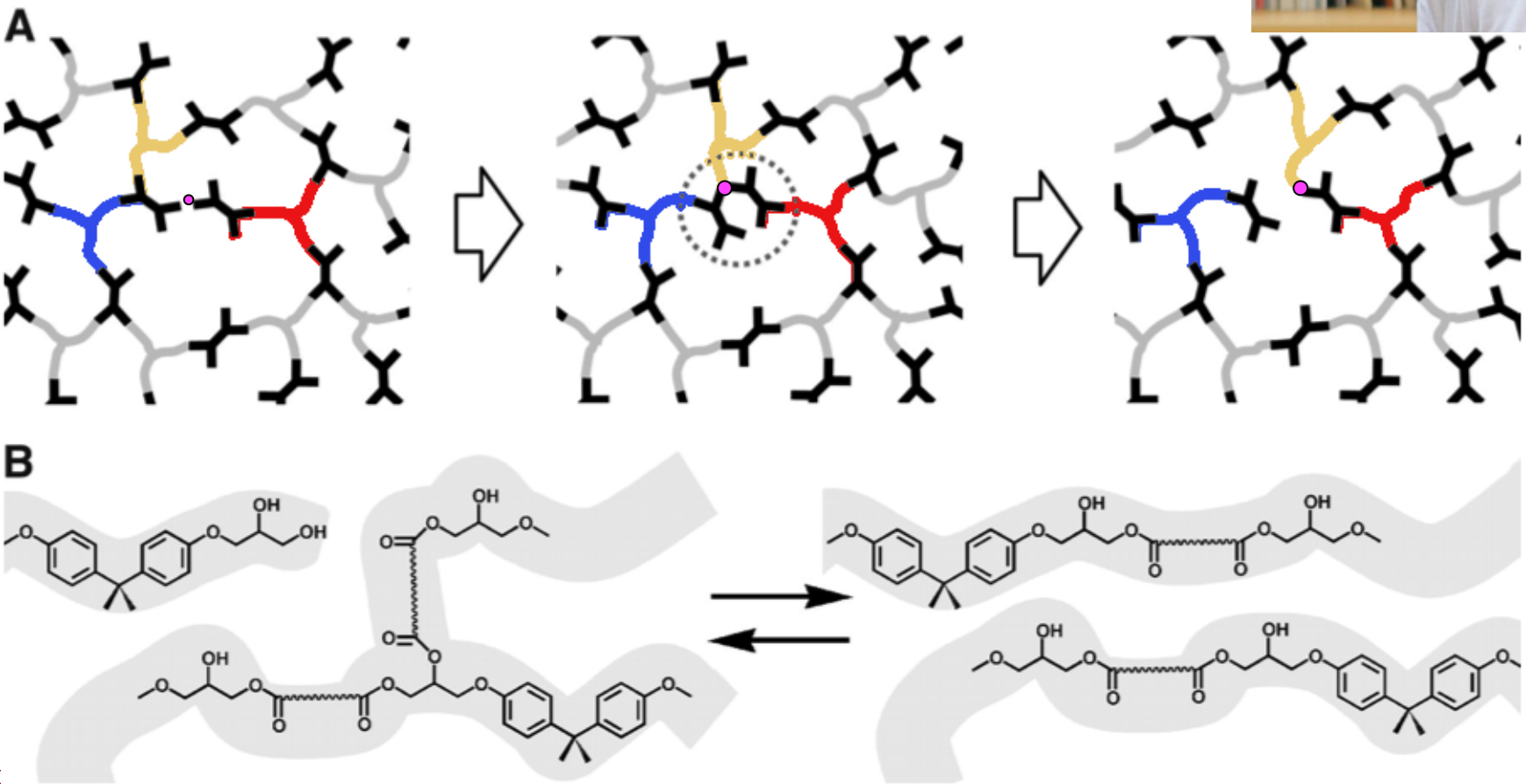
COLLDENSE
COLLOIDS with DESIGNED RESPONSE

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



Silica-Like Malleable Materials from Permanent Organic Networks

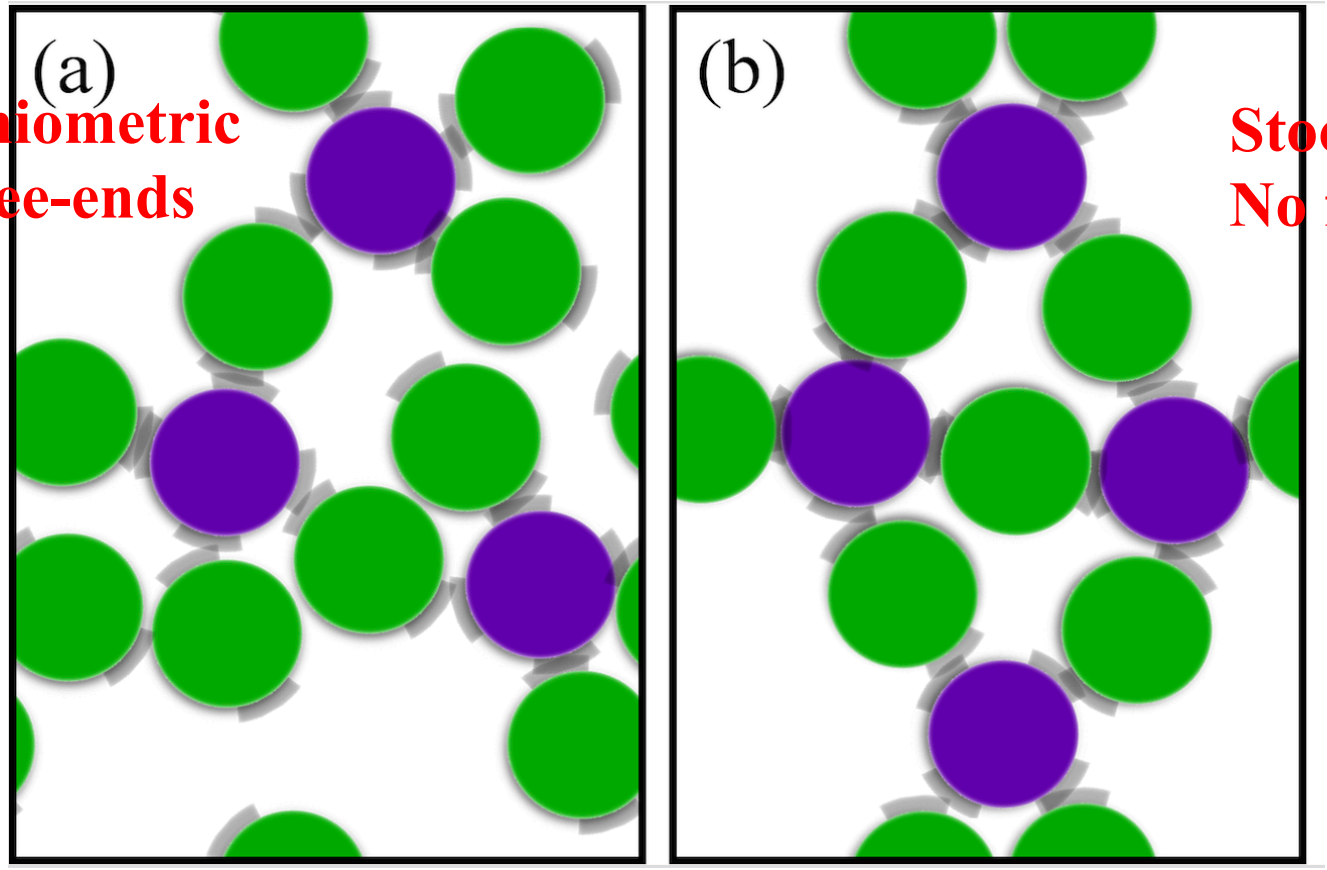
Damien Montarnal, Mathieu Capelot, François Tournilhac, Ludwik Leibler*



The essence of the vitrimers:

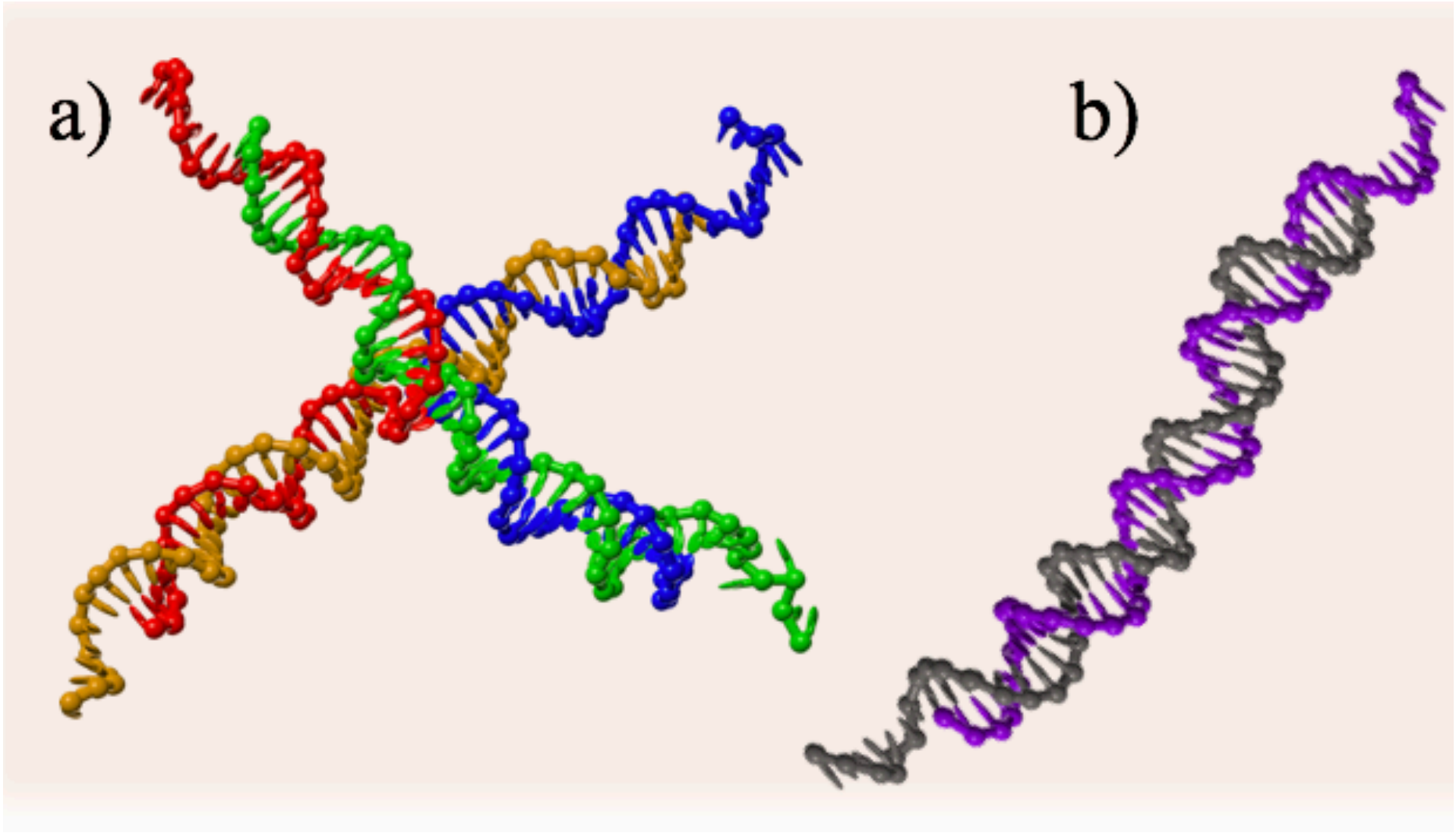
1) non-stochiometric binary mixture of limited valence particles

Non-Stochiometric
Several free-ends

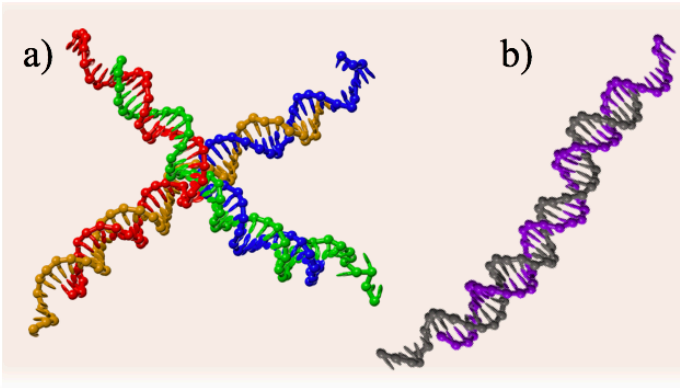


Stochiometric
No free-ends

2) swap mechanism


a)
b)

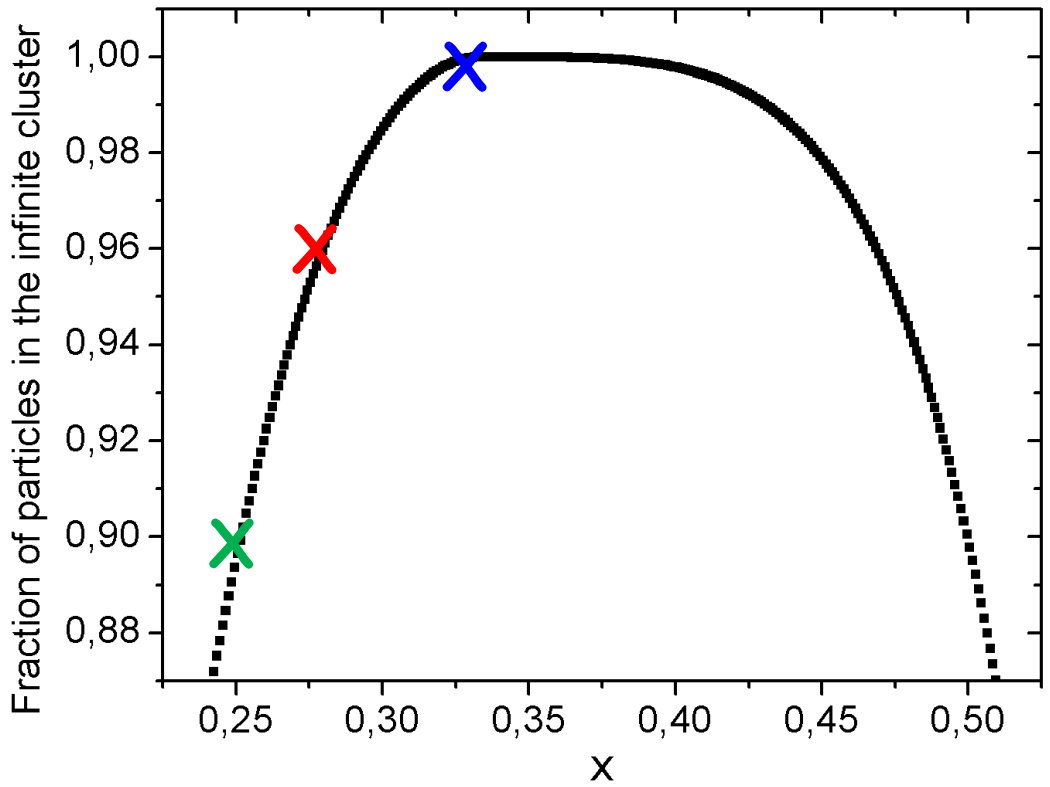
What do we expect according to Flory-Stockmayer in the limit where all possible bonds are formed



x = 0.33

x = 0.28

x = 0.25

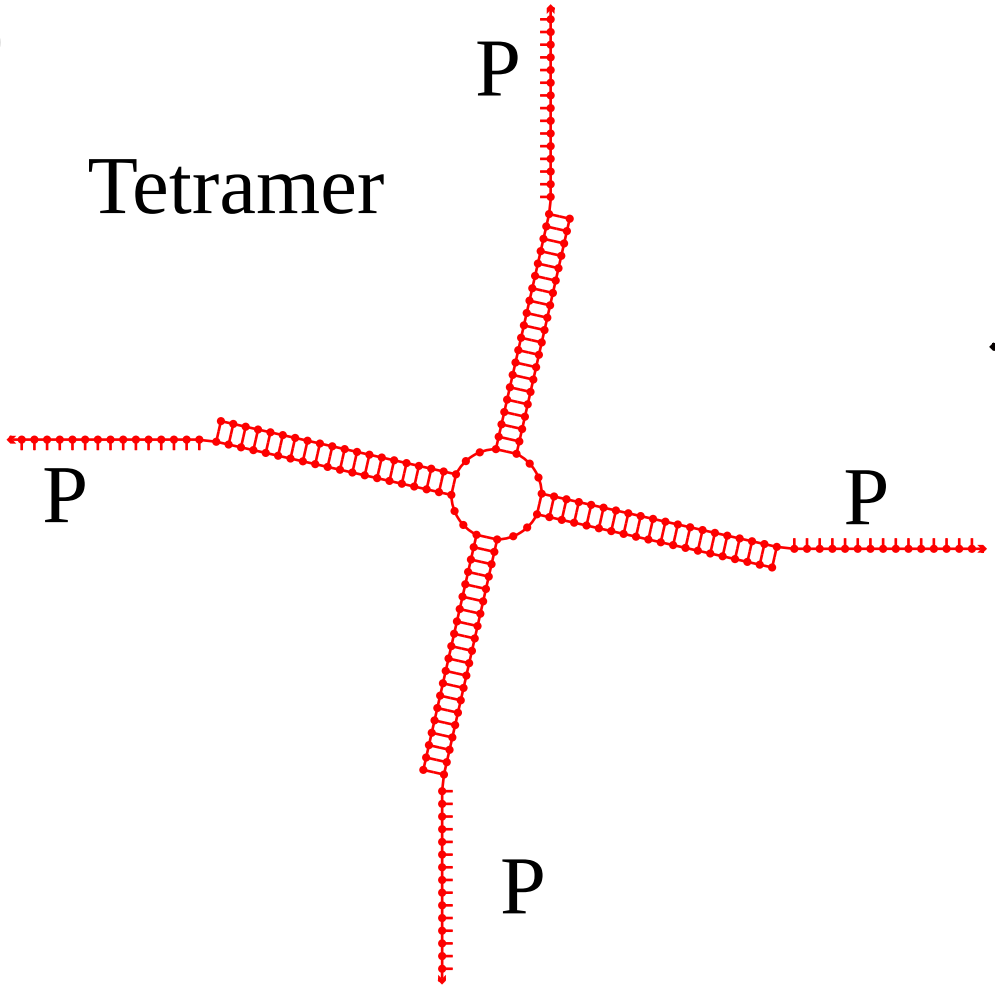


FLUID | GEL | FLUID

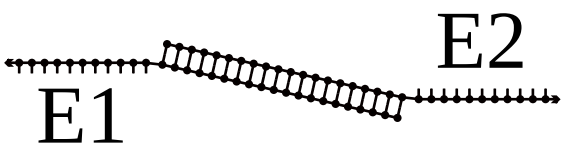
x

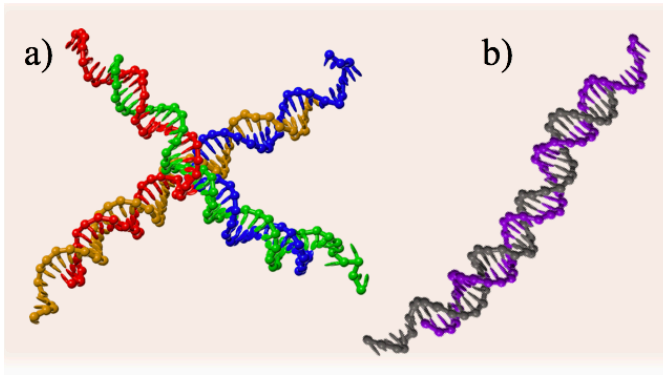
(only a-b bonds)

An all DNA vitrimer !



Bridge





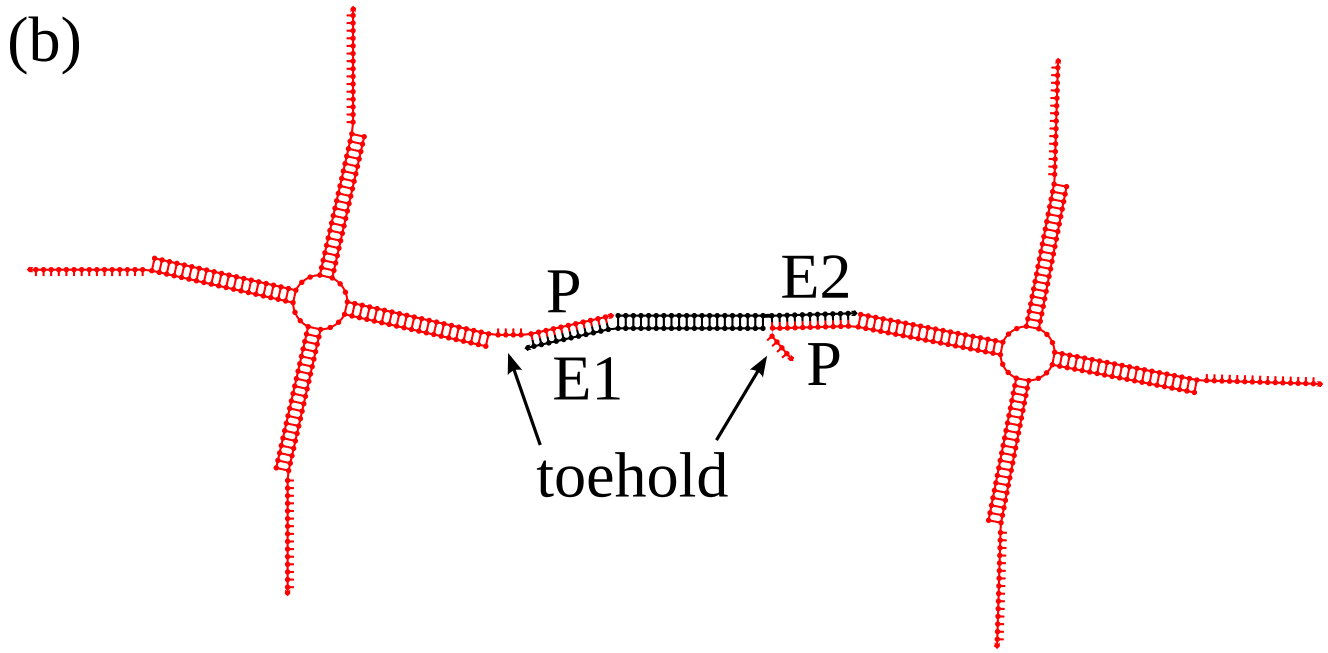
$E1$	5′-GGTTCGACACG-3′
P	3′-CCAAGCTGTGCTCAC-5′
$E2$	5′-CGACACGAGTG-3′

114, 078104 (2015) PHYSICAL REVIEW LETTERS

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

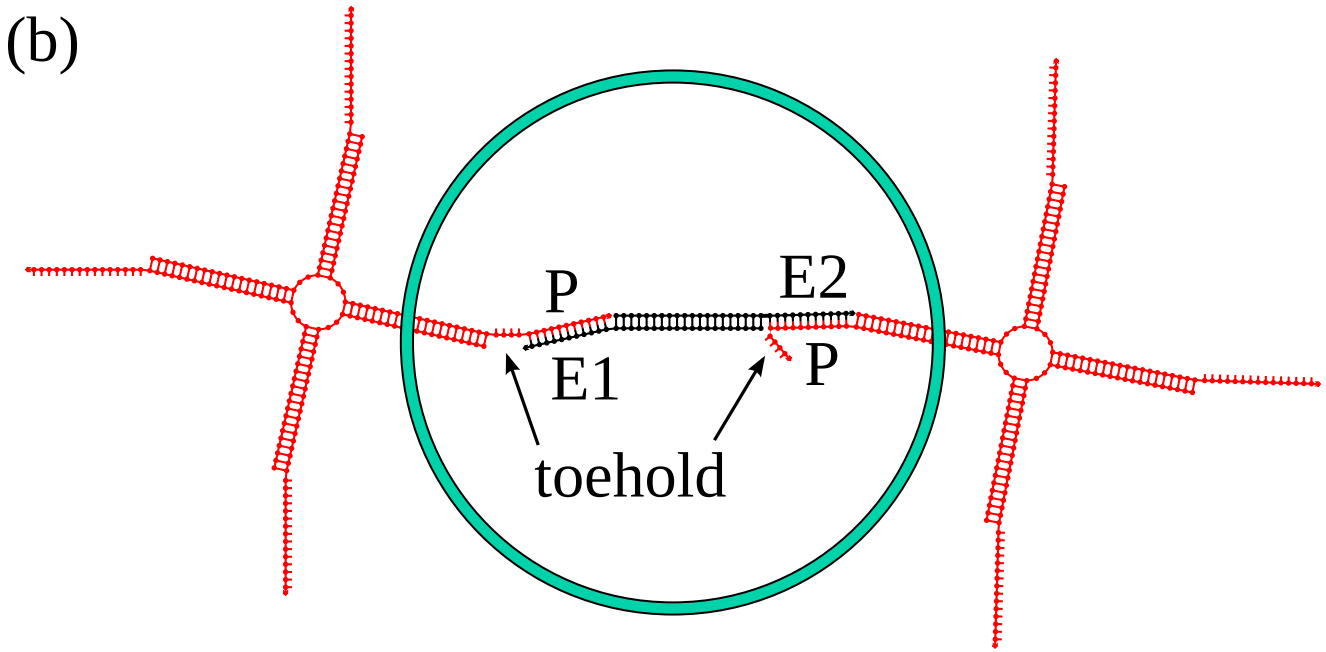
Flavio Romano[1] and Francesco Sciortino[2]

An all DNA vitrimer !



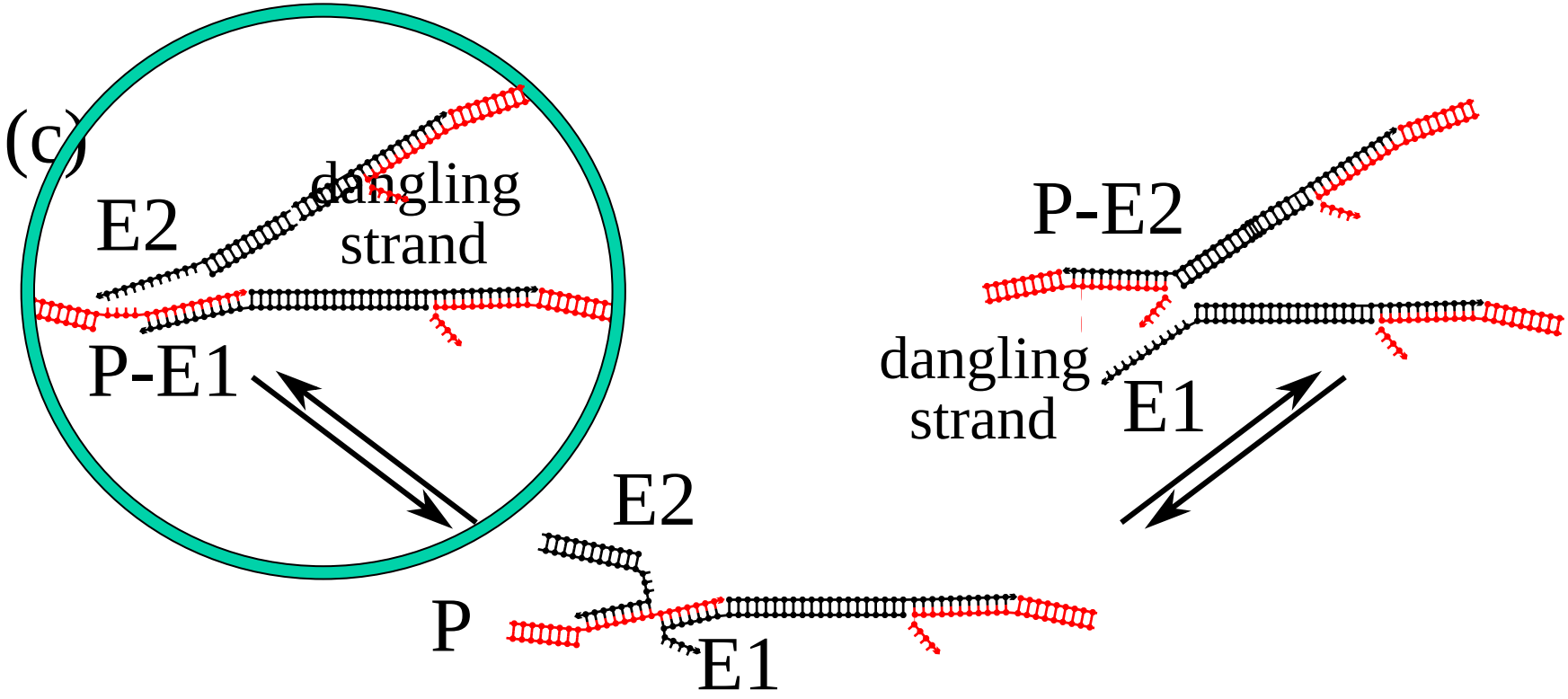
Toehold mediated strand displacement

An all DNA vitrimer !



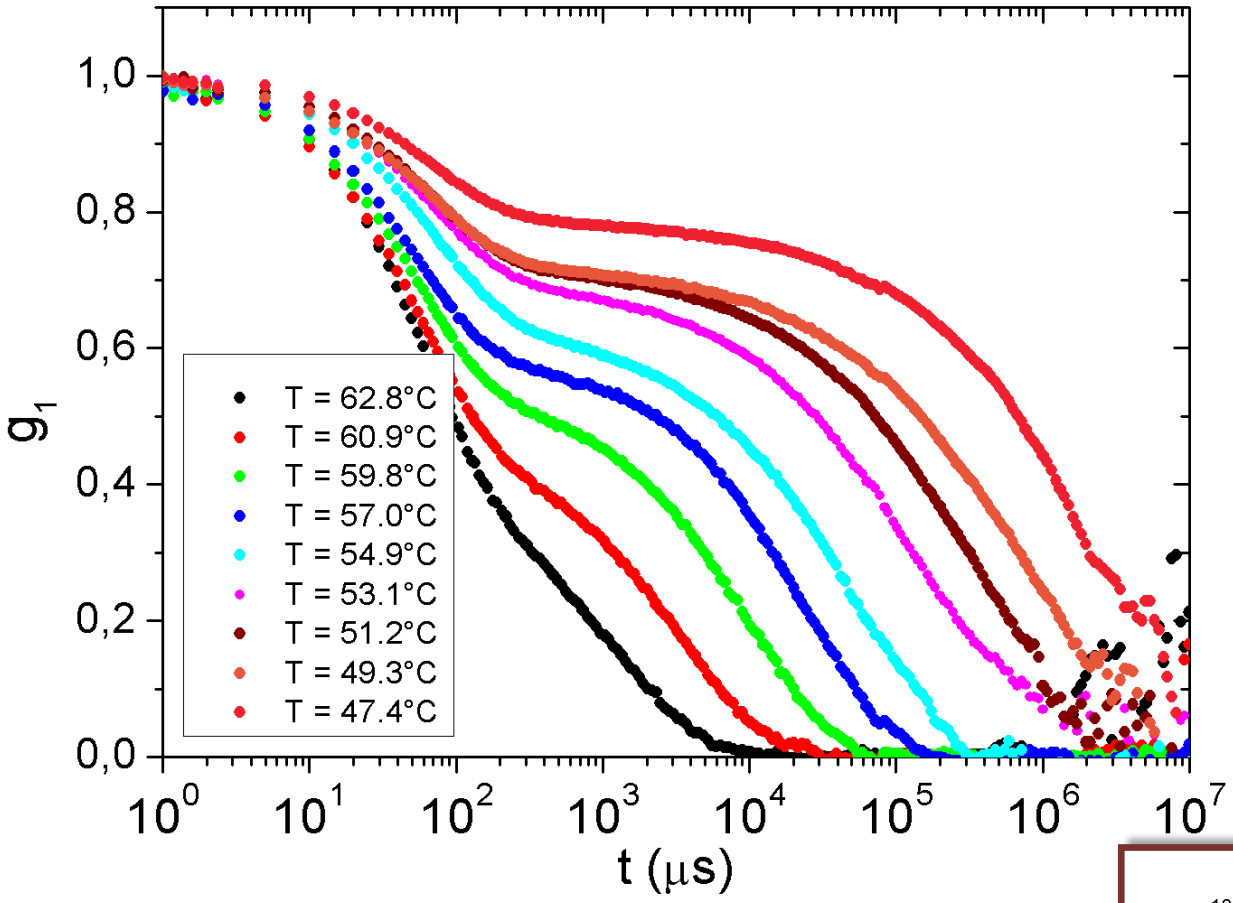
Toehold mediated strand displacement

An all DNA vitrimer !



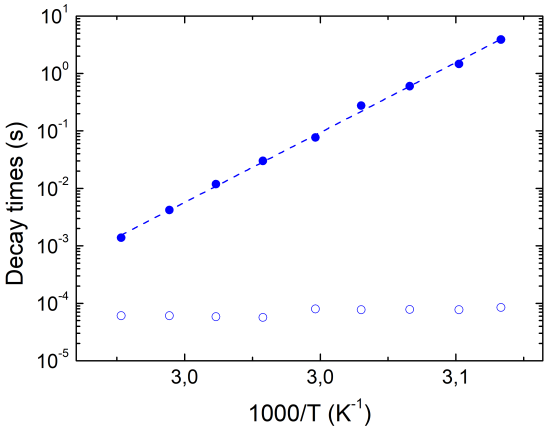
$E1$	5′-GGTTCGACACG-3′
P	3′-CCAAGCTGTGCTCAC-5′
$E2$	5′-CGACACGAGTG-3′

Onset of a equilibrium gels of long-living bonds



x = 0.33

No free-ends



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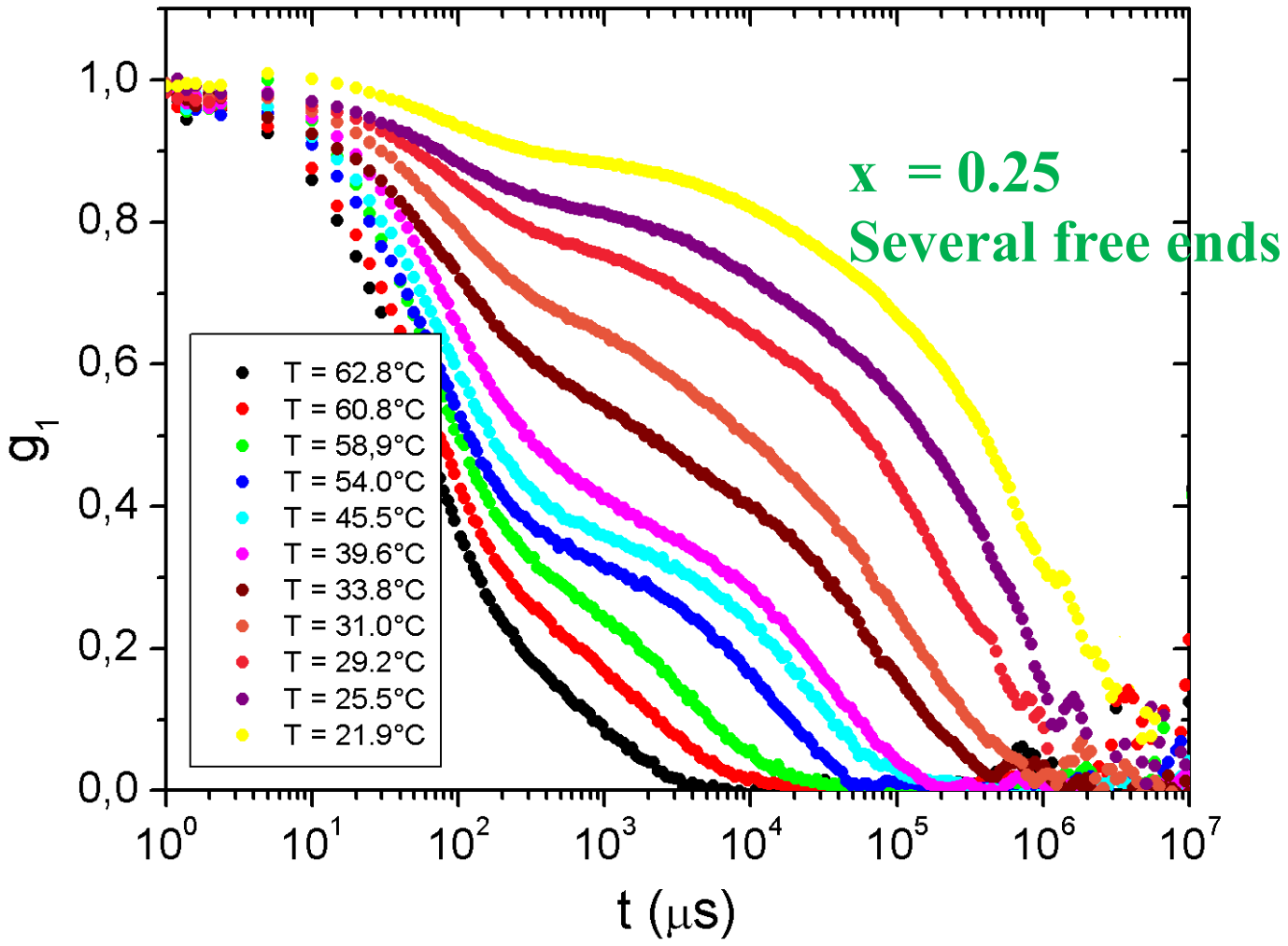
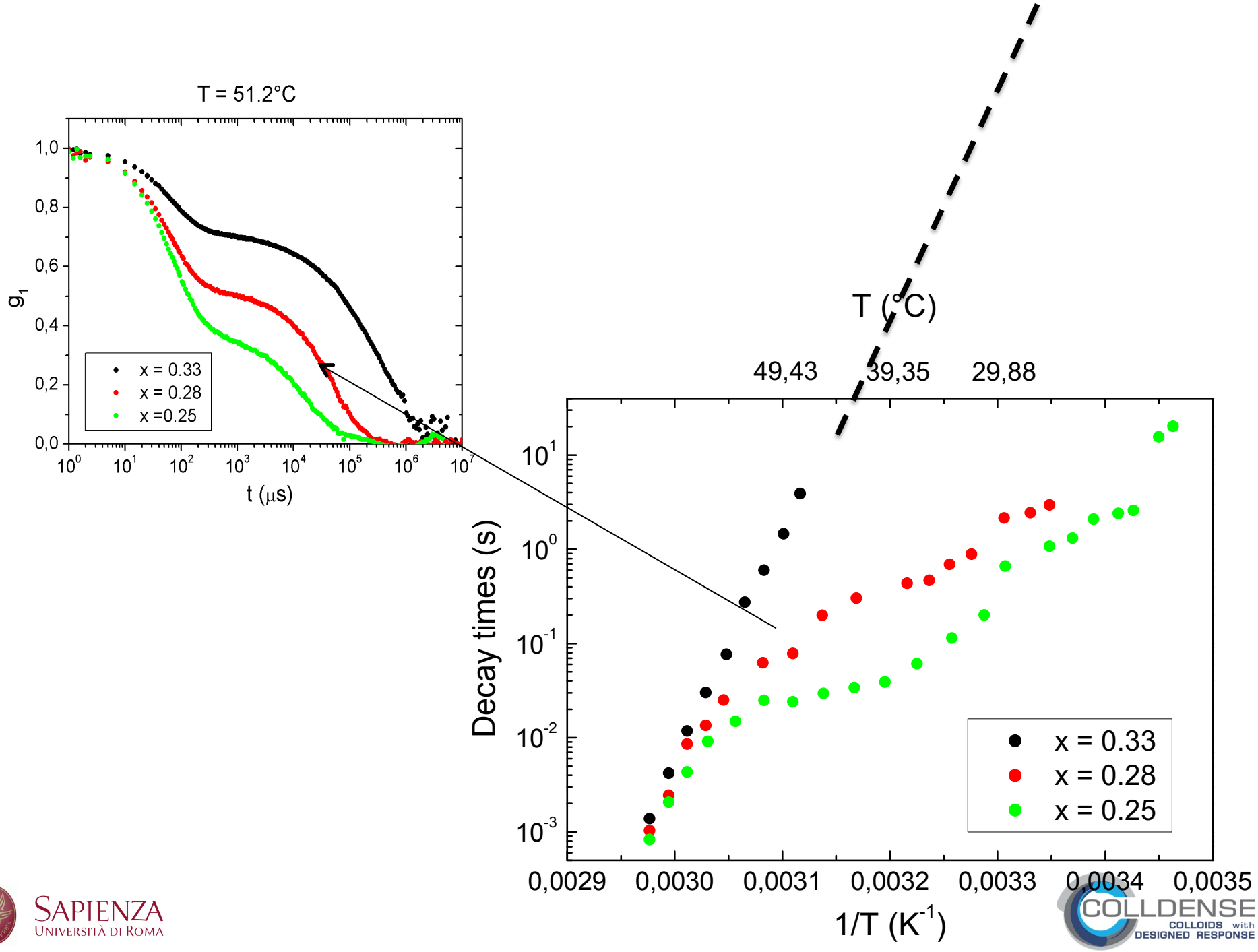
Fast-restructuring gel





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COLLDENSE
COLLOIDS with DESIGNED RESPONSE

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

Swapping gel

Who did the work

Lorenzo Rovigatti - DNA simulations

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

Frank Smallenburg – Phase behavior of Colloids

Tommaso Bellini, Roberto Cerbino, Giovanni Nava, Silvia Biffi, Francesca Bomboi, Javier Castanon, Patriza Filetici, Manuela Leo, Federico Bordi, Debora Caprara – (DNA experiments)

Animation by L. Rovigatti

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COLLDENSE