Bangalore, January 2010

Francesco Sciortino
Universita' di Roma *La Sapienza*

"Colloidal glasses and other glassy states in soft materials"

La Sapienza
Università degli Studi di Roma

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

http://pacci.phys.uniroma1.it/

erc

Outline

Aims:

1) Review the rich variety of glass-behaviors observed in colloidal systems (and discuss the possible origins). What MCT can and what can not do.

2) Discuss some recent ideas on the routes to gel formation and possible connections/differences between gel and glasses.

Glasses:

Hard Colloids: Hard Spheres …..

Soft Colloids: Star polymers …….

Attractive Colloids: Depletion …..

Repulsive Colloids: Yukawa….

Gels:

Competing Interactions

Limited valence potentials

La Sapienza
Università degli Studi di Roma

erc

Colloid

From Wikipedia, the free encyclopedia

A **colloid** is a type of chemical mixture in which one substance is dispersed evenly throughout another.[1] The particles of the dispersed substance are only suspended in the mixture, unlike in a solution, in which they are completely dissolved. This occurs because the particles in a colloid are larger than in a solution - small enough to be dispersed evenly and maintain a homogeneous appearance, but large enough to scatter light and not dissolve. Because of this dispersal, some colloids have the appearance of solutions. A colloidal system consists of two separate phases: a **dispersed phase** (or **internal phase**) and a **continuous phase** (or **dispersion medium**). A colloidal system may be solid, liquid, or gaseous.

Many familiar substances are colloids, as shown in the chart below. As well as these naturally occurring colloids, modern chemical process industries utilise high shear mixing technology to create novel colloids.

The subsequent table compares particle(s) diameters of colloids, homogeneous and heterogeneous mixture:

Size

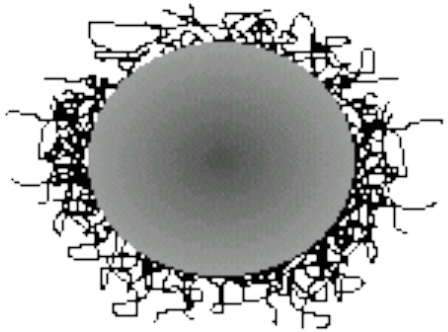
Particles in a solvent

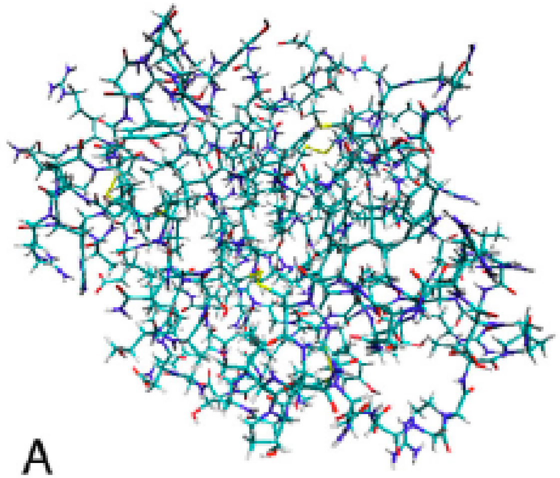
Particle size		
less than 10^{-9} m	10^{-9} – 10^{-6} m	greater than 10^{-6} m
homogenous mixture	colloids	non-homogeneous mixtures

Disperse phase	Dispersion medium	Notation	Technical name	Examples
Solid	Gas	S/G	Aerosol	Smoke
Liquid	Gas	L/G	Aerosol	Hairspray, mist, fog
Solid	Liquid	S/L	Sol or dispersion	Printing ink, paint
Liquid	Liquid	L/L	Emulsion	Milk, mayonnaise
Gas	Liquid	G/L	Foam	Fire-extinguisher foam
Solid	Solid	S/S	Solid dispersion	Ruby glass; some alloys
Liquid	Solid	L/S	Solid emulsion	Road paving; ice cream
Gas	Solid	G/S	Solid foam	Insulating foam

Examples

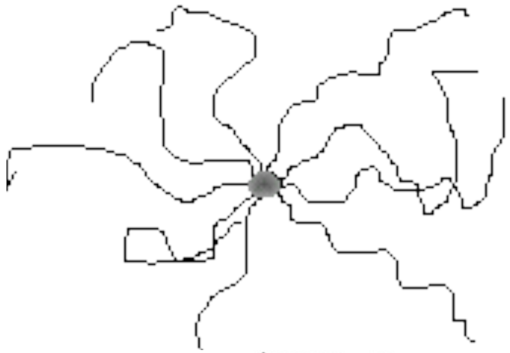
Adsorbed Polymer.
Polymers physically adsorbed to large particle.



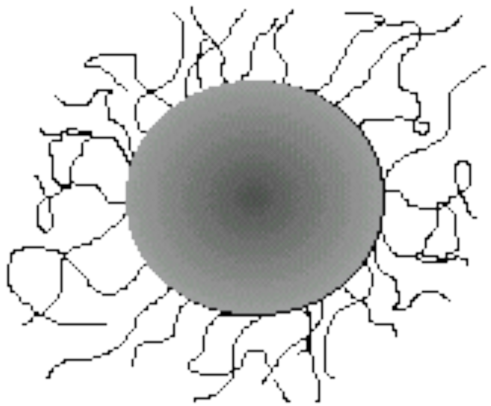


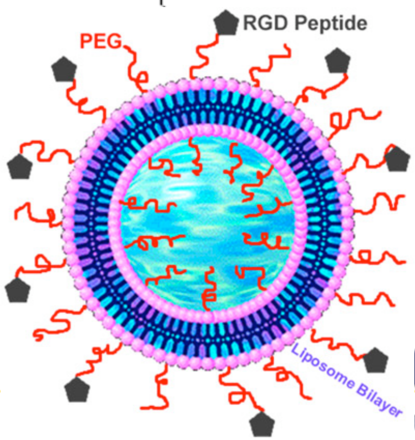
Lysozime

Star Polymer.
Chain ends chemically attached to small core.

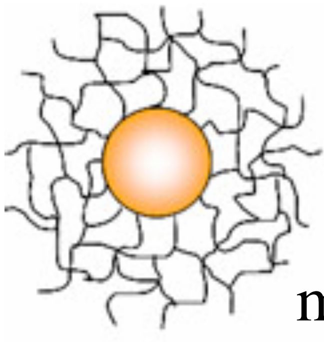


Grafted Polymer.
Chain ends chemically attached to large particle.





liposomes



microgel

Laponite

Colloidal Interactions

Attraction:

$$V_{\mathrm{vdW}}(r) = -\frac{1}{6}A\left[\frac{2R^2}{r^2-4R^2}+\frac{2R^2}{r^2}+\ln\left(\frac{r^2-4R^2}{r^2}\right)\right]$$

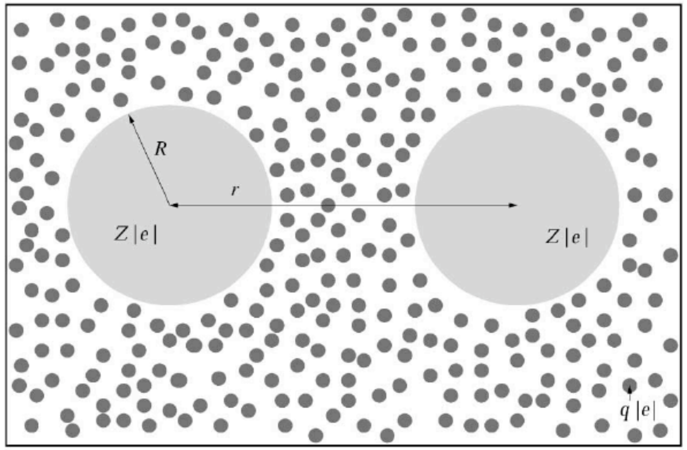
$A=A(n_1,n_2)$

Repulsion

$$V_{\mathrm{C}}(r) = \frac{(\tilde{Z}e)^2\exp(-\kappa r)}{\varepsilon r}$$

$\kappa=\kappa(\textit{salt concentration})$

$$V_{\mathrm{DLVO}}(r) = \begin{cases} \infty & \text{if } r < 2R \\ V_{\mathrm{vdW}}(r) + V_{\mathrm{C}}(r) & \text{if } r \geq 2R \end{cases}$$



La Sapienza
Università degli Studi di Roma

erc

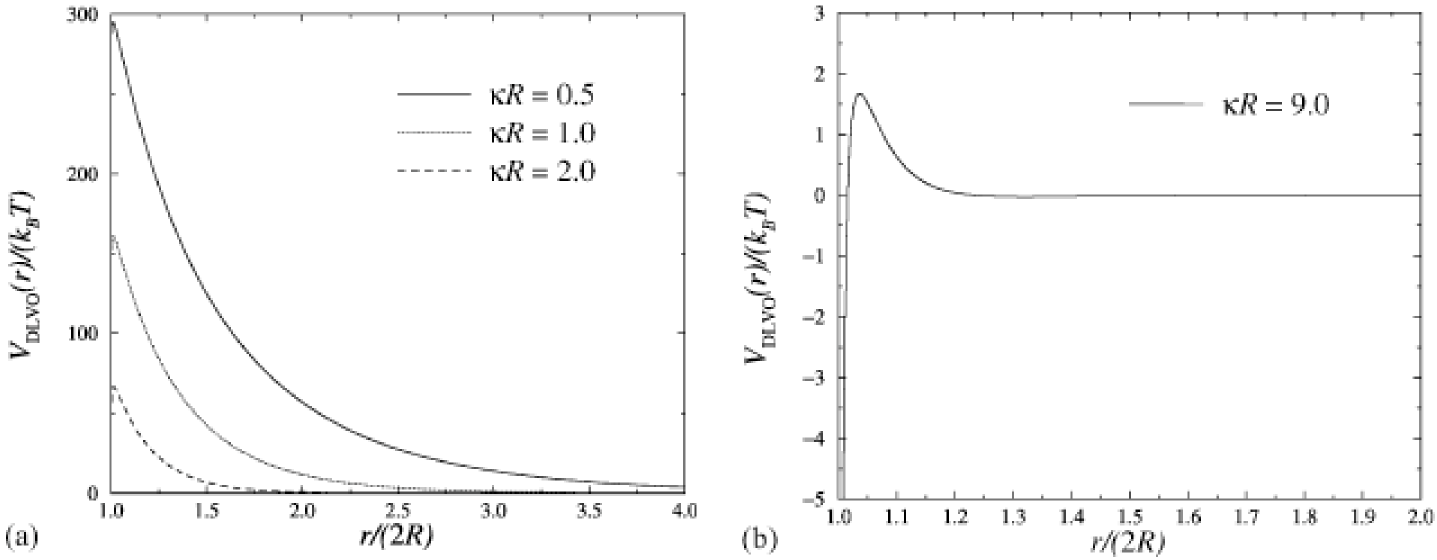
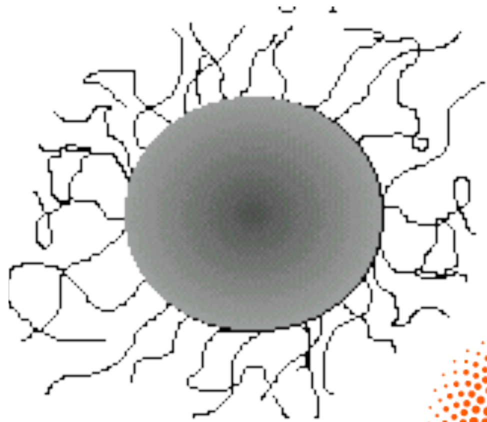


Fig. 3. The sum of the van der Waals potential of Eq. (2.10) and the screened Coulomb repulsion of Eq. (2.12) for realistic values of the parameters and for various degrees of screening. For the plots, we have chosen $A = 10^{-20}$ J; $\varepsilon = 80$; $R = 1$ μm; $Z^* = 1000$; $T = 300$ K. In (a) we show typical results for weak screening, where the electrostatic repulsion completely dominates the van der Waals attraction. In (b) the potential barrier is barely capable of keeping the particles apart. Notice also the very shallow secondary minimum of the potential at about $r/(2R) = 1.3$. The hard-sphere repulsion for $r < 2R$ is not shown.



To prevent aggregation:
Charge Stabilization
Steric Stabilization

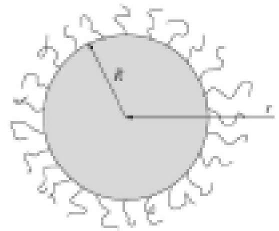
La Sapienza
Università degli Studi di Roma

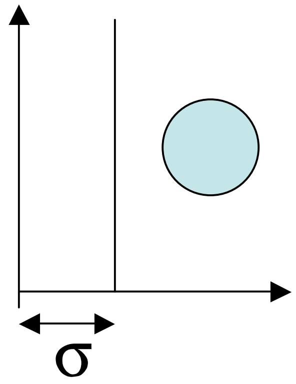
C.N. Likos / Physics Reports 348 (2001) 267–439

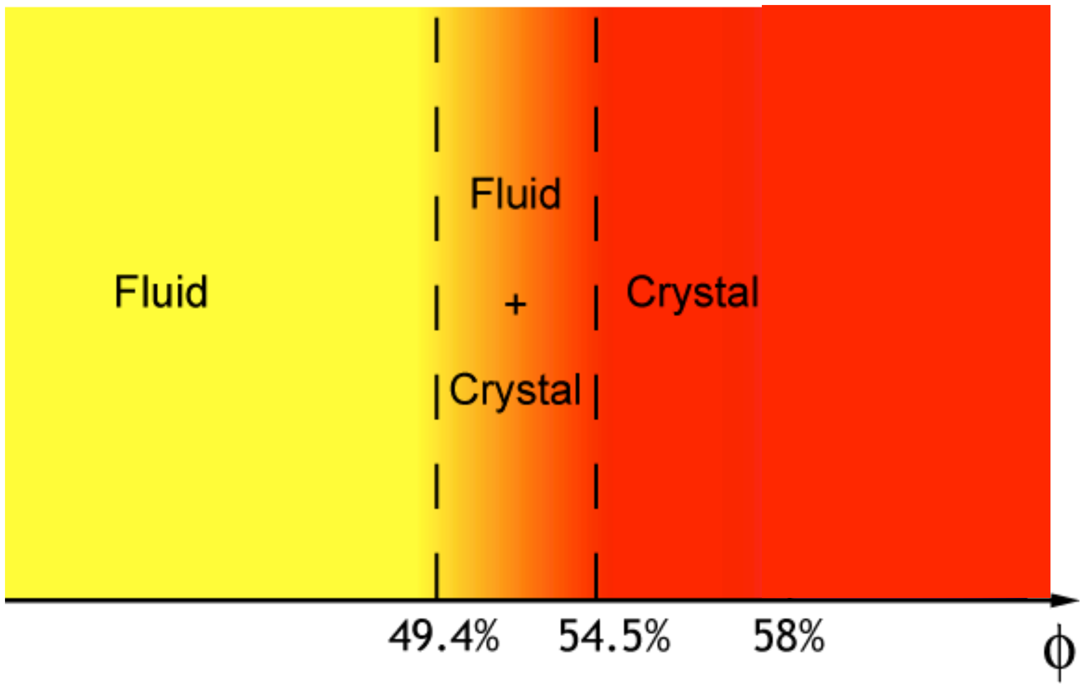
erc

Hard Spheres (HS)

Equilibrium properties







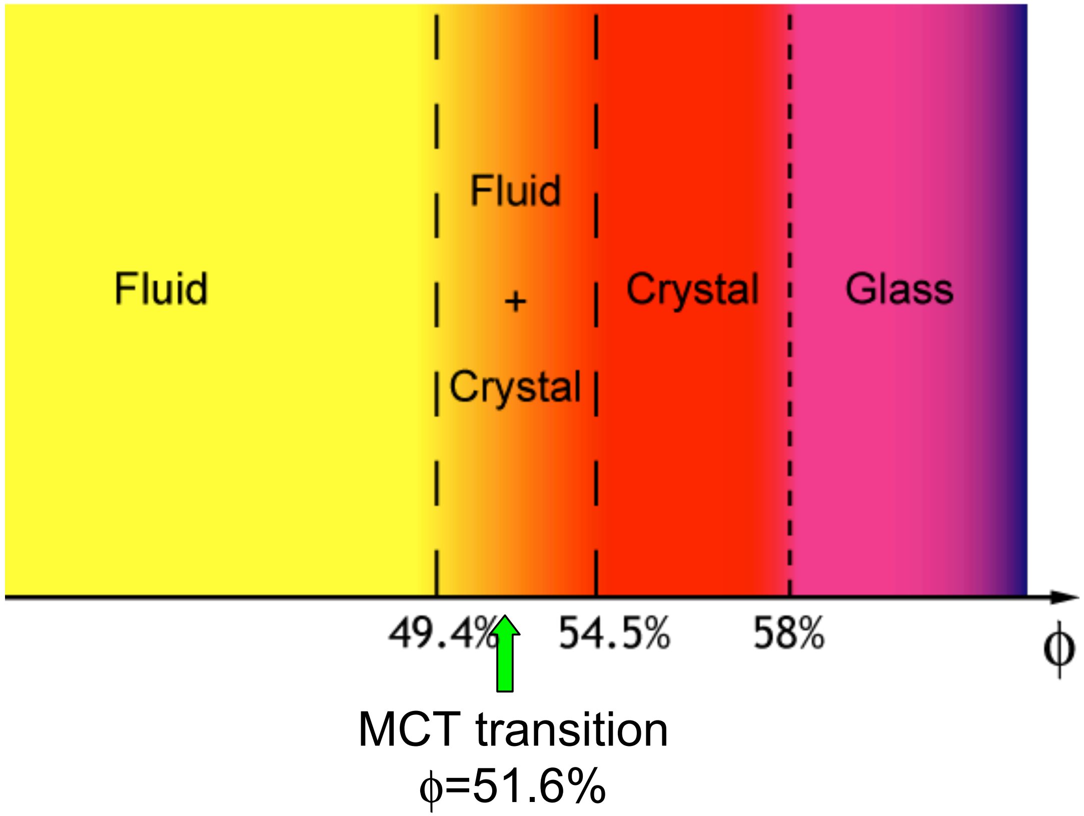
- **Hard spheres present a a fluid–solid phase separation due to entropic effects**

Sterically stabilized PMMA particles (polydispersity 5-10 %)

Hard Spheres (HS)

• Hard spheres present a a fluid–solid phase separation due to entropic effects

•Experimentally, at ϕ=0.58% the system freezes forming disordered aggregates. (1)



1. W. van Megen and P.N. Pusey *Phys. Rev.* A **43**, 5429 (1991)

La Sapienza
Università degli Studi di Roma

erc

HS MCT-Exp
(density correlations)

Once the location of the glass line has been rescaled. MCT accounts for experimental data within 15% accuracy level

Fit in $(\phi - \phi_{MCT})$

W. van Megen and S.M. Underwood

Phys. Rev. Lett. **70**, 2766 (1993)

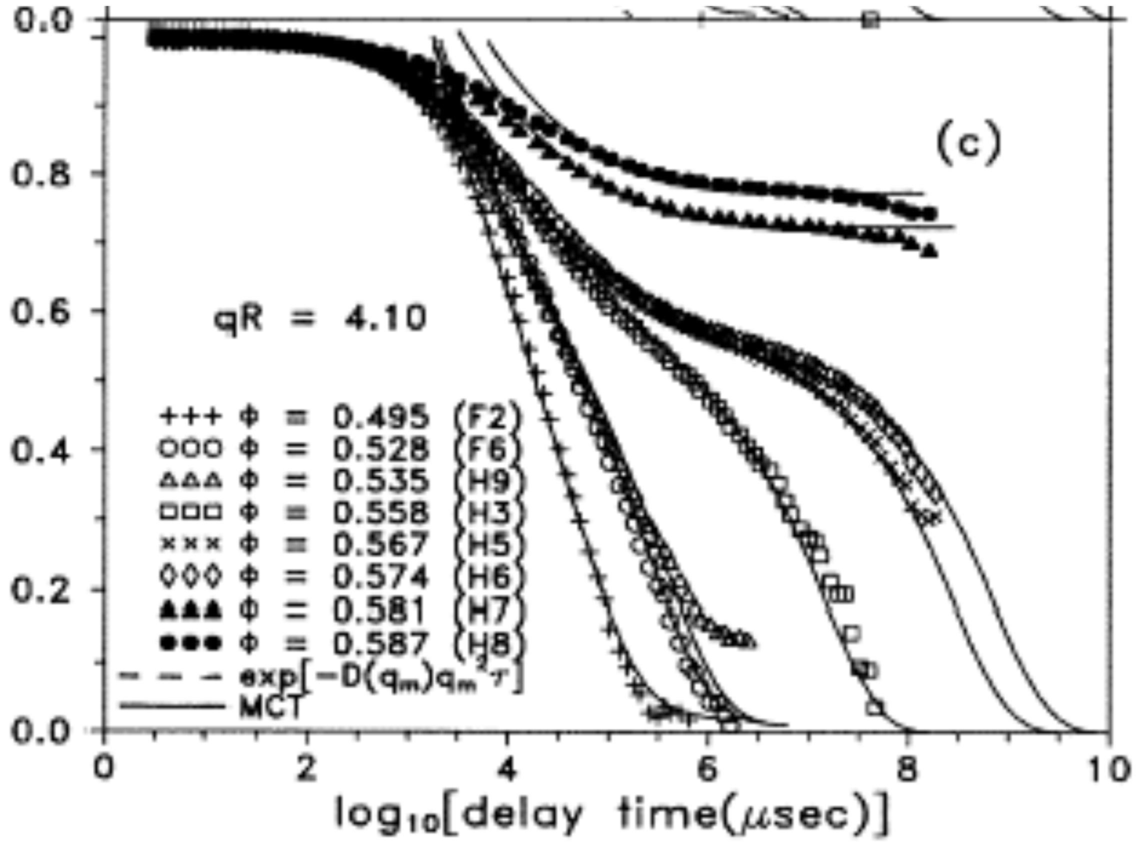
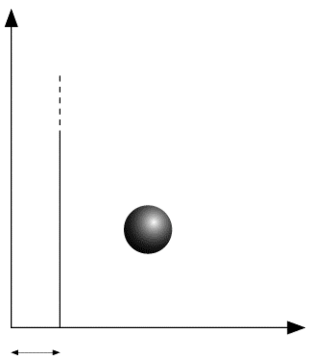
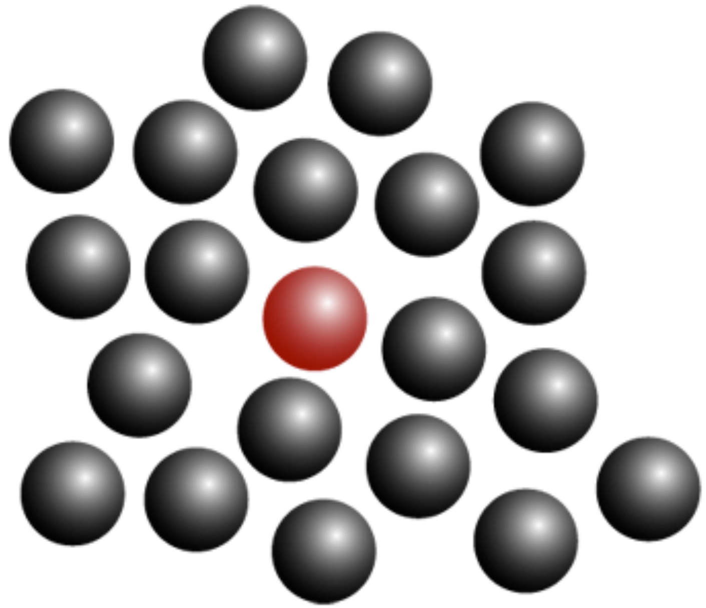


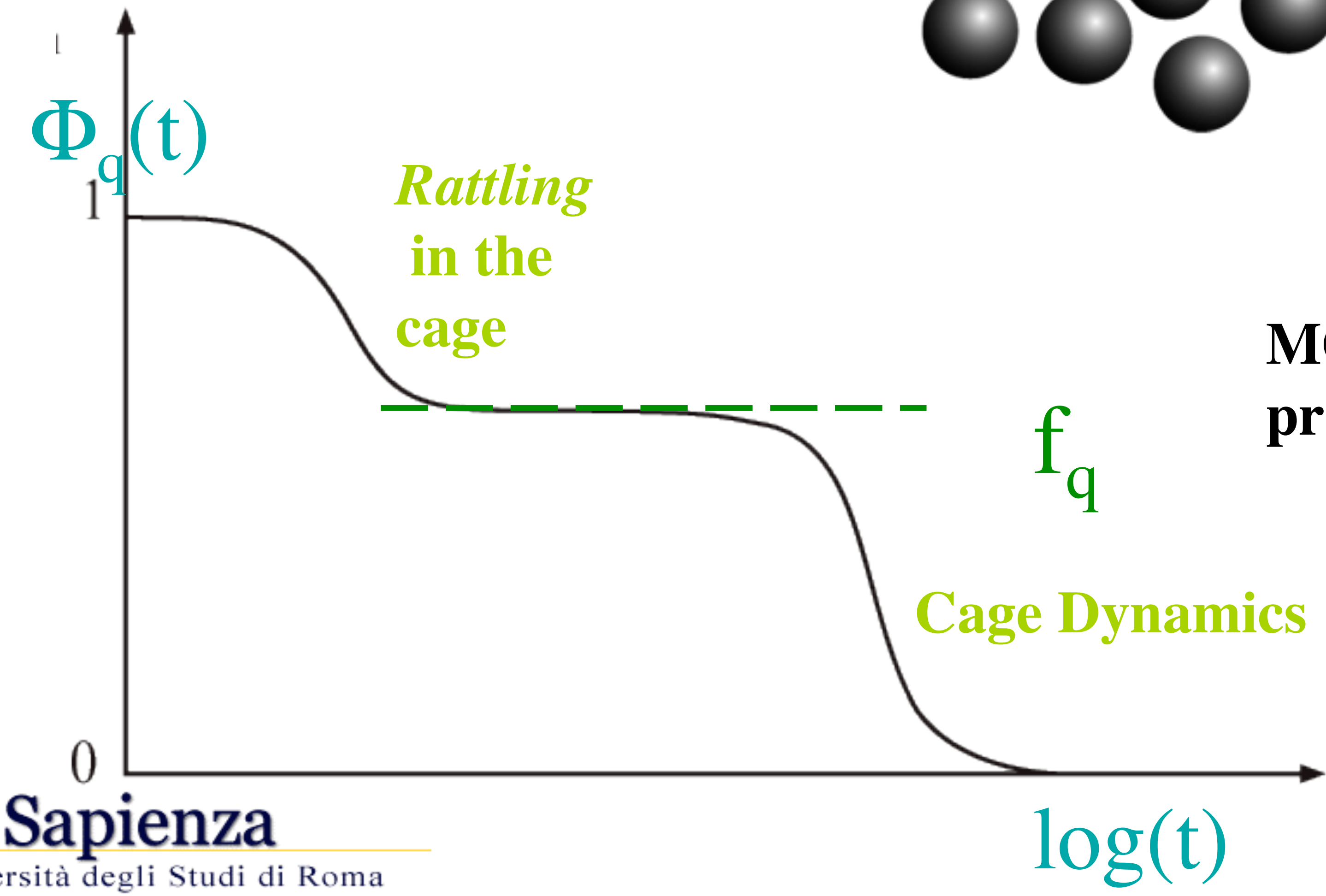
FIG. 1. Intermediate scattering functions for indicated values qR, the product of the scattering vector and the particle radius; the main maximum in $S(q)$ for the hard sphere fluid at freezing is located at $q_m R = 3.46$. The symbols refer to the experimental data for volume fractions indicated. The solid curves are the MCT fits. The dashed curve in (b) is the quantity $\exp[-q^2 D(q)\tau]$ representative of the microscopic dynamics, where $D(q)$ is the short-time q-dependent collective diffusion coefficient.

La Sapienza
Università degli Studi di R

Cage Effect







MCT predicts f_q

The MCT equations of motion (thanks Kuni !)

$$\ddot{\Phi}_q(t)+\nu_q\dot{\Phi}_q(t)+\Omega_q^2\Phi_q(t)+\Omega_q^2\int_0^t ds\, m_q(t-s)\dot{\Phi}_q(s)=0.$$

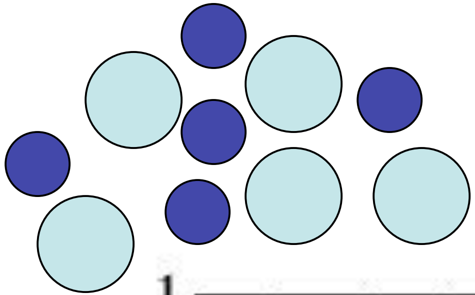
Long time limit: $\Phi(\infty)=f_q \quad \dot{\Phi}(\infty)=0 \quad \ddot{\Phi}(\infty)=0$

$$f_q + m_q(\infty)\int_0^\infty \dot{\Phi}_q(s)ds = 0$$

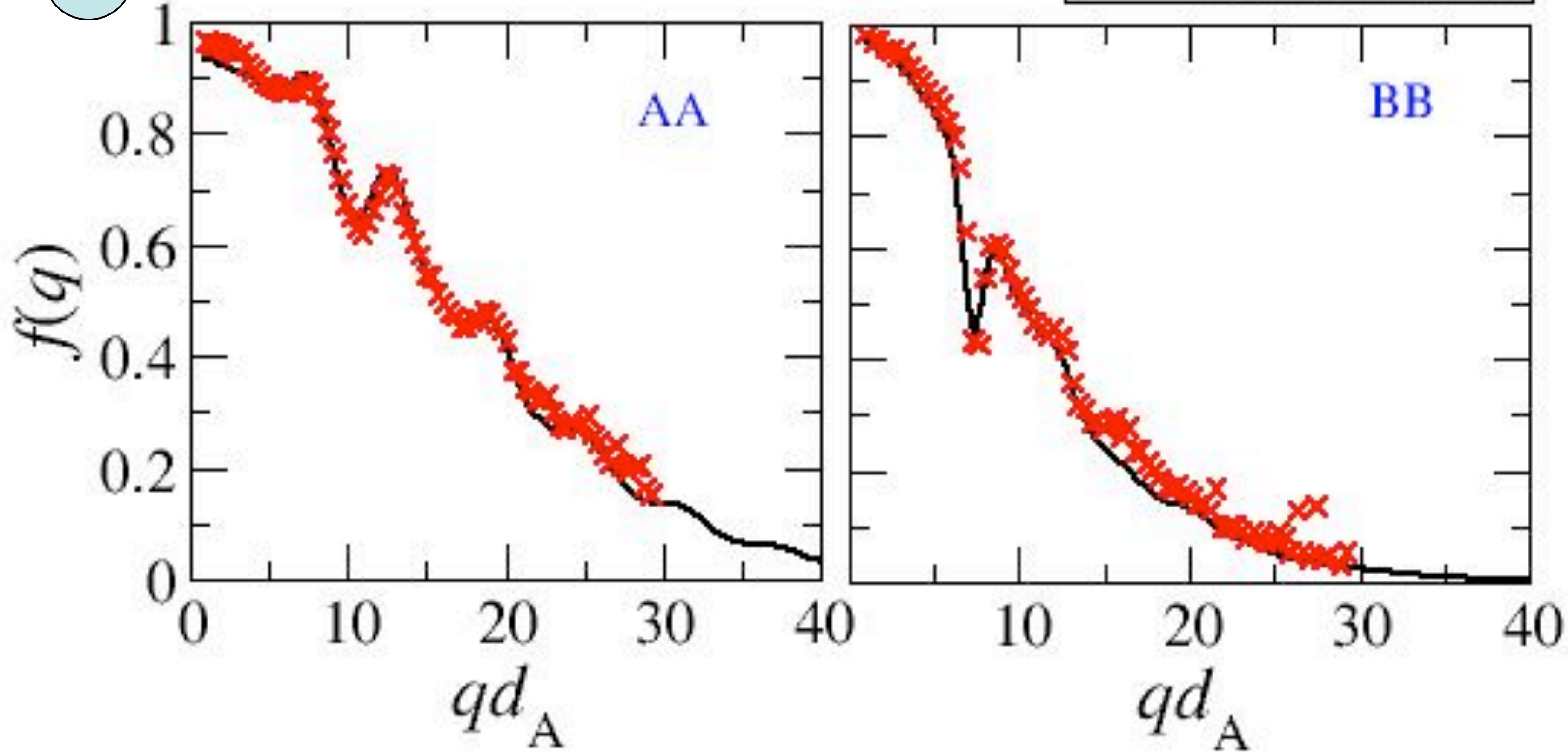
$$f_q + m_q(\infty)(f_q-1)=0$$

$$m_q(\infty)=\frac{f_q}{1-f_q} \qquad f_q=\frac{m_q(\infty)}{1+m_q(\infty)}$$

MCT --- Comparison for the non-ergodicity factore Binary HS



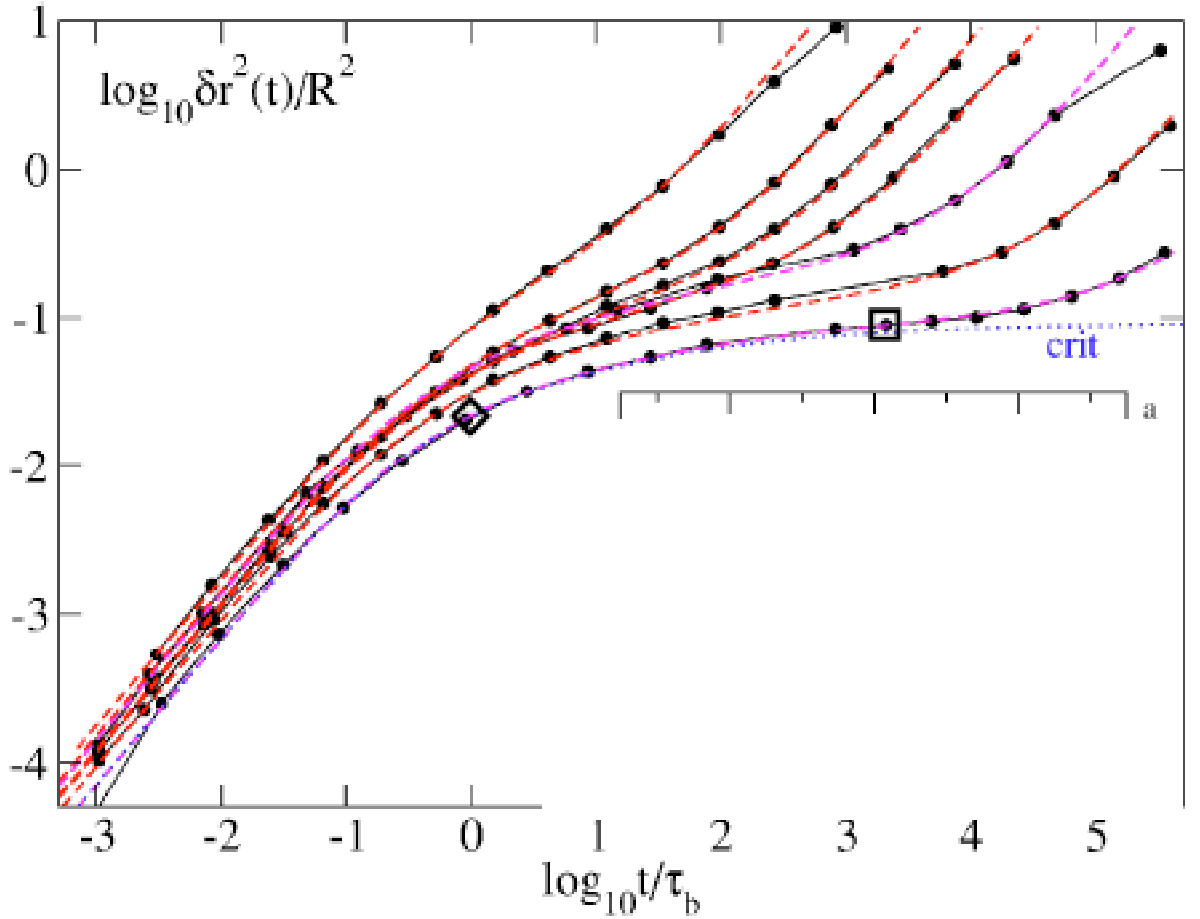
d_B=0.6d_A



Foffi et al prl 2003

The HS MSD close to the glass transition

EXP: W. van Megen et al. PRE 58, 6073 (1998) (symbols+lines)
MCT: M. Sperl, PRE 71 060401 (2005) (red dashed lines)



Cage size

FIG. 3. (Color online.) Fit of the mean-squared-displacement data from [11] (full circles and curves) by the solutions of mode-coupling theory (dashed)

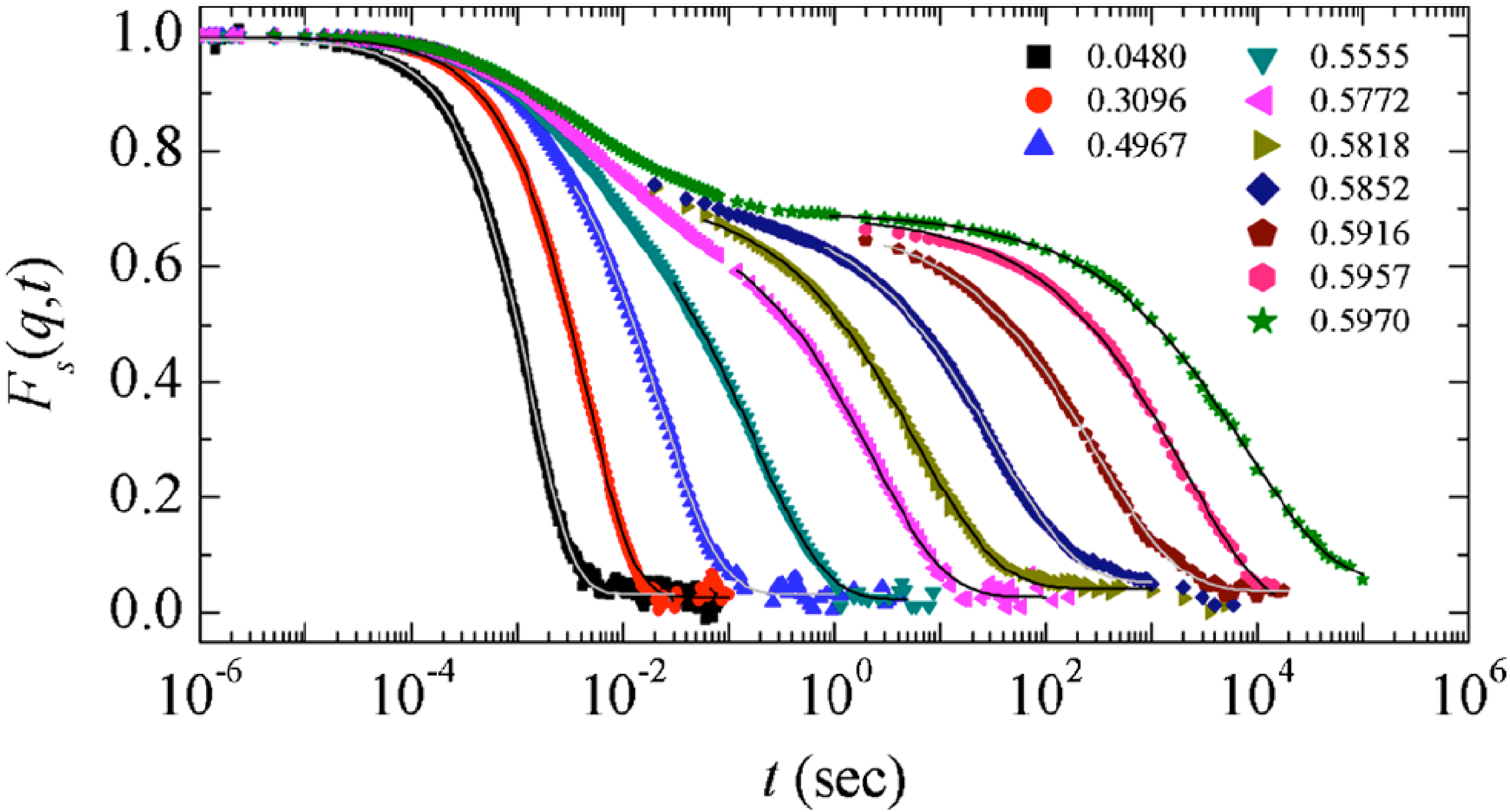
La S
Univer

Probing the Equilibrium Dynamics of Colloidal Hard Spheres above the Mode-Coupling Glass Transition

Brambilla et al. PRL **102**, 085703 (2009)

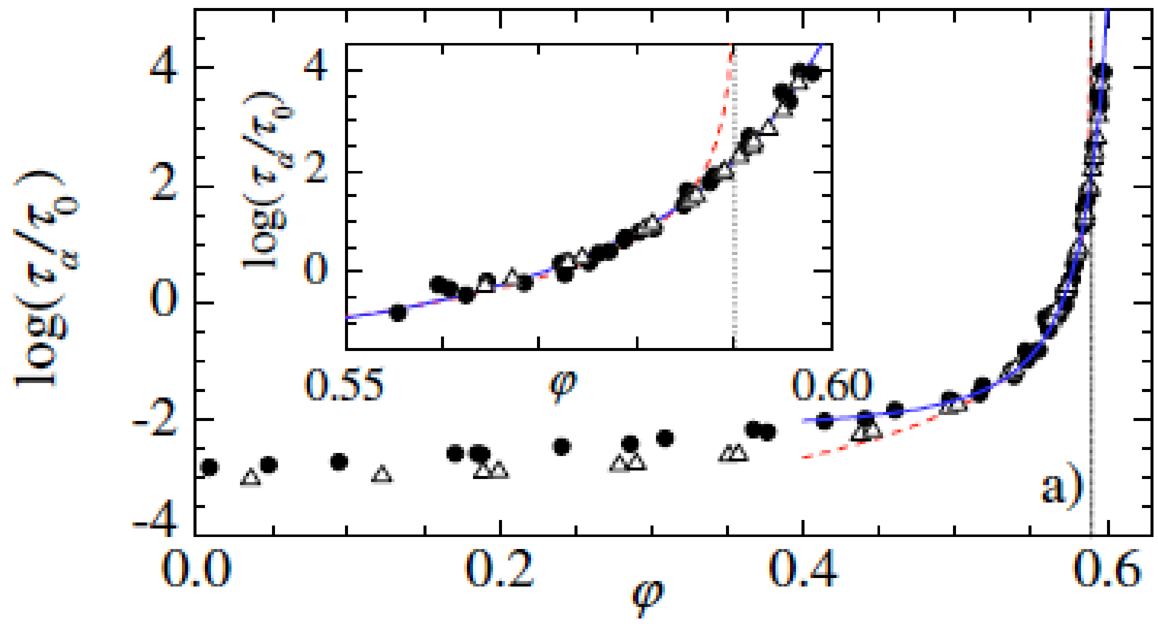
PMMA 260 nm (grafted polymer)

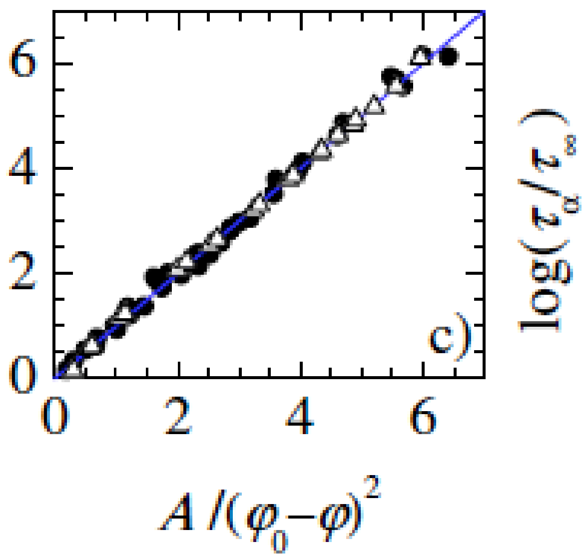
10 % polidispersity (no cryst over several months)



Brambilla et al. PRL **102**, 085703 (2009)

Exp and MC simul





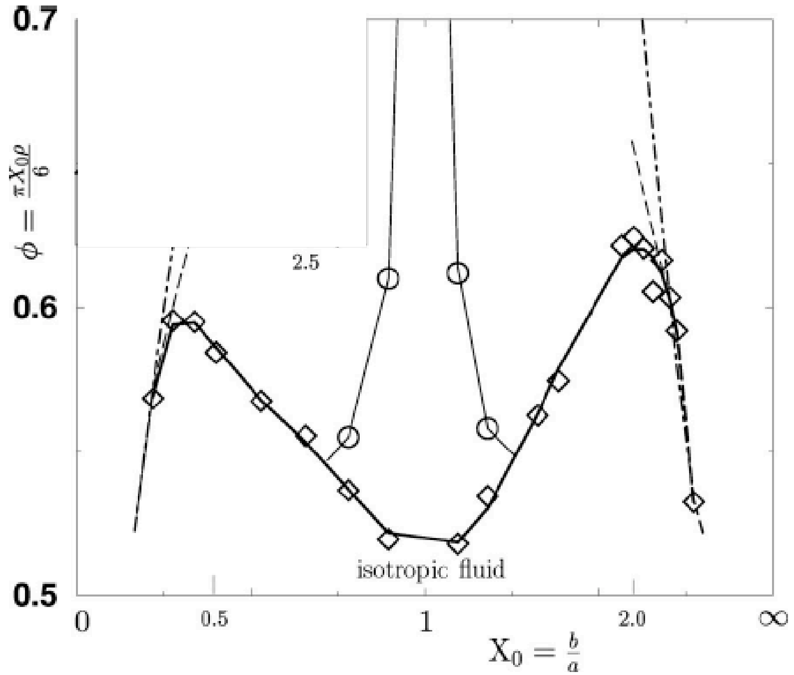
$$\tau_\alpha(\varphi) = \tau_\infty \exp\left[\frac{A}{(\varphi_0 - \varphi)^\delta}\right]$$

$$\delta = 2.0 \pm 0.2$$

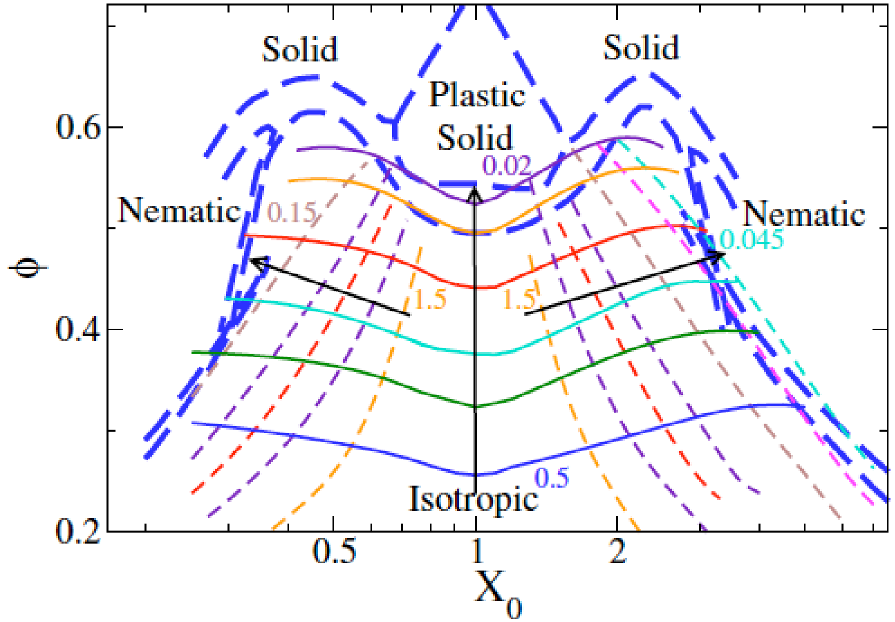
$$\varphi_0 \approx 0.637 \pm 0.002$$

Other
hard
bodies…

Letz et al. PRE 62 5173

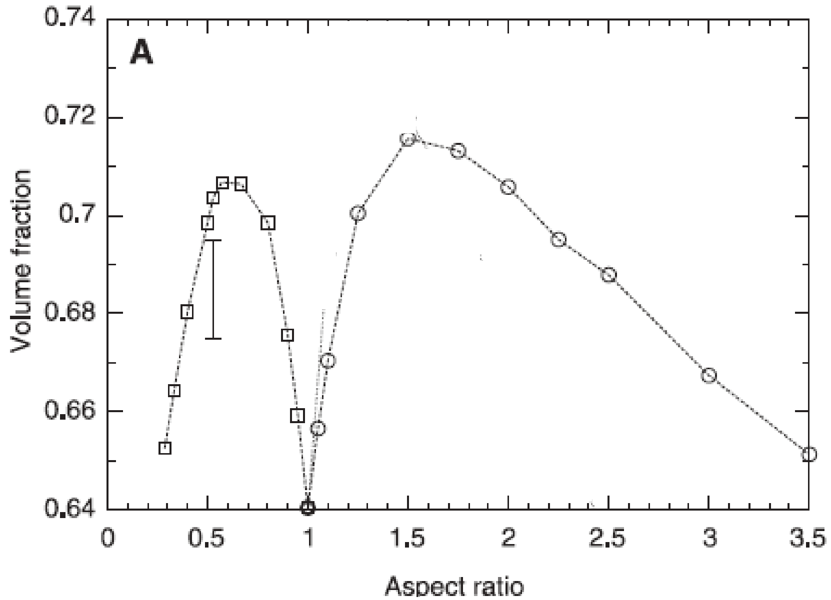


De Michele et al.
PRL **98,** 265702 (2007)



Donev et al

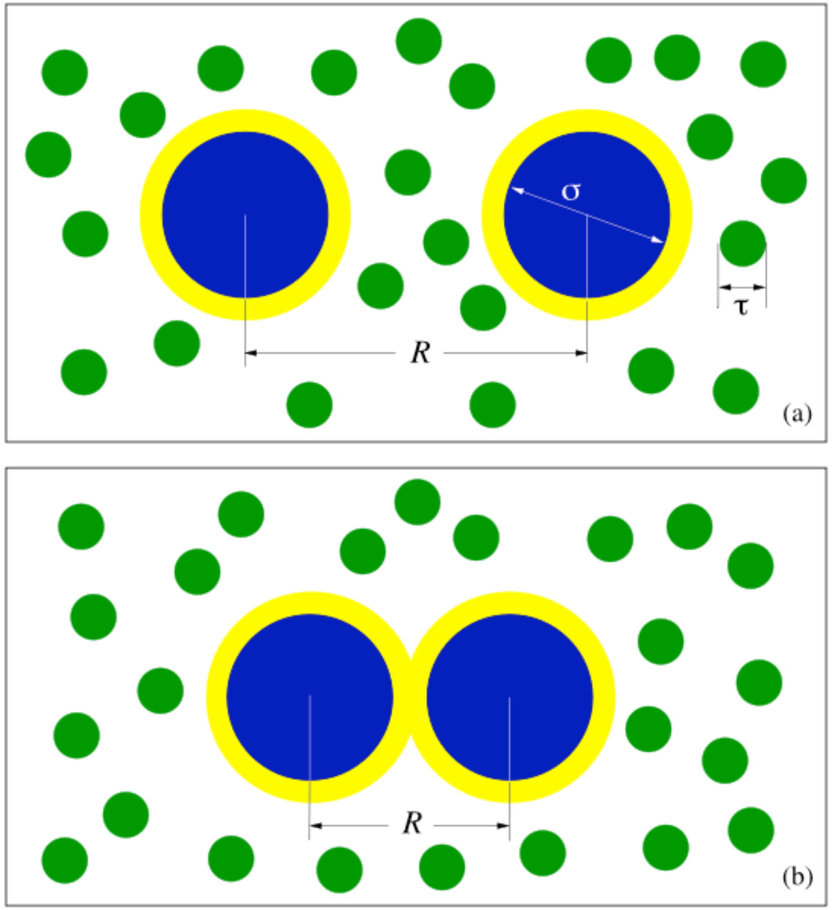
Science **303**, 990 (2004);



See also works on dumbbell (Chong, Moreno..)

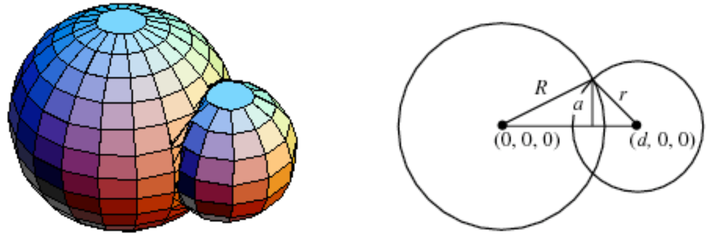
Adding Attractions between Colloids

Depletion Interactions



Sphere-Sphere Intersection

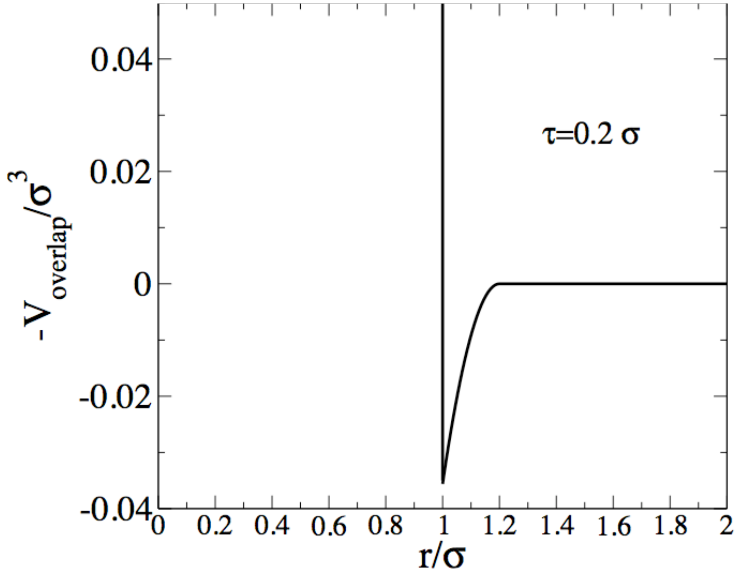
DOWNLOAD *Mathematica* Notebook



Letting $R_1 = R$ and $R_2 = r$ and summing the two caps gives

$$V = V(R_1, h_1) + V(R_2, h_2) = \frac{\pi (R + r - d)^2 \left(d^2 + 2\,d\,r - 3\,r^2 + 2\,d\,R + 6\,r\,R - 3\,R^2\right)}{12\,d}.$$

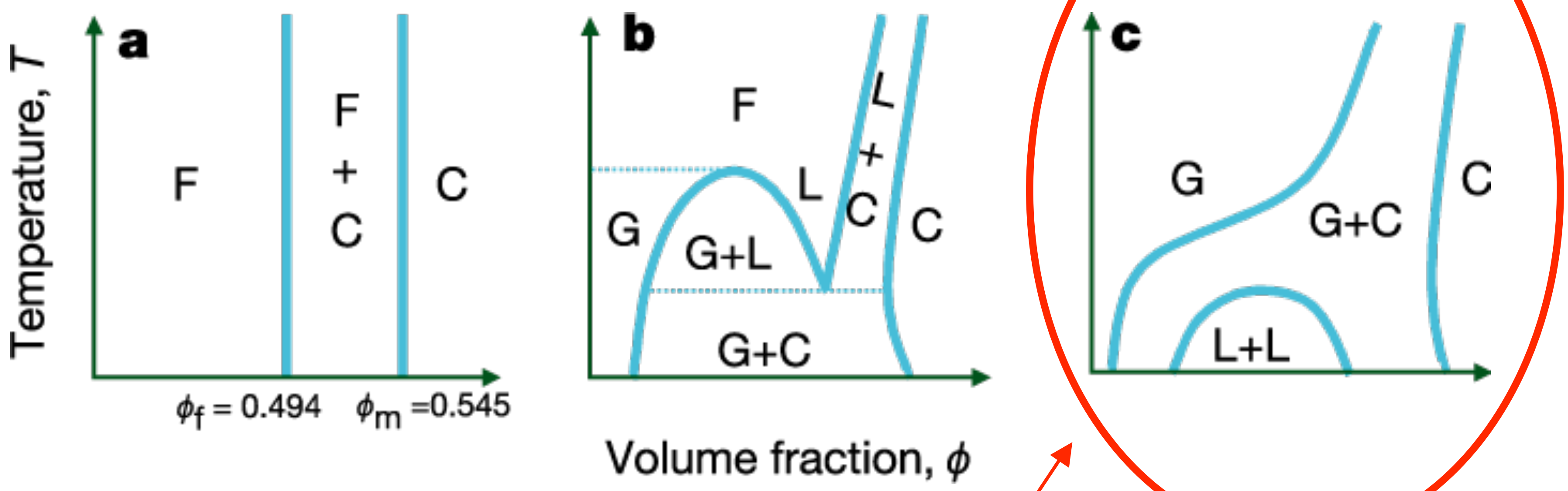
$$V_{overlap} = \frac{\pi}{12}[2(\sigma + \tau) + r)][(\sigma + \tau) - r]^2$$



$$u(r) = \begin{cases} \infty & 0 < r < \sigma \\ -\Pi V_{overlap} & \sigma < r < \sigma + \tau \\ 0 & r > \sigma + \tau \end{cases}$$

Phase diagram of spherical potentials -role of the range

Hard-Sphere | **Large Range** | **Short Range**



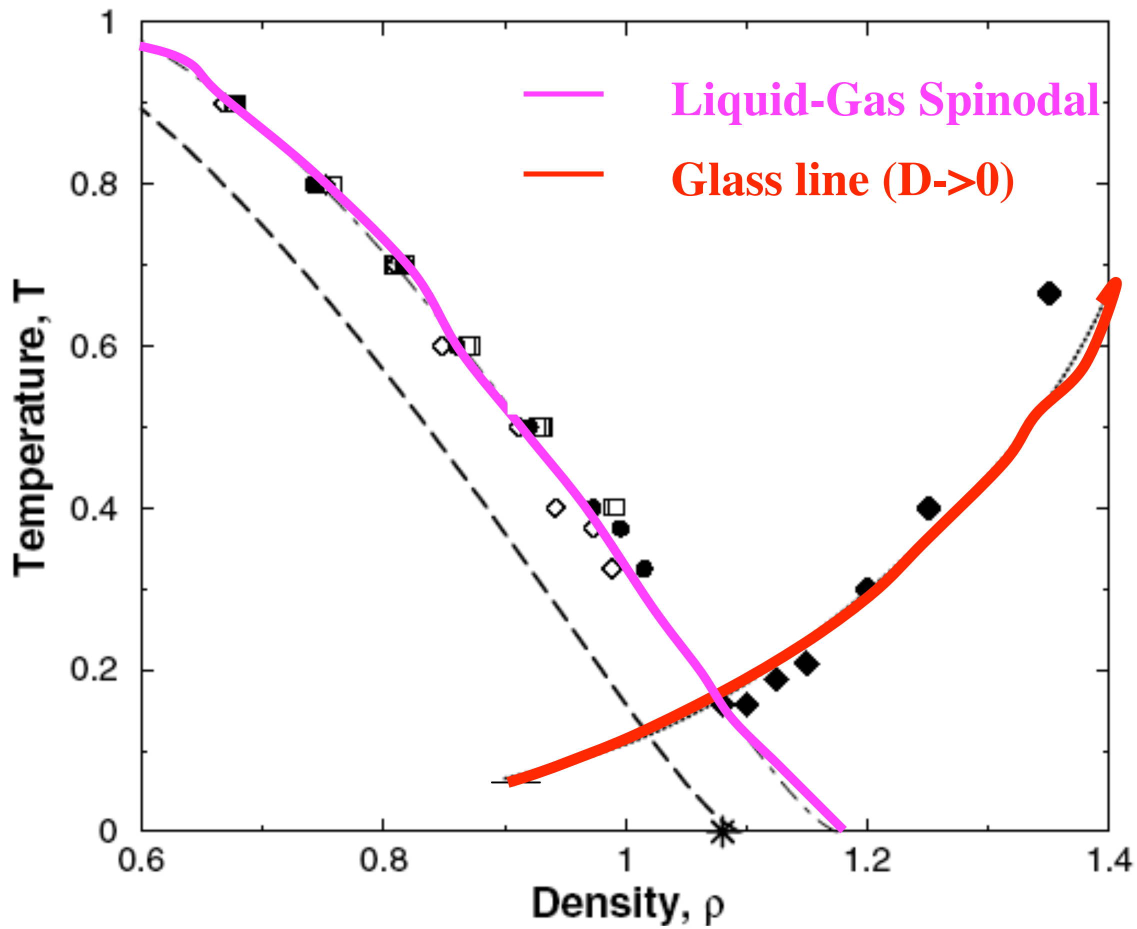
V.J. Anderson and H.N.W. Lekkerkerker *Nature* **416**, 811 (2002)

Interplay between glass formation and phase separation

Possible with proteins and colloids

La Sapienza
Università degli Studi di Roma

erc



What happen to the glass line with attractions ?

Binary Mixture LJ particles

“*Equilibrium*”
“homogeneous”
arrested states only for large packing fraction

VOLUME 85, NUMBER 3 PHYSICAL REVIEW LETTERS 17 JULY 2000

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)

erc

spherical potentials*

(excluding crystals)

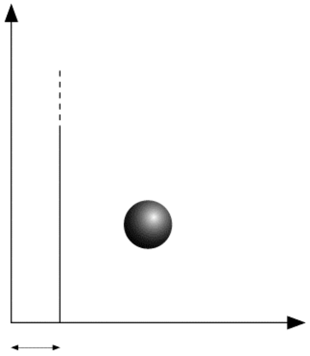
$0.13<\phi_c<0.27$

*One component, "Hard-Core" plus attraction

Do we see the same with colloids ?

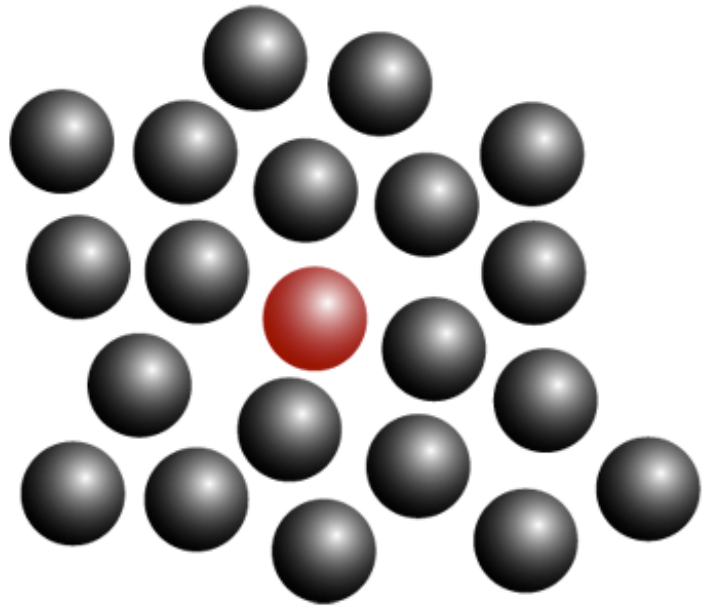
Adding to HS a short-range attraction….

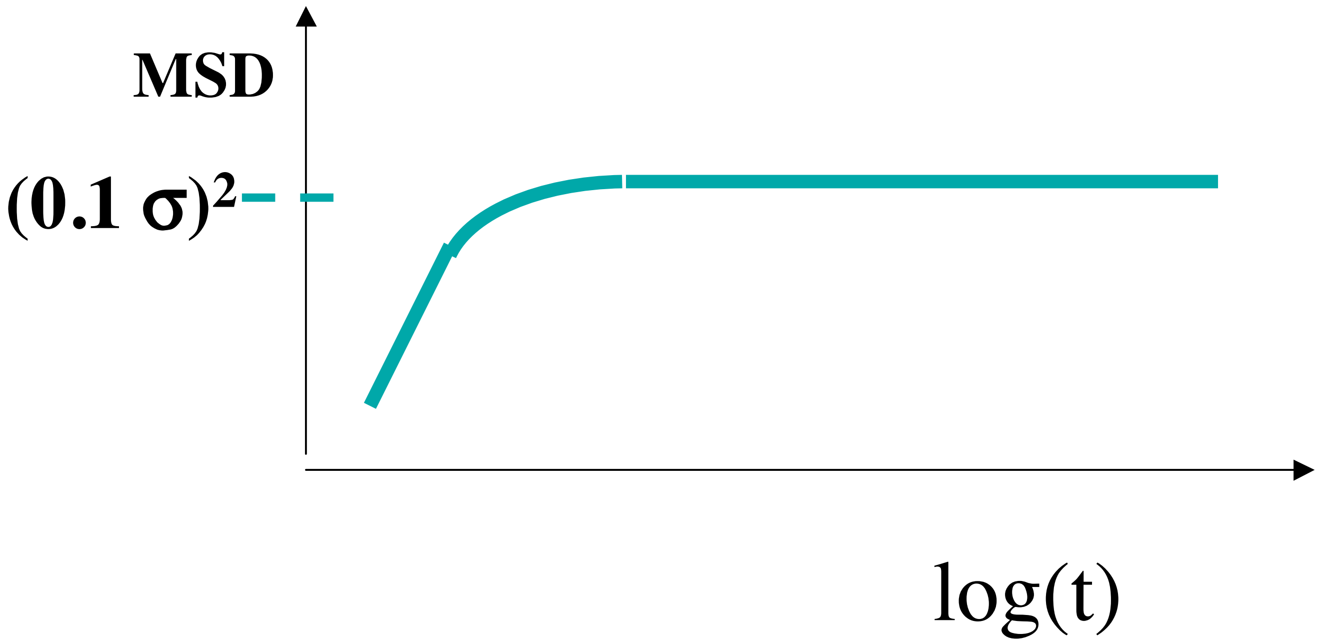
(play with T [polymer depletant] in addition to ϕ)



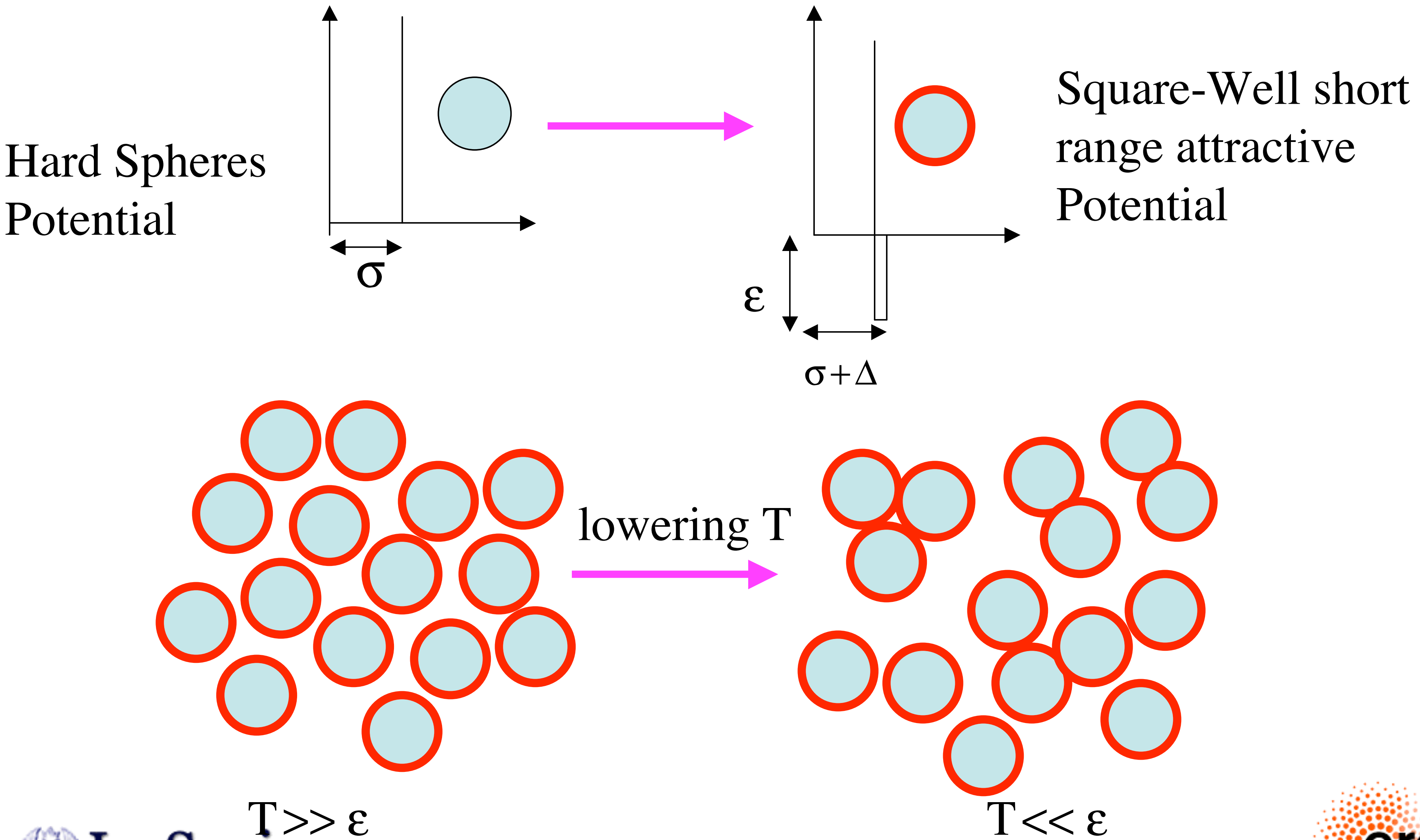
Quadratic mean square displacement

(in the glass)



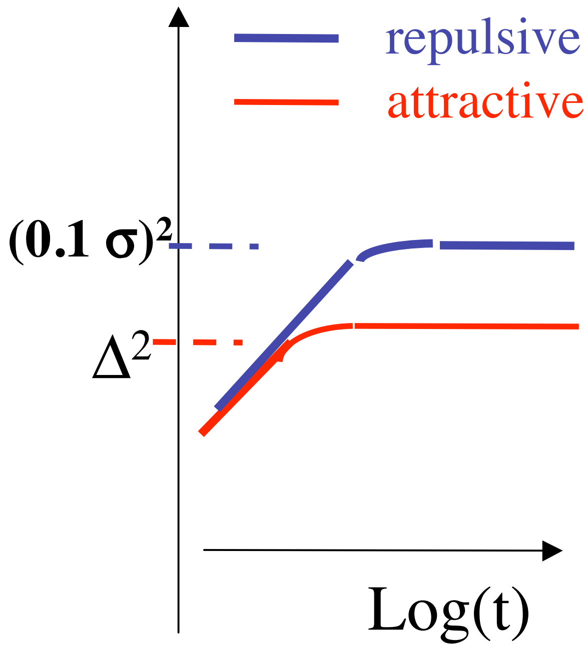


Adding a short-range attraction



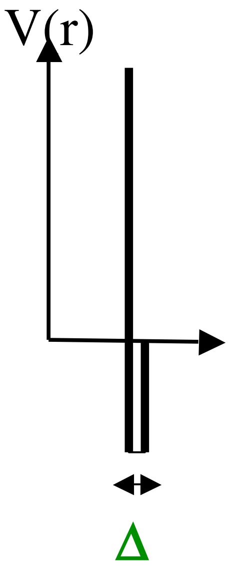
La Sapienza
Università degli Studi di Roma

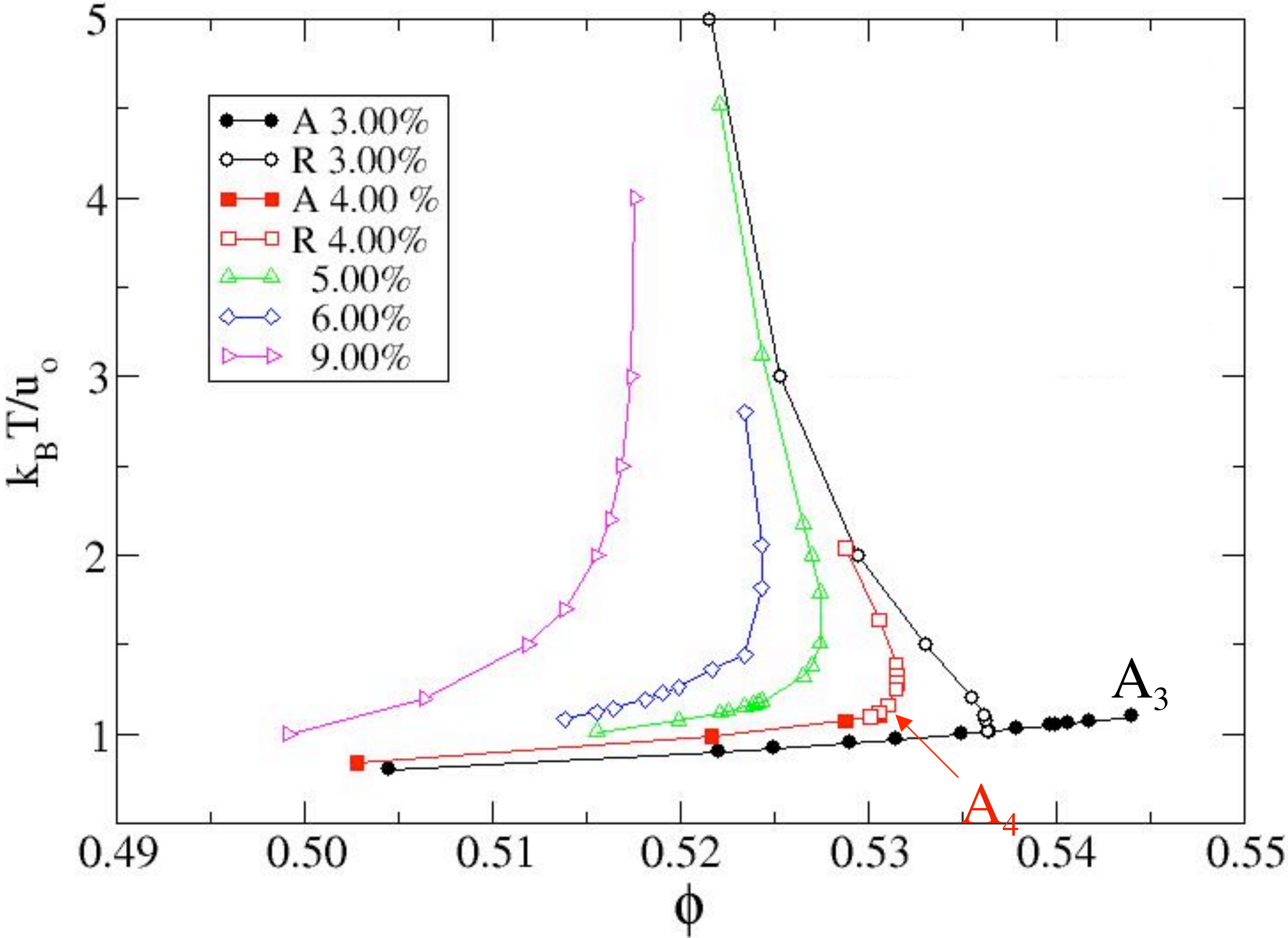
Mean squared displacement



How does the system change from one (glass) to the other one ? Let's ask MCT.

MCT IDEAL GLASS LINES (PY) - SQUARE WELL MODEL - CHANGING Δ

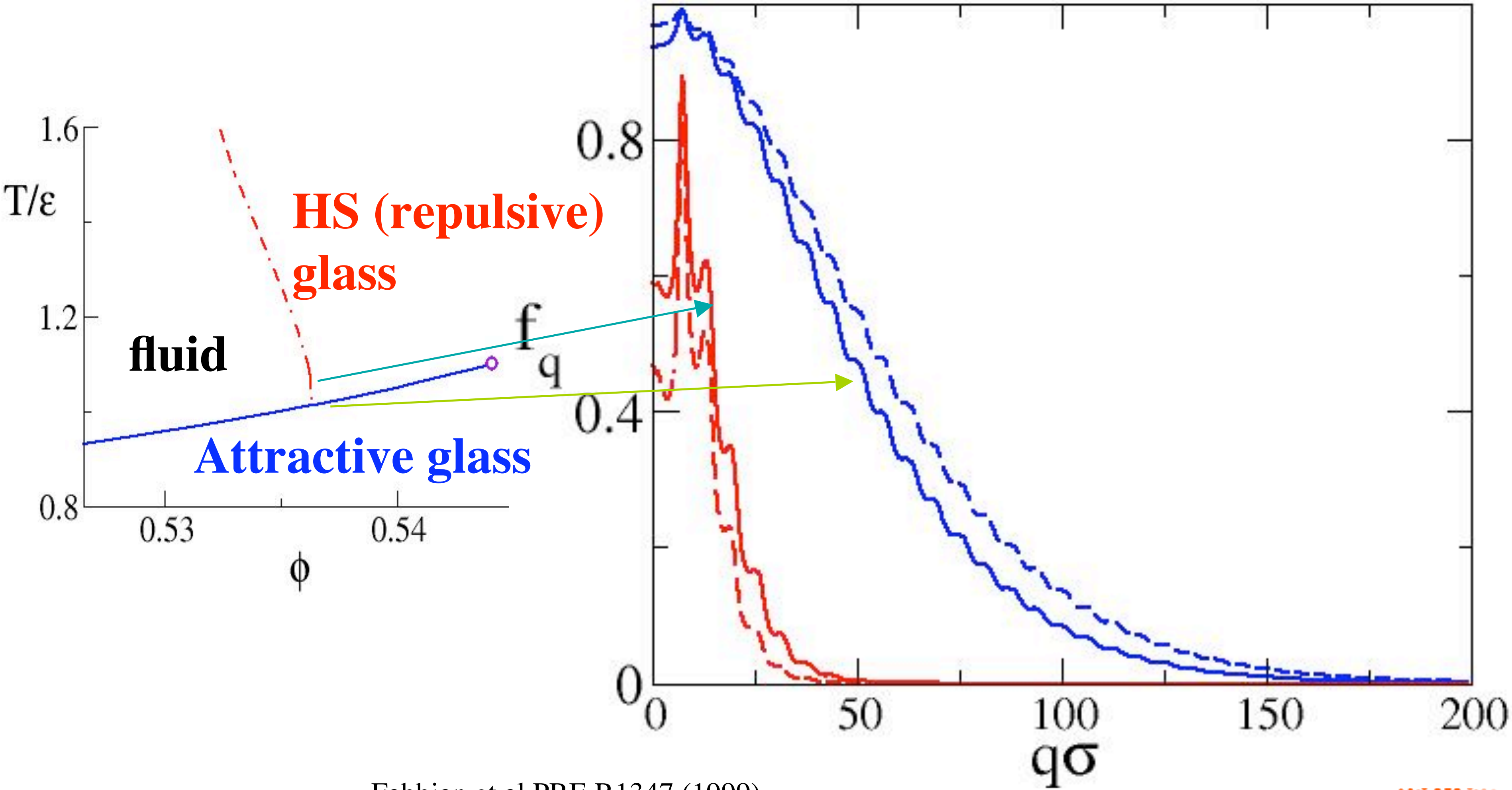




La Sapienza
Università degli Studi di Roma

PRE-63-011401-2001

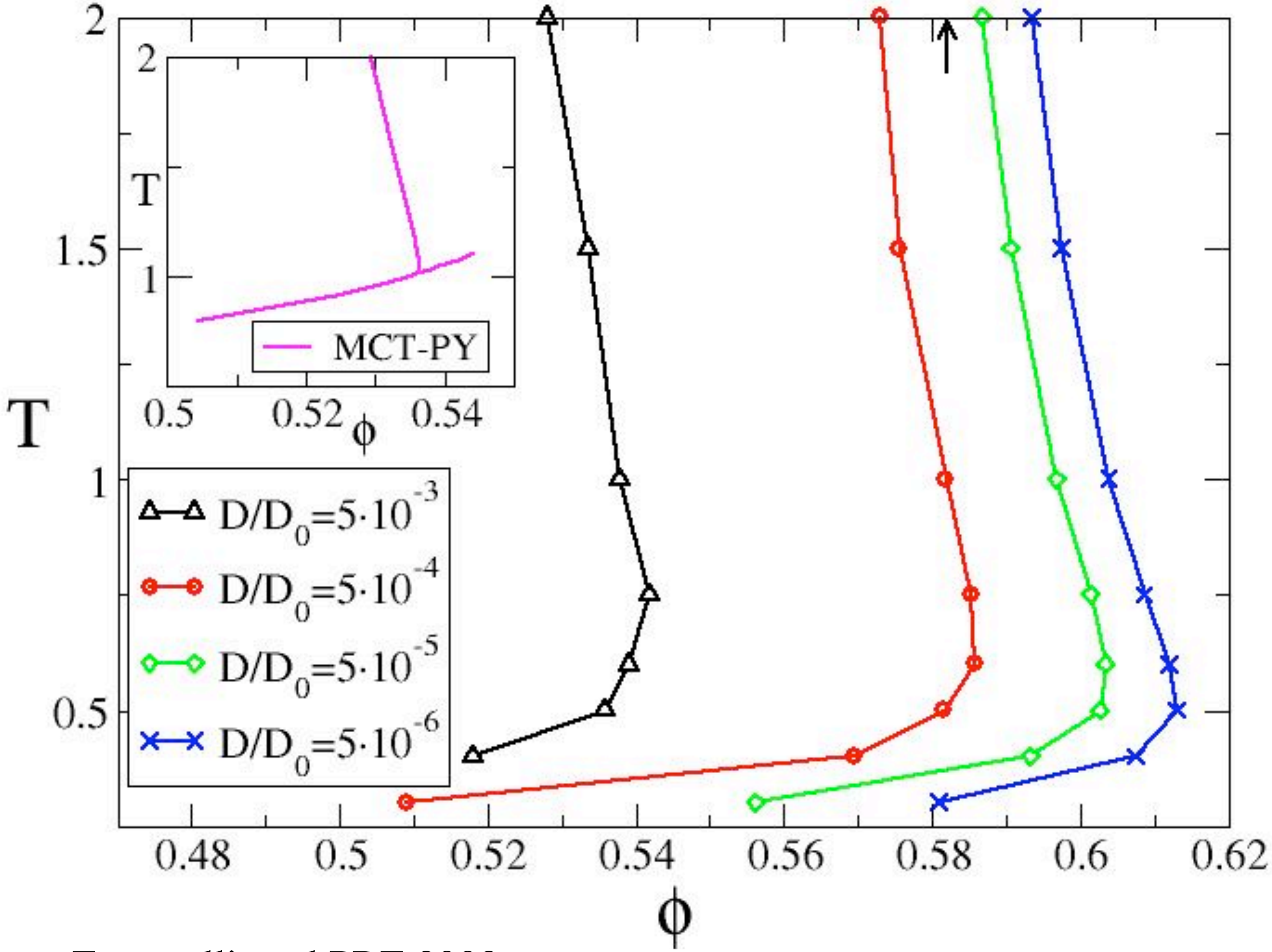
MCT Predictions:
Wavevector dependence of the non ergodicity parameter (plateau) along the glass line



Fabbian et al PRE R1347 (1999)
Bergenholtz and Fuchs, PRE 59 5708 (1999)

La Sapienza
Università degli Studi di Roma

Isodiffusivity curves (Event Driven MD)

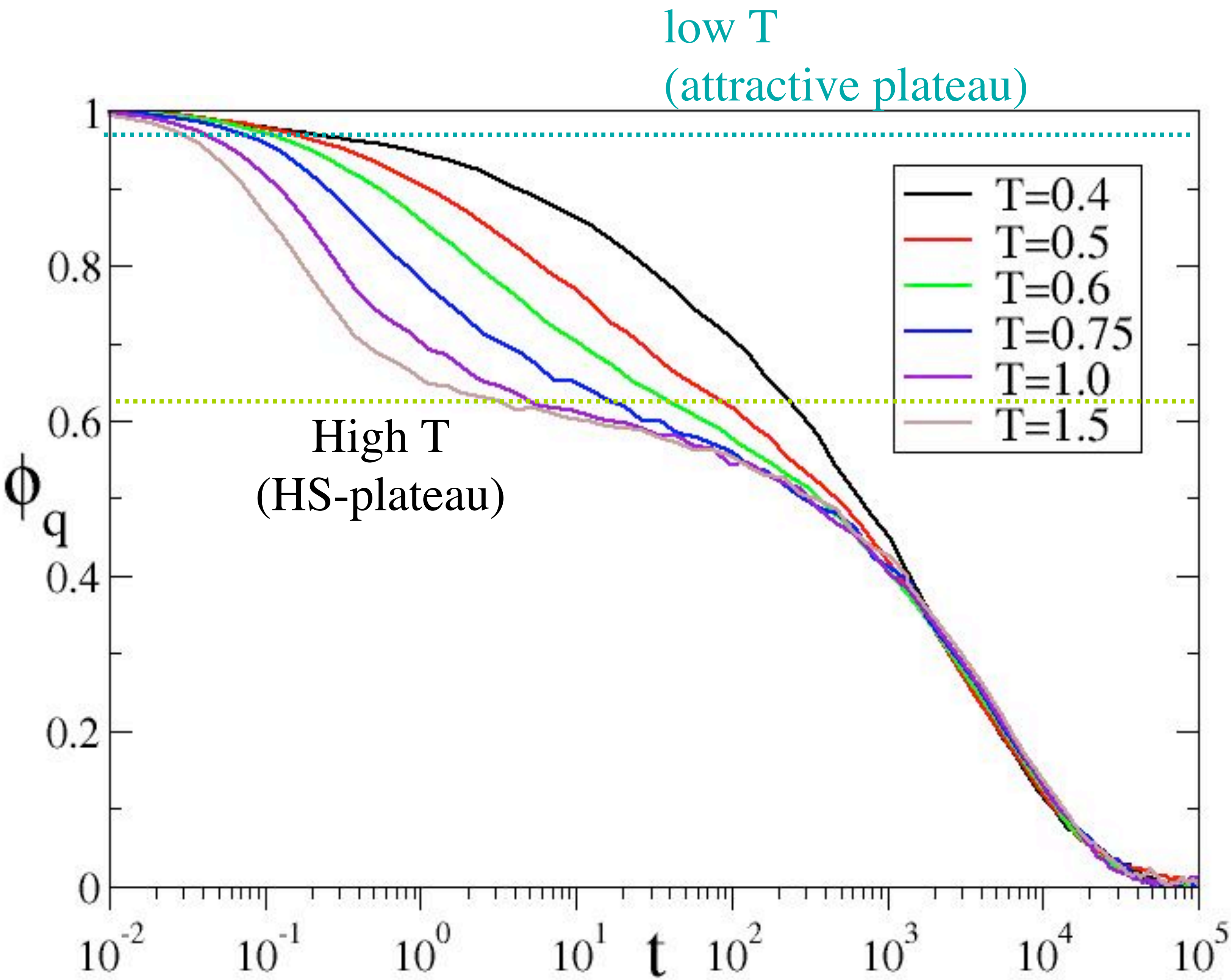


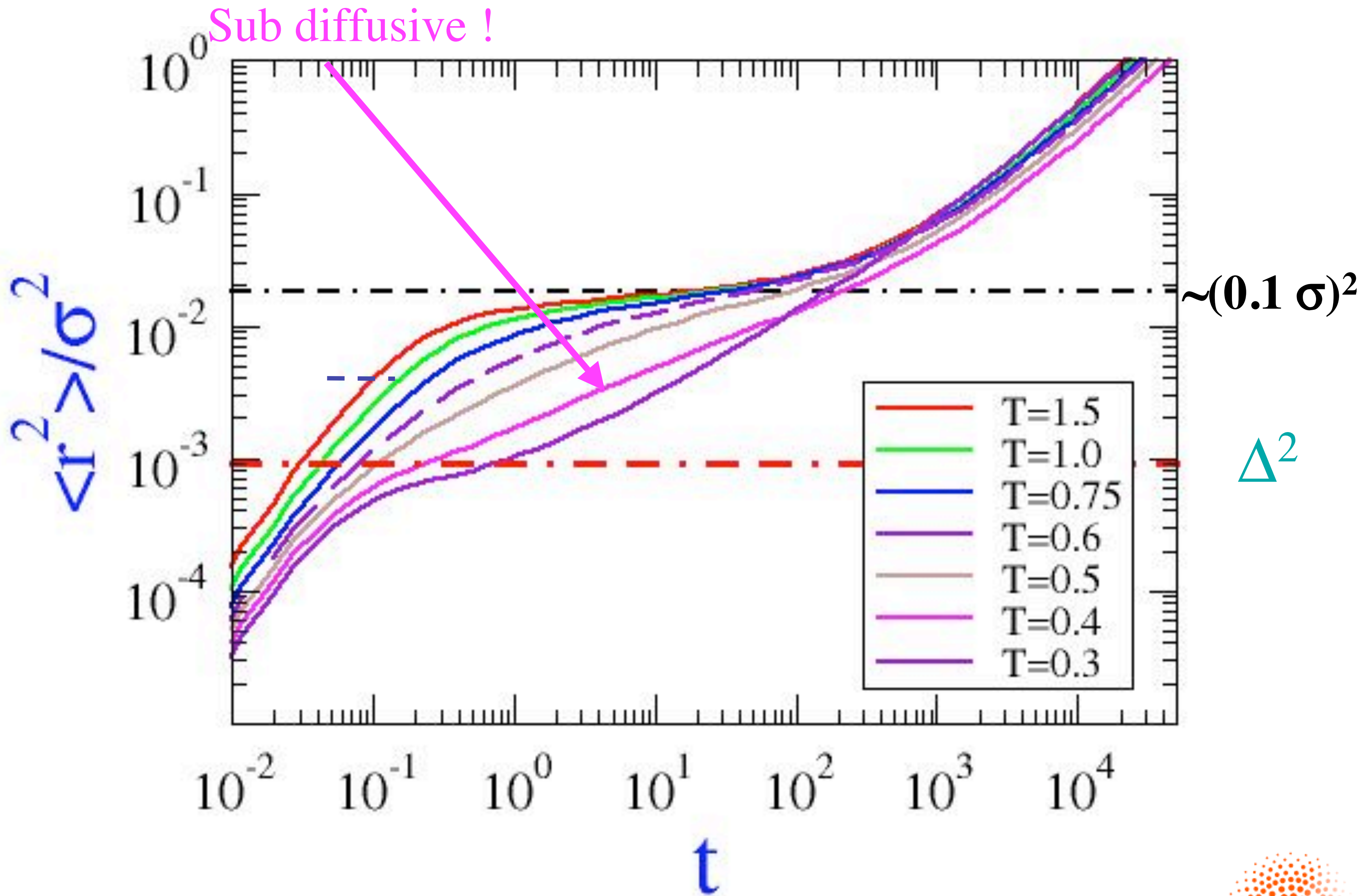
Zaccarelli et al PRE 2002

La Sapienza
Università degli Studi di Roma

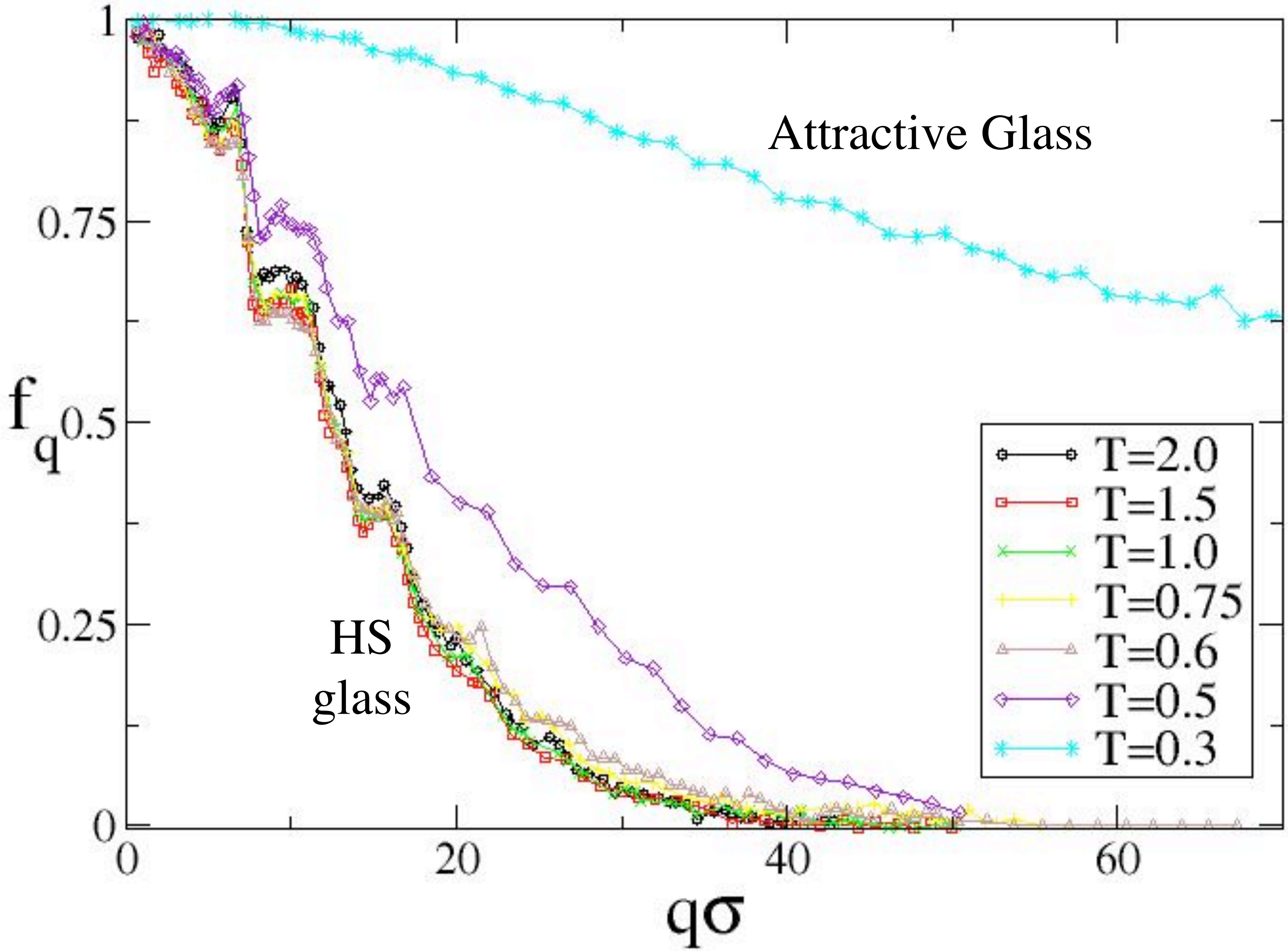
erc

Decay of correlation along an isochrone





La Sapienza
Università degli Studi di Roma

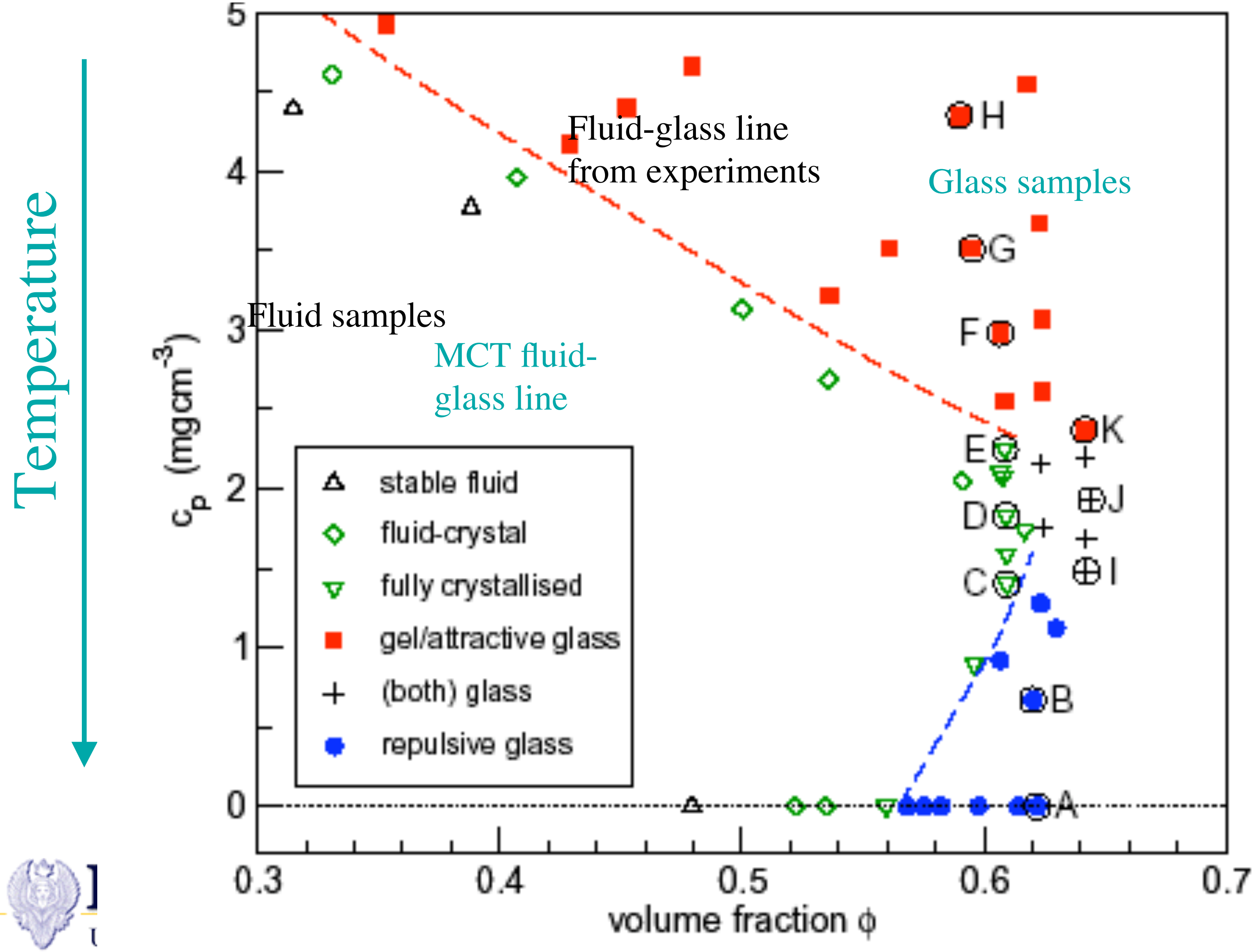


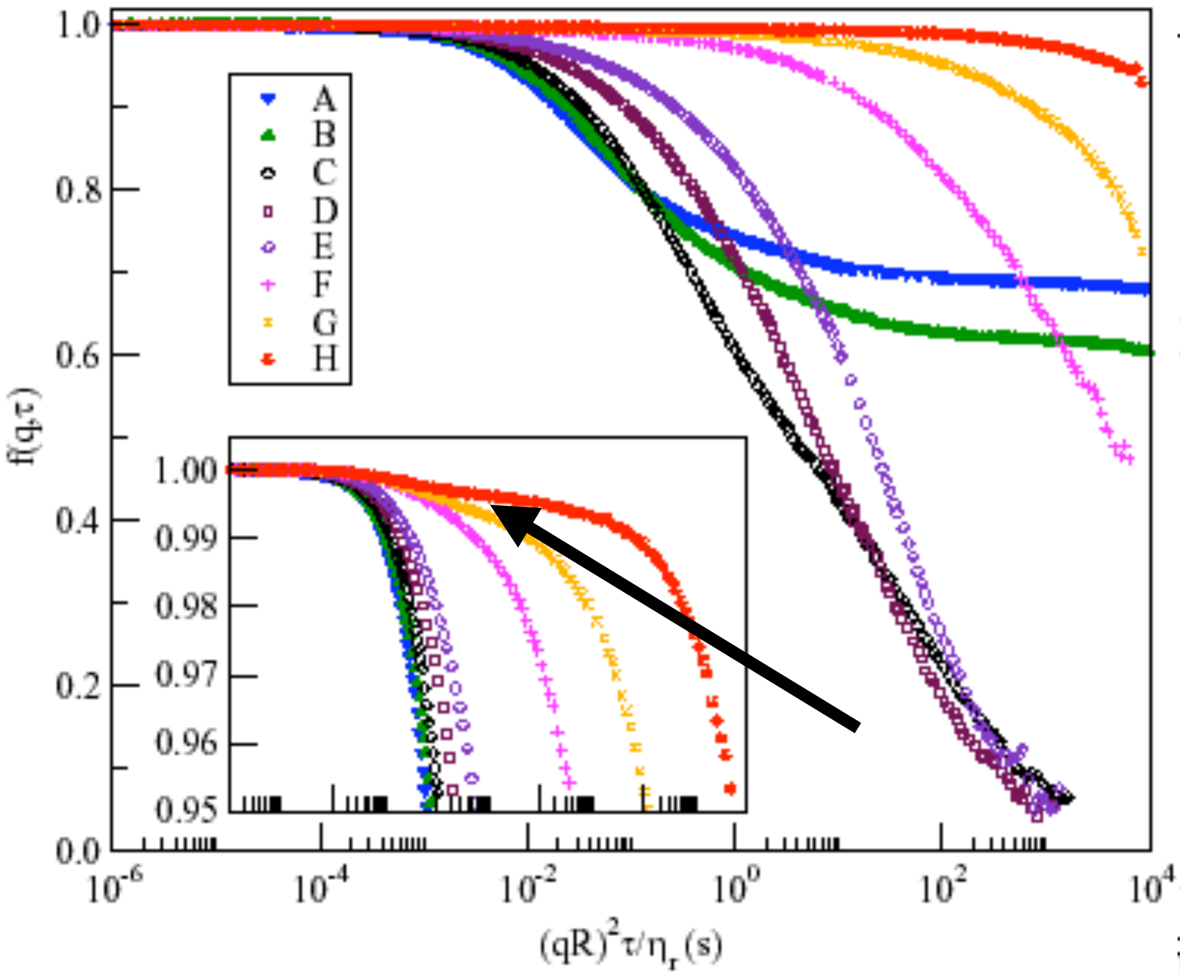
Attractive Glass
HS
glass
T=2.0
T=1.5
T=1.0
T=0.75
T=0.6
T=0.5
T=0.3
f_q
$q\sigma$
0
0.25
0.5
0.75
1
0
20
40
60

Experimental Verifications

Multiple Glassy States in a Simple Model System

N. Pham,[1] A. M. Puertas,[1,2] J. Bergenholtz,[3] S. U. Egelhaaf,[1]
A. Moussaïd,[1] P. N. Pusey,[1] A. B. Schofield,[1] M. E. Cates,[1]
M. Fuchs,[1] W. C. K. Poon[1*]





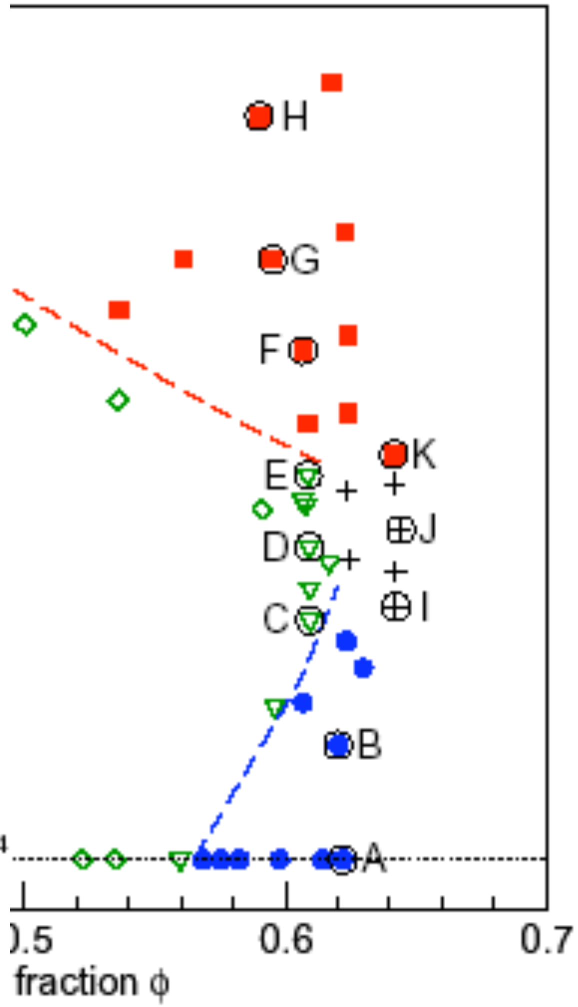
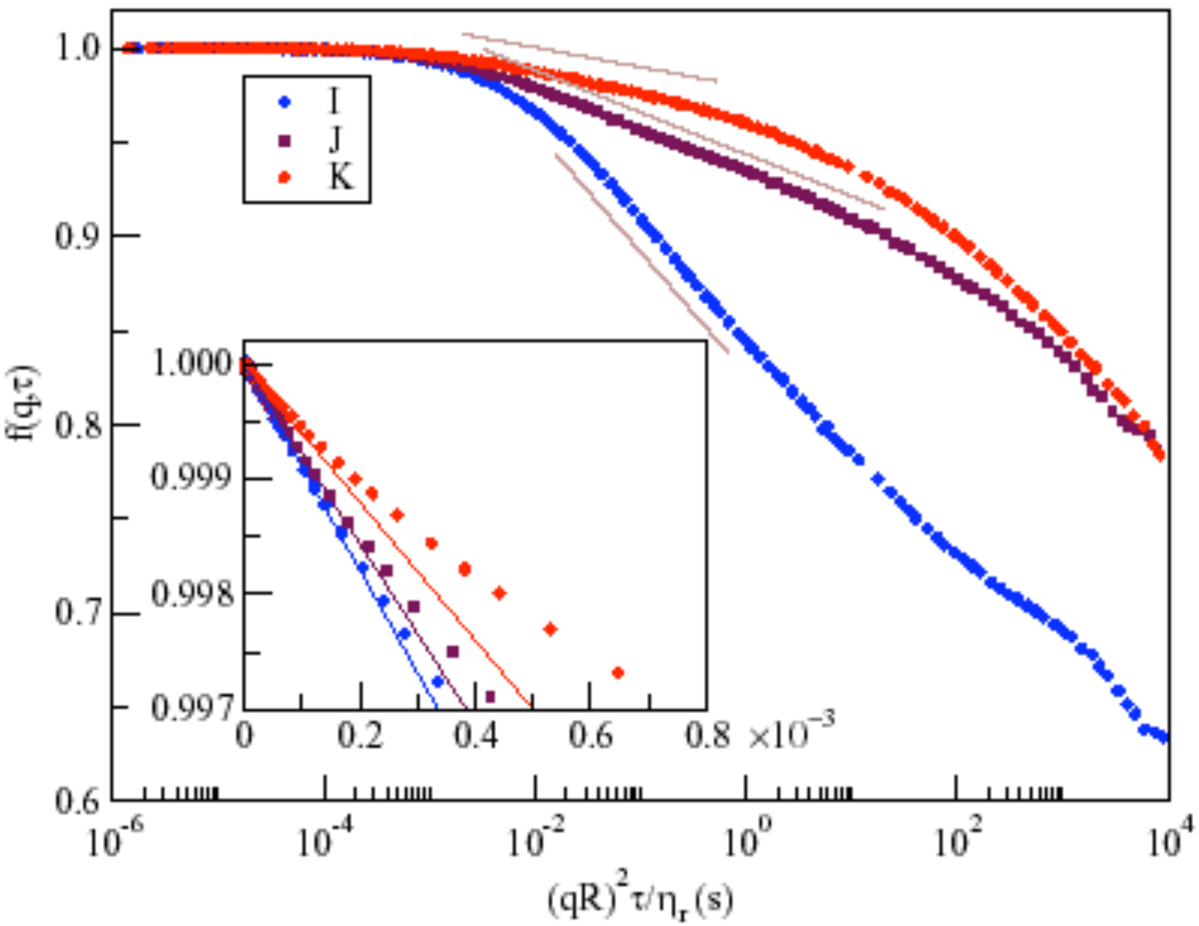


FIG. 6: Collective dynamic structure factors at $qR = 1.50$ from samples A–H spanning the re-entrant region. The time axis is scaled to dimensionless length scale $(qR)^2$ and relative polymer solution viscosity η_r. The inset shows the same plots on an expanded vertical axis.

La Sapienza
Università degli Studi di Roma

erc



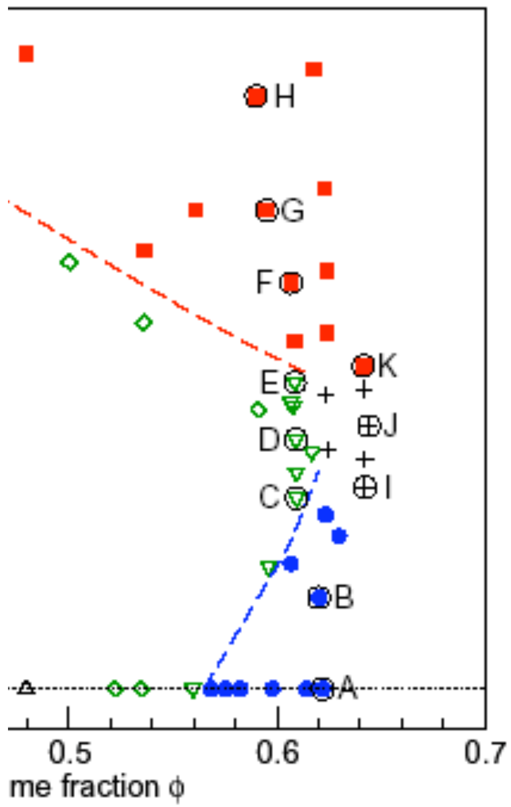
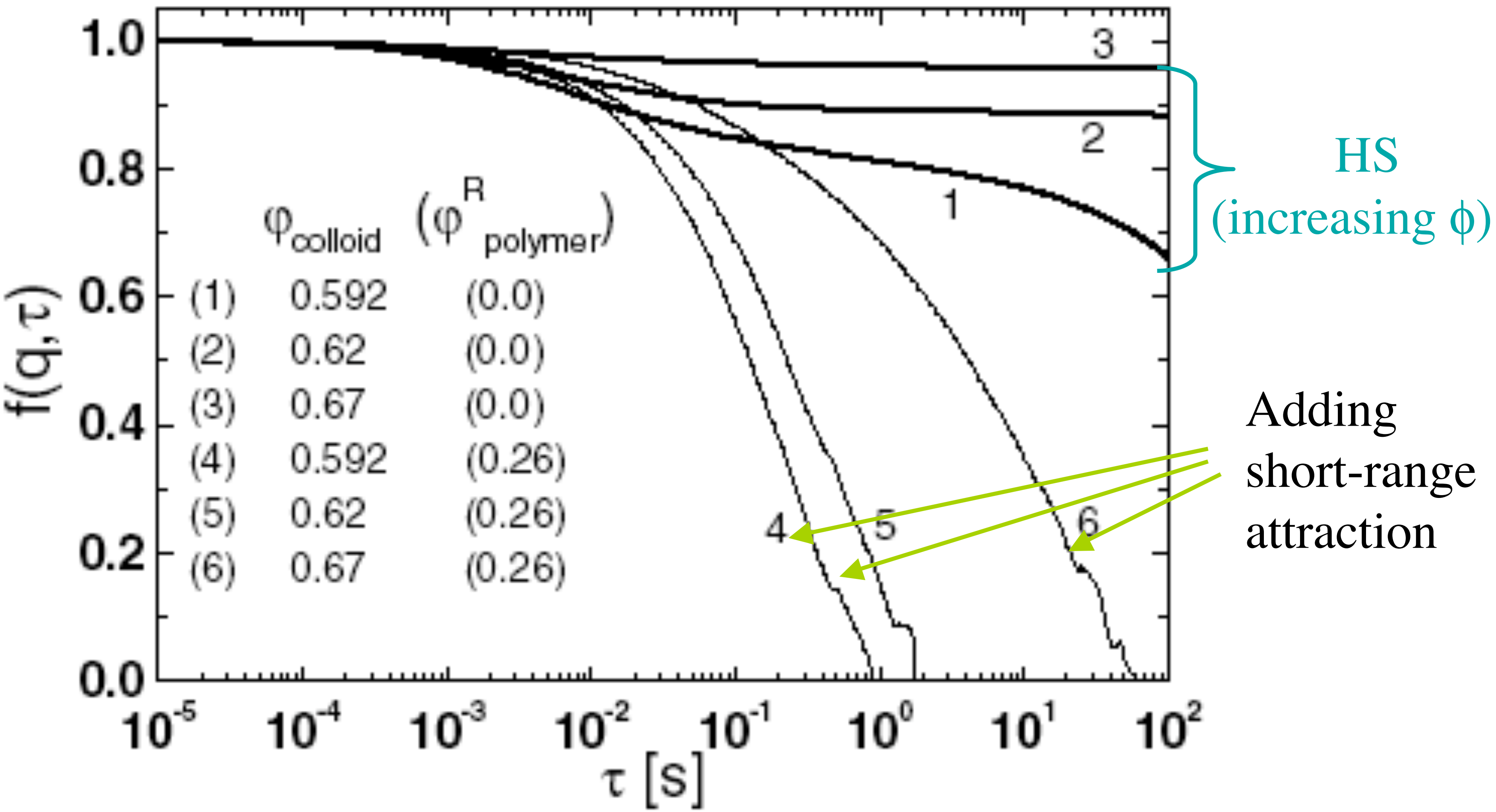


FIG. 12: The DSFs at $qR = 1.50$ for samples I–K with $\phi \sim 0.64$. Extremely stretched relaxation is found in all three samples with logarithmic decay over long ranges of τ (straight lines). The inset shows the short-time dynamics, which deviate from the diffusive regime from very early times.



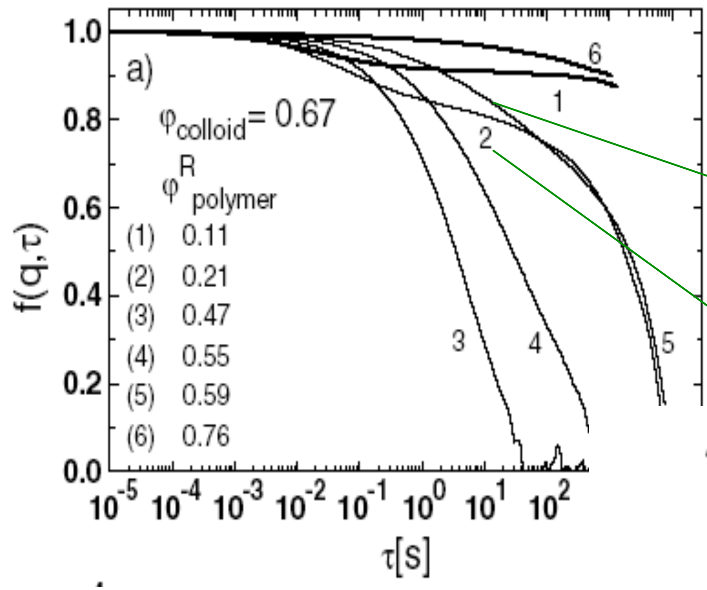
T. Eckert and E. Bartsch

Colloidal-Polymer Mixture with Re-entrant Glass Transition in a Depletion Interactions

Phys.Rev. Lett. 89 125701 (2002)

FIG. 1. Comparison of the density autocorrelation functions $f(q, \tau)$ of a hard sphere colloidal suspension (see text) before (thick solid lines) and after (thin solid lines) the addition of linear polymer chains (size ratio $\delta = R_{g,\text{polymer}}/\langle R_{\text{colloid}}\rangle = 0.054$). The colloid volume fractions of each set of $f(q, \tau)$ increase from left to right as indicated in the figure. The dynamics is probed at a scattering vector corresponding to the peak maximum of $S(q)$ of the pure colloid suspension at its glass-transition volume fraction $\varphi_g \approx 0.595$ [22].

La Sapienza
Università degli Studi di Roma



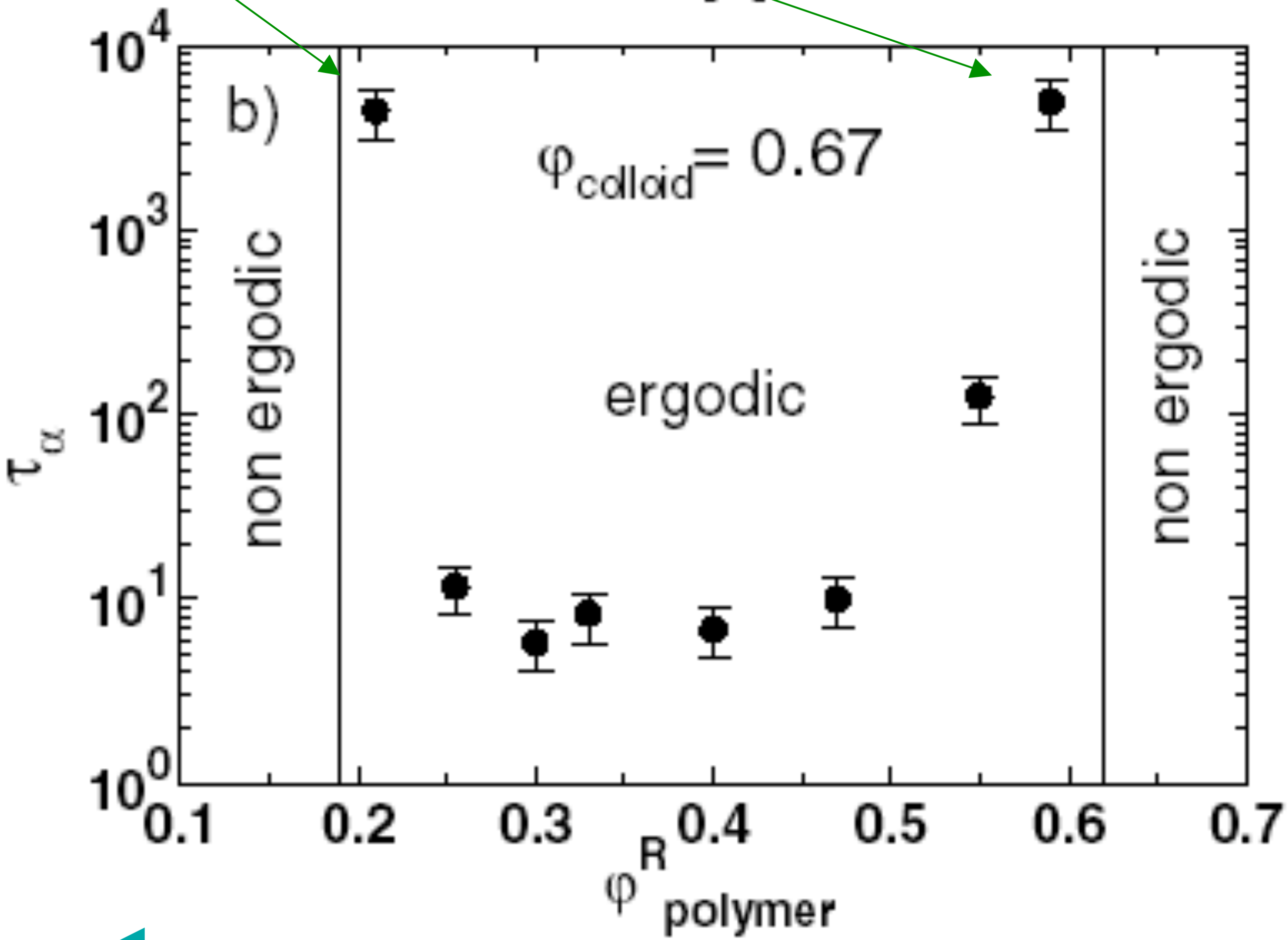
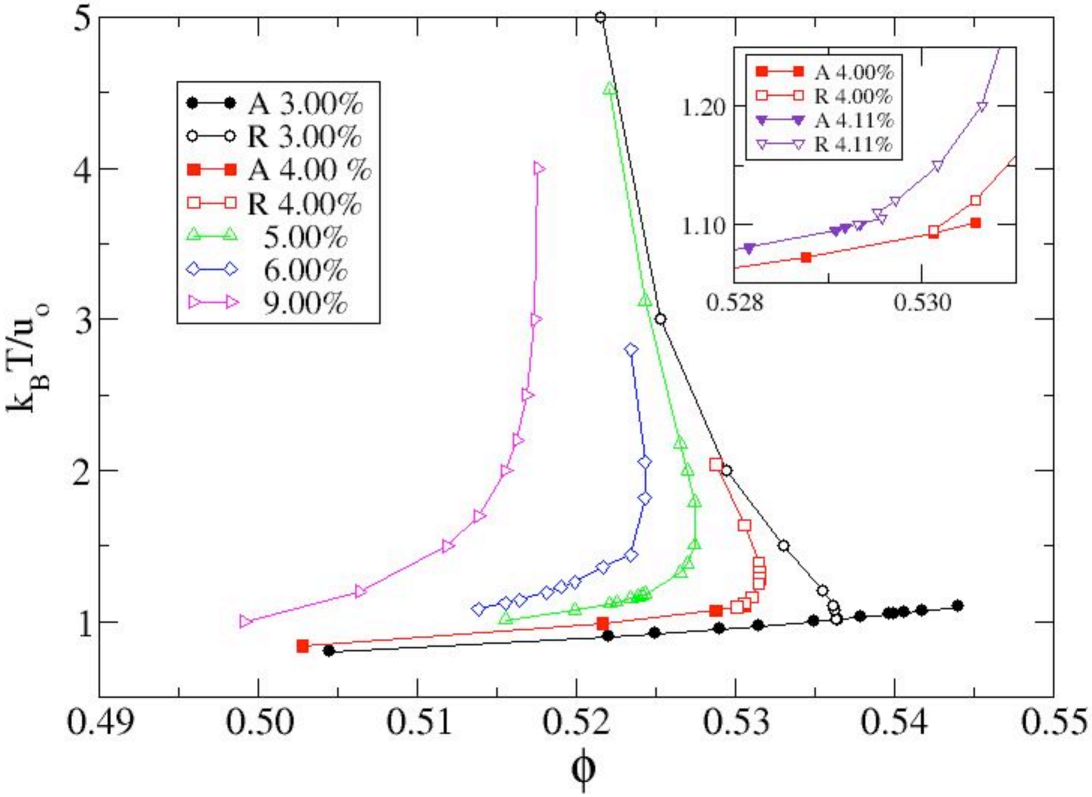


FIG. 3. Effect of increasing the free polymer volume $\varphi^R_{polymer}$ on the dynamics of a colloid suspension in state close to random close packing ($\varphi_{colloid} = 0.67$) in the phenomenon of re-entrant melting. (a) Density au lation functions $f(q,\tau)$ (probed at the same scattering in Fig. 1). The polymer reservoir volume fractions indicated by the numbers at the curves. The thi lines correspond to nonergodic (glassy) sampl (b) Structural relaxation times τ_α versus polymer volume fraction $\varphi^R_{polymer}$. The vertical lines schemati dicate the transition lines to the respective nonergodi

Temperature

La Sapienza
Università degli Studi di Roma

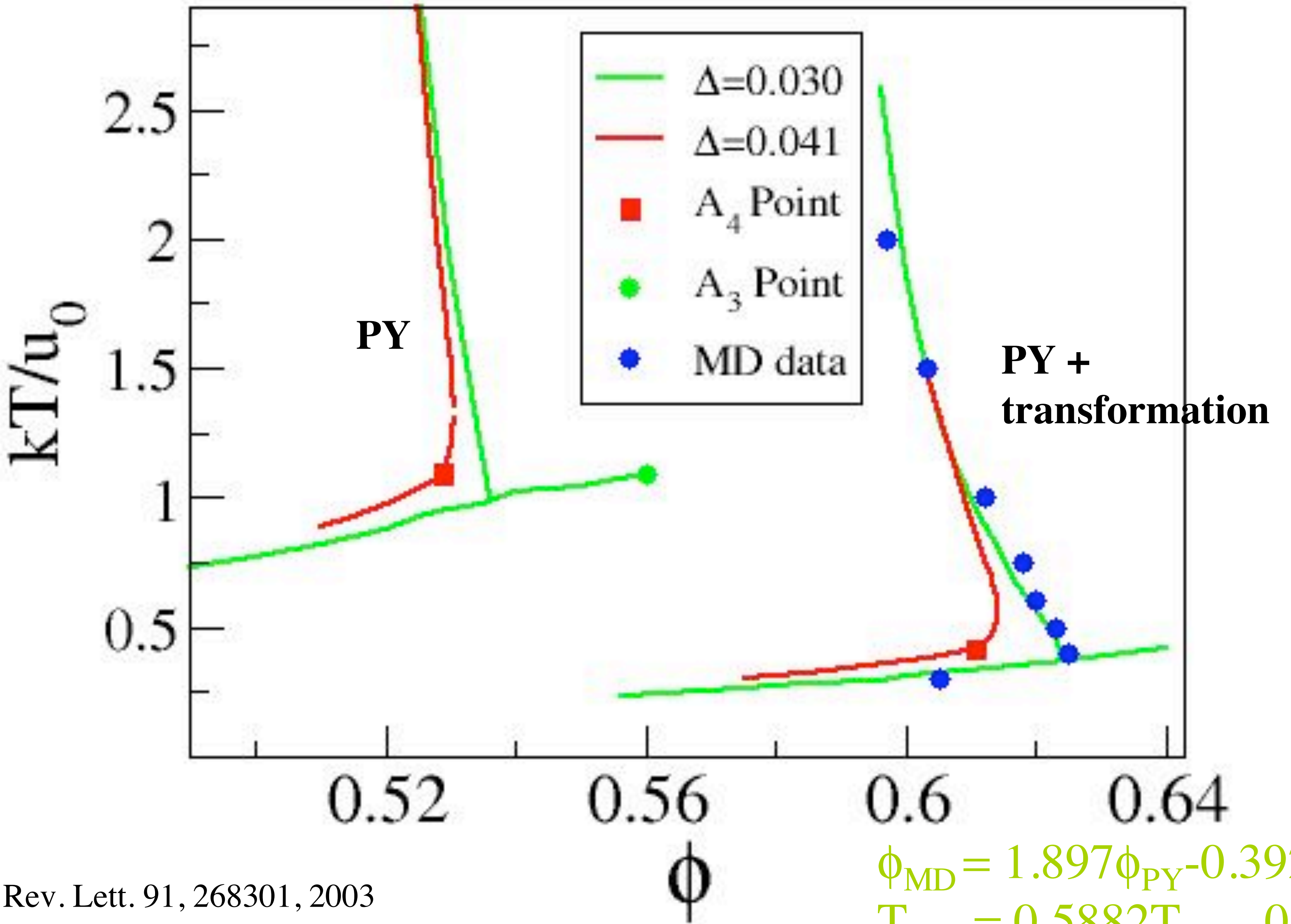
The A_4 point !



La Sapienza
Università degli Studi di Roma

erc

- Tracing the A_4 point: Theory and Simulation



Phys. Rev. Lett. 91, 268301, 2003

$\phi_{MD} = 1.897\phi_{PY} - 0.3922$

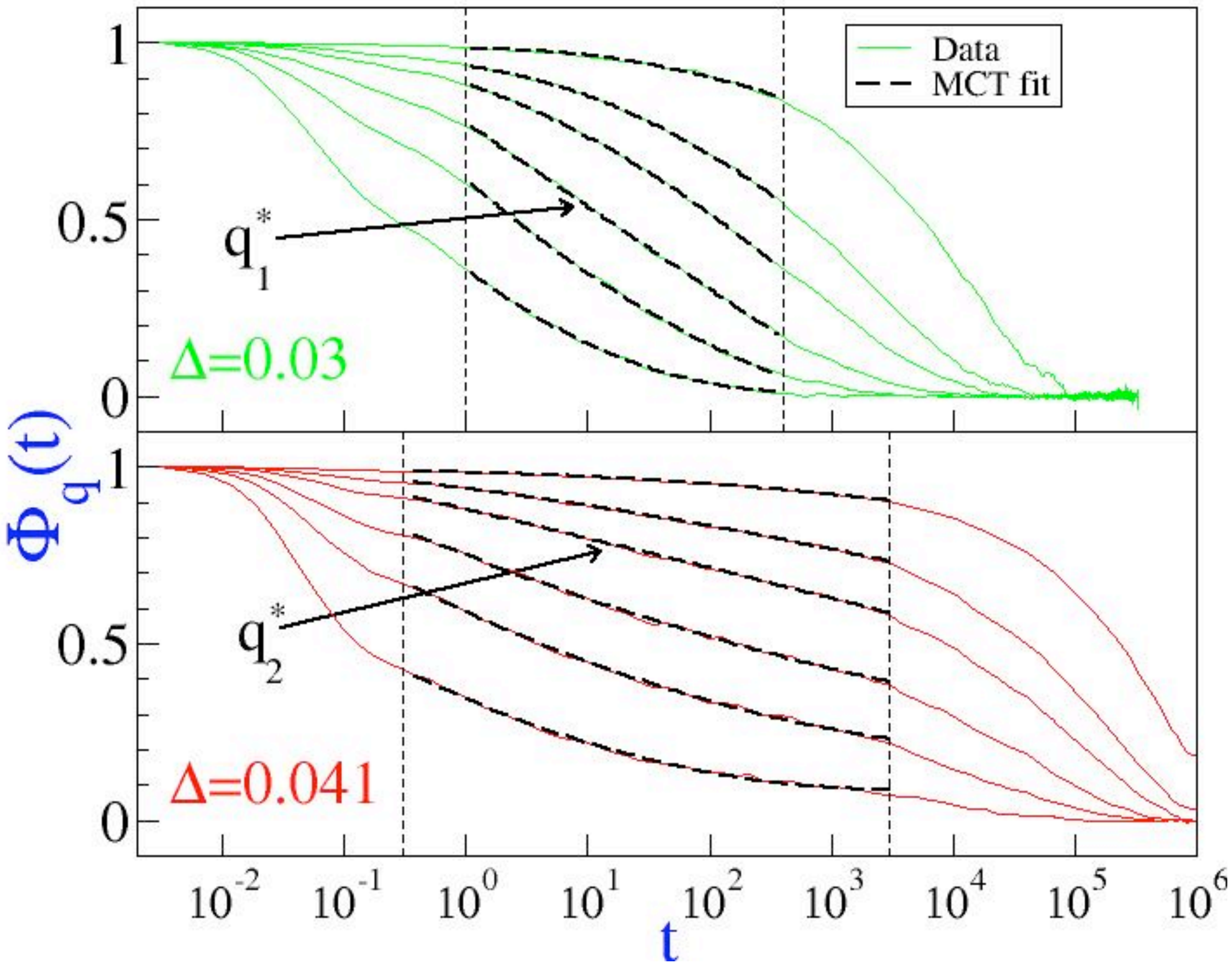
$T_{MD} = 0.5882T_{PY} - 0.225$

La Sapienza
Università degli Studi di Roma

PY-MCT overestimates ideal attractive glass T by a factor of 2

erc

Same T and ϕ, different Δ

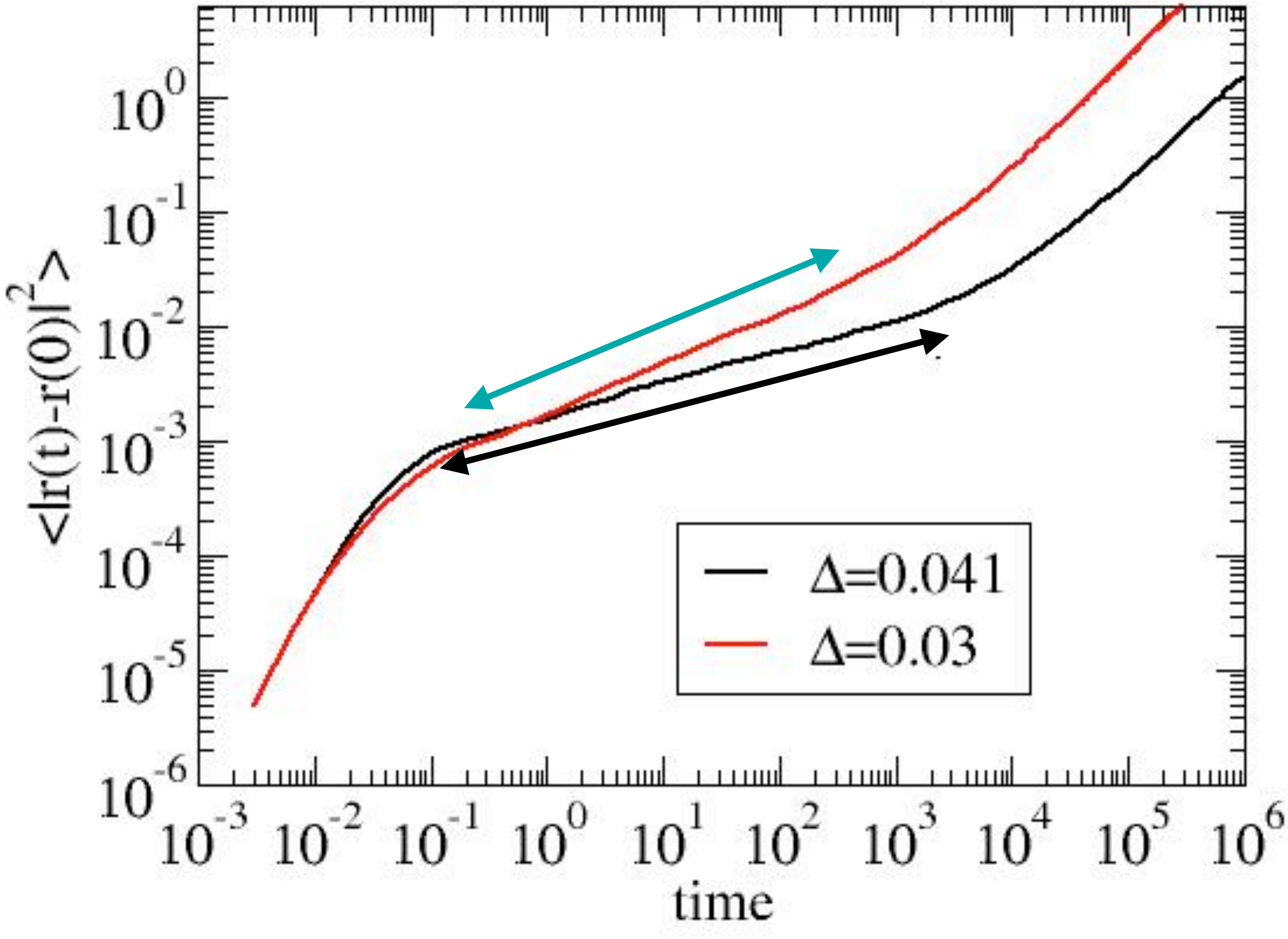


$$\Phi_q(t)=f_q-h_q\,[B^{(1)}\ln(t/\tau)+B^{(2)}_q\ln^2(t/\tau)]$$

La Sapienza
Università degli Studi di Roma

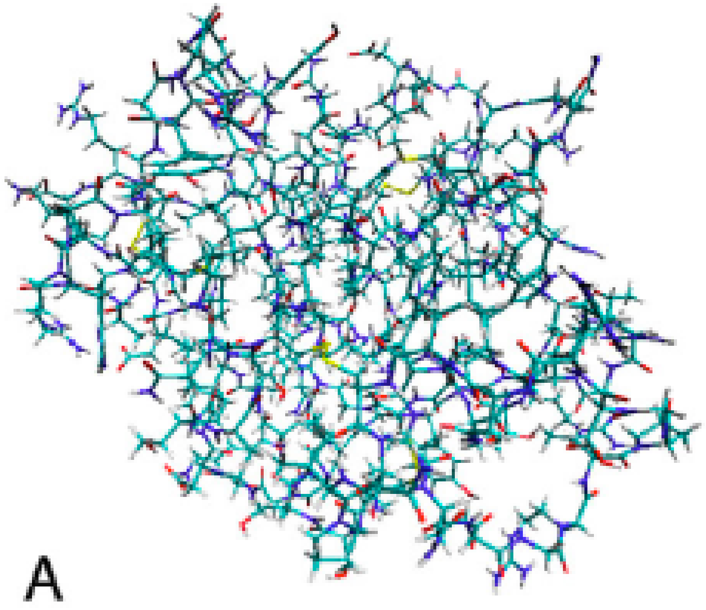
erc

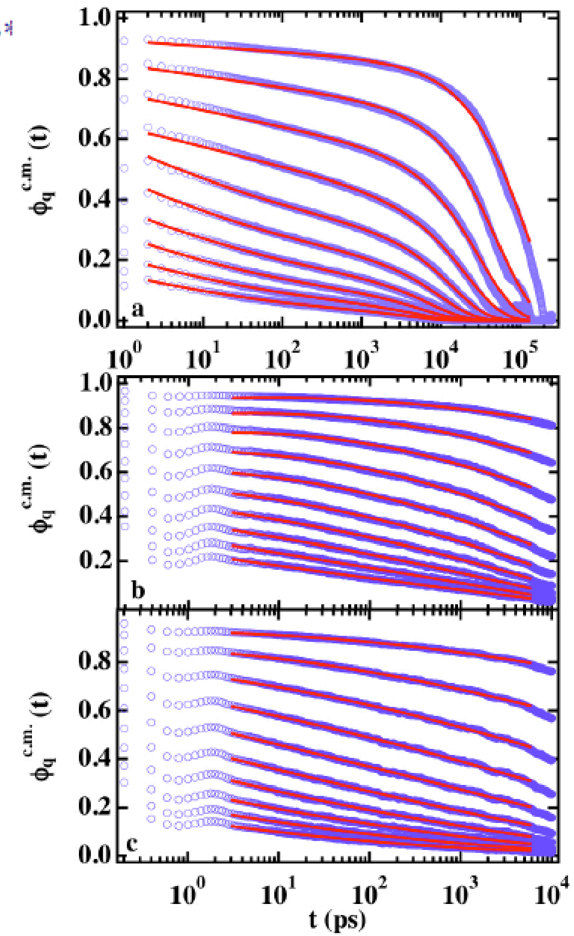
Sub-diffusive MSD for five decades….



Logarithmic Decay in Single-Particle Relaxation of Hydrated Lysozyme Powder

Marco Lagi,[1,2] Piero Baglioni,[2] and Sow-Hsin Chen[1,*]

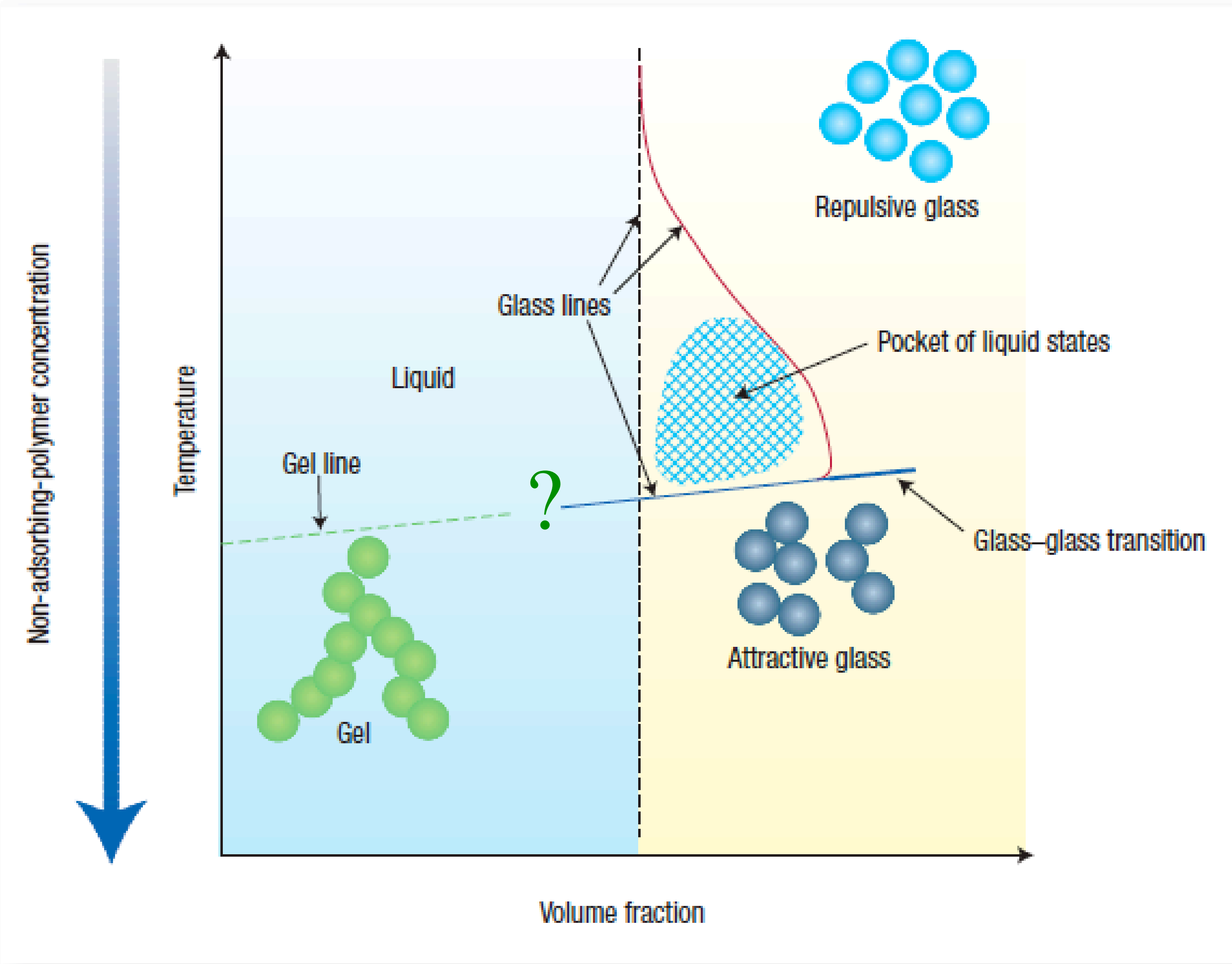




2 (color online). Q vector and temperature dependence
e self-intermediate scattering functions for the c.m. of the
o acid residues. (a) $T = 310$ K, (b) $T = 280$ K, (c) $T =$
K. Ten different wave vectors are displayed, from 1.6 to
$^{-1}$ with a 0.8 Å^{-1} interval (from top to bottom).
continuous lines are the best fits with Eq. (2) (a) and
1) (b),(c).

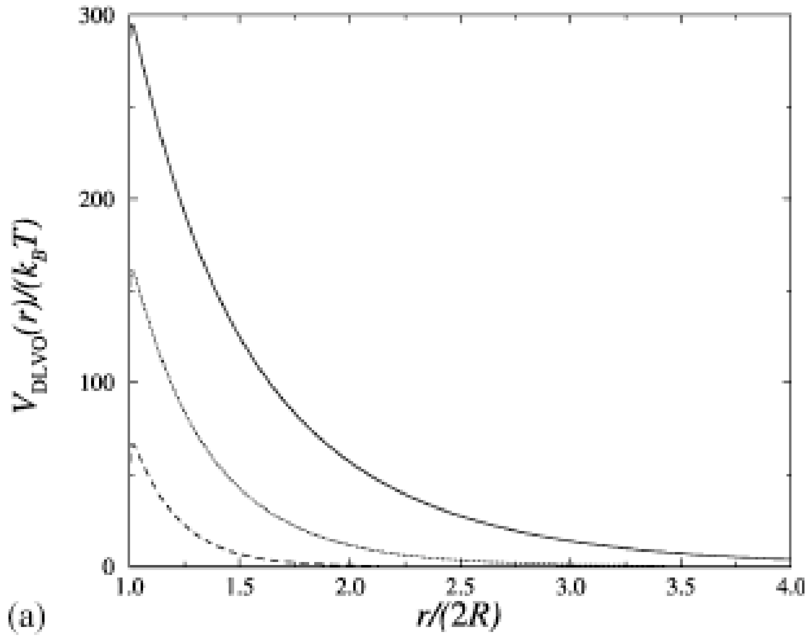
$$\phi_q^S(t) \sim [f_q - H_q' \ln(t/\tau^\beta) + H_q'' \ln^2(t/\tau^\beta)]\exp(-t/\tau_q^\alpha),$$

La Sapienza
Università degli Studi di Roma


Non-adsorbing-polymer concentration
Temperature
Repulsive glass
Glass lines
Pocket of liquid states
Liquid
Gel line
?
Glass–glass transition
Attractive glass
Gel
Volume fraction

Long range Repulsion

Effective Potential for Charged Colloids (Poisson-Boltzmann)



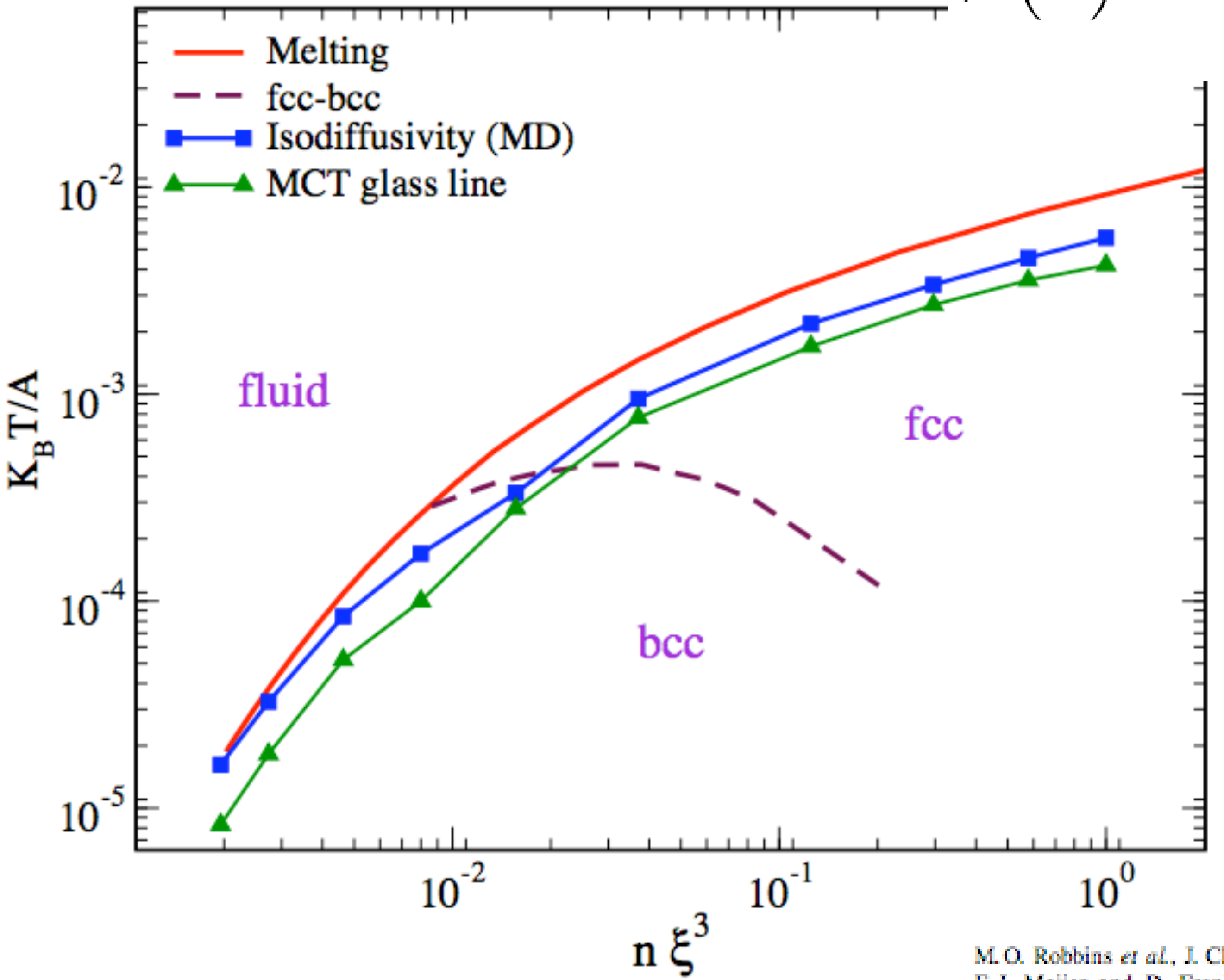
$$V(r) = A\frac{e^{-r/\xi}}{r/\xi}$$

Screening length controlled by salt and colloid

BELLONI L., *J. Chem. Phys.*, **85** (1986) 519.

Yukawa phase diagram (neglecting HS)

$$V(r) = A\frac{e^{-r/\xi}}{r/\xi}$$



M. O. Robbins *et al.*, J. Chem. Phys. **88**, 3286 (1988).
E. J. Meijer and D. Frenkel, J. Chem. Phys. **94**, 2269 (1991).

JOURNAL OF CHEMICAL PHYSICS VOLUME 111, NUMBER 17

The glass transition of charged and hard sphere silica colloids

Ch. Beck, W. Härtl, and R. Hempelmann[a)]
Physikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken, Germany

H. M. Lindsay and P. M. Chaikin, J. Chem. Phys. **76**, 3774 (1982).

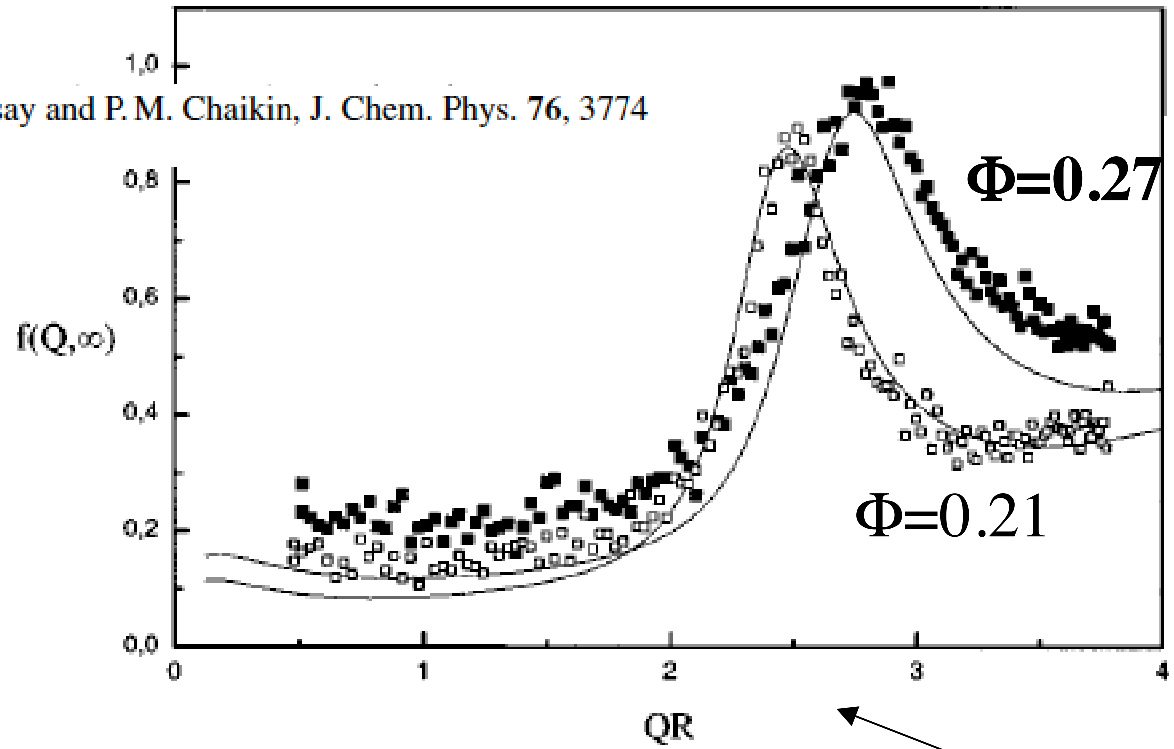


FIG. 6. Nonergodicity functions $f(Q,\infty)$, also called Debye-Waller factors, for charged colloidal systems in the glassy state at two different volume fractions [$\varphi(\blacksquare)=0.27$, $\varphi(\square)=0.21$]. Solid lines: predictions of the MCT according to Eq. (9); data points: dynamic light scattering experimental results.

Note peak shift

La Sapienza
Università degli Studi di Roma

erc

Yukawa Glasses….

$$V_{ij}(r) = A_{ij}\frac{\exp(-r/\xi_{ij})}{r/\xi_{ij}}.$$

J. Bosse and S.D. Wilke, Phys. Rev. Lett. **80**, 1260 (1998).
S.D. Wilke and J. Bosse, Phys. Rev. E **59**, 1968 (1999).

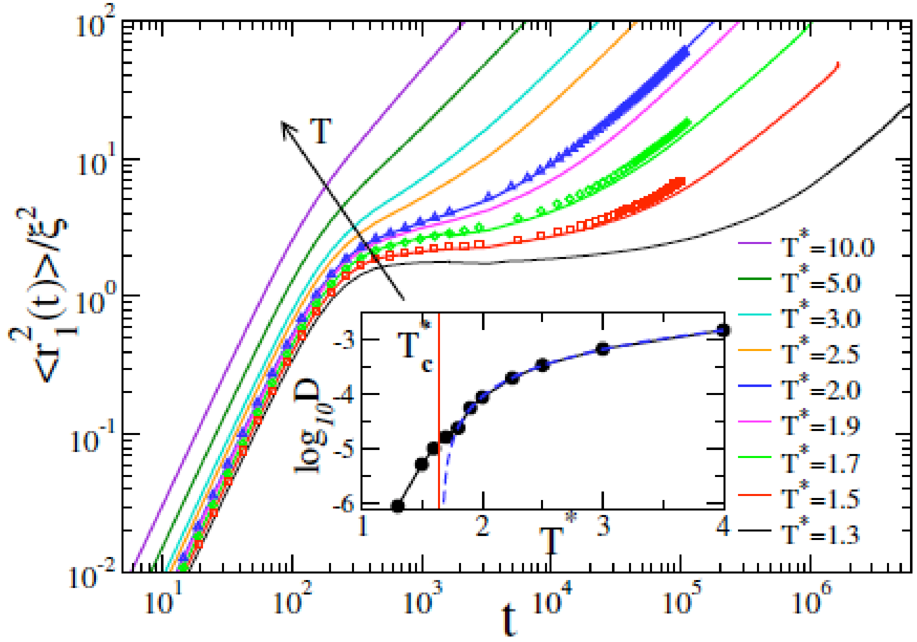


FIG. 3 (color online). $\langle r_1^2(t)\rangle$ for type-1 particles with decreasing T^*. Lines and symbols refer, respectively, to simulations with $N = 10^3$ and $N = 10^4$ particles. Inset: Power-law fit to the diffusion coefficient D, with exponent $\gamma_D = 1.45$ and $T_c^* \simeq 1.67$.

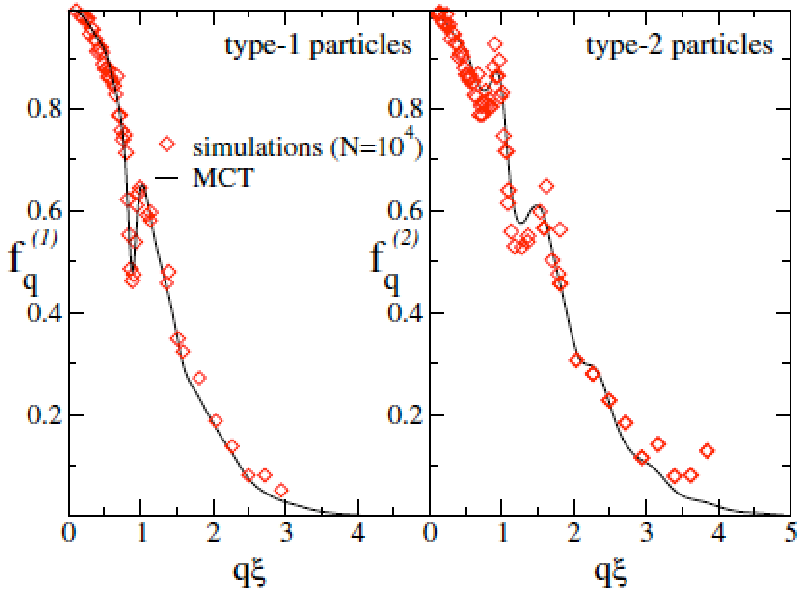
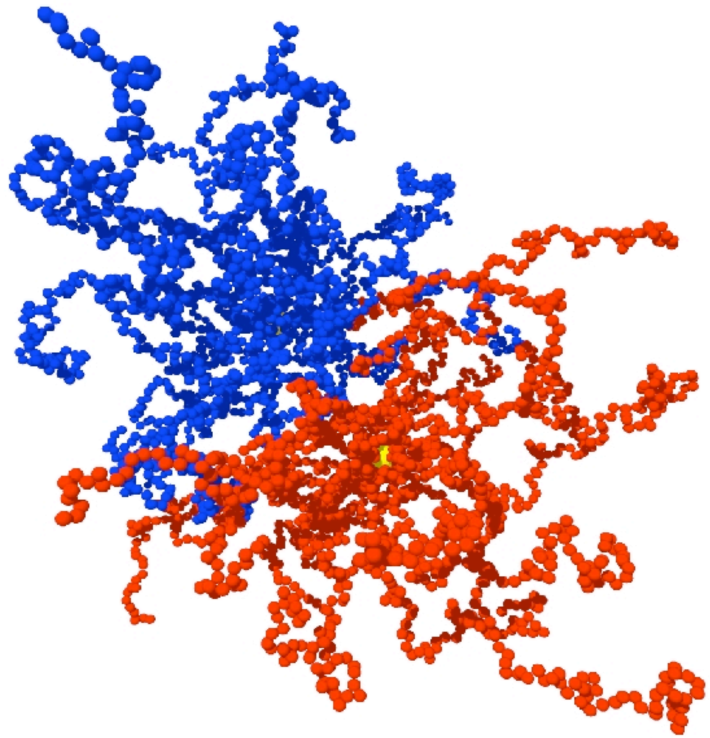


FIG. 4 (color online). Debye-Waller factors from simulations extracted from stretched exponential fits (symbols) and from MCT calculations (lines) for type-1 (left) and type-2 (right) particles, respectively. The simulation temperature is $T^* = 2.0$, while for MCT calculations we report results at the critical temperature $T^*_{\mathrm{MCT}} = 2.81$.

Again…
MCT failure and success

E. Zaccarelli et al, Phys. Rev. Lett. 100, 195701 (2008).

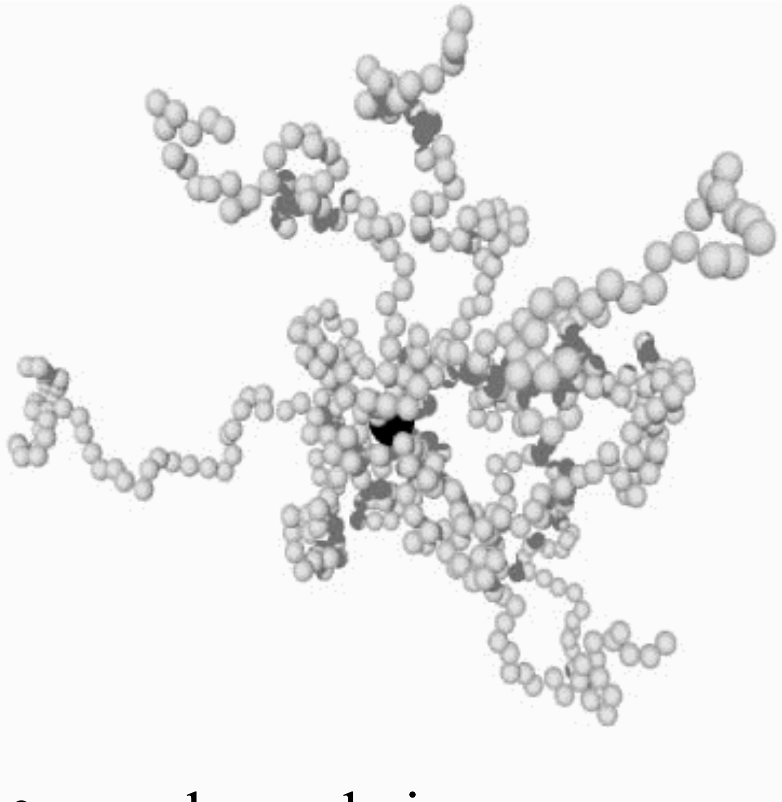
Soft Colloids: Star Polymers

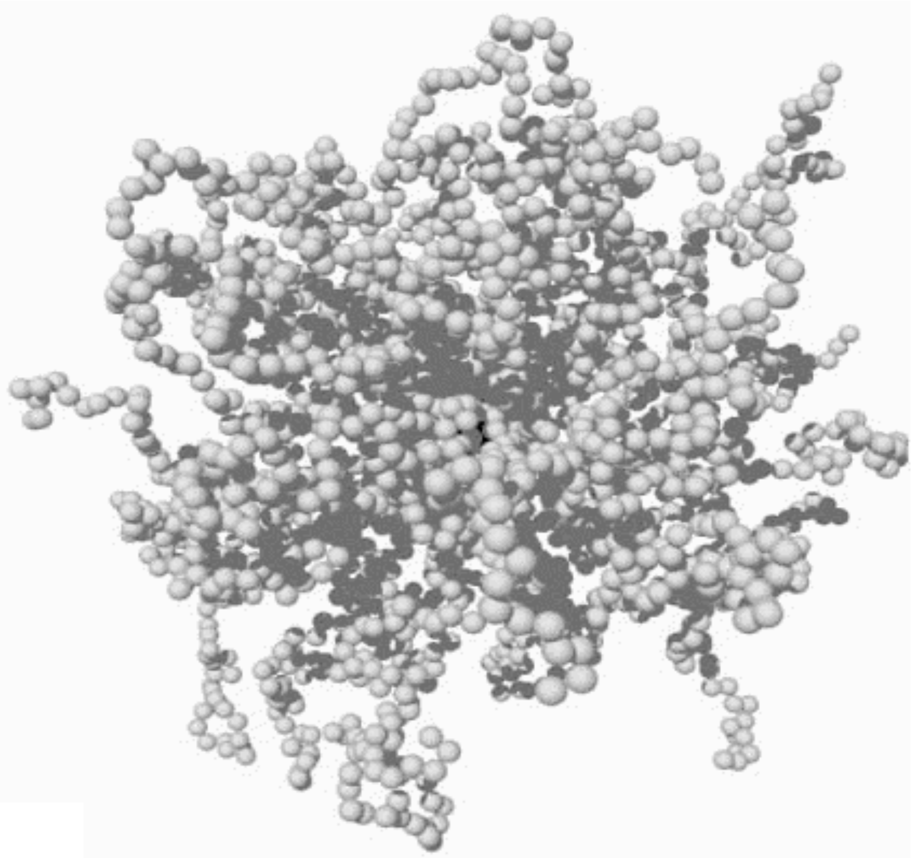


La Sapienza
Università degli Studi di Roma

erc

Star Polymers





- very long chains
- microscopic core

control parameters:

f functionality/arm number, **σ** diameter ~ R_h

f=2 *polymer chains;* ***f*** $\rightarrow \infty$ *hard spheres*

La Sapienza
Università degli Studi di Roma

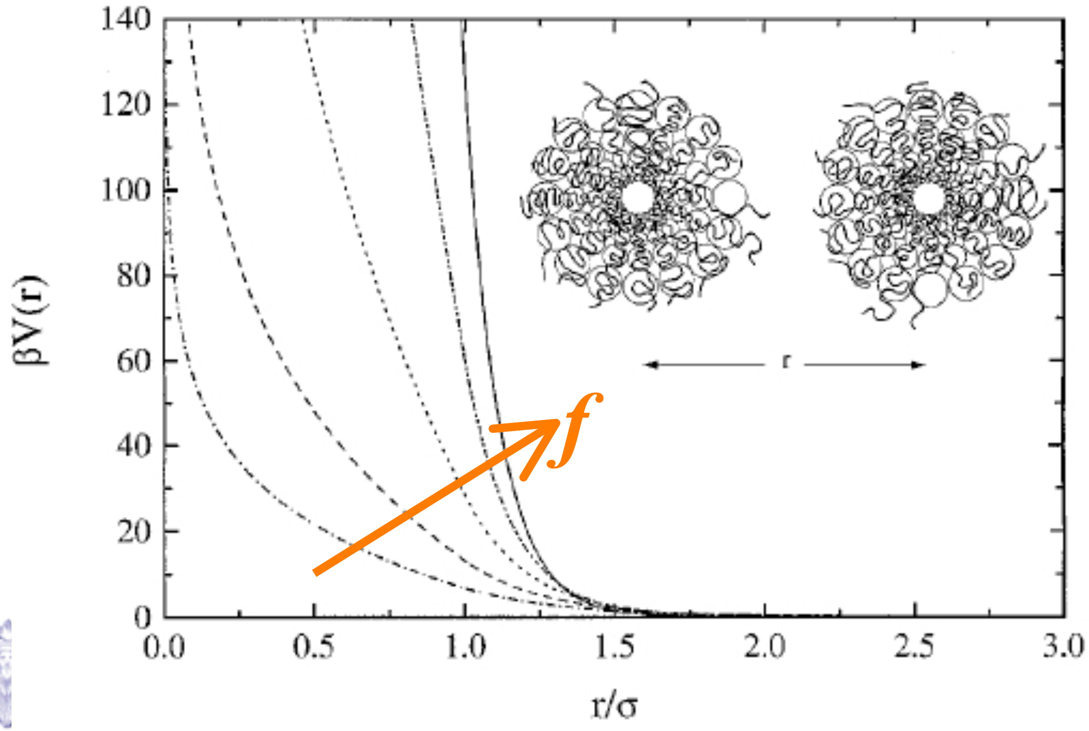
erc

Effective interactions: ultrasoftness

$$\beta V(r) = \frac{5}{18} f^{3/2} \left[-\ln\left(\frac{r}{\sigma}\right) + \frac{1}{1+\sqrt{f}/2} \right], \qquad r \leq \sigma$$

$$= \frac{5}{18} f^{3/2} \frac{\sigma/r}{1+\sqrt{f}/2} \exp\left[-\frac{\sqrt{f}(r-\sigma)}{2\sigma} \right], \quad r \geq \sigma$$

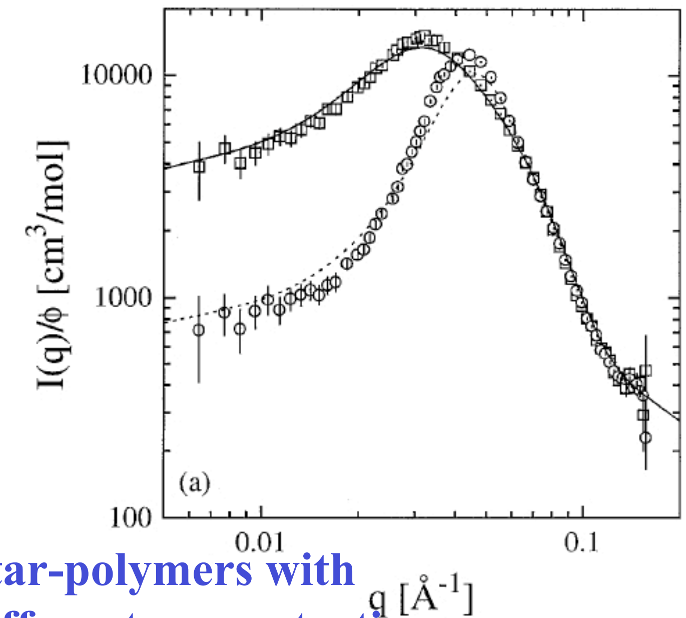
logarithmic divergence (from scaling arguments)
+ Yukawa tail



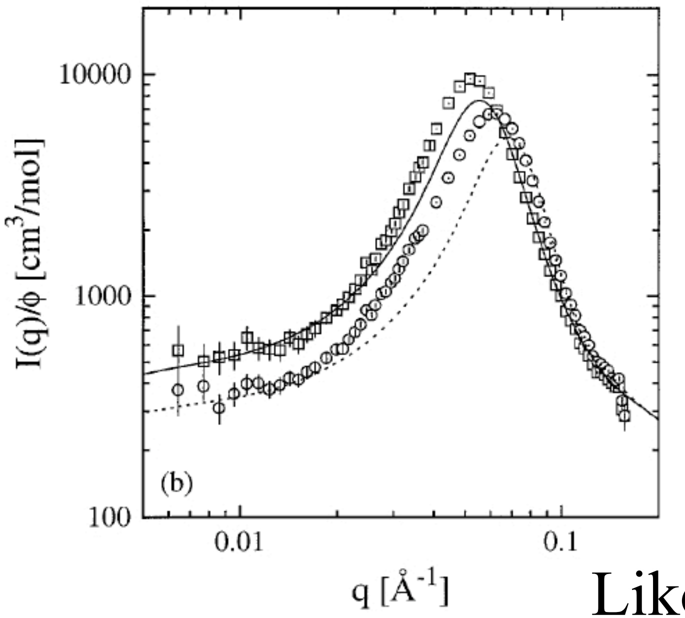
- potential is athermal
- interactions are purely repulsive
- tunable softness with ***f***

Likos et al PRL (1998)

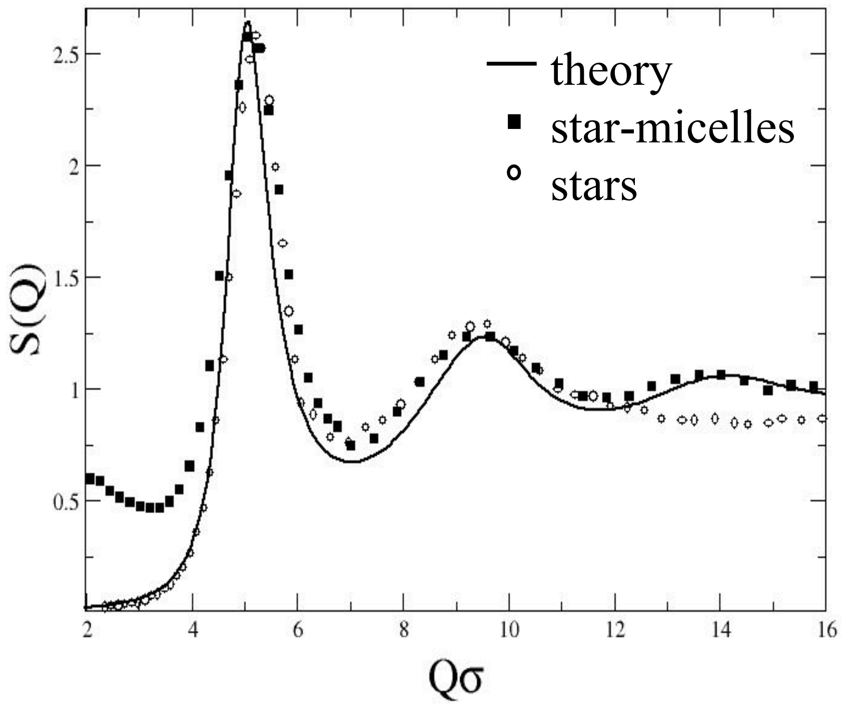
Validation of potential against experiments



Star-polymers with different concentration



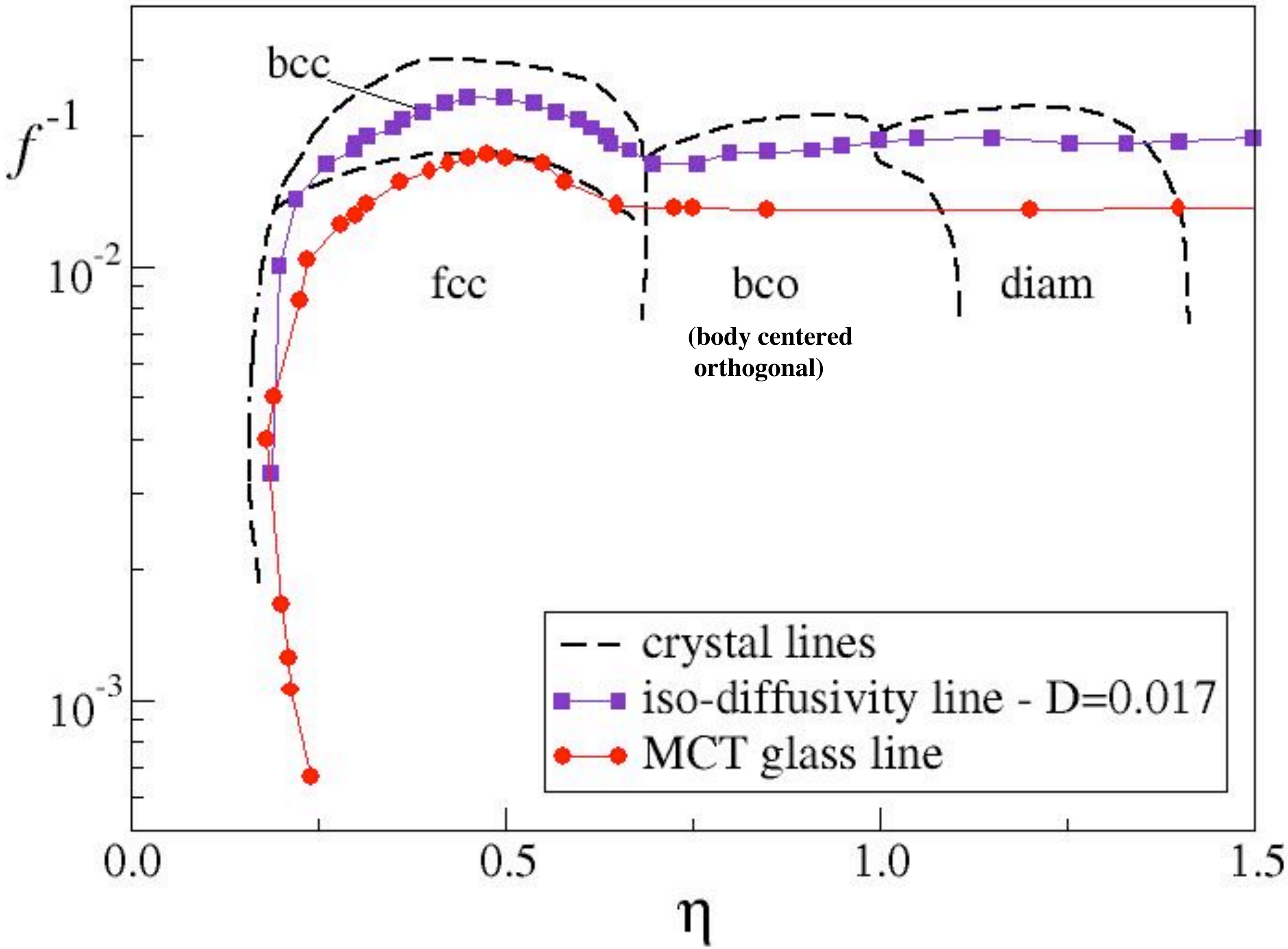
Likos et al PRL (1998)



asymmetric PEP-PEO star-like micelles

Laurati et al PRL (2005)

Star Polymer Phase Diagram



Watzlawek, Likos, Löwen PRL (1999)
Foffi et al PRL (2003)

Binary mixtures of stars: theory and experiments

large stars

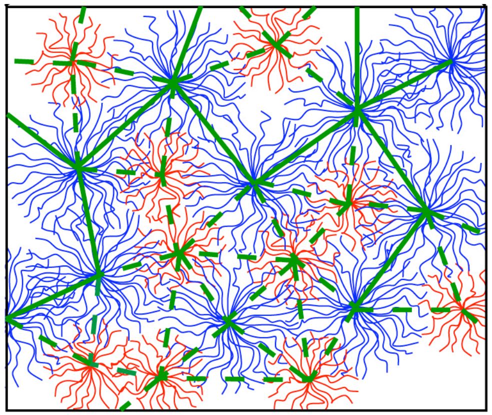
f_1 =263

ρ_1 =0.345 → *glass*

small stars

f_2 = 16,32,64

control parameters: $q = \sigma_2/\sigma_1$, ρ_2

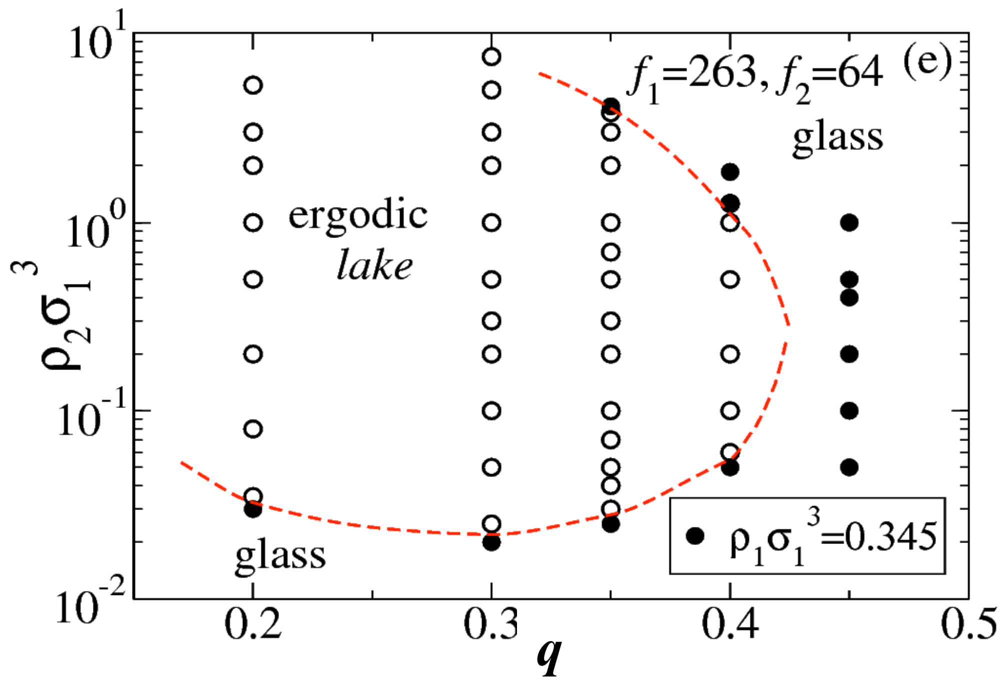


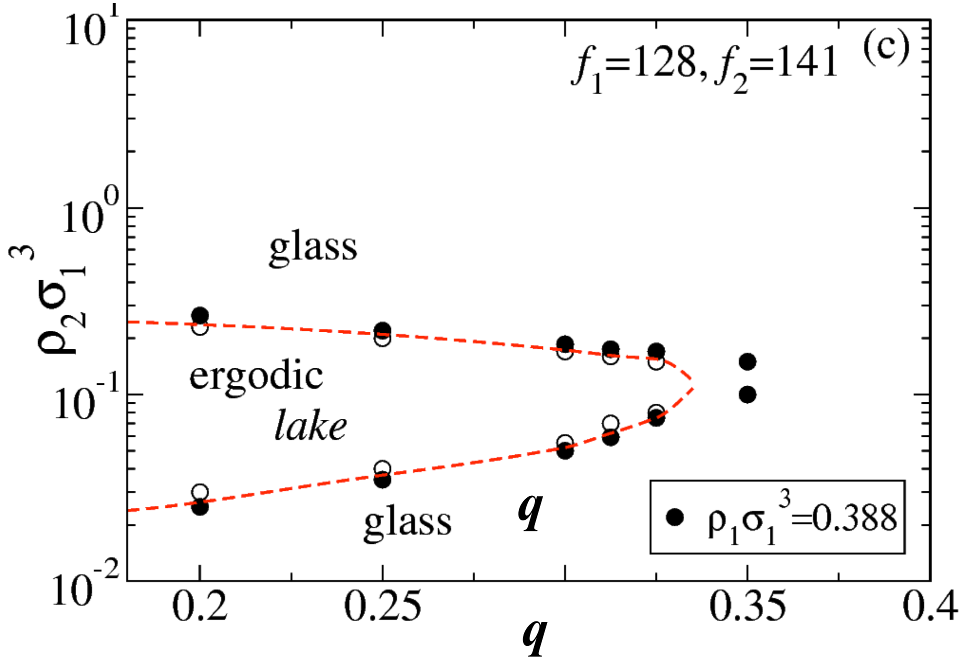
La Sapienza
Università degli Studi di Roma

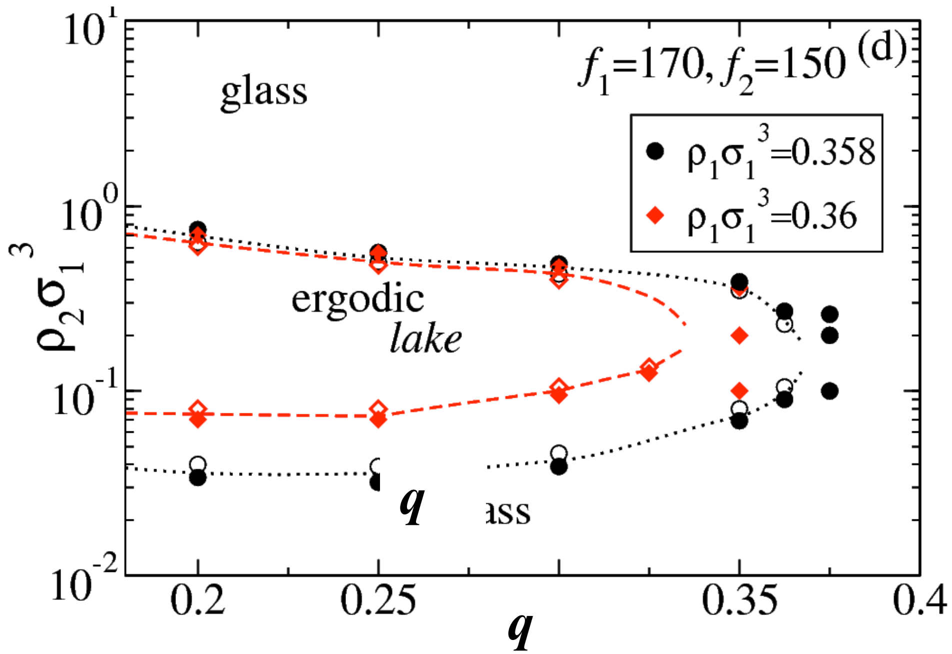
erc

Mayer et al Nature Materials 7, 780 (2008)

MCT calculations for several f_1-f_2 pairs

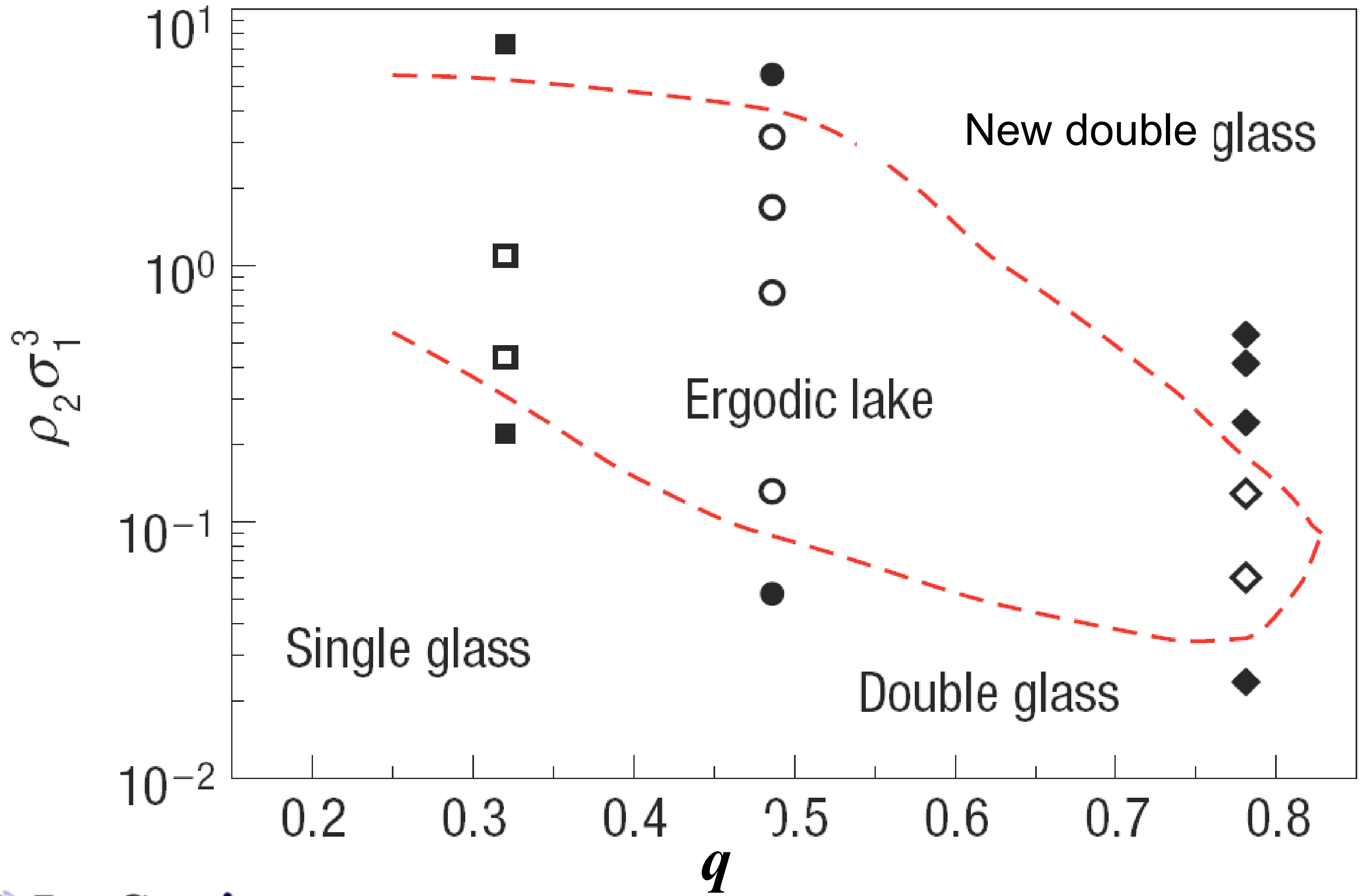






...and experiments:

different *f1/f2* combinations



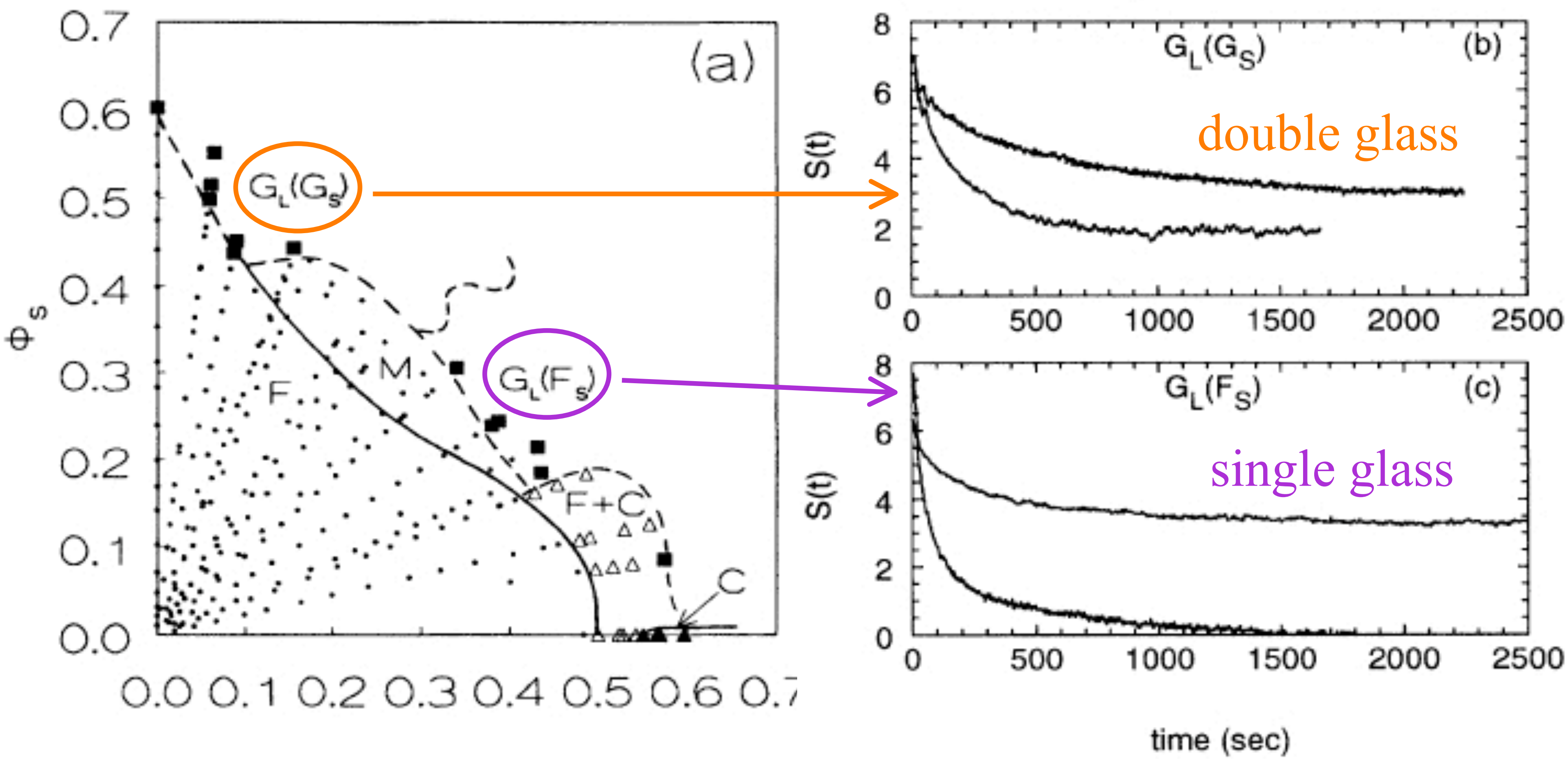
La Sapienza
Università degli Studi di Roma

C. Mayer et al Nature Materials 7, 780 (2008)

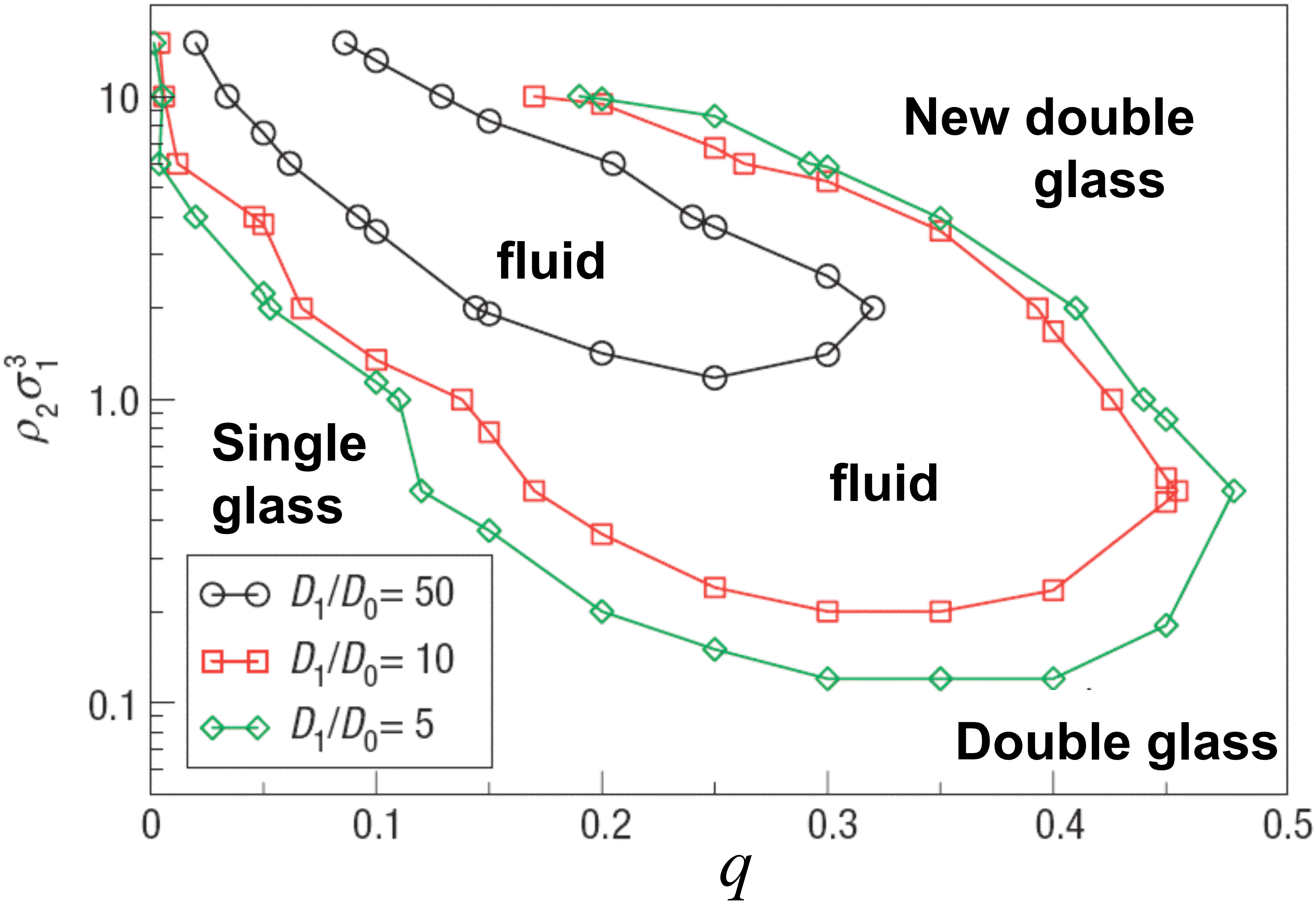
erc

Similarity with asymmetric binary hard sphere mixtures

Imhof & Dhont PRL 75, 1662 (1995)



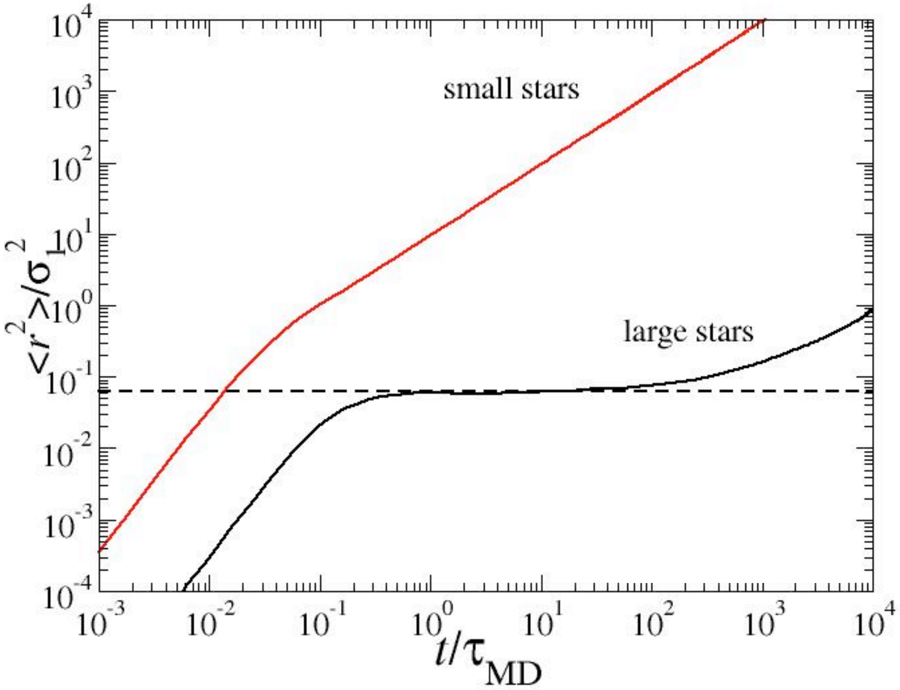
Iso-diffusivity curves from MD Simulations



La Sapienza
Università degli Studi di Roma

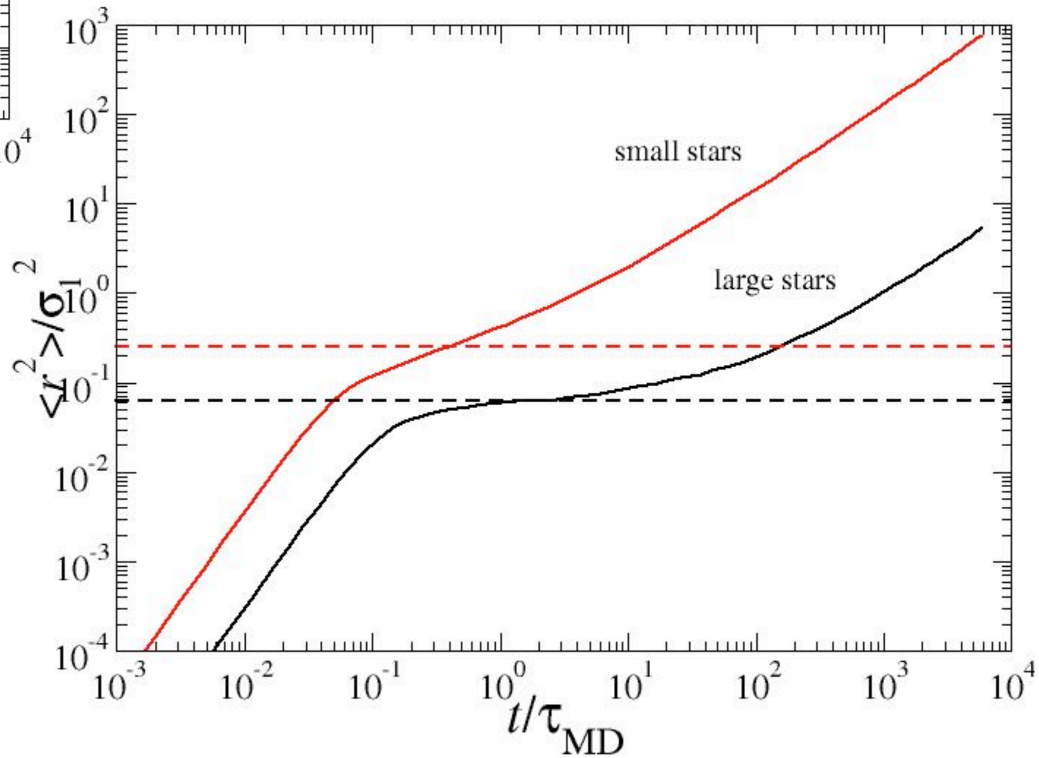
erc

Partial Mean Squared Displacements



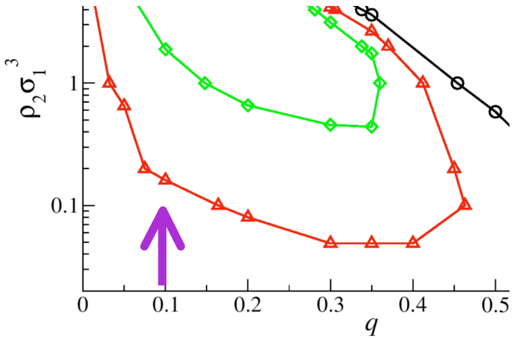
single glass

double glass

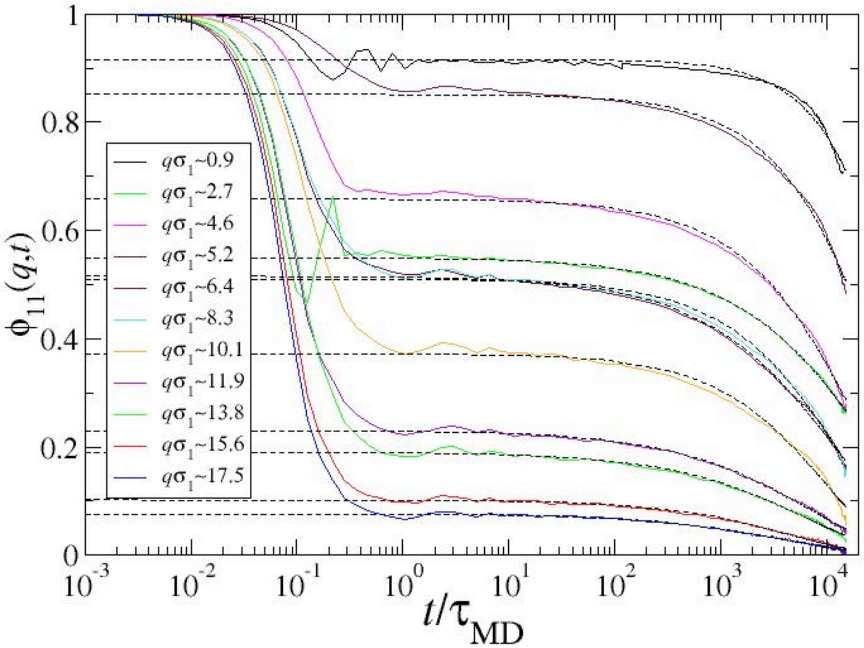


La Sapienza
Università degli Studi di Roma

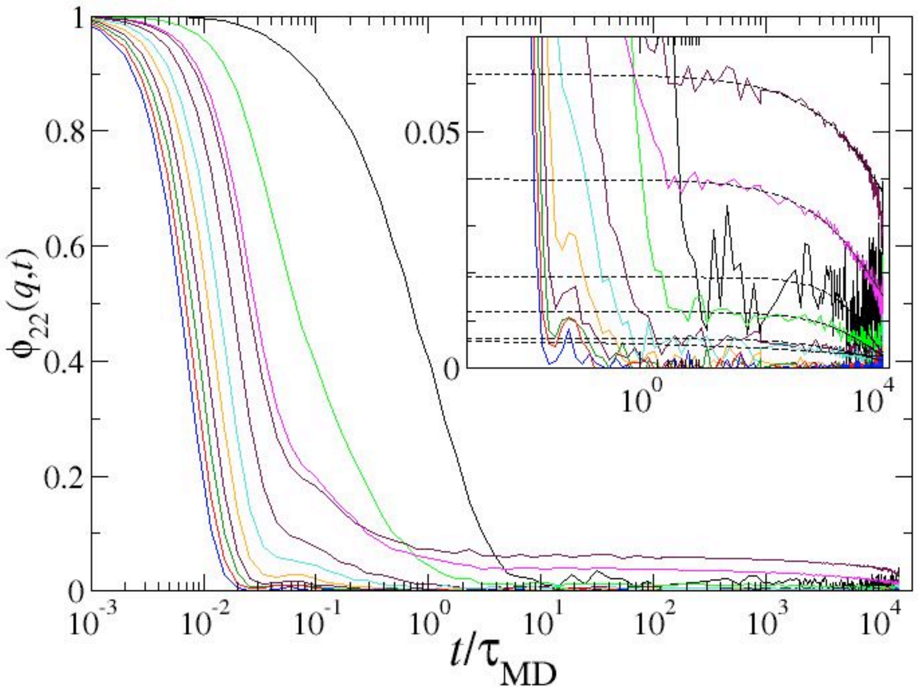
Partial density autocorrelation functions:
single glass



Large stars



Small stars

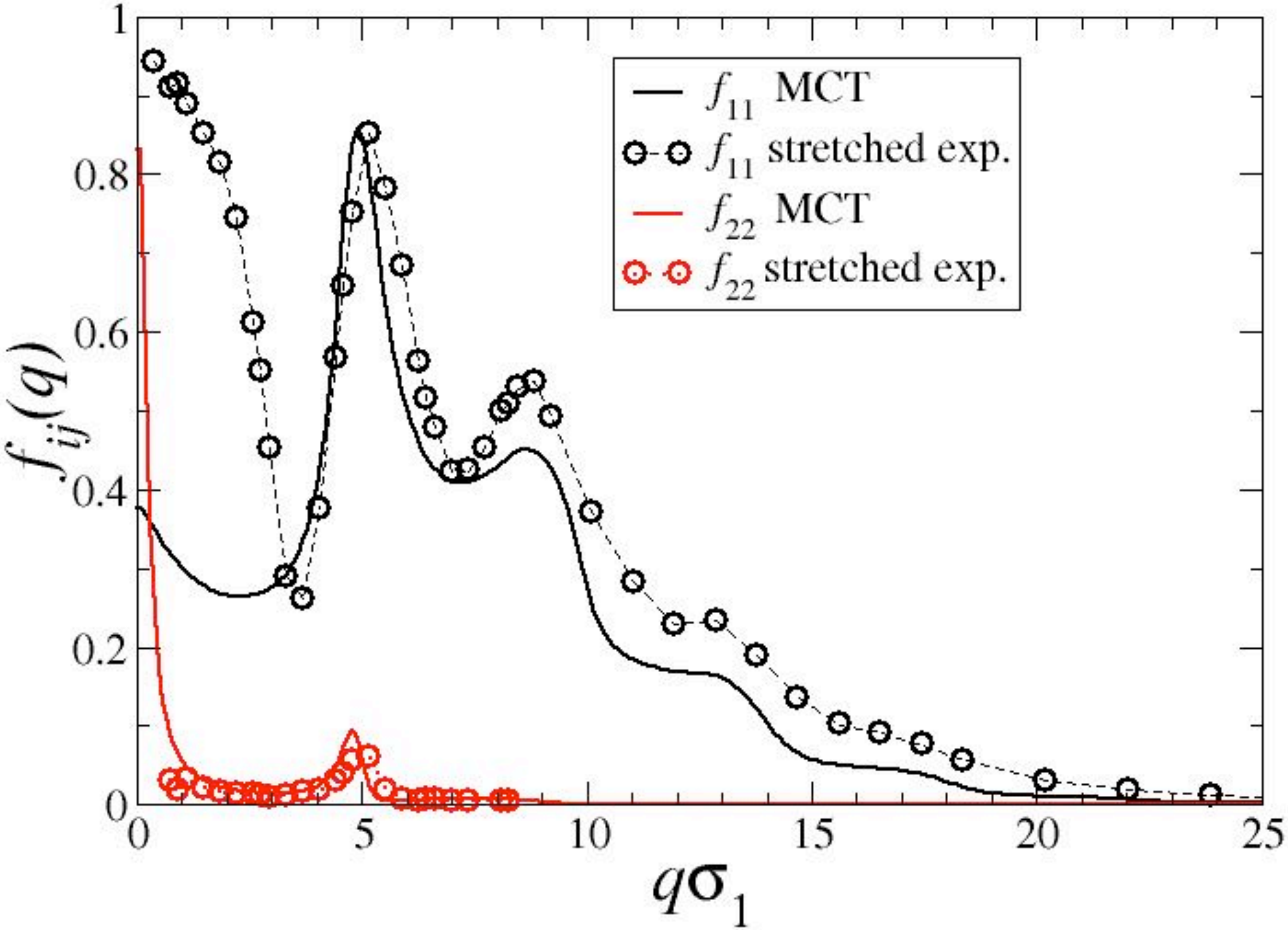


dashed curves are stretched exponential fits

La Sapienza
Università degli Studi di Roma

erc

Partial non-ergodicity parameters:
single glass



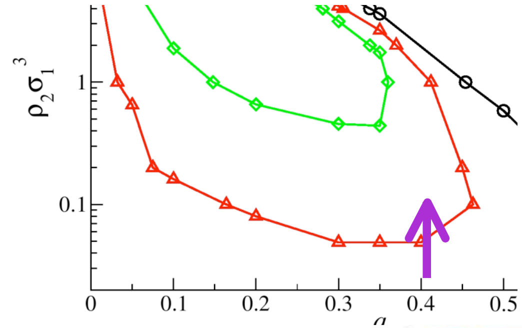
Università degli Studi di Roma

Mayer et al Macromolecules 42, 423 (2009)

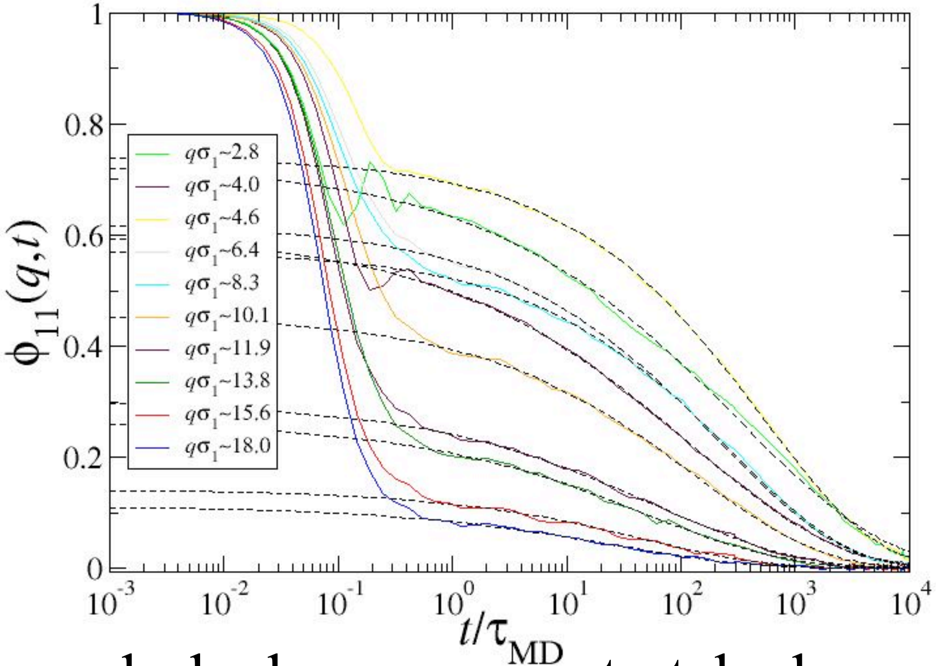
Partial density autocorrelation functions:

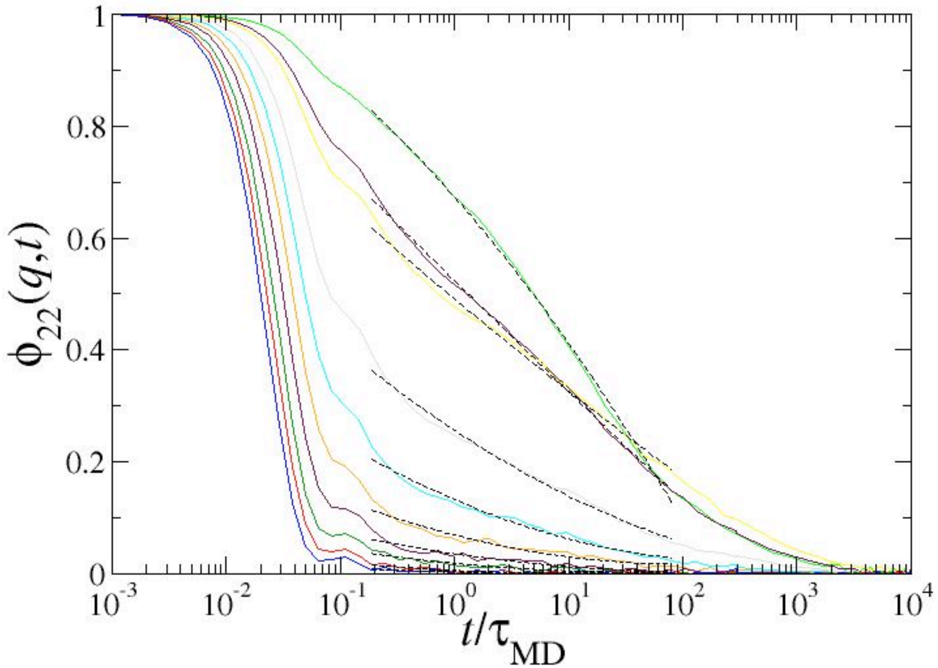
double glass

Large stars



small stars





dashed curves are stretched exponential fits

dashed curves are logarithmic fits:

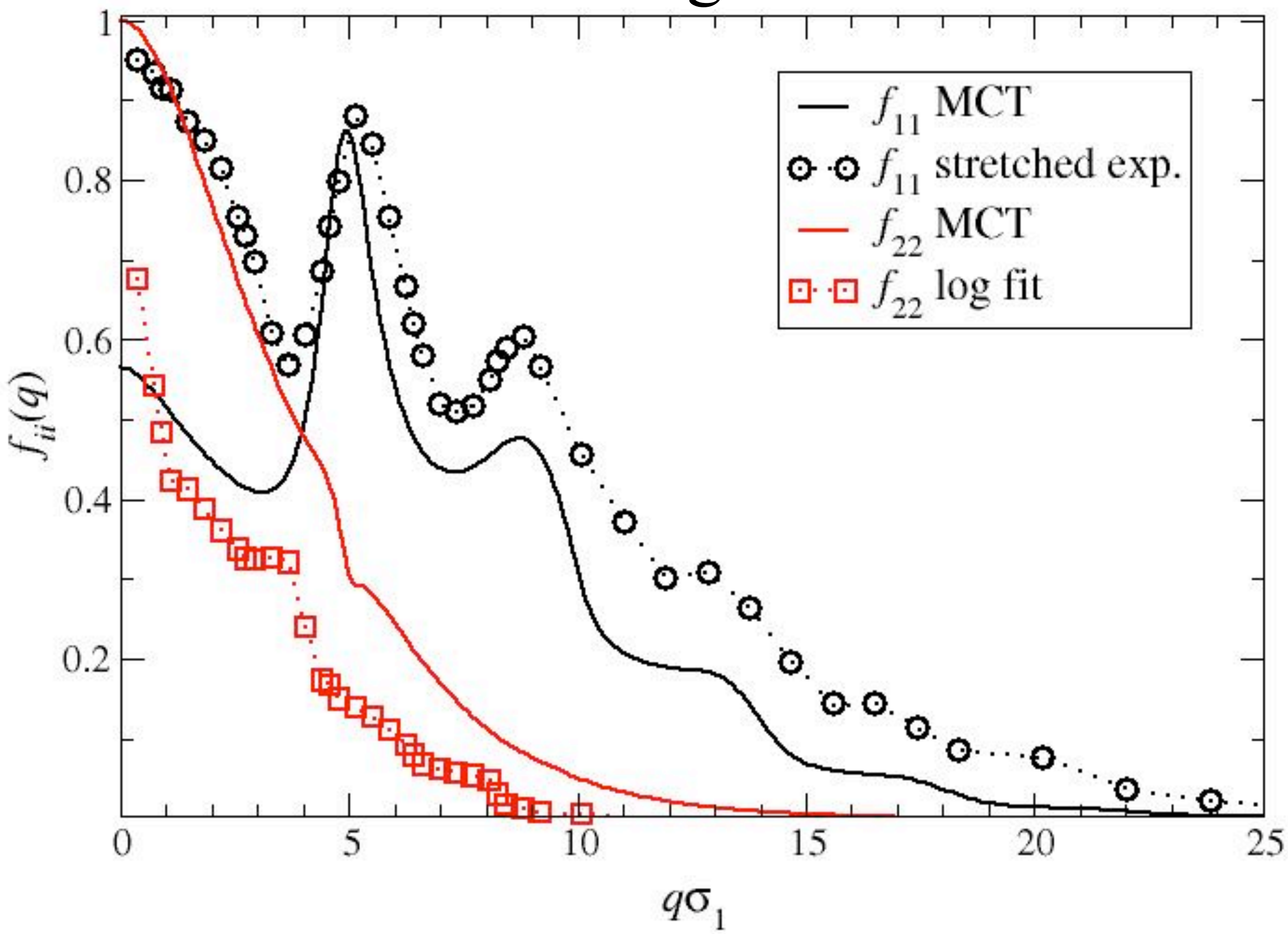
$\sim f_q - h_q[A \ln(t/\tau) + B_q \ln^2(t/\tau)]$

La Sapienza

Università degli Studi di Roma

erc

Partial non-ergodicity parameters:
double glass



Density correlators for small stars display LOG behavior, as close to a glass-glass transition according to MCT

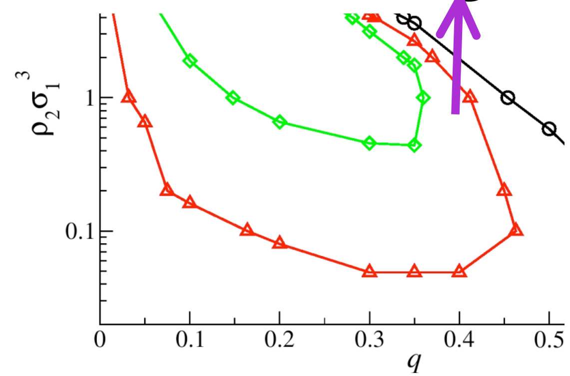
La Sapienza
Università degli Studi di Roma

C. Mayer et al Macromolecules 42, 423 (2009)

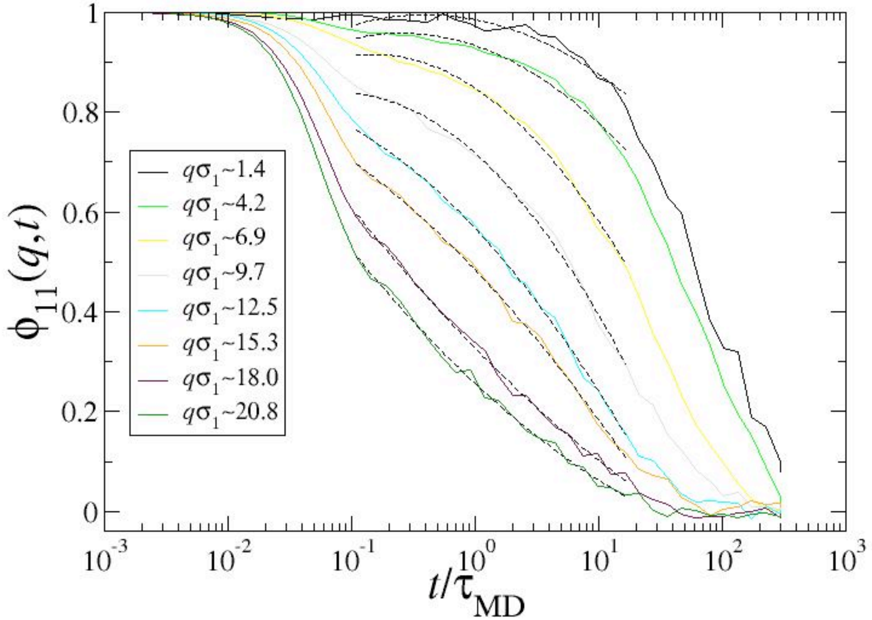
erc

Partial density autocorrelation functions:

new double glass



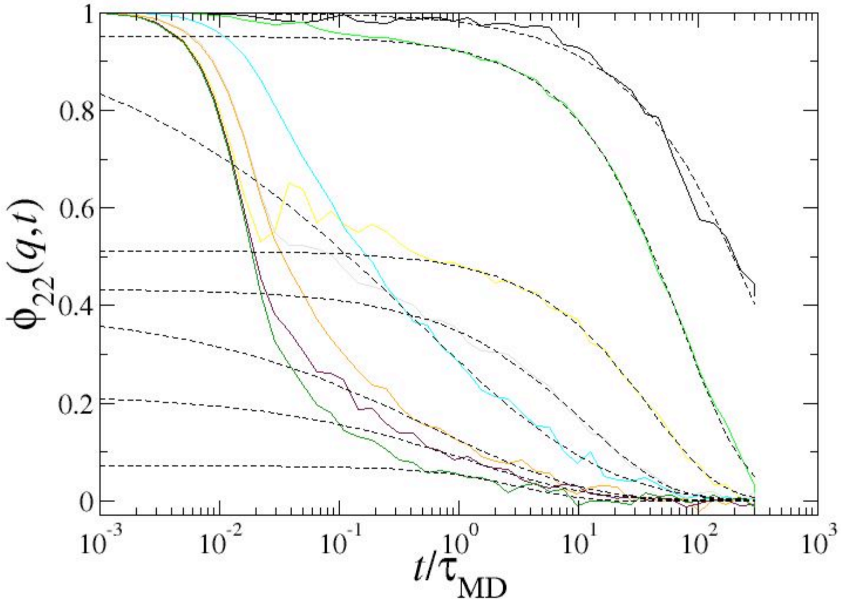
Large stars



dashed curves are logarithmic fits:

$\sim f_q - h_q[A \ln(t/\tau) + B_q \ln^2 (t/\tau)]$

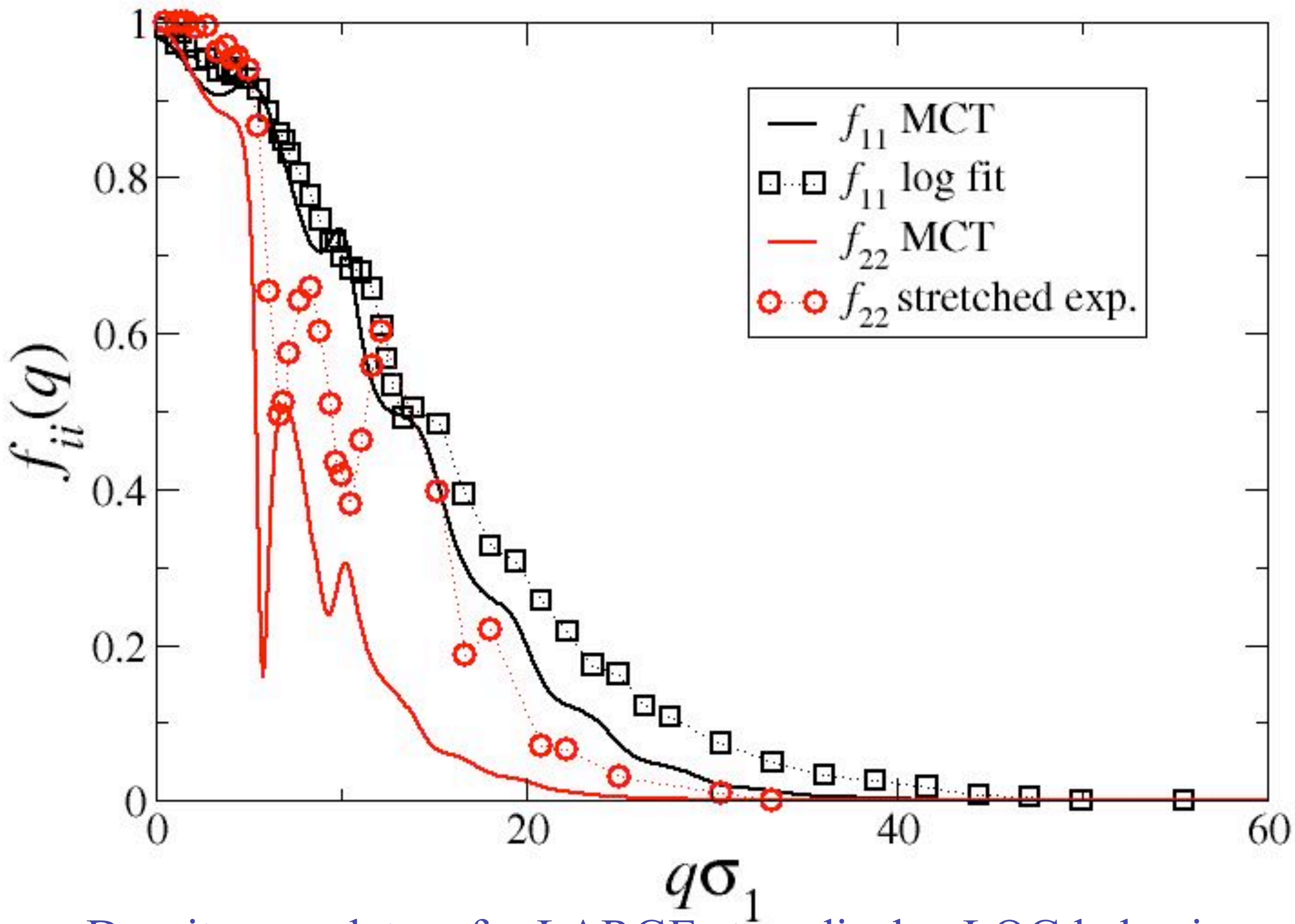
Small stars



dashed curves are stretched exponential fits

La Sapienza
Università degli Studi di Roma

Partial non-ergodicity parameters:
new double glass

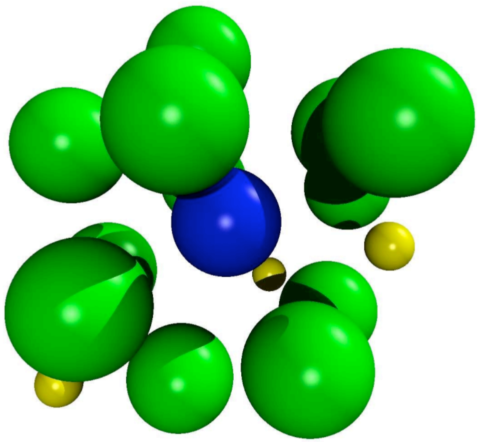


Density correlators for LARGE stars display LOG behavior:
a large star glass-glass transition?

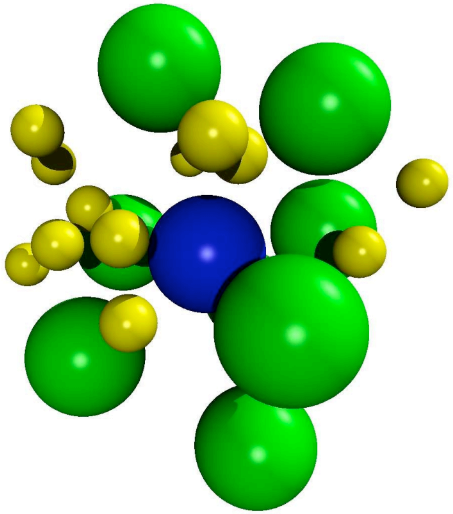
La Sapienza
Università degli Studi di Roma

erc

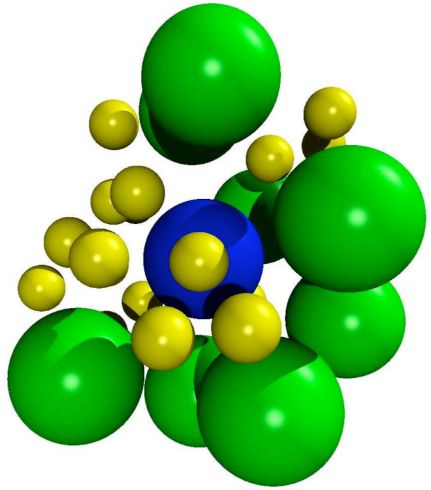
Snapshots of nearest-neighbours cages around a Large Star



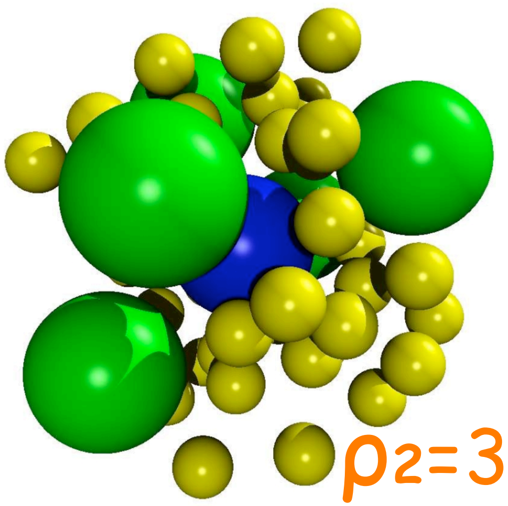
$\rho_2=0.05$



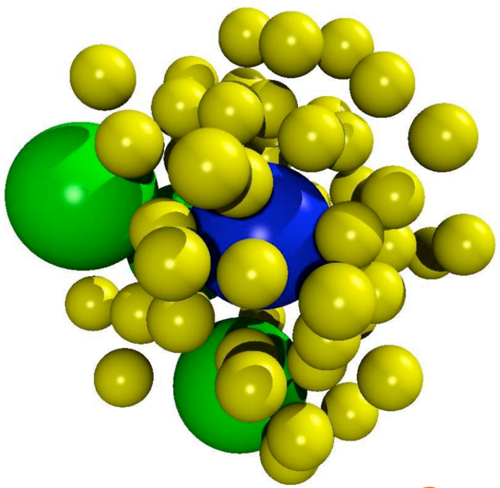
$\rho_2=0.5$



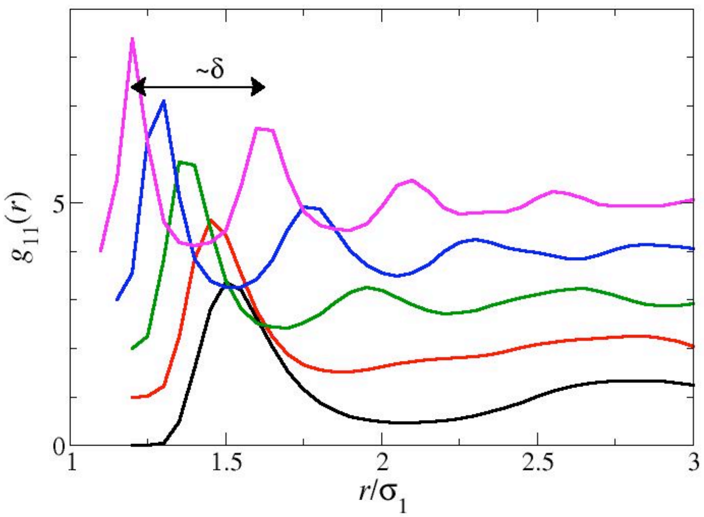
$\rho_2=1.5$



$\rho_2=3.0$



$\rho_2=4.0$



La Sapienza
Università degli Studi di Roma

erc

nature Vol 462|5 November 2009|

Soft colloids make strong glasses

Johan Mattsson[1]†, Hans M. Wyss[1]†, Alberto Fernandez-Nieves[1]†, Kunimasa Miyazaki[2]†, Zhibing Hu[3], David R. Reichman[2] & David A. Weitz[1]

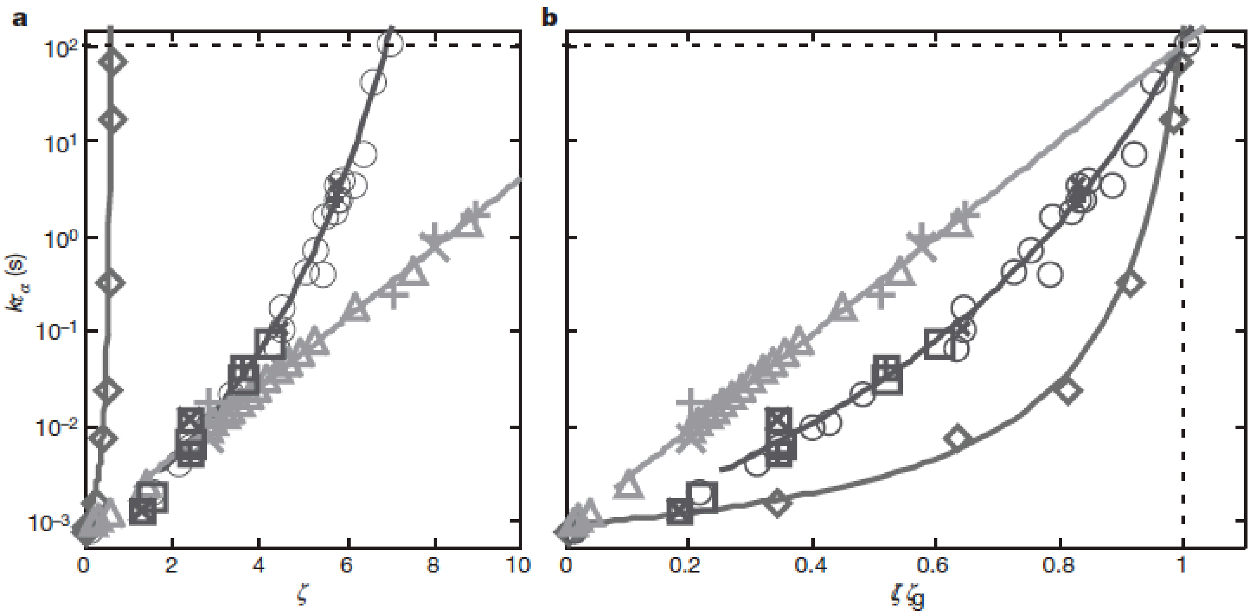
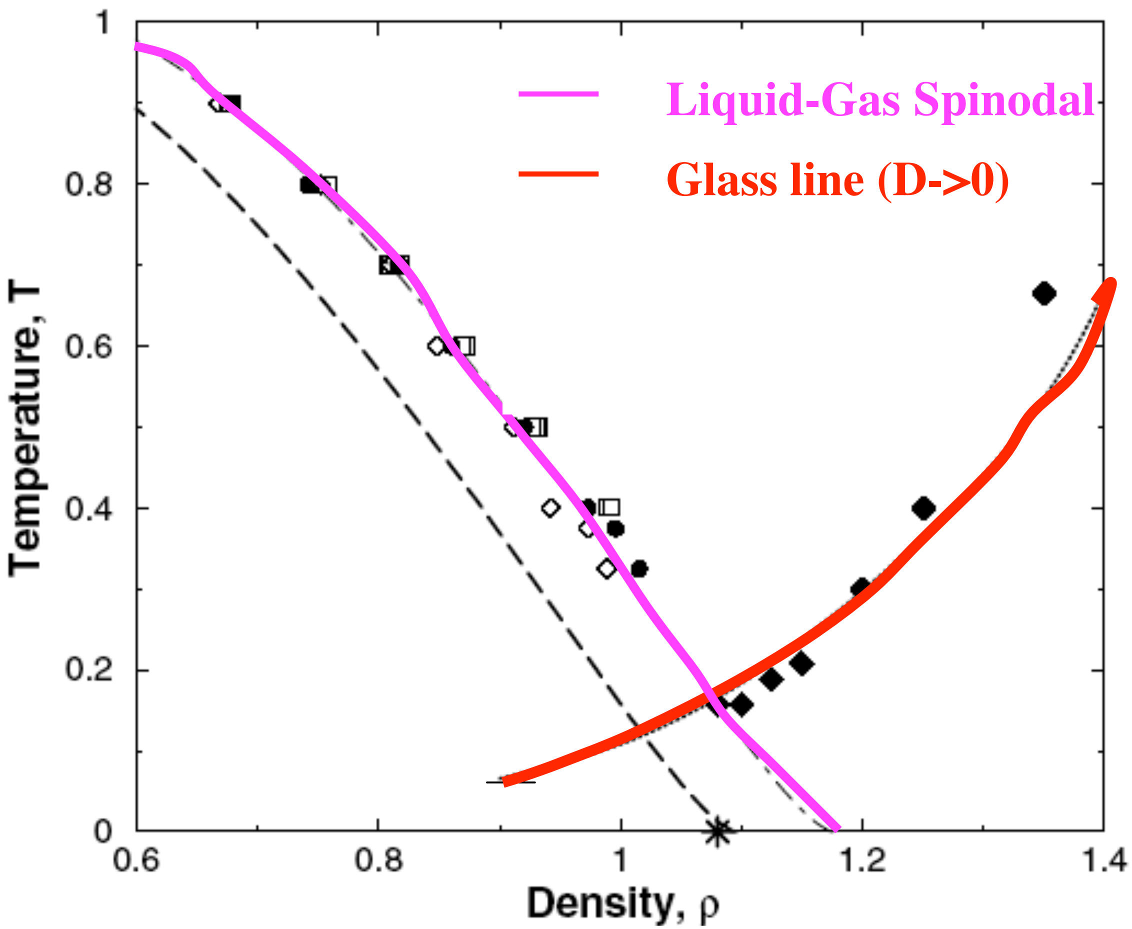


Figure 2 | Fragility range for colloids. a, Plot of $k\tau_\alpha$ versus ζ for stiff (diamonds, $R_0 = 95$ nm)[8], intermediate (empty circles, $R_0 = 92$ nm) and soft (triangles, $R_0 = 80$ nm) microgels, where k is chosen to collapse the data onto those of the intermediate sample at low ζ values. Data for a second intermediate sample (empty squares, $R_0 = 168$ nm) scale onto those of the first for $\zeta > \zeta^*$, as expected. Rescaled shear viscosities (intermediate: crosses in circles, $R_0 = 92$ nm, and crosses in squares, $R_0 = 168$ nm; soft: crosses, $R_0 = 80$ nm) and rheological structural relaxation times (intermediate: pluses in circles, $R_0 = 92$ nm, and pluses in squares, $R_0 = 168$ nm; soft: pluses, $R_0 = 80$ nm). **b,** Same as **a**, with ζ normalized by $\zeta_g = \zeta(\tau_\alpha = 100\,\text{s})$.

Microgel particles of varying elasticity

La Sapienza
Università degli Studi di Roma

Glasses and Gels….



What happen with attractions ?

Binary Mixture LJ particles

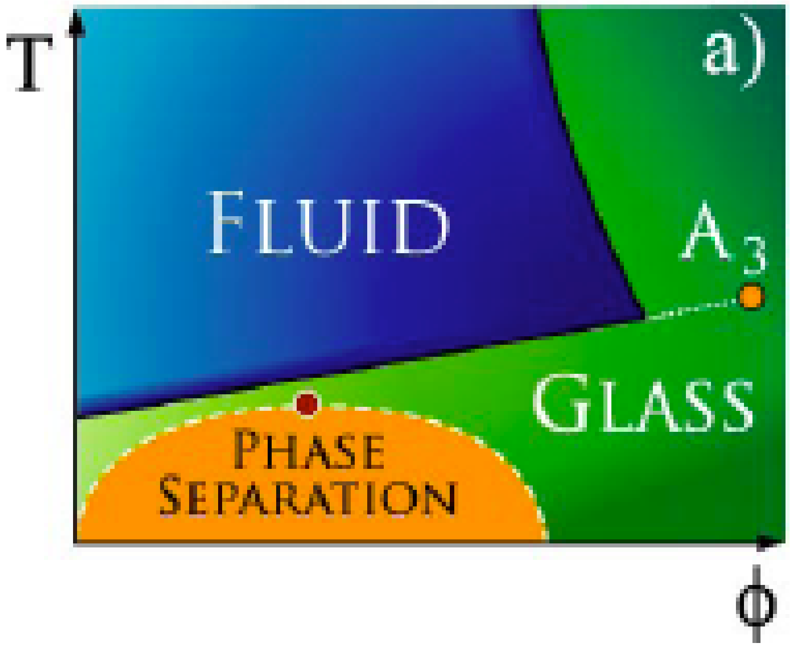
“*Equilibrium*”
“homogeneous”
arrested states only for large packing fraction

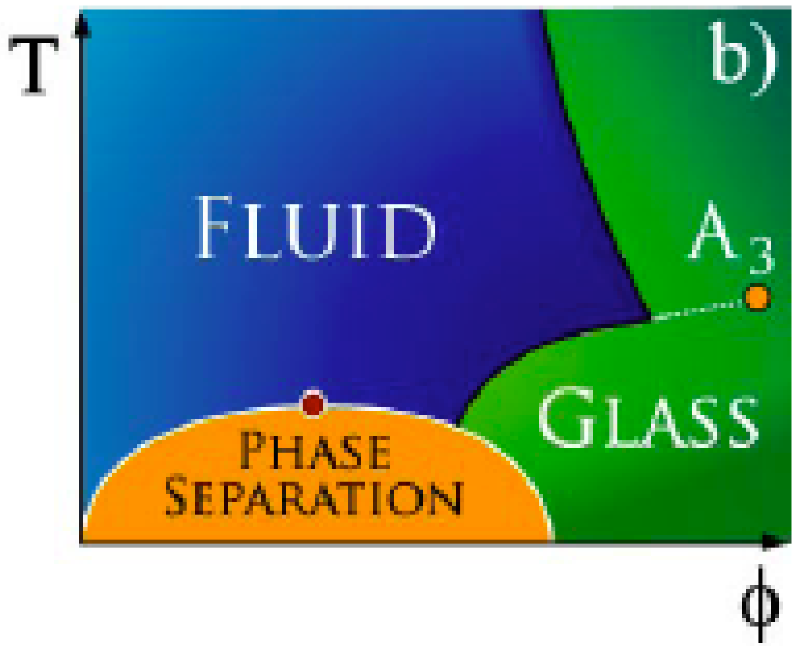
VOLUME 85, NUMBER 3 PHYSICAL REVIEW LETTERS 17 JULY 2000

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)

Two possibilities, on reducing the range of interaction (depletion interactions, proteins)





Contradictory exp results
MCT (Fuchs, Bergenholtz)

Simulations Supported
(Foffi et al PRL **94, 078301, 2005)**

La Sapienza
Università degli Studi di Roma

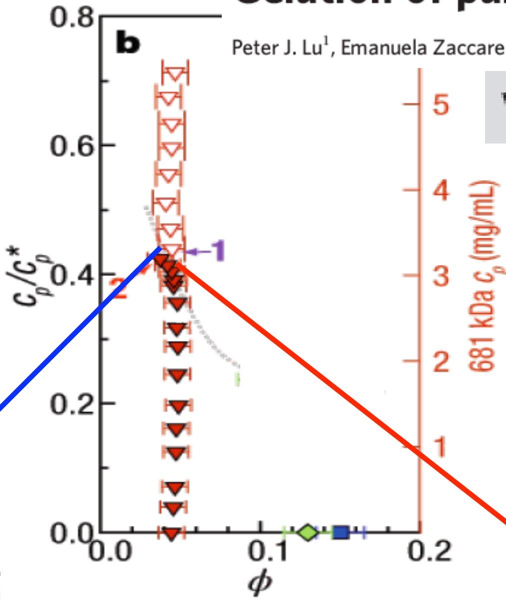
erc

For depletion interactions, arrest at low ϕ (gelation) is the result of a phase separation process interrupted by the glass transition

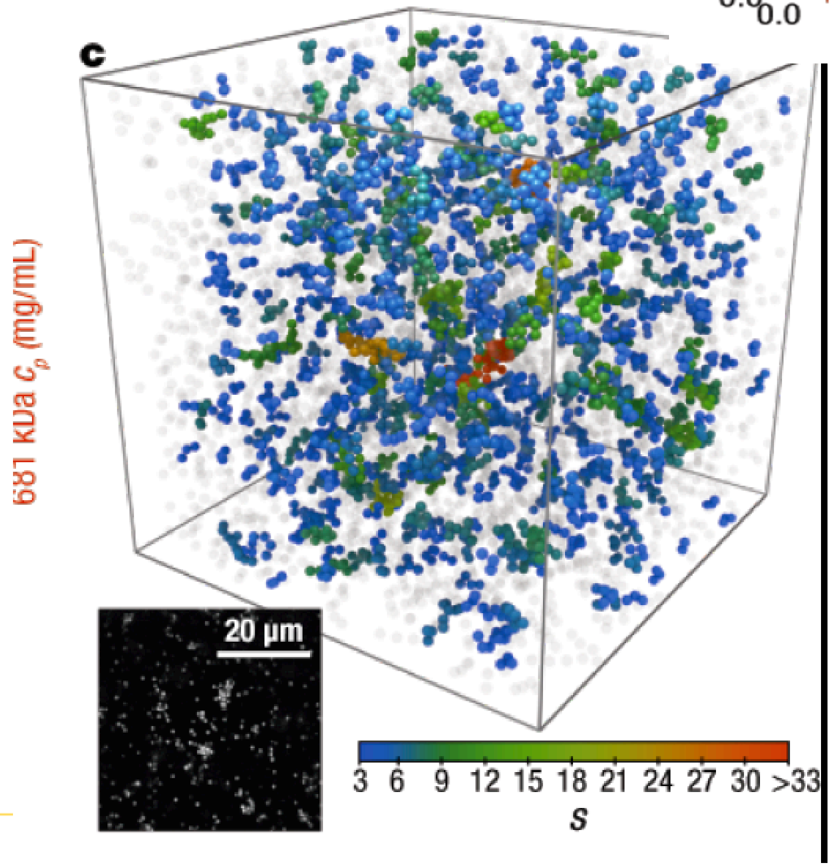
Gelation of particles with short-range attraction

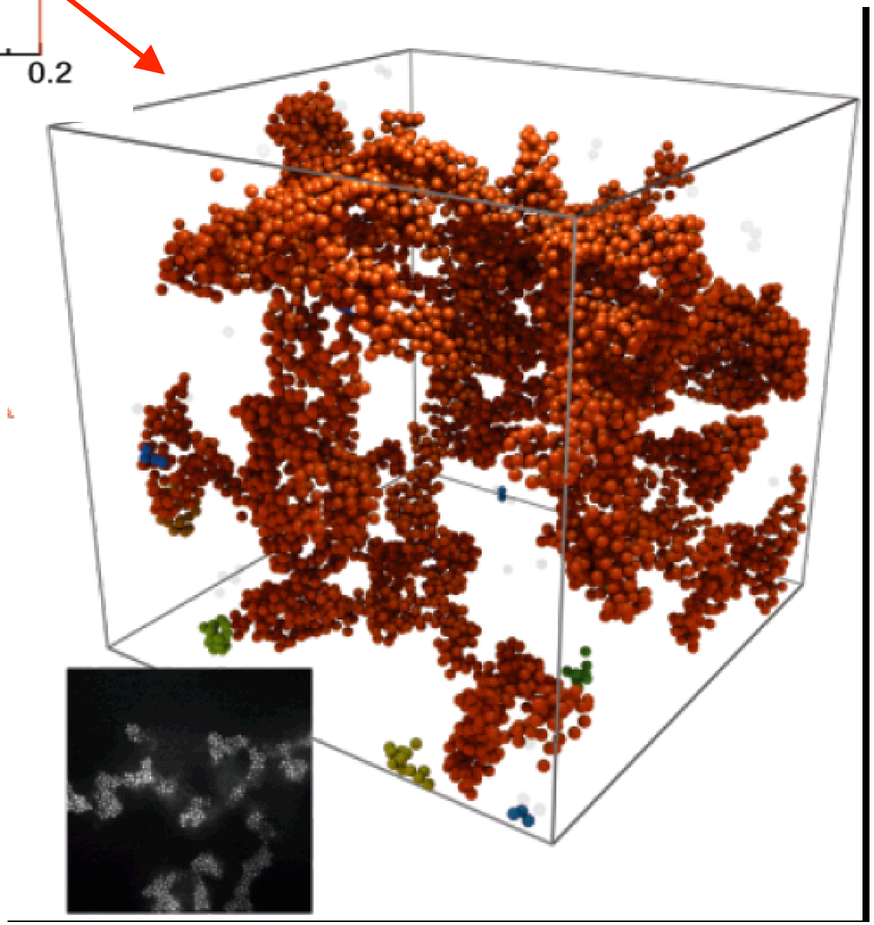
Peter J. Lu[1], Emanuela Zaccarelli[3,4], Fabio Ciulla[3], Andrew B. Schofield[5], Francesco Sciortino[3,4] & David A. Weitz[1,2]

Vol 453 | 22 May 2008 | doi:10.1038/nature06931



CONFOCAL IMAGES
First Order Transition

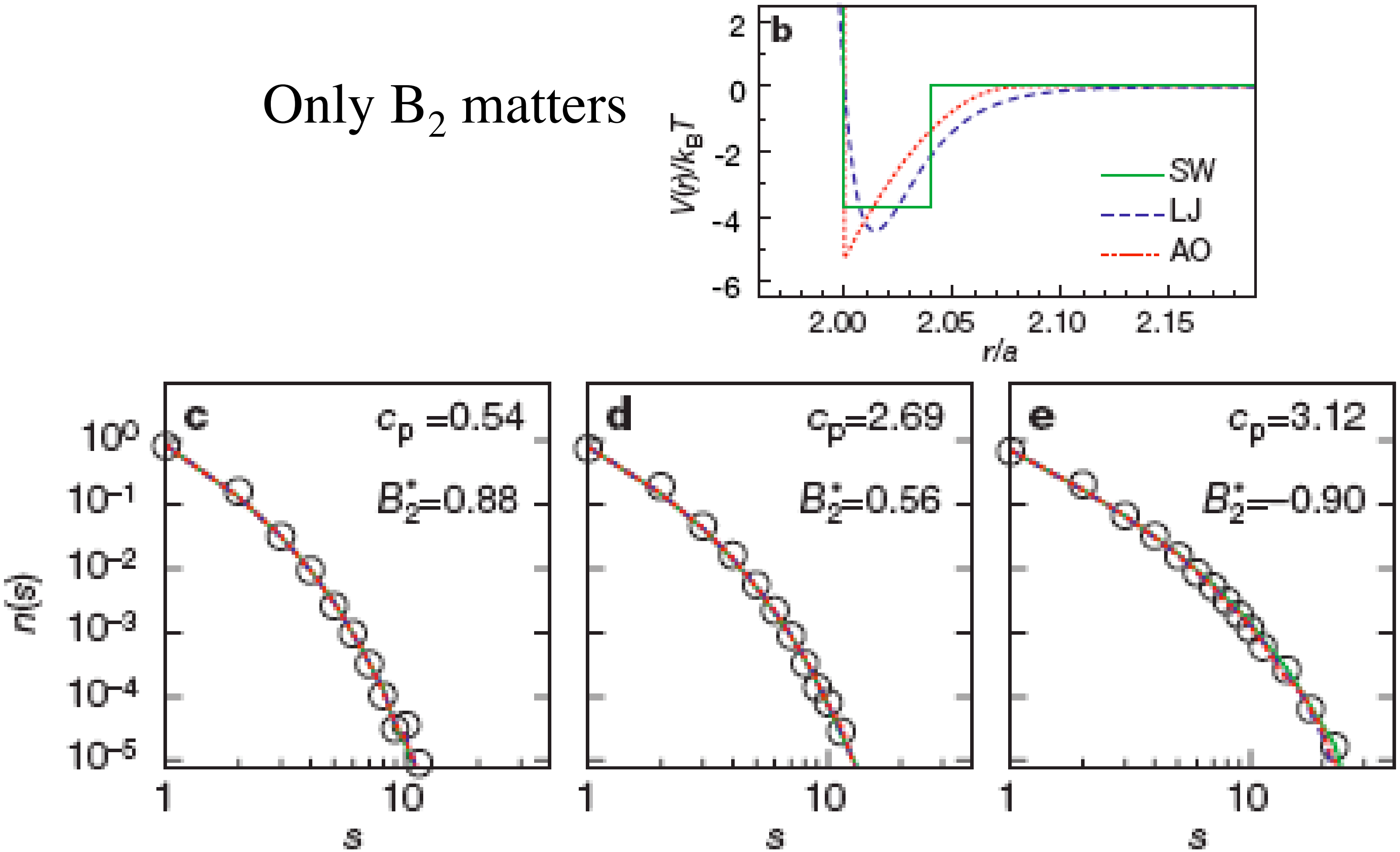


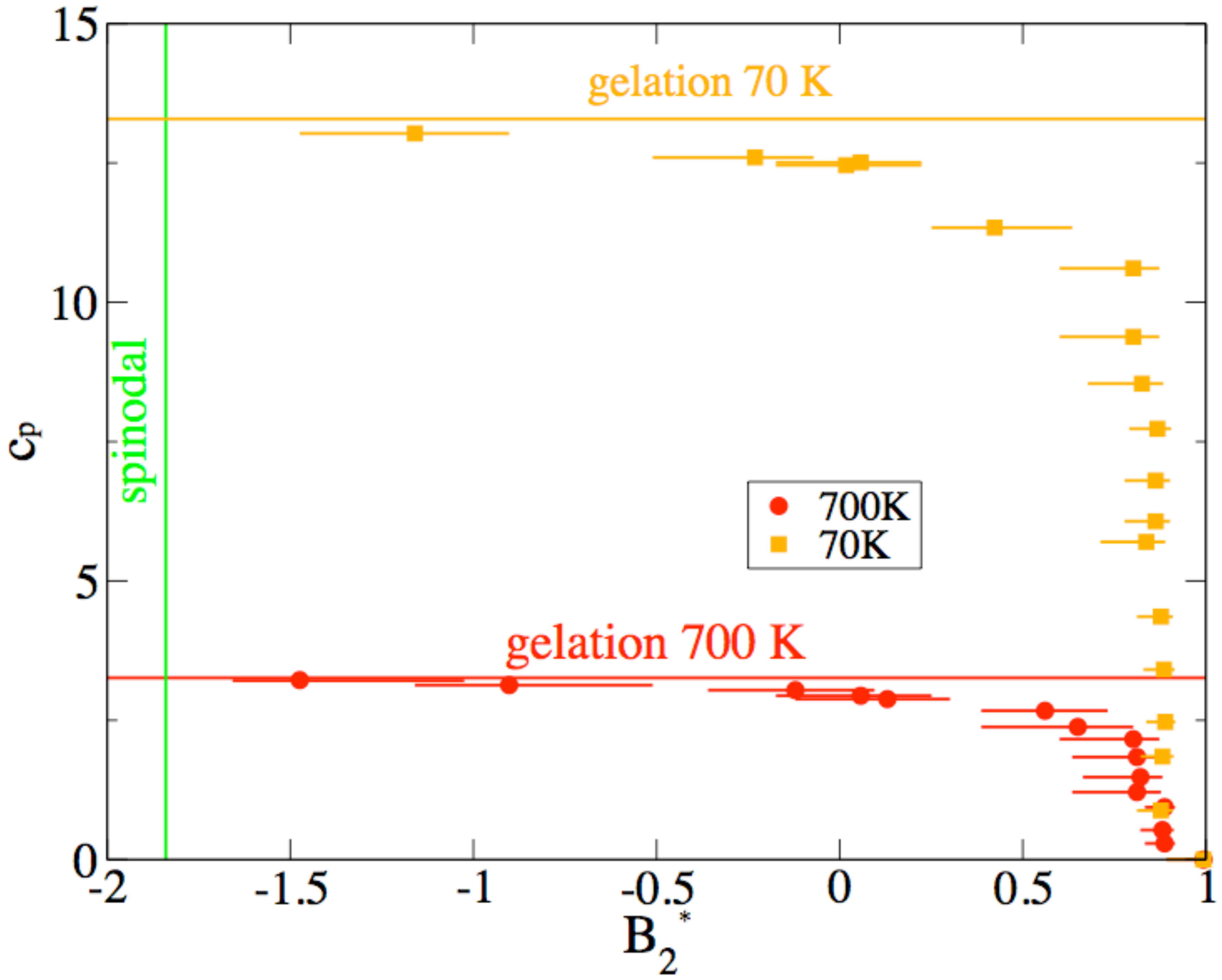


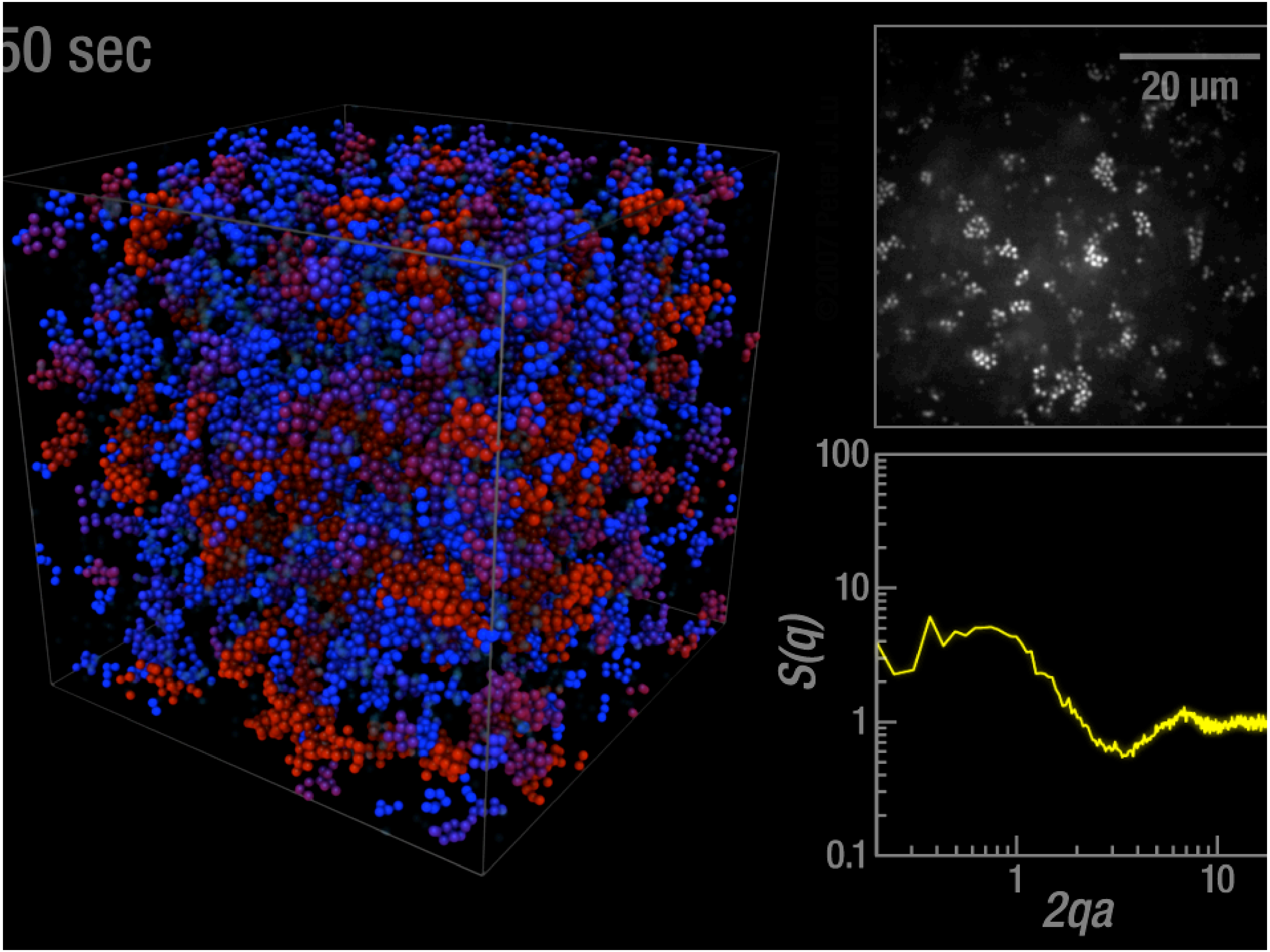
How relevant is the shape of the interaction potential
When the potential is short-ranged ?

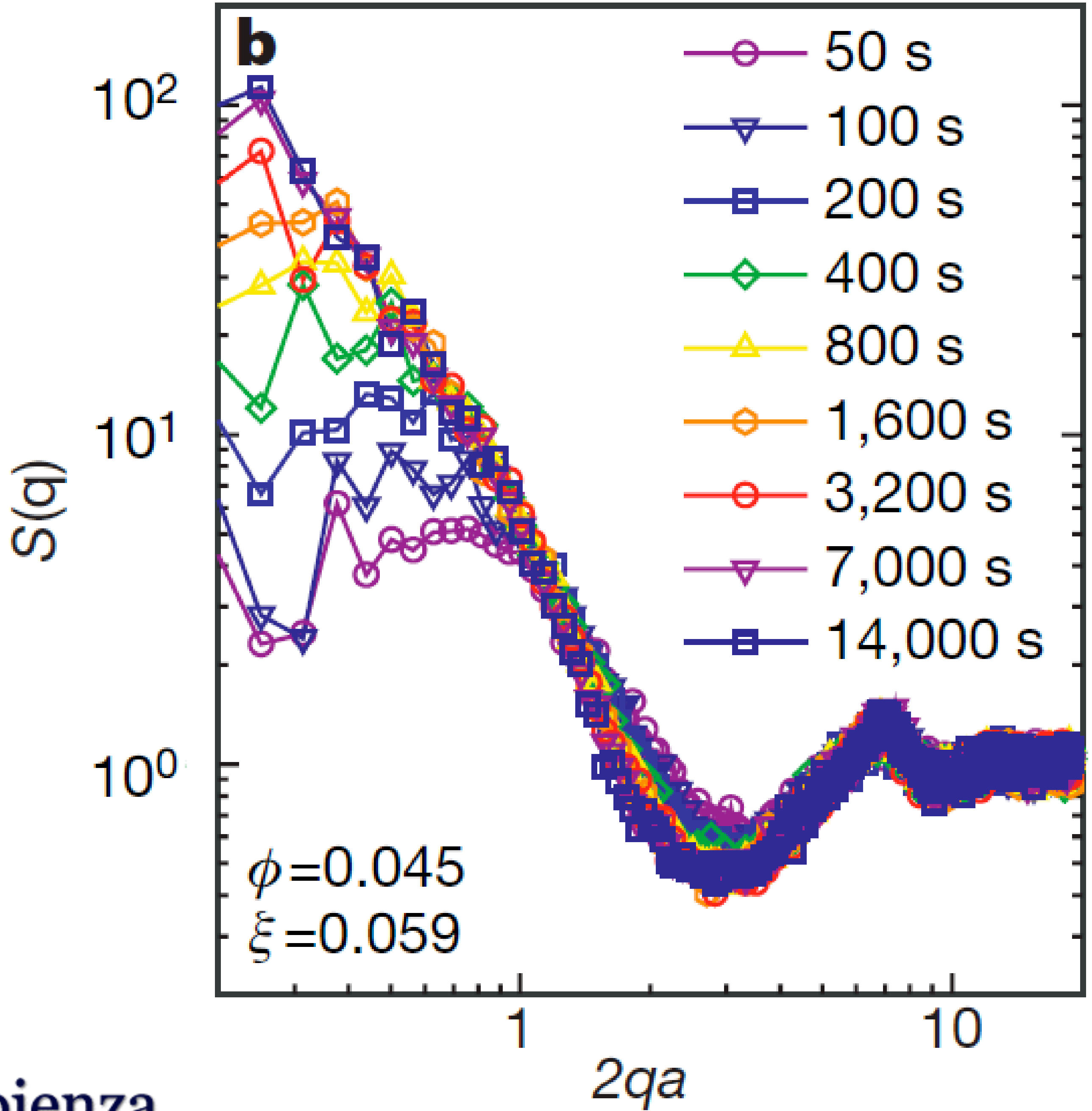
Noro-Frenkel: Extended corresponding-states behavior for particles with variable range attractions, J. Chem. Phys. 113, 2941 (2000)

Only B_2 matters




gelation 70 K
gelation 700 K
spinodal
700K
70K
c_p
B_2^*
15
10
5
0
-2
-1.5
-1
-0.5
0
0.5
1


50 sec
20 µm
100
10
1
0.1
S(q)
1
10
2qa

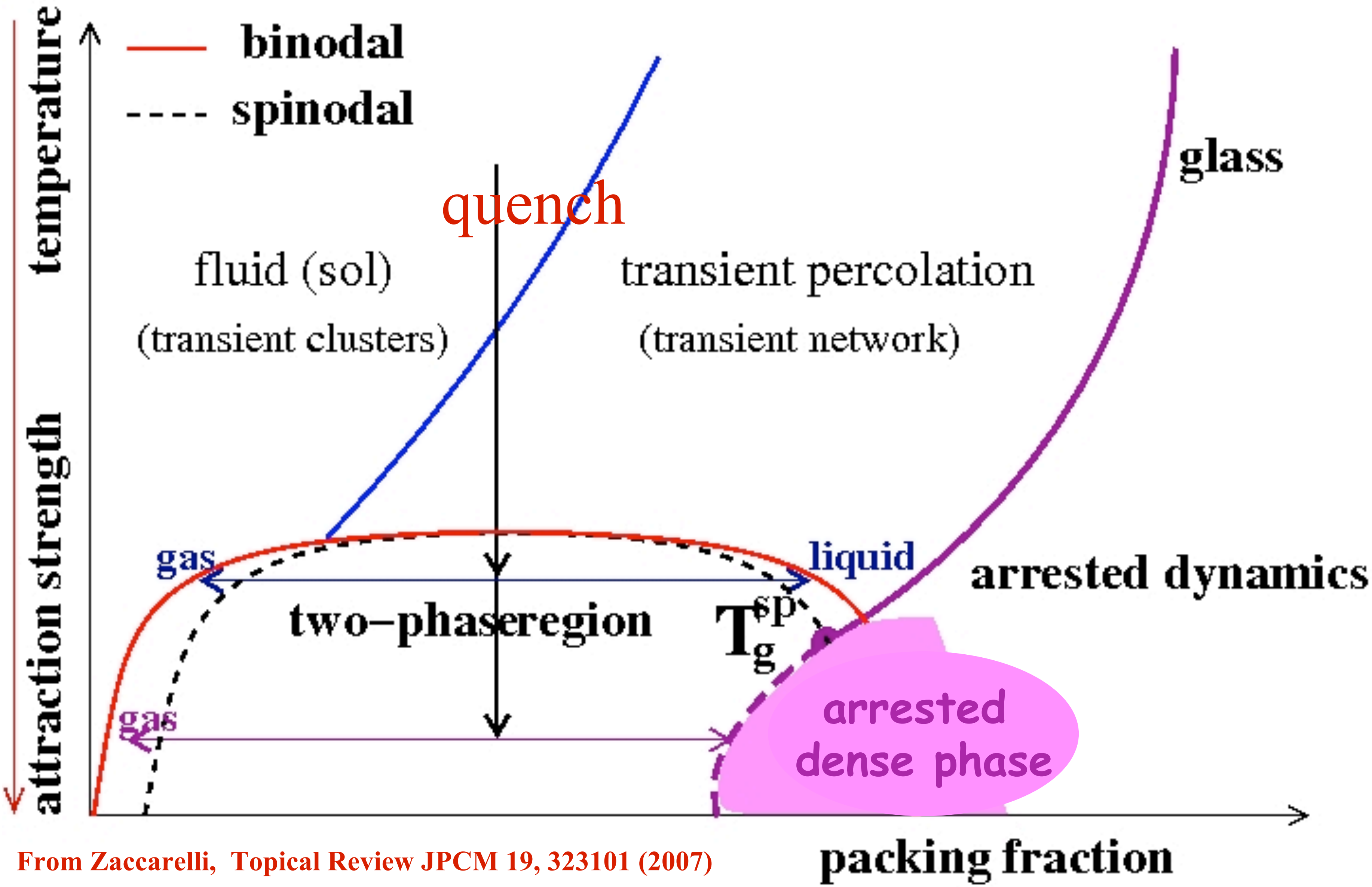


La Sapienza
Università degli Studi di Roma

erc

Non-equilibrium route to gelation

Spherical potentials: arrested phase separation
(interrupted by the glass transition)



From Zaccarelli, Topical Review JPCM 19, 323101 (2007)

PRL **99,** 118301 (2007) PHYSICAL REVIEW LETTERS week ending 14 SEPTEMBER 2007

Interplay between Spinodal Decomposition and Glass Formation in Proteins Exhibiting Short-Range Attractions

Frédéric Cardinaux,* Thomas Gibaud, Anna Stradner, and Peter Schurtenberger†
Department of Physics, University of Fribourg, CH-1700 Fribourg, Switzerland
(Received 16 December 2006; published 13 September 2007)

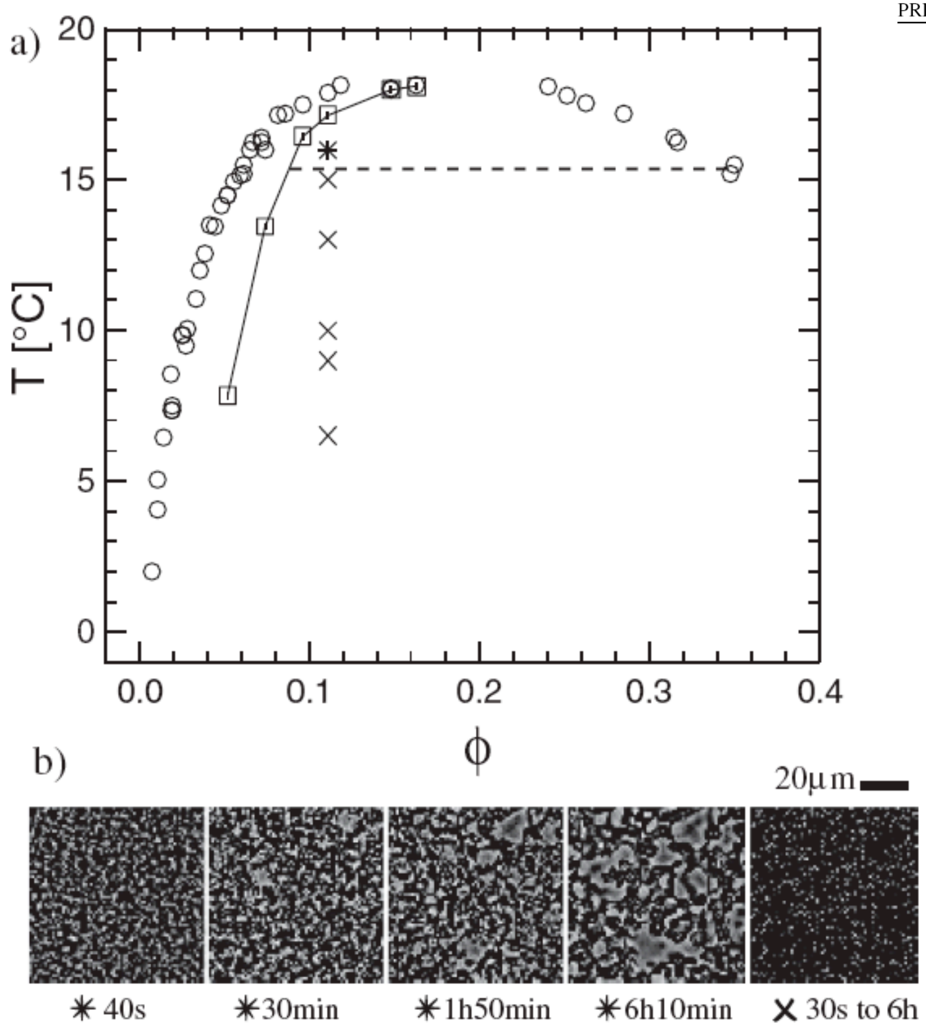
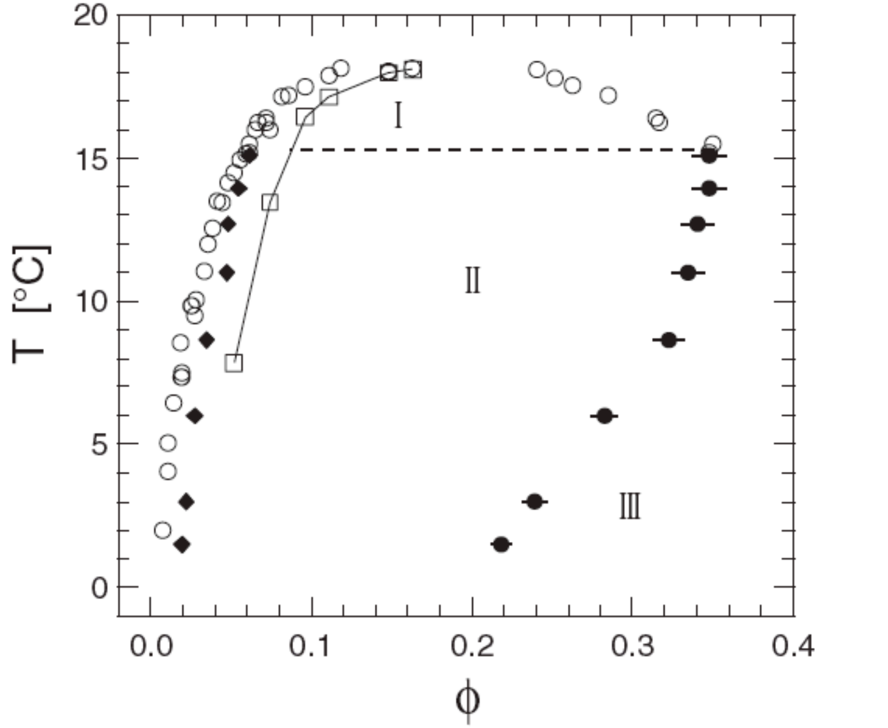


FIG. 1. (a) T-ϕ plane of the phase diagram of aqueous lysozyme solutions (20 mM Hepes buffer, pH = 7.8, 0.5M NaCl). Liquid-liquid coexistence curve (○), spinodal (□). Also shown are state points in the unstable region investigated with rheology where liquidlike (*) and solidlike (×) behavior has been observed. (b) Phase contrast micrographs of samples at $\phi = 0.11$ showing the coarsening at 16.8 °C (*) and the freezing at 13 °C (×) of the bicontinuous texture in the spinodal region.

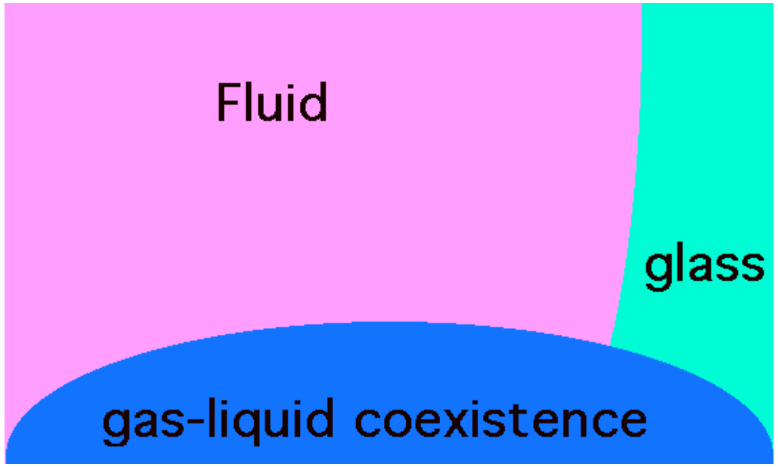
RL **99,** 118301 (2007) PHYSICAL RE



IG. 4. Kinetic phase diagram of aqueous lysozyme solutions howing regions of complete demixing (I), gel formation (II), nd glasses (III). Full symbols stand for the results of the centrifugation experiments: (●) arrested dense phase, (◆) dilute phase.

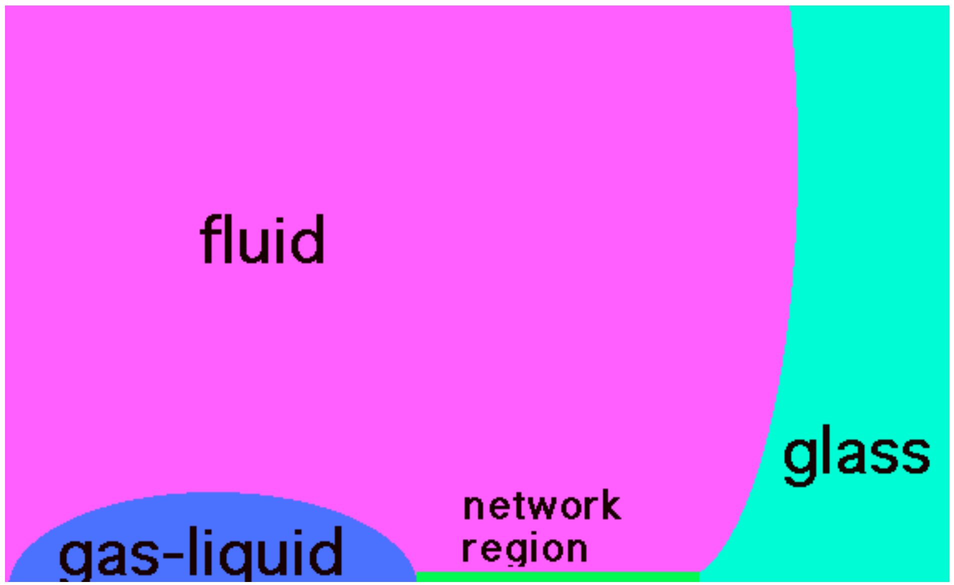
How to go to low T at low ϕ (in metastable equilibrium)

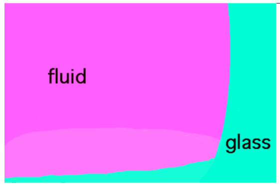
How to suppress phase separation ?



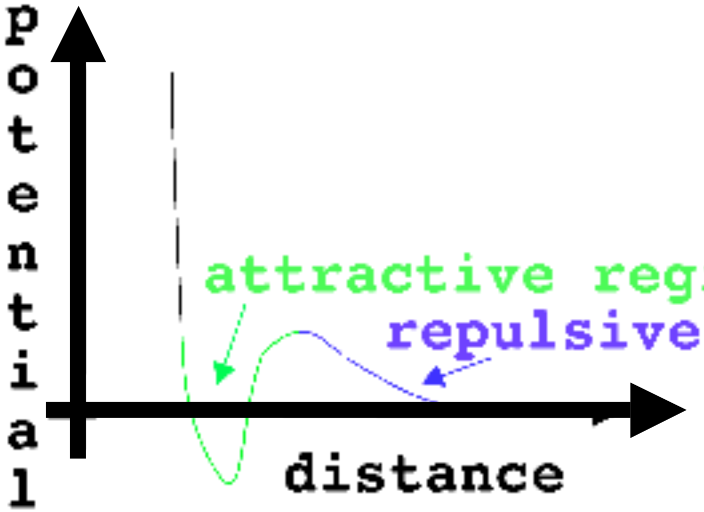
Competing interactions

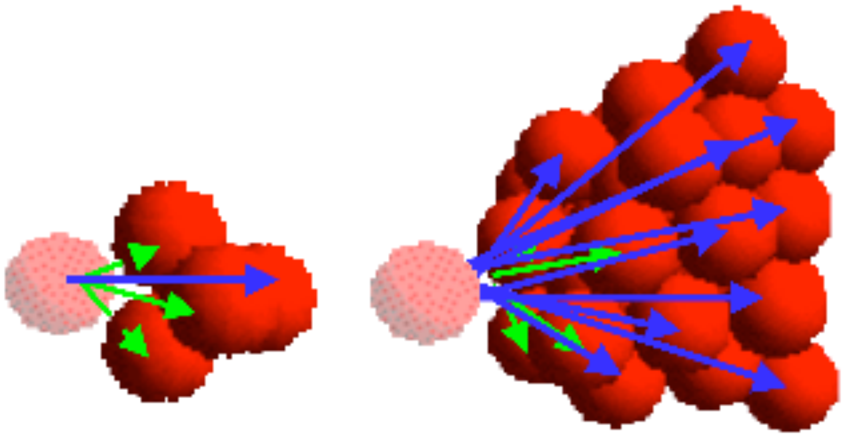
Reducing "valence"



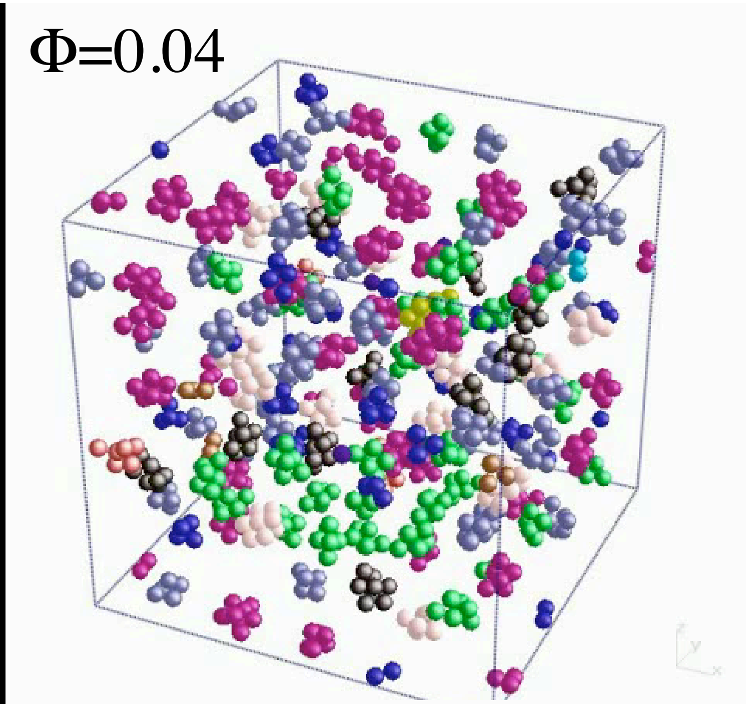


Competing Interactions





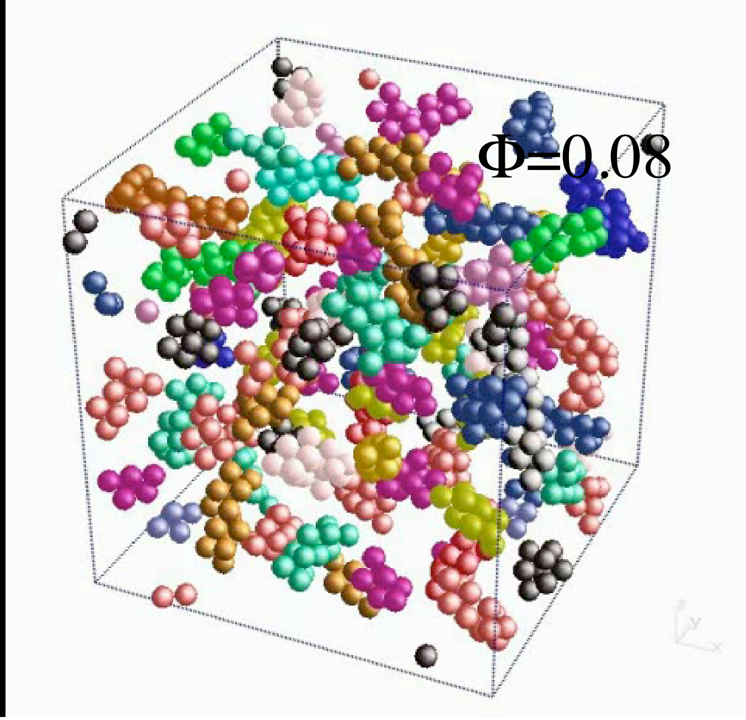
Phase separation is suppressed - Cluster phases (microphase separation)

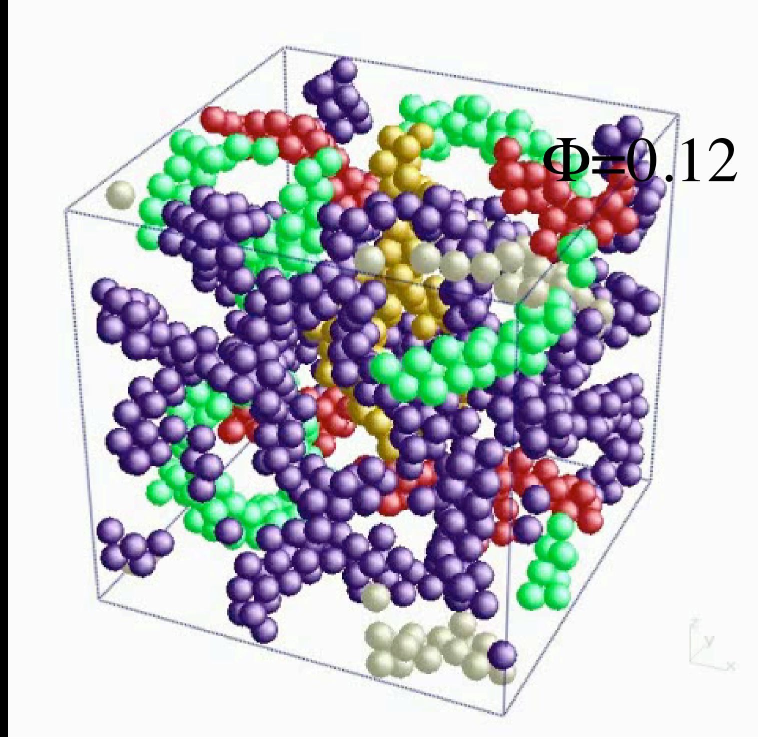


Toledano JCF, FS, Zaccarelli E
Colloidal systems with competing interactions: from an arrested repulsive cluster phase to a gel
Soft Matter 5, 2390-2398 (2009)

$kT/A=2 \quad kT/\varepsilon=0.1$

$\xi=2\sigma$



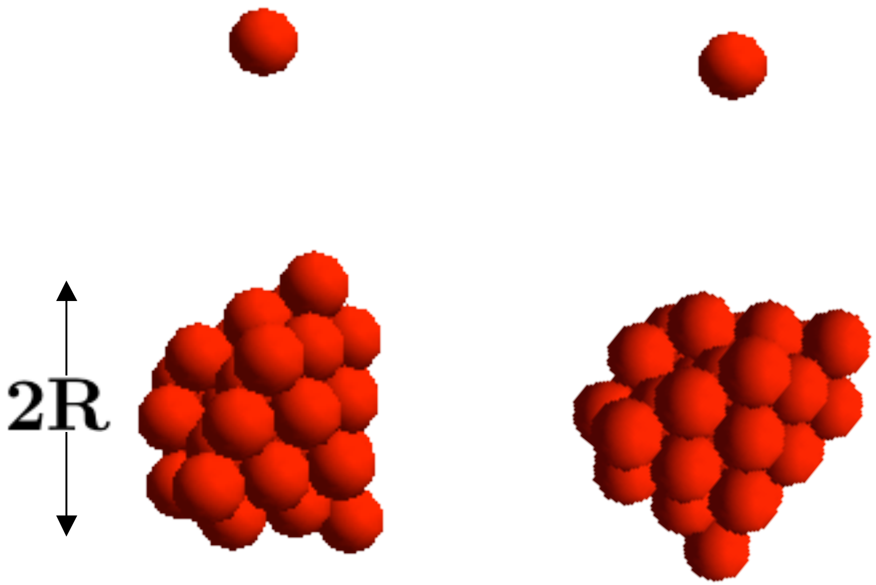


Two questions:

1) Why a glass of cluster at low packing

2) Why one-dimensional shapes at larger packing

How do "spherical" clusters interact ?



$$\mathbf{V(r) = A\ \frac{e^{-r/\xi}}{r/\xi}}.$$

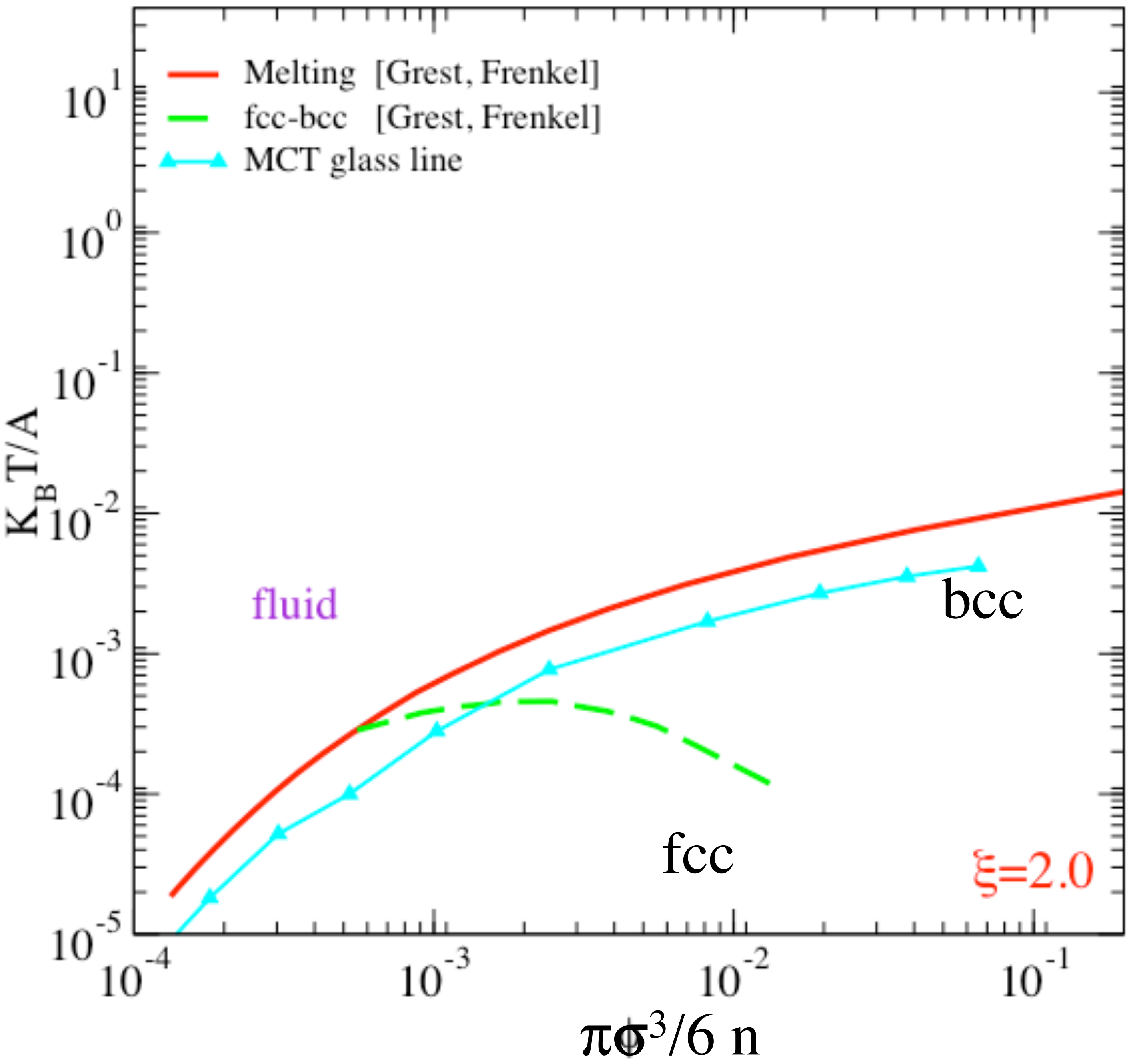
$$\mathbf{V_{RR}(r) = A(R)\ \frac{e^{-r/\xi}}{r/\xi}}.$$

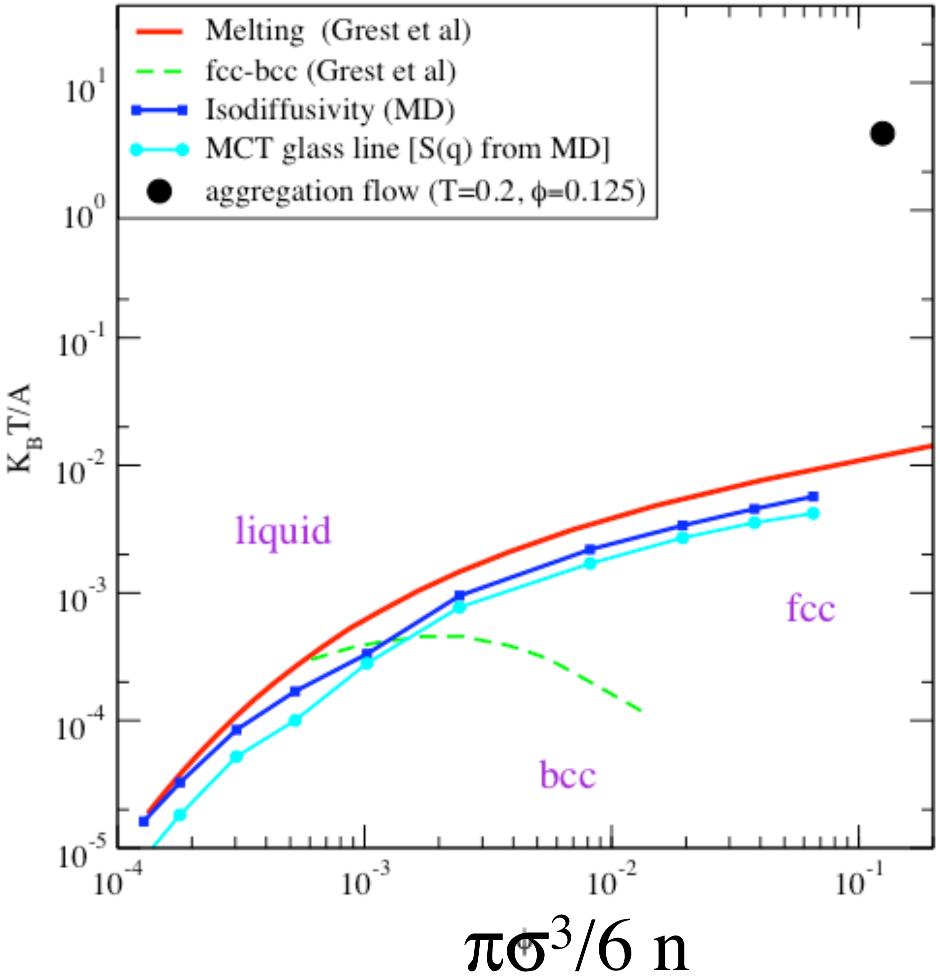
$$\mathbf{\frac{A(R)}{A} = \left\{2\pi\xi^3\rho e^{-R/\xi}\left[1+\frac{R}{\xi}+\left(\frac{R}{\xi}-1\right)e^{2R/\xi}\right]\right\}^2}.$$

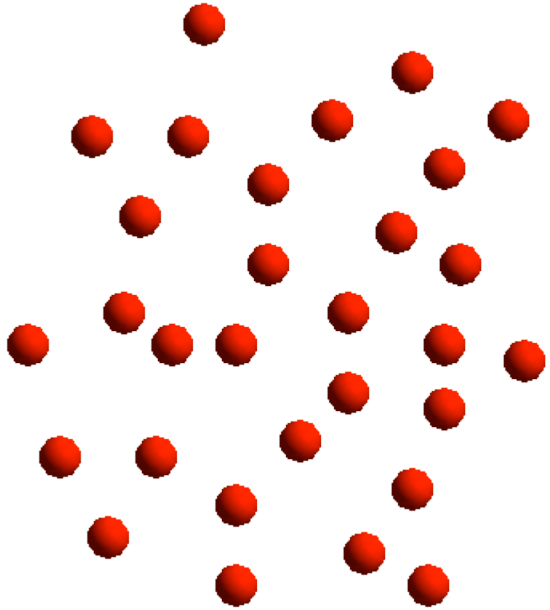
La Sapienza
Università degli Studi di Roma

erc

Yukawa Phase Diagram



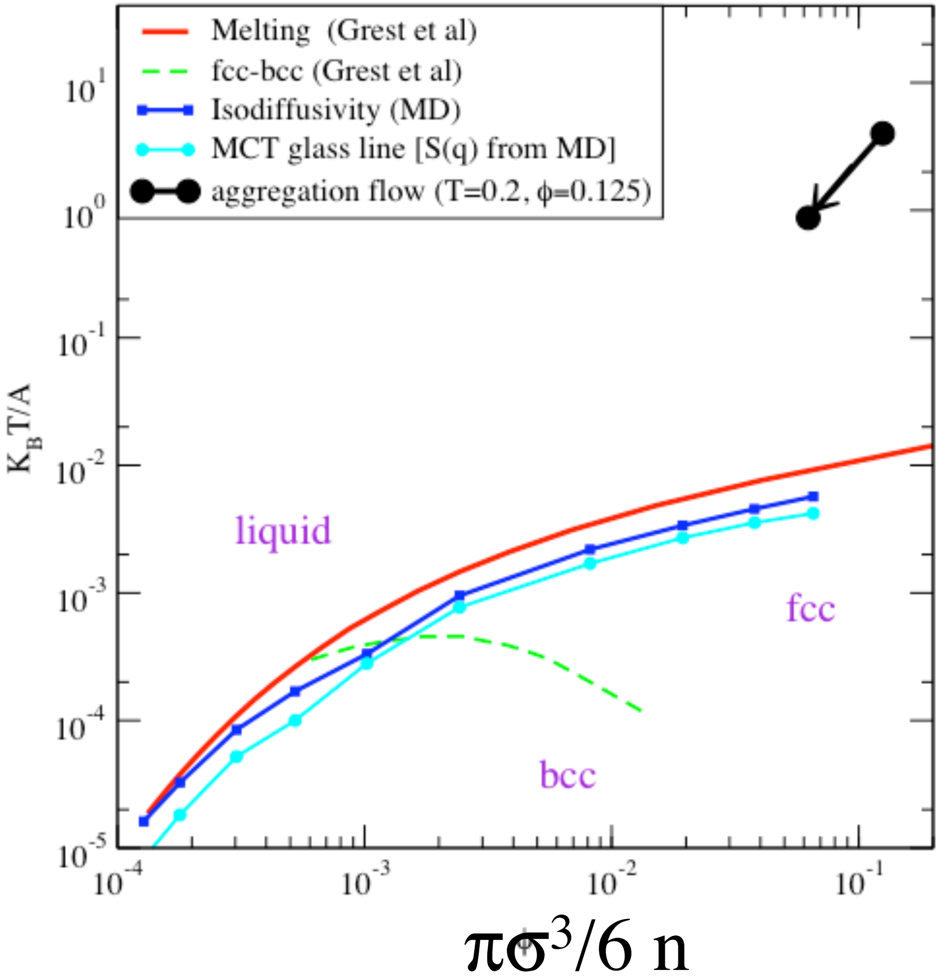


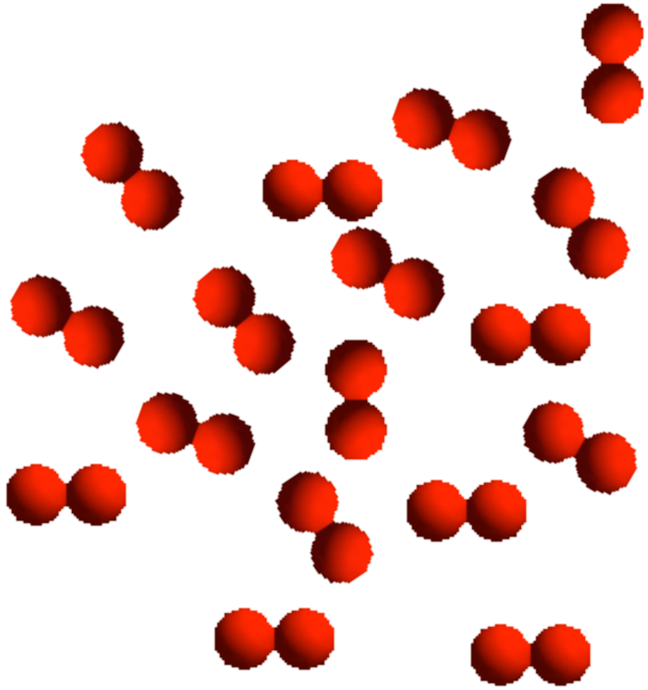


N=1

La Sapienza
Università degli Studi di Roma

erc

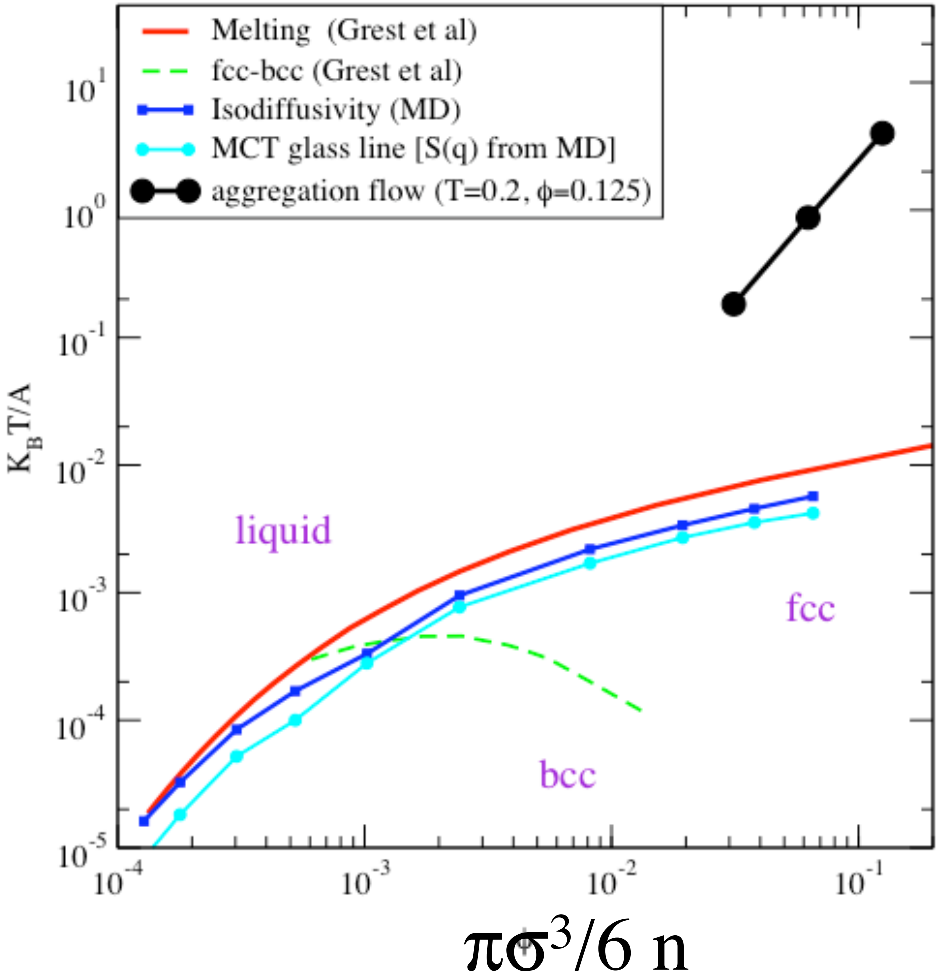


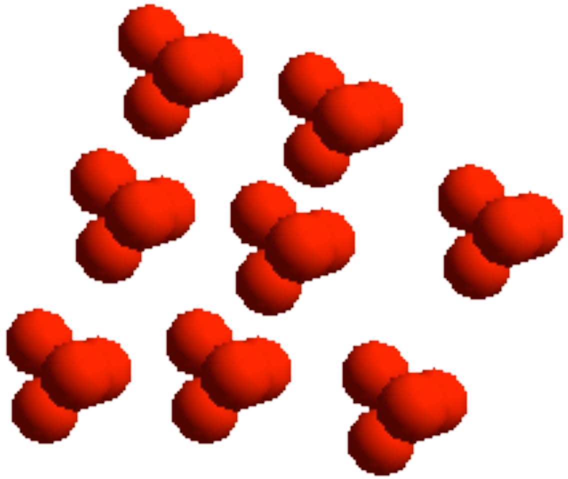


N=2

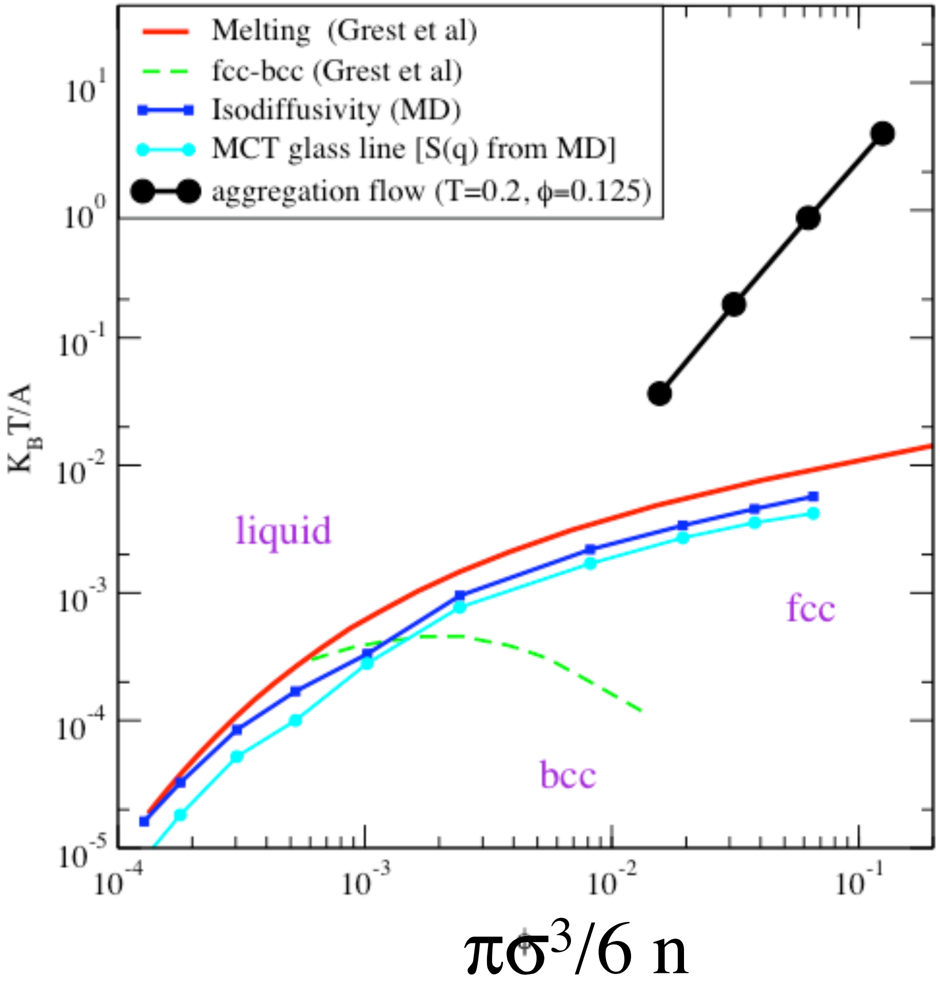
La Sapienza
Università degli Studi di Roma

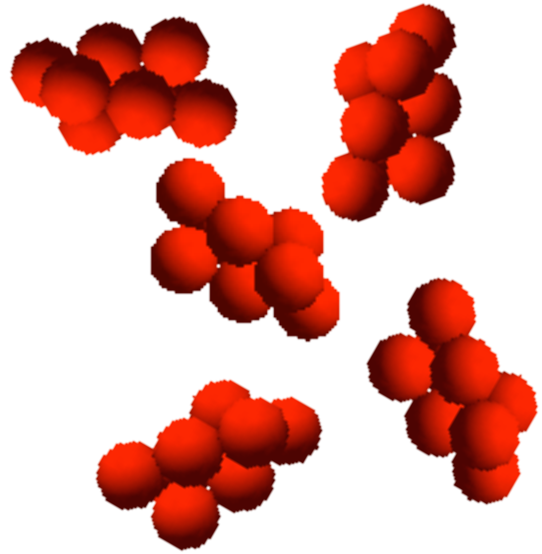
erc


Melting (Grest et al)
fcc-bcc (Grest et al)
Isodiffusivity (MD)
MCT glass line [S(q) from MD]
aggregation flow (T=0.2, φ=0.125)
$K_B T/A$
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
liquid
fcc
bcc
10^{-4}
10^{-3}
10^{-2}
10^{-1}
$\pi\sigma^3/6\ n$

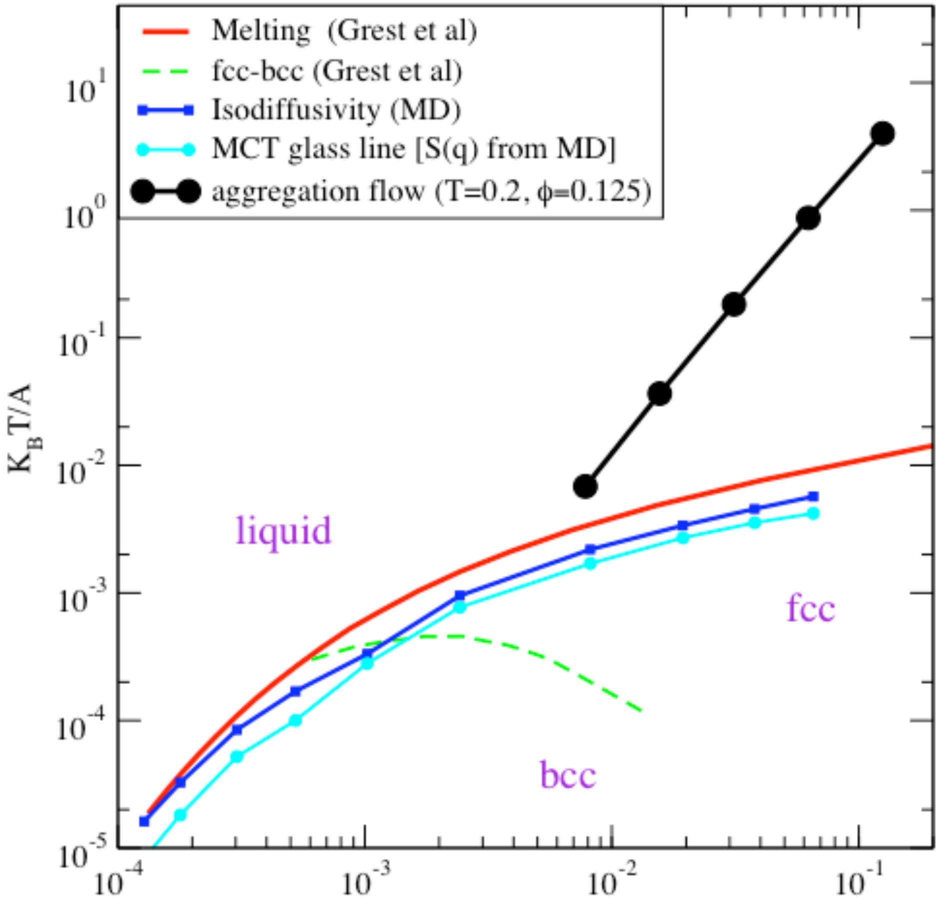


N=4

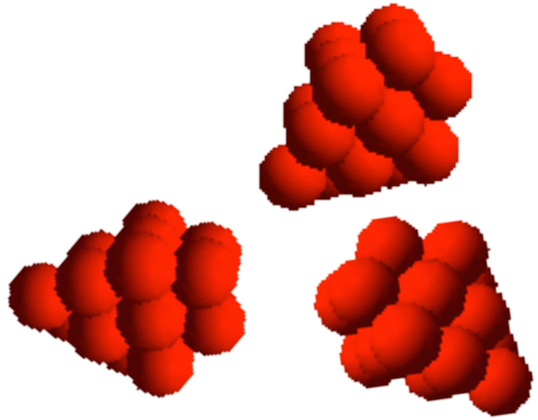

Melting (Grest et al)
fcc-bcc (Grest et al)
Isodiffusivity (MD)
MCT glass line [S(q) from MD]
aggregation flow (T=0.2, ϕ=0.125)
liquid
fcc
bcc
$K_B T/A$
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
$\pi\sigma^3/6\ n$



N=8



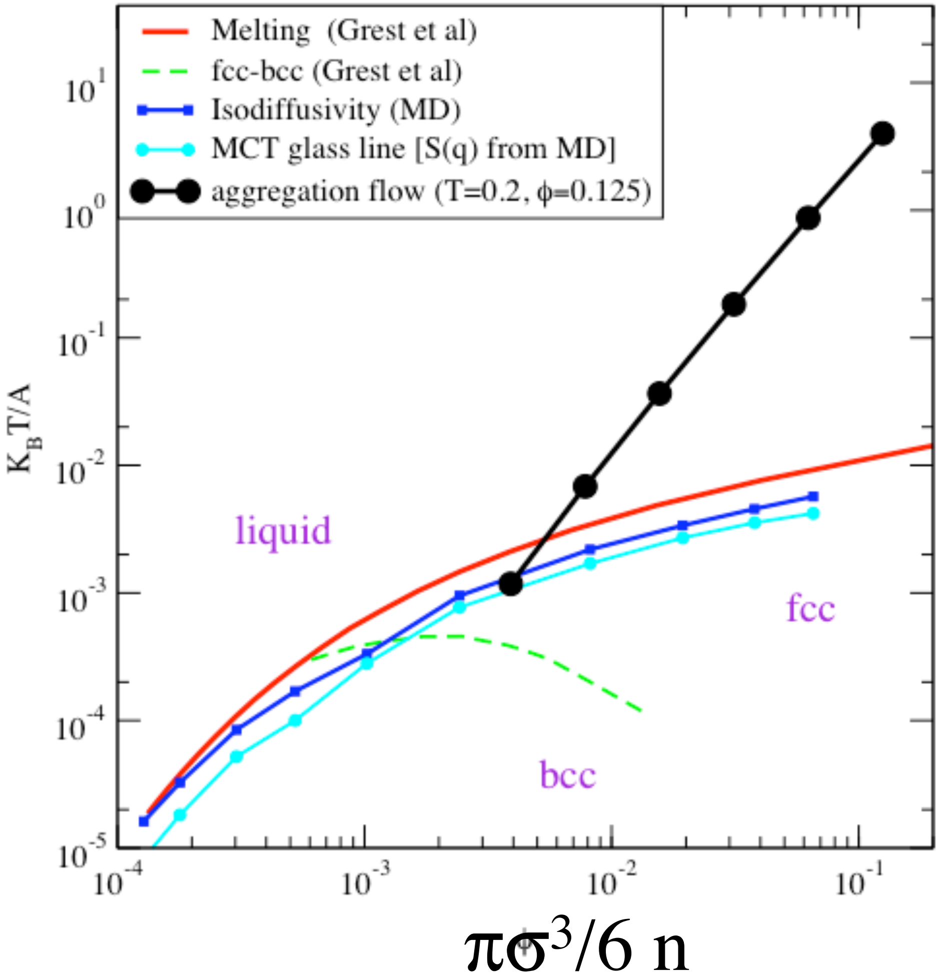
$\pi\sigma^3/6\ n$

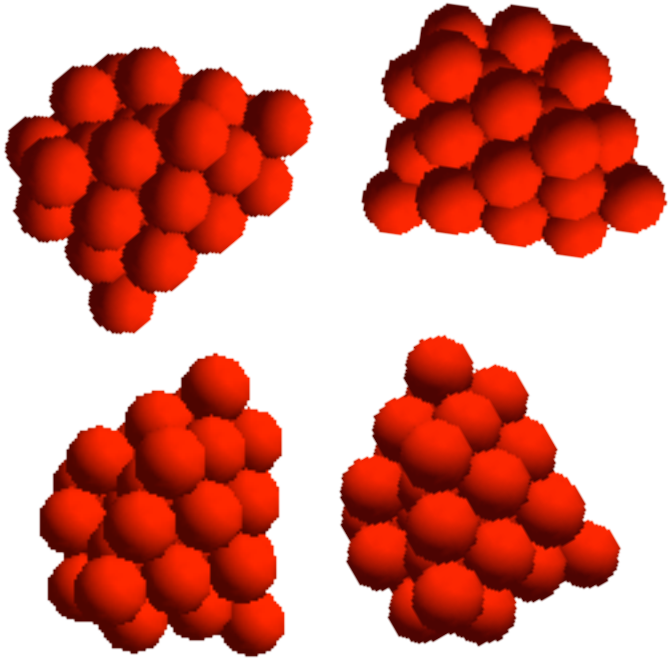


N=16

La Sapienza
Università degli Studi di Roma

erc

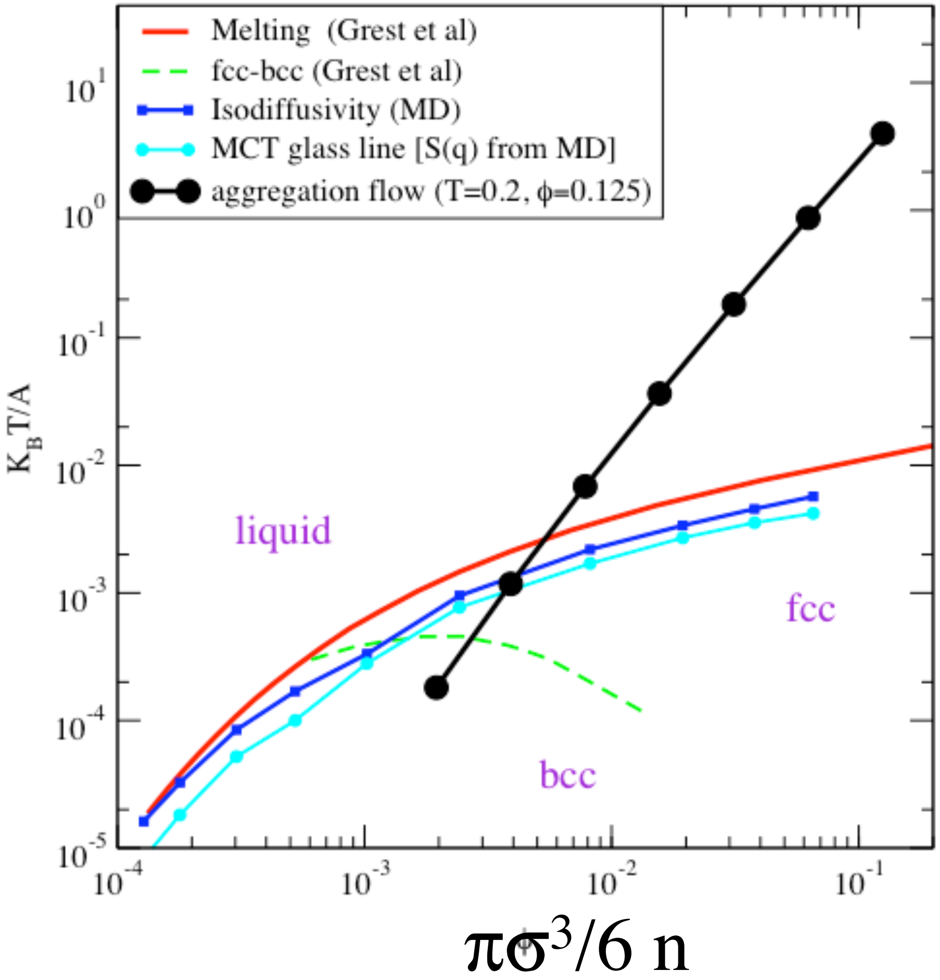


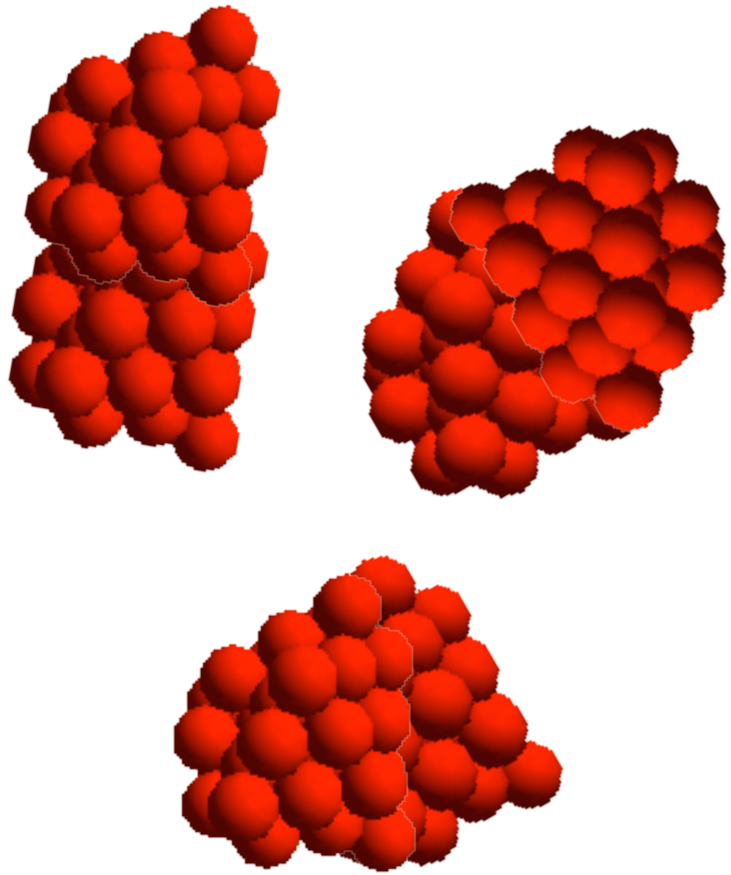


N=32

La Sapienza
Università degli Studi di Roma

erc





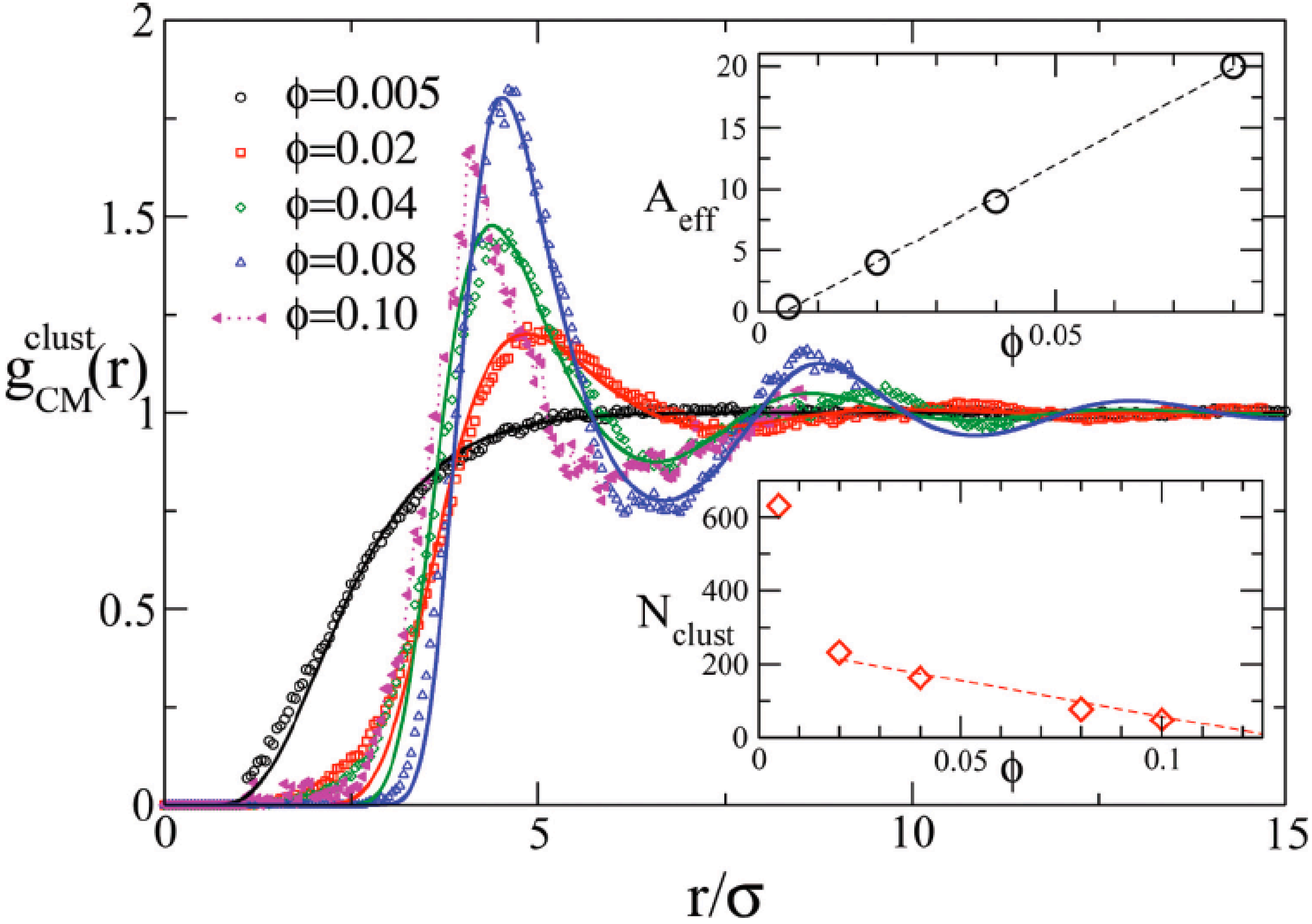
N=64

La Sapienza
Università degli Studi di Roma

erc

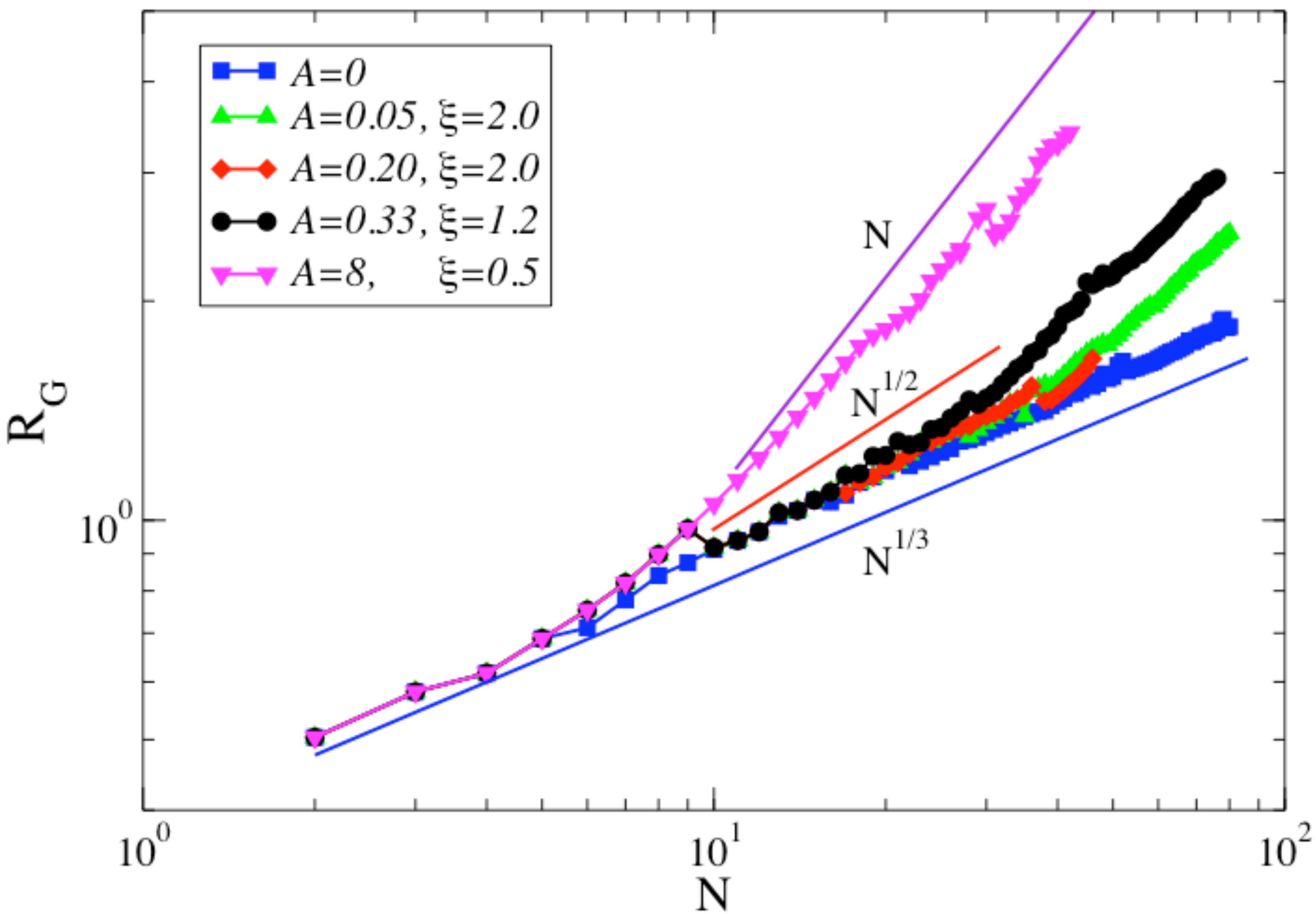
Comparison between theoretical and simulation g(r)

$$\mathbf{V}(\mathbf{r}) = \mathbf{A}(\mathbf{R}) \; \frac{\mathbf{e}^{-\mathbf{r}/\xi}}{\mathbf{r}/\xi}.$$



Why one dimensional growth….

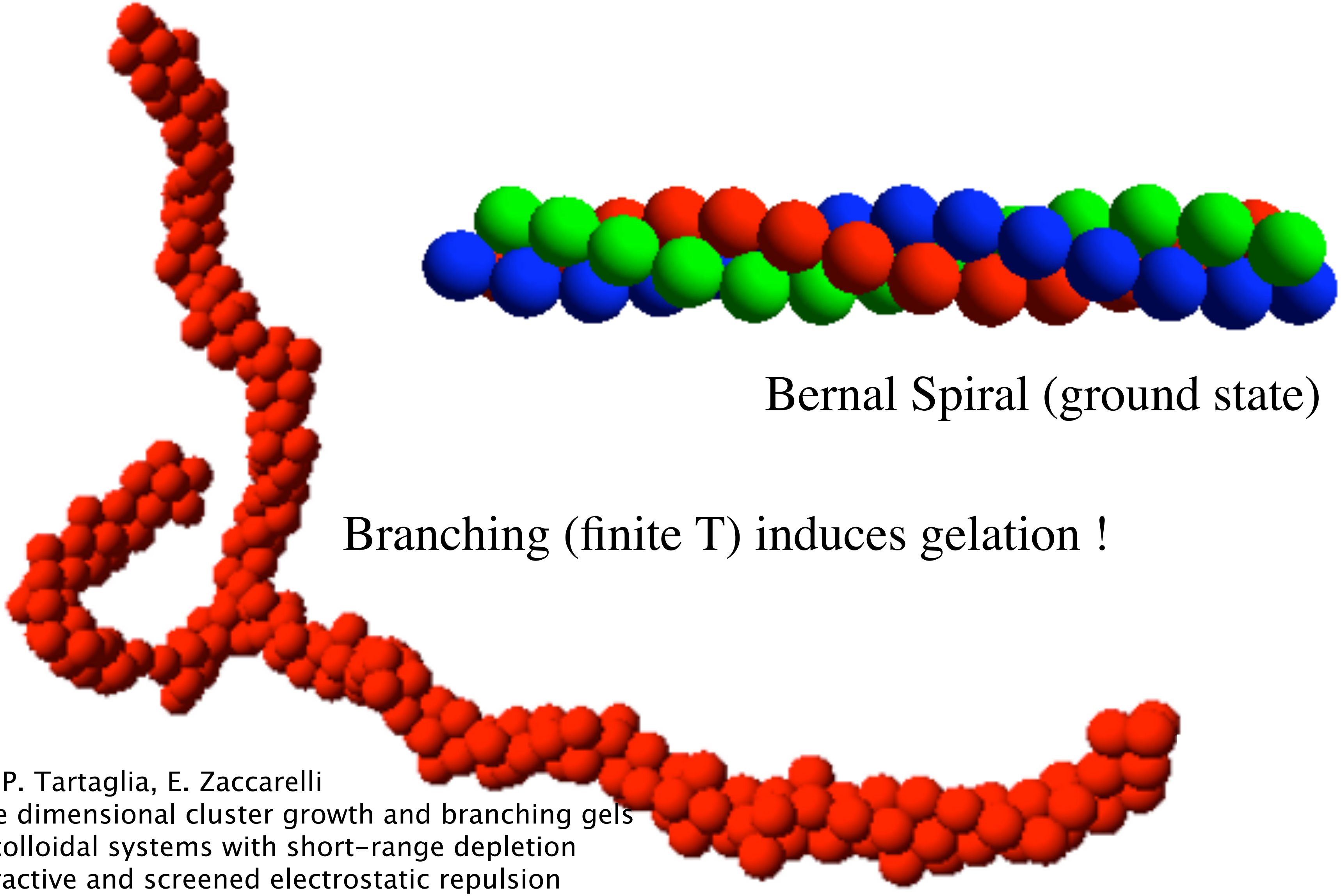
Ground-state clusters (S. Mossa et al, Langmuir 20, 10756, 2004)



La Sapienza
Università degli Studi di Roma

erc

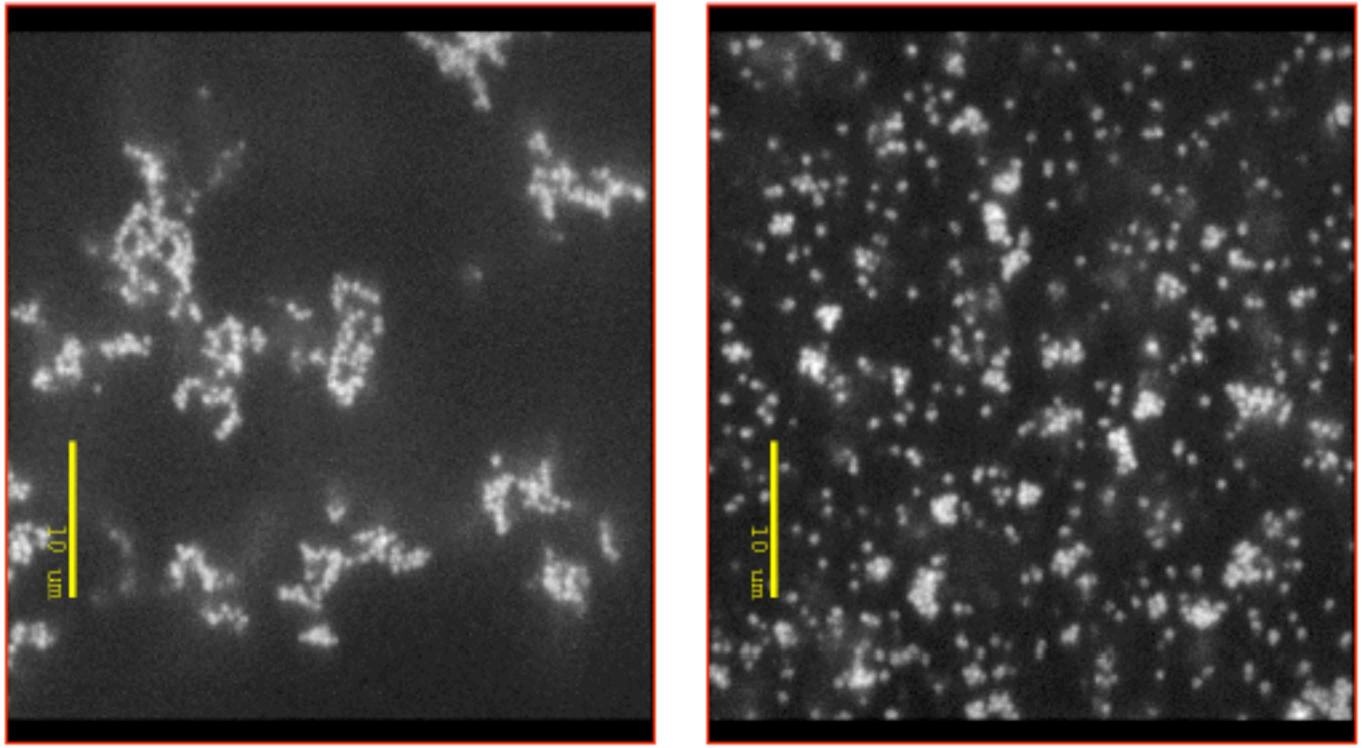
Cluster shapes for large but significantly screened repulsions



Bernal Spiral (ground state)

Branching (finite T) induces gelation !

FS, P. Tartaglia, E. Zaccarelli
One dimensional cluster growth and branching gels in colloidal systems with short-range depletion attractive and screened electrostatic repulsion
J. Phys. Chem. B 109, 21942-21953, 2005



Direct imaging of three-dimensional structure and topology of colloidal gels

A D Dinsmore[1,2] and D A Weitz[1]

La Sapienza
Università degli Studi di Roma

erc

Dynamical Arrest in Attractive Colloids: The Effect of Long-Range Repulsion

Andrew I. Campbell, Valerie J. Anderson, Jeroen S. van Duijneveldt, and Paul Bartlett
School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom
(Received 6 December 2004; published 23 May 2005)

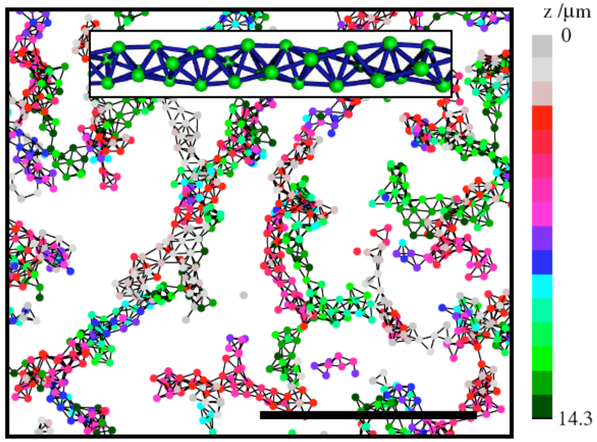


FIG. 3 (color online). A two-dimensional projection of the particle centers within a slab of gel (14.3 μm deep) at $\phi_c = 0.1$. Particles are colored as a function of their depth within the sample and drawn 40% of their actual size for clarity. The bar is 20 μm long. Inset: A spiral chain formed from tetrahedra of particles sharing faces.

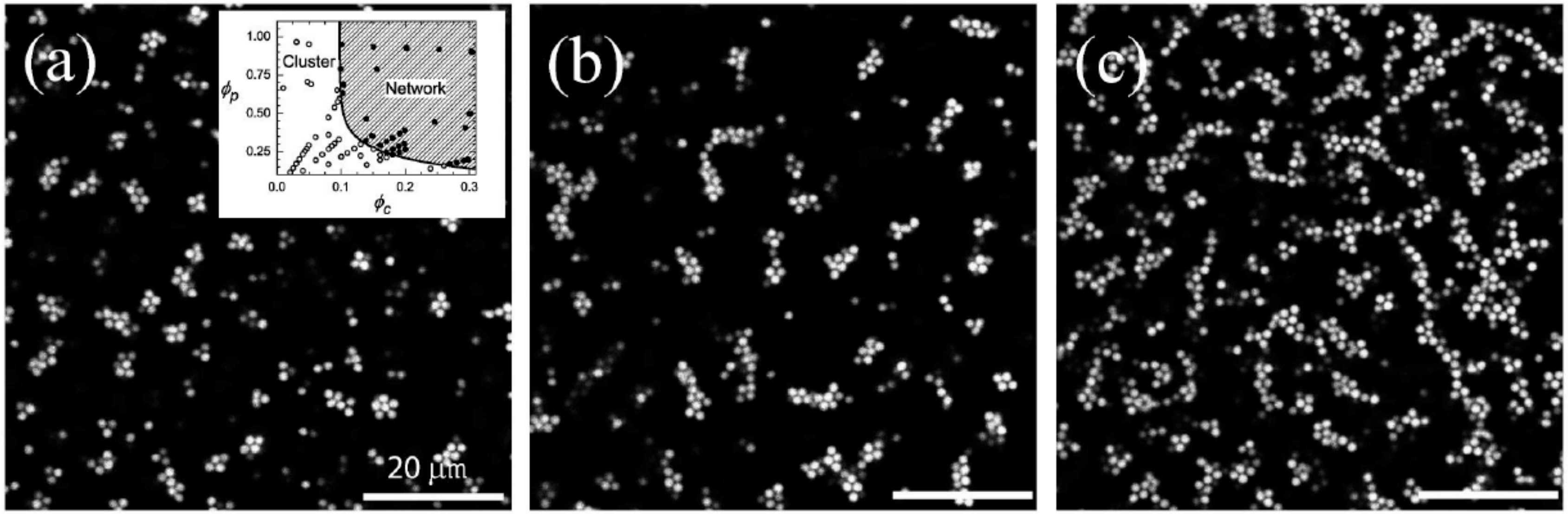
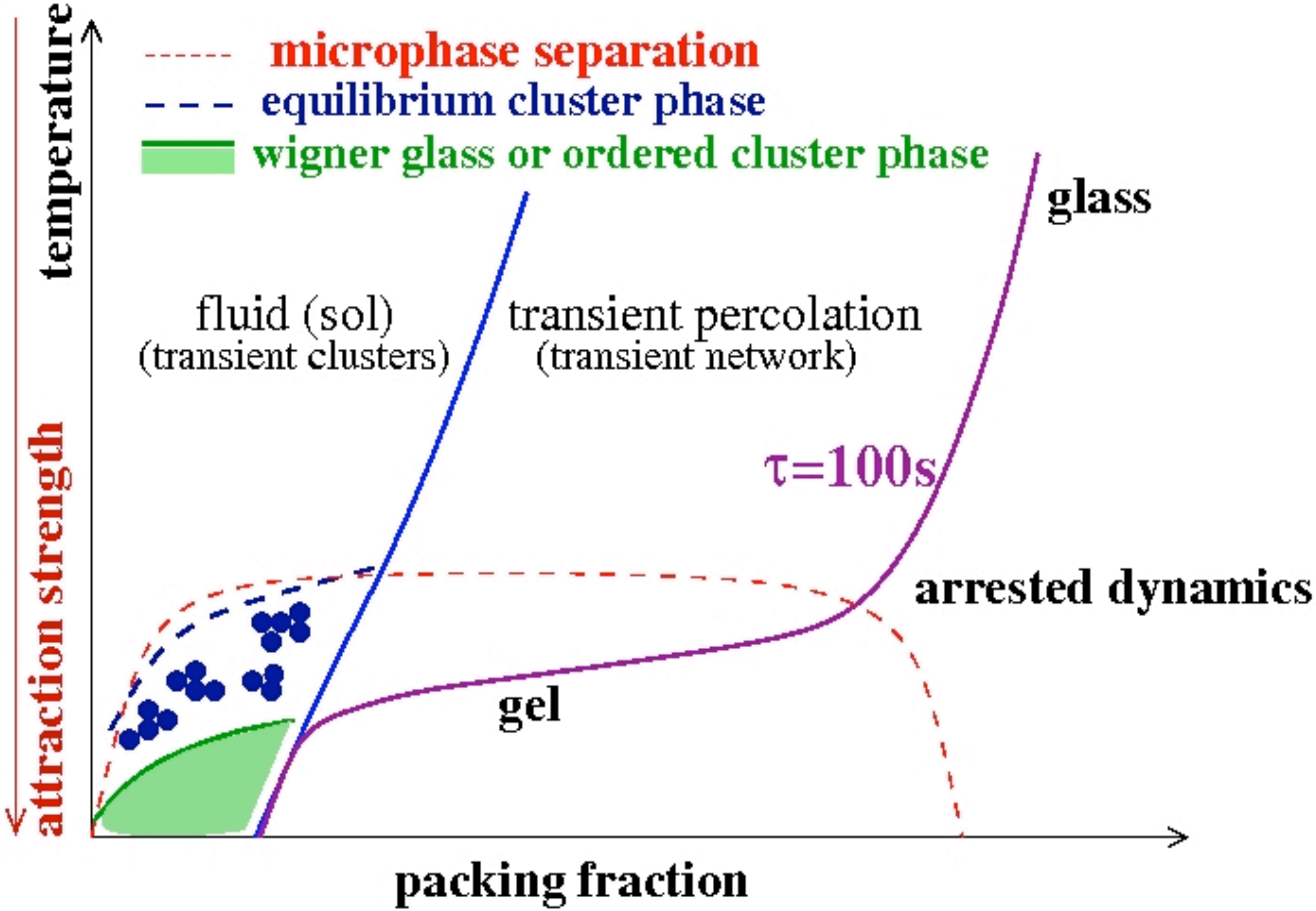


FIG. 1. Confocal microscope images of colloid-polymer mixtures at different volume fractions. From left to right: $\phi_c = 0.080$, 0.094, and 0.156. The attractive interactions are the same in all samples, $U_{\mathrm{SR}} = -9k_BT$ ($\phi_p = 0.69$). Images (a) and (b) contain clusters while (c) shows a network phase. The bars are 20 μm long. Inset: Phases observed as a function of the volume fractions of colloid (ϕ_c) and polymer (ϕ_p).


microphase separation
equilibrium cluster phase
wigner glass or ordered cluster phase
temperature
attraction strength
fluid (sol)
(transient clusters)
transient percolation
(transient network)
glass
τ=100s
arrested dynamics
gel
packing fraction

Equilibrium cluster formation in concentrated protein solutions and colloids

Anna Stradner[1], Helen Sedgwick[2], Frédéric Cardinaux[1], Wilson C. K. Poon[2], Stefan U. Egelhaaf[2,3] & Peter Schurtenberger[1]

NATURE | VOL 432 | 25 NOVEMBER 2004 |

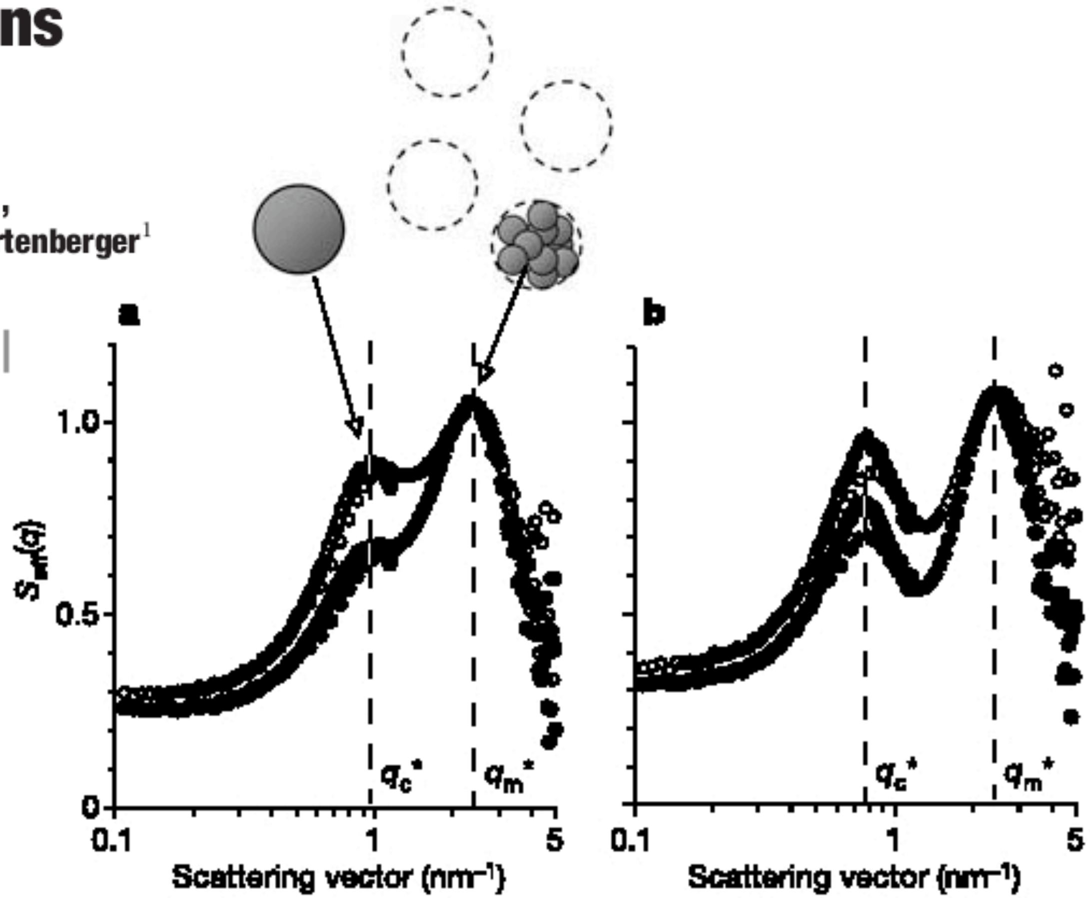
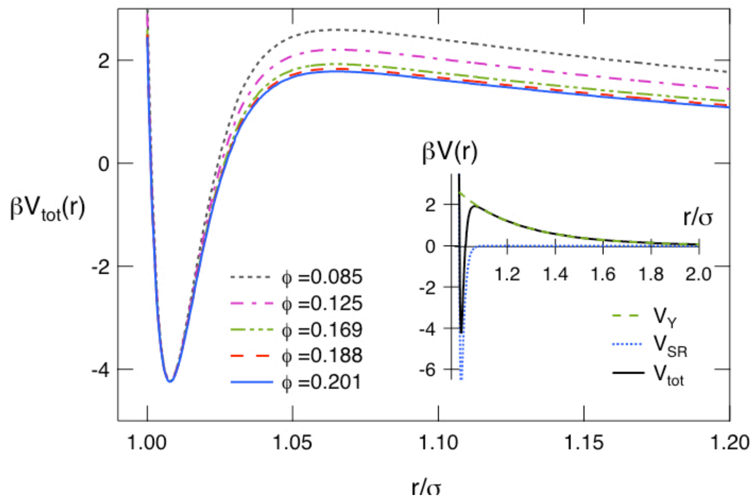


Figure 2 Effect of concentration and temperature on the effective structure factor $S_{eff}(q)$ as obtained by SANS. **a**, 254 mg ml^{-1} (filled symbols) and 169 mg ml^{-1} (open symbols) lysozyme solutions at 25 °C. **b**, The same samples at 5 °C. The dashed lines highlight that both peak positions are independent of lysozyme concentration. The second peak (corresponding to internal monomer–monomer correlations within the dense particle clusters) changes neither with concentration nor with temperature. The cluster–cluster correlation peak at lower q is also concentration independent but shows a strong temperature dependence, indicating fewer but larger aggregates at lower temperatures.

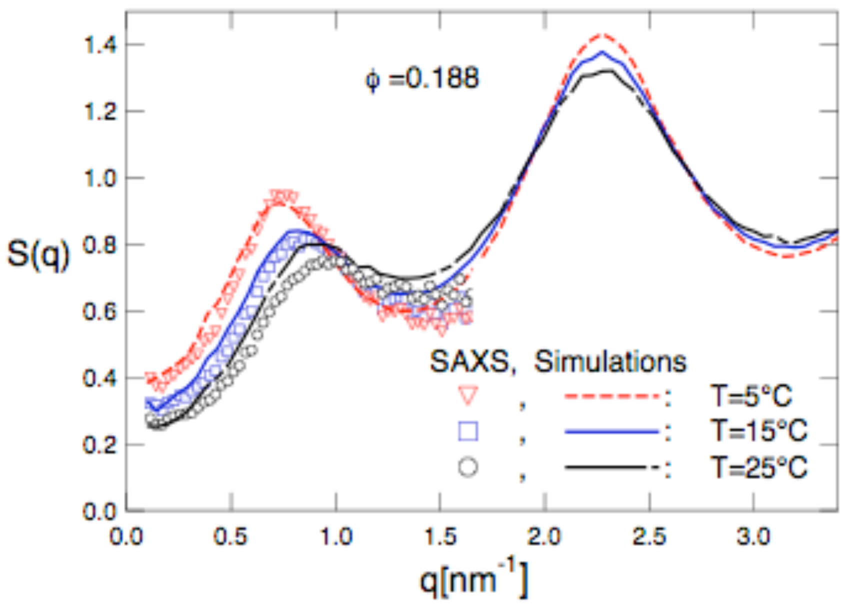
F. Cardinaux, A. Stradner, P. Schurtenberger, FS and E. Zaccarelli
Europhysics Letter, 77, 48004, 2007

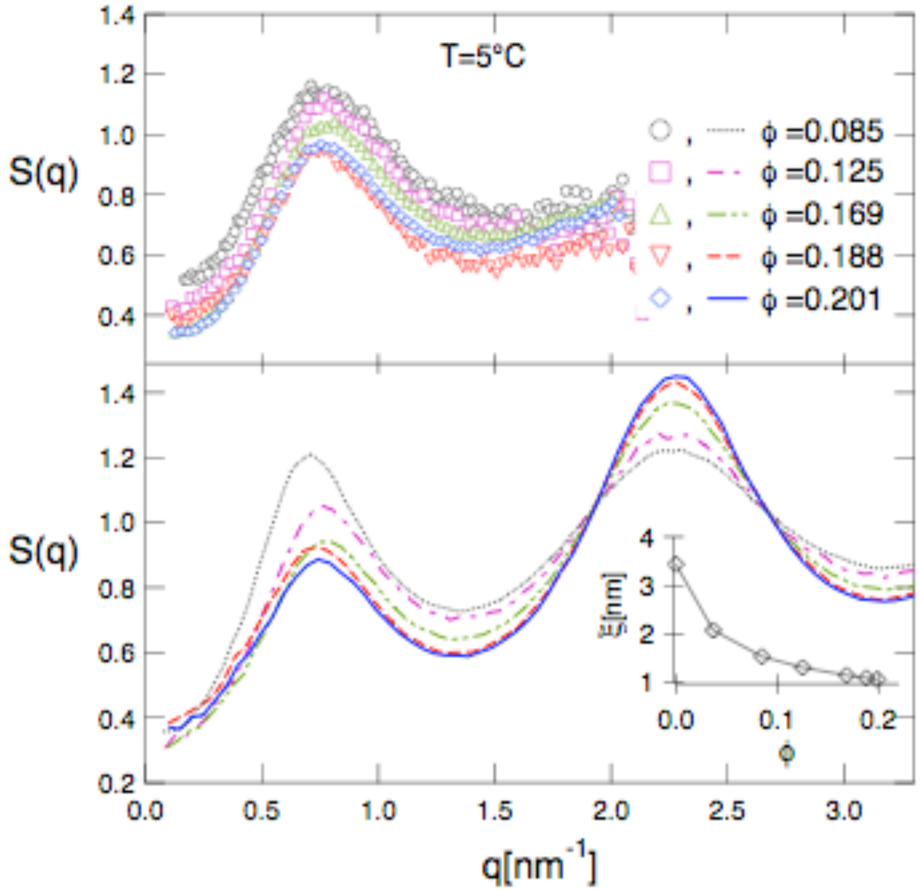


Modeling cluster phases in lysozyme solutions

within a simple model
short-ranged attraction
+ density-dependent repulsion

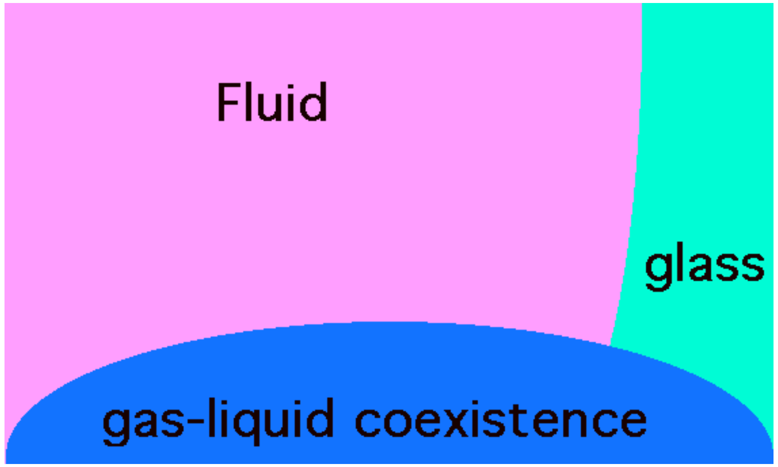
One-Component Microion Approach - Belloni L., J. Chem. Phys., 85 (1986) 519.





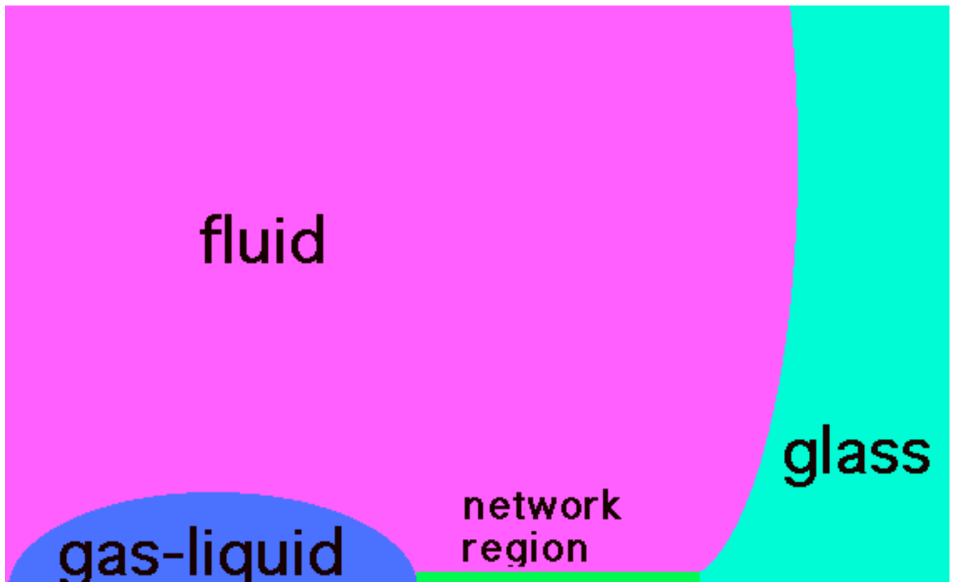
How to go to low T at low ϕ (in metastable equilibrium)

How to suppress phase separation ?



Competing interactions

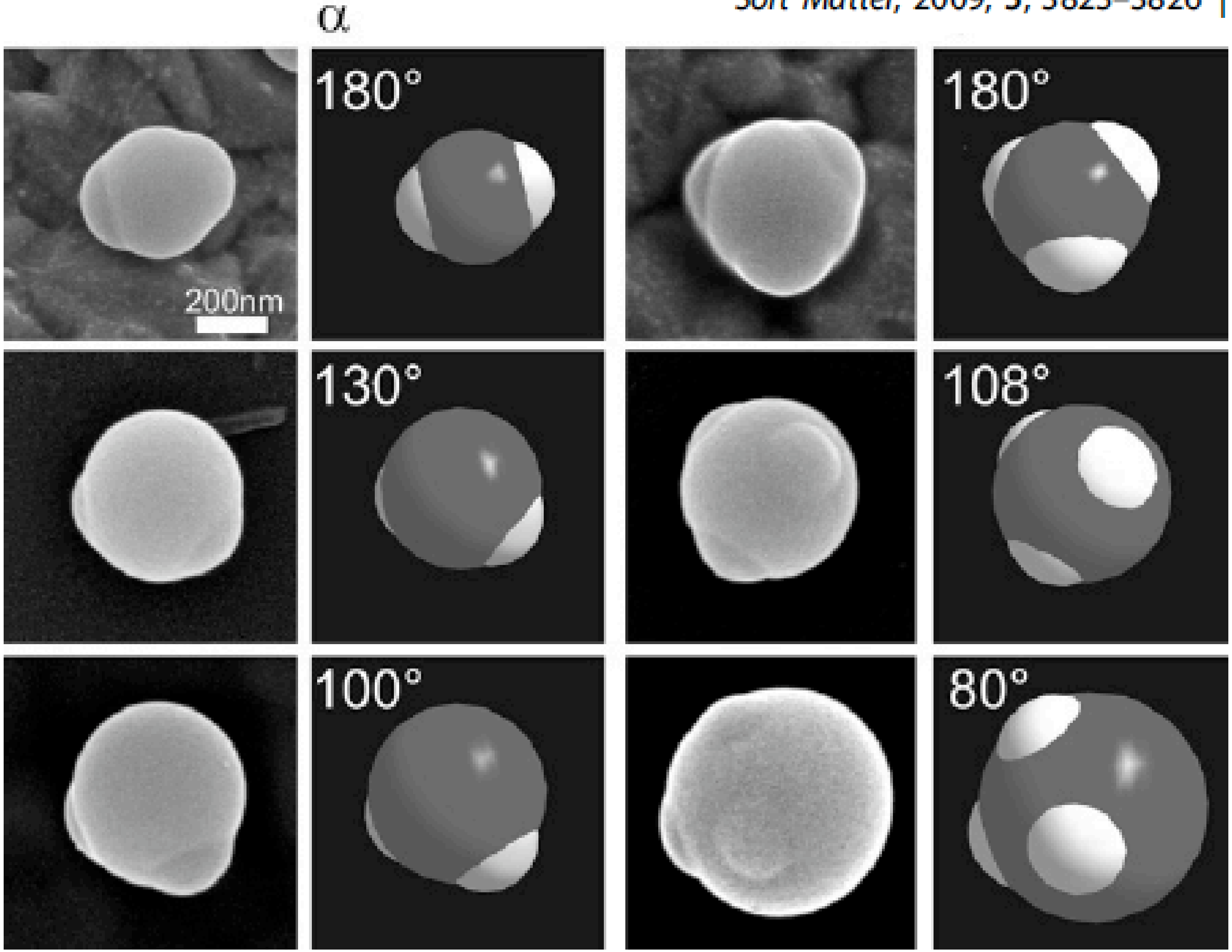
Reducing "valence"



Colloidal molecules with well-controlled bond angles†

Daniela J. Kraft,* Jan Groenewold and Willem K. Kegel*

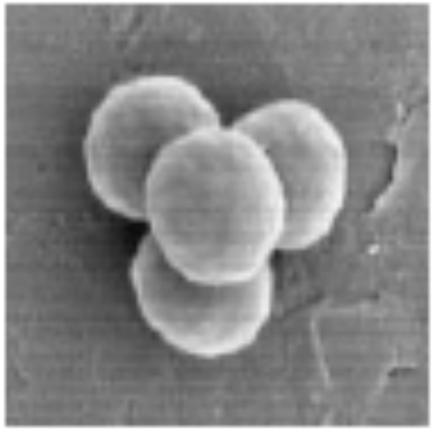
Soft Matter, 2009, **5**, 3823–3826 | 3823



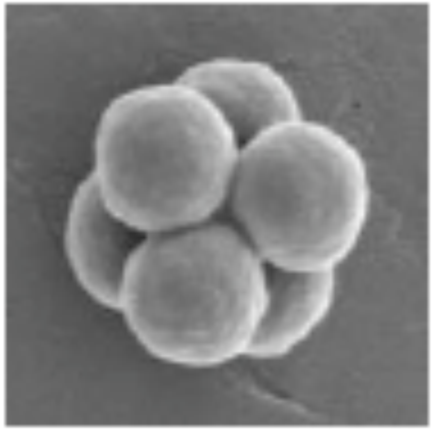
Monomer swollen cross-linked polymer particles

Vinothan N. Manoharan,[1] Mark T. Elsesser,[1] David J. Pine[1,2*]
25 JULY 2003 VOL 301 SCIENCE

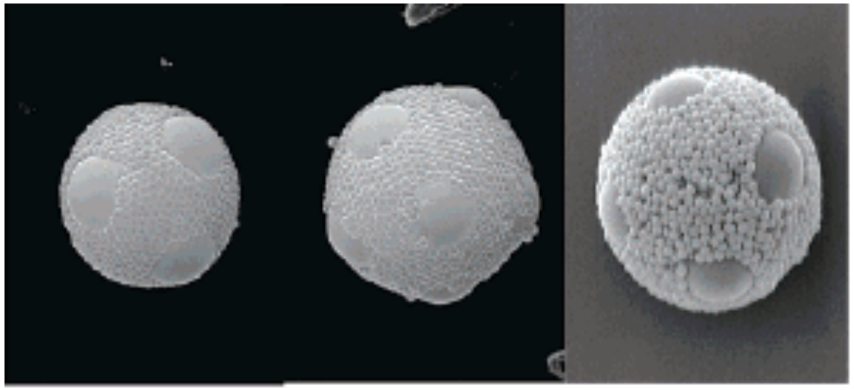
Pine's particles

4


5


6


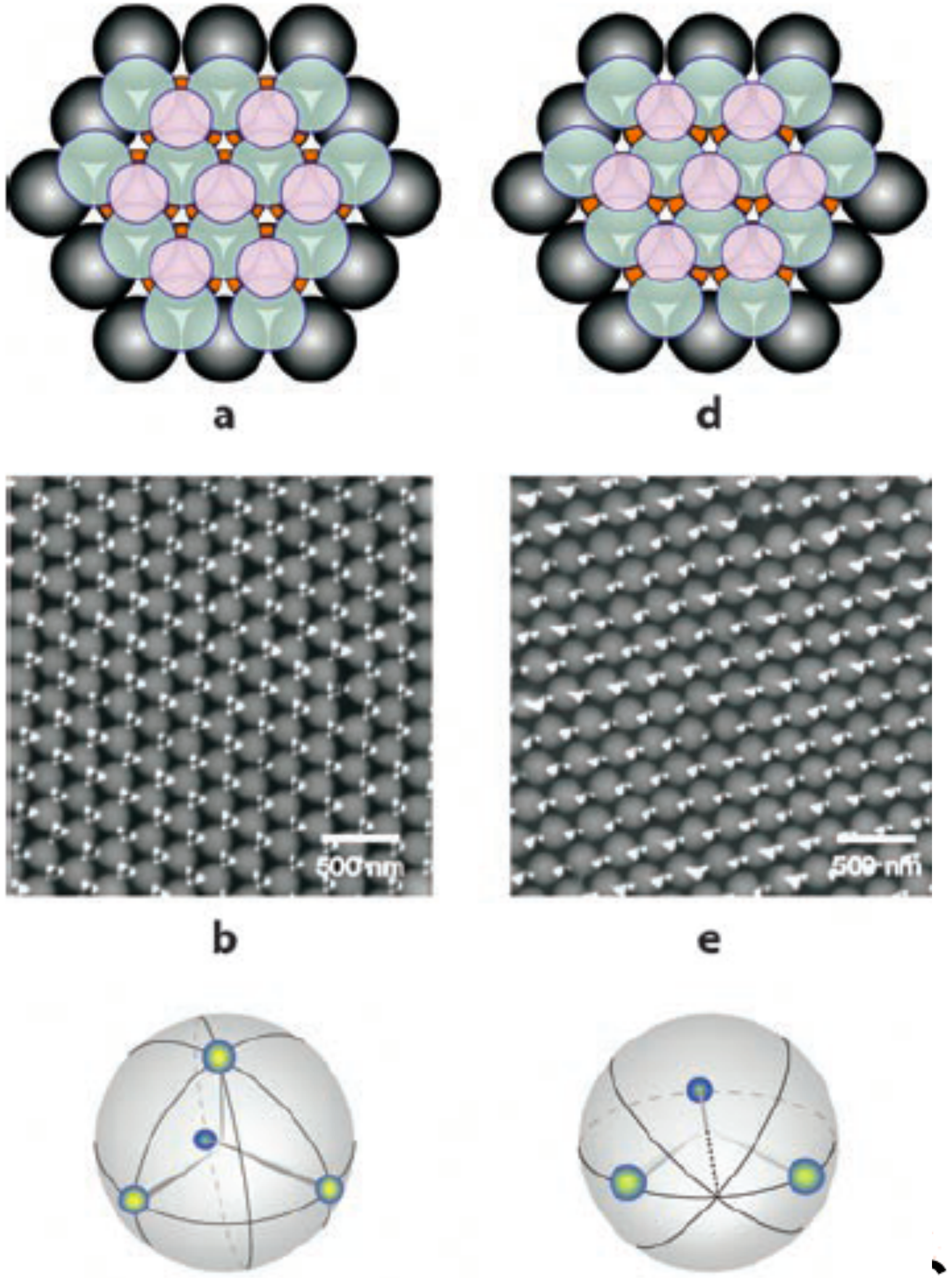
Self-Organization of Bidisperse Colloids in Water Droplets
Young-Sang Cho, Gi-Ra Yi, Jong-Min Lim, Shin-Hyun Kim, Vinothan N. Manoharan,, David J. Pine, and Seung-Man Yang J. Am. Chem. Soc.; **2005**; *127*(45) pp 15968 - 15975;



Decoration of Microspheres with Gold Nanodots—Giving Colloidal Spheres Valences**

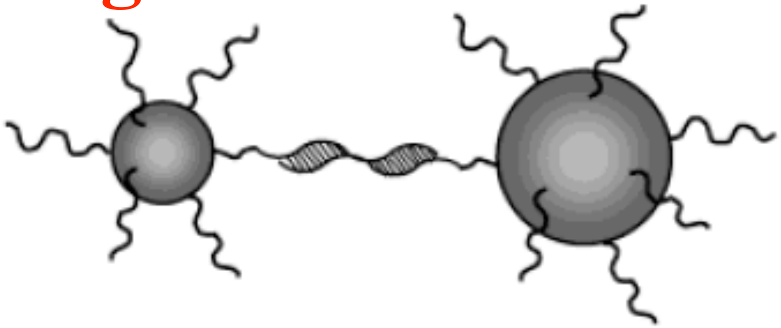
Gang Zhang, Dayang Wang, and Helmuth Möhwald*

Angewandte Chemie



a d b e c f

DNA functionalized particles: modulating the interaction



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*[,†,‡,§]

nature materials | VOL 6 | AUGUST 2007 |

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

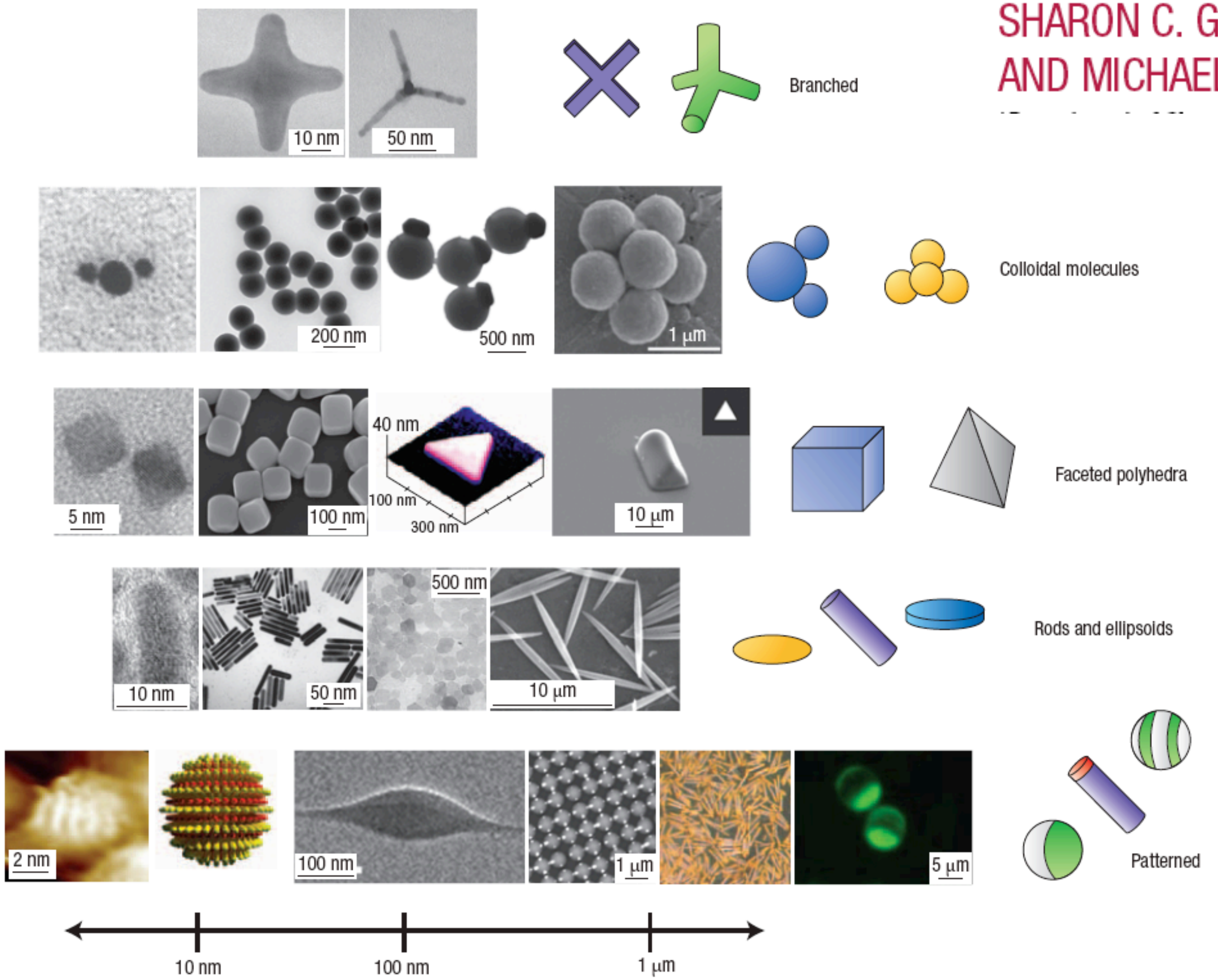
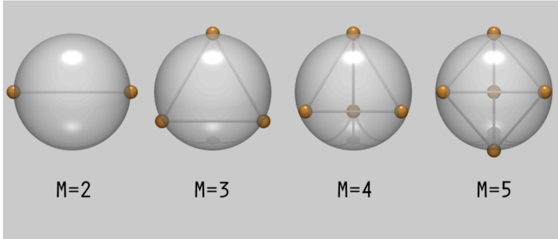


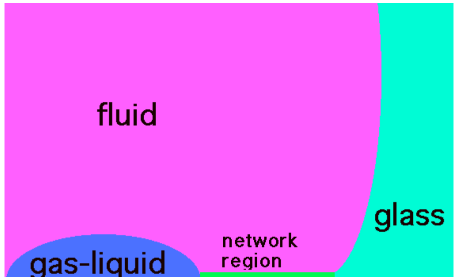
Figure 1 Representative examples of recently synthesized anisotropic particle building blocks. The particles are classified in rows by anisotropy type and increase in size from left to right according to the approximate scale at the bottom. From left to right, top to bottom: branched particles include 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.

Phase Diagram - Theory and Simulations

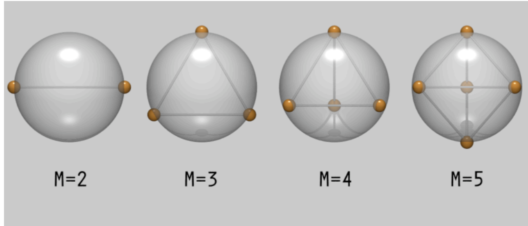


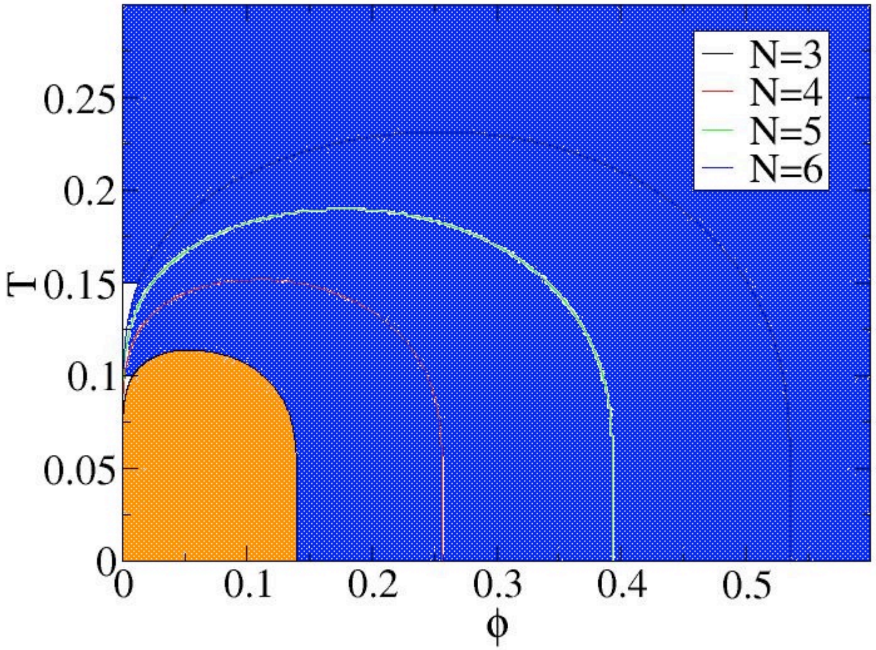
What happens to the gas-liquid critical point ?

What happen to the "arrest" lines ?

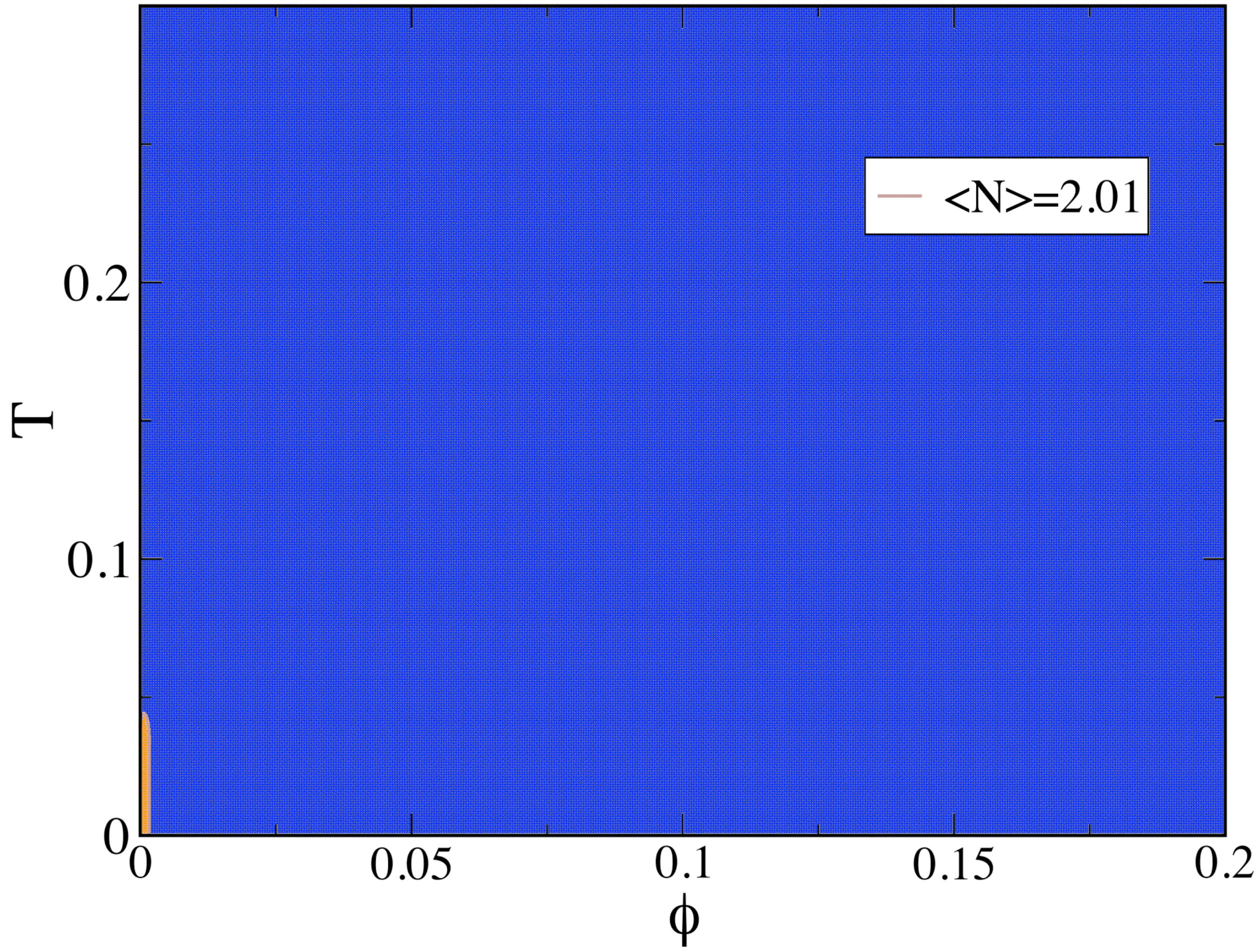


Valence Reduction



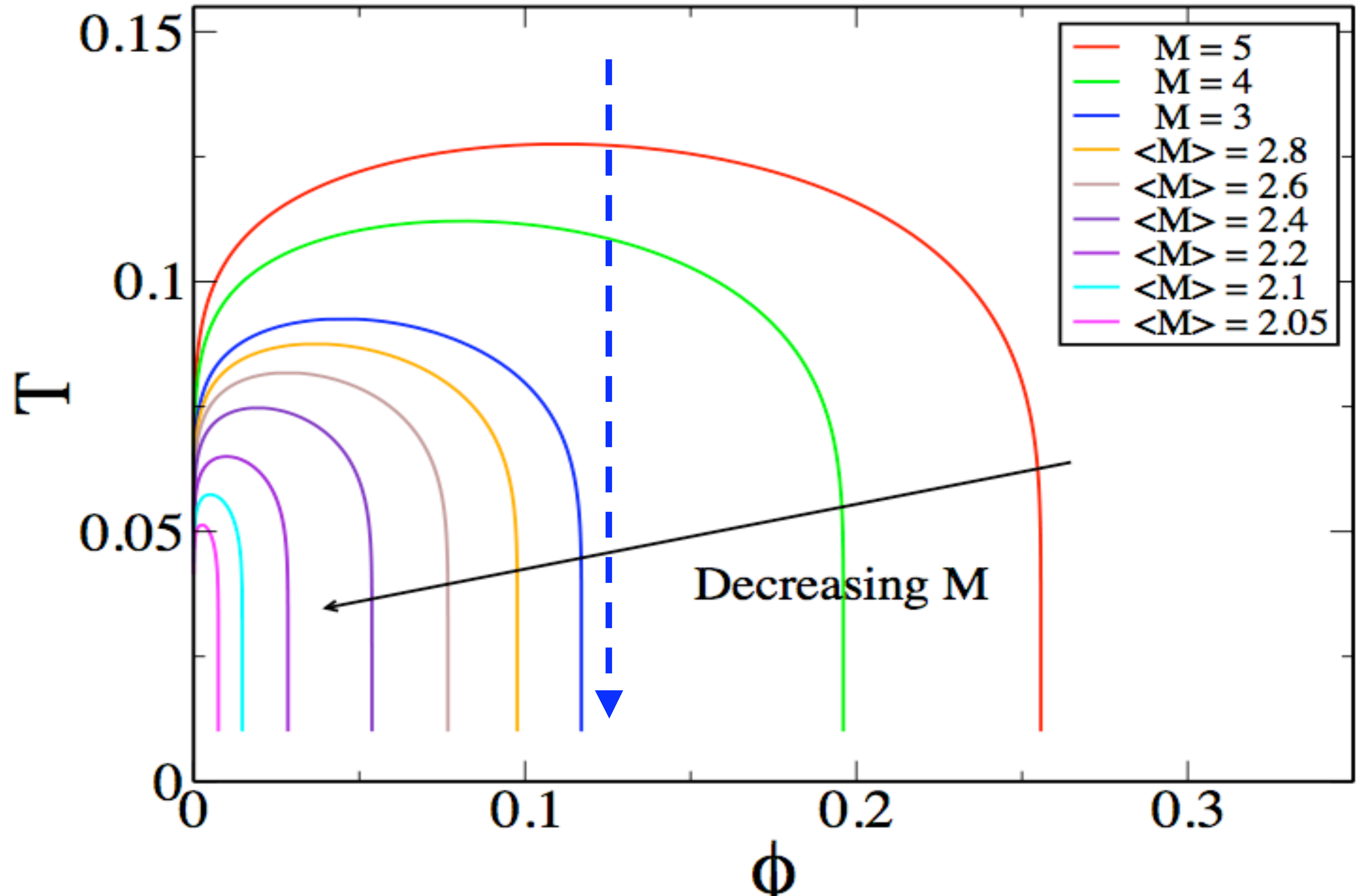


Average valence less than 2….



La Sapienza
Università degli Studi di Roma

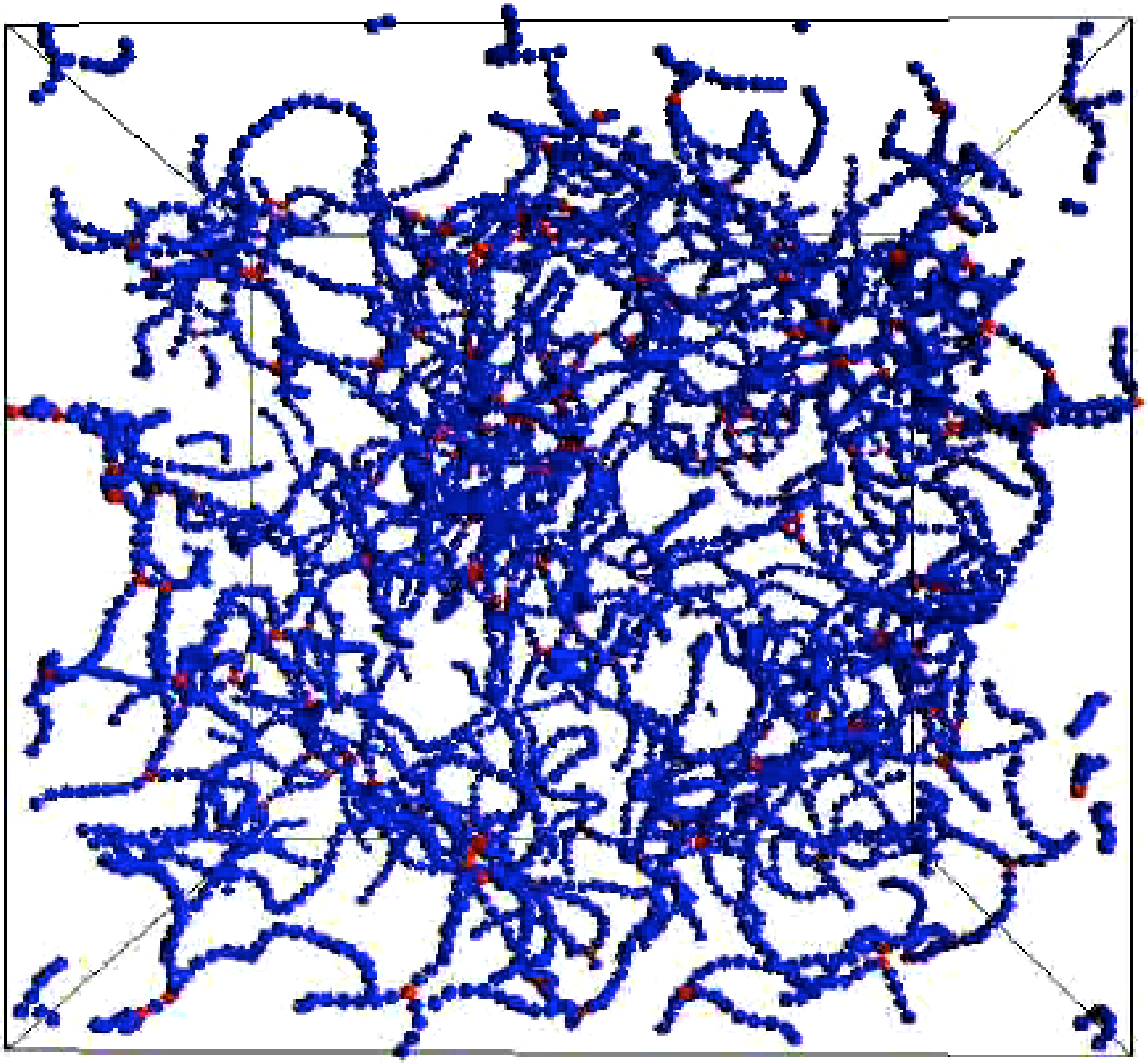
erc



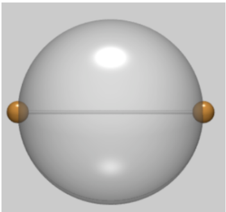
Empty liquids!

Cooling the liquids without phase separating!

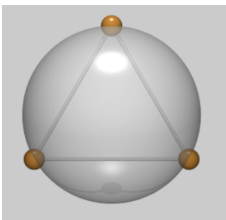
A snapshot of <M>=2.025



$N_2=5670$



$N_3=330$



T=0.05, ϕ=0.01

La Sapienza
Università degli Studi di Roma

See also S. `Saw et al PRL 2009

Wertheim TPT for associated liquids

(particles with M identical sticky sites)

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

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

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

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

$$g_{HS}(r) \approx 1 \qquad f(r) \approx e^{\beta u_0} \quad (bond\ volume)\ V_b$$

$$0 \quad (otherwise)$$

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

La Sapienza
Università degli Studi di Roma

erc

Wertheim (in a nut-shell)

$$\#_{clusters} = V \sum \rho_l$$
$$N = V \sum l \rho_l$$

(ideal gas of loop-less clusters of independent bonds) (Jackson)

$$p_b = \frac{\#_b}{\#_b^{max}} \qquad \#_b^{max} = \frac{fN}{2} \qquad \rho_1 = \rho(1-p_b)^f$$

$$\#_{clusters} = N - \#_b = N(1 - p_b \frac{f}{2})$$

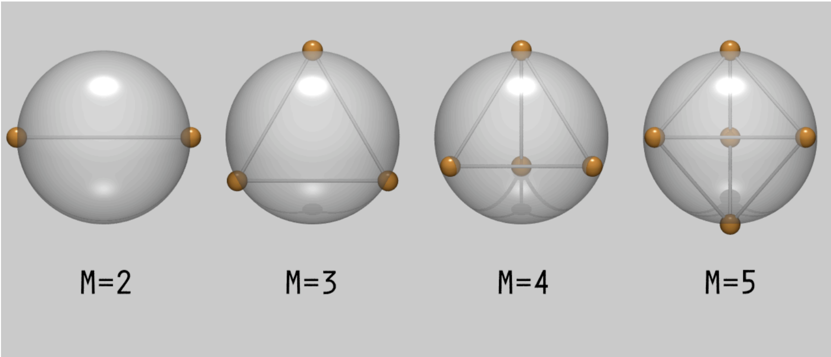
$$\beta F = \beta\mu_1 N - \beta PV \qquad \beta PV = \#_{clusters}$$

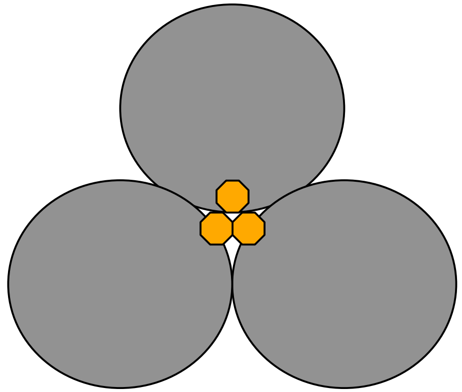
$$\frac{\beta F}{V} = \rho \ln \rho (1-p_b)^f - \rho(1 - \frac{f}{2} p_b)$$

$$\frac{\beta F}{V} = \frac{\beta A_{bond}}{V} + \rho \ln \rho - \rho$$

La Sapienza
Università degli Studi di Roma

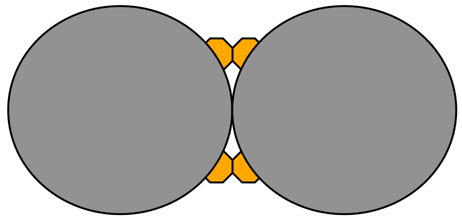
erc



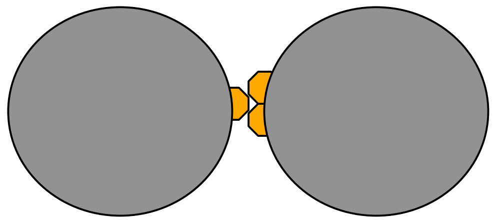


Steric incompatibilities

satisfied if SW width δ <0.11



No double bonding



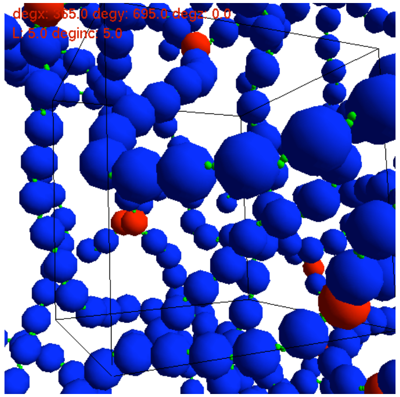
Single bond per bond site

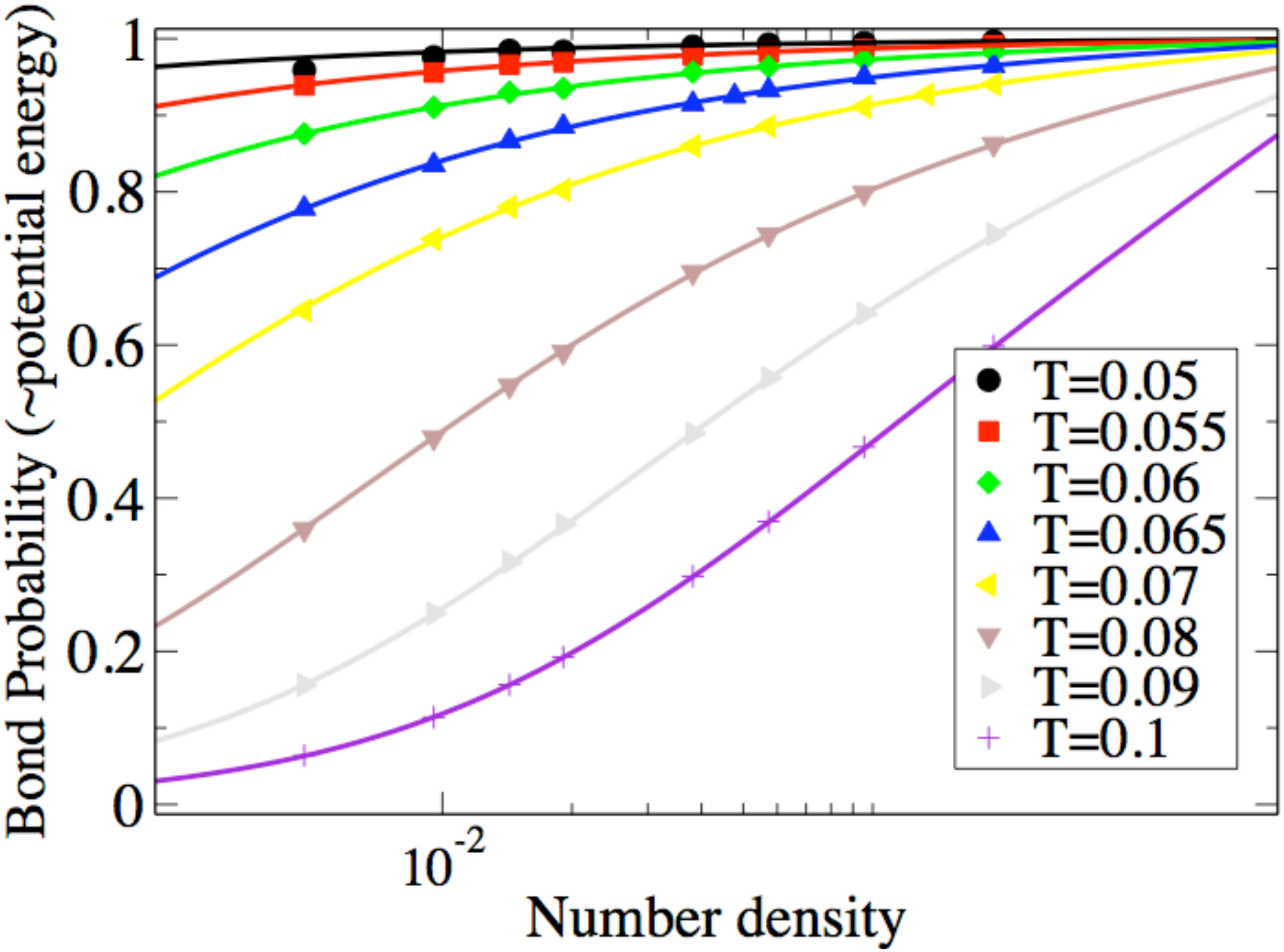
No ring configurations !

Wertheim theory predicts p_b extremely well (in this model) !

(ground state accessed in equilibrium !!!!!)

<M>=2.055

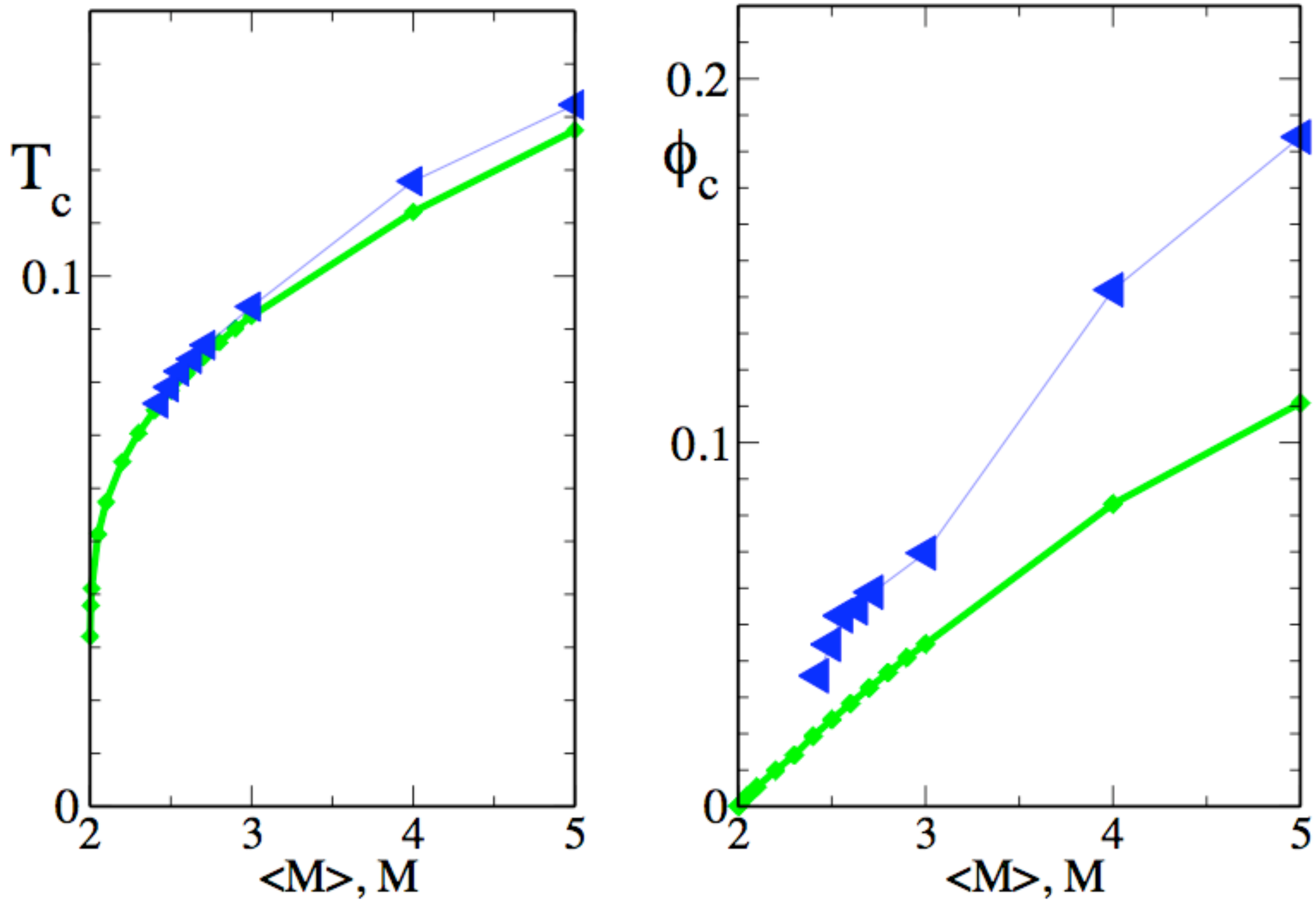




Emanuela Bianchi, Piero Tartaglia, Emilia La Nave and FS, Fully Solvable Equilibrium Self-Assembly Process: Fine-Tuning the Clusters Size and the Connectivity in Patchy Particle Systems, J. Phys. Chem. B 111, 11765 (2007).

Patchy particles - Critical Parameters

Comparison between theory (green) and simulations (blue)

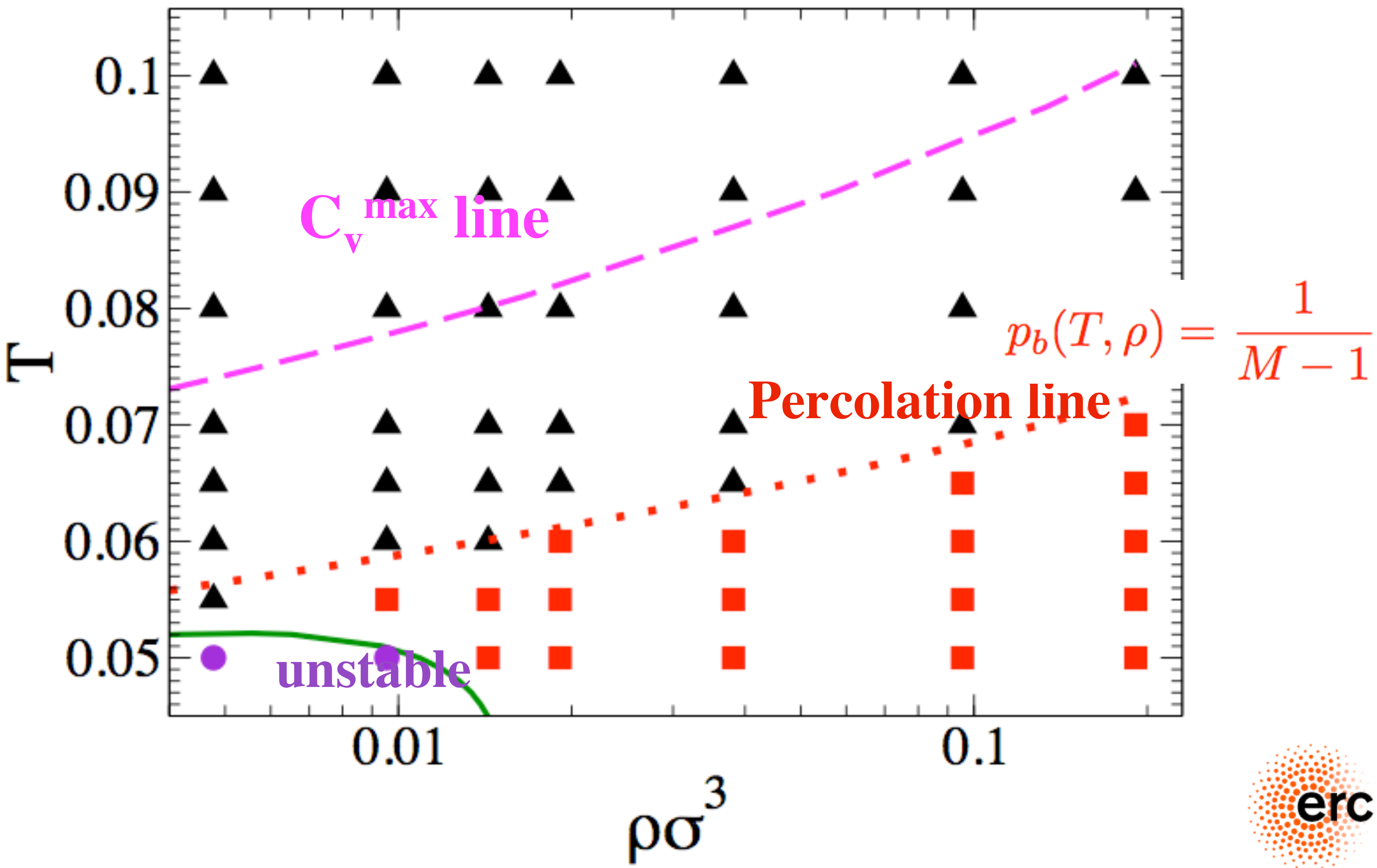


T_c and ϕ_c tend to vanish when valence approaches two

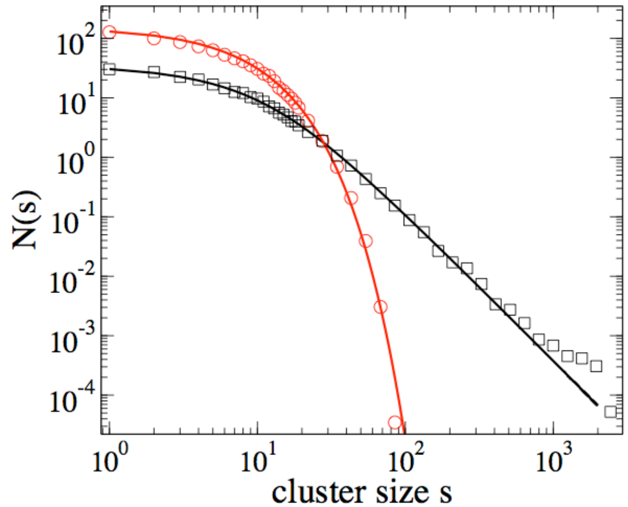
La Sapienza
Università degli Studi di Roma

erc

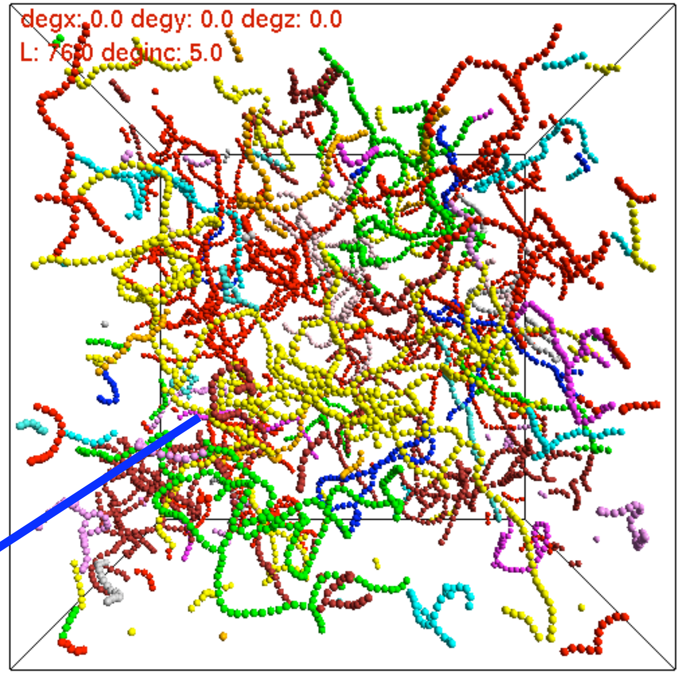
Generic features of the phase diagram
Branching introduces percolation and phase-separation!

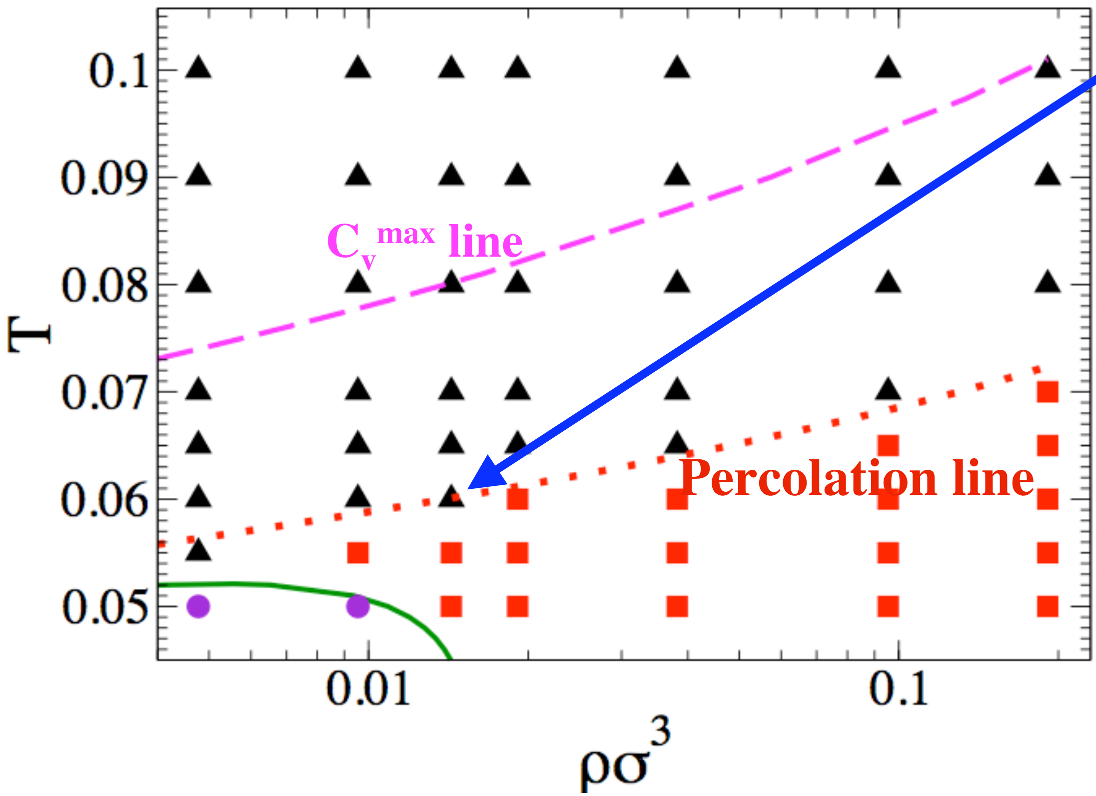


Phase diagram, Connectivity properties and cluster size distributions

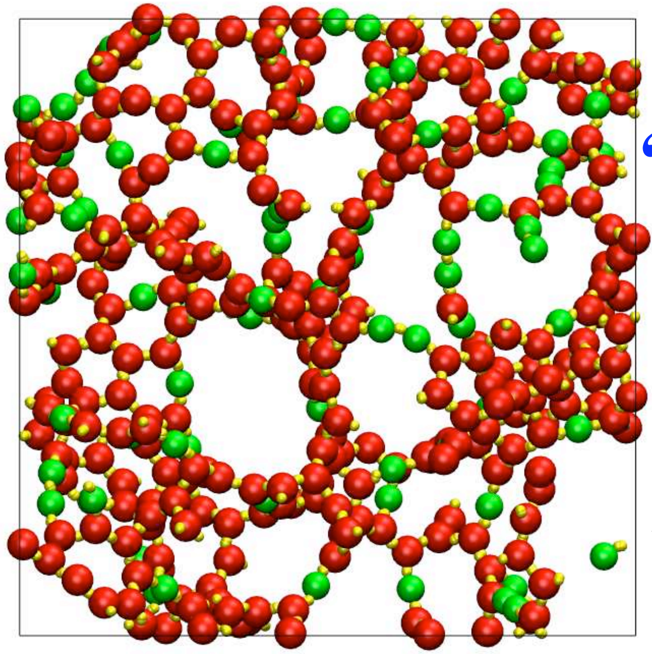


Branching introduces percolation and phase-separation!

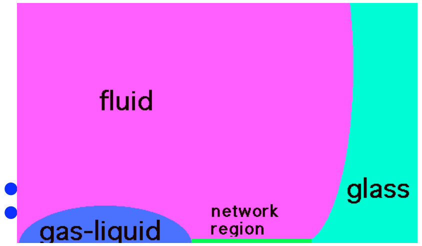




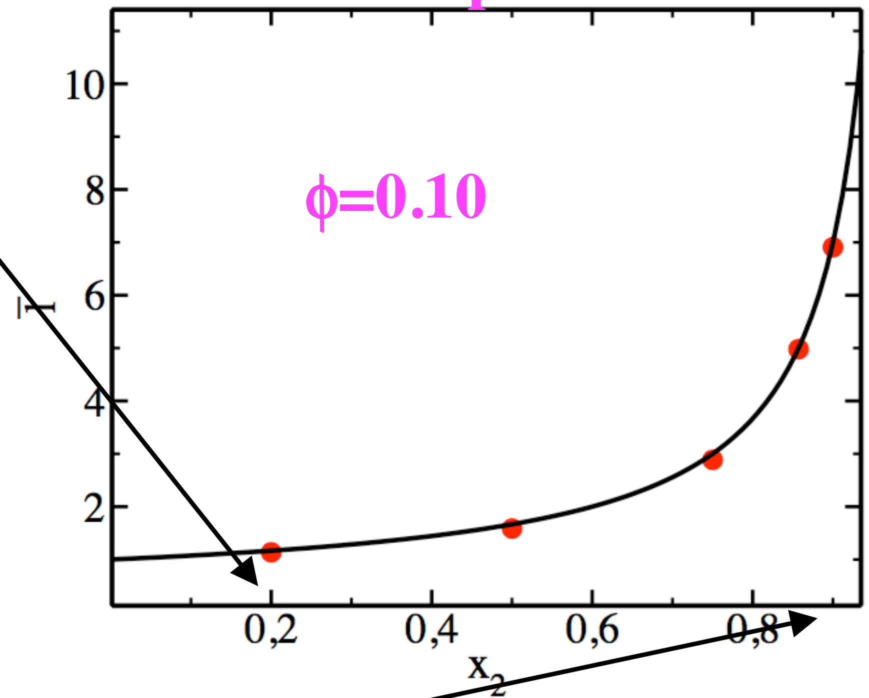
Flory-Stockmayer cluster size distributions observed

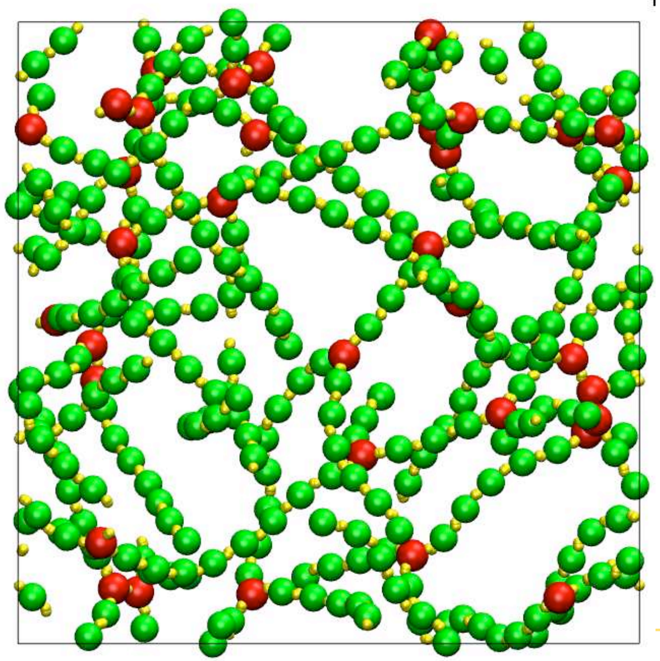


The structure of the "fully connected network":

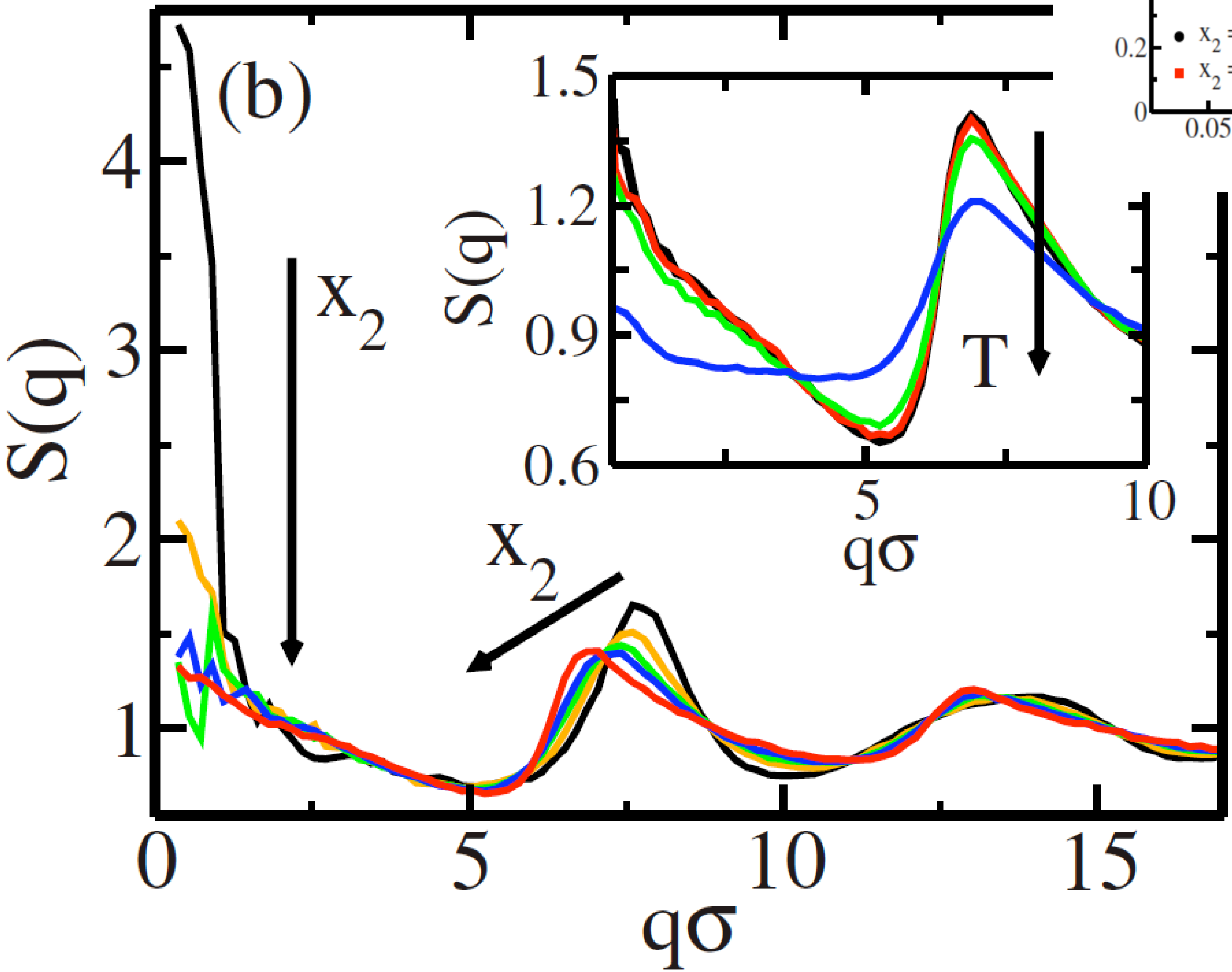


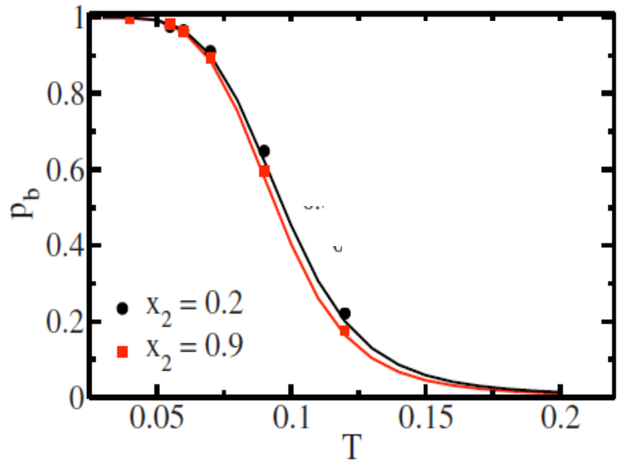
Average length connecting 3-functional particles

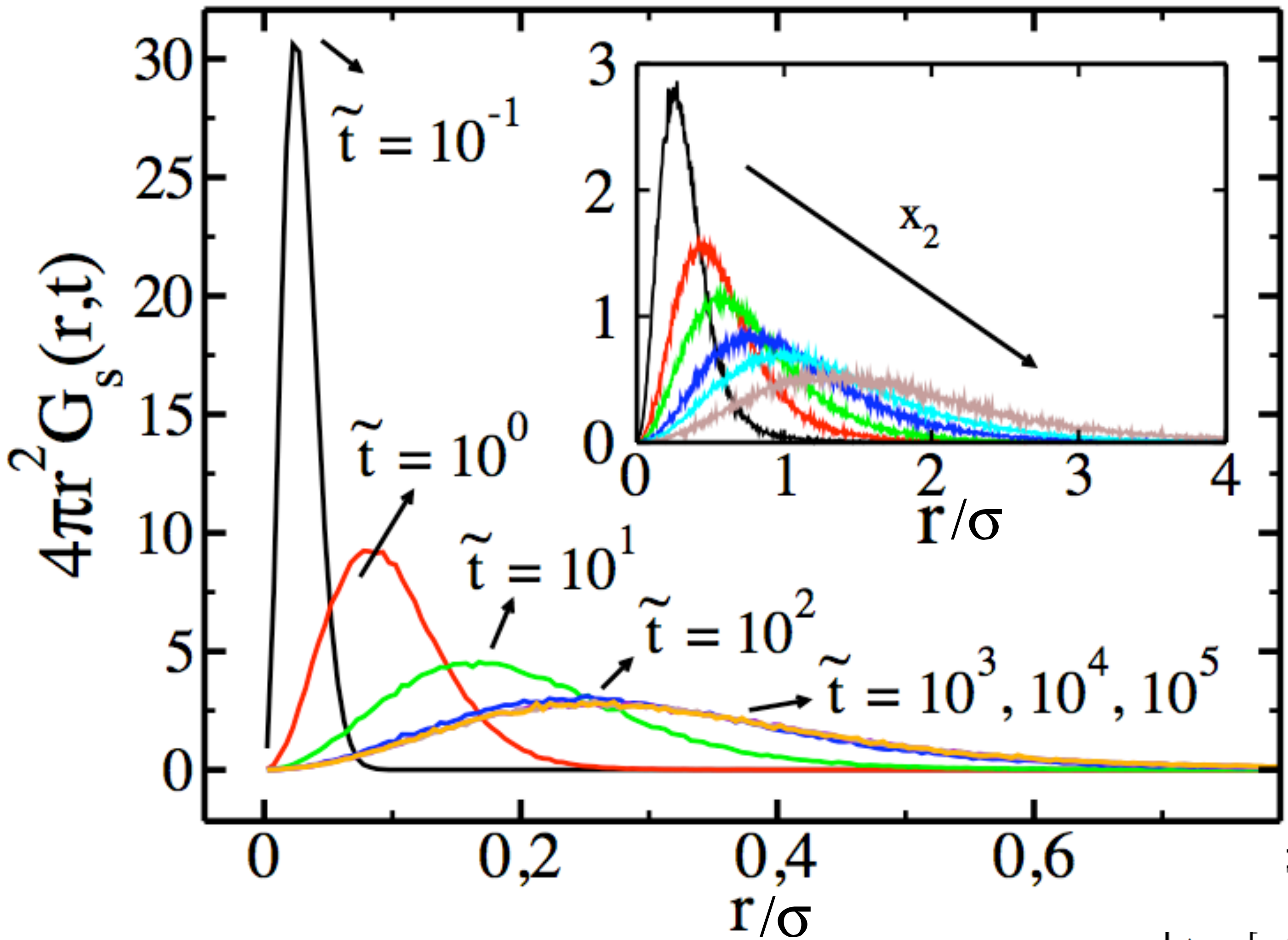




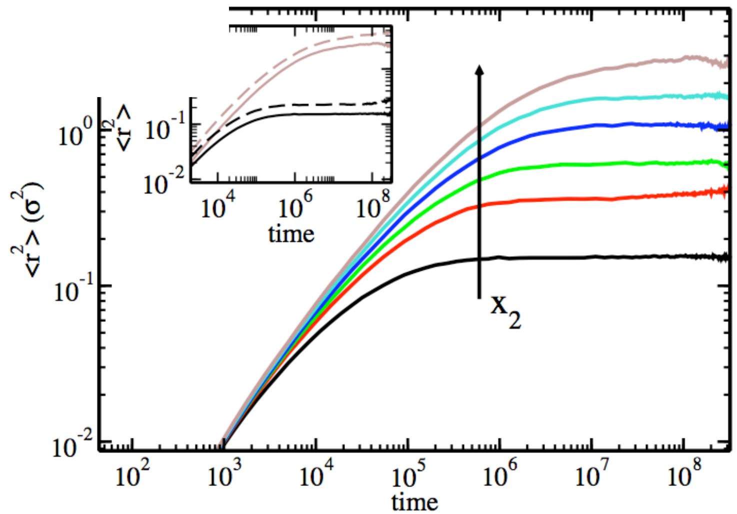
S(q) with the valence







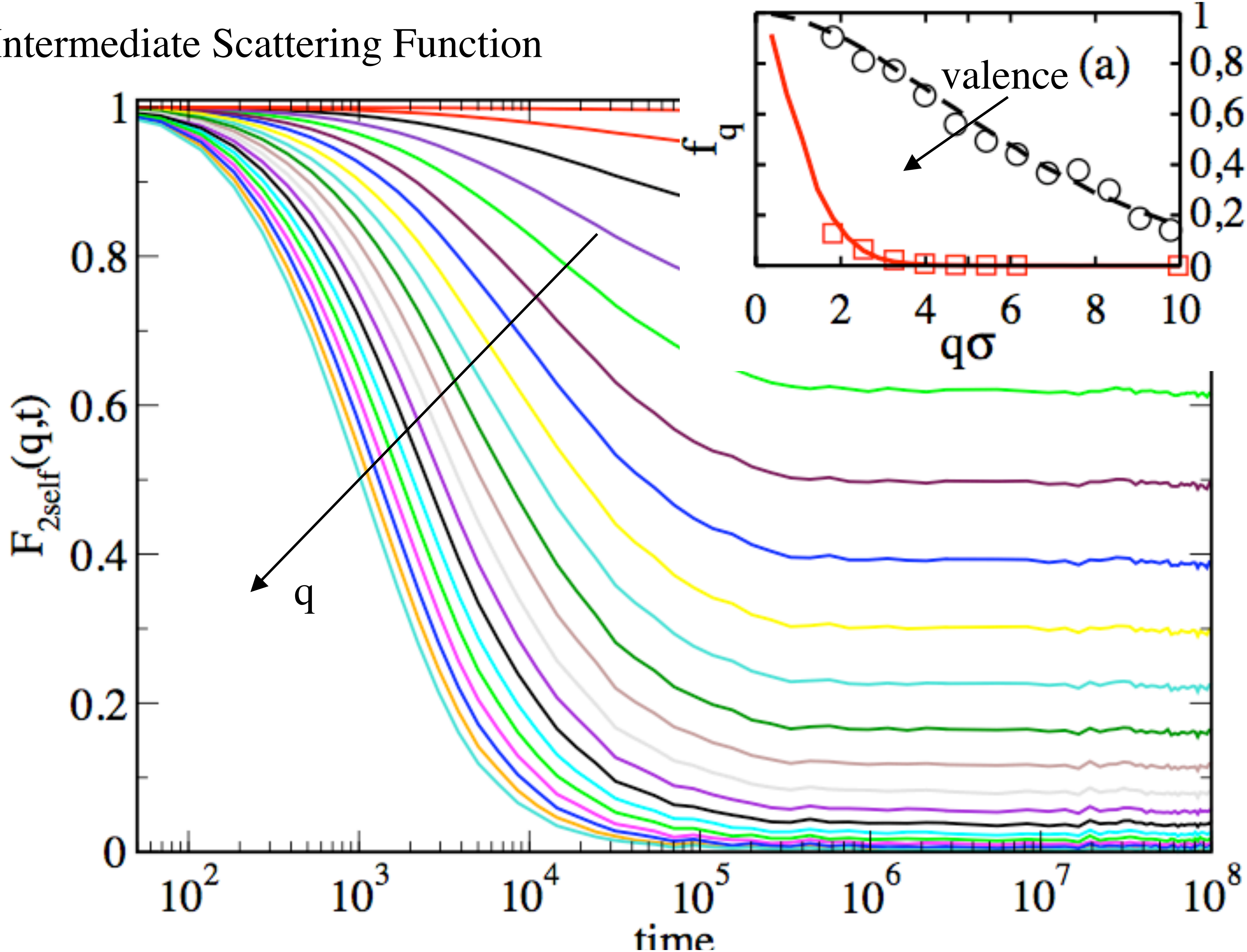
Dynamics in the fully connected gel



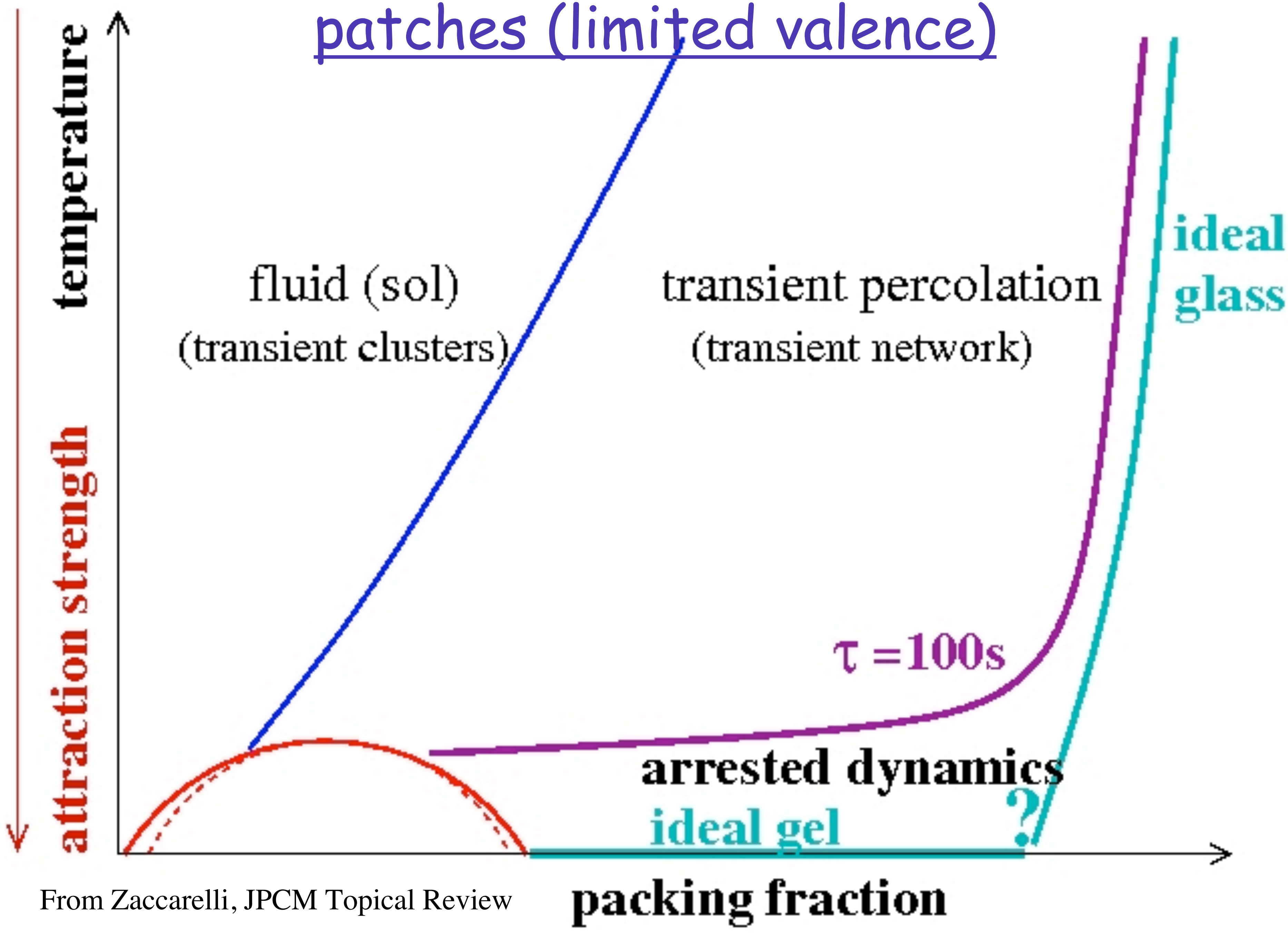
Reversible gels of patchy particles: Role of the valence.
J. Russo, P. Tartaglia, FS, J. Chem. Phys., 131 (2009)

La Sapienza
Università degli Studi di Roma

Intermediate Scattering Function



equilibrium route to gelation with patches (limited valence)

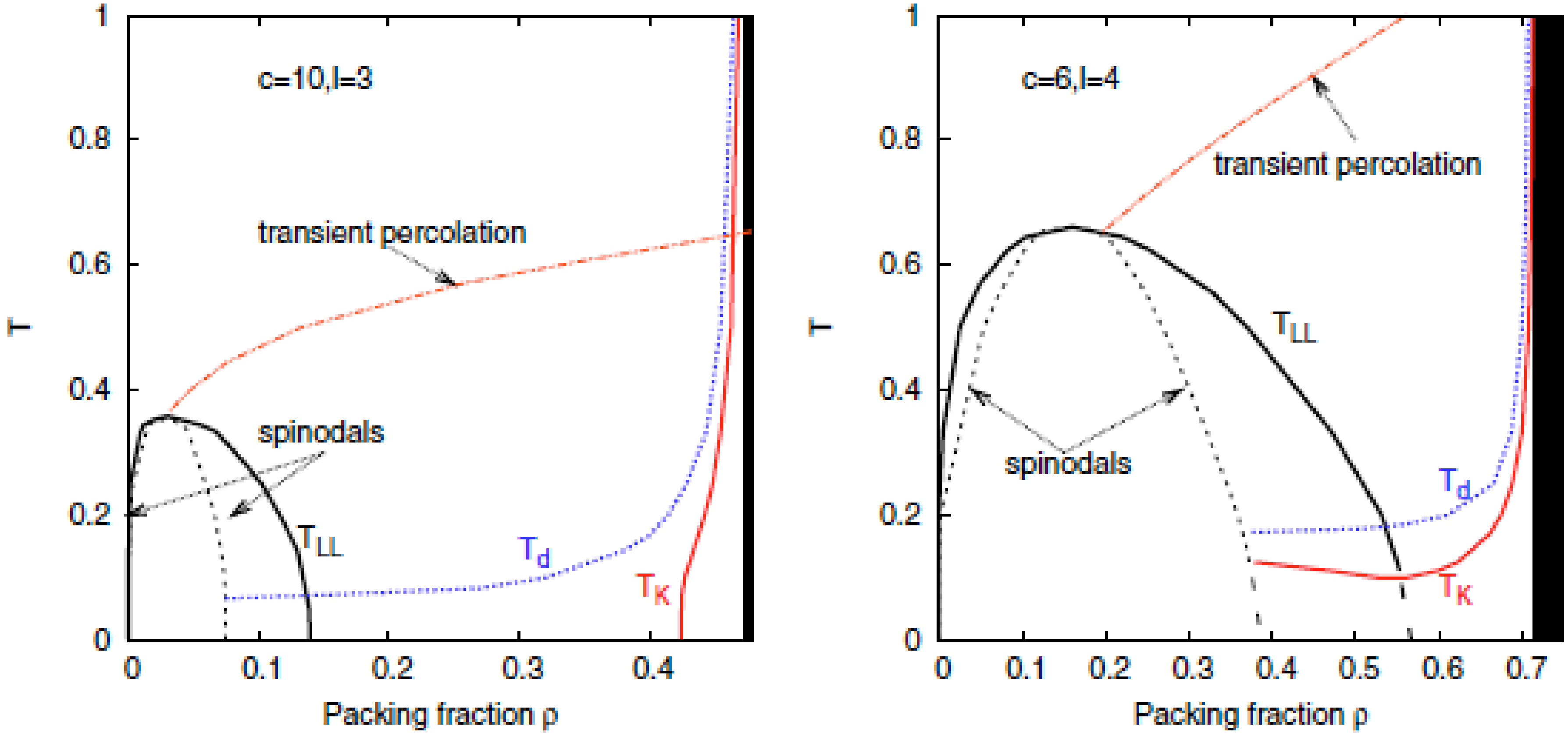


From Zaccarelli, JPCM Topical Review

PRL 101, 165702 (2008) PHYSICAL REVIEW LETTERS week ending 17 OCTOBER 2008

Lattice Model for Colloidal Gels and Glasses

Florent Krzakala,[1] Marco Tarzia,[2] and Lenka Zdeborová[3,4]

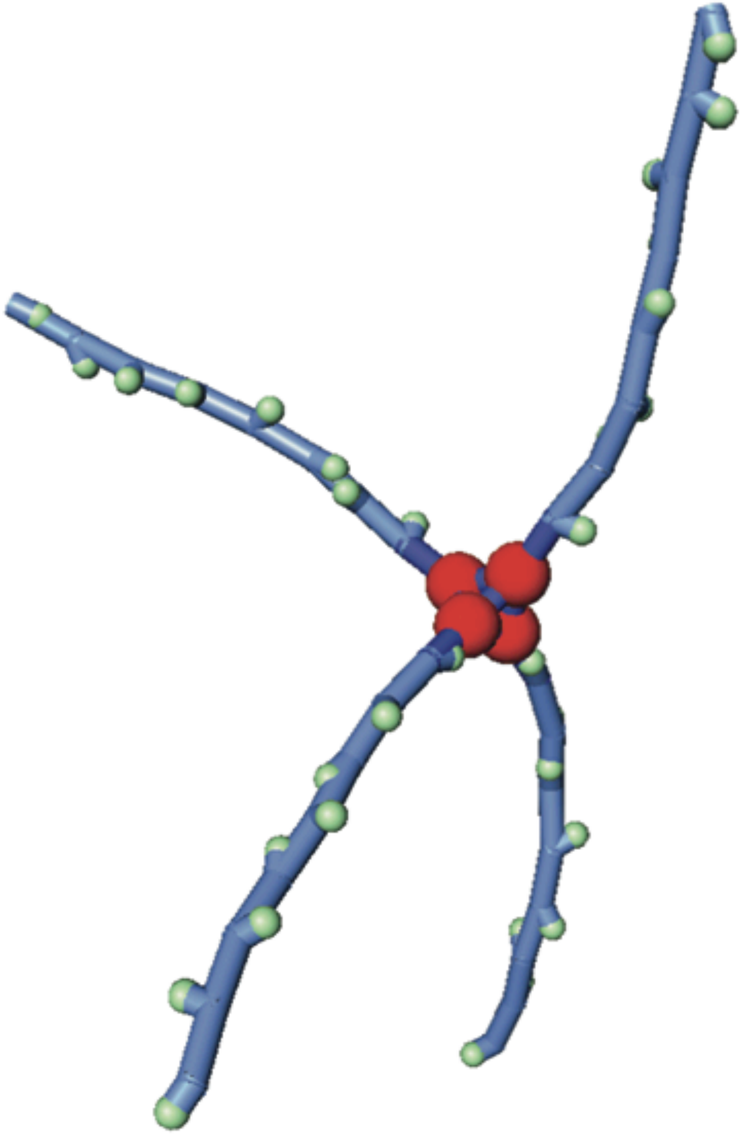


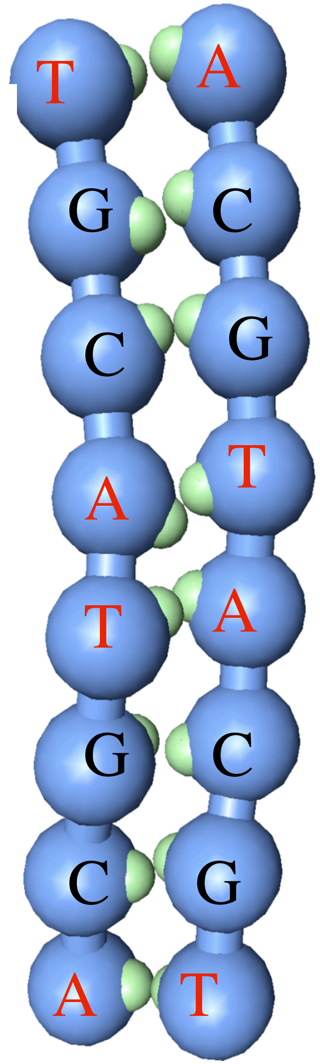
La Sapienza
Università degli Studi di Roma

See also S. Sastry, E. La Nave, F. Sciortino
Maximum valency lattice gas models
J. Stat. Mech. 12010, 2006

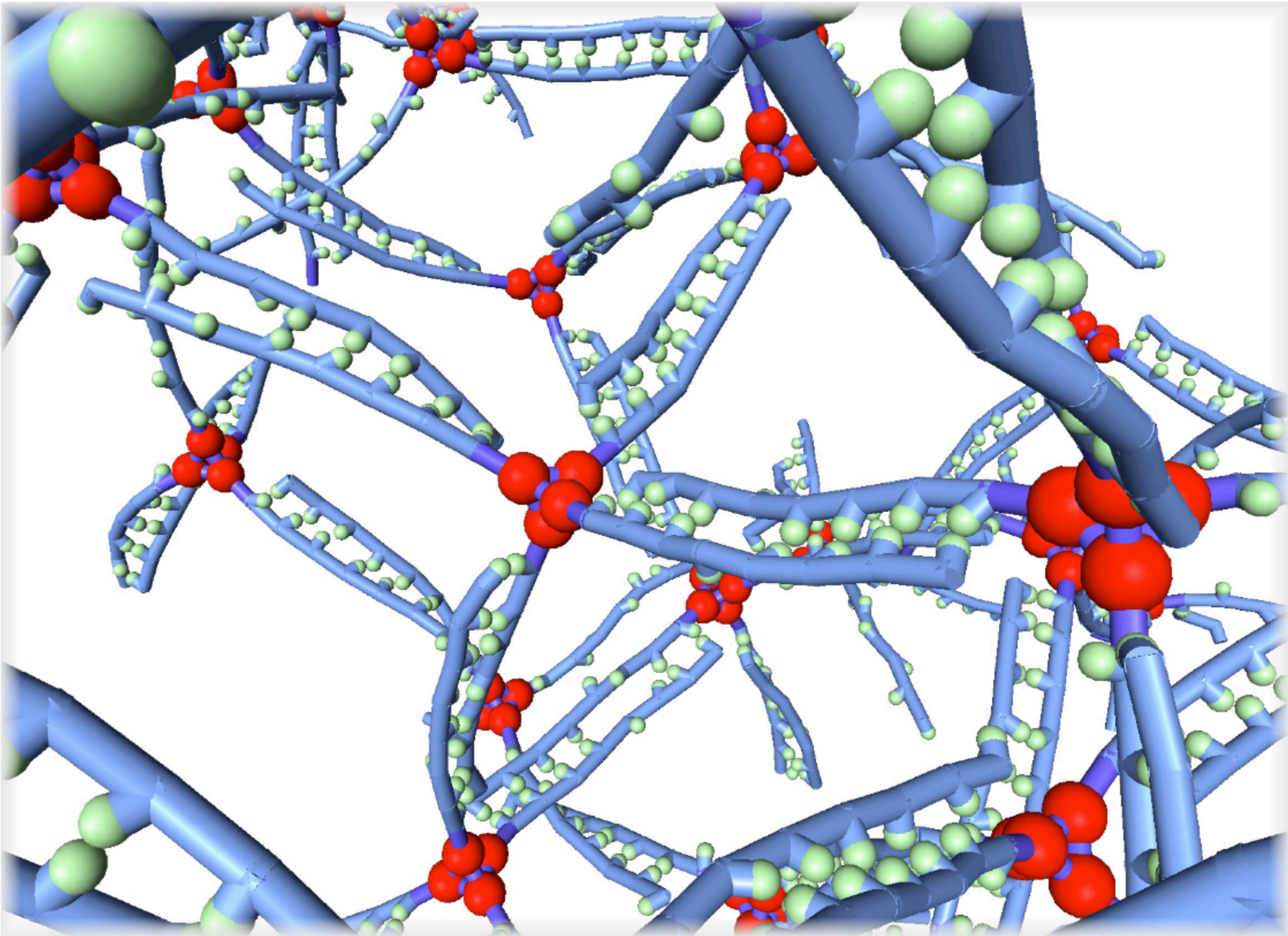
erc

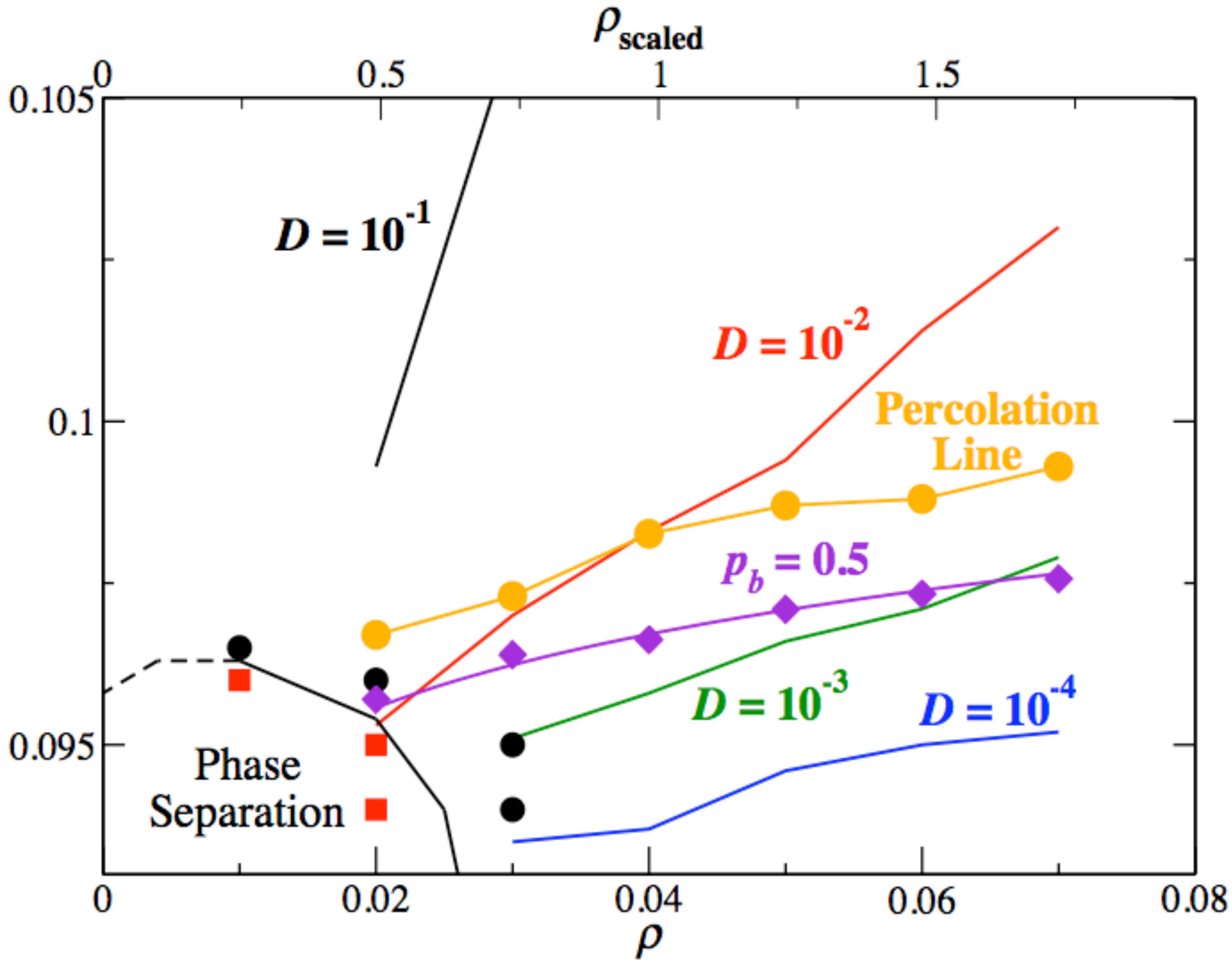
DNA dendrimers: bond selectivity - Valence 4





Langmuir **2007**, *23*, 5896−5905



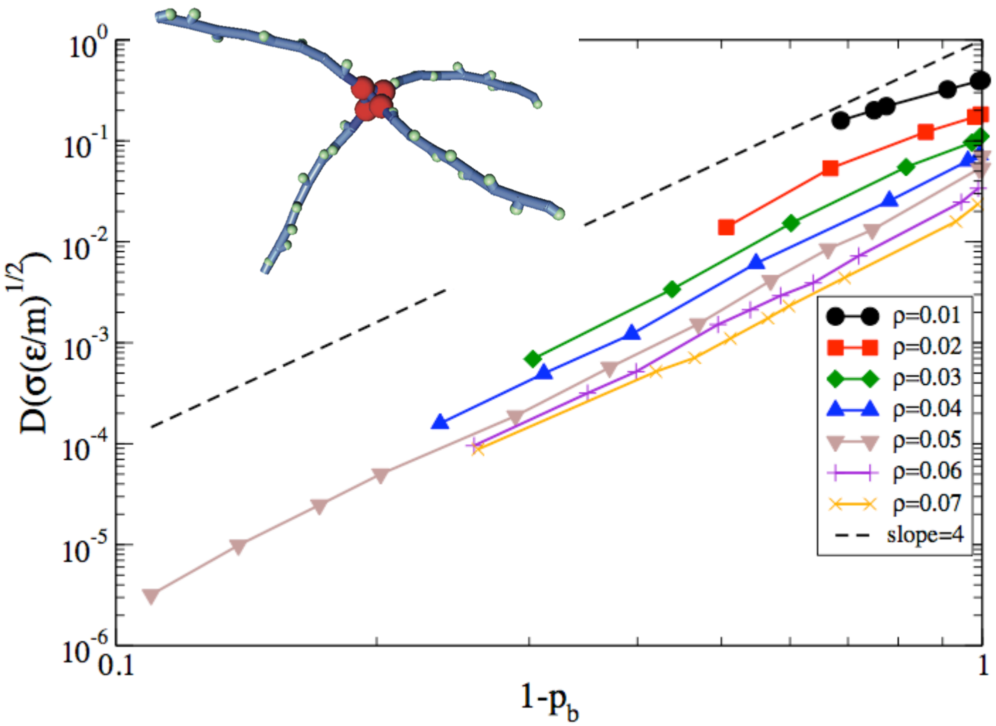


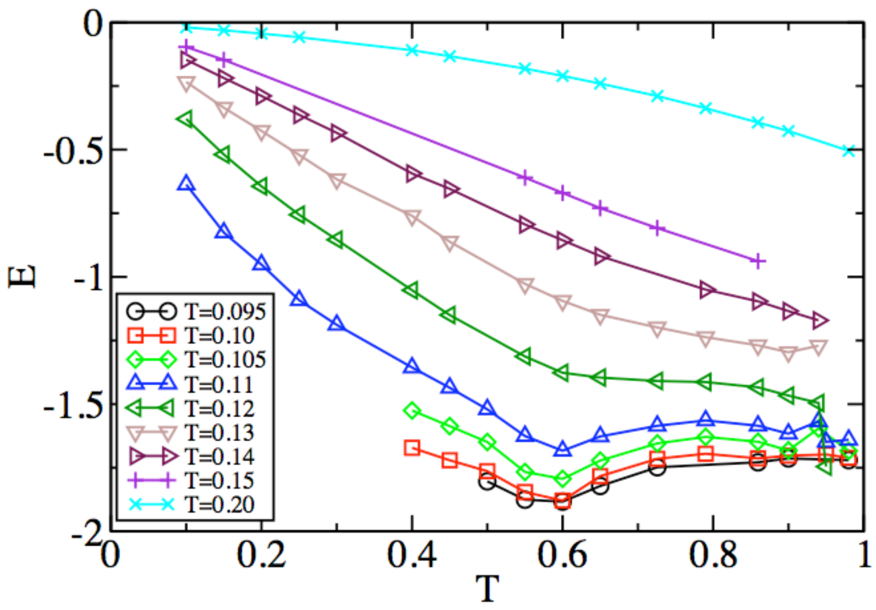
ρ_{scaled}
0
0.5
1
1.5
0.105
0.1
0.095
$D = 10^{-1}$
$D = 10^{-2}$
Percolation Line
$p_b = 0.5$
$D = 10^{-3}$
$D = 10^{-4}$
Phase Separation
0
0.02
0.04
0.06
0.08
ρ

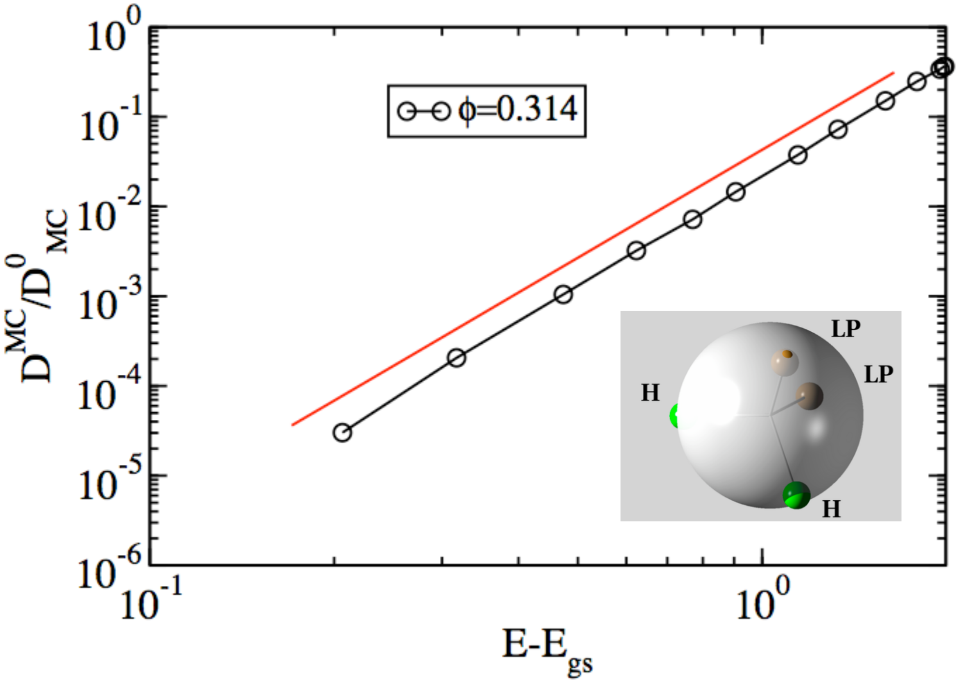
$$D = D_0(1 - p_b)^4$$

Arrhenius Dynamics
at low T

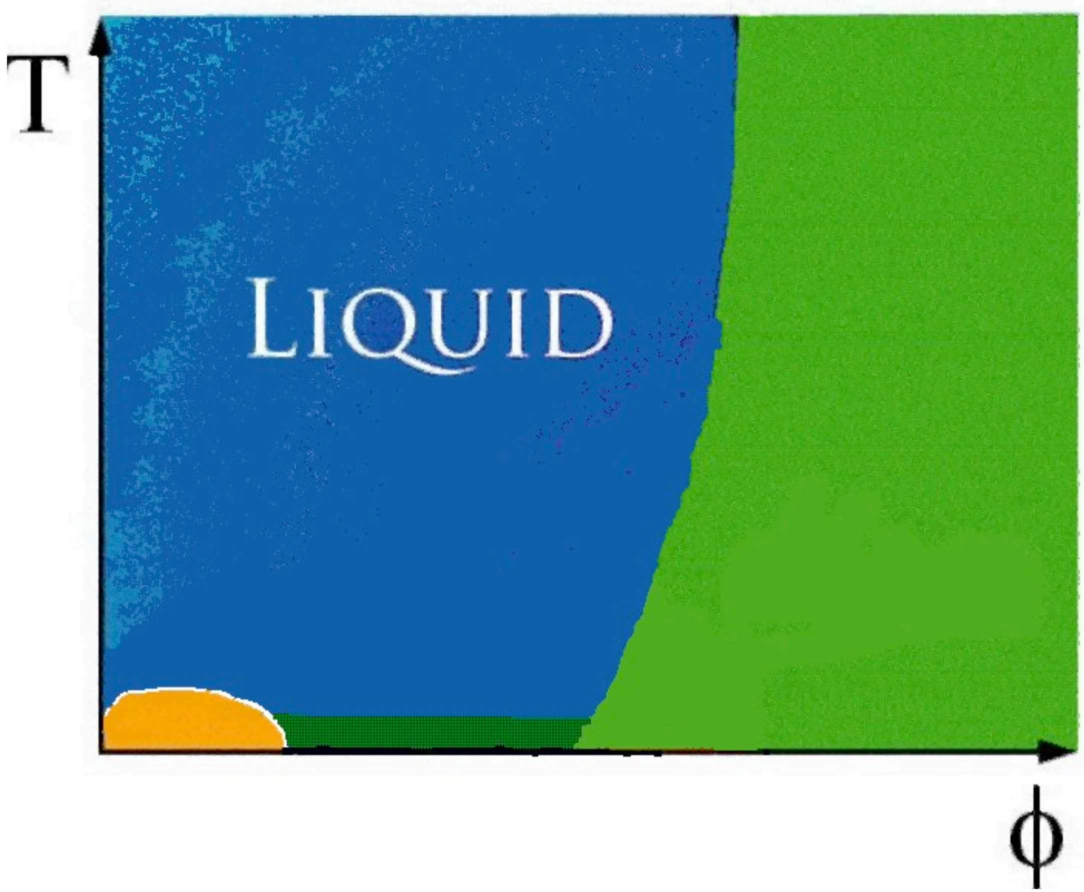
STRONG LIQUIDS







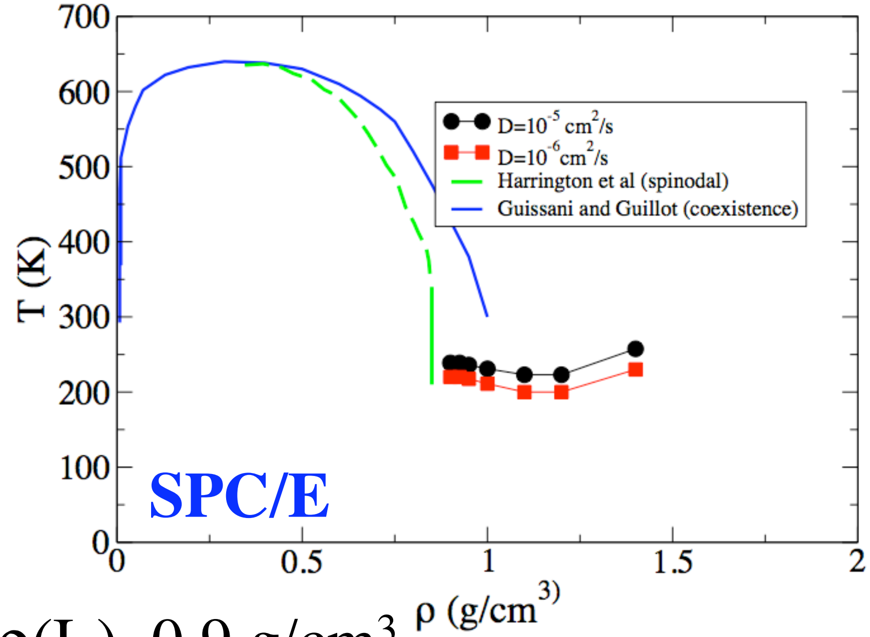
Reduced Valence in atomic and molecular systems



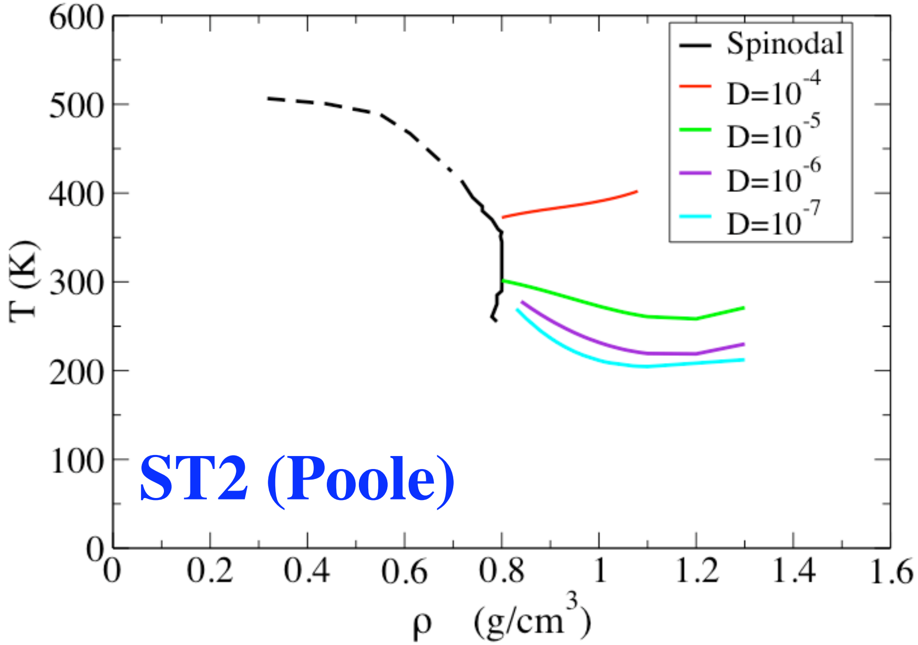
La Sapienza
Università degli Studi di Roma

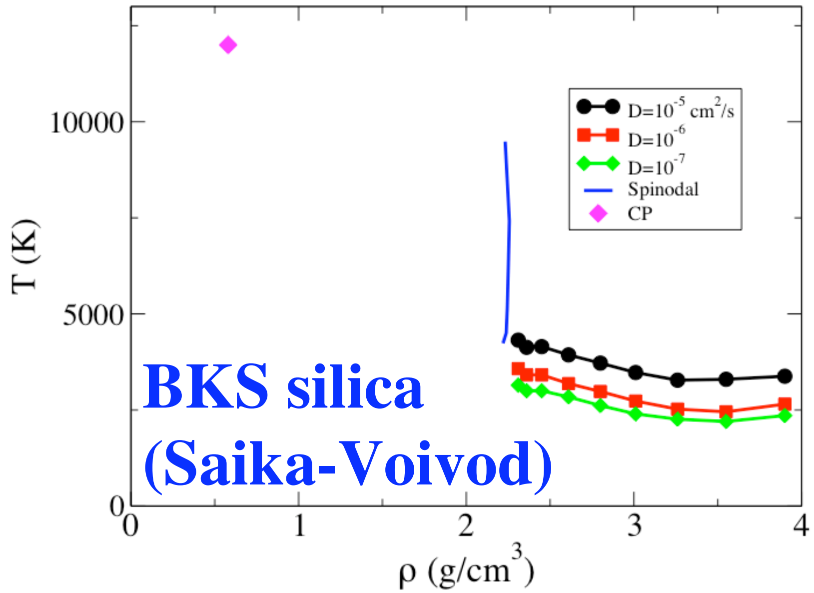
erc

Analogies with other network-forming potentials



$\rho(I_h)\sim 0.9$ g/cm^3





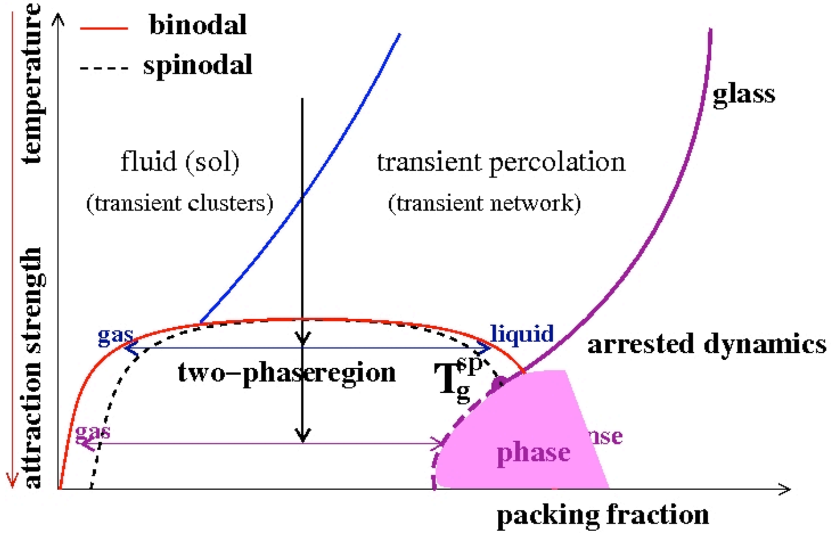
La Sapienza
Università degli Studi di Roma

erc

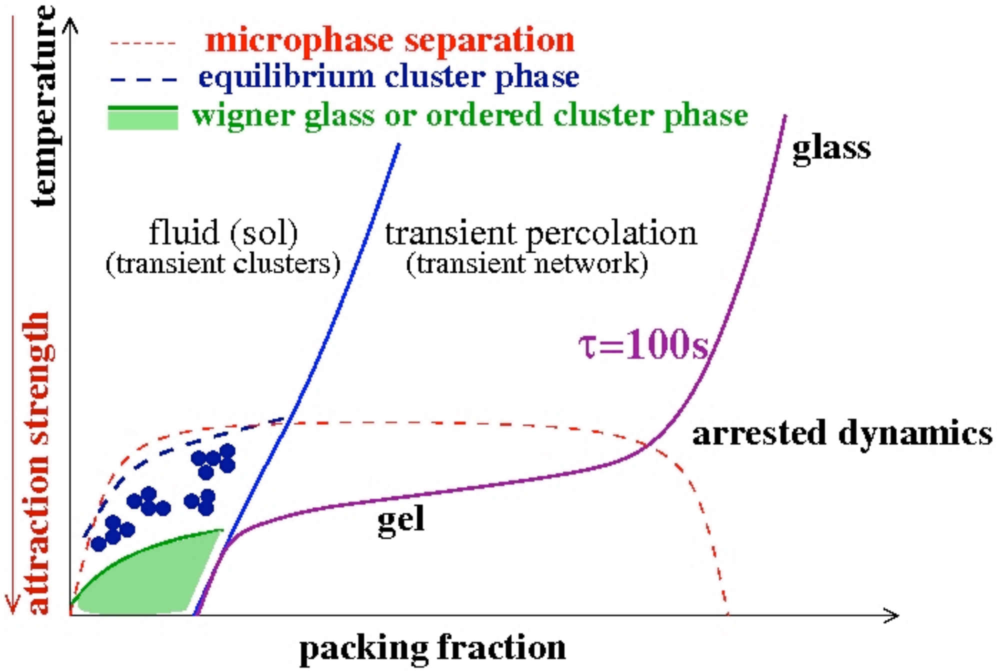
Summary: routes to gels

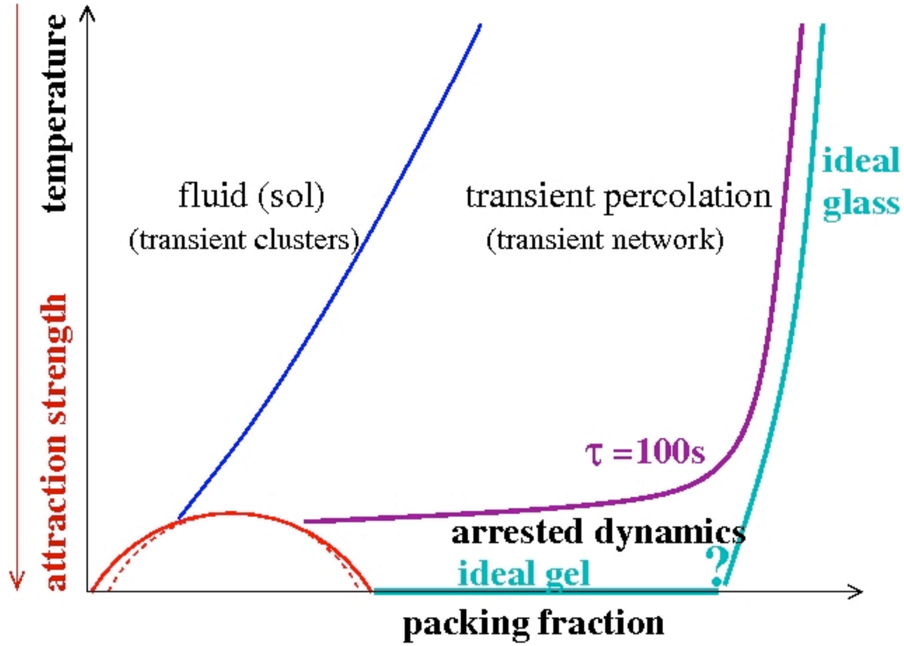
Zaccarelli, JPCM 19, 323101 (2007)

arrested phase separation:
non-equilibrium route



Equilibrium routes to gelation:
with long-range repulsion / with patches





Kinetics of the self-assembly process

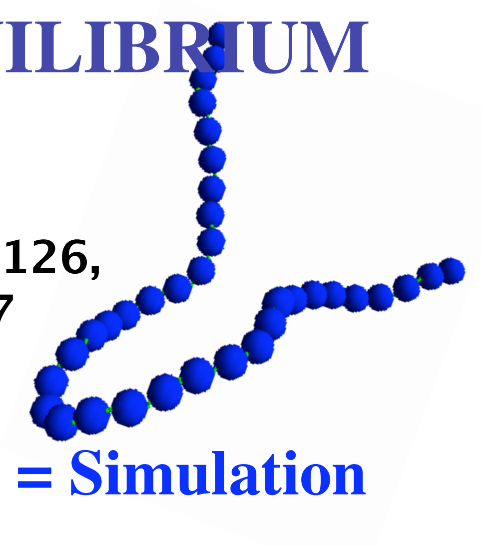
(some ideas for aging)

La Sapienza
Università degli Studi di Roma

erc

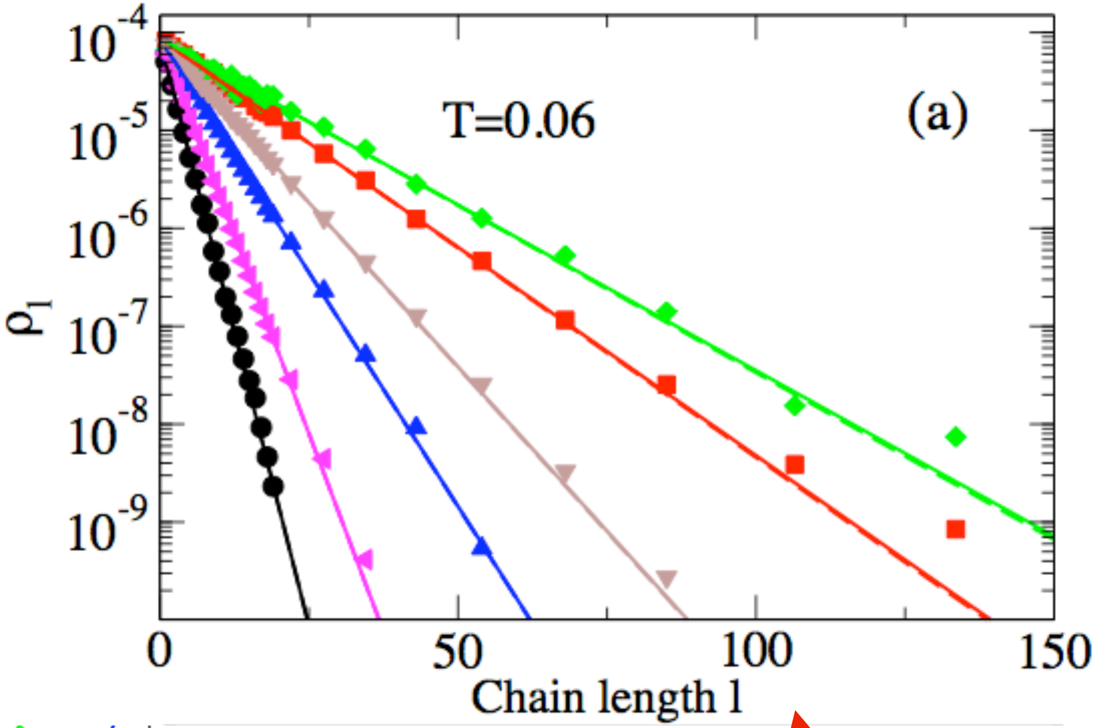
M=2 EQUILIBRIUM (Chains)

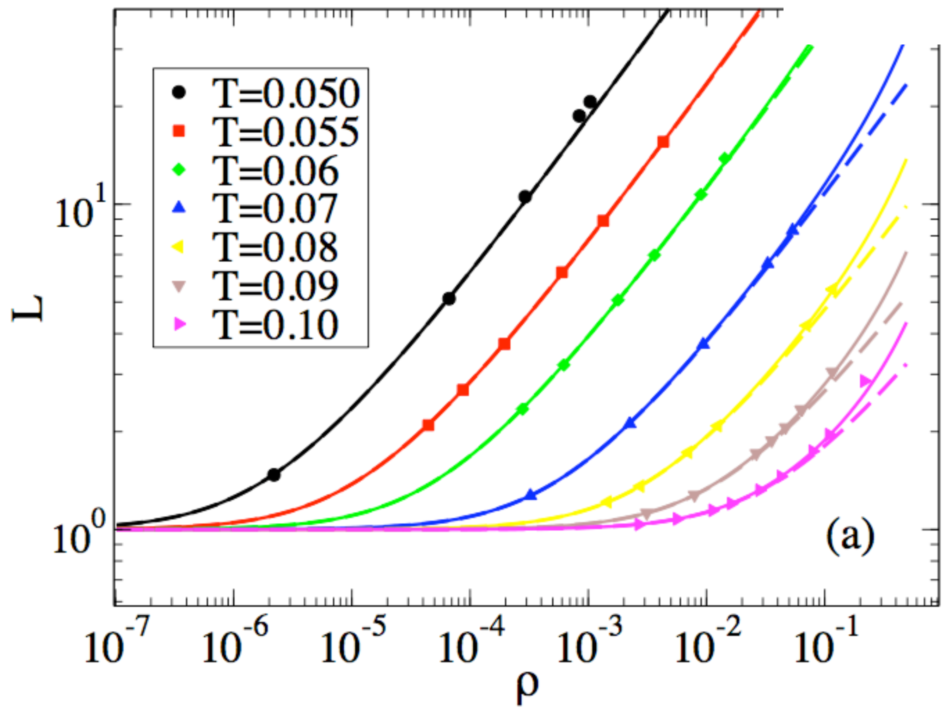
FS et al
J. Chem.Phys.126, 194903, 2007



Symbols = Simulation

Lines = Wertheim Theory





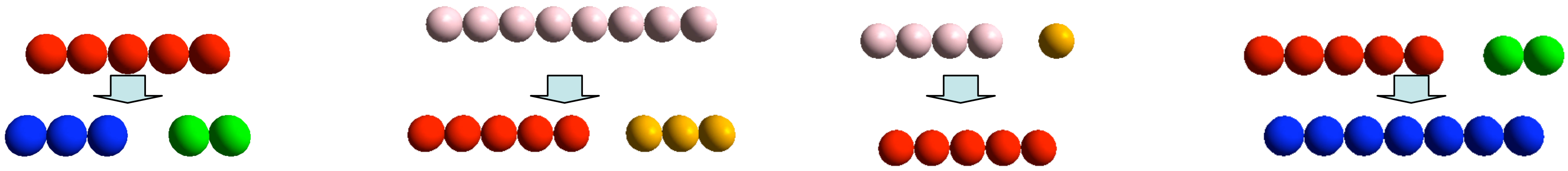
Chain length distributions

$$N_l = \frac{N}{L^2}\left(1 - \frac{1}{L}\right)^{l-1}$$

Average chain length L

M=2 EQUILIBRATION (Growth of the Chains -Cates)

$$\frac{dN_l}{dt} = -k_{breaking}(l-1)N_l + 2k_{breaking}\sum_{j=l+1}^{\infty} N_l + \frac{1}{2}\frac{k_{bonding}}{V}\sum_{j=1}^{l-1} N_j N_{l-j} - N_l \frac{k_{bonding}}{V}\sum_{j=1}^{\infty} N_j .$$



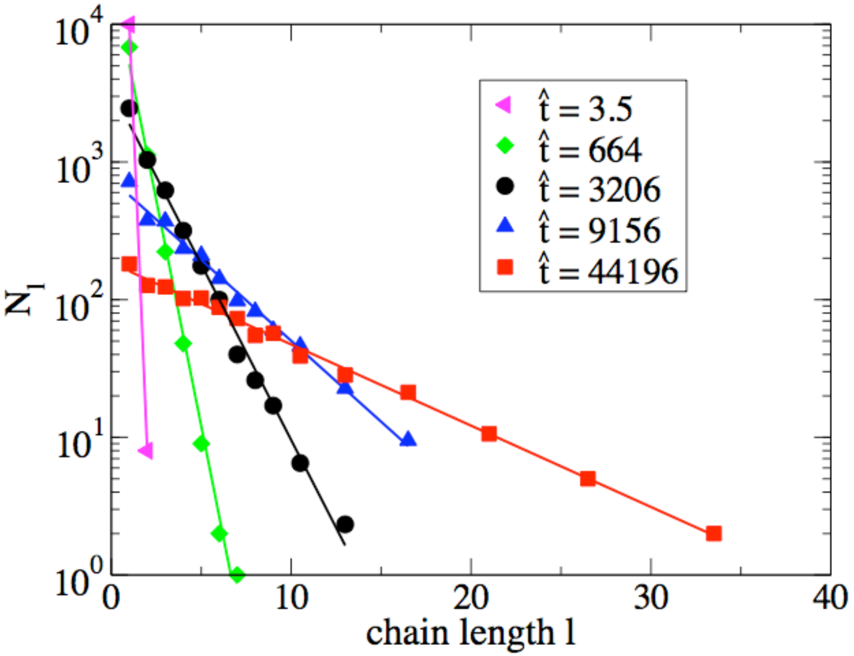
$$N_l(t) = \frac{N}{\bar{l}(t)^2}\left(1 - \frac{1}{\bar{l}(t)}\right)^{l-1}$$

$$\bar{l}(t) = \frac{1 + (2\bar{l} - 1)\tanh[\frac{k_{breaking}t}{2}(2\bar{l} - 1) + \phi]}{2}$$

Low T limit: $\bar{l}(t) = 1 + \frac{k_{bonding}\rho t}{2}$ $\qquad \tanh[\phi] = \frac{2\bar{l}(0) - 1}{2\bar{l} - 1}$

FS, C. De Michele and J. Douglas
Growth of equilibrium polymers under non-equilibrium conditions
J. Phys. Condensed Matter 20, 155101 (2008)

M=2 EQUILIBRATION (Growth of the Chains)

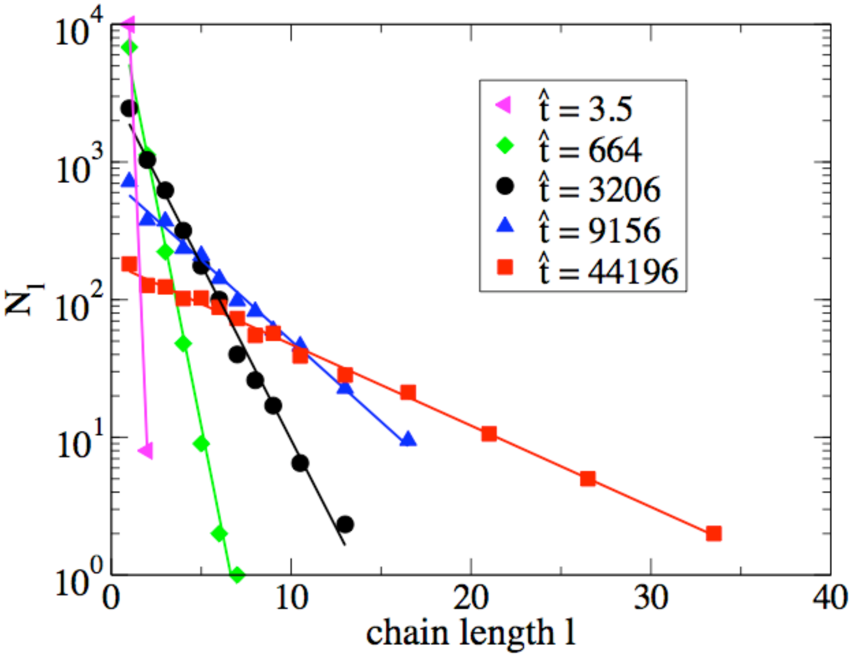


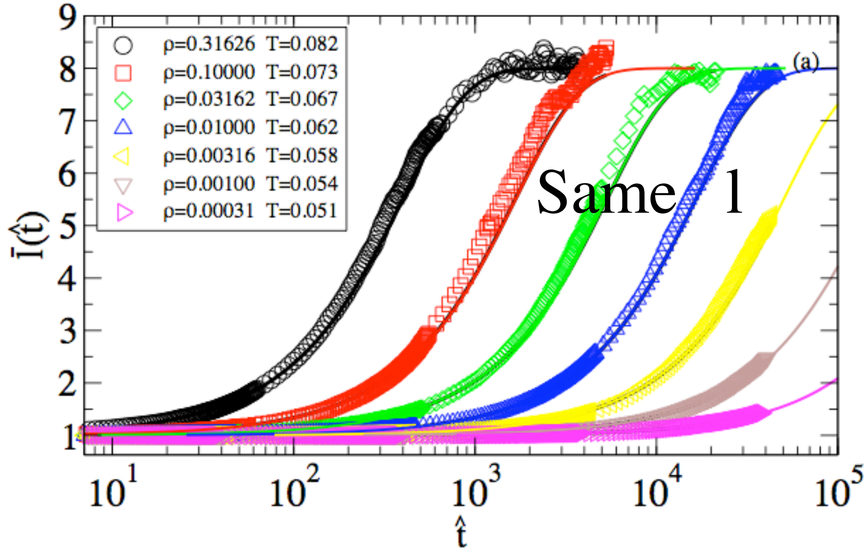
$$N_l(t) = \frac{N}{\bar{l}(t)^2}\left(1 - \frac{1}{\bar{l}(t)}\right)^{l-1}$$

FS, C. De Michele and J. Douglas
Growth of equilibrium polymers under non-equilibrium conditions
J. Phys. Condensed Matter 20, 155101 (2008)

M=2 EQUILIBRATION (Growth of the Chains)

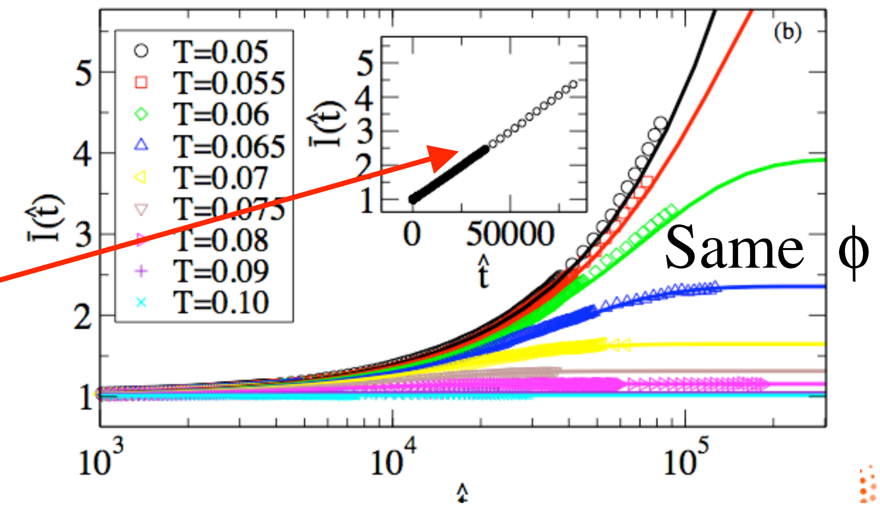
$$\bar{l}(t) = \frac{1 + (2\bar{l} - 1)\tanh[\frac{k_{breaking} t}{2}(2\bar{l} - 1) + \phi]}{2}$$





$$N_l(t) = \frac{N}{\bar{l}(t)^2}\left(1 - \frac{1}{\bar{l}(t)}\right)^{l-1}$$

Low T limit: $\bar{l}(t) = 1 + \frac{k_{bonding}\rho t}{2}$



FS, C. De Michele and J. Douglas
Growth of equilibrium polymers under non-equilibrium conditions
J. Phys. Condensed Matter 20, 155101 (2008)

La Sapienza
Università degli Studi di Roma

Equilibration (to a finite T) in the presence of branching (but no loops !)

(P. van Dongen and M. Ernst, J. Stat Phys 37, 301 (1984).)

$$\frac{dN_k}{dt} = -k^{site}_{breaking}(k-1)N_k + \sum_{j=k+1}^{\infty} k^{k,j-k}_{breaking} N_j + \frac{1}{2}\sum_{j=1}^{k-1} \frac{k^{j,k-j}_{bonding}}{V} N_j N_{k-j} - N_k \sum_{j=1}^{\infty} \frac{k^{k,j}_{bonding}}{V} N_j .$$

At all times, the cluster size distribution is the same as the equilibrium one, but with p(t) instead of p_{eq}

$$\rho_n = \rho\omega_n (1-p_b(t))^f \left[p_b(t)(1-p_b(t))^{f-2}\right]^{n-1}$$

La Sapienza
Università degli Studi di Roma

erc

Equilibration (to a finite T) in the presence of branching (but no loops !)

(P. van Dongen and M. Ernst, J. Stat Phys 37, 301 (1984).)

$$\frac{dN_k}{dt} = -k^{site}_{breaking}(k-1)N_k + \sum_{j=k+1}^{\infty} k^{k,j-k}_{breaking} N_j + \frac{1}{2}\sum_{j=1}^{k-1} \frac{k^{j,k-j}_{bonding}}{V} N_j N_{k-j} - N_k \sum_{j=1}^{\infty} \frac{k^{k,j}_{bonding}}{V} N_j .$$

At all times, the cluster size distribution is the same as the equilibrium one, but with p(t) instead of p_{eq}

$$\rho_n = \rho\omega_n (1-p_b(t))^f \left[p_b(t)(1-p_b(t))^{f-2}\right]^{n-1}$$

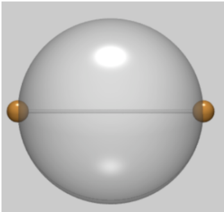
The resulting equation for p(t) CAN be solved analytically !!!

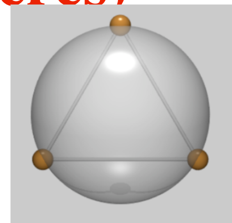
$$p(t) = 1 + \frac{(1-p_{eq})^2 - (1-p_{eq}^2)\coth\left(\frac{1+p_{eq}}{1-p_{eq}} \frac{k^{site}_{breaking} t}{2} - \ln p_{eq}\right)}{2p_{eq}}$$

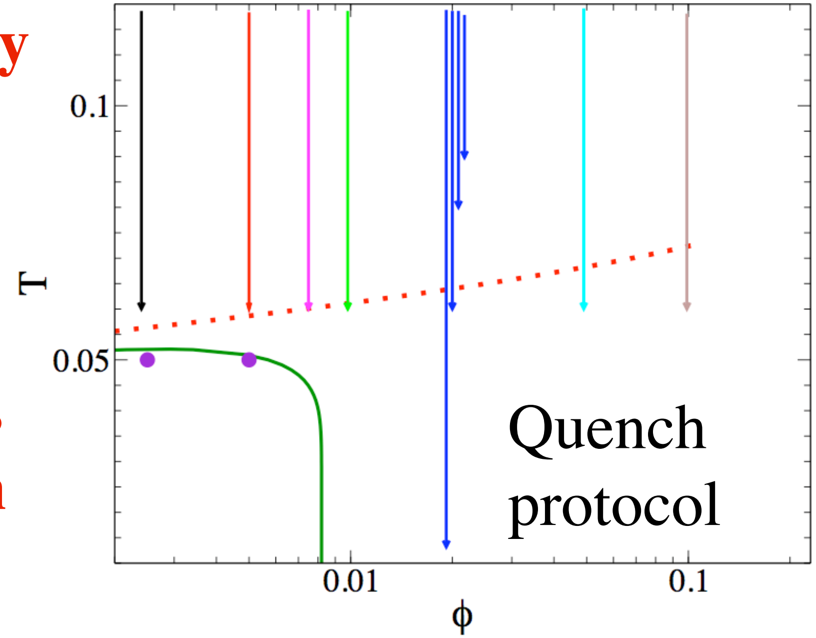
At low T
(irreversible coagulation) $\longrightarrow$

$$p_b(t) = \frac{f k_{bonding}\rho t}{1 + f k_{bonding}\rho t}$$

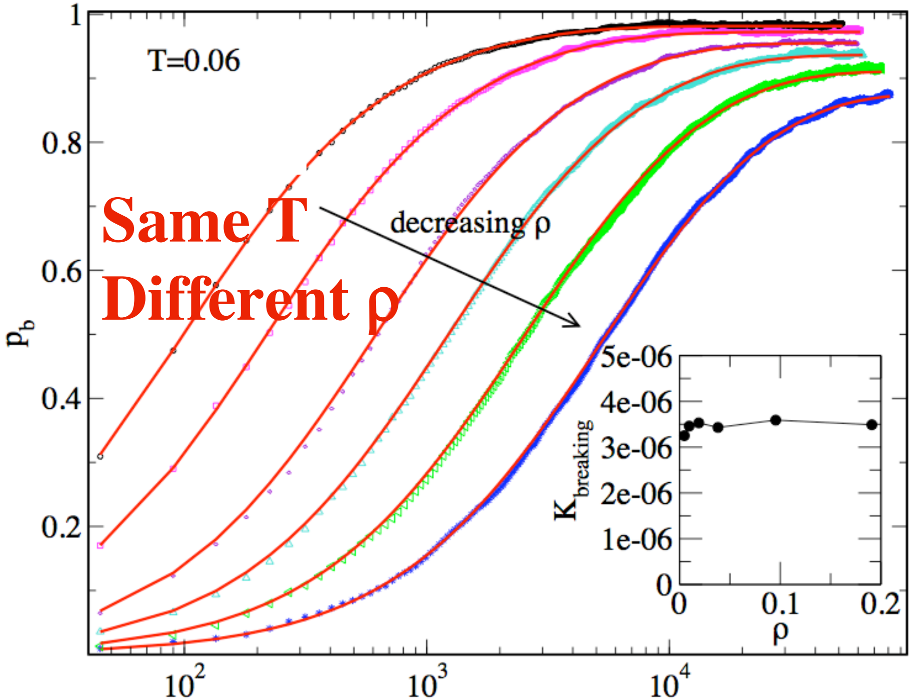
Comparing simulation and theory (for patchy spheres)

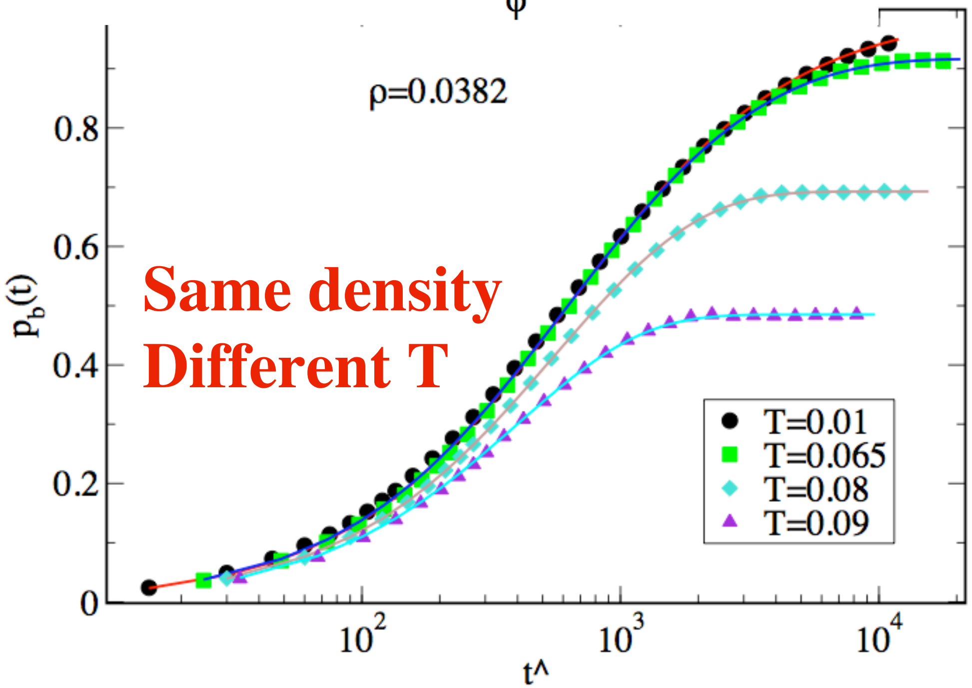






Evolution of the number of bonds following a T-jump, starting from high-T

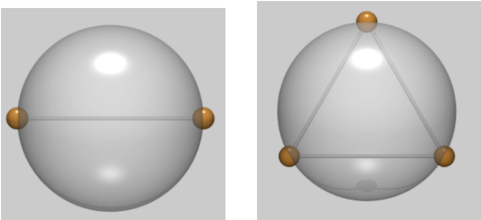




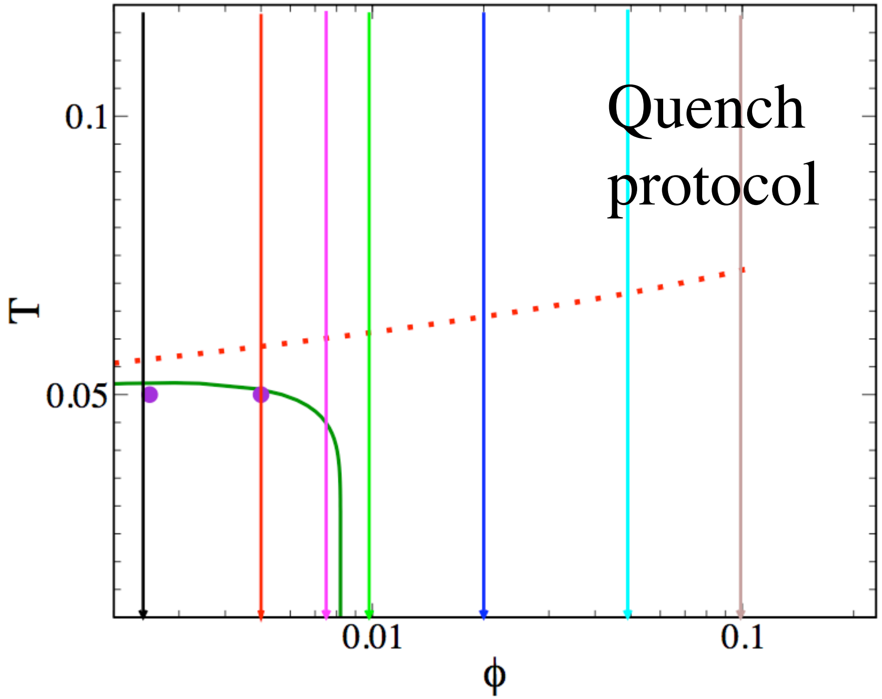
A parameter-free description of the kinetics of formation of loop-less branched structures and gels
FS, Cristiano De Michele, Silvia Corezzi, John Russo, Emanuela Zaccarelli and Piero Tartaglia,
Soft Matter, 5, 2571, 2009

Chemical Gels…..

Irreversible aggregation in the absence of bond loops

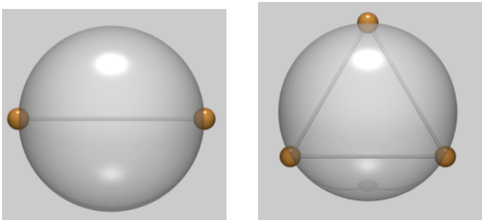


$$p_b(t) = \frac{f k_{bonding} \rho t}{1 + f k_{bonding} \rho t}$$

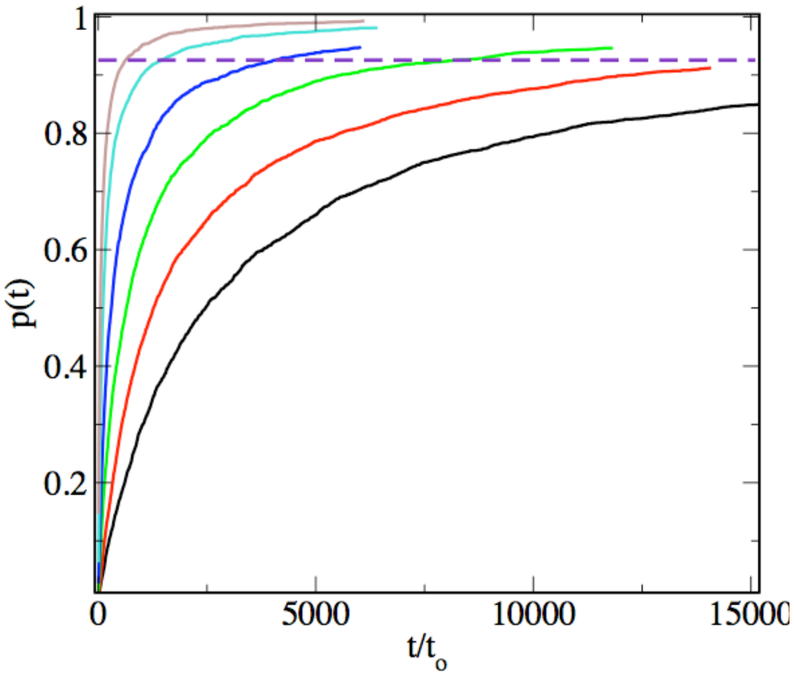


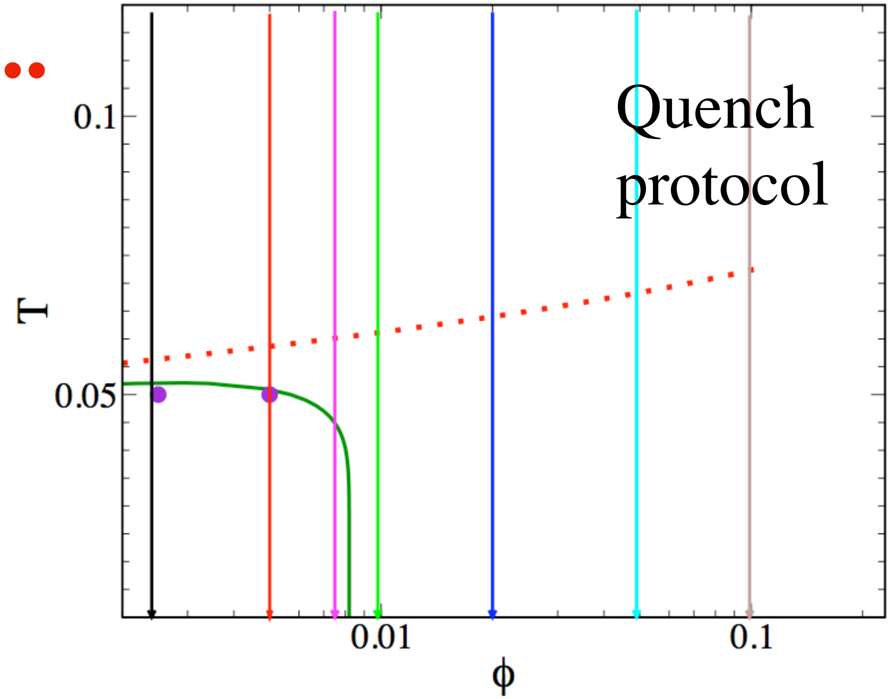
Chemical Gel limit…..

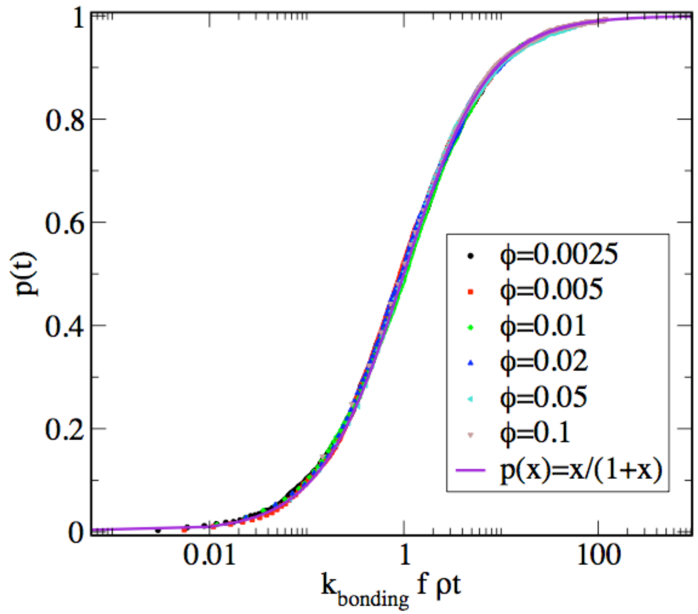
Irreversible aggregation in the absence of bond loops



$$p_b(t) = \frac{f k_{bonding} \rho t}{1 + f k_{bonding} \rho t}$$

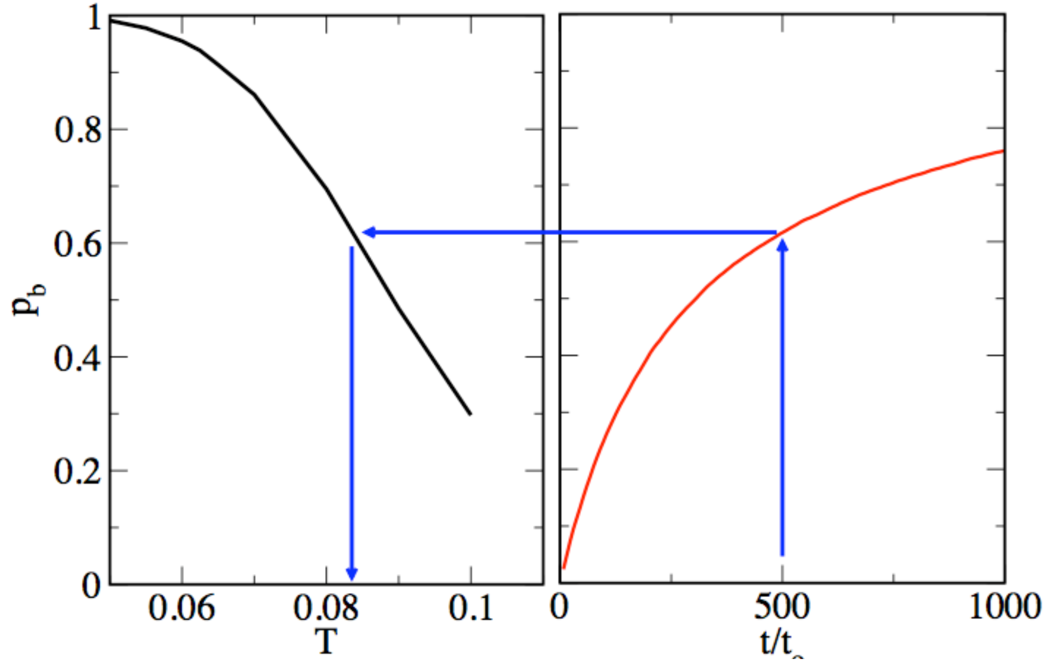






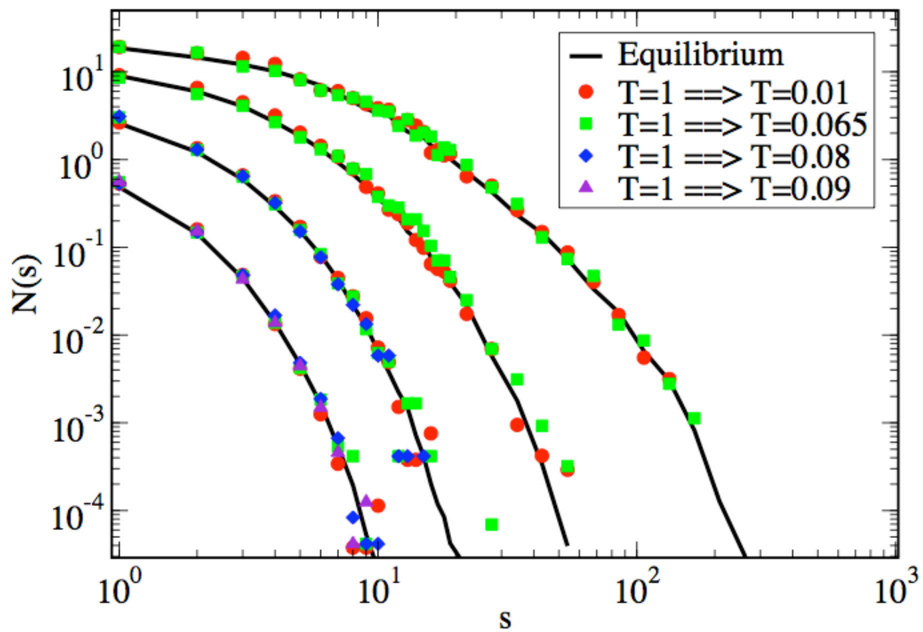
Smoluchowski coagulation works !

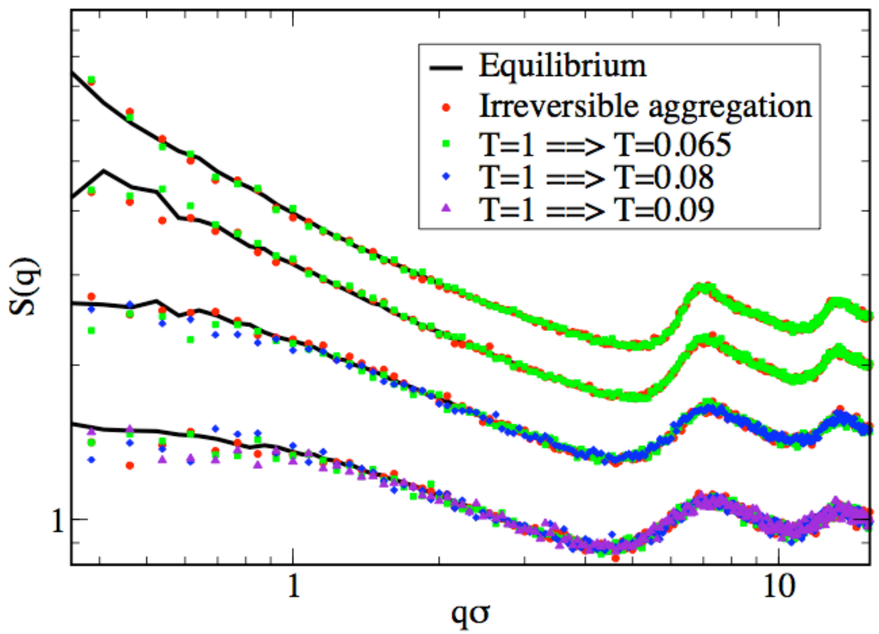
Chemical and physical gelation (in the absence of loops)



t <---->T

At p(t) =p(T)





A parameter-free description of the kinetics of formation of loop-less branched structures and gels
FS, Cristiano De Michele, Silvia Corezzi, John Russo, Emanuela Zaccarelli and Piero Tartaglia,
Soft Matter, 5, 2571, 2009

Thanks to…

Emanuela Bianchi, Fabio Ciulla, Cristiano De Michele, Giuseppe Foffi, Julio Largo, Cristian Mayer, Stefano Mossa, John Russo, Piero Tartaglia, Emanuela Zaccarelli (Roma along the years)

Silvia Corezzi, Daniele Fioretto (Perugia)
Jack Douglas (NIST)
Francis Starr (Wesleyan)
Peter Lu, David Weitz (Harvard)

La Sapienza
Università degli Studi di Roma

erc