Growth of Order and its Role in the Dynamics of Supercooled Liquids

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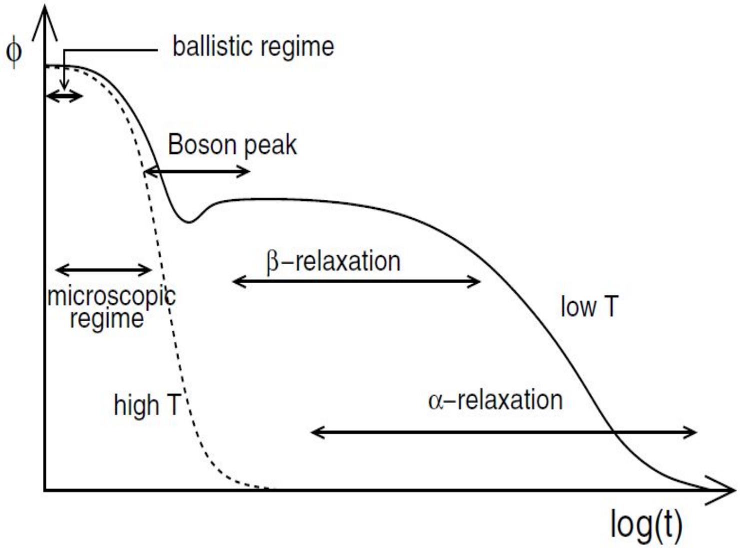
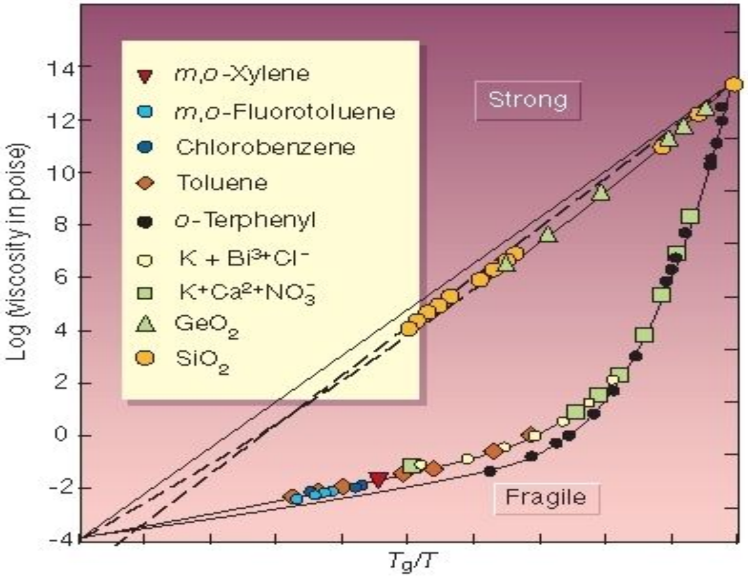
Entropy, Infromation and Order in Soft Matter,
ICTS, 2018

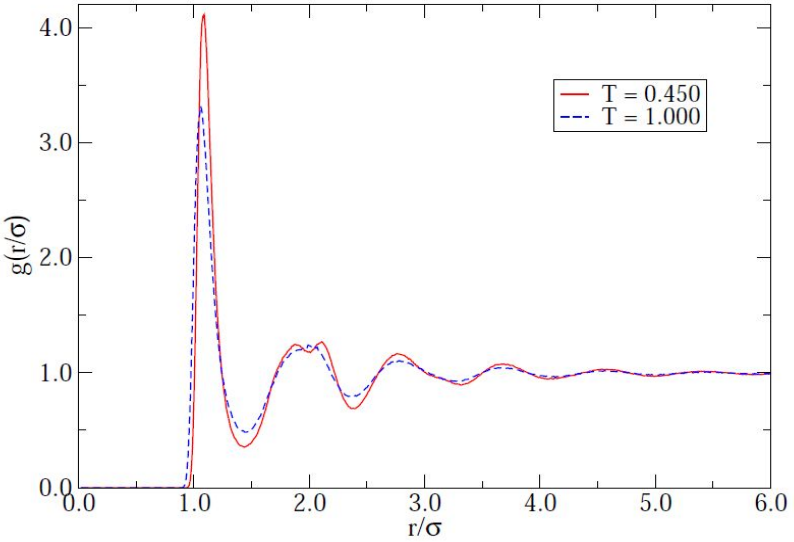
Glassy Systems

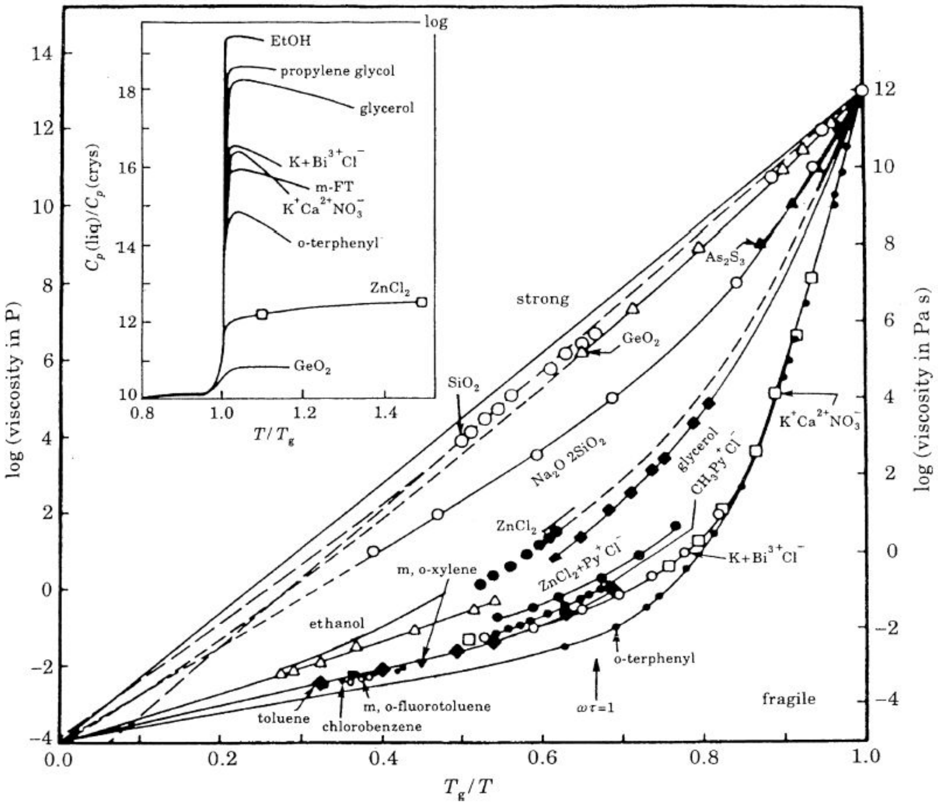
- Cool rapidly enough such that crystallization is avoided → supercooled state → glass (lower temperature)
- It is a non-equilibrium state which depends strongly on the cooling rate
- Relaxation time increses many orders of magnitude with temperature change of ~ 100K
- Stretched exponential relaxation → indicating multiple relaxation times in the system.
- Super-Arrhenius temperature dependence





Phenomenology of Supercooled Liquid

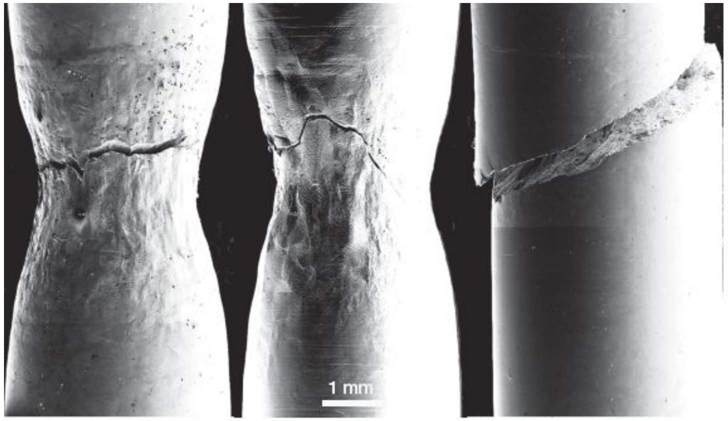




- No dramatic structural changes with decresing temperature.
- Rapid increase in relaxation time and Viscosity changes by 16 orders of magnitude over a temperture change of around hundred degrees.

- Super-Arrhenius temperature dependence.

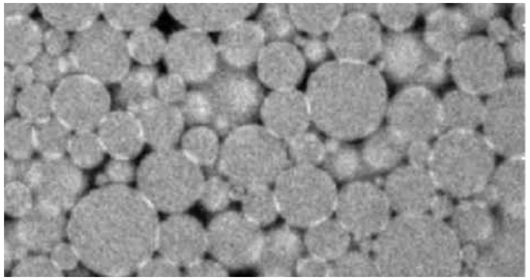
Systems with Glassy Dynamics



metallic glasses

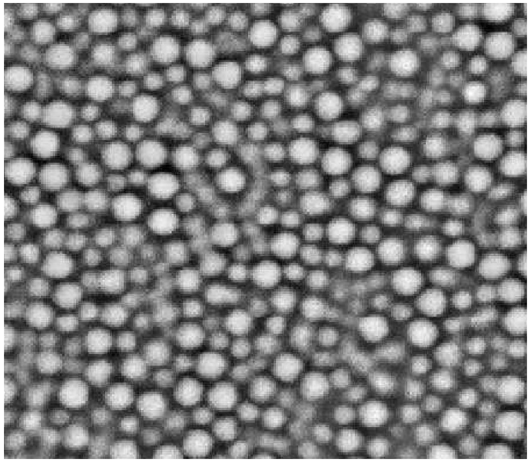
Model glass former

Emulsions



Model glass former with crystalline order

Colloids



- **Rapid increase of relaxation time** in Glass with decreasing temperature is very similar to the **phenomena of critical slowing down** near a continuous phase transition.
- Possibility of a **growing length scale** associated with the dramatic slowing down in dynamics.
- **Static** length scale or **Dynamic** length scale?

Numerous attempts to extract a growing length scale

Growing length and time scales in glass-forming liquids

Smarajit Karmakar[a], **Chandan Dasgupta**[a,b,1], **and Srikanth Sastry**[b]

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Edited by H. Eugene Stanley, Boston University, Boston, MA, and approved January 9, 2009 (received for review November 6, 2008)

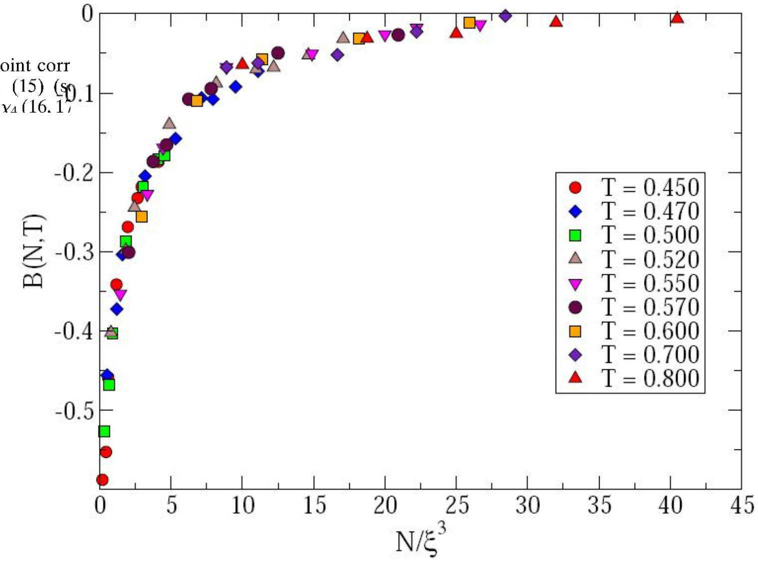
The glass transition, whereby liquids transform into amorphous solids at low temperatures, is a subject of intense research despite decades of investigation. Explaining the enormous increase in

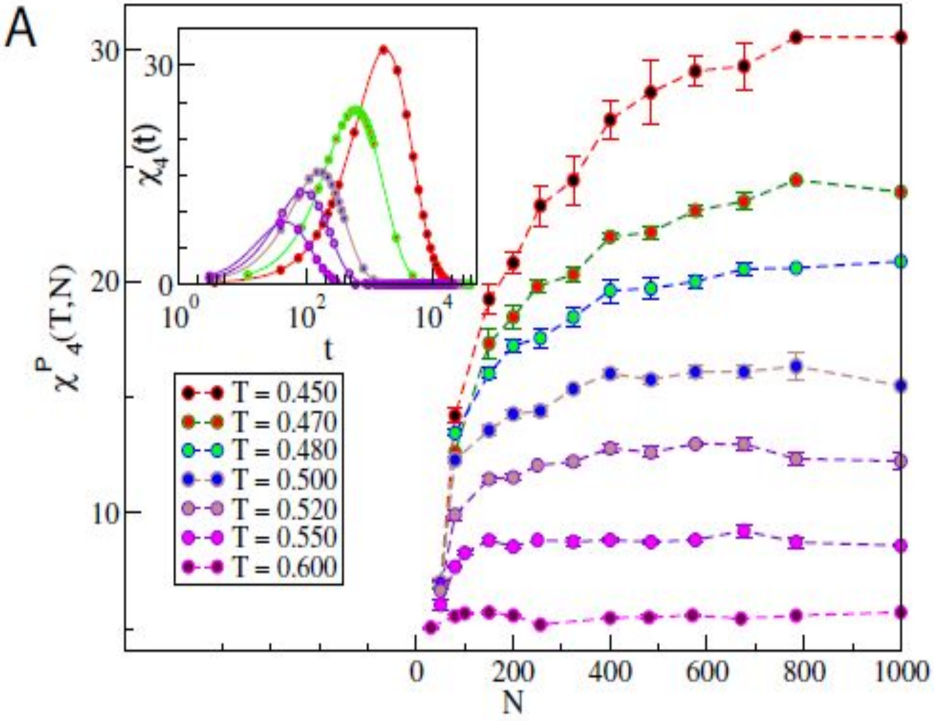
dependent) length scale, ξ, through analysis of a 4-point corr lation function first introduced by Dasgupta, *et al.* (15) (s *Methods*), and the associated dynamical susceptibility χ_4 (16, 17

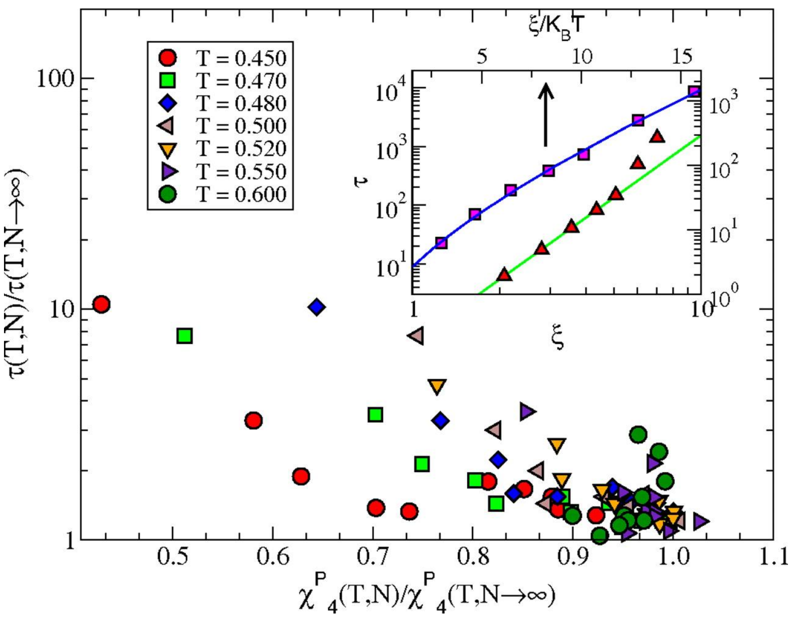
$$\chi_4(t) = \frac{1}{N}\left[\langle Q^2(t)\rangle - \langle Q(t)\rangle^2\right].$$

$$Q(t) = \int d\vec{r}\rho(\vec{r},t_0)\rho(\vec{r},t+t_0) \sim \sum_{i=1} w(|\vec{r}_i(t_0) - \vec{r}_i(t_0+t)|)$$

$$B(N,T) = \frac{< [Q_\tau - < Q_\tau >]^4 >}{3 < [Q_\tau - < Q_\tau >]^2 >^2} - 1$$



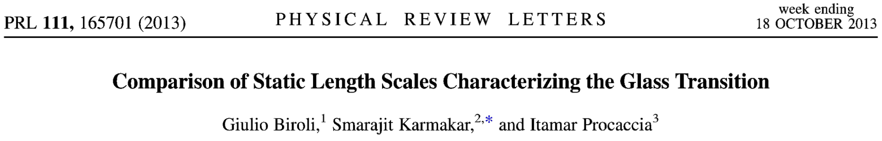




Static Length scale of Amorphous Order

- Different methods for calculating static length scale:
  - Point-to-set Correlation function
  - Patch Repetition Length Scale
  - Curvature of local potential energy minimum (Hessian Matrix)
  - Finite size scaling of relaxation time

All these methods are involved in nature and sometime require a lot of microscopic details. Thus they are not practical for real glass forming liquids and are mostly studied for model liquids in simulations.



PRL **111,** 165701 (2013) PHYSICAL REVIEW LETTERS week ending 18 OCTOBER 2013

Comparison of Static Length Scales Characterizing the Glass Transition

Giulio Biroli,[1] Smarajit Karmakar,[2,*] and Itamar Procaccia[3]

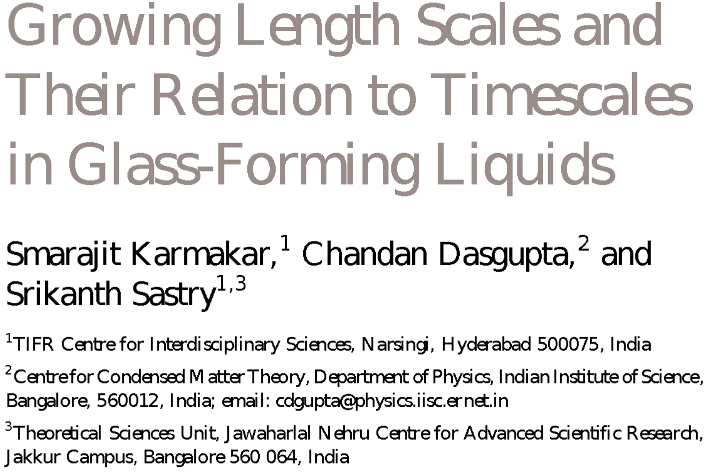
IOP Publishing Reports on Progress in Physics

Rep. Prog. Phys. 79 (2016) 016601 (36pp) doi:10.1088/0034-4885/79/1/016601

Review Article

Length scales in glass-forming liquids and related systems: a review

Smarajit Karmakar[1], Chandan Dasgupta[2] and Srikanth Sastry[3]



Growing Length Scales and Their Relation to Timescales in Glass-Forming Liquids

Smarajit Karmakar,[1] Chandan Dasgupta,[2] and Srikanth Sastry[1,3]

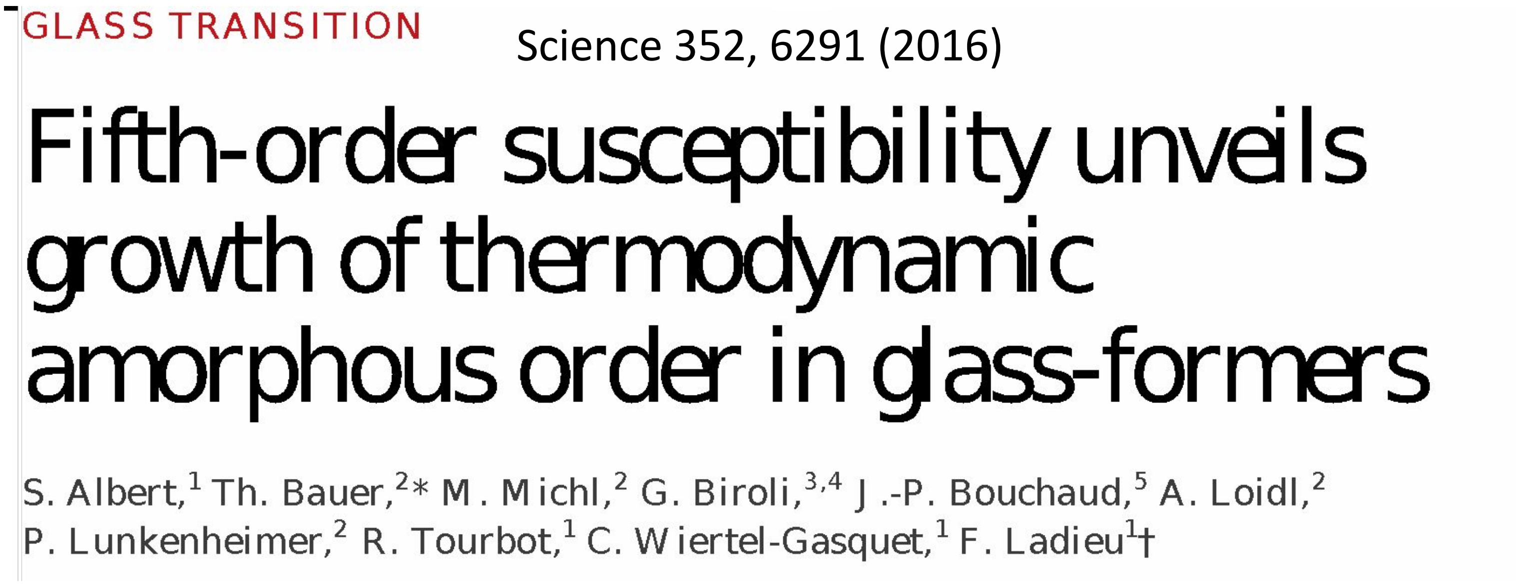
[1]TIFR Centre for Interdisciplinary Sciences, Narsingi, Hyderabad 500075, India

[2]Centre for Condensed Matter Theory, Department of Physics, Indian Institute of Science, Bangalore, 560012, India; email: cdgupta@physics.iisc.ernet.in

[3]Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560 064, India

Static Length scale of Amorphous Order

- Experimental determination of this static length scale remained a major challenge.



GLASS TRANSITION

Science 352, 6291 (2016)

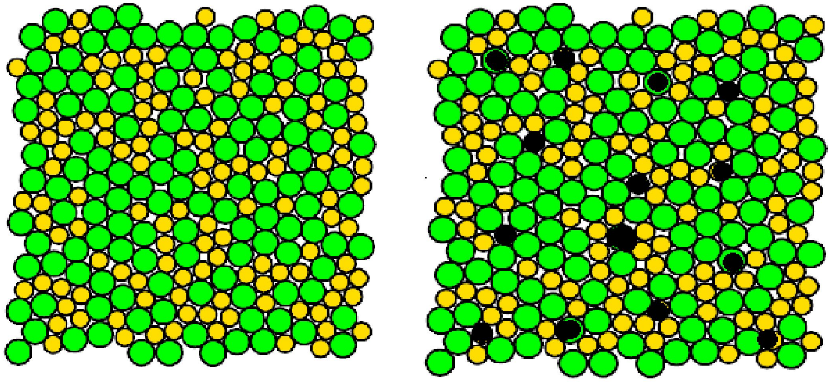
Fifth-order susceptibility unveils growth of thermodynamic amorphous order in glass-formers

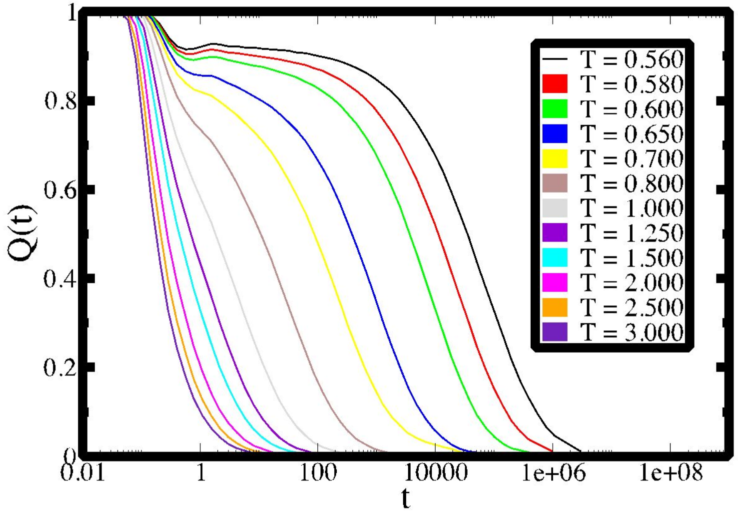
S. Albert,[1] Th. Bauer,[2]* M. Michl,[2] G. Biroli,[3,4] J.-P. Bouchaud,[5] A. Loidl,[2]
P. Lunkenheimer,[2] R. Tourbot,[1] C. Wiertel-Gasquet,[1] F. Ladieu[1]†

- Measuring the higher order non-linear dielectric susceptibilities is extremely difficult as they are many orders of magnitude smaller than the leading linear contribution. Special experimental techniques were developed to reliably measure these higher order susceptibilities.

Pinning Susceptibility: A novel method to study Static Length scale of Amorphous Order

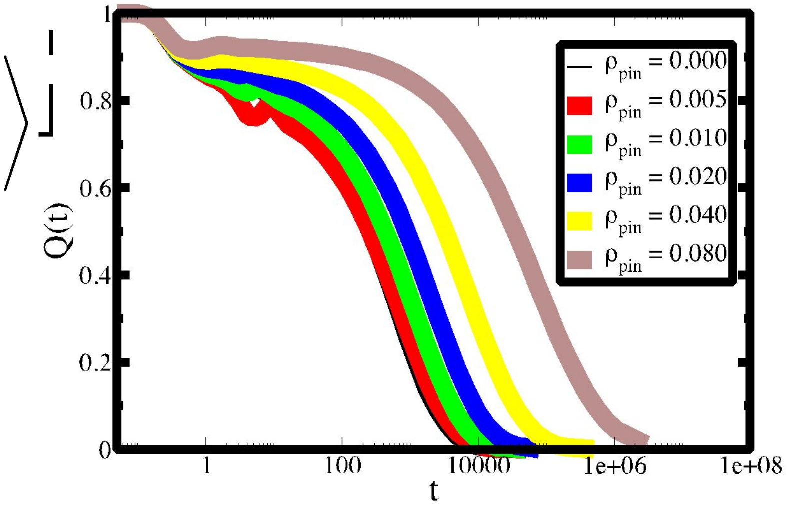
We proposed a new susceptibility : **Pinning Susceptibility** to extract the static length scale very easily. This will be also very simple to implement in experiments.





$$\chi_P(t) = \left.\frac{\partial Q(t)}{\partial \rho_{pin}}\right|_{\rho_{pin}=0}$$

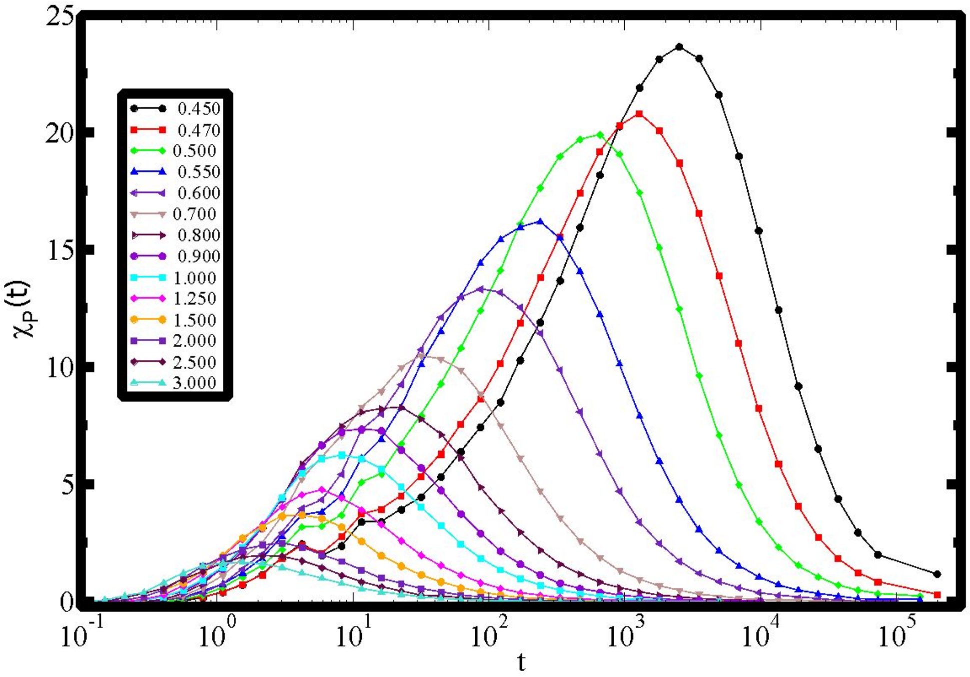
$$Q(T,c,t) = \frac{1}{(1-c)N}\left[\left\langle \sum_{i=1}^{(1-c)N} w(|\vec{r}_i(t) - \vec{r}_i(0)|)\right\rangle\right]$$



Pinning Susceptibility : A Novel Method to Study Growth of Amorphous Order in Glass-forming Liquids, R. Das, S. Chakrabarty, S. Karmakar, Soft Matter 2017.

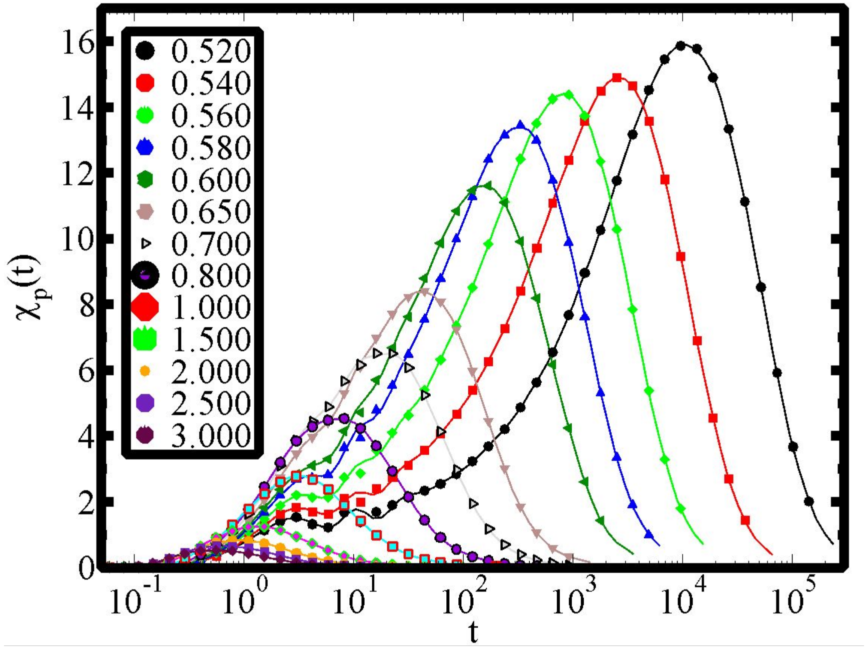
Pinning Susceptibility

This susceptibility looks very similar to $\chi_4(t)$ but the main difference is that peak height of $\chi_4(t)$ depends on the dynamic length-scale where as peak height of $\chi_p(t)$ is directly proportional to the static correlation volume in the liquid. There is no unknown exponent involved in the analysis.



In 3 dimensions

In 2 dimensions



- At time much larger than the short time relaxation, Q(c,t) can approximated very well by stretched exponential function :

$$Q(c,t) \sim \exp\left[-\left(\frac{t}{\tau_\alpha(c,T)}\right)^{\beta}\right], t \gg \tau_\beta .$$

- Differentiating this above Eq. with respect to c and then letting $t \sim \tau_\alpha$

$$\chi_p^{max}(T) \sim \frac{\beta}{e\tau_\alpha(c,T)} \frac{\partial \tau_\alpha(c,T)}{\partial c}\bigg|_{c=0}$$

- Now for small pinning concentration c, relaxation time obeys the following scaling function if certain conditions are satisfied :

$$\boxed{\log\left[\frac{\tau_\alpha(c,T)}{\tau_\alpha(0,T)}\right] = f\left[c\xi_p^d(T)\right]}$$

- The scaling function f(x) goes to zero as x goes to 0. So in the limit x -> 0, we can approximate $f(x) \sim x$

$$\chi_p^{max}(T) = \frac{\beta}{e}\xi_p^d(T).$$

Conditions for Existence of Scaling Function

- First find out if there is an optimum value of the pinning fraction, c_P, at which the temporal peak of the pinning susceptibility takes its highest value for a given temperature.

- Set the derivative of $\chi_p[c, T, \tau_\alpha(c, T)]$ with respect to c to zero.

$$\tau_\alpha \frac{\partial^2 \tau_\alpha}{\partial c_P^2} = \left(\frac{\partial \tau_\alpha}{\partial c_P} \right)^2 . \tag{1}$$

- Solving this, we get,

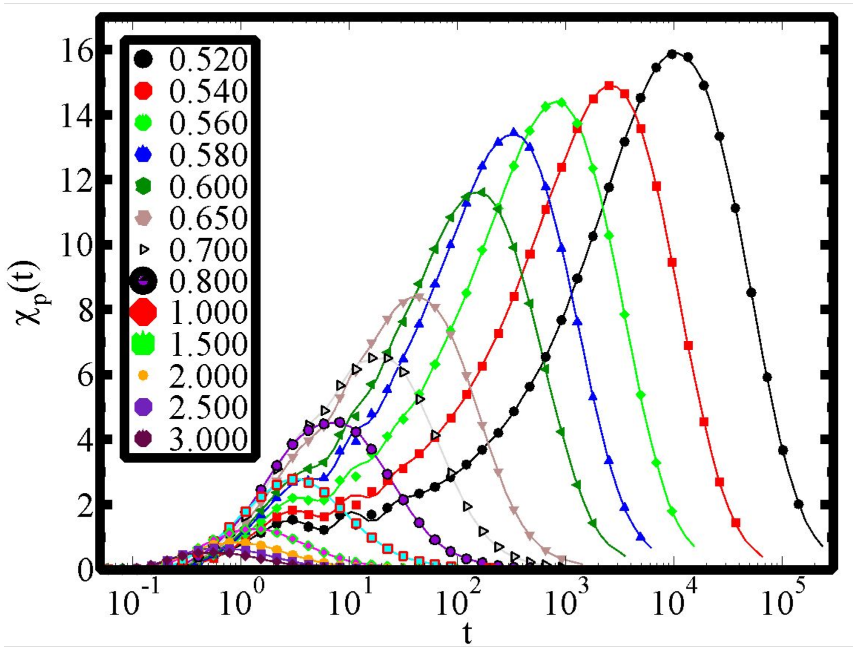
$$\tau_\alpha(c_P, T) = A(T) \exp\left[B(T) c_P\right] . \tag{2}$$

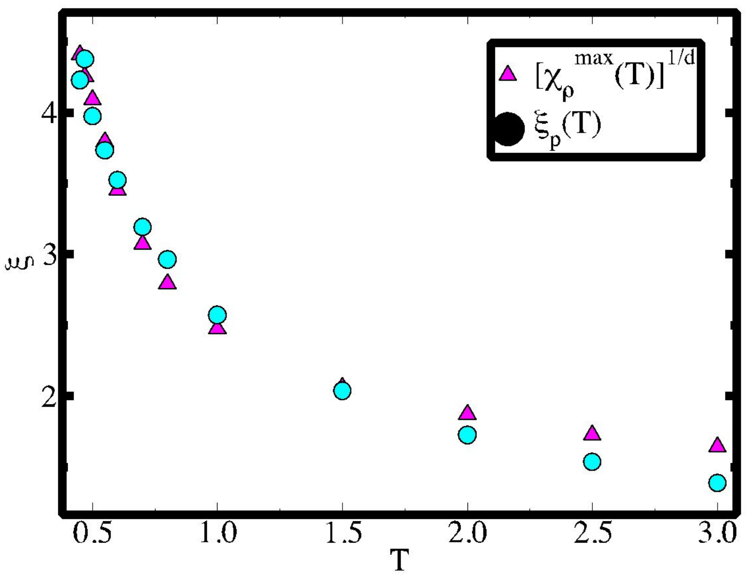
- A corollary to this is that if the peak height of $\chi_p(t)$ for a given temperature is independent of c, then the derivative considered to get the maximum in the above analysis vanishes for all values of c. In that case, we get after renaming $A(T)$ and $B(T)$ appropriately,

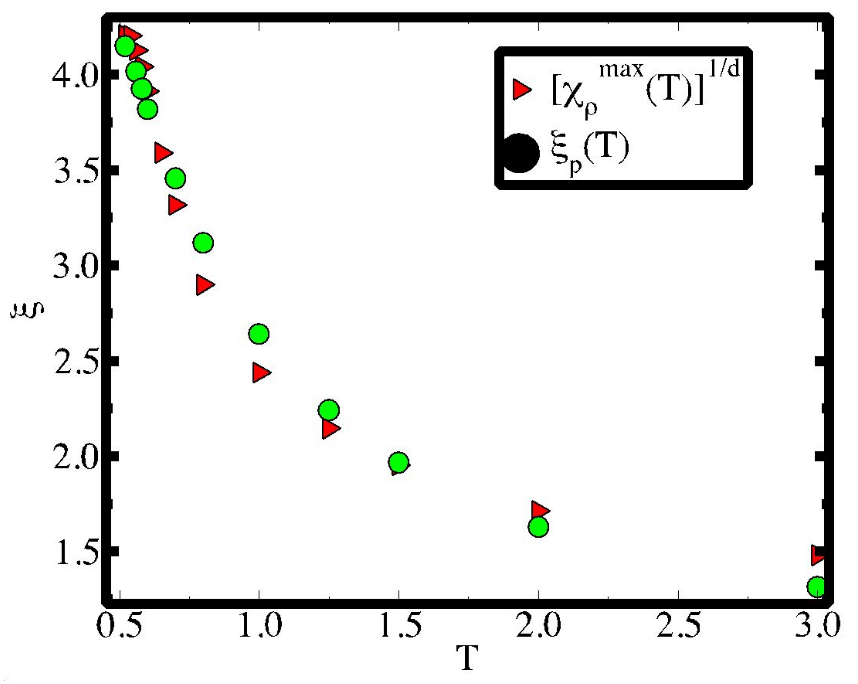
$$\tau_\alpha(c, T) = \tau_\alpha(0, T) \exp[c \xi_p^d(T)]. \tag{3}$$

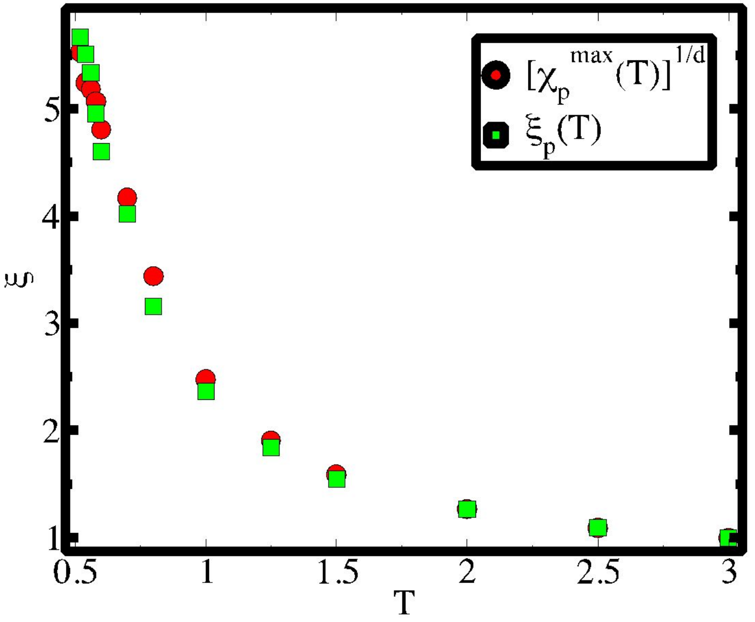
- Thus it is essential for the existence of the proposed scaling function that the peak height of $\chi_p(t)$ for a given temperature is independent of the pinning concentration, c.

Pinning Susceptibility

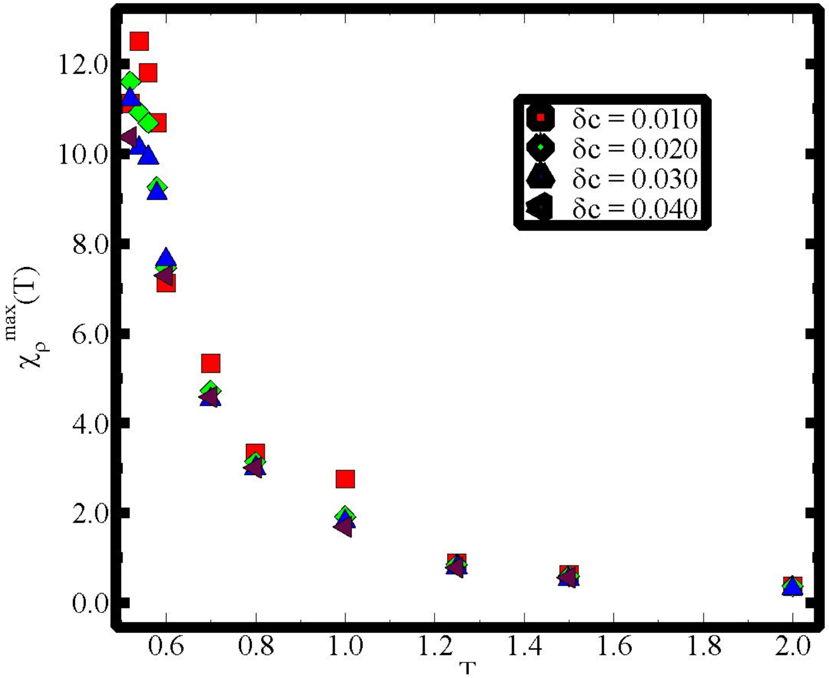






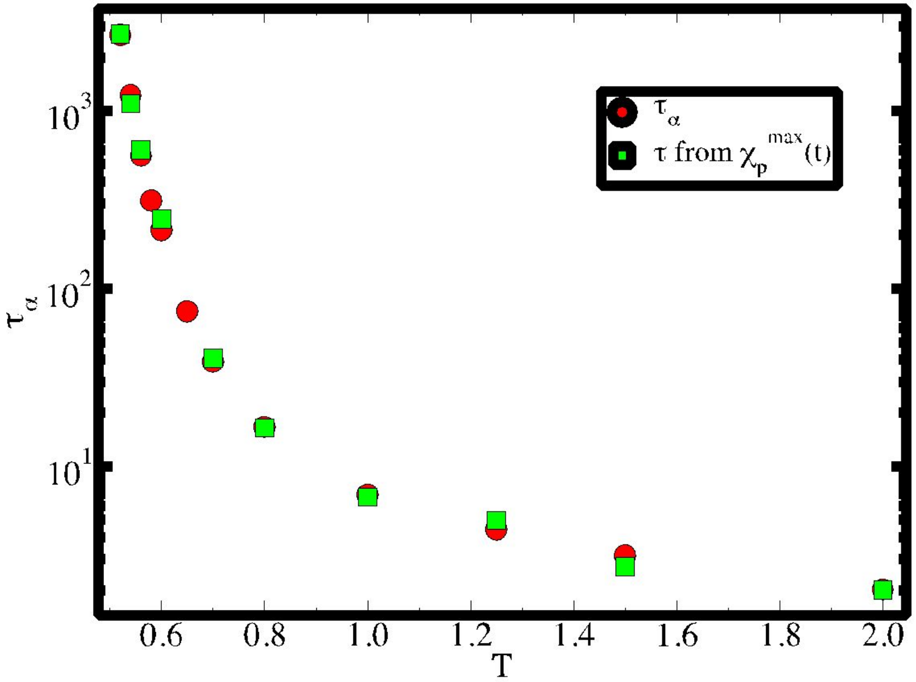


Consistency Check



Pinning Susceptibility does not depend much even for larger δc

Time at which the peak of pinning susceptibility appears is proportional to the α relaxation time.



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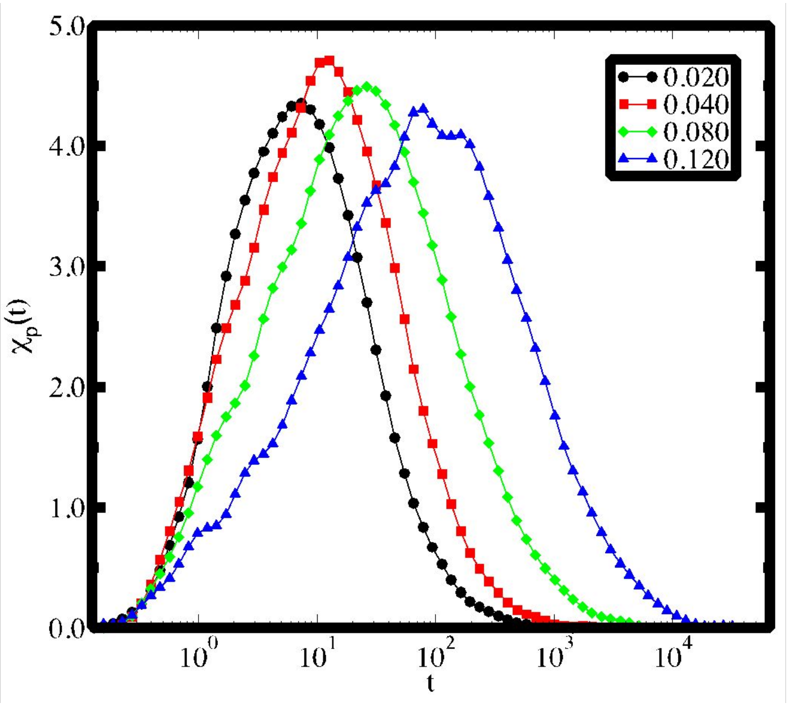
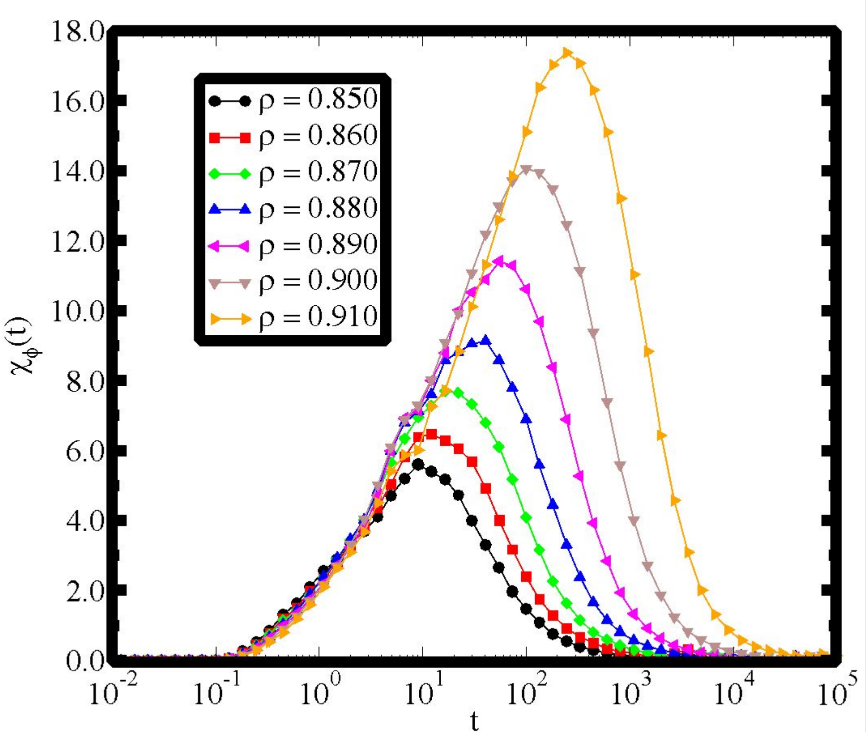


Peak height of Pinning Susceptibility indeed does not depend even if it is calculated at different pinning concentration. This is essential for the existence of the scaling function.

Peak height of $\chi_\phi \equiv \partial Q/\partial \phi$ does depend on packing fraction if it is calculated at different packing fraction. Similar Scaling function will not exist for this susceptibility.



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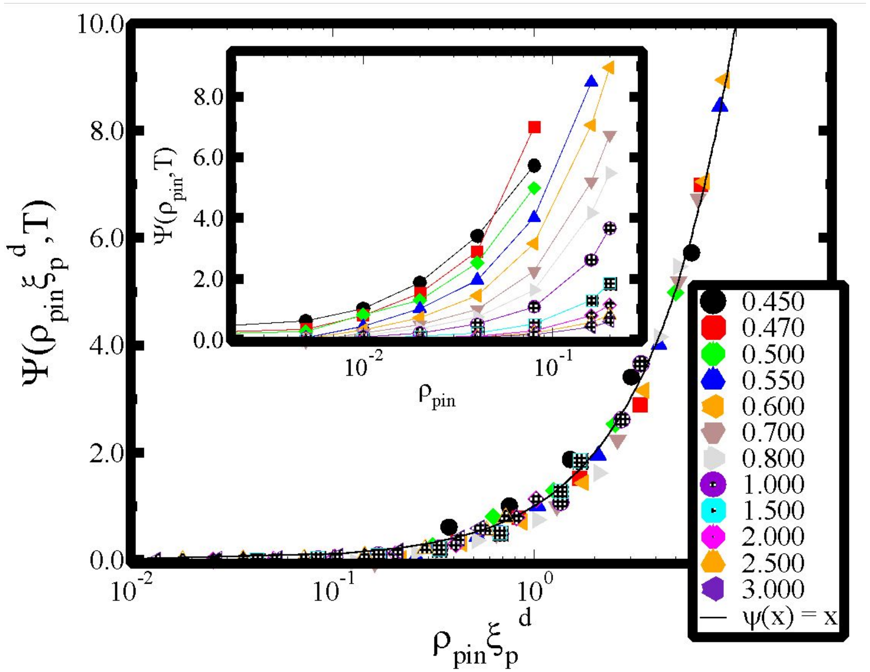
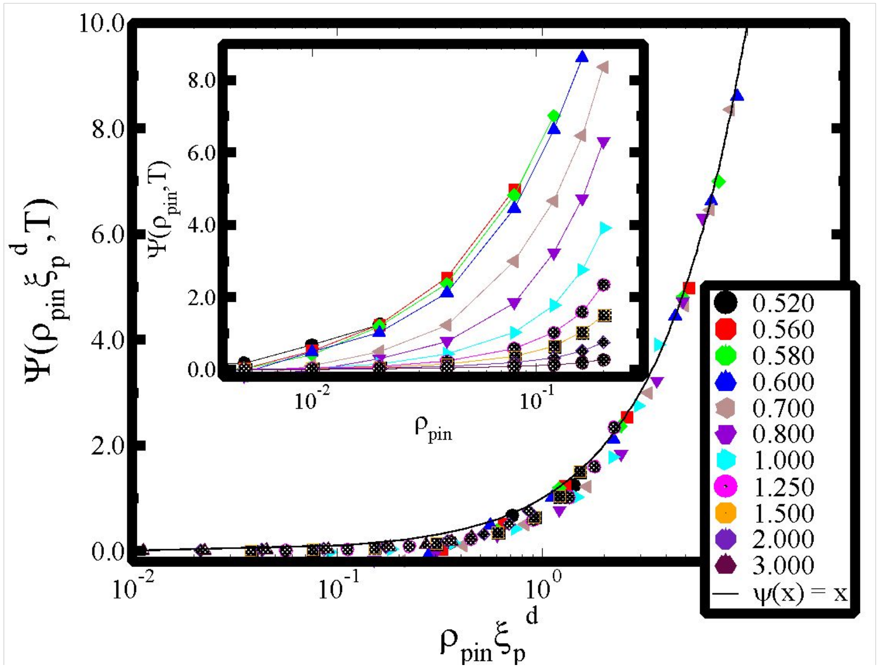
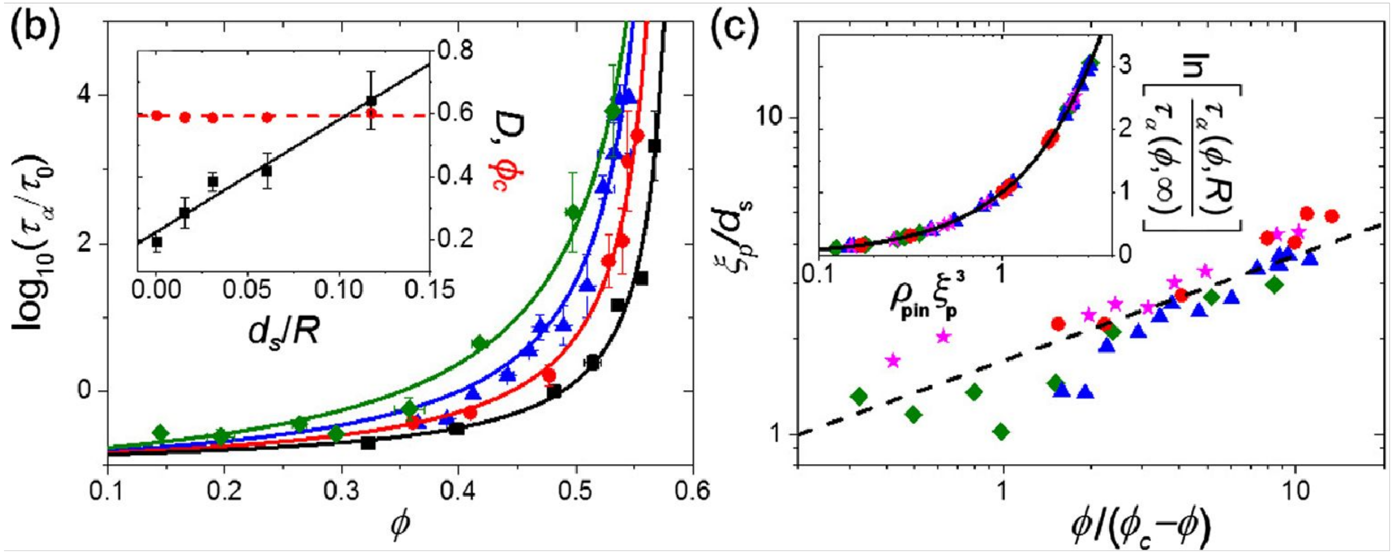


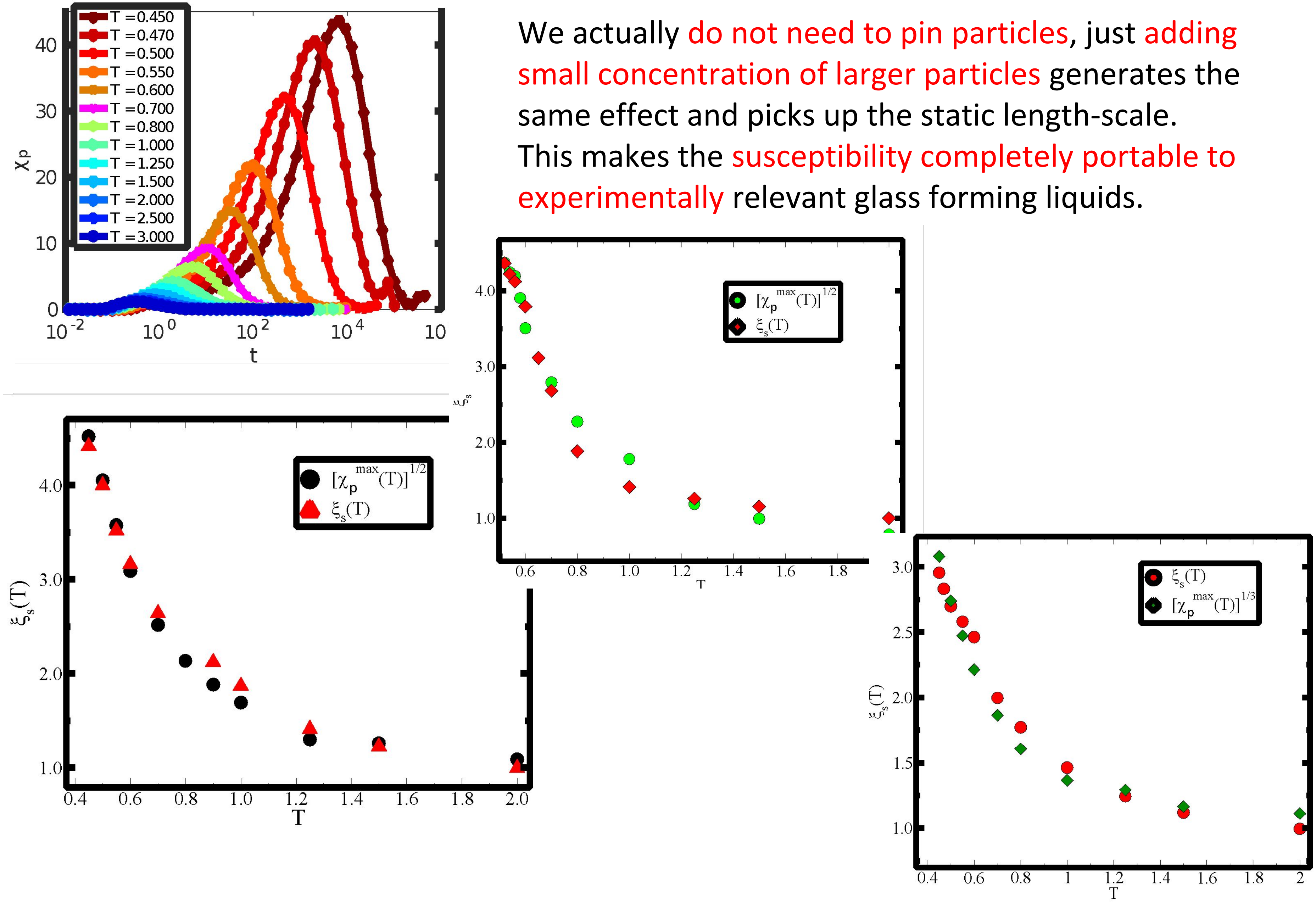




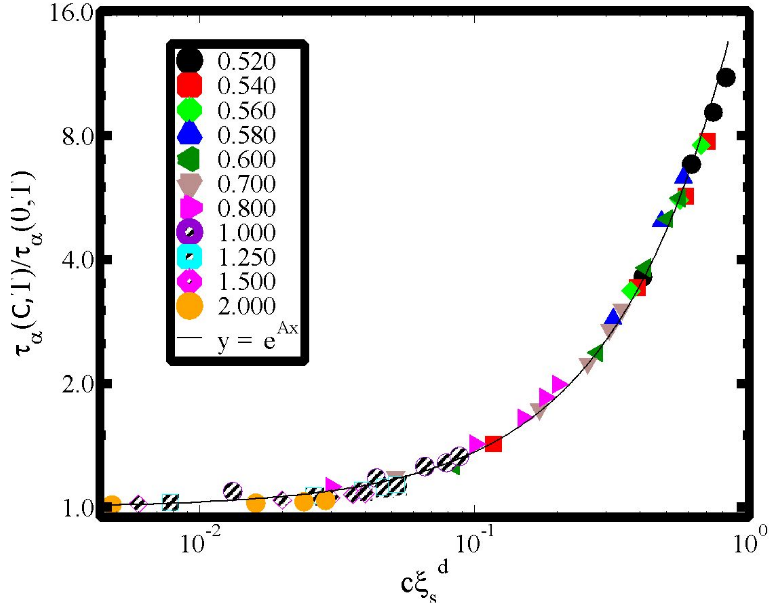
Colloidal Experiments, PRL 116, 098302 (2016)

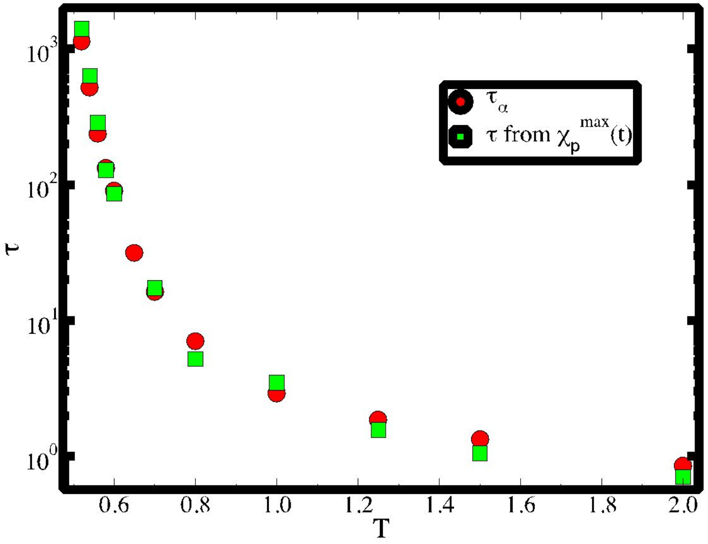
Pinning Susceptibility without pinning

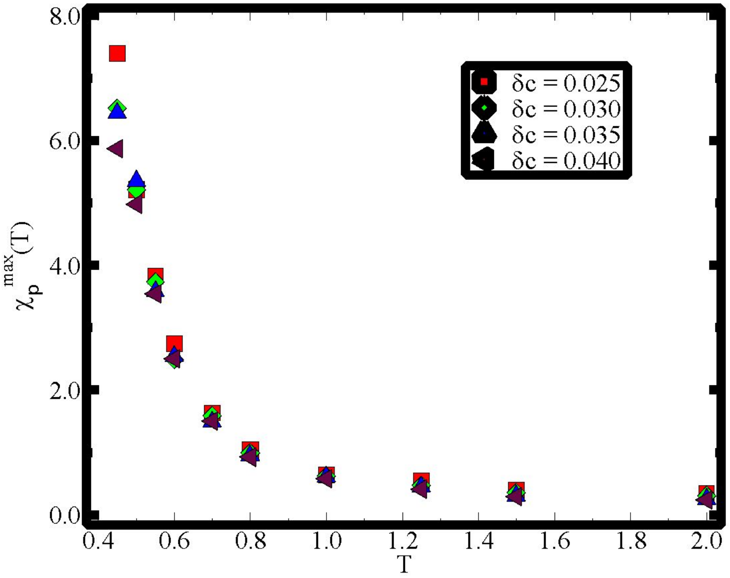
We actually do not need to pin particles, just adding small concentration of larger particles generates the same effect and picks up the static length-scale. This makes the susceptibility completely portable to experimentally relevant glass forming liquids.

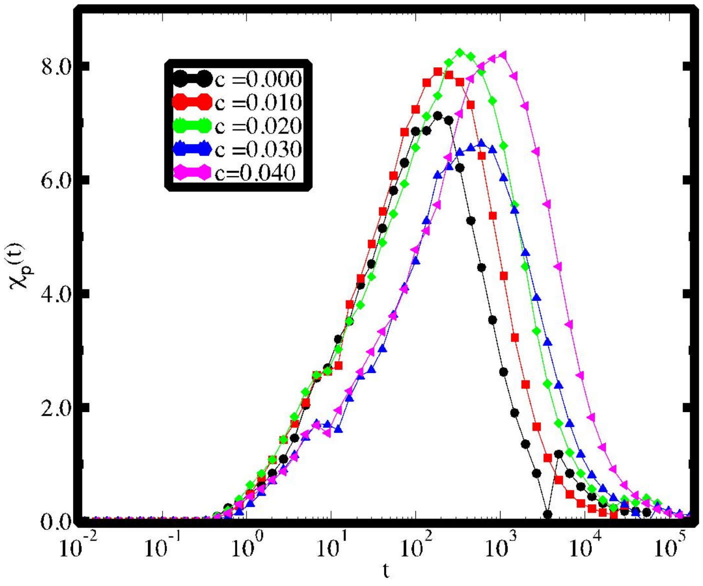


Similar consistency checks

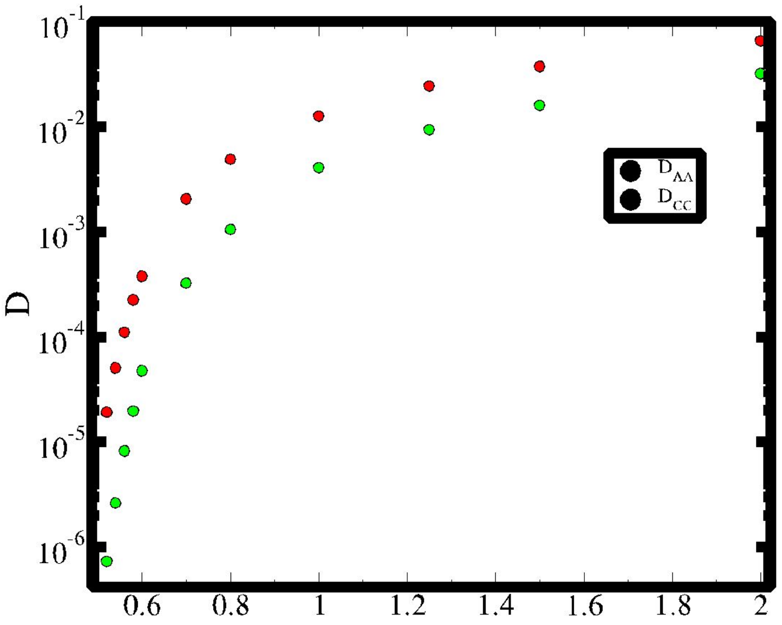


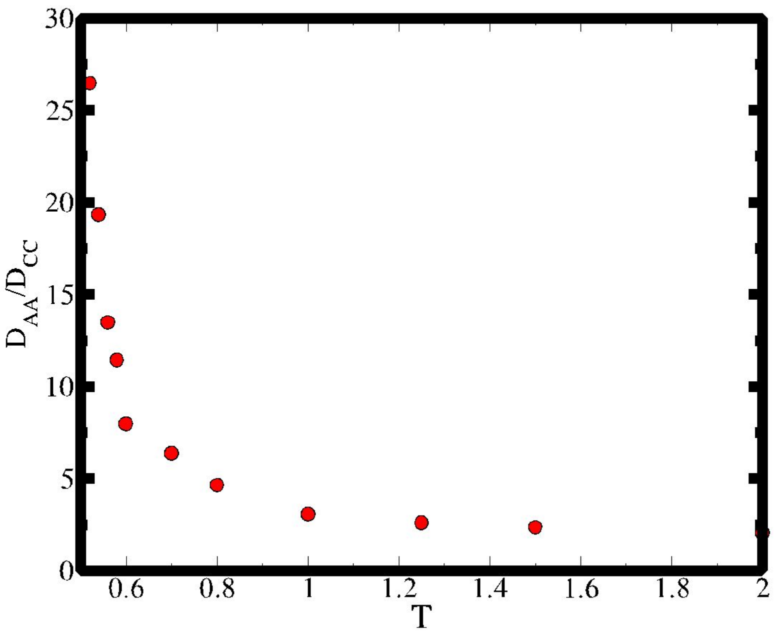




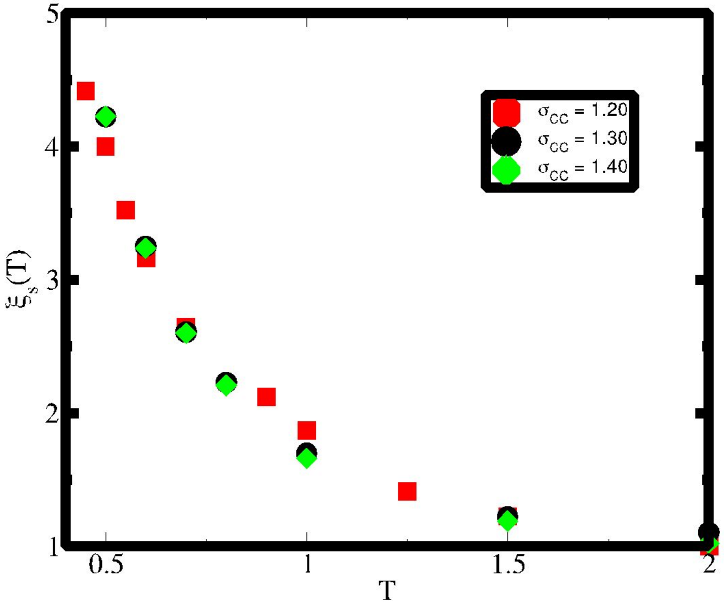


Consistency Checks

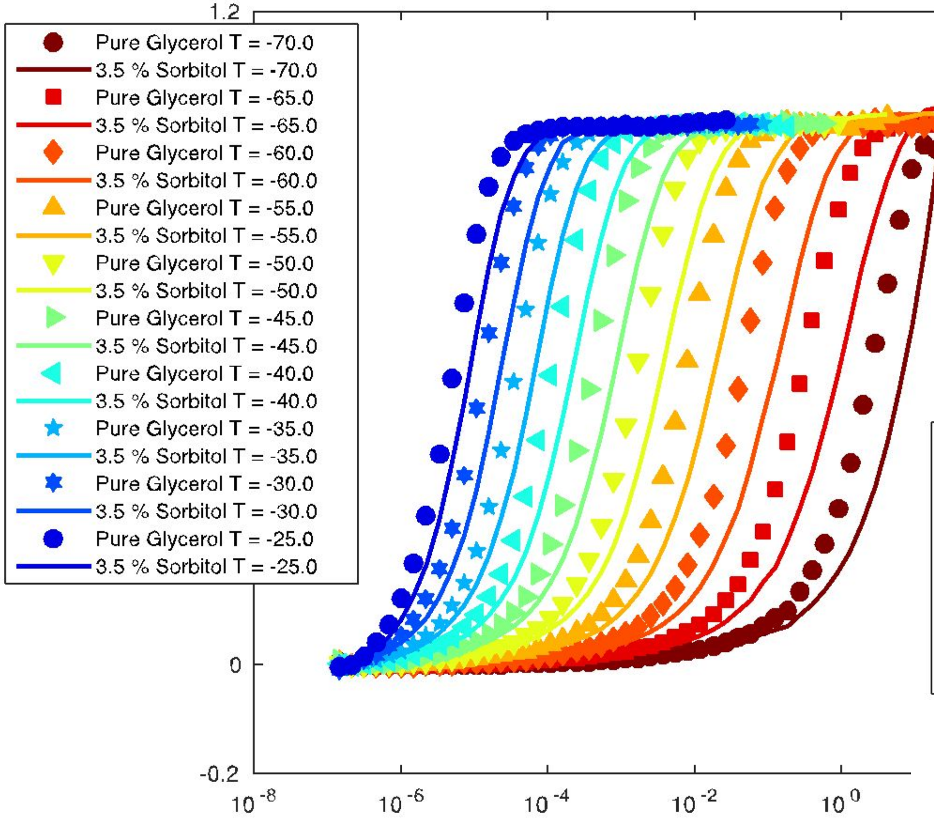


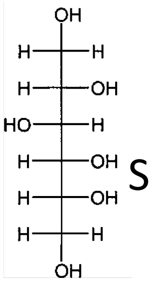


- Diffusion constant of C particle is around an order of magnitude smaller than the solvent particles.
- Pinning Susceptibility does not depend on the size of the C particles within the studied size range.



Initial data with Glycerol + Sorbitol Mixture

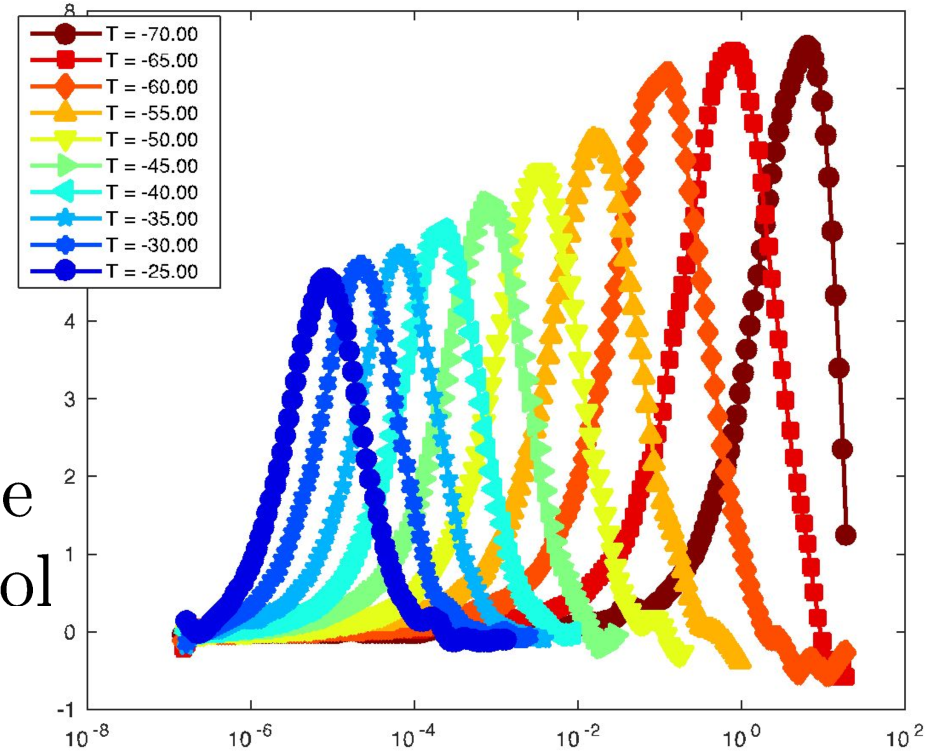




Sorbitol

Glycerol

Dielectric storage modulus, ϵ'



$\chi_p \equiv \partial\epsilon'/\partial c$, where c is the molar concentration of Sorbitol

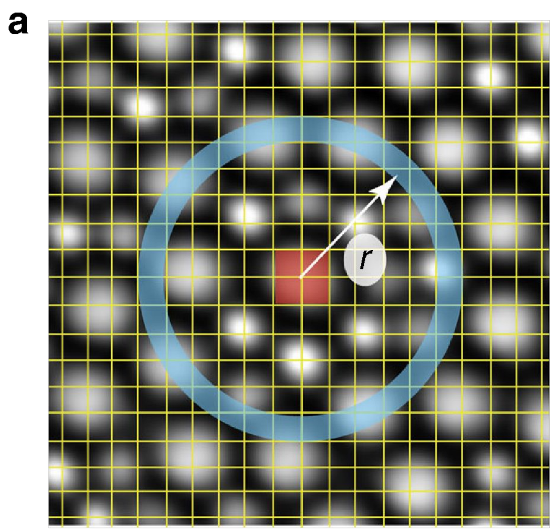
nature COMMUNICATIONS

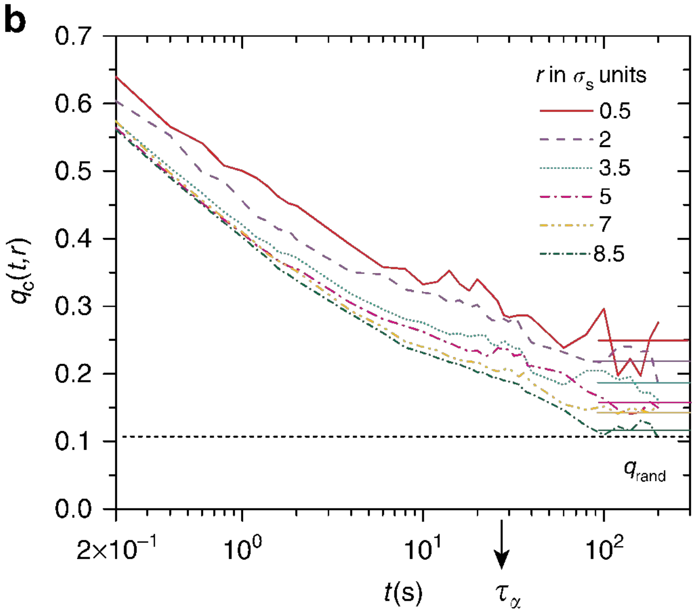
ARTICLE

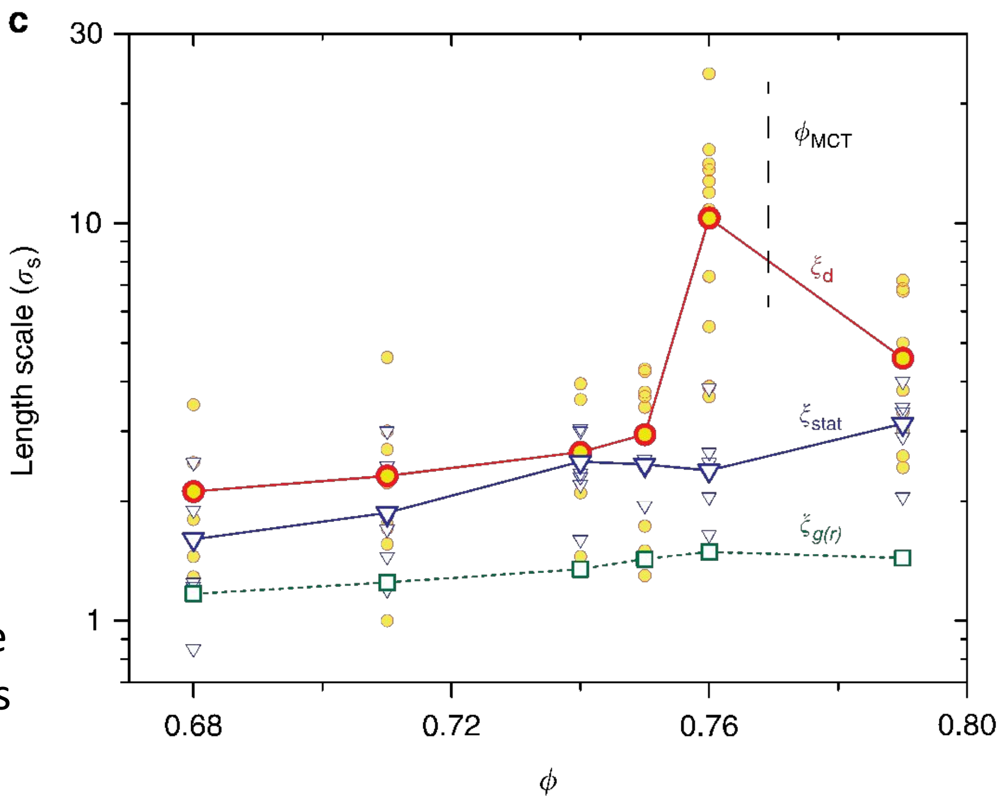
DOI: 10.1038/s41467-018-02836-6 OPEN

Measurements of growing surface tension of amorphous–amorphous interfaces on approaching the colloidal glass transition

Divya Ganapathi[1], K. Hima Nagamanasa[2,5], A.K. Sood[1,3] & Rajesh Ganapathy[3,4]





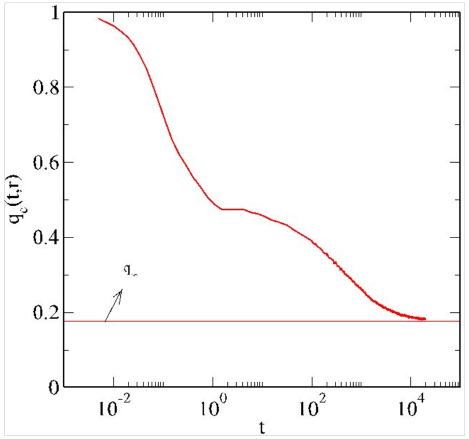


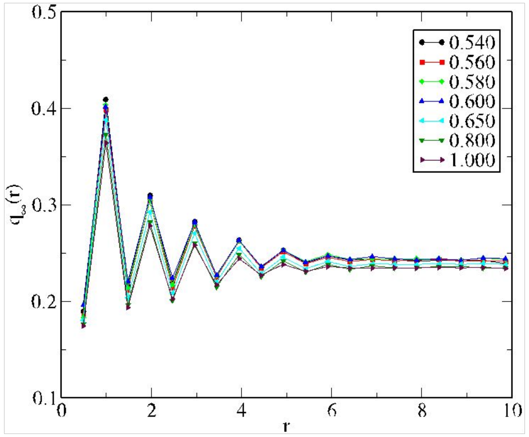
Some particles are **softly pinned** over the measurement time window and the correlation around that particle extends over static length scale.

Random Pinning Case:

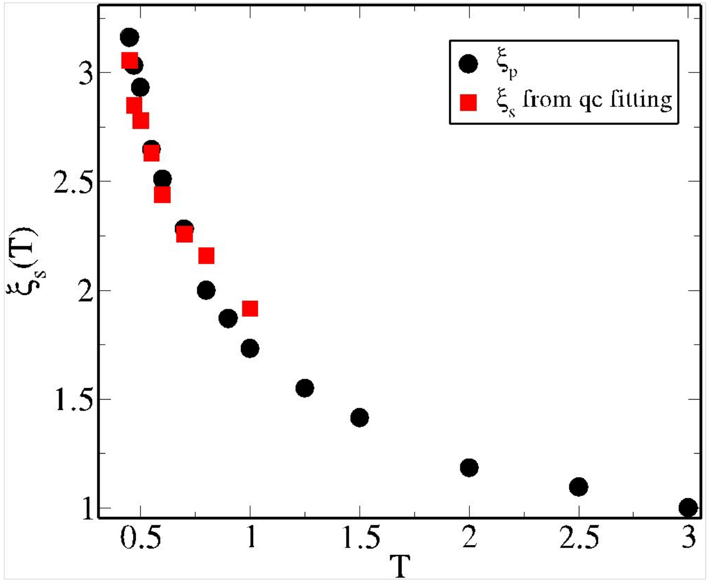
$$q_c(t) = \frac{< n_i(t) n_i(0) >}{< n_i(0) >}.$$

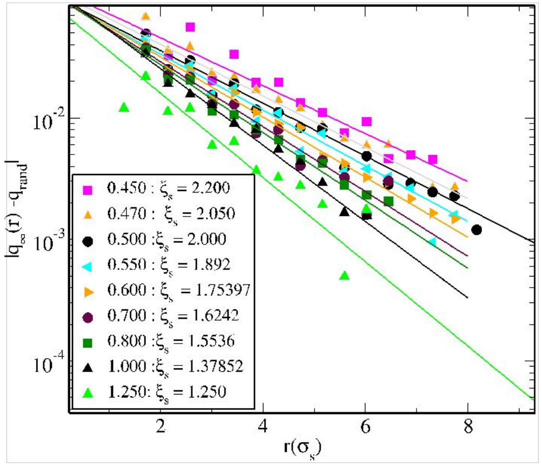
If a box is occupied by a particle then $n_i(t) = 1$ else $n_i(t) = 0$.

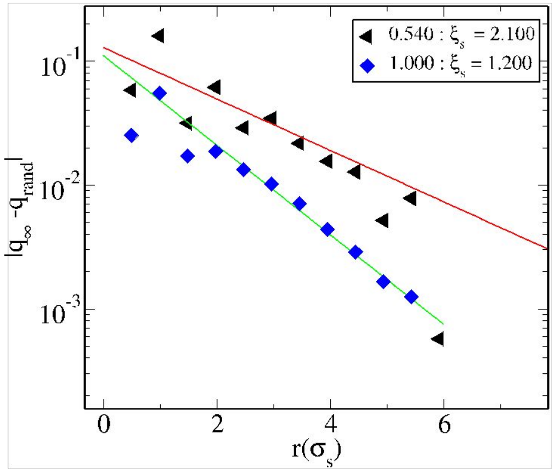




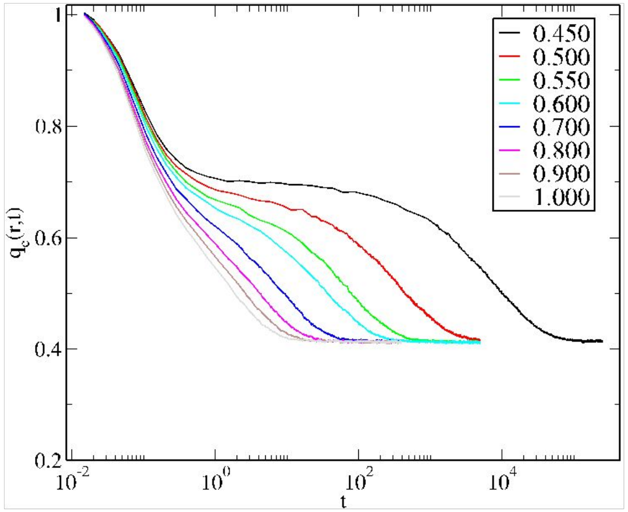
$$|q_\infty(r) - q_{rand}| = B \exp(-r/\xi_{stat})$$

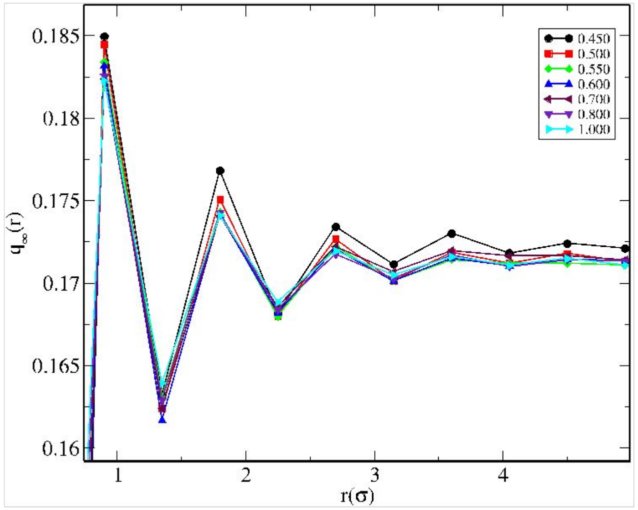


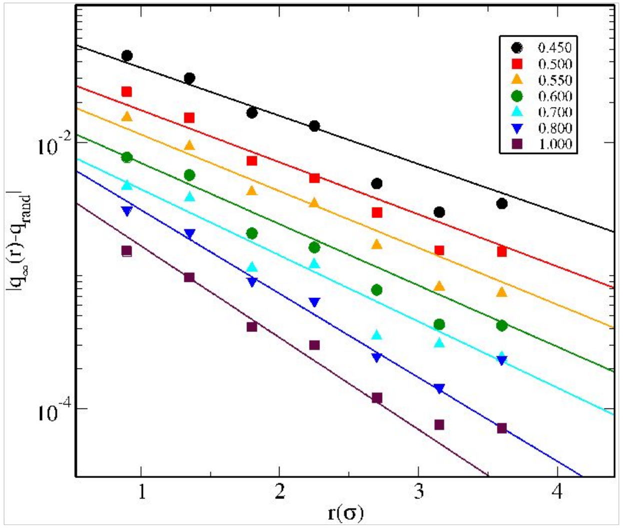


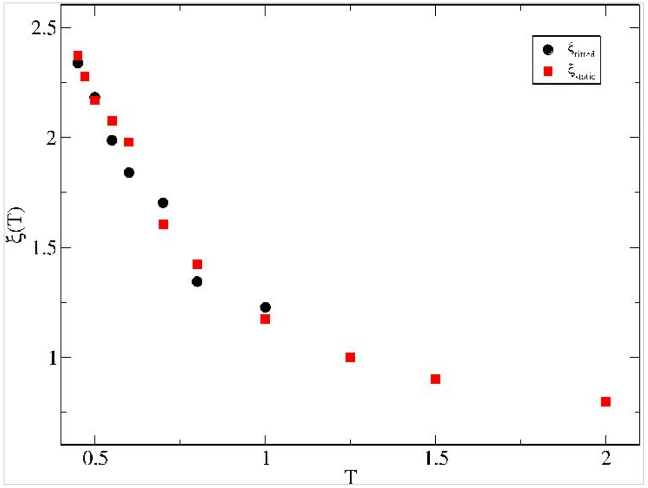


Soft Pinning Case:







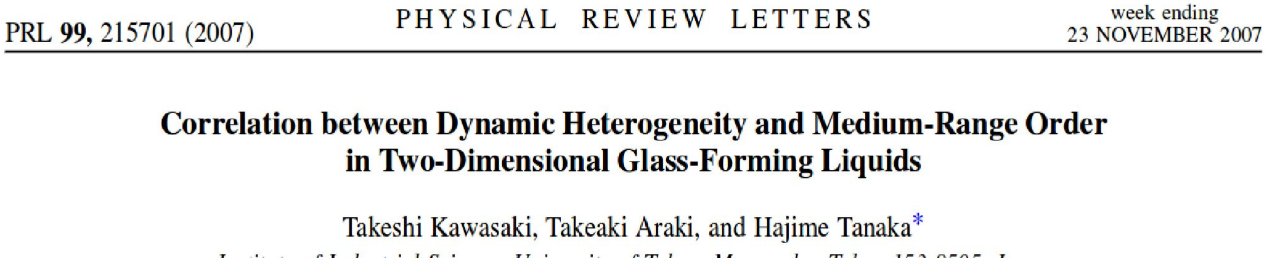


Conclusion : Part 1

- Proposed a new susceptibility which is easy to calculate in experimentally relevant glass forming liquids.
- The peak height of this susceptibility is directly proportional to the static correlation volume without any unknown scaling exponents.
- Initial experimental results are encouraging and hope that we will have some idea about the growth of amorphous order in real glass forming liquids in near future close to Tg.

Systems with Medium Range Crystalline Order

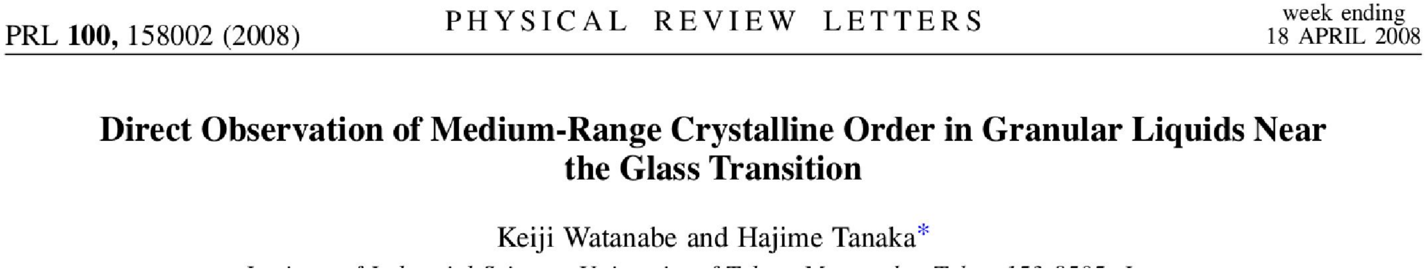
- Are glass formers with medium range crystalline order generically same as other glass formers?
- How different length-scales are connected to slowing down in supercooled liquid for glasses with and without medium range crystalline order?



PRL **99,** 215701 (2007) PHYSICAL REVIEW LETTERS week ending 23 NOVEMBER 2007

Correlation between Dynamic Heterogeneity and Medium-Range Order in Two-Dimensional Glass-Forming Liquids

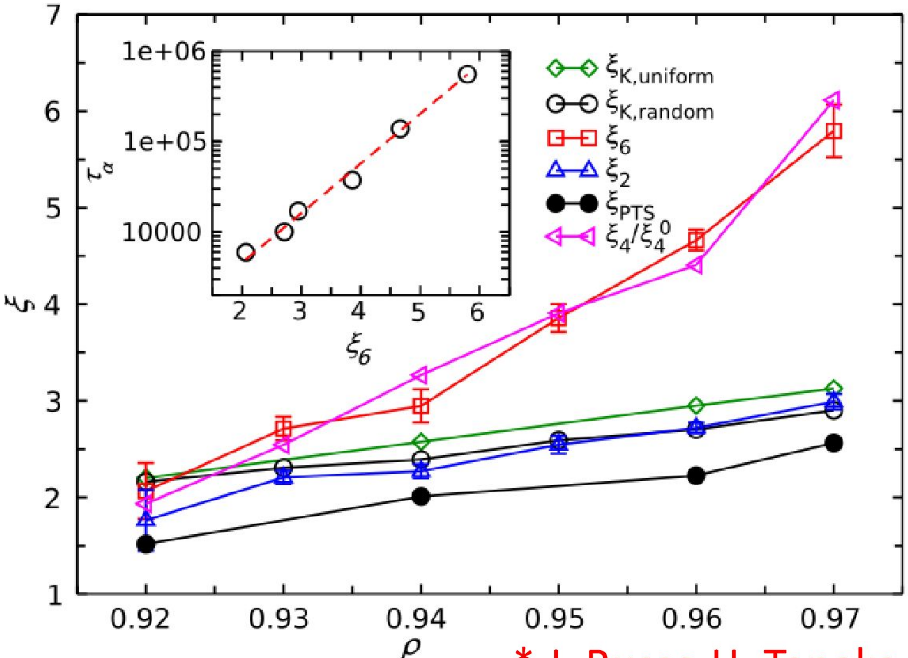
Takeshi Kawasaki, Takeaki Araki, and Hajime Tanaka*

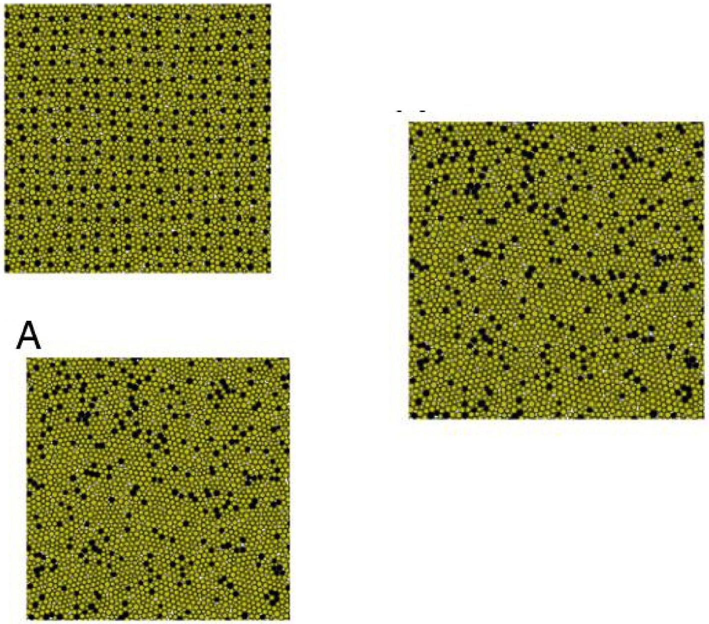


PRL **100,** 158002 (2008) PHYSICAL REVIEW LETTERS week ending 18 APRIL 2008

Direct Observation of Medium-Range Crystalline Order in Granular Liquids Near the Glass Transition

Keiji Watanabe and Hajime Tanaka*





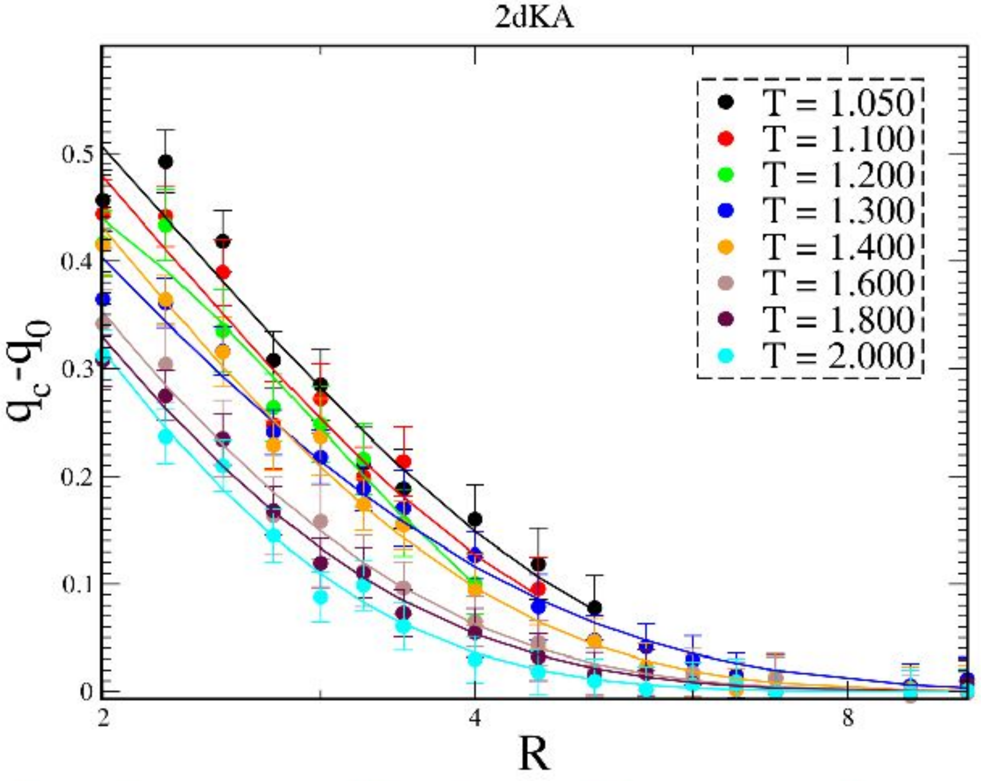
* J. Russo H. Tanaka, Proc. Nat. Acad. Sci. (USA) 112 (2015) 6920-6924

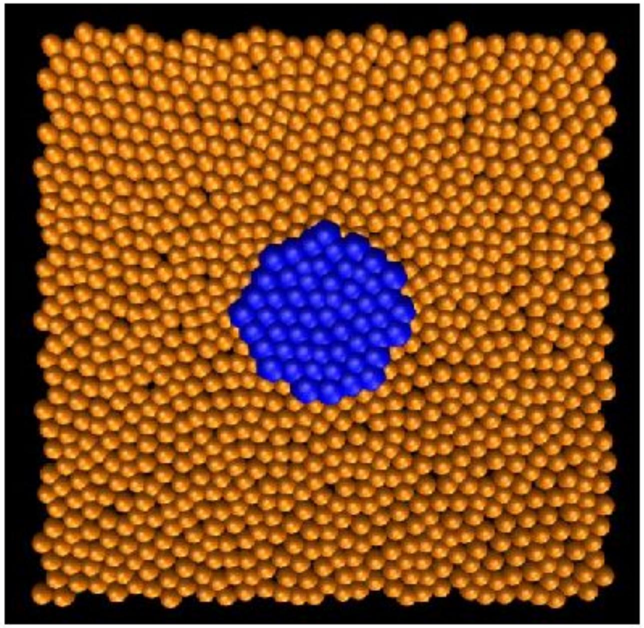
Point to set Length Scale

Point to set length scale in cavity geometry Ref. [*].

The overlap function is defined as

$$q_c(R) = \frac{1}{l^2 N_\nu} \sum_{i \in \nu} < n_i(t_0) n_i(t_0 + \infty) >$$





$$q_c(R) - q_0 = Aexp(-\left(\frac{R-1}{\xi_{pts}}\right)^{\eta}$$ fits all the data at all temperature.

$$q_0 = \rho l^2$$

This Method is order agnostic

* Hocky GM, Markland TE, Reichman DR Phys. Rev Lett. 108(22):225506

* Birilo G, Bouchad J-P, Cavagna A, Grigera T S and Verrocchio P 2008 Nat Phys. 4 771

Dynamic Length-Scale

Four point Dynamics Susceptibility $\chi_4(t)$

$$\chi_4 = \frac{1}{N}[< Q_p^2(t) > - < Q_p(t) >^2]$$

$$Q_p(t) = \sum_{i,j=1}^{N} \delta(r_i(0) - r_j(t))$$

$$S_4(q,t) = \frac{1}{N}(< Q(q,t)Q(-q,t) > \quad - Q(q,t) >^2)$$

$$Q(q,t) = \sum_{i=1}^{N} \exp[iq.r_i(o)w(|r_i(0) - r_i(t)|)]$$

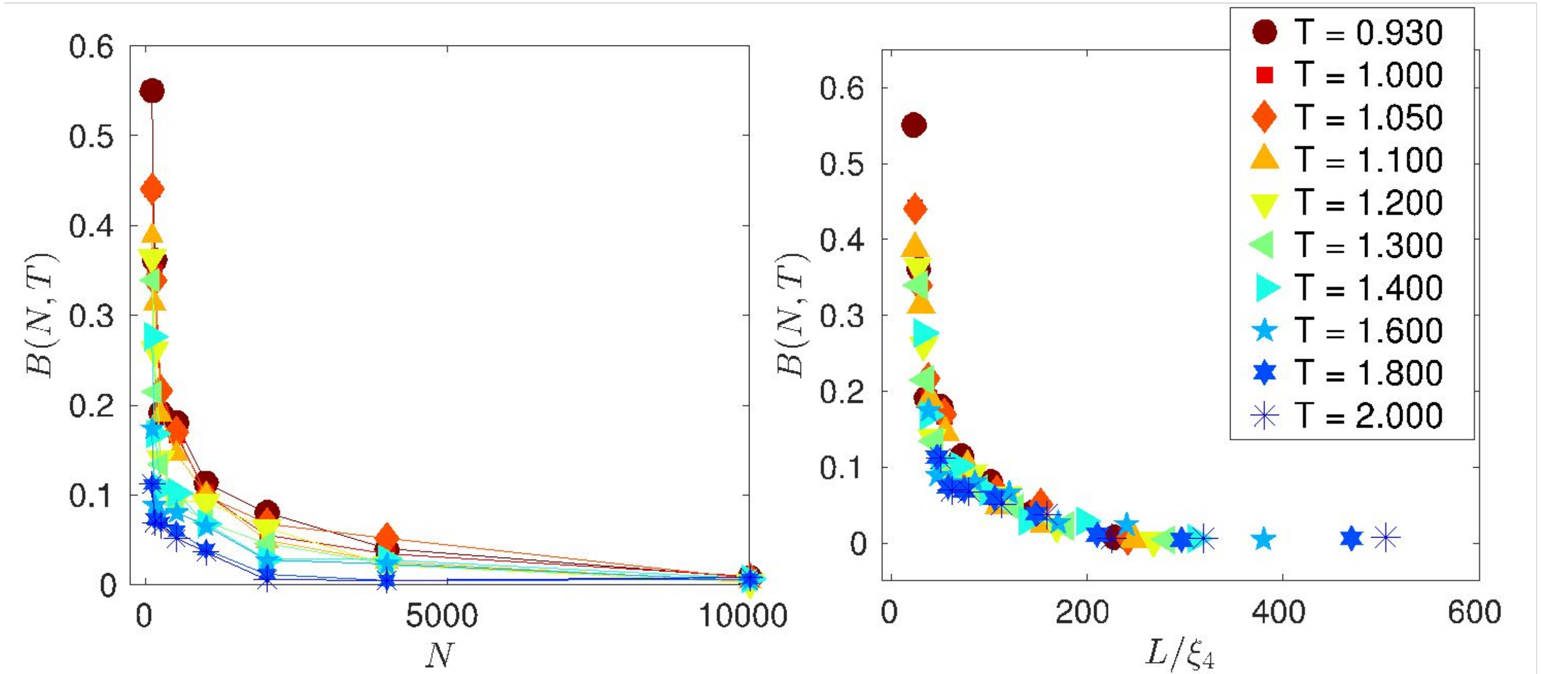
we assume the functional form of $S_4(q,t)$ at t =τ in $q \rightarrow 0$

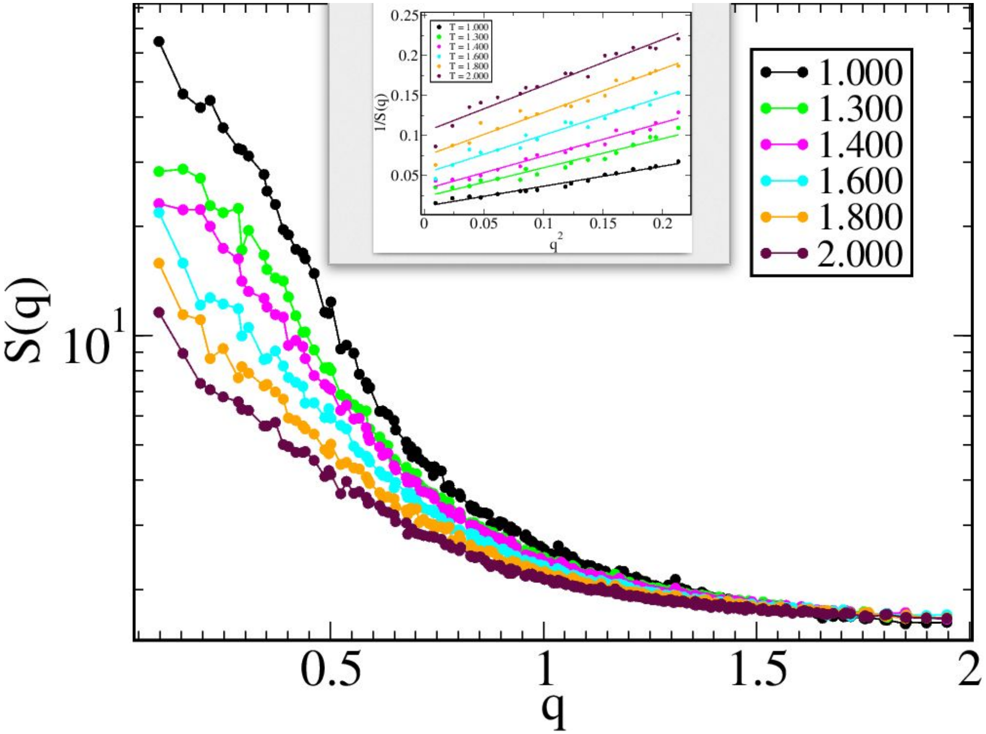
$$S_4(q,\tau,T) = \frac{S_4(0,\tau,T)}{1 + [q\xi(T)]^{\alpha}}$$

B(N,T) is the ratio of fourth and second moments of Q(τ_4) .

$$B(N,T) = 1 - \frac{< [Q(\tau_4) - < Q(\tau_4) >]^4 >}{3 < [Q(\tau_4) - < Q(\tau_4) >]^2 >^2}$$

It is a scaling function of N/ξ_{dyn}^d without any pre-factor. B(L,T) = $g(\frac{L}{\xi_{dyn}^d})$





Dynamic length-scale is obtained from the finite size scaling of Binder Cummulant and also from four point structure factor of bond breakage correlation function.

Hayato Shiba, Yasunori Yamada, Takeshi Kawasaki, and Kang Kim, PRL 117, 245701 (2016)

Hexatic Order

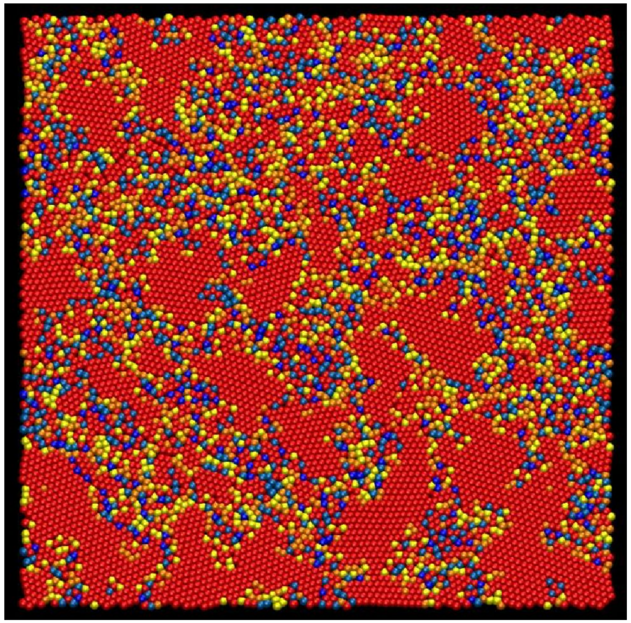
Calculation of hexatic order parameter:

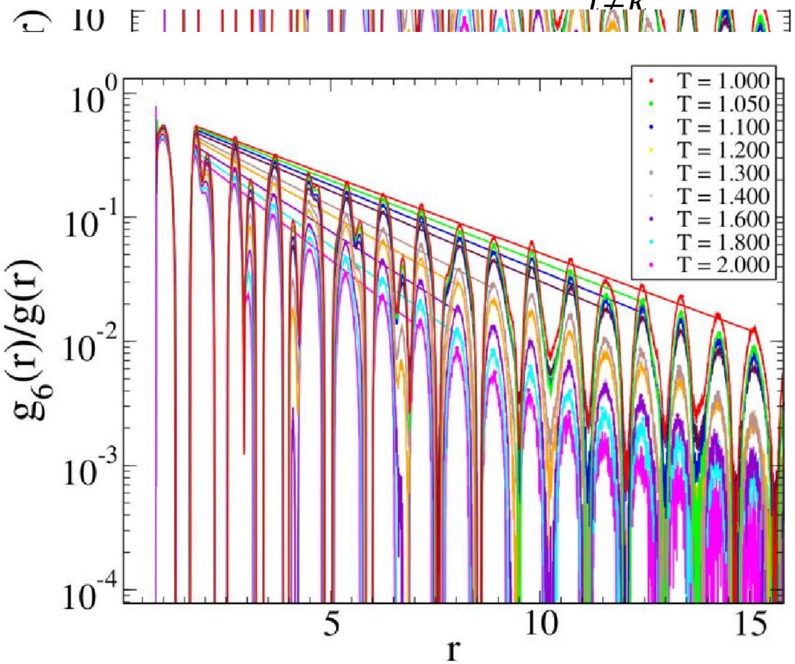
$$\psi_6^i = \frac{1}{n_i}\sum_{m=1}^{n_i} e^{j6\theta_{im}}$$

The spatial correlation of ψ_6^i is calculated as

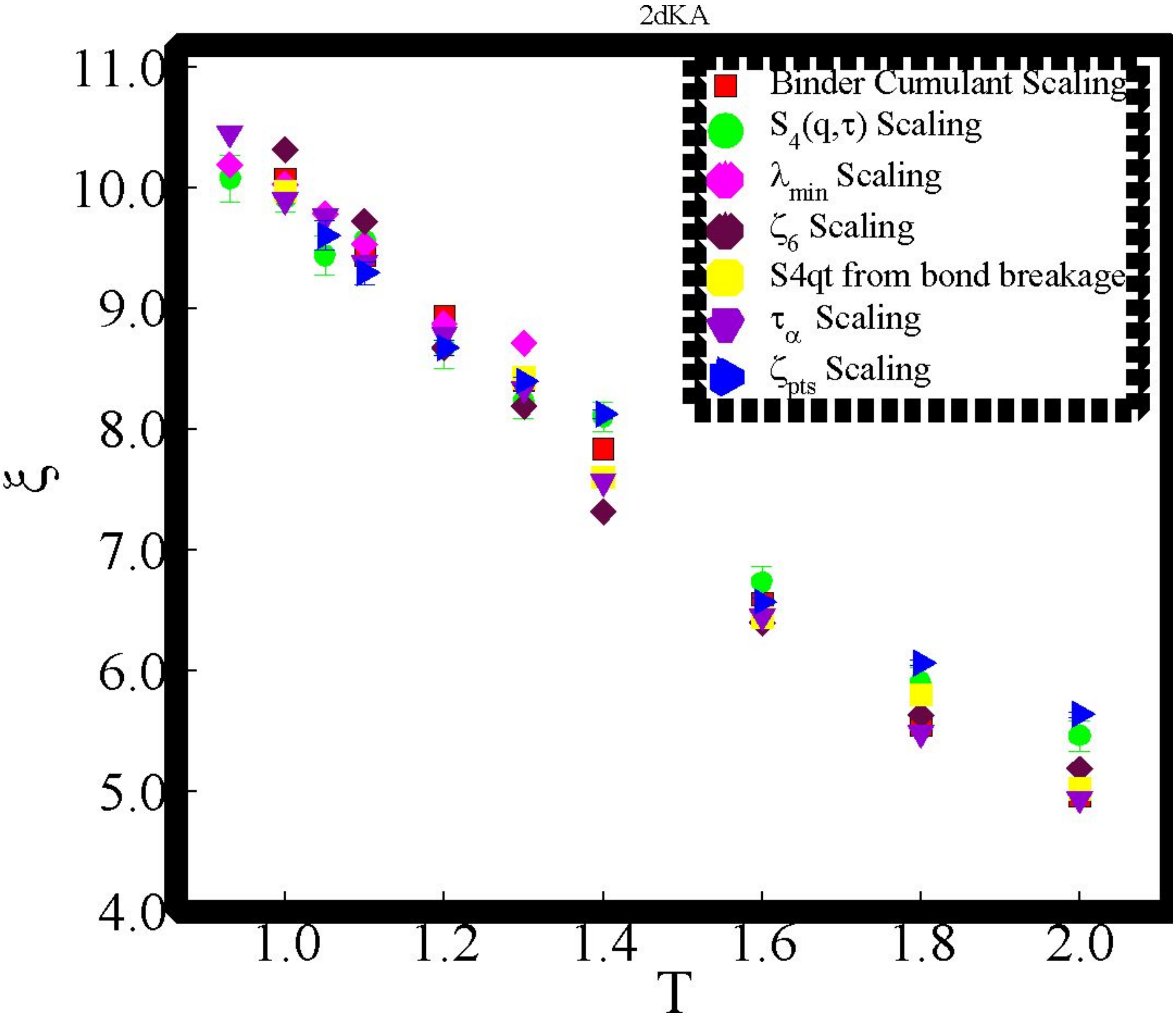
$$g_6(r) = \left(\frac{L^2}{2\pi r \Delta r N(N-1)}\right)\sum_{i\neq k}\delta(r-|r_{ik}|)\,\psi_6^i\psi_6^{k*}$$

- 🟥 0.80 <= hop < 1.00
- 🟧 0.60 <= hop < 0.80
- 🟨 0.40 <= hop < 0.60
- 🟦 0.20 <= hop < 0.40
- 🟦 0.00 <= hop < 0.20





The correlation length of the hexatic order, ξ_6 ,obtain by fitting the exponential decay of the peaks of the correlation function.



Static and Dynamic Length-scales are same at all temperatures

System without MRCO : 2dR10

Simulation Details:

B. 2d R10 model is a 50:50 binary mixture of particles interacting via purely repulsive soft sphere potential.

$$V_{\alpha\beta}\left(\frac{r_{\alpha\beta}}{\sigma_{\alpha\beta}}\right) = \epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{10} + \sum_{l=0}^{2} C_{2l}\left(\frac{r_{\alpha\beta}}{\sigma_{\alpha\beta}}\right)^{2l}\right], r_{\alpha\beta<cutoff}$$

$$= 0, r_{\alpha\beta} > cutoff$$

Parameter of the system:

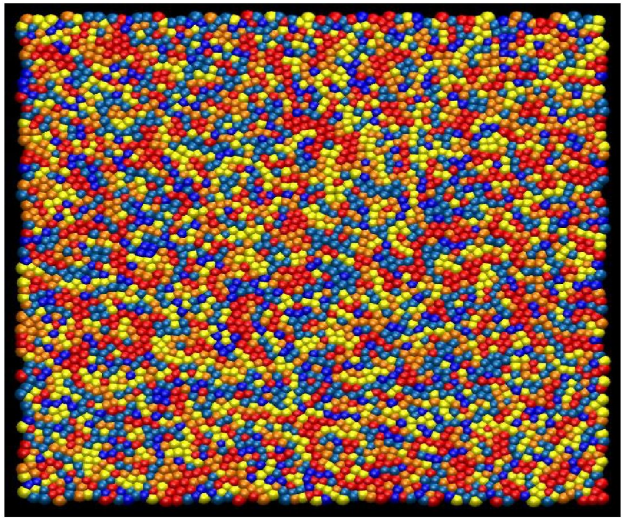
$\epsilon_{AA} = 1.0, \epsilon_{AB} = 1.0, \epsilon_{BB} = 1.0, \sigma_{AA} = 1.0, \sigma_{AB} = 1.18, \sigma_{BB} = 1.40.$

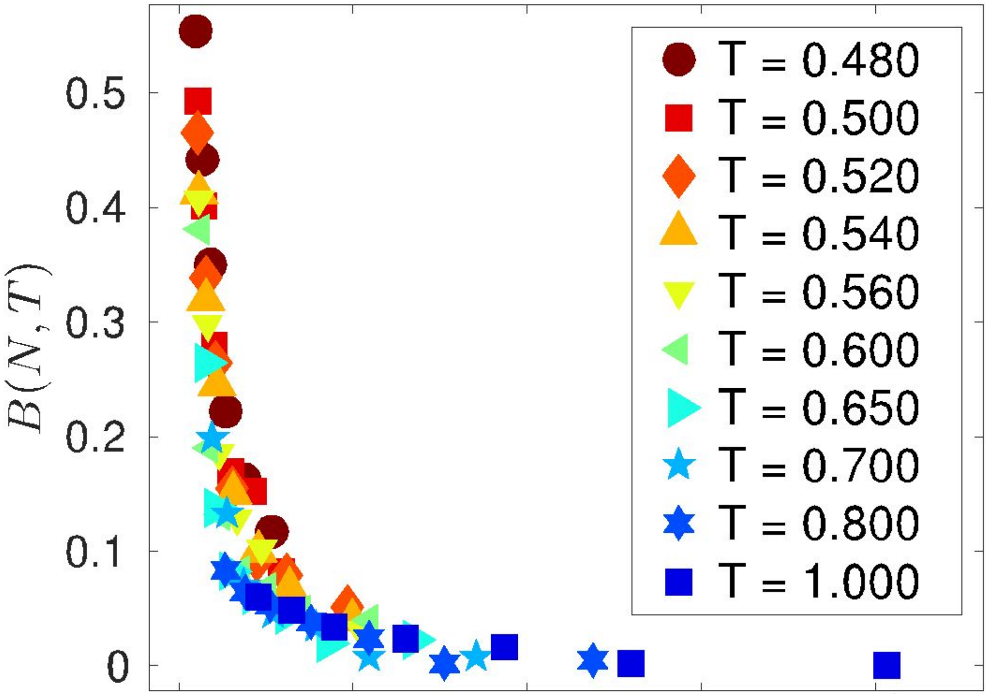
The interaction potential cut-off $1.3854\sigma_{\alpha\beta}$.

$\rho = 0.85.$

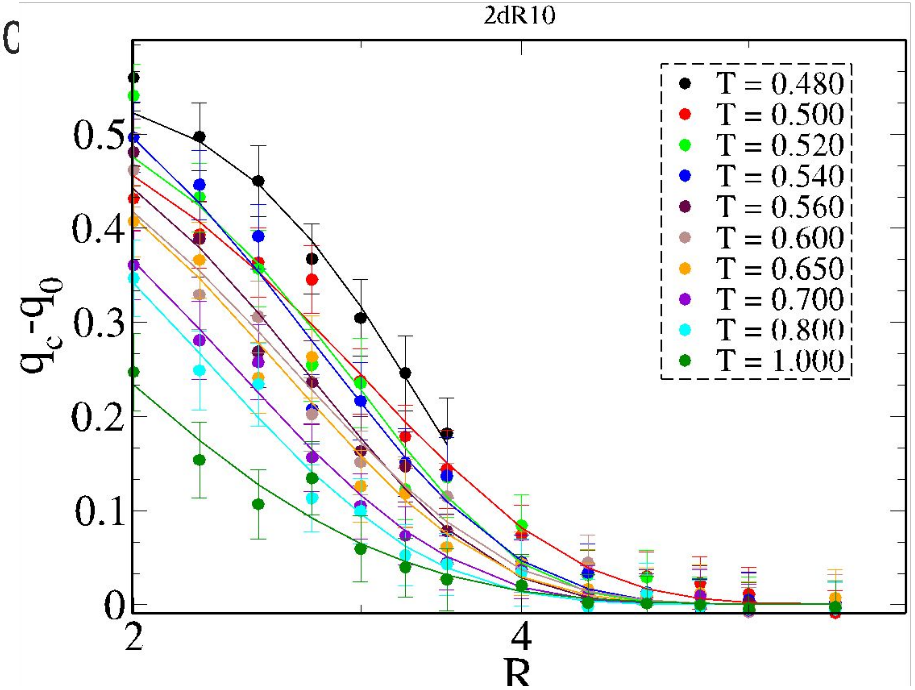
No prominent hexatic order is observed at the lowest temperature studied.

🔴 0.80 <= hop < 1.00
🟠 0.60 <= hop < 0.80
🟡 0.40 <= hop < 0.60
🔵 0.20 <= hop < 0.40
🔵 0.00 <= hop < 0.20



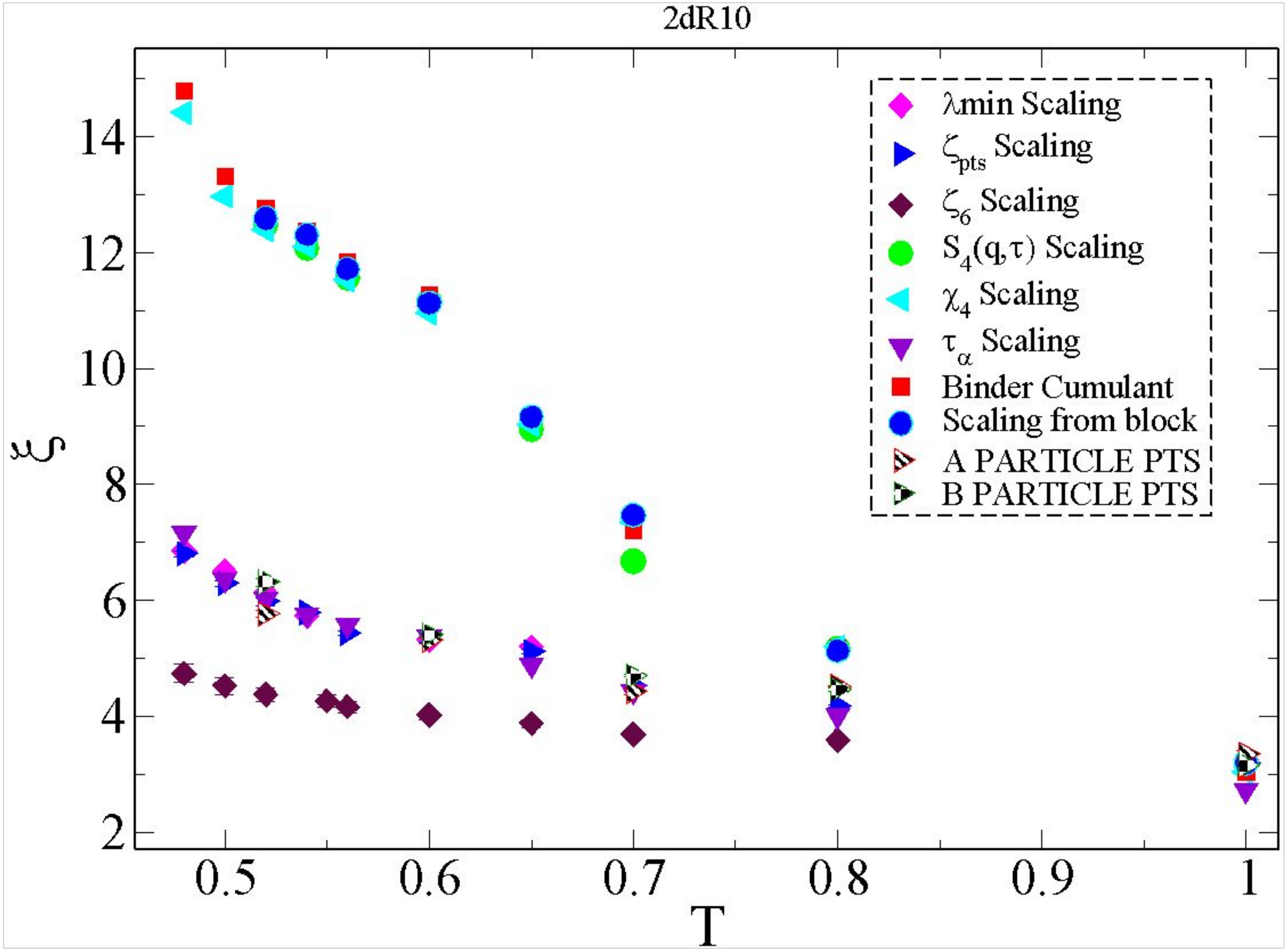


FSS of Binder Cummulant



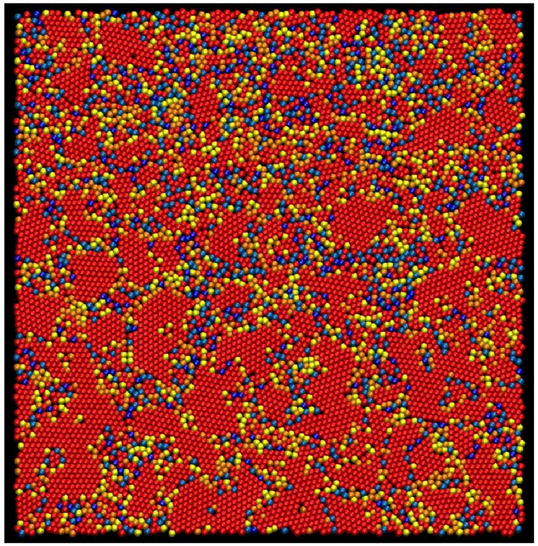
Point-to-set Length scale with cavity geometry

Comparison of different Length-scale

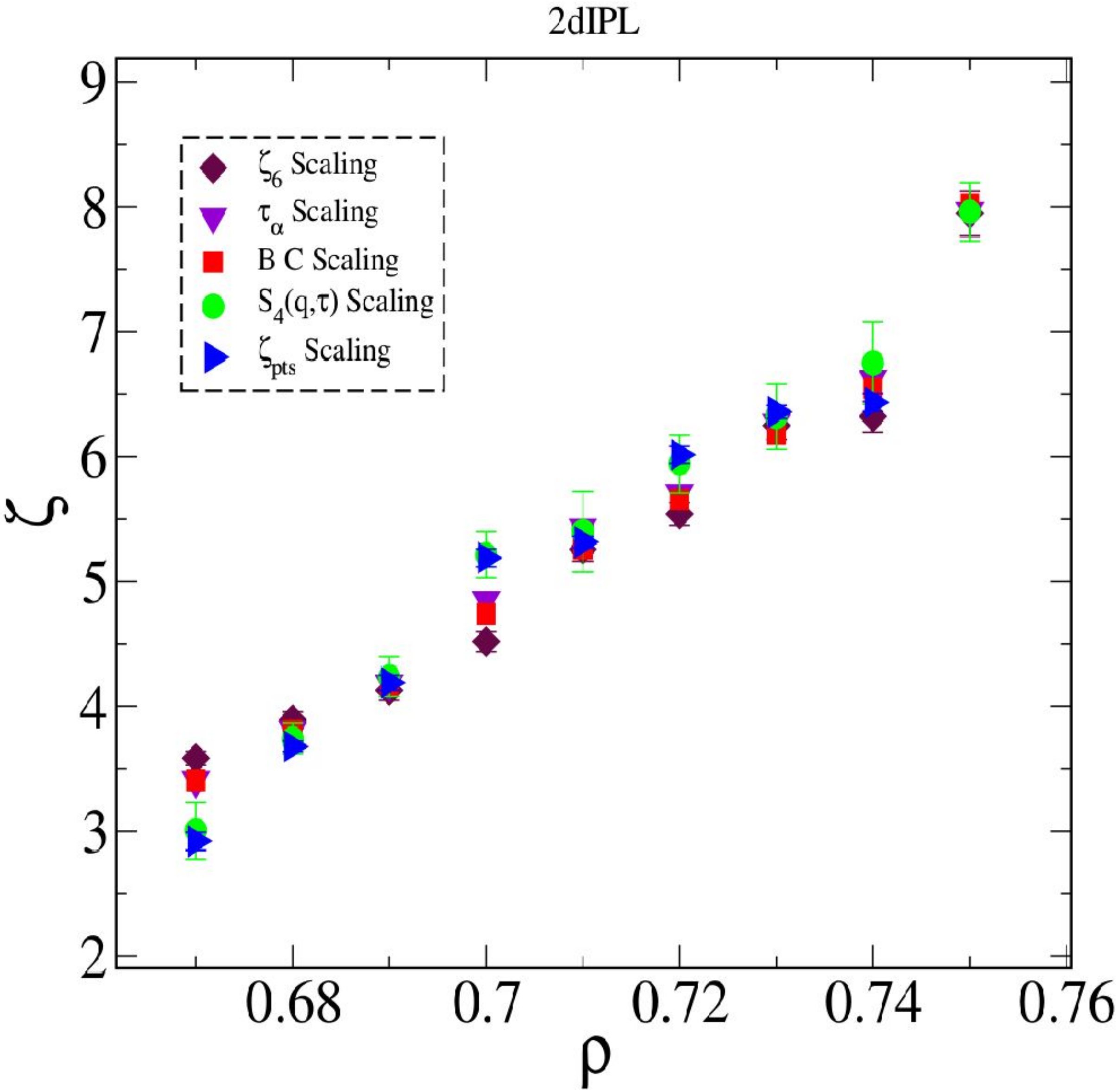


Static and Dynamic Length-scales decouple from each other.

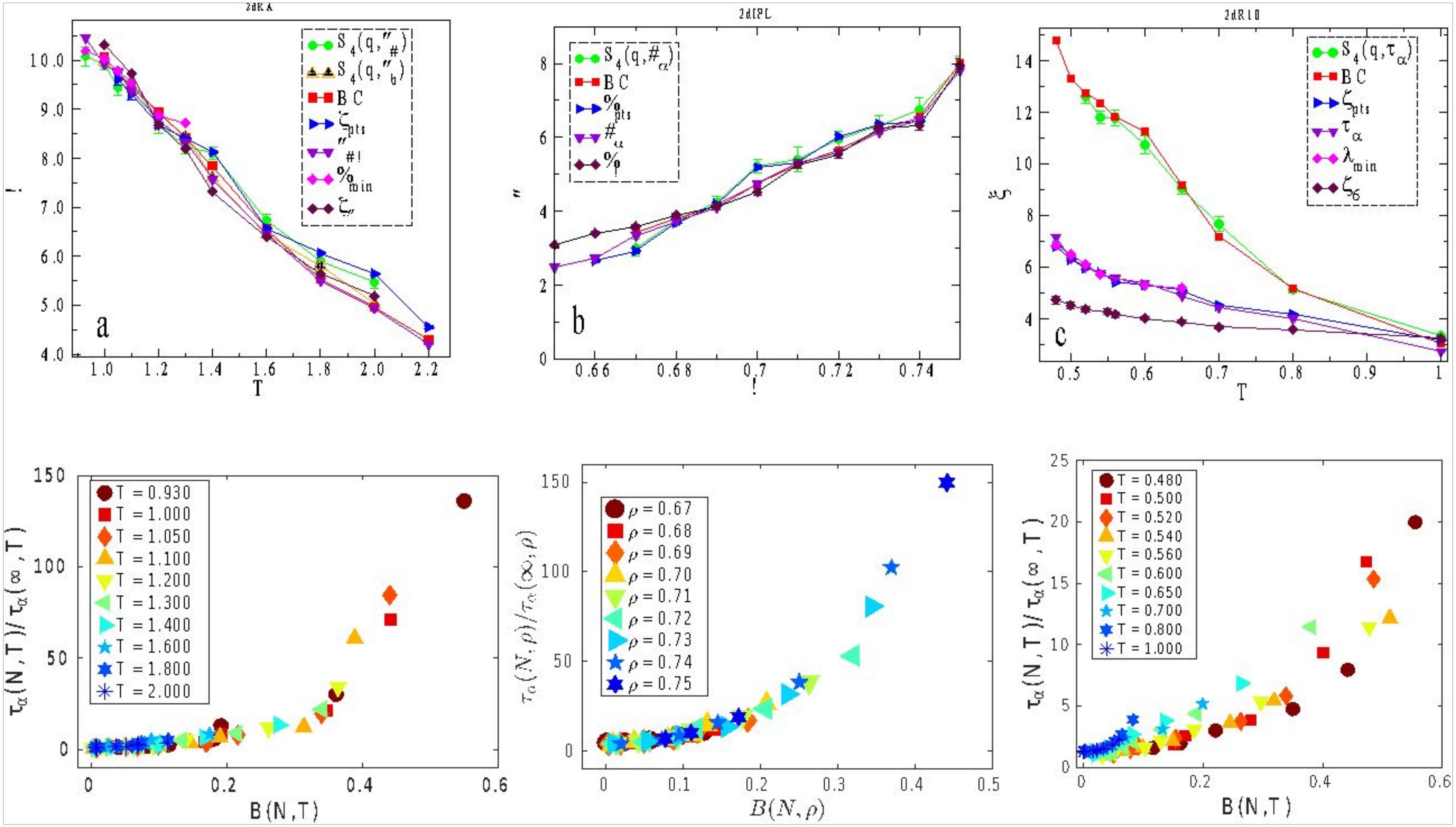
2dIPL model: Density as control parameter



● 0.80 <= hop < 1.00
● 0.60 <= hop < 0.80
● 0.40 <= hop < 0.60
● 0.20 <= hop < 0.40
● 0.00 <= hop < 0.20



MRCO vs non-MRCO glassy Liquids



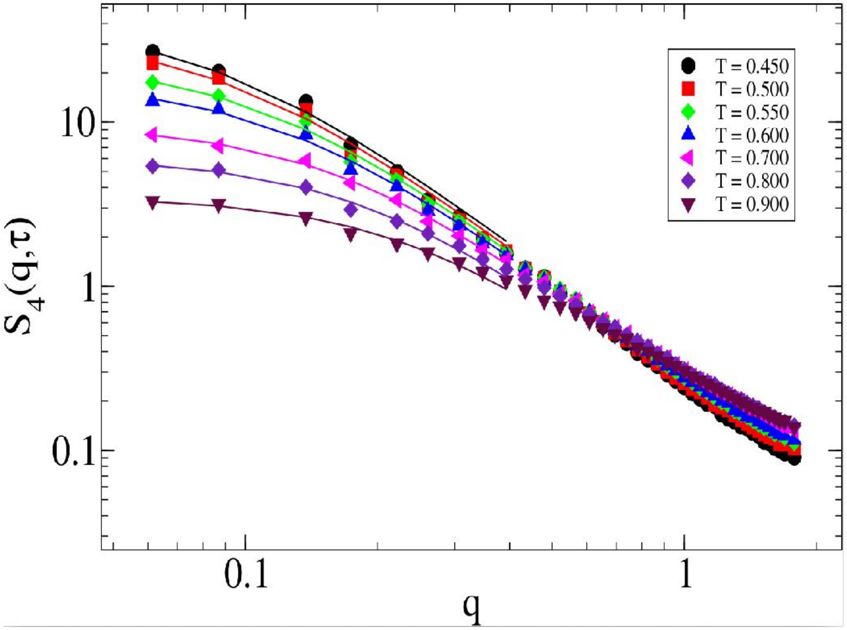
Polydisperse Model:

$$\text{Polydispersity } (\eta) = \frac{\sqrt{<\sigma^2> - <\sigma>^2}}{<\sigma>}$$

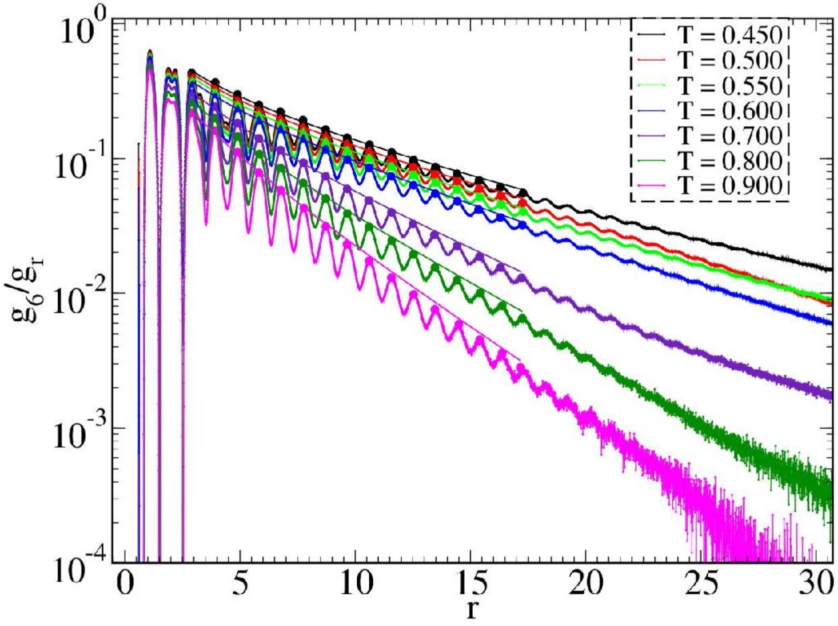
We choose $\eta = 11\%$

The particles interact with Weeks-Chandler-Anderson potential

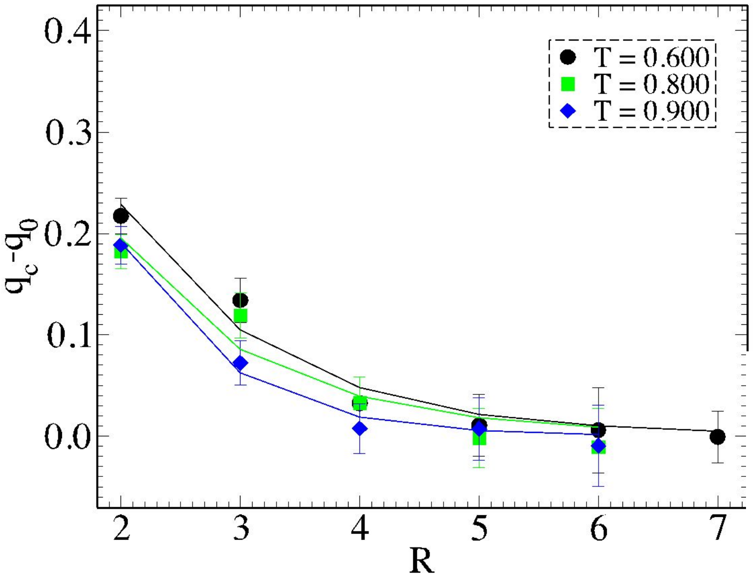
Dynamical length scale from $S_4(q,\tau)$ for Polydisperse system



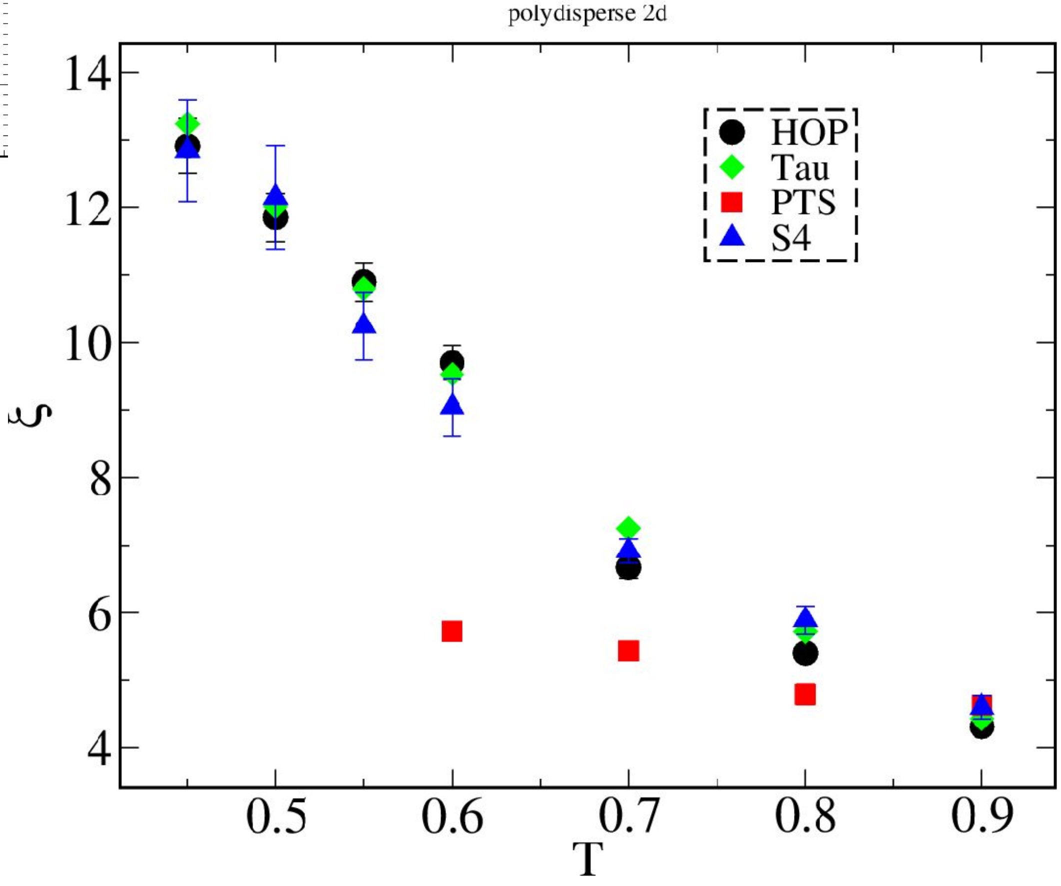
The spatial correlation of ψ_6^i for Polydisperse system:



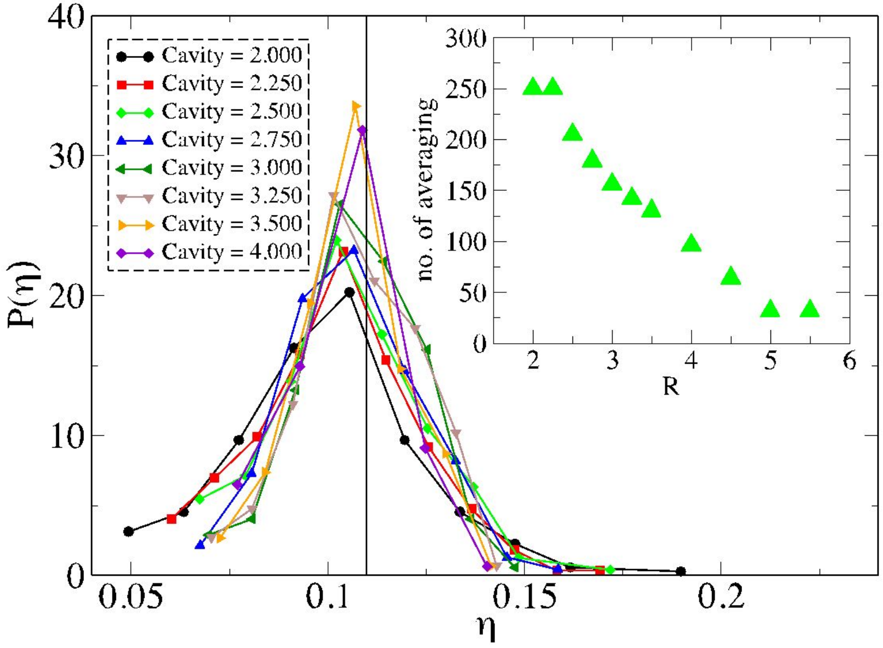
Point-to-Set Length-scale



PTS length-scale does not grow rapidly. Consistent with Russo & Tanaka, PNAS 2015 work.

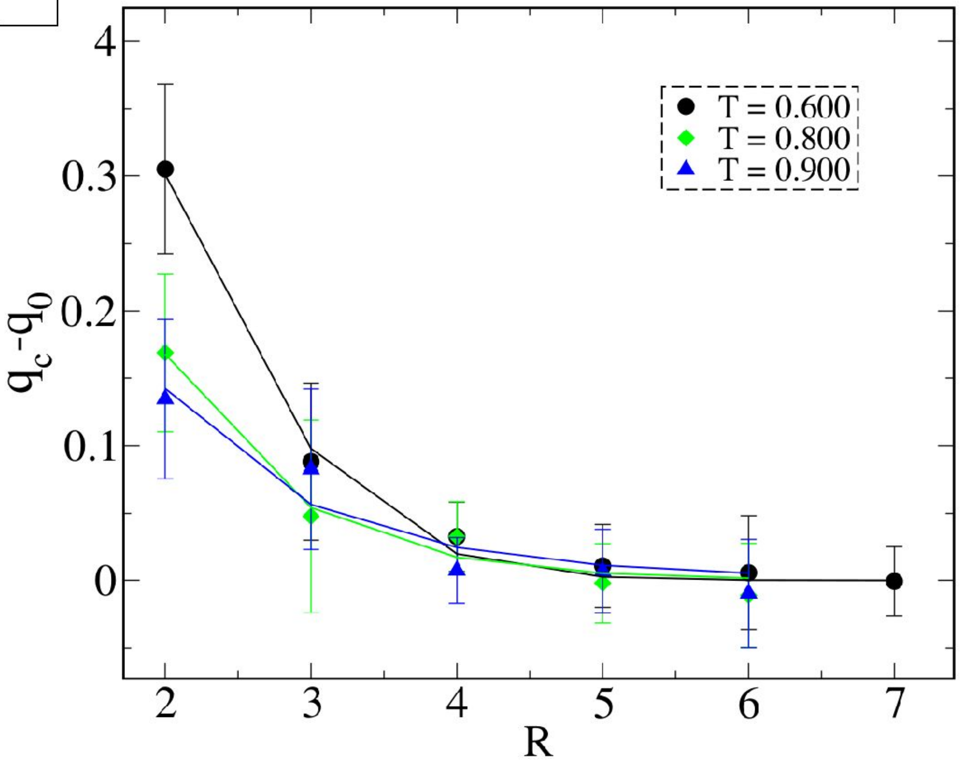


Probability distribution of Polydispersity (η).

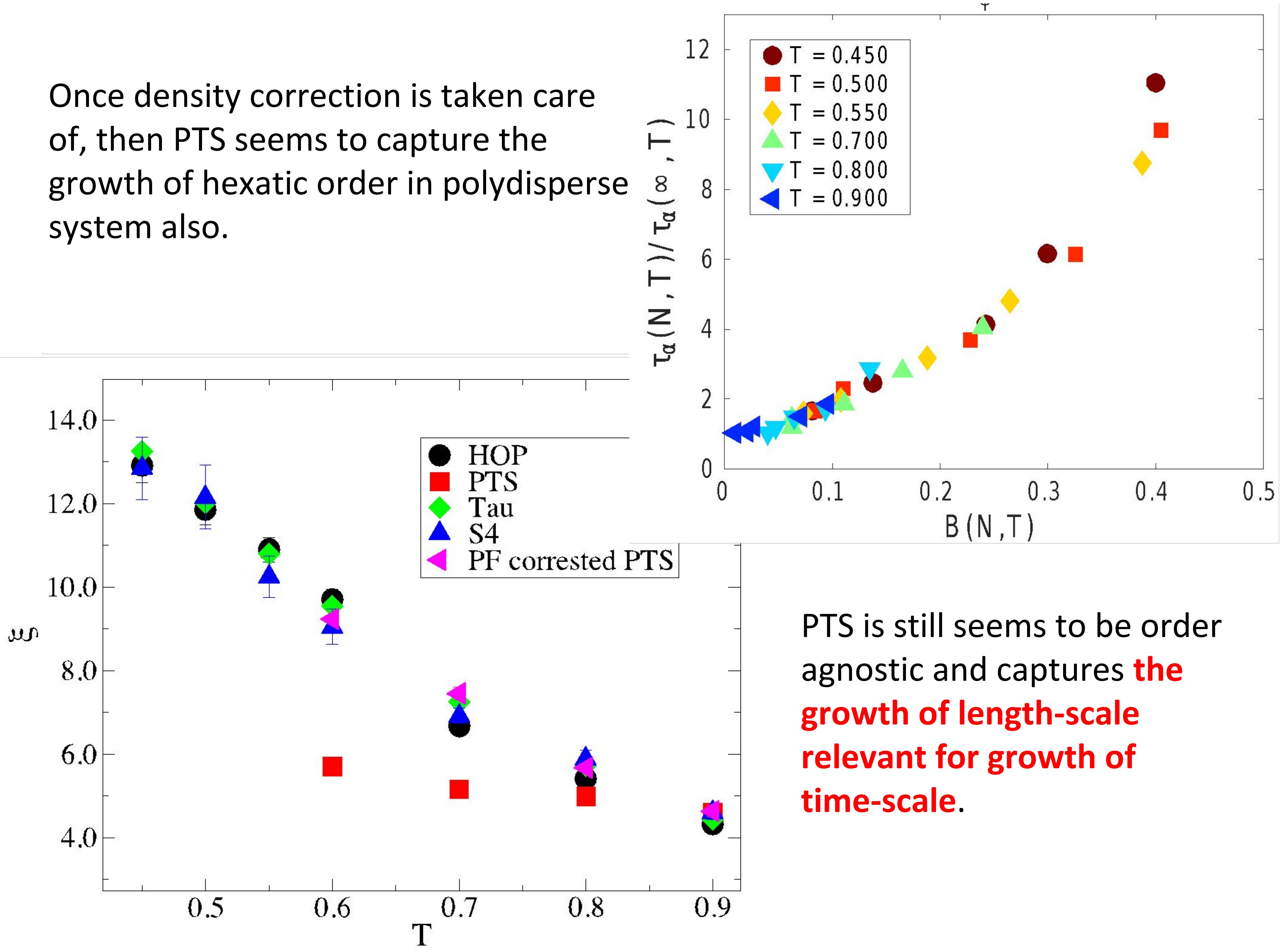


Very large variation of polydispersity and density for different cavities. This is really a concern when one calculate PTS length-scale using cavity geometry.

If we take only those cavities whose densities are close (within 2%) to the bulk density and recalculate the overlap and Point-to-set length-scale, then indeed overlap decays slowly for lower temperature.

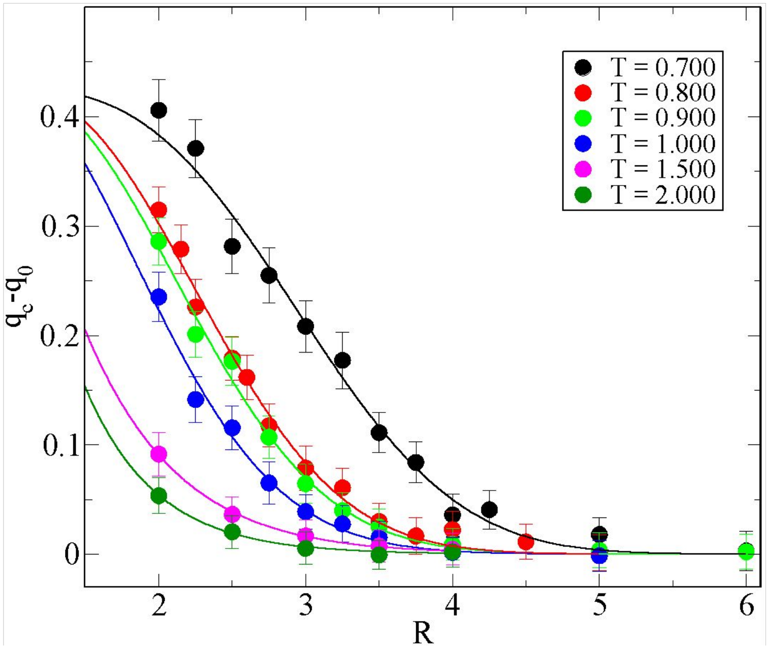


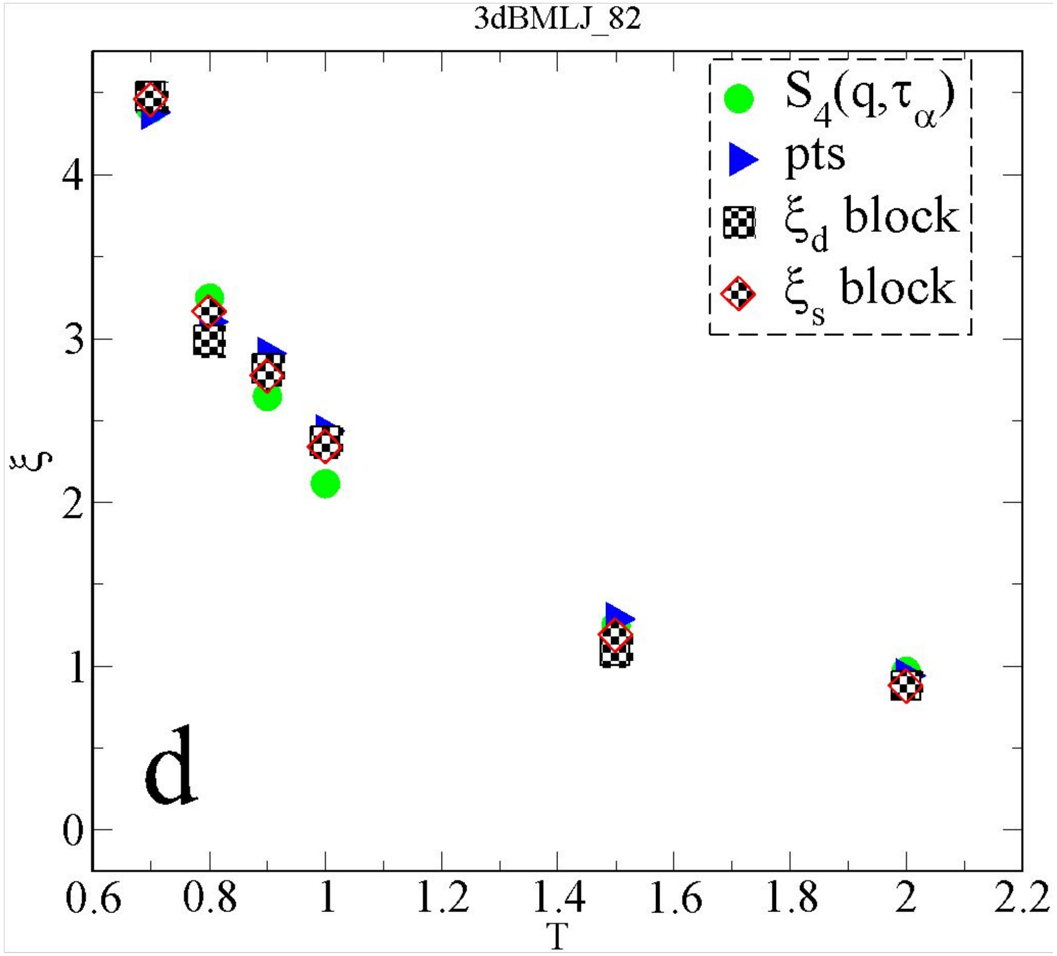
Once density correction is taken care of, then PTS seems to capture the growth of hexatic order in polydisperse system also.

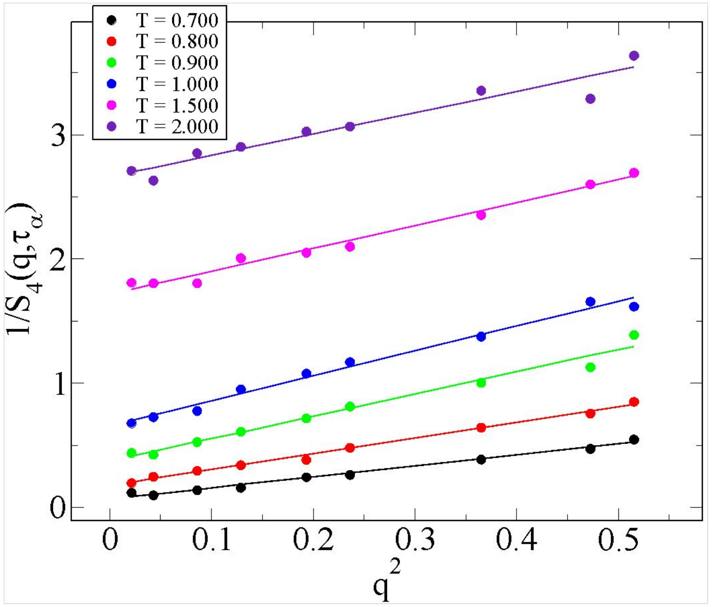


PTS is still seems to be order agnostic and captures **the growth of length-scale relevant for growth of time-scale**.

3d BMLJ System





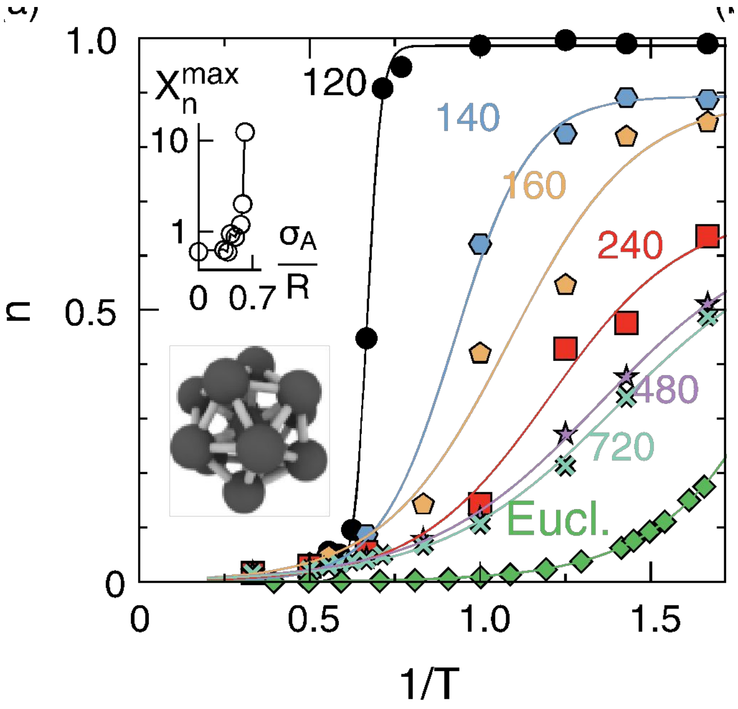


Static and Dynamic Length scales are strongly coupled **: Growth of Locally Favored Structures (LFS) may possibly be the reason**.

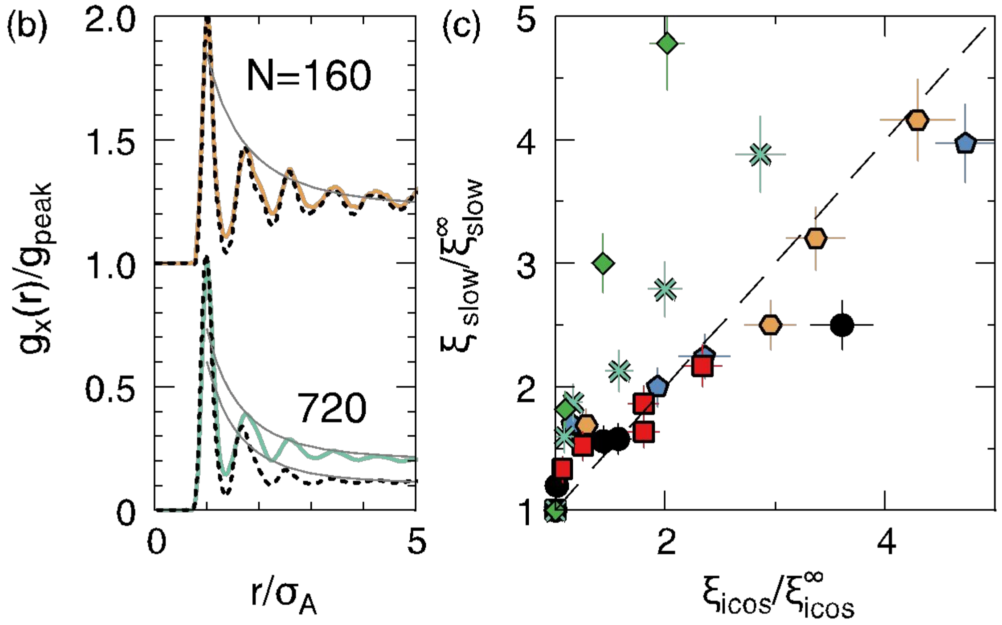
PRL **118,** 215501 (2017) PHYSICAL REVIEW LETTERS week ending 26 MAY 2017

From Glass Formation to Icosahedral Ordering by Curving Three-Dimensional Space

Francesco Turci,[1,*] Gilles Tarjus,[2] and C. Patrick Royall[1,3,4,5]

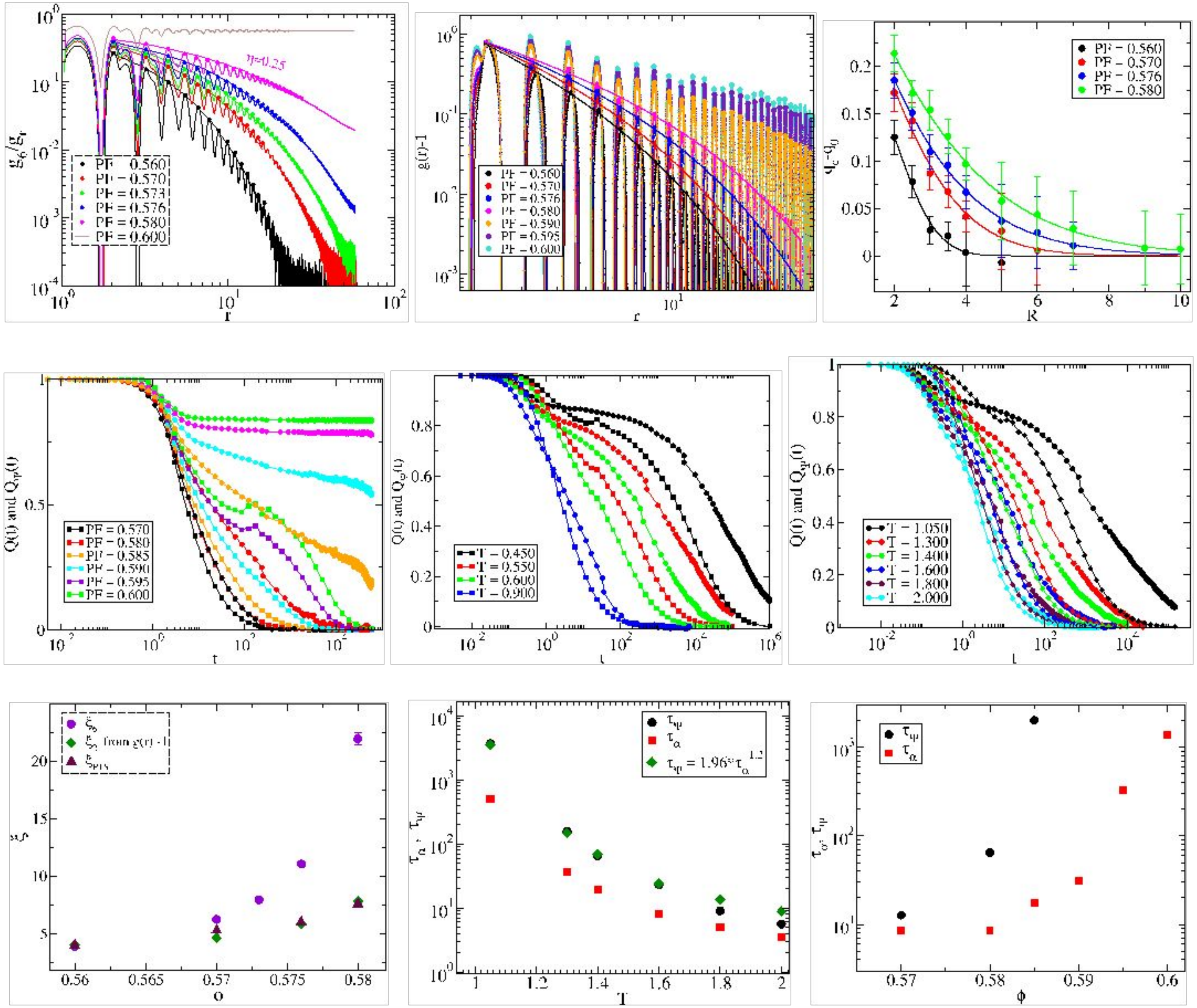


With increasing curvature, icosahedral order becomes much more prominent and static and dynamic length scale becomes strongly coupled.



Icosahedra is the structural motif which is like MRCO region in 2d systems.

Mono-disperse Systems



Conclusion : Part 2

- The growth of different length scales in supercooled liquids with medium range crystalline order (MRCO) are completely different from the generic glass forming liquid where MRCO is not prominent.
- Dynamic heterogeneity and relaxation times are controlled by one unique length scale for glass forming liquids with MRCO.
- Systems with no prominent medium range crystalline order, dynamic heterogeneity and relaxation times are controlled by two different length scales. Increase in relaxation time with decreasing temperature is controlled by the static length scale not the dynamic one.
- PTS length scale correctly picks up the hexatic order. This is actually order agnostic.
- Metallic glasses seem to have also local crystalline order and thus glass transition in metallic glasses might be different from the conventional glass transition.
- Extension to this work in other three dimensional models with MRCO/LFS is in progress and it will be great to see whether similar physics also applies to those systems.

Collaborators : Part 1

Theory &
Simulations

Rajsekhar Das

Saurish Chakrabarty

Experiments:

Bhanu Prasad Bhowmick

Dr. Anand B Puthirath

Dr. T.N. Narayanan

Collaborators : Part 2

Indrajit Tah

Dr. Shiladitya Sengupta

Prof. Srikanth Sastry

Prof. Chandan Dasgupta