# Block Analysis for the Calculation of Dynamic and Static Length Scales in Glass-Forming Liquids

## Smarajit Karmakar
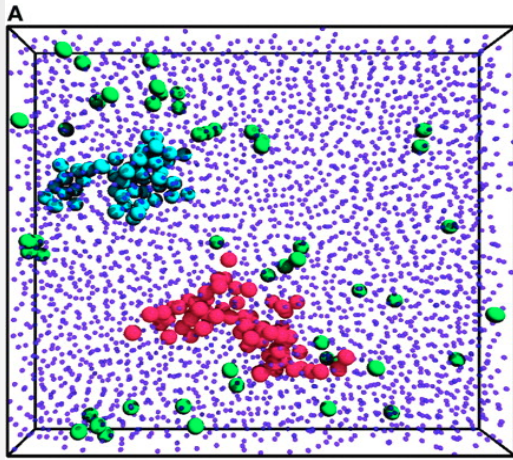
### Center for Interdisciplinary Sciences, Tata Institute of Fundamental Research, Hyderabad

**Phys. Rev. Lett, 119 205502 (2017).**

**Collaborators:**
**Saurish Chakrabarty (ICTS), Indrajit Tah (TIFR-H), Chandan Dasgupta (IISc)**

# Dynamic Heterogeneity:  Coexistence of "slow" and "fast" regions



The locations of the fastest particles (large spheres) and the other particles (smaller spheres). The spheres are drawn smaller for clarity; the particles all have the same physical size, which is the size of the large spheres shown in this figure. (**A**) "Supercooled" sample with φ = 0.56, $\Delta t^*$ = 1000 s; the fastest particles had a displacement >0.67 μm. The red cluster contained 69 particles; the light blue cluster contained 50 particles.

Dynamical heterogeneity  Weeks et al. Science 2000
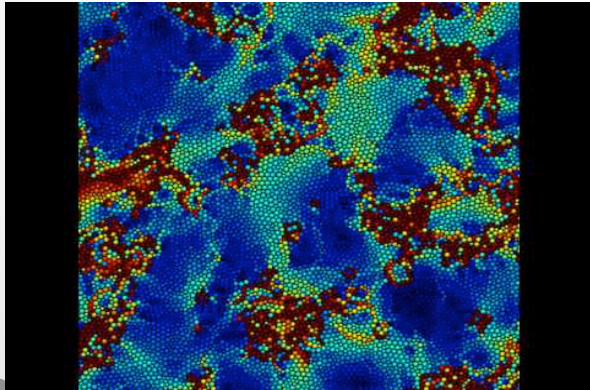
Aaron S. Keys, Lester O. Hedges, Juan P. Garrahan, Sharon C. Glotzer, and David Chandler Phys. Rev. X 1, 021013
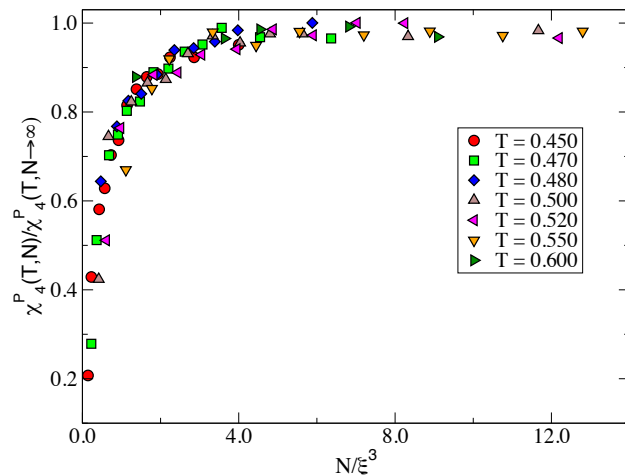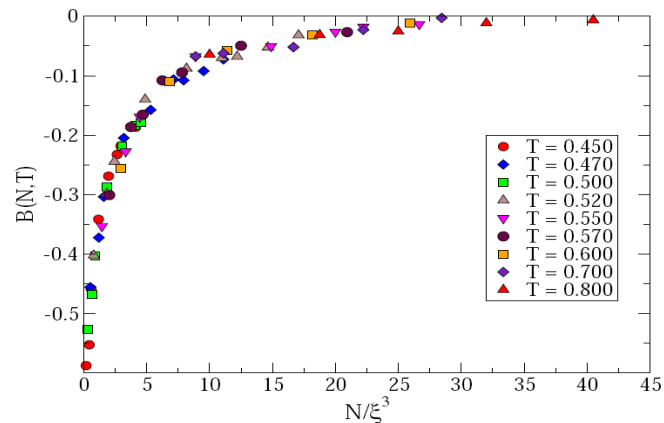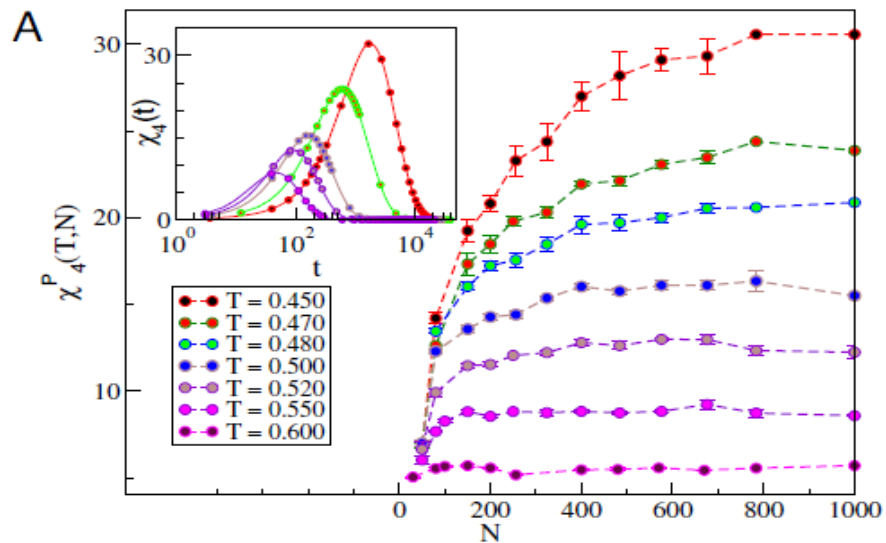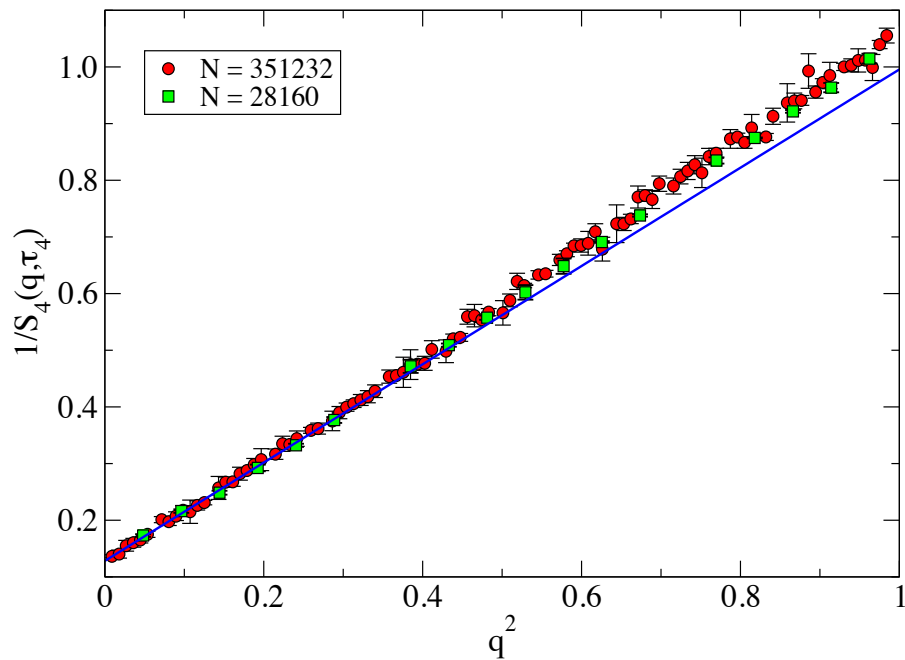
# Dynamic Heterogeneity Length Scale

[ Karmakar et al. PNAS 106, 3675 (2009) ]

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

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

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

$$\lim_{q \to 0} S_4(q, t) = \chi_4(t)$$

This relation does not hold
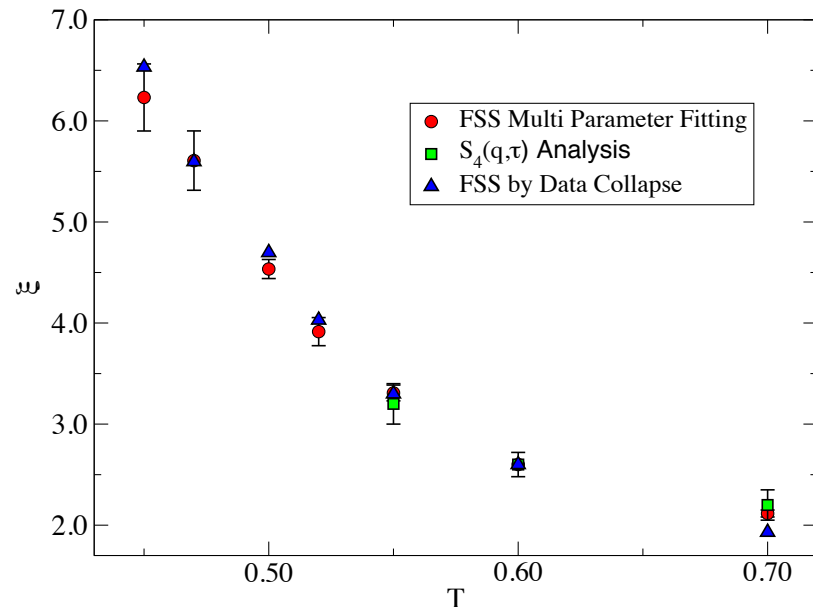in the canonical ensemble

- FSS results are in complete agreement
  with conventional methods.
- FSS method are robust and does not
  require simulation of very large system
  size.

# 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 microscopic details. Thus they are not practical for real glass forming liquids and are mostly studied for model liquids in simulations.

**Comparison of Static Length Scales Characterizing the Glass Transition**

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

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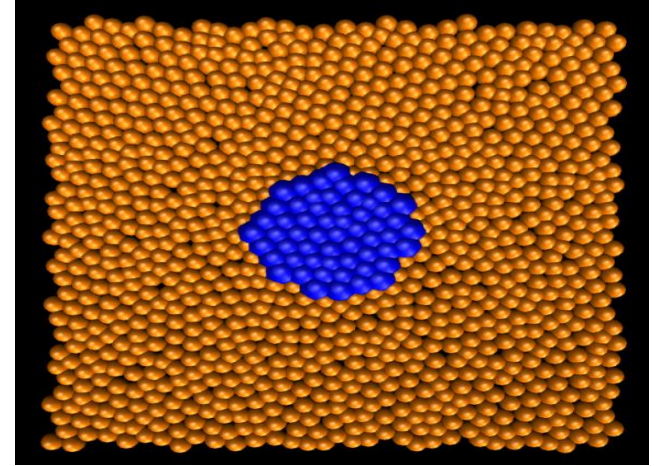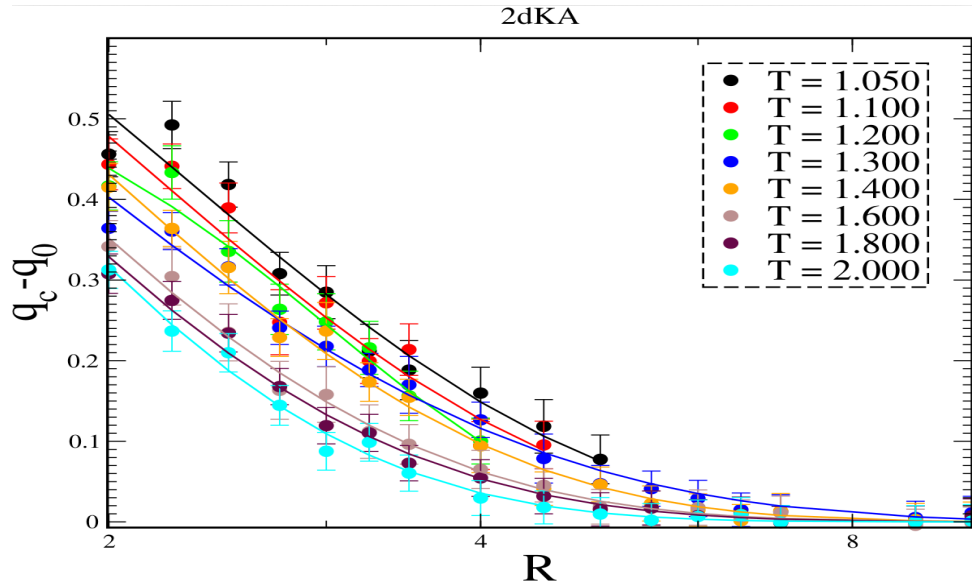
[3]Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560 064, India

# Point to set Length Scale

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

The overlap function is defined as

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





2dKA

$$q_c(R) - q_0 = A exp\left(-\left(\frac{R-1}{\xi_{pts}}\right)^\eta\right) \text{ fits all}$$

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

# Static Length scale of Amorphous Order

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

# 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.

# Colloidal Experiments
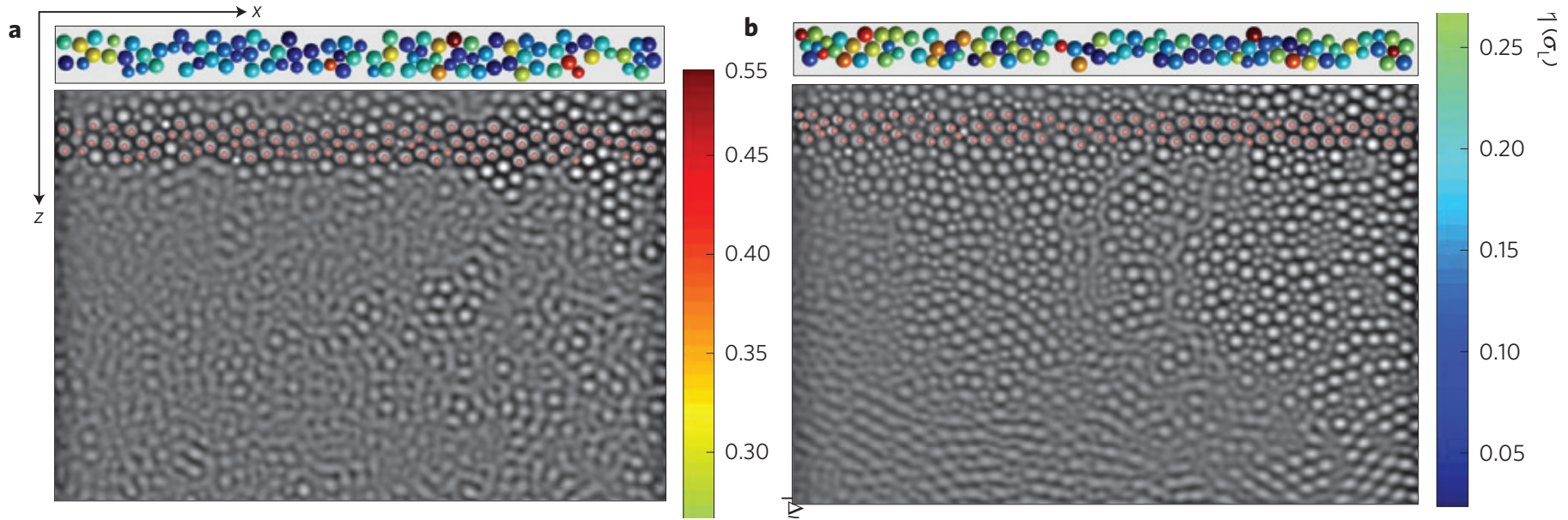


KH Nagamanasa, S Gokhale, AK. Sood and R. Ganapathy, Nat. Phys. 2015

# Schematic diagram for block analysis



$$L_B = L/n$$
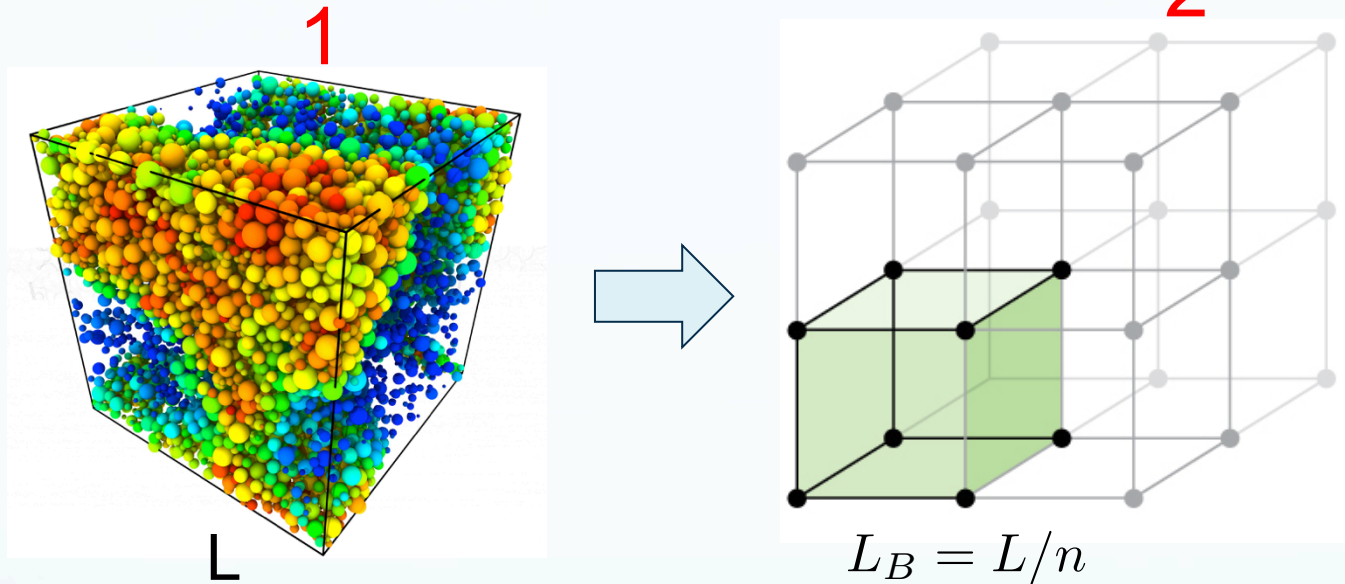
In colloidal experiments, only portion of the system is imaged using microscope and thus that portion is already in grand canonical ensemble. This is ideal for block analysis.

static and dynamic length scales can be obtained in one go. Static length scale using PTS method is very computationally expensive and not easy to implement at low temperatures.

# Models and Methods:

**3dKA** – 80:20 binary mixture.
L-J potential,

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right].$$

$$\epsilon_{AA} = 1.0, \ \epsilon_{AB} = 1.5, \ \epsilon_{BB} = 0.5,$$

$$\sigma_{AA} = 1.0, \ \sigma_{AB} = 0.80, \ \sigma_{BB} = 0.88.$$

$$\rho = 1.2.$$

**3dIPL-** This model is a variant of the 3dKA model with purely repulsive pairwise interaction

$$V_{\alpha\beta}(r) = 1.945\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{15.48}\right]$$

**3dR10** – A 50:50 binary mixture interacting in three dimensions via the potential

$$V_{\alpha\beta}(r) = \epsilon_{\alpha\beta}\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{10}.$$

**Here,** $\epsilon_{\alpha\beta} = 1.0, \ \sigma_{AA} = 1.0,$
$\sigma_{AB} = 1.22$ **and** $\sigma_{BB} = 1.40.$
$\rho = 0.81.$

**3dHP-** This is 50:50 binary mixture of harmonic spheres with diameter ratio of 1.4. $\rho$ =0.82.

$$V_{\alpha\beta}(r) = \epsilon\left[1 - \left(\frac{r_{\alpha\beta}}{\sigma_{\alpha\beta}}\right)\right]^{2}$$

**3dPOL-** This is a polydisperse mixture of soft spheres with the diameter $\sigma$. The spheres chosen from a Gaussian distribution. The polydispersity ($\Delta$) is defined as

$$\Delta = \frac{\sqrt{\langle \sigma^2 \rangle - \langle \sigma \rangle^2}}{\langle \sigma \rangle}$$

Here $\Delta = 8\%$.

The interaction potential is

$$V_{ij}(r) = 4\epsilon_{ij} \left[ (\frac{\sigma_{ij}}{r})^{12} - (\frac{\sigma_{ij}}{r})^6 + \frac{1}{4} \right]$$

if $r < 2^{1/6}\sigma_{ij}$, **else** $0$. **Here**
$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$.

## Self Overlap Correlation:

$$Q(L_B, t) = \frac{1}{N_B} \sum_{i=1}^{N_B} \frac{1}{n_i} \sum_{j=1}^{n_i} w(|\vec{r}_j(t) - \vec{r}_j(0)|)$$

$$w(x) = \Theta(a - x)$$

## The dynamical susceptibility associated with blocks of size $L_B$

$$\chi_4(L_B, t) = \frac{NL_B^3}{L_0^3} \langle [Q(L_B, t) - \langle Q(L_B, t) \rangle]^2 \rangle$$

$$\chi_4(L_B, t)$$
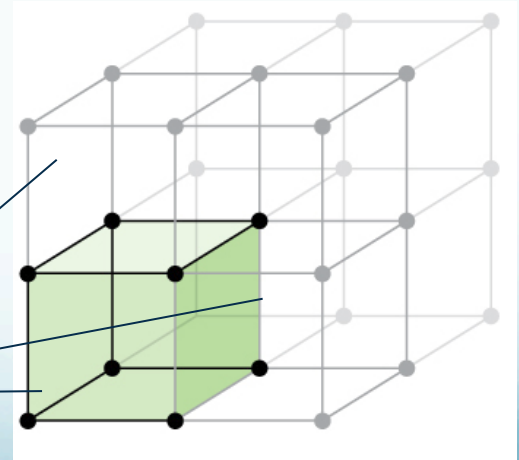
Block size dependence of $\chi_4^P$ and finite size scaling:

# 3dKA



$$\chi_4^P(L_B, T) = \chi_0(T)\mathcal{F}\left(\frac{L_B}{\xi_d}\right)$$

$$\chi_0(T) \equiv \lim_{L_B \to \infty} \chi_4^P(L_B, T)$$

S. Karmakar, C. Dasgupta and S. Sastry Proc. Natl. Acad.Sci. U.S.A. 106, 3675 (2009)
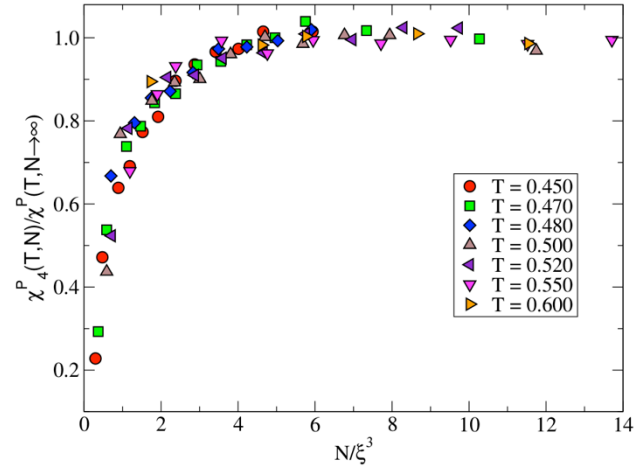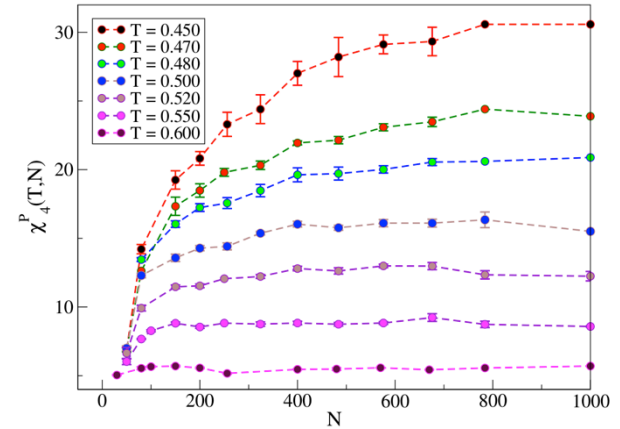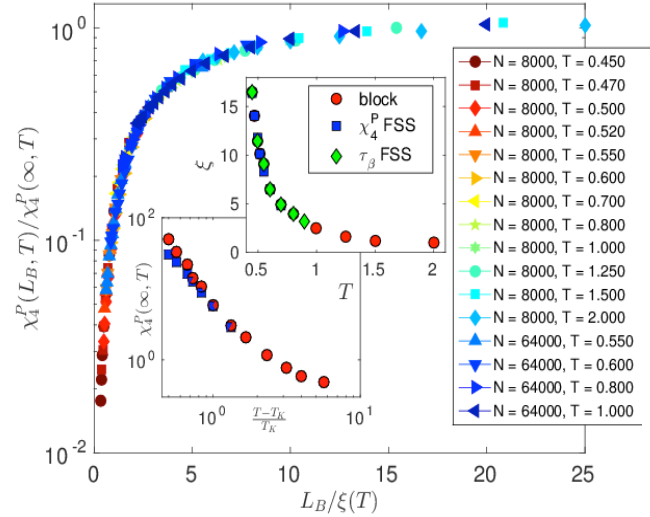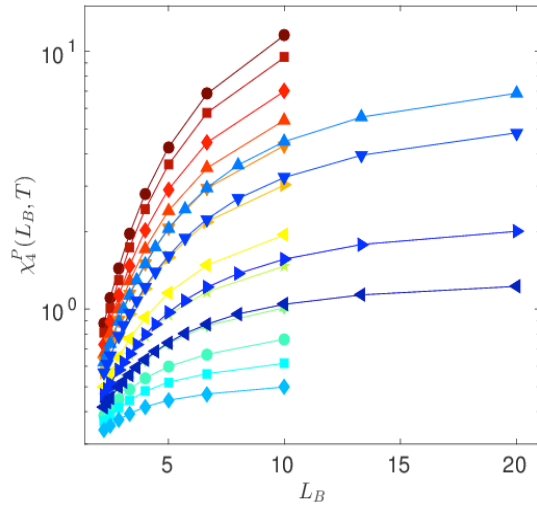
3dR10
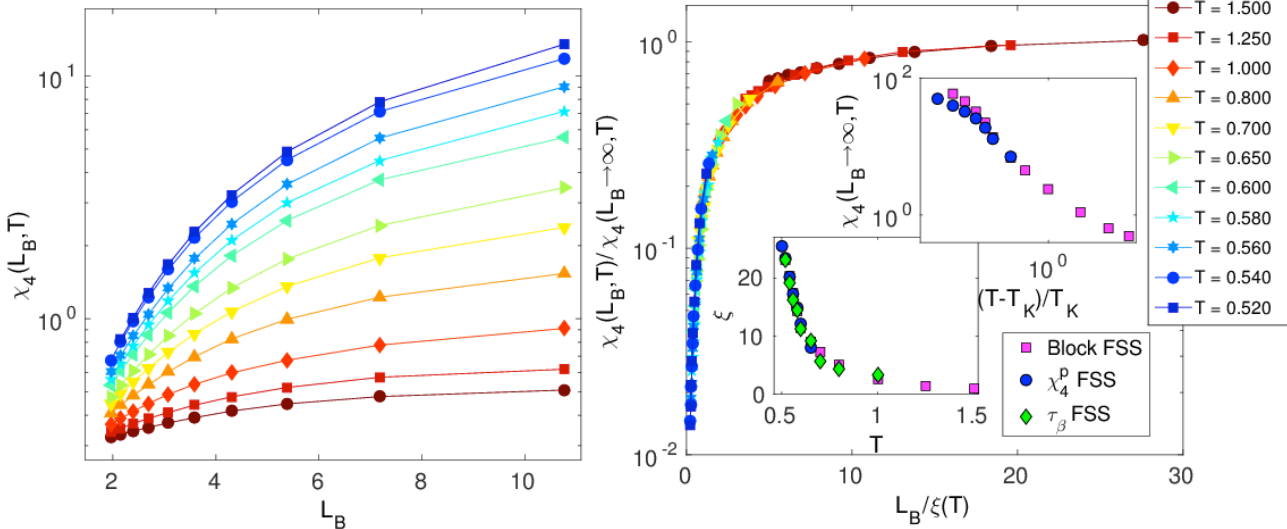
3dIPL
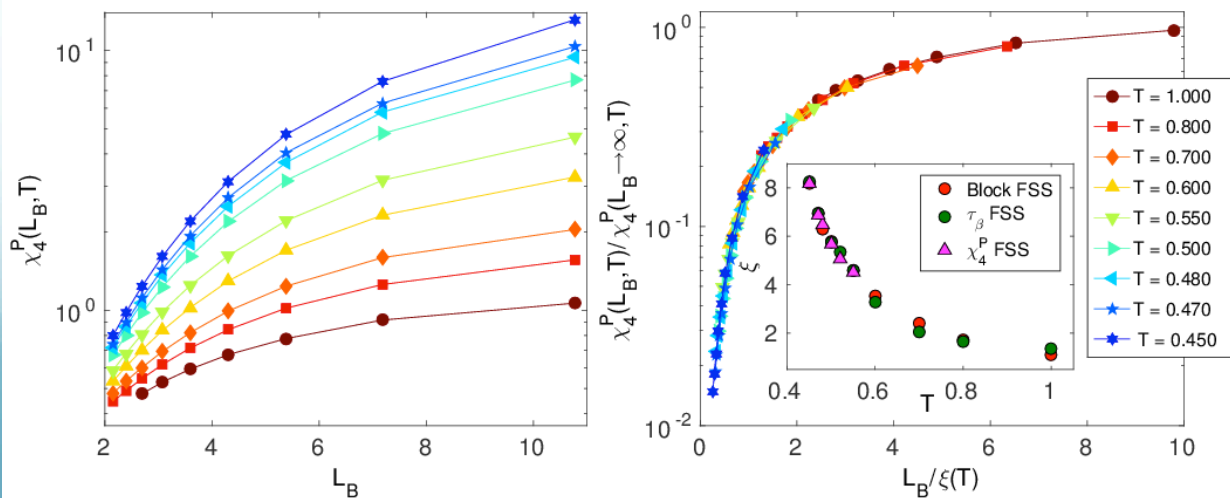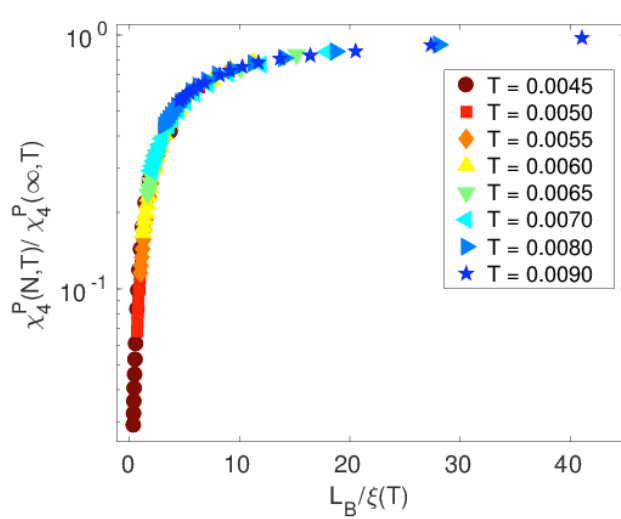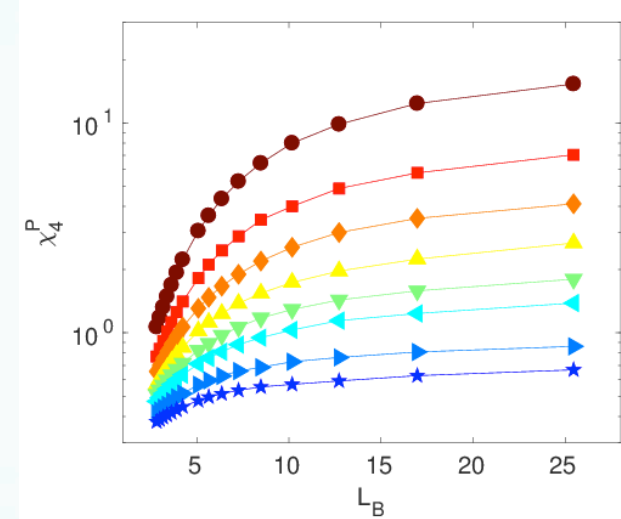
3dHP
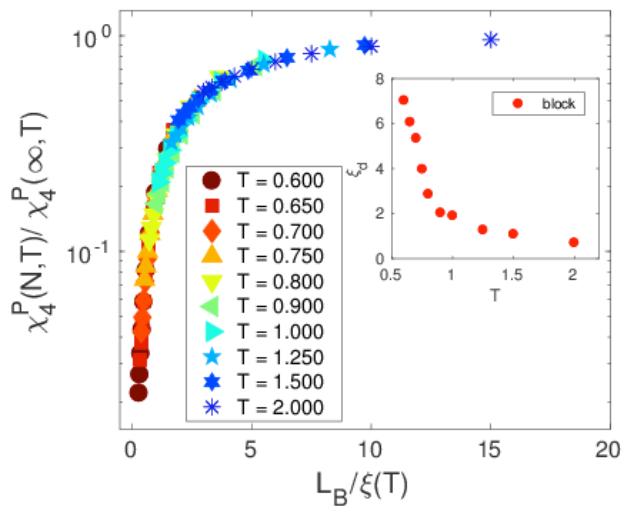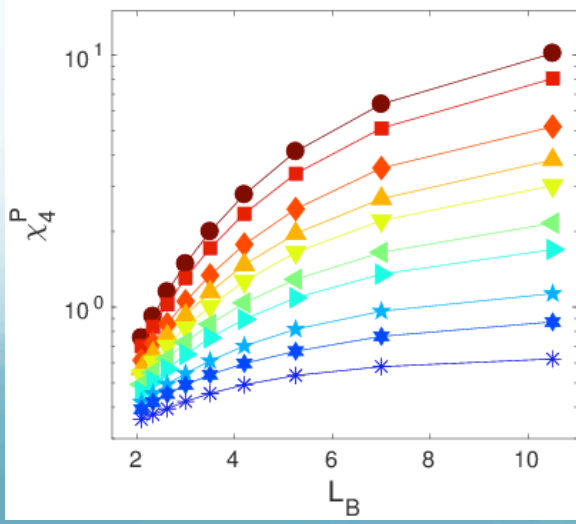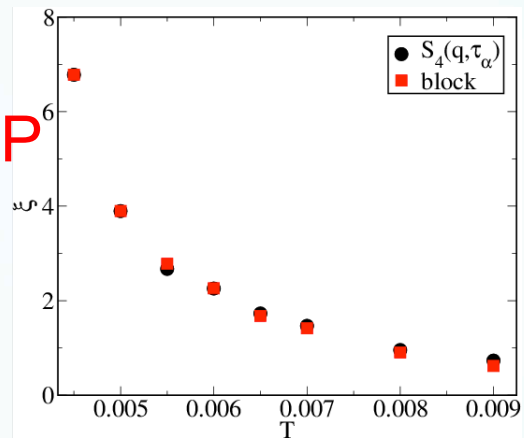
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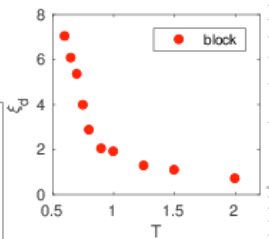
# Scaling function and the scaling exponent:

Scaling form we have used in our analysis

$$\chi_4^P(L_B, T) = \chi_0(T) \mathcal{F}\left(\frac{L_B}{\xi_d}\right)$$ where $\chi_0(T) \equiv \lim_{L_B \to \infty} \chi_4^P(L_B, T)$

$$\chi_0(T) \propto \xi_d^{2-\eta}$$

$L_B \gg \xi_d$ $L_B$ Dependence on $\chi_4^P$ should go away. $F(x)$ goes to const at $x \gg 1$

For small $L_B$ or $\xi_d \to \infty$ one expect the dependence of $\chi_4^P$ on $\xi_d$ should go away

Which implies the scaling function $F(x)$ should be proportional to $x^{2-\eta}$

$$\chi_4^P(L_B, T) \text{ should grow as } L_B^{2-\eta} \text{ as } \xi_d \to \infty.$$
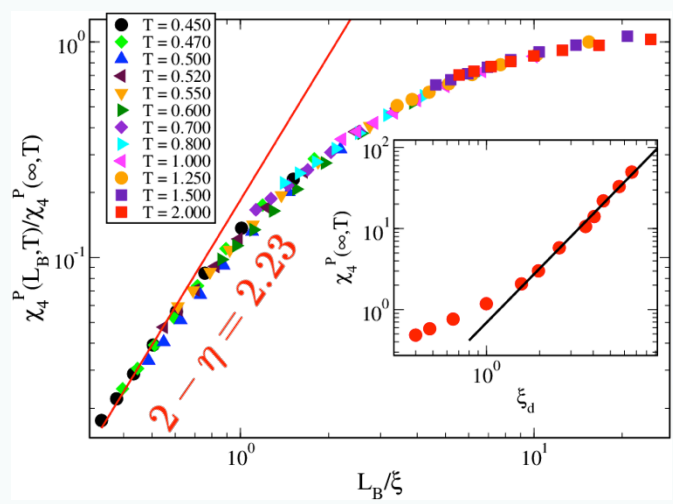
3dKA
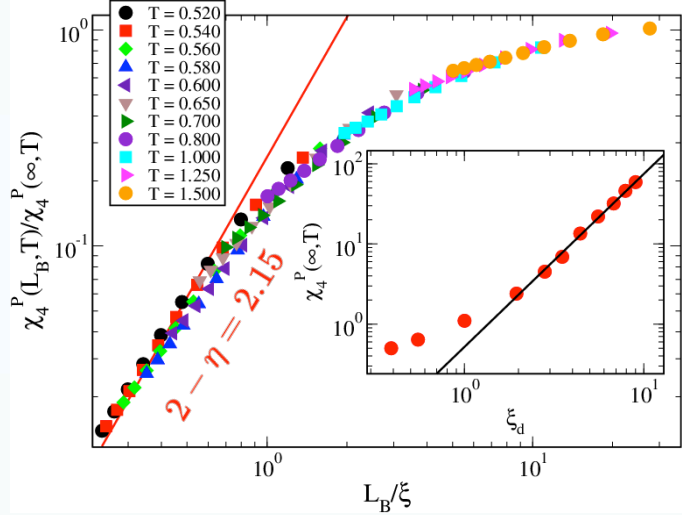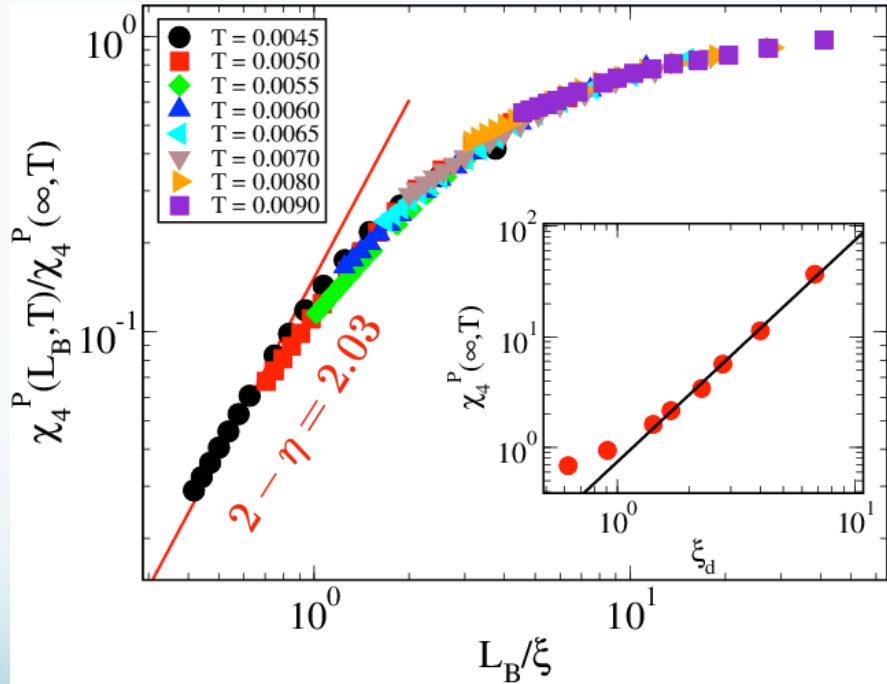
3dR10
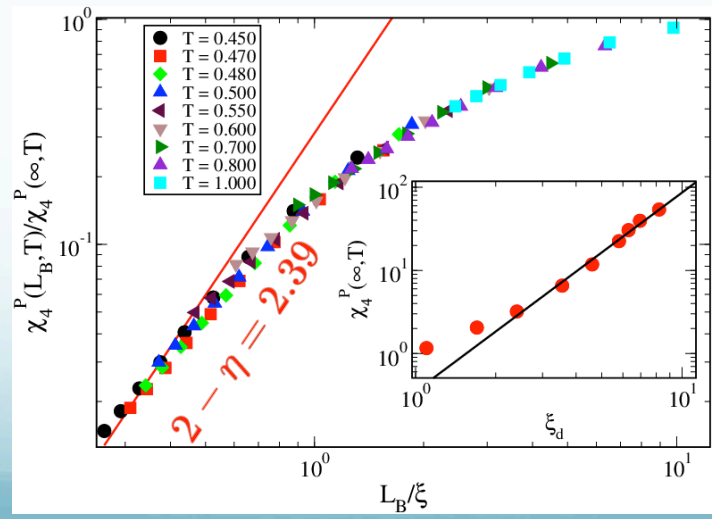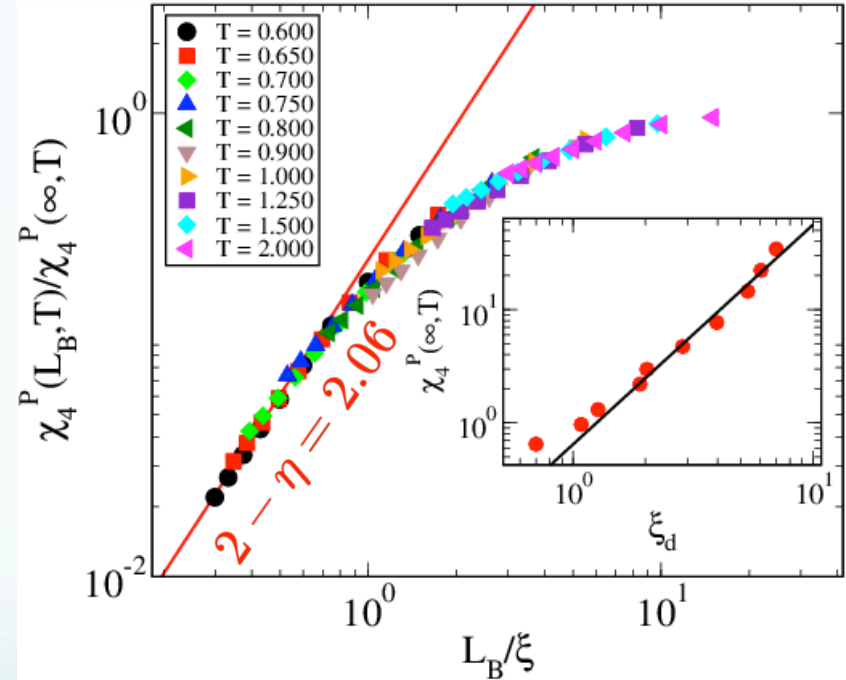
3dIPL

Here $\eta \approx 0$ which seems to be universal. This results would not have been obtained without this proposed method of block analysis
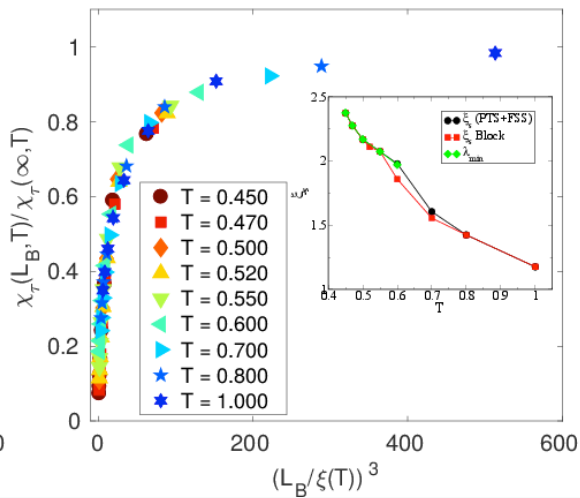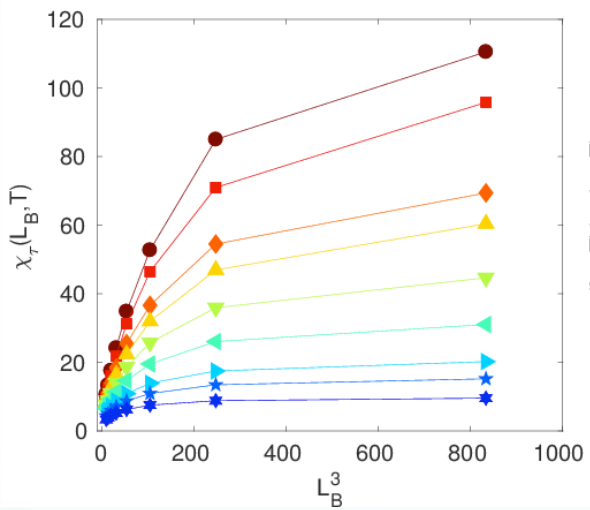
# Static length scale

The statistics of $\tau_\alpha$ and the calculation of the static length Scale

$$\chi_\tau(L_B, T) = L_B^3 \left\langle \frac{\frac{1}{N_B} \sum_{i=1}^{N_B} [\Delta\tau_\alpha^{(i)}(L_B)]^2}{\overline{[\tau_\alpha^{(i)}(L_B)]}^2} \right\rangle$$
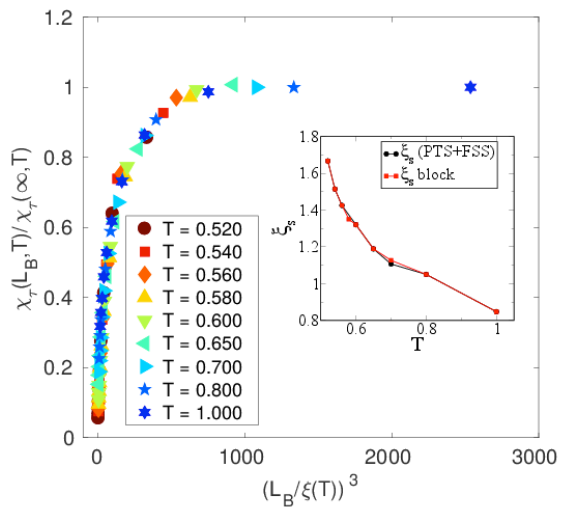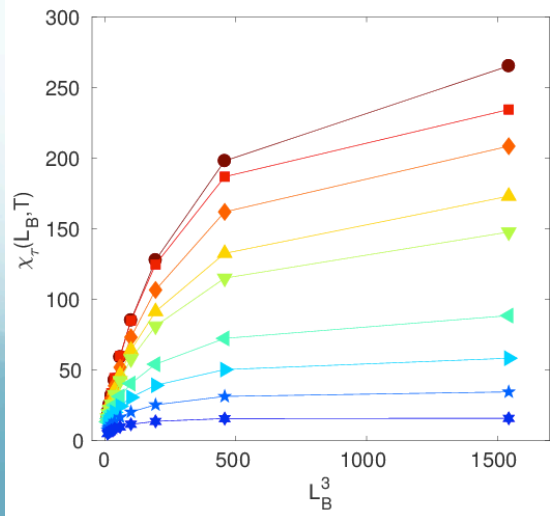
Why the variation of the average $\tau_\alpha$ with block size is very weak?
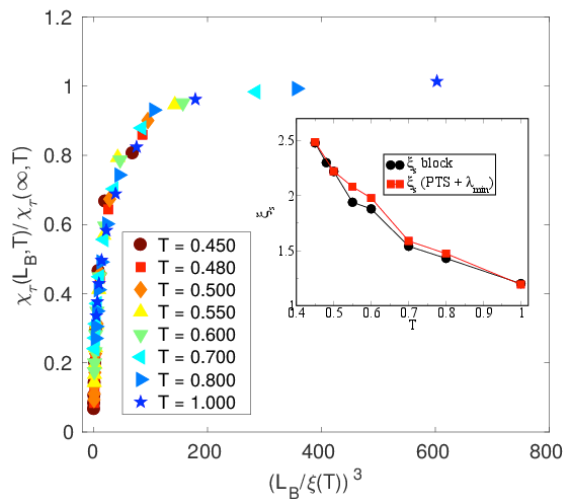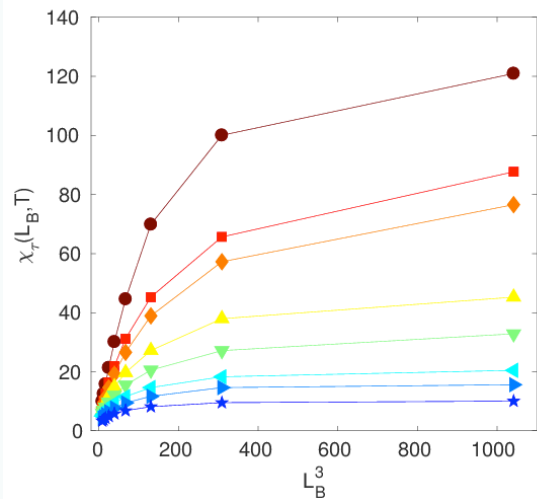
Why the variance of $\tau_\alpha$ is related to the static length scale?
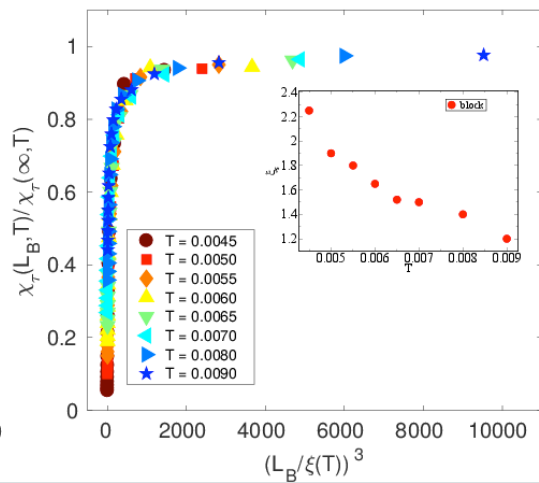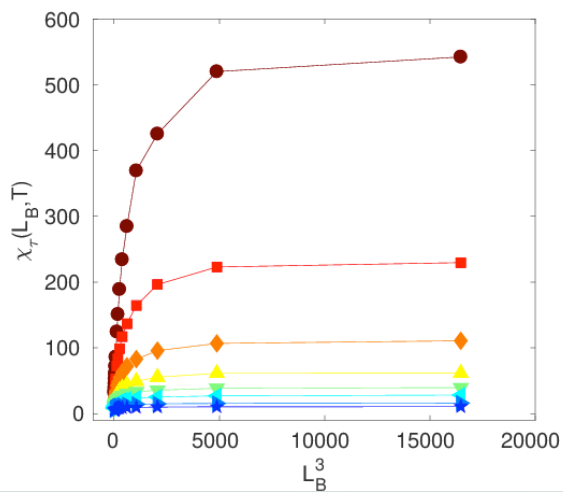
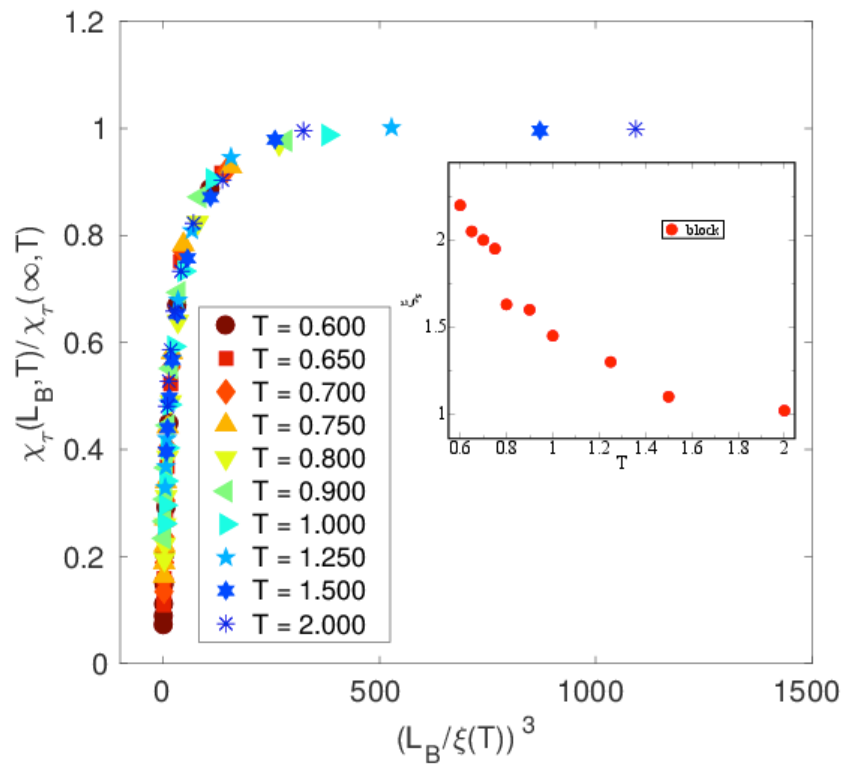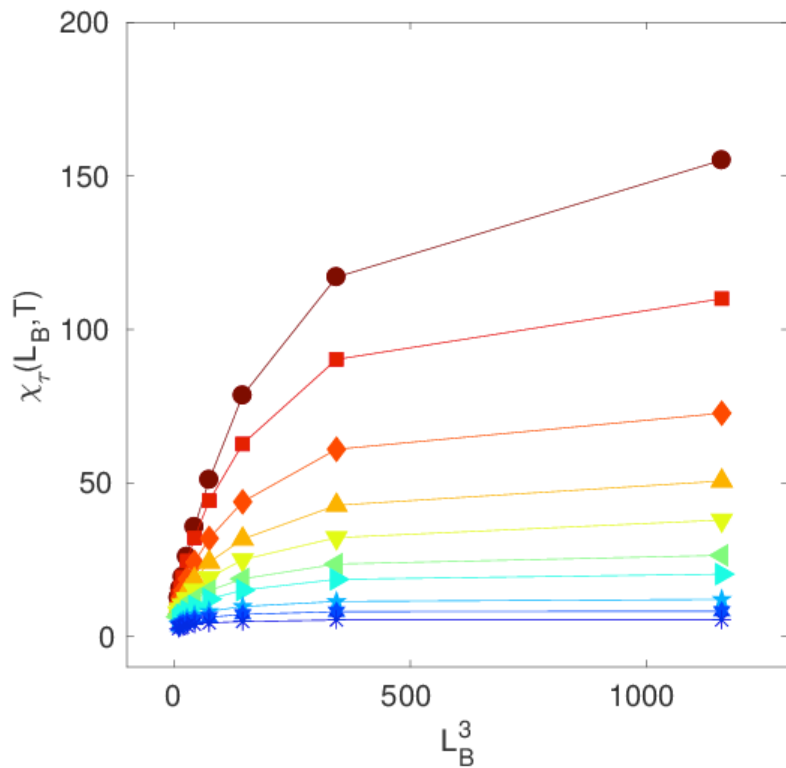No clear answer. Need further understanding

3dKA

3dR10

3dIPL

3dHP

# 3dpolydisperse

# CONCLUSION:

- **We present an efficient method which can be used in simulations as well as in colloidal experiments on glass forming liquids to obtain both static and dynamic length scale.**

- **This methods capturing all the important fluctuations in the system which is not possible in simulations in the canonical ensemble for varying system sizes.**

- **Block analysis also provides extremely well averaged results without any additional computational overhead in simulation.**

- **It can be implemented very easily in colloidal glass experiments.**

**Phys. Rev. Lett, 119 205502 (2017).**