Controlling and understanding local structure in supercooled liquids

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Frank Smallenburg
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Overview

1. Introduction

    1.1 What is a glass?
    1.2 How to model glasses/supercooled liquids?

2. How to control dynamics (or local structure)?

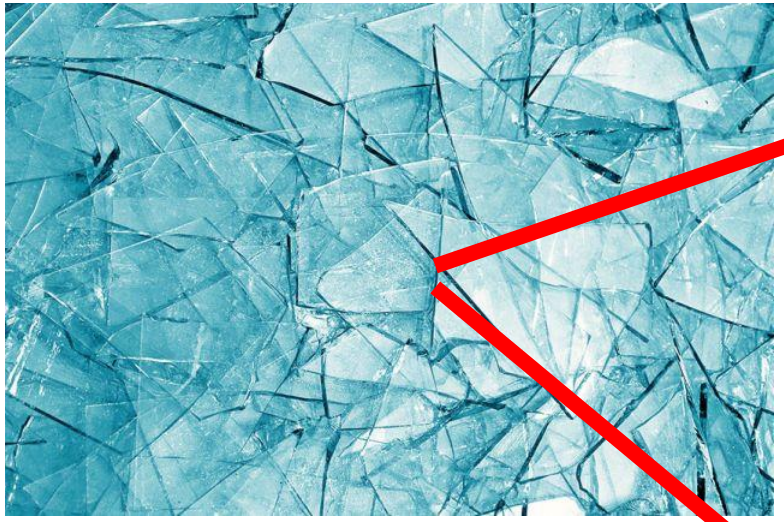
    2.1 Interactions
    2.2 Change on shape
    2.3 Size distribution

3. Conclusions

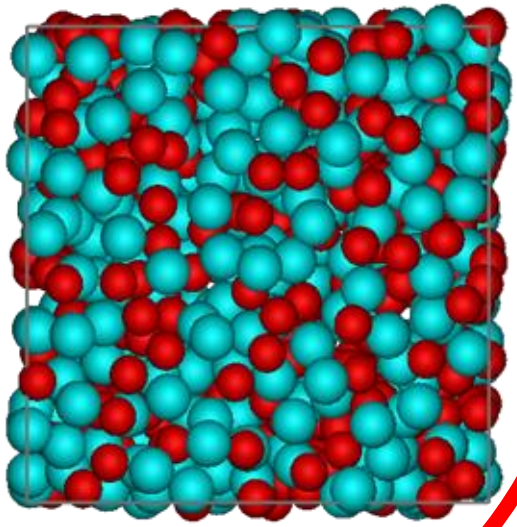
What is a glass?

Liquid

Avoiding crystallization



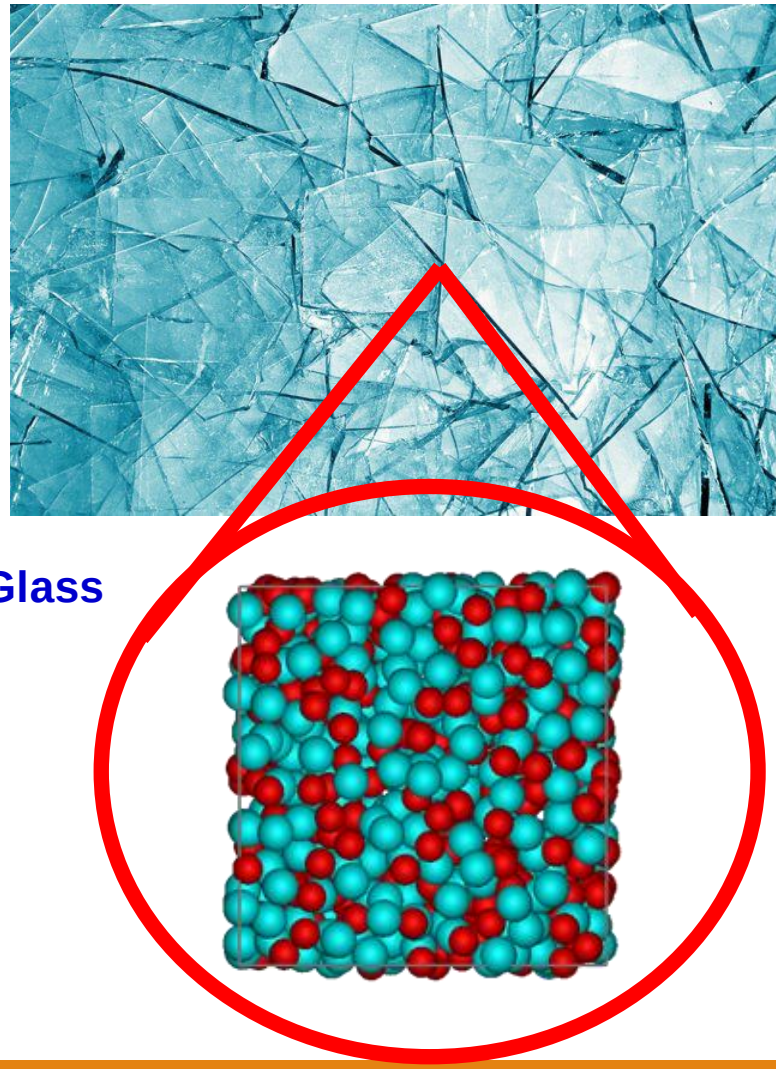
Glass



Temperature

- No long range order
  - Arrested system
    - Out of equilibrium

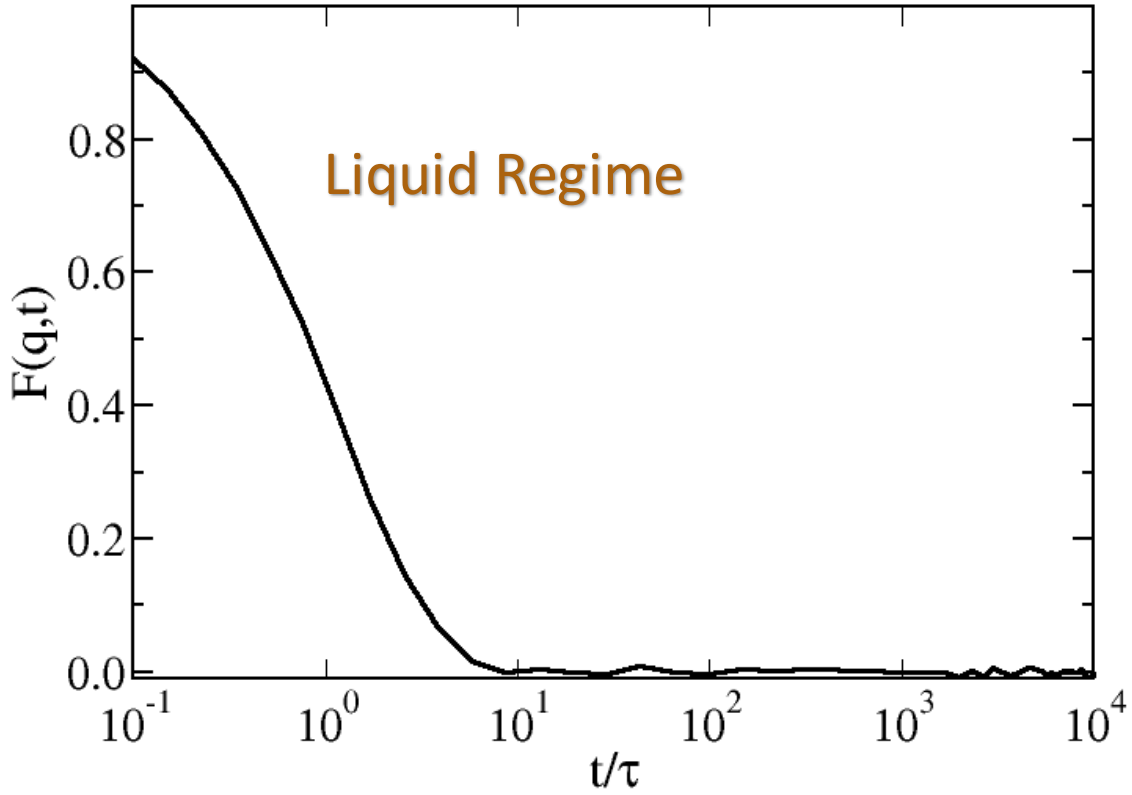
When can we call it a glass?



Glass

Relaxation Time

Intermediate Scattering Function



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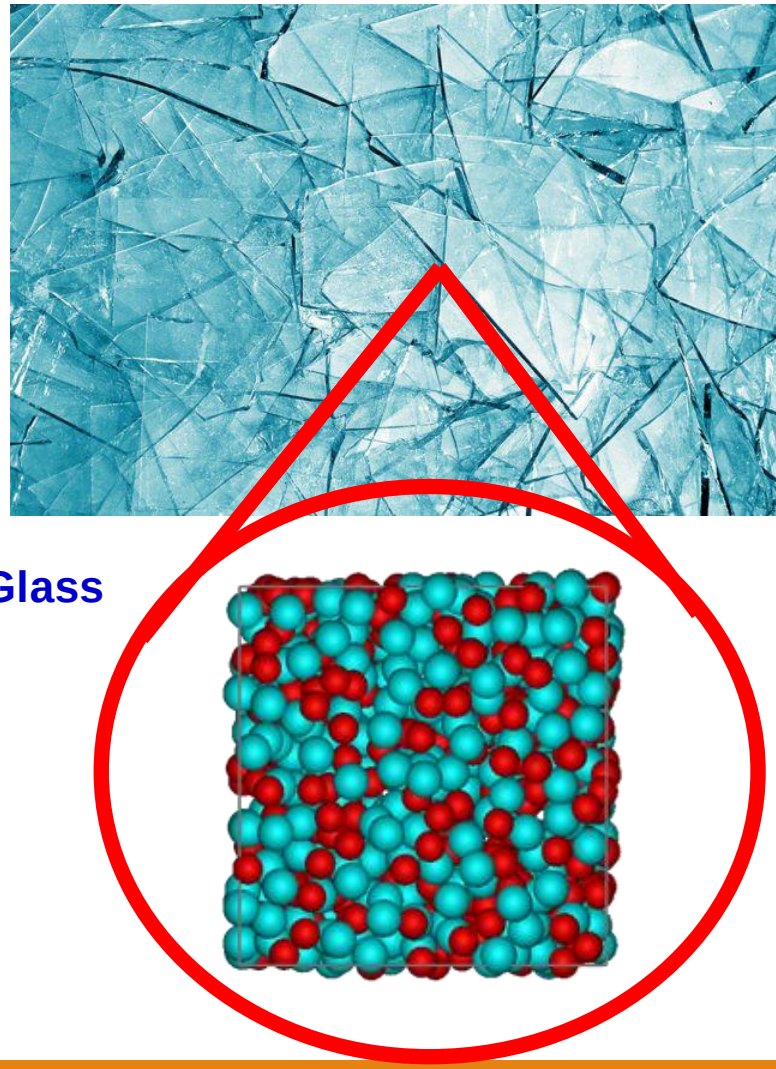

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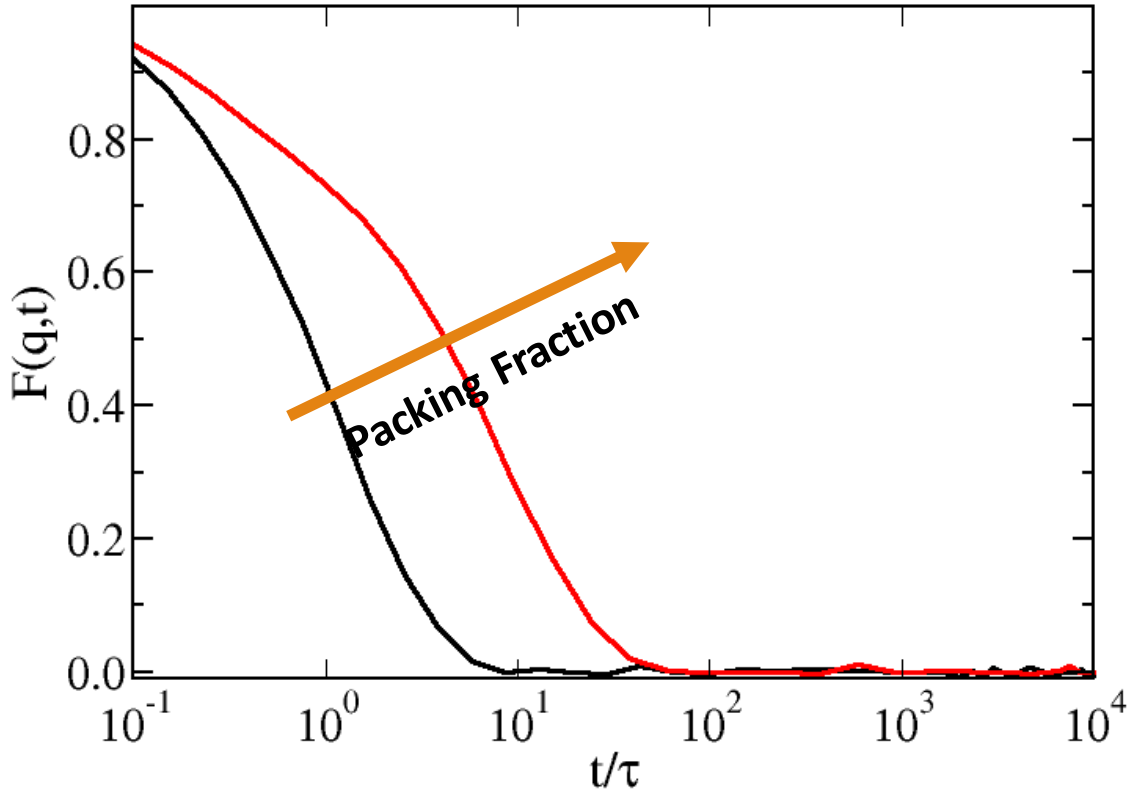

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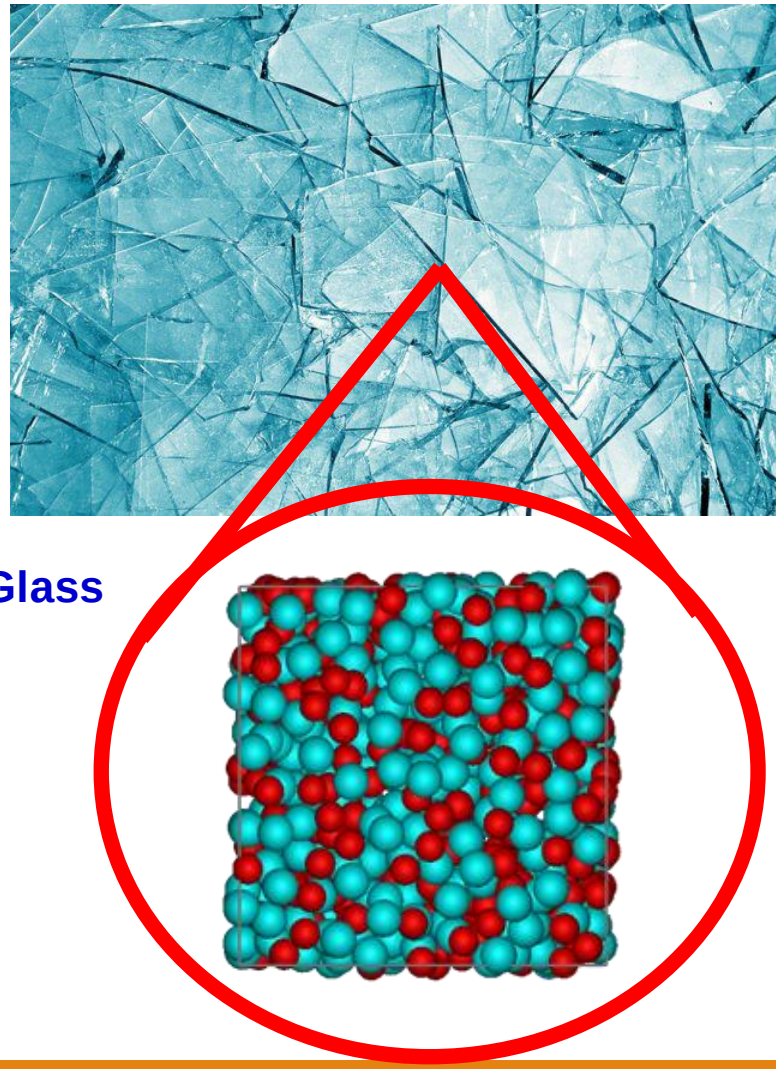

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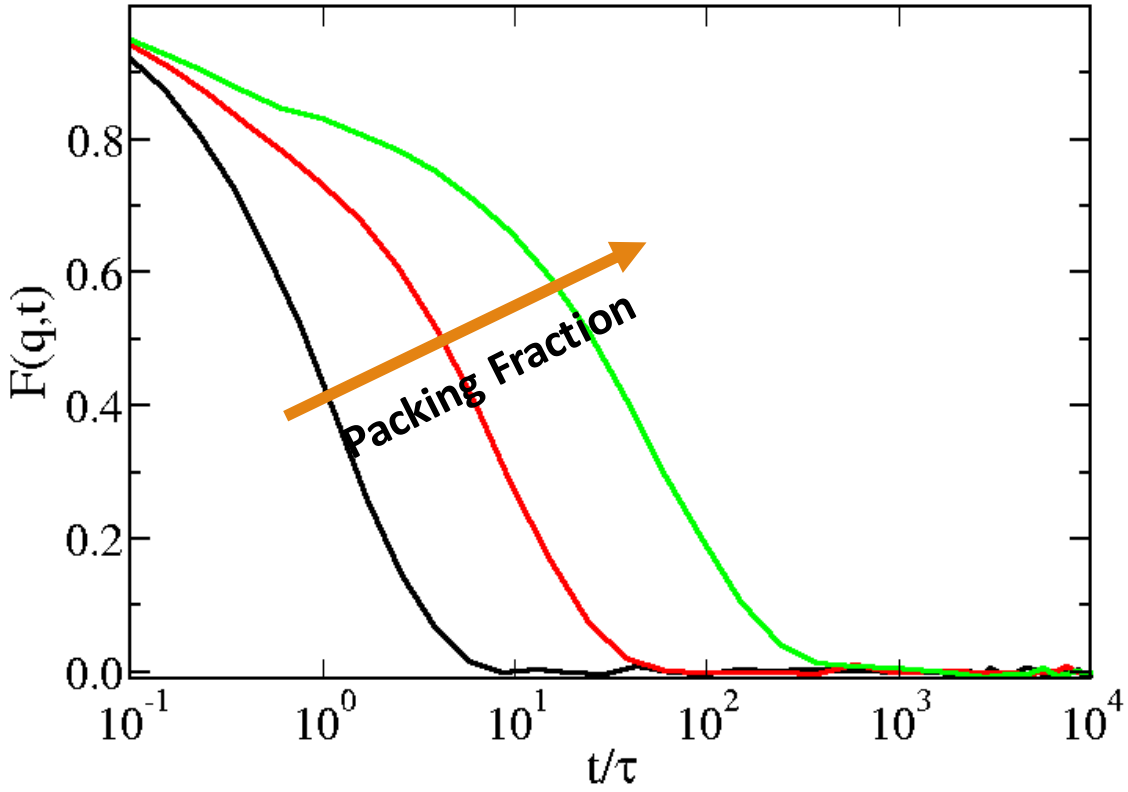

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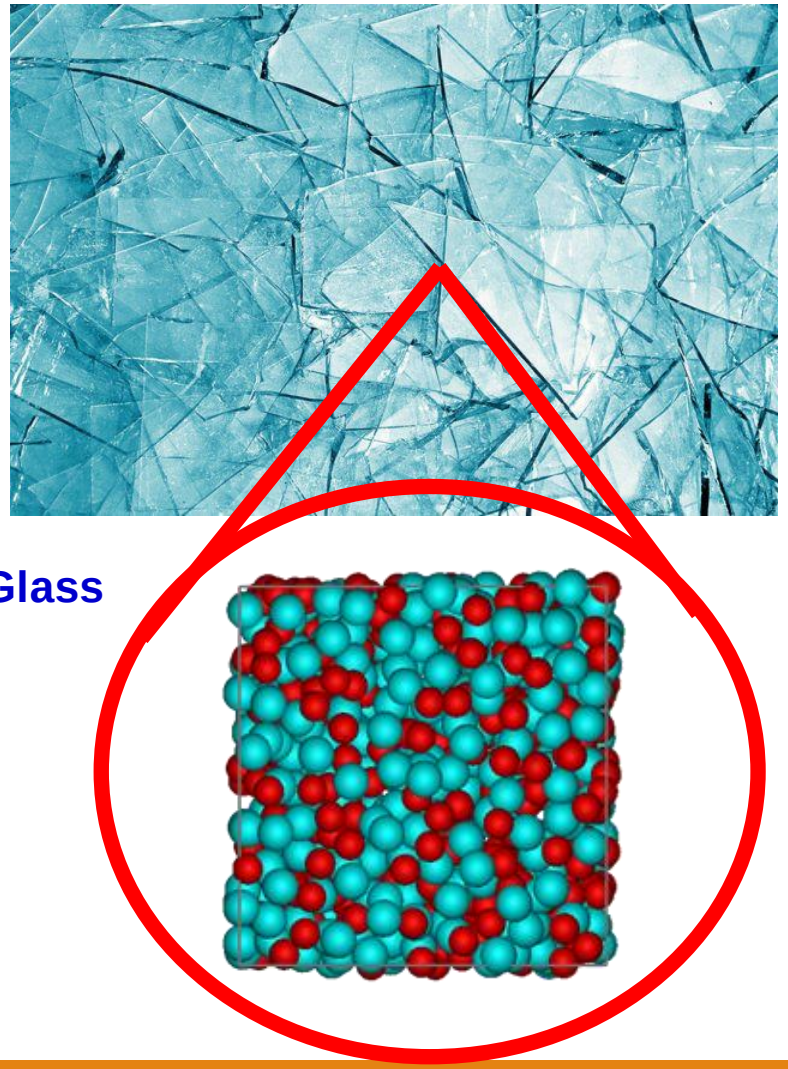

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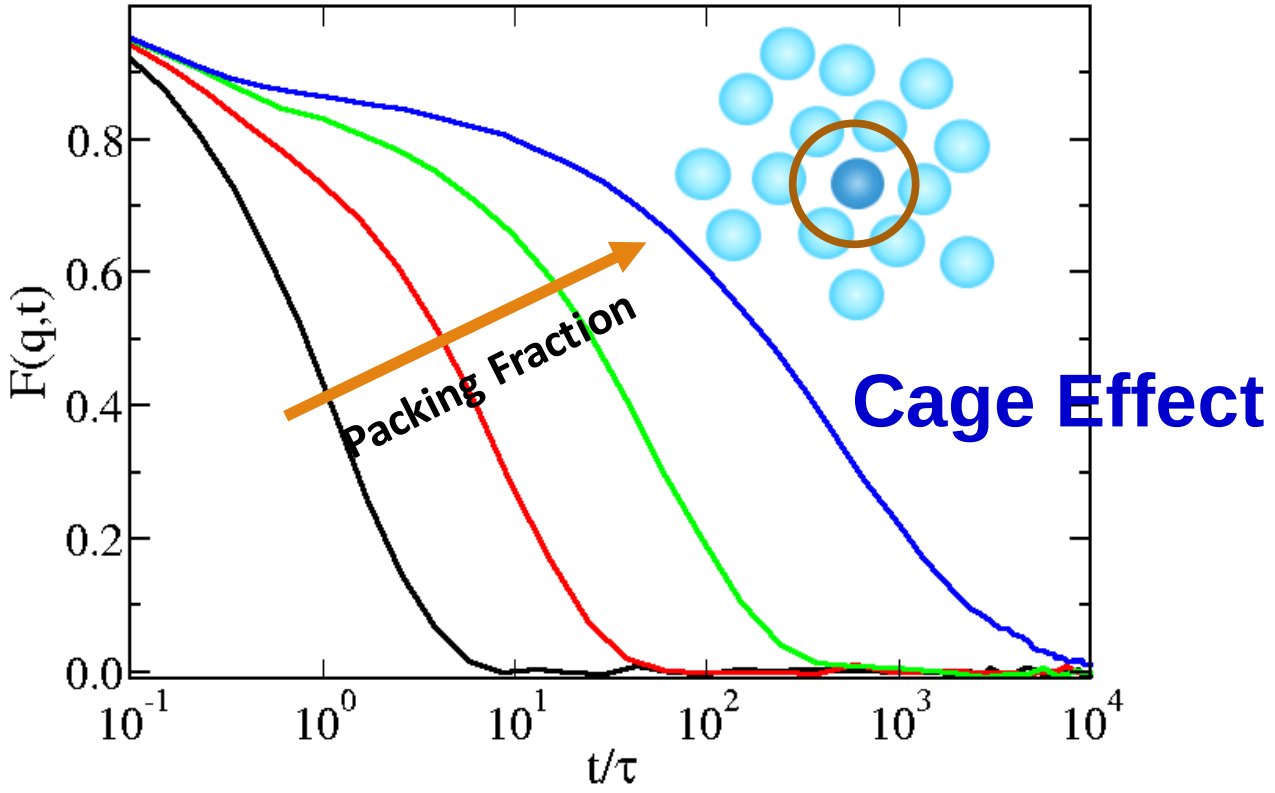
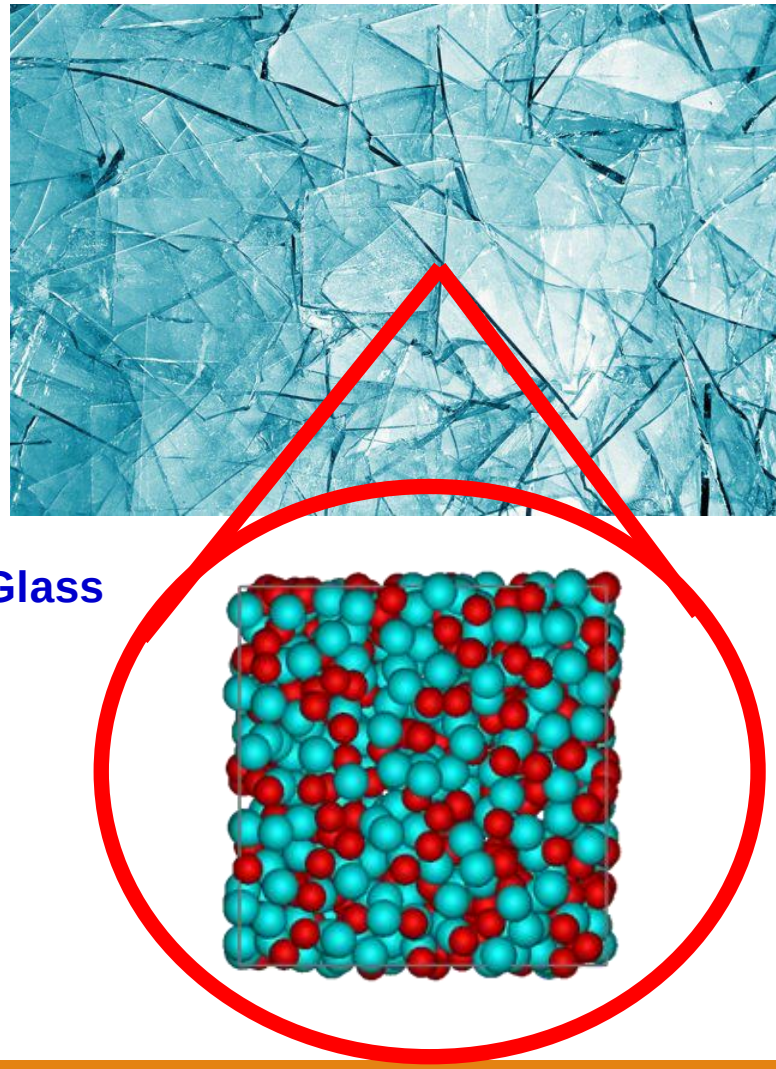


Cage Effect

When can we call it a glass?



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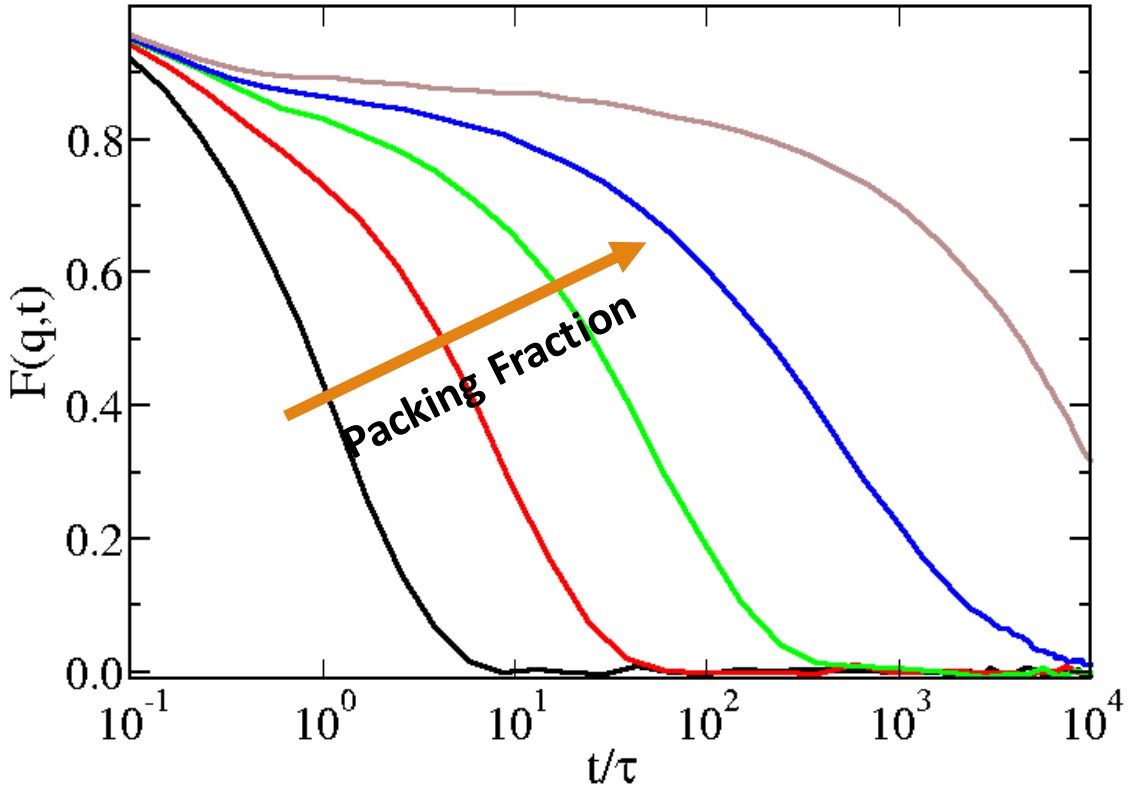

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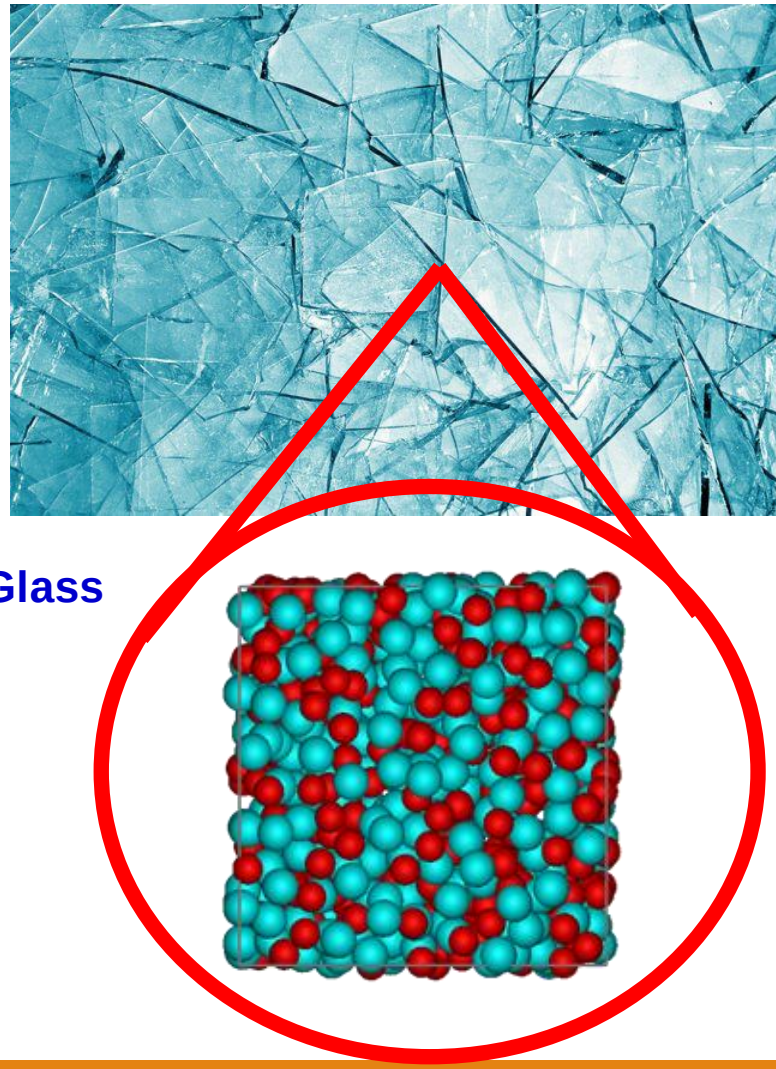

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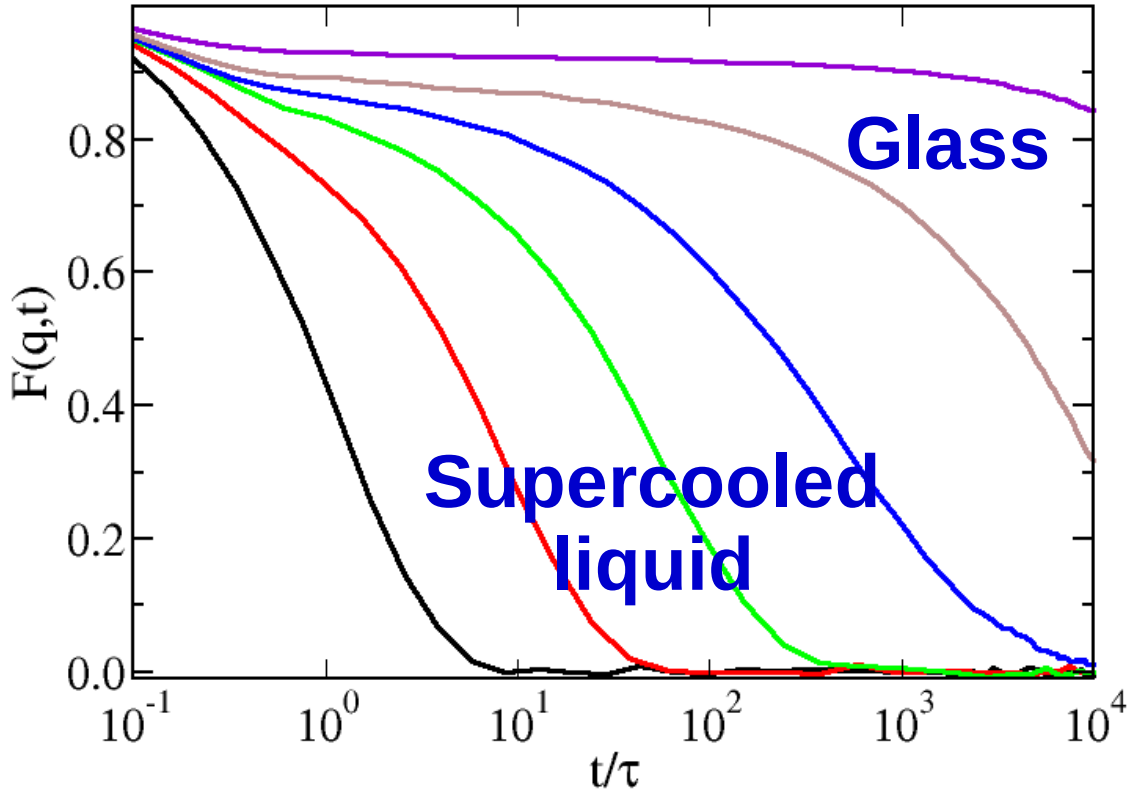

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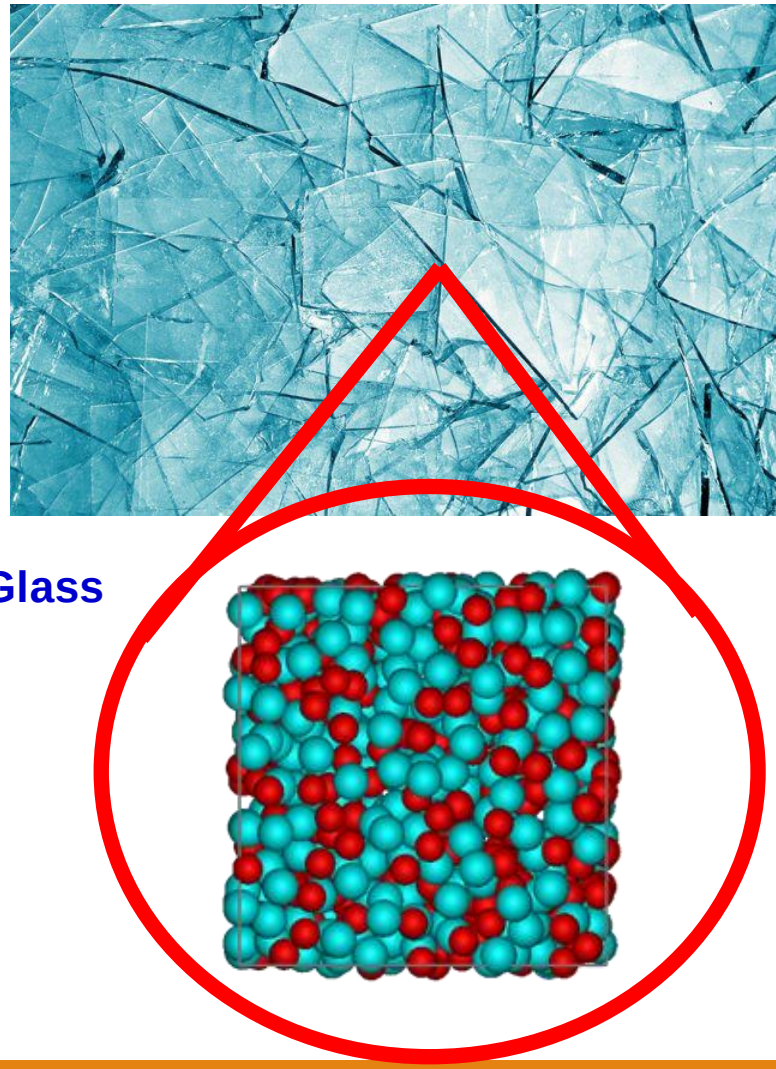

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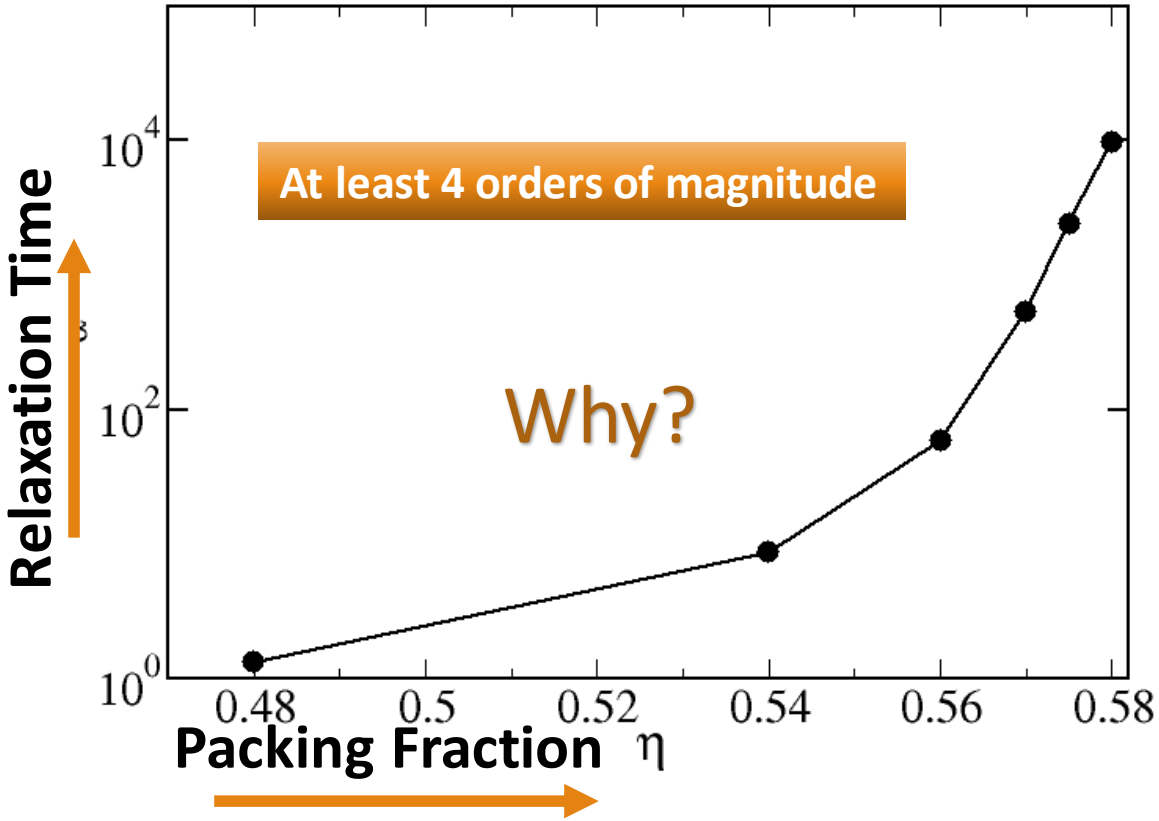
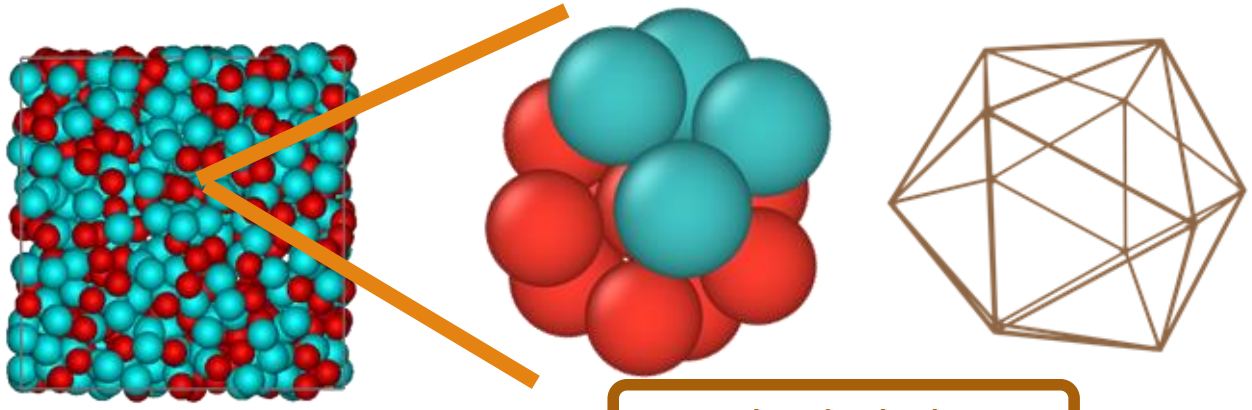


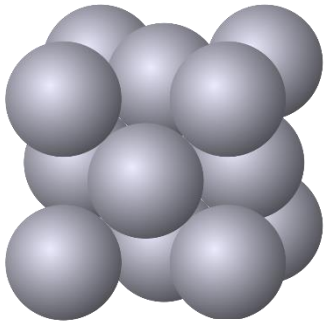
Local Structural Changes



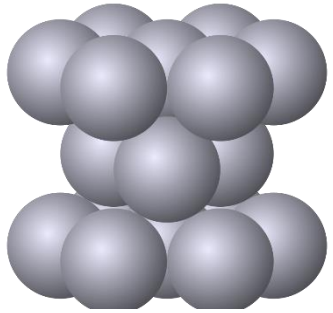
Icosahedral Cluster

1952

Frank, *P. ROY. SOC. A-MATH PHY*, **215,** 1120 (1952)

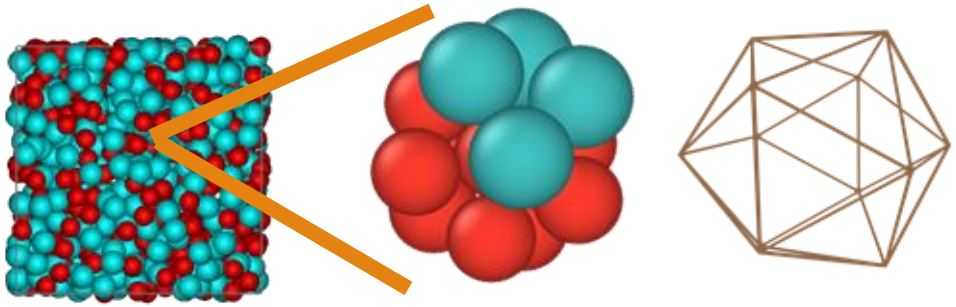


FCC



HCP

Local Structural Changes



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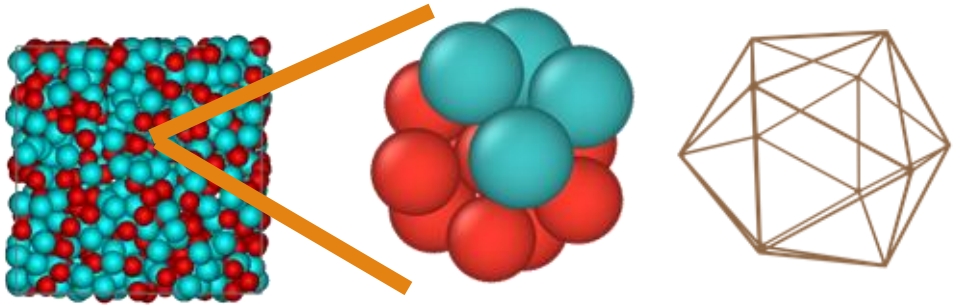

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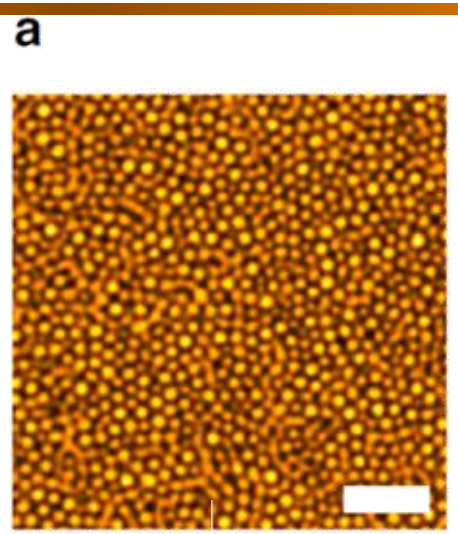

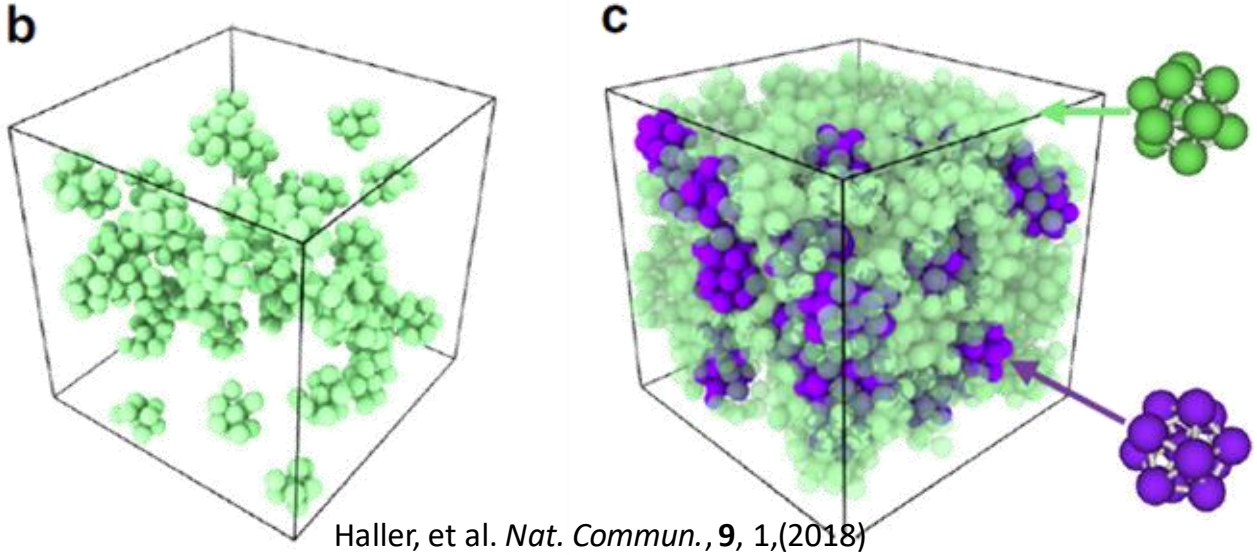

Defective Icosahedral Cluster

Icosahedral Cluster

Haller, et al. *Nat. Commun.*, **9**, 1,(2018)

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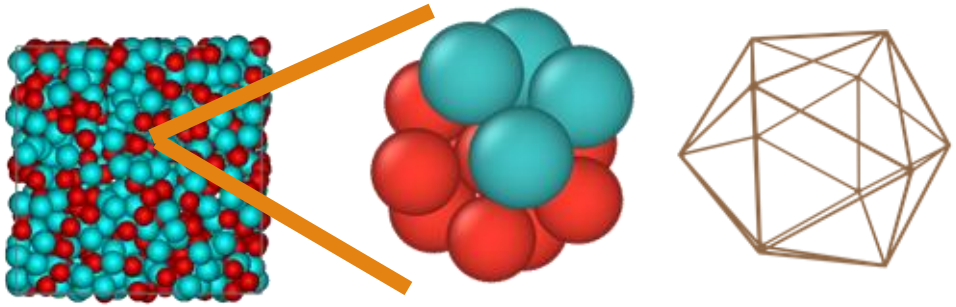

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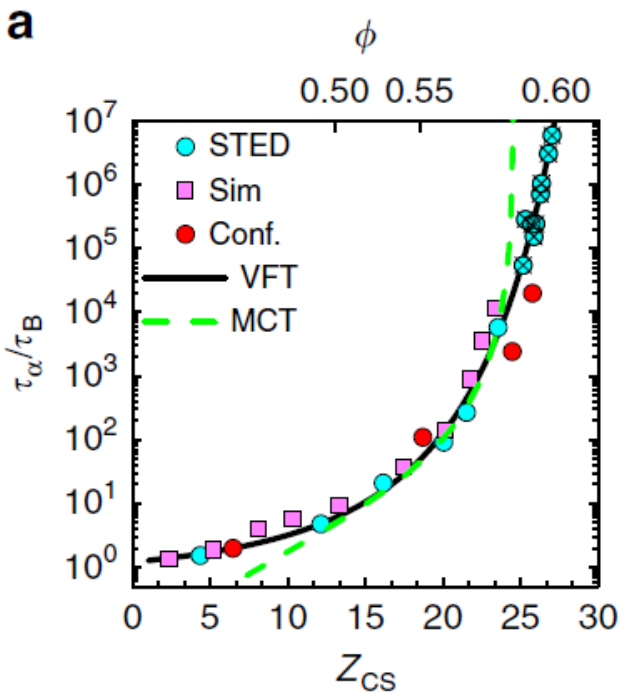

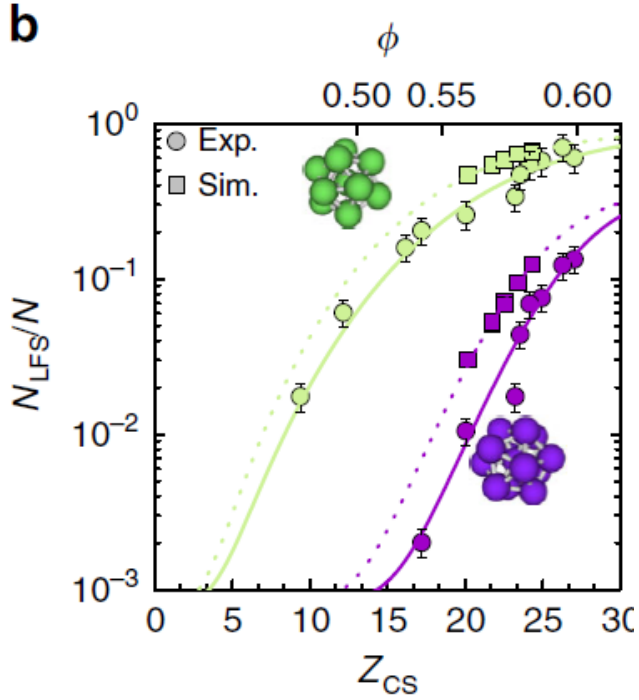

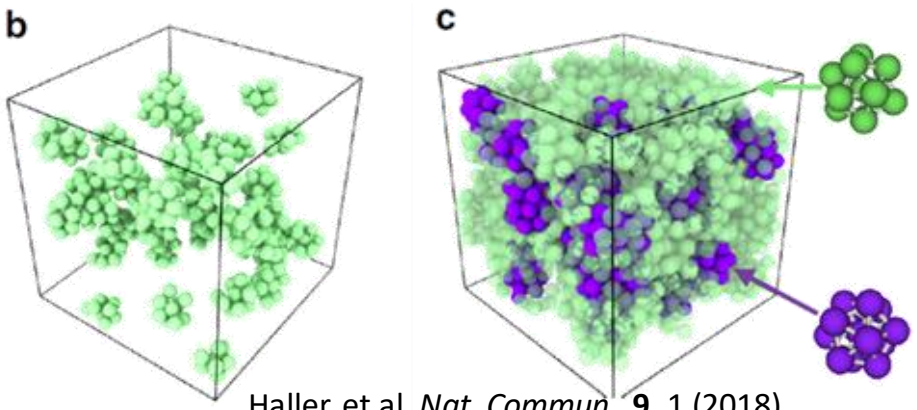

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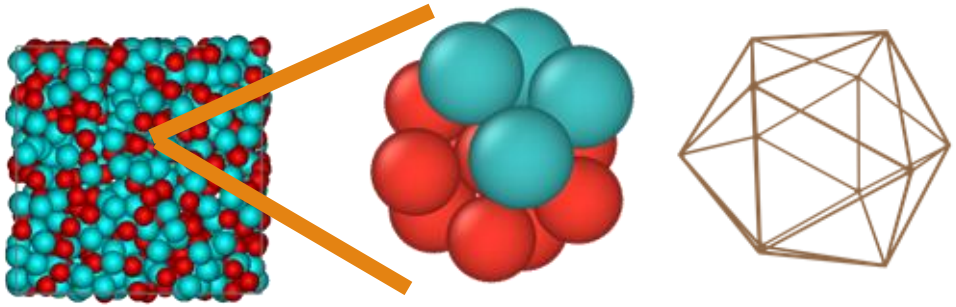

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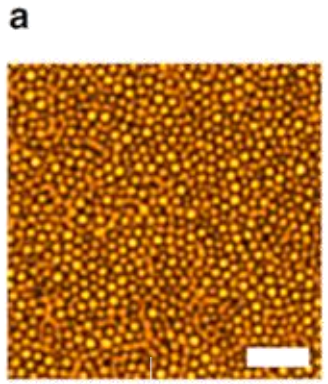

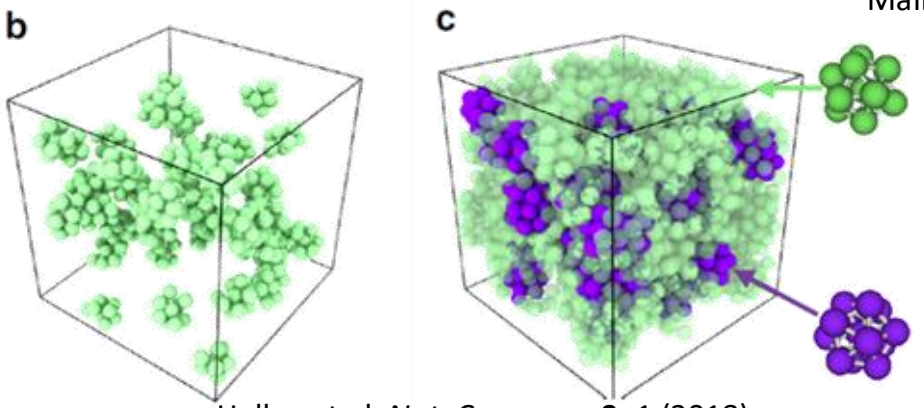

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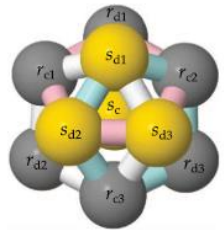
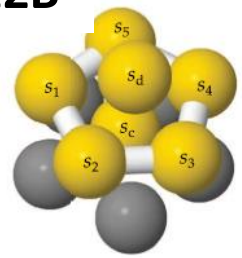
Other cluster with similar trends:

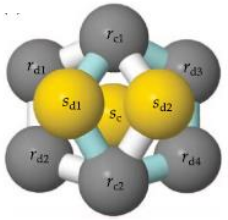
10B



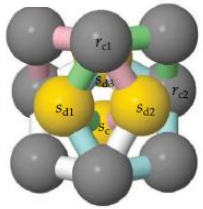
12B



9B



12D



Malins, et al. JCP **139**, 234506 (2013)

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How can we study glasses/supercooled liquids?

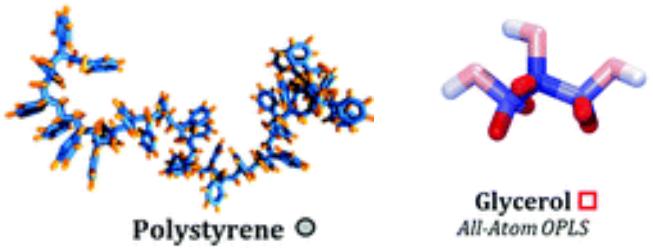
Simulations

- Molecular Dynamics
- Monte Carlo

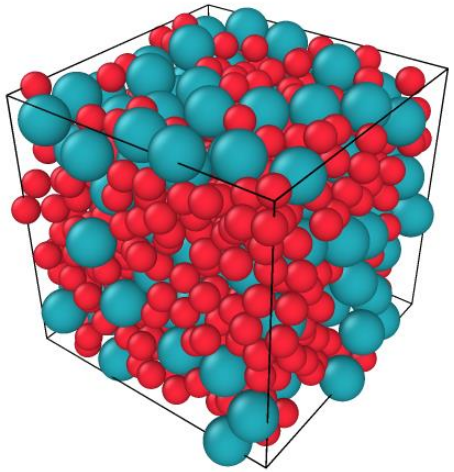
→ Interaction Potential

How the particles interact between each other

Atomistic models



Hung, et al. *Soft Matter*, **15**, 6,(2019)



Colloidal particles

- **Lennard-Jones**
- **Square-Well**
- **Hard-spheres**

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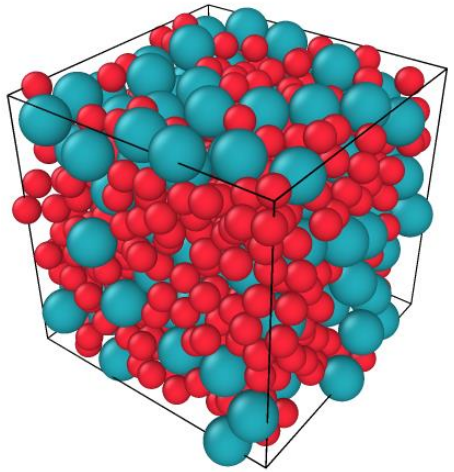

Colloidal particles

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Event-Driven Molecular Dynamics
EDMD

STEPS:

1. **Initial configuration (positions and velocities)**
2. **Find the next time where two particles will collide**
3. **Solve collision**
4. **Update velocities and positions**

How can we study glasses/supercooled liquids?

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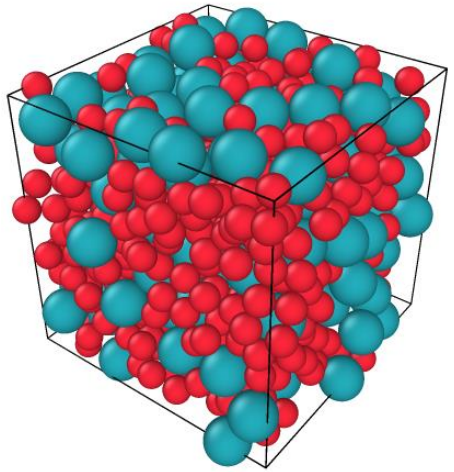

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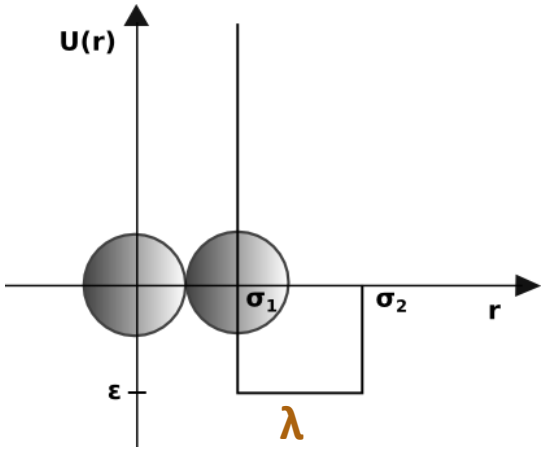
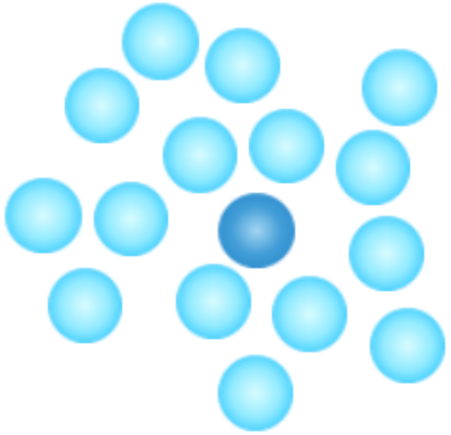


RESULTS:

- **Dynamical properties: diffusion coefficient, mean square displacement, relaxation times, ISF, …**
- **Static properties: S(q), g(r), compresibility…**

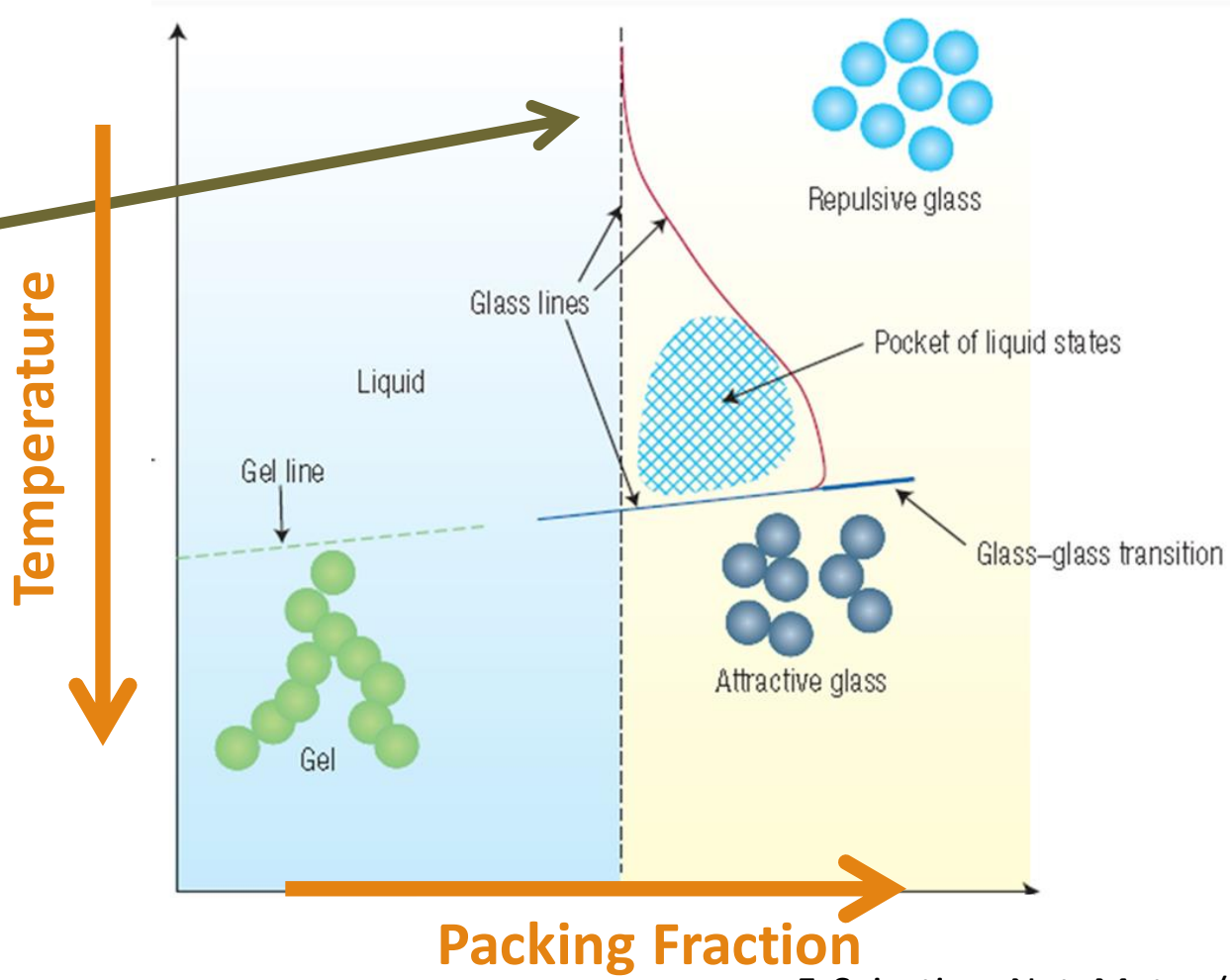
Short range potentials: Two glassy states

Repulsive glass:



Temperature

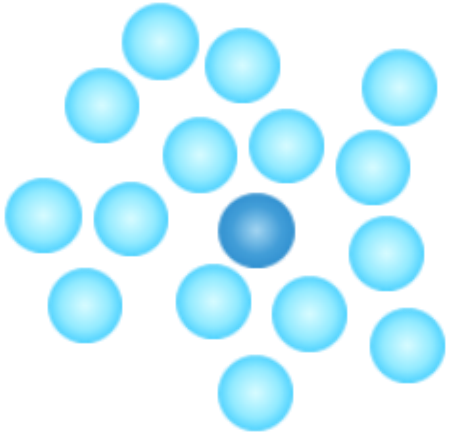
Particles trapped by **repulsions** from their neighbors.



F. Sciortino, Nat. Mater. (2002)

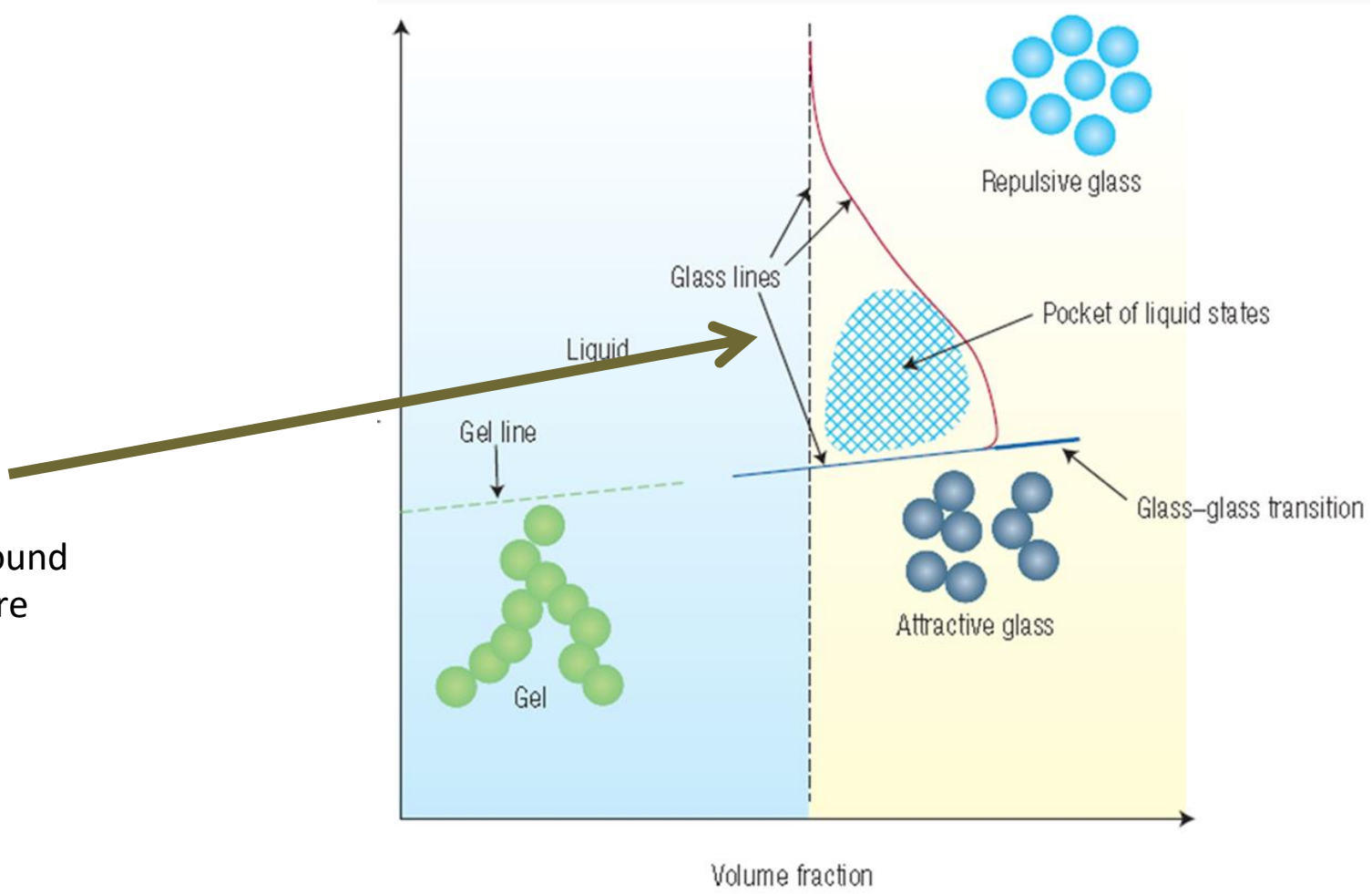
Short range potentials: Two glassy states

Intermediate fluid:



Temperature

Some particles tightly bound to neighbors, others more **free to move**.



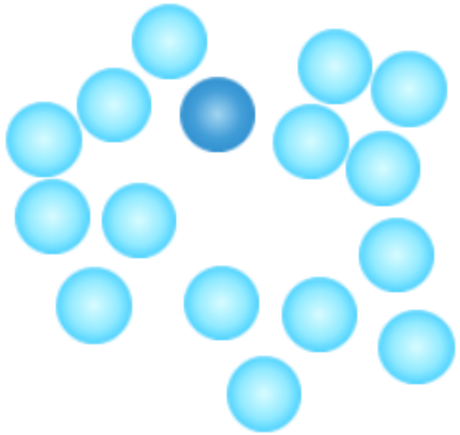
F. Sciortino, Nat. Mater. (2002)

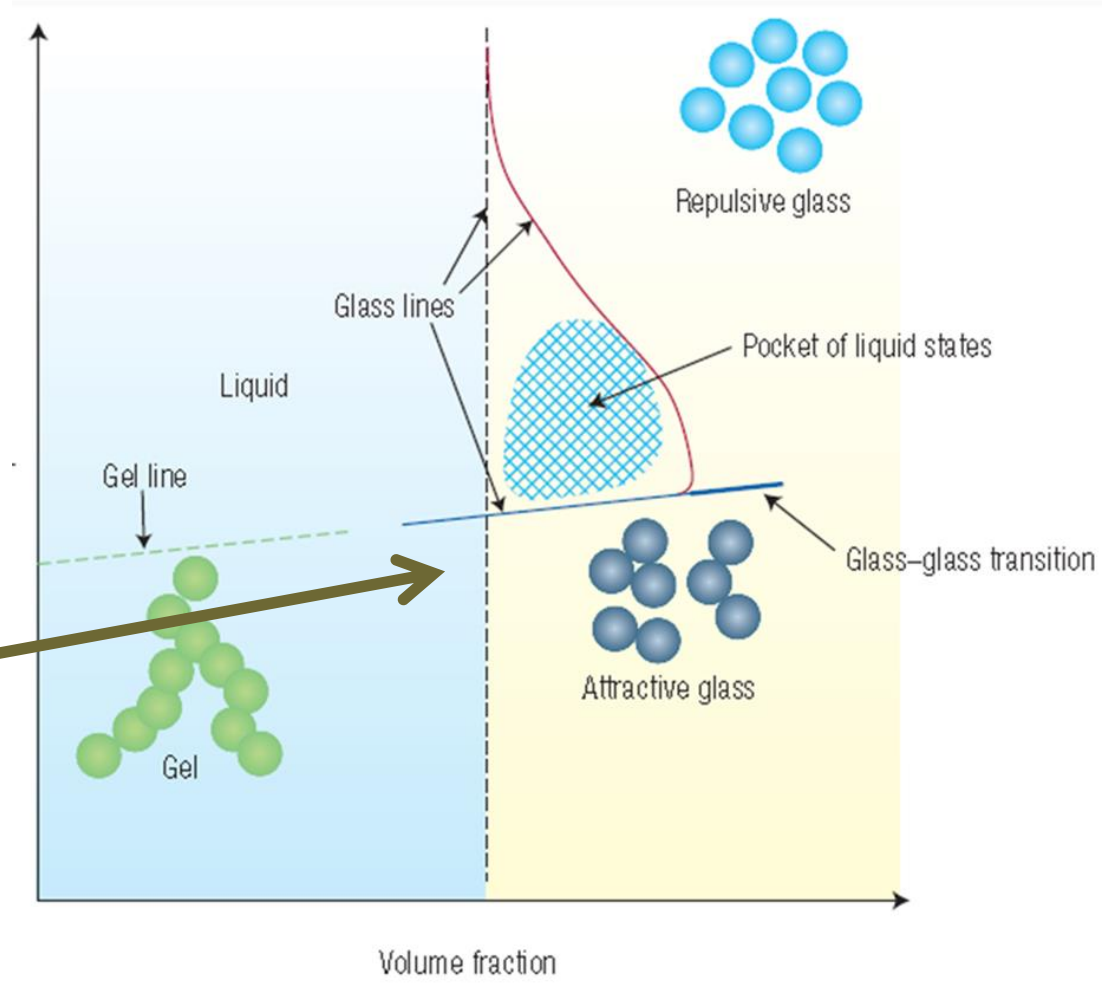
Short range potentials: Two glassy states

Temperature

Attractive glass:

Particles trapped by **attractions** to their neighbors.





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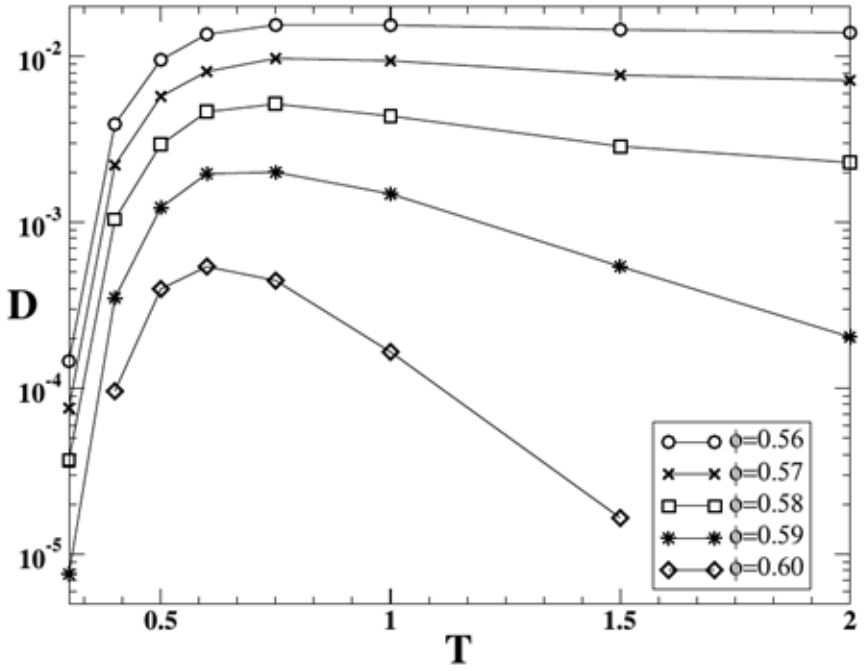
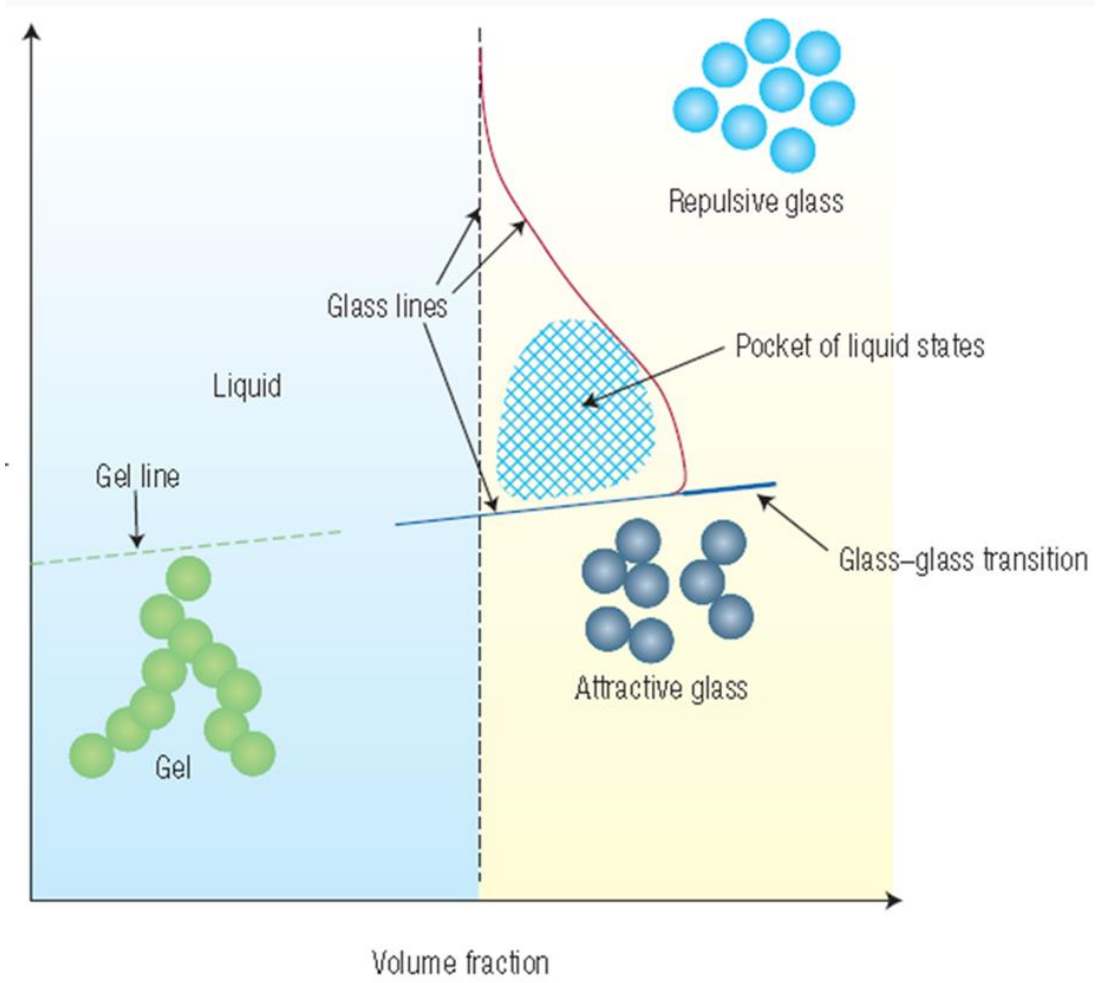
Short range potentials: Two glassy states



Temperature

Zaccarelli *et al.*, PRE **66**, 041402 (2002)



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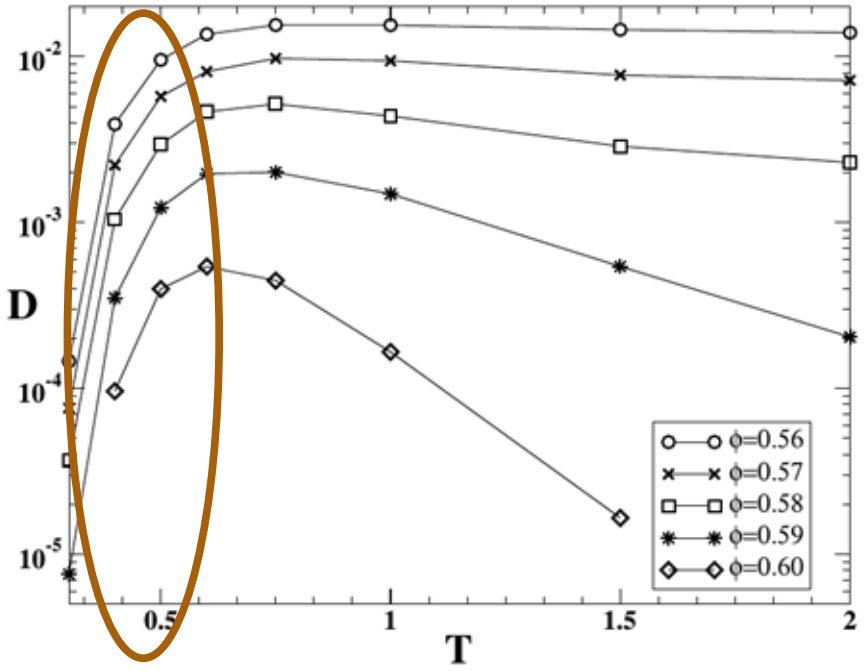
Short range potentials: Two glassy states

Attractive



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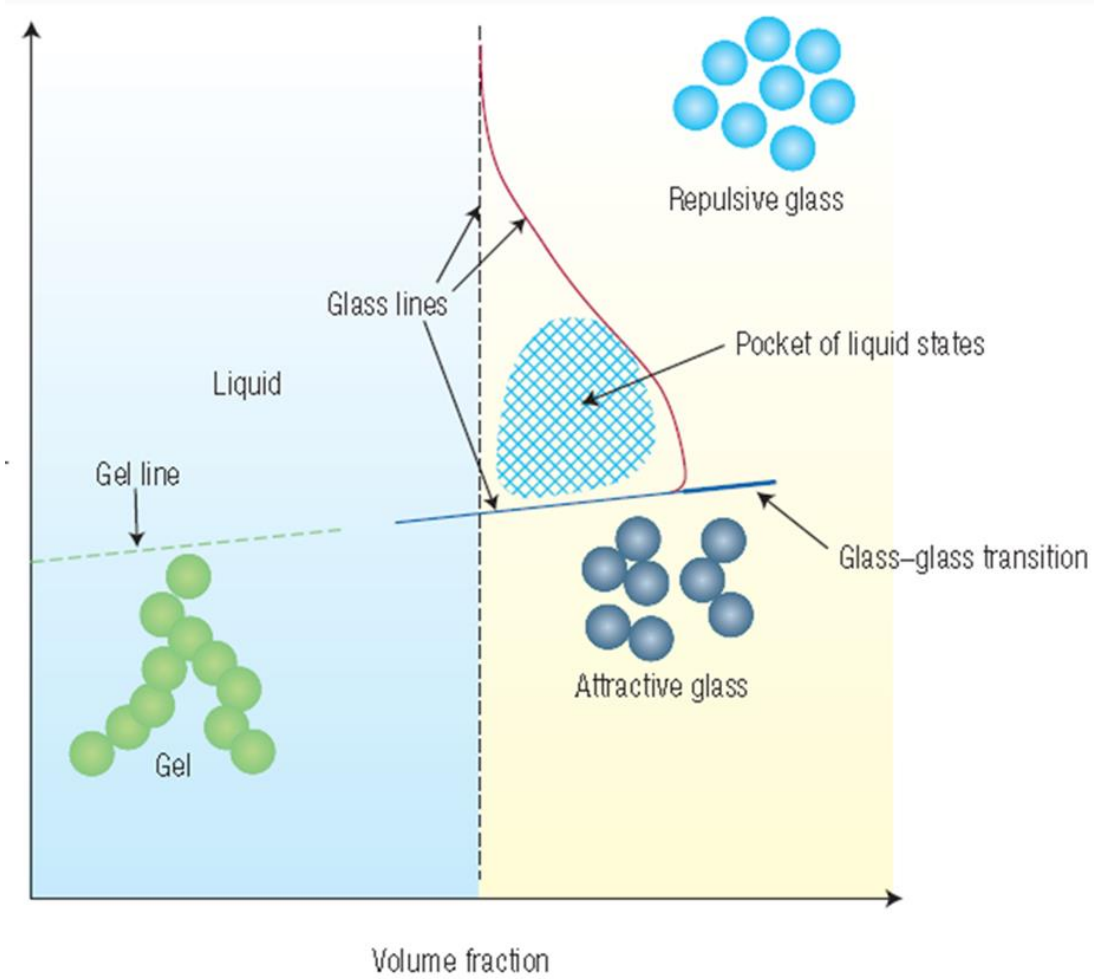

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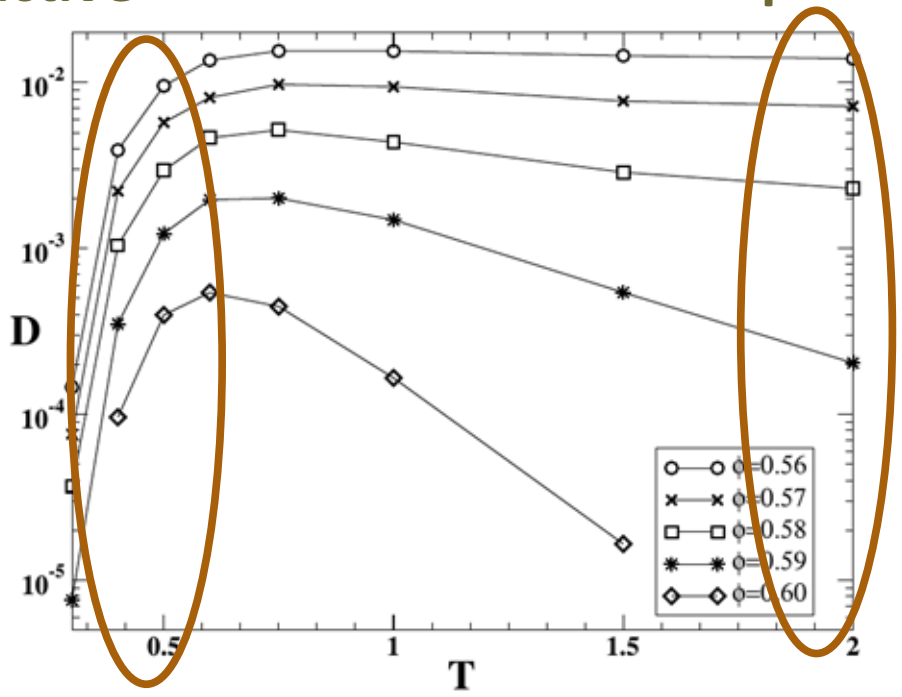
Short range potentials: Two glassy states

Attractive **Repulsive**



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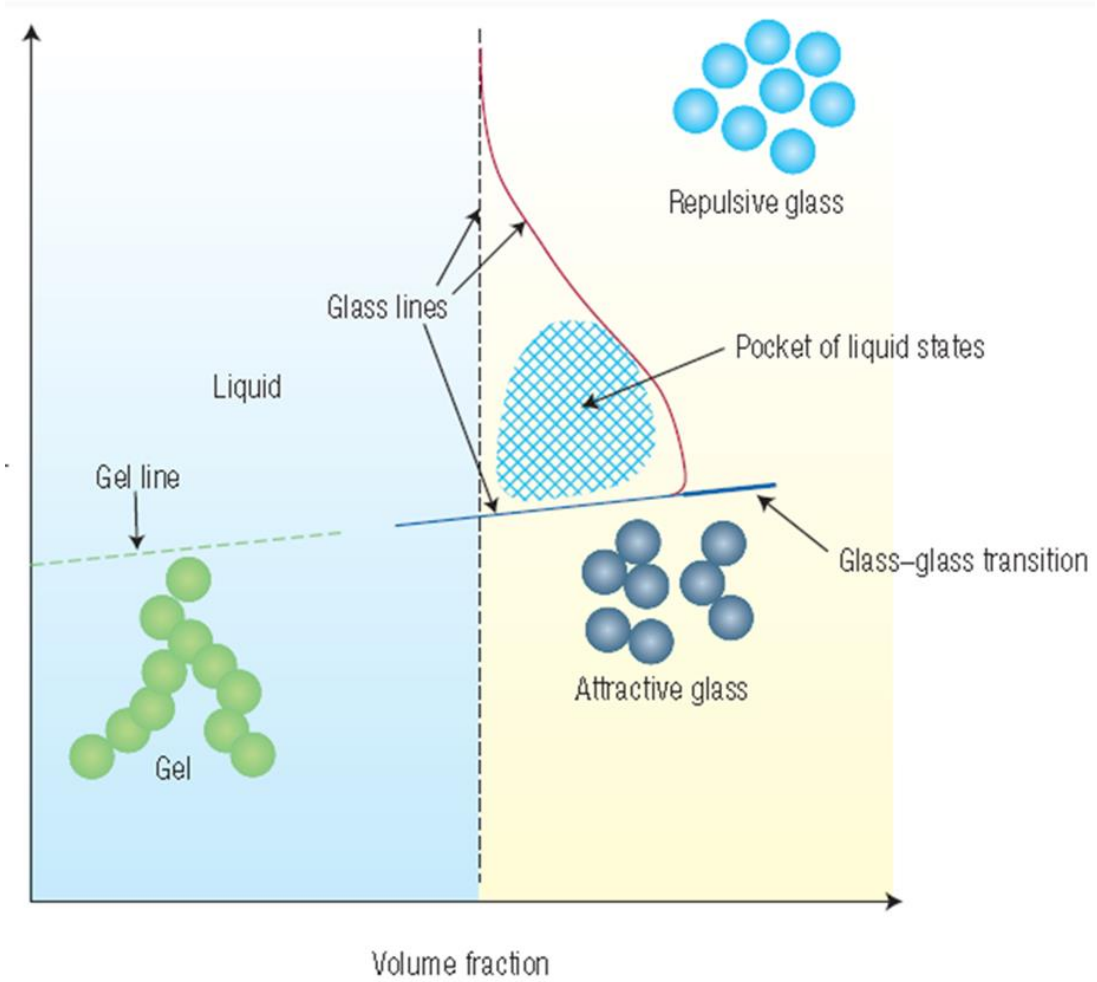
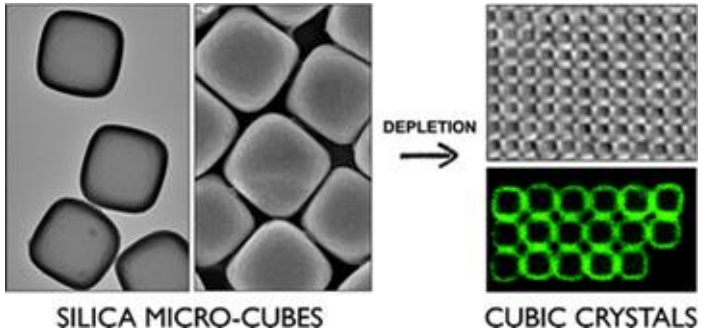


F. Sciortino, Nat. Mater. (2002)

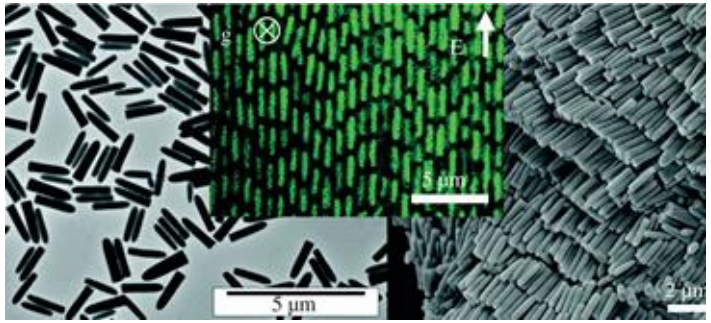
How to control dynamics (or local structure)?

Colloids: ideal playground for studying glasses.

Shape

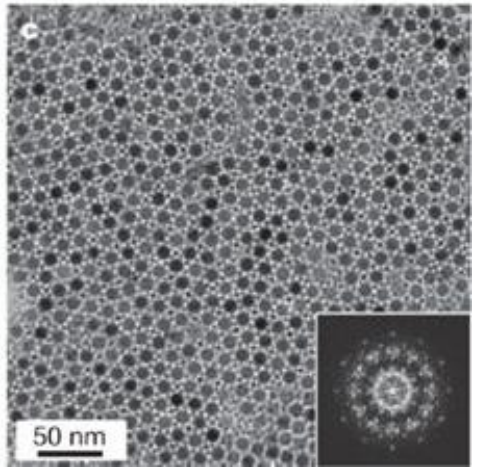


Rossi *et al.*, Soft Matter **7**, 4139 (2011)



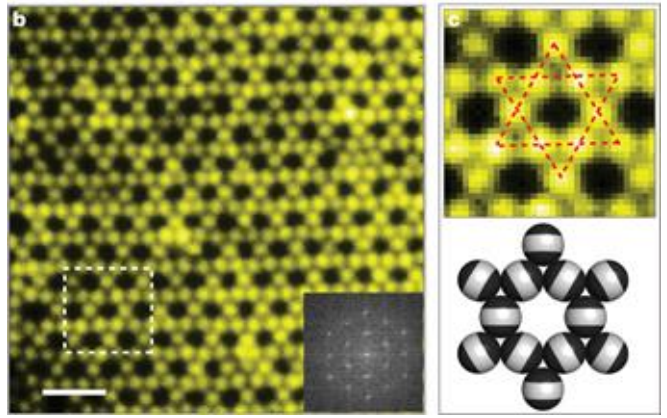
Kuijk *et al.*, J. Am. Chem. Soc. **133**, 2346 (2011)

Size distribution

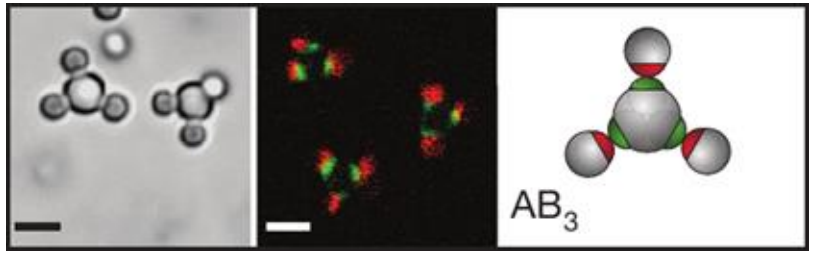


Talapin *et al.*, Nature **461**, 964 (2009)

Surface chemistry



Chen *et al.*, Nature **469**, 381 (2011)



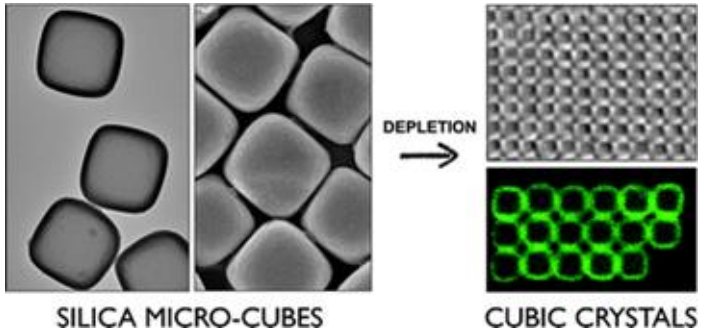
Y. Wang *et al.*, Nature **491**, 51 (2012)

What about the glassy regime?

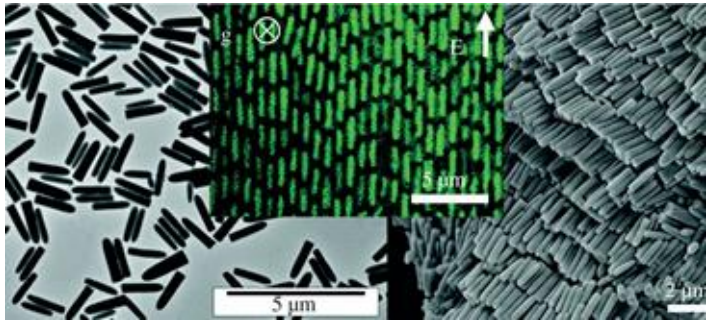
How to control dynamics (or local structure)?

Colloids: ideal playground for studying glasses.

Shape



Rossi *et al.*, Soft Matter **7**, 4139 (2011)



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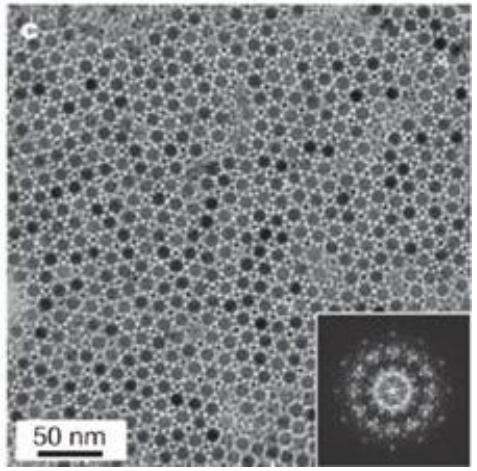
Size distribution



Talapin *et al.*,
Nature **461**,
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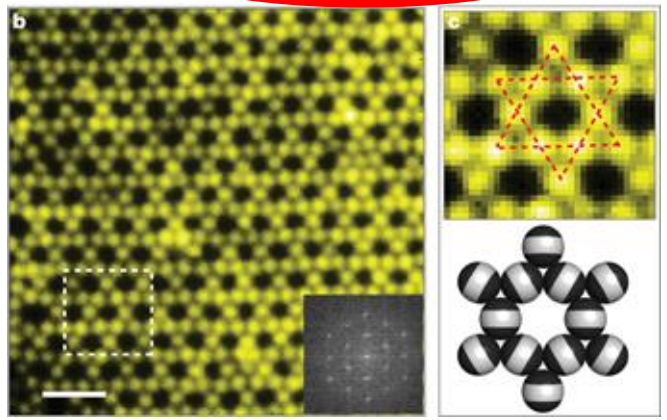
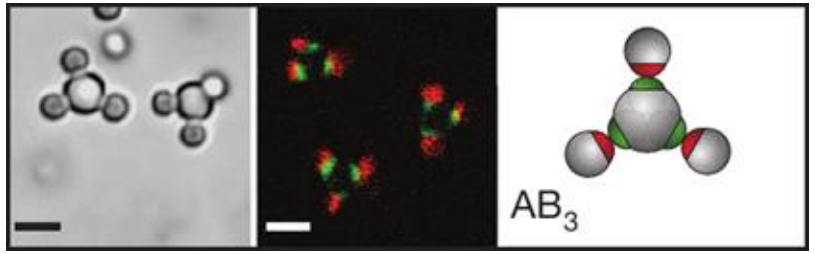
Surface chemistry



Chen *et al.*, Nature **469**, 381 (2011)



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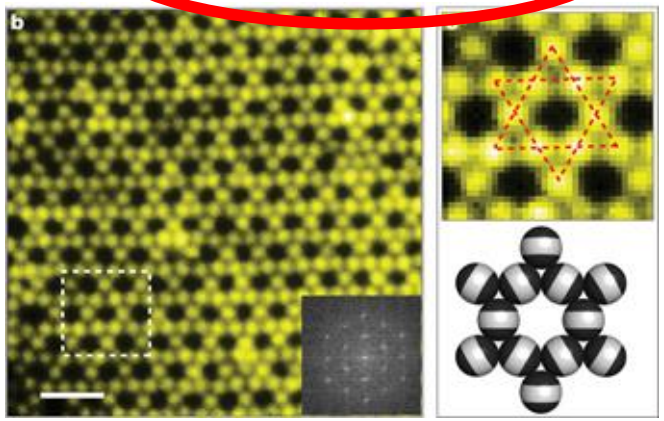
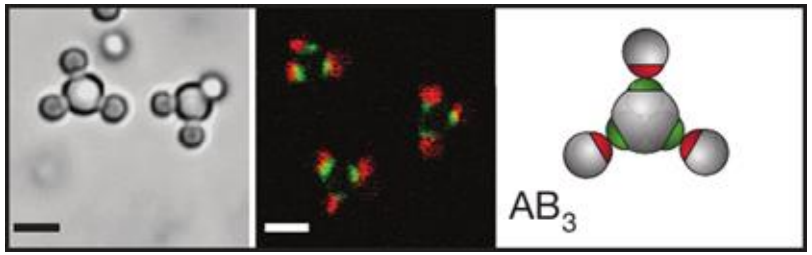


Chen *et al.*, Nature **469**, 381 (2011)

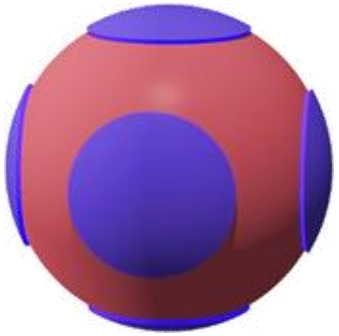


Y. Wang *et al.*, Nature **491**, 51 (2012)

How to modify the cage?

Patchy Particles

Directional Interactions



→ Kern-Frenkel Model

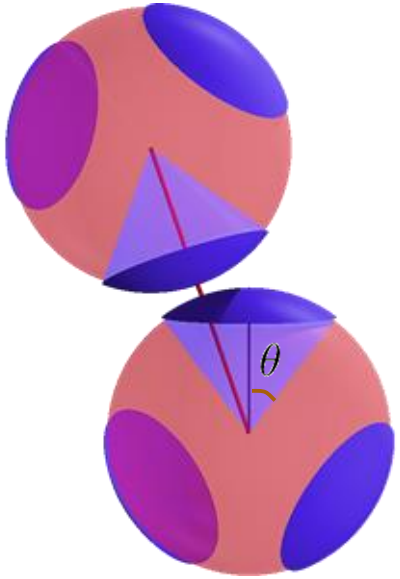
$$U_{ij}(\mathbf{r}_{ij}) = \begin{cases} -\epsilon & \begin{cases} \text{for any two patches face to face and,} \\ r_{ij} \leq \lambda \end{cases} \\ 0 \end{cases}$$

Hard spheres decorated with **attractive square-well patches** on the surface.

Two particles bond when:

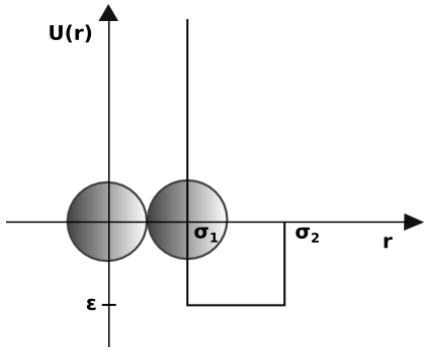
- The distance between them is less than the potential range.

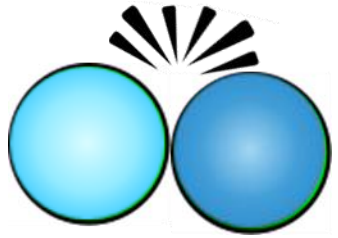
- The line connecting them goes through a patch on both surfaces.



How to?

Event-Driven Molecular Dynamics



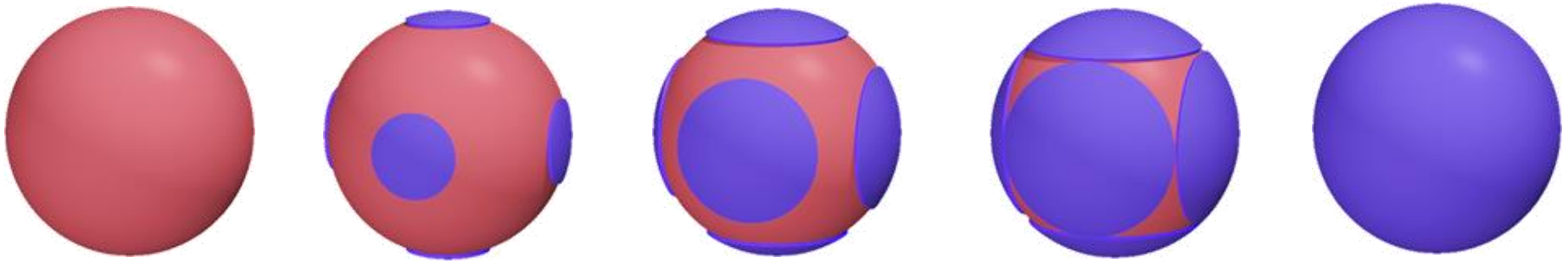


- Binary mixture
- N= 700
- λ=1.03σ
- q=0.833 (size ratio)

Change patch size

Hard sphere

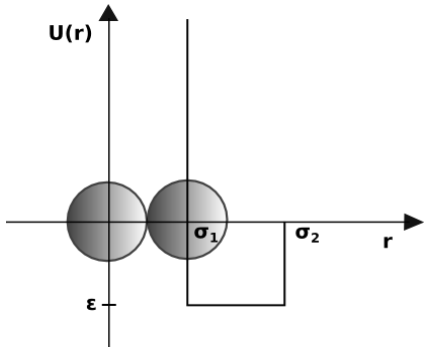
Square well

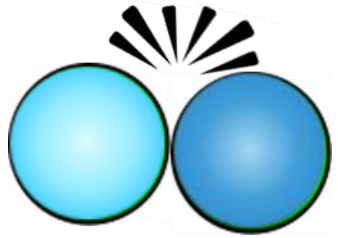


Increasing patch size (θ)

How to?

Event-Driven Molecular Dynamics





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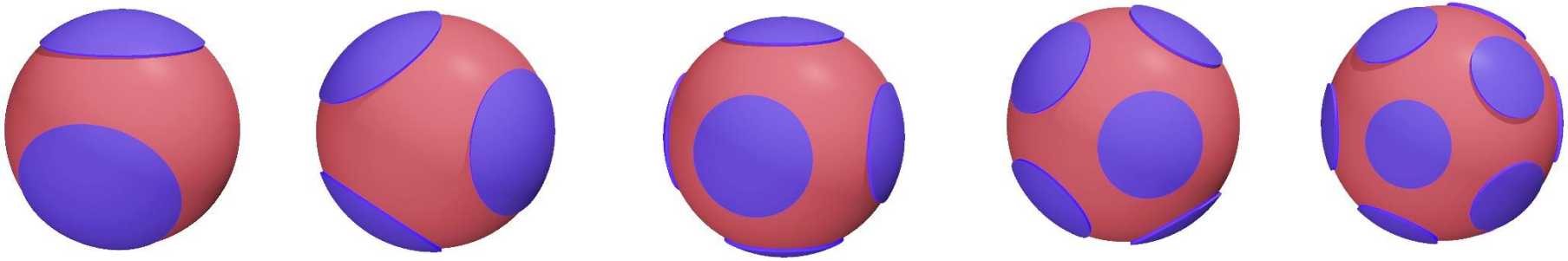
Change patch geometry



n = 3 (Triangle)

n = 4 (Tetrahedron)

n= 6 (Octahedron)

n = 8 (Rotated square prism)

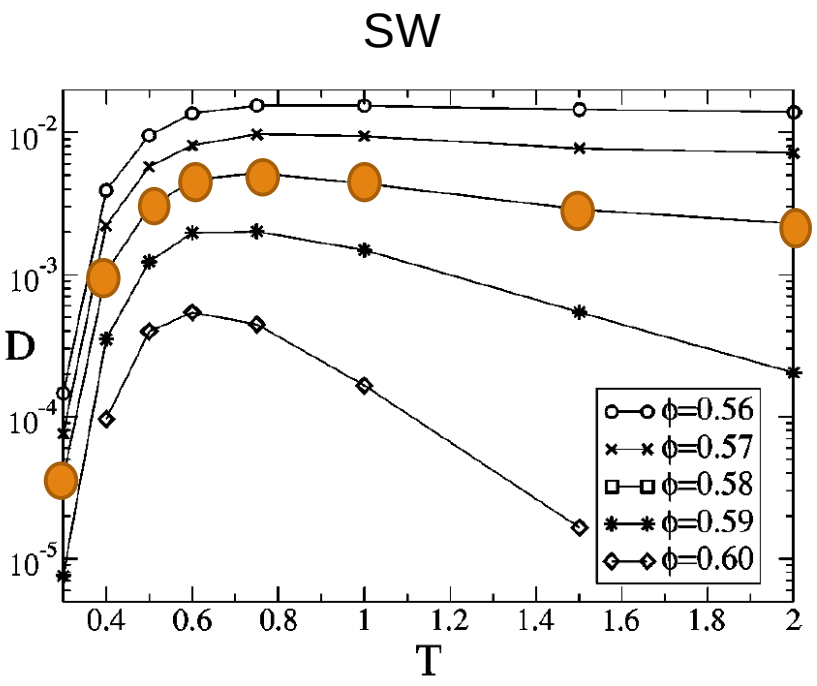
n = 12 (Icosahedron)

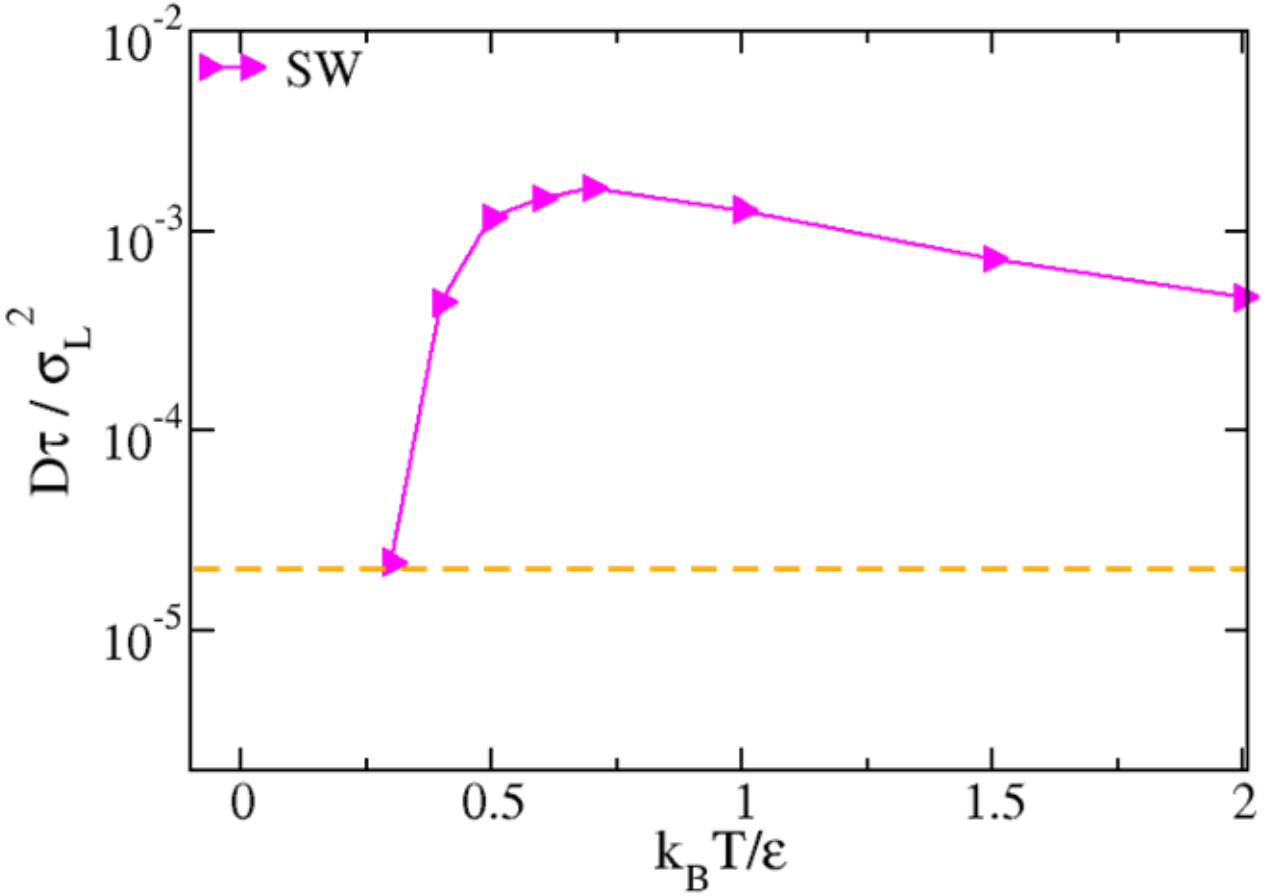
Increasing number of patches (n)

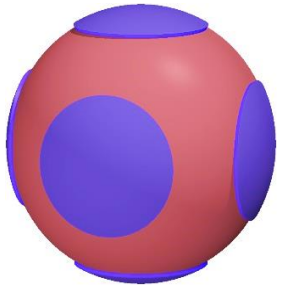
Reentrance in patchy particle systems

Reentrance remains intact for patchy interactions.

η=0.58







6 patches
(Octahedron)

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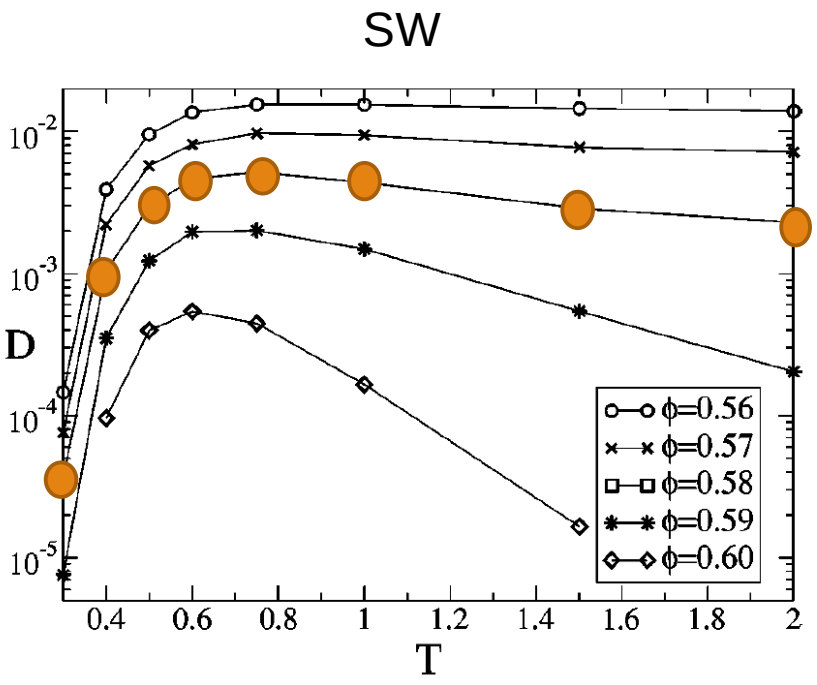

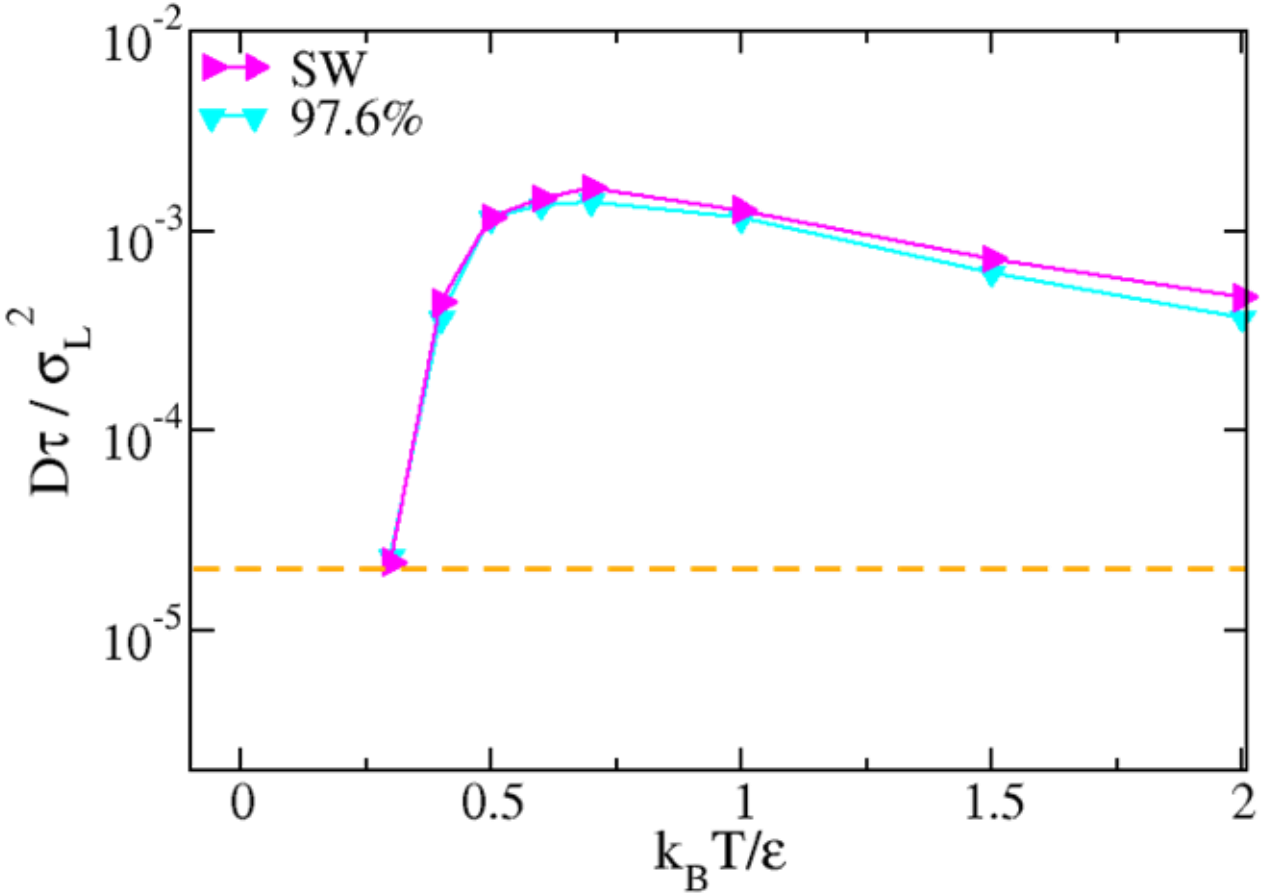

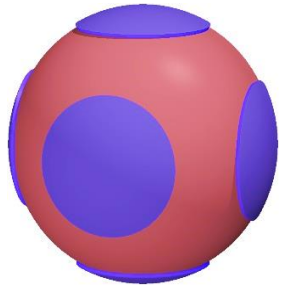

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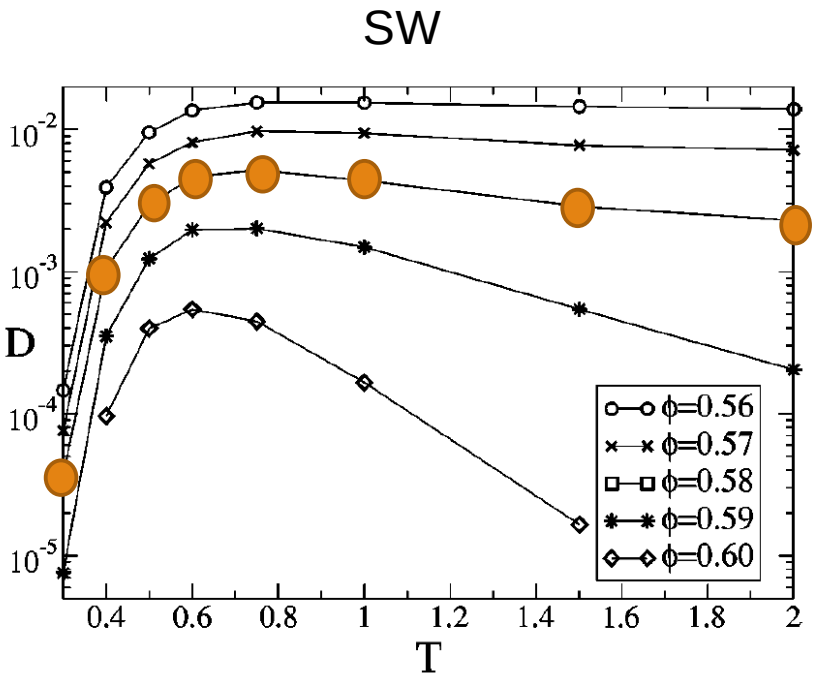

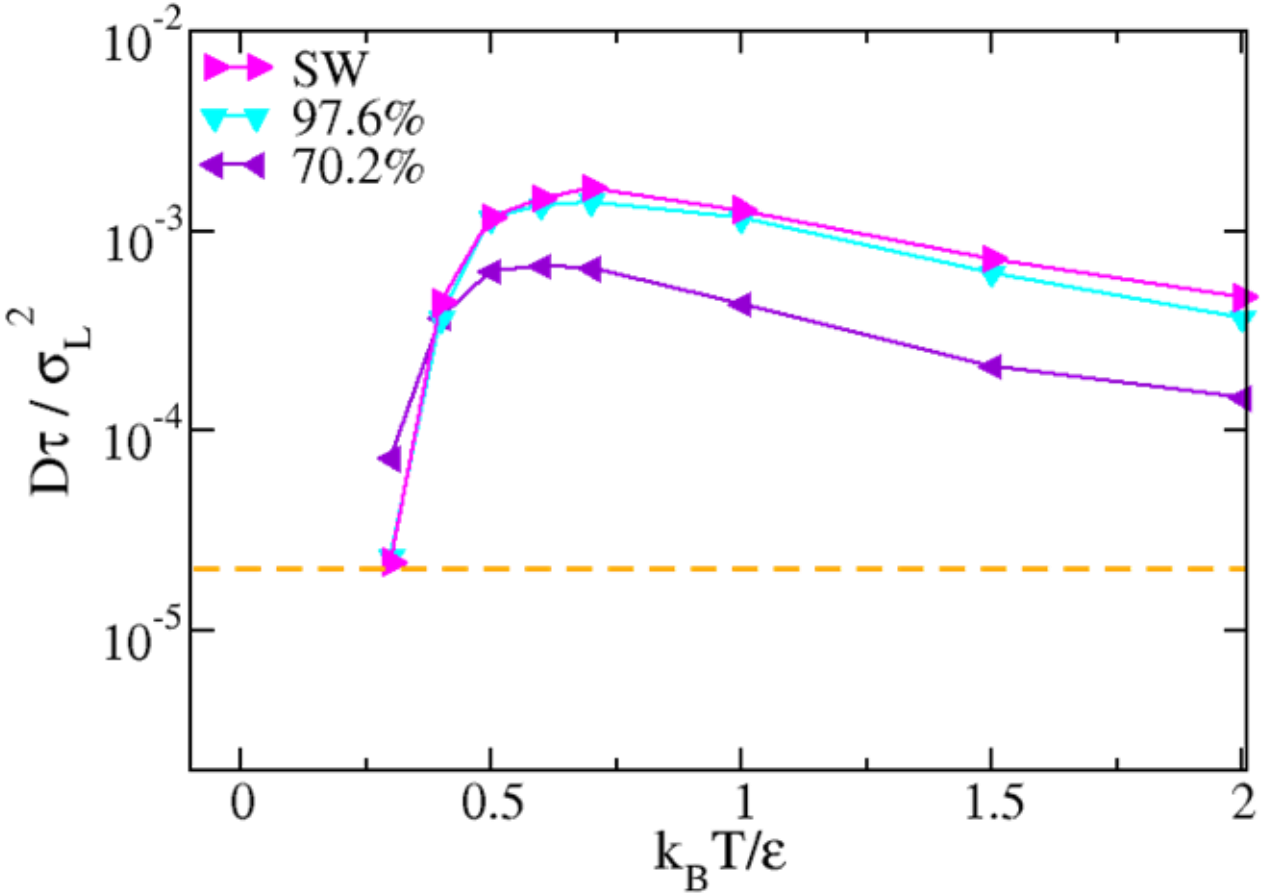

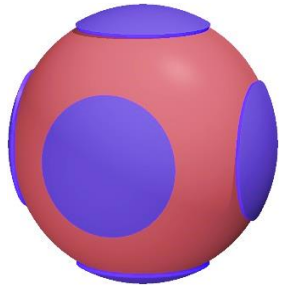

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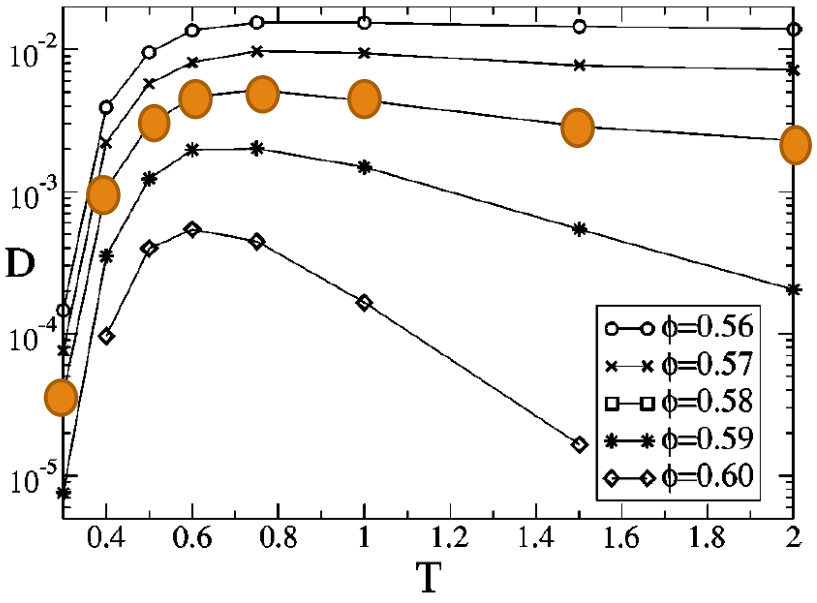
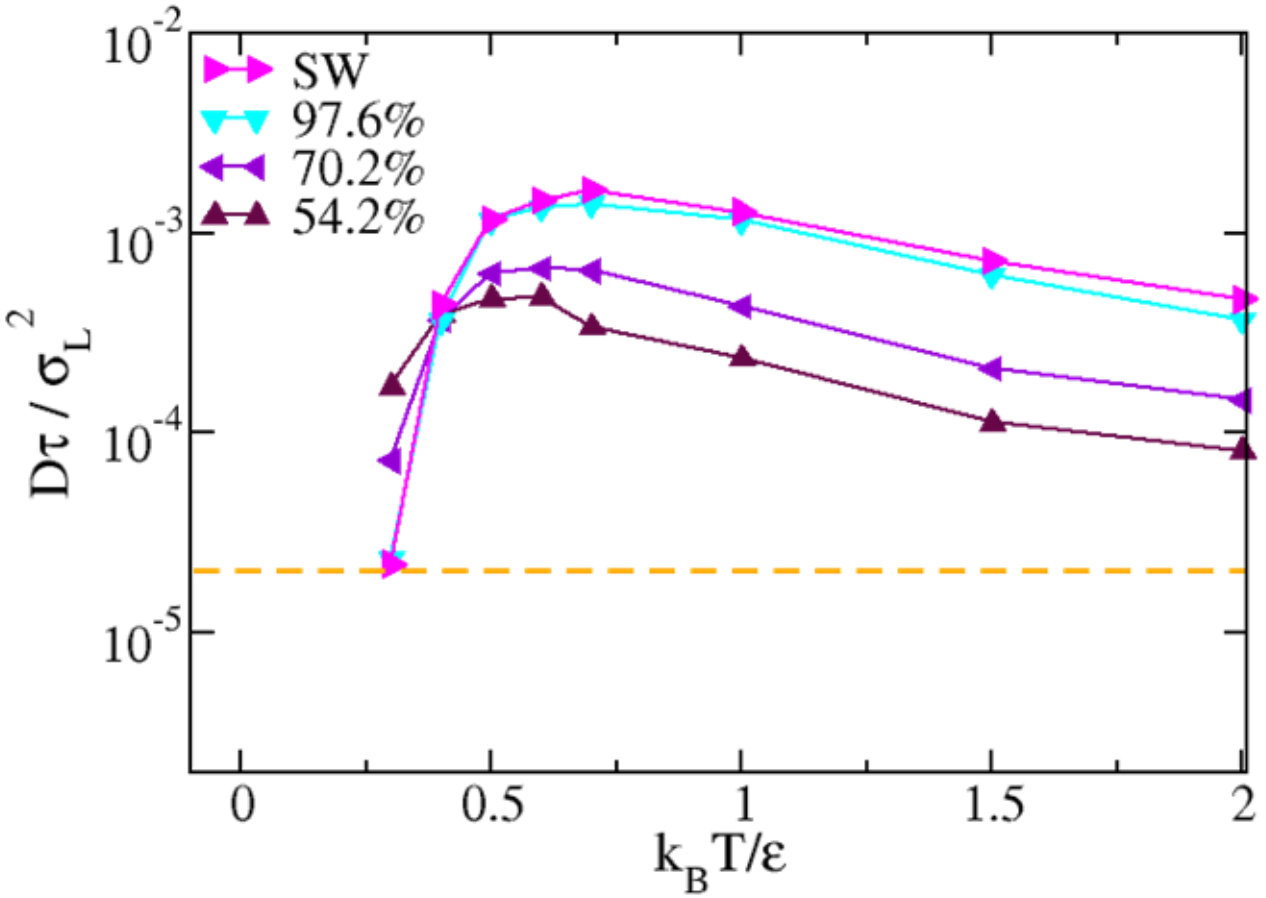
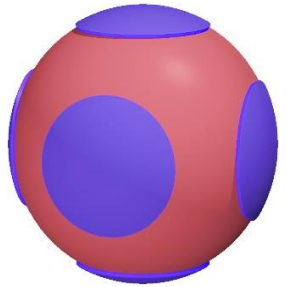
SW







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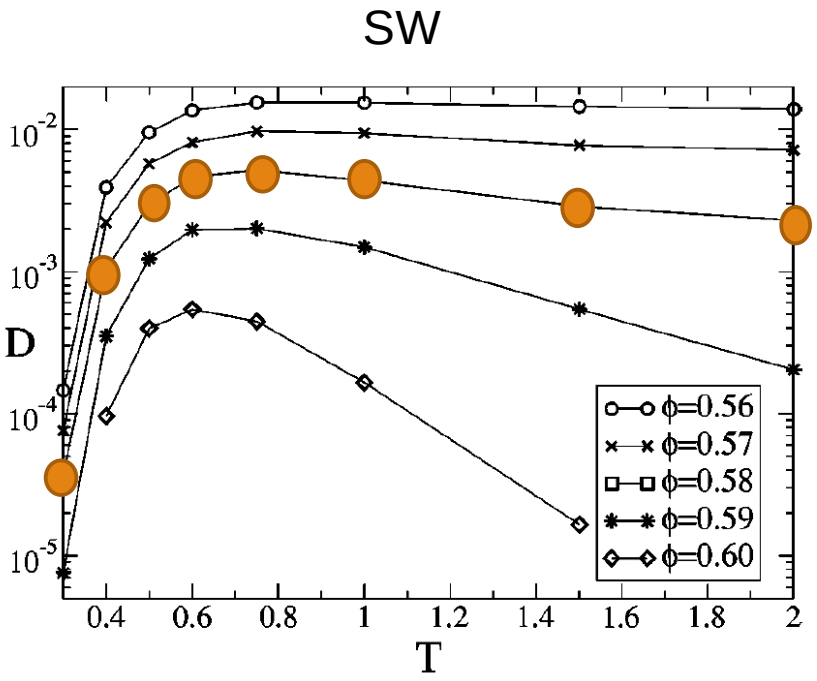

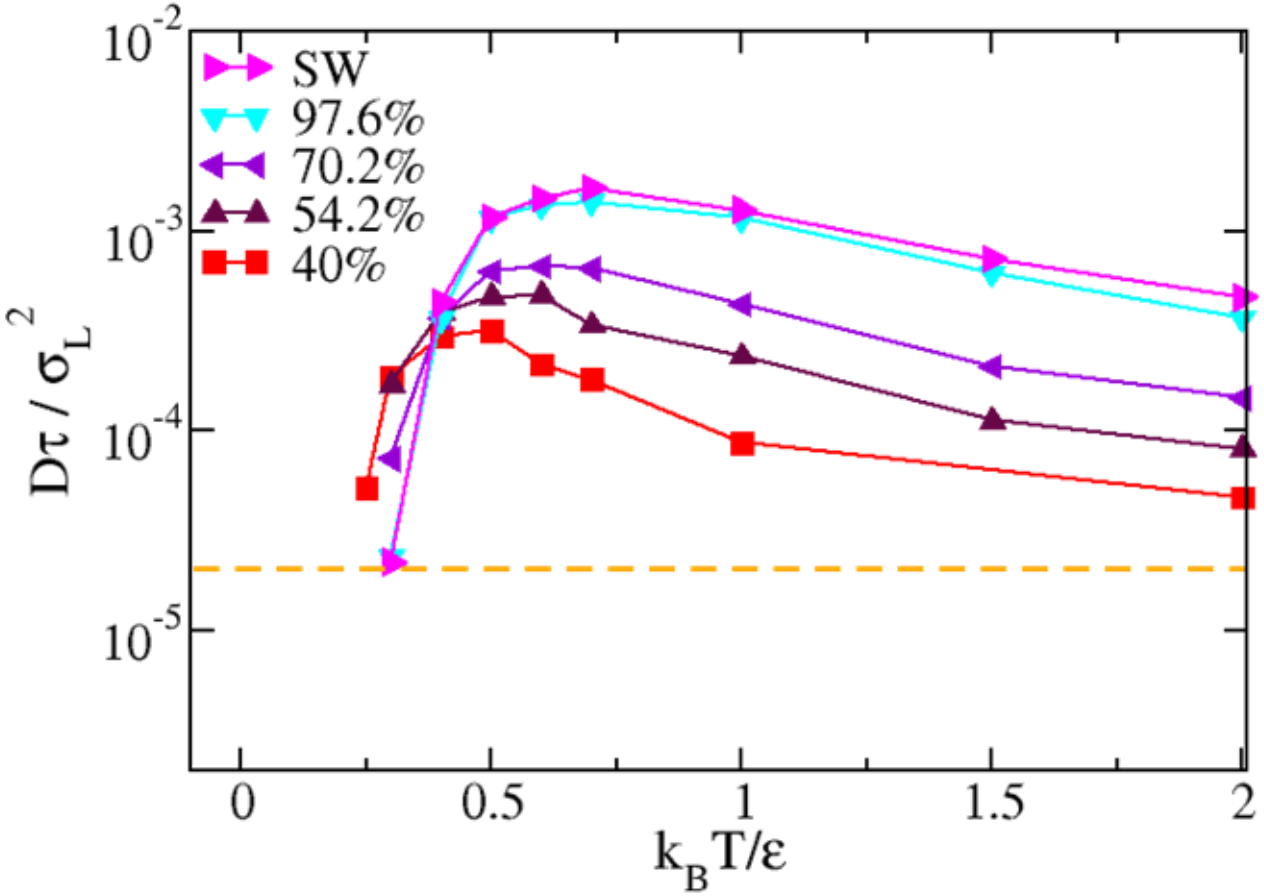

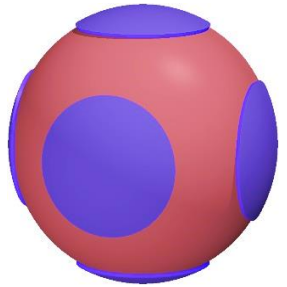

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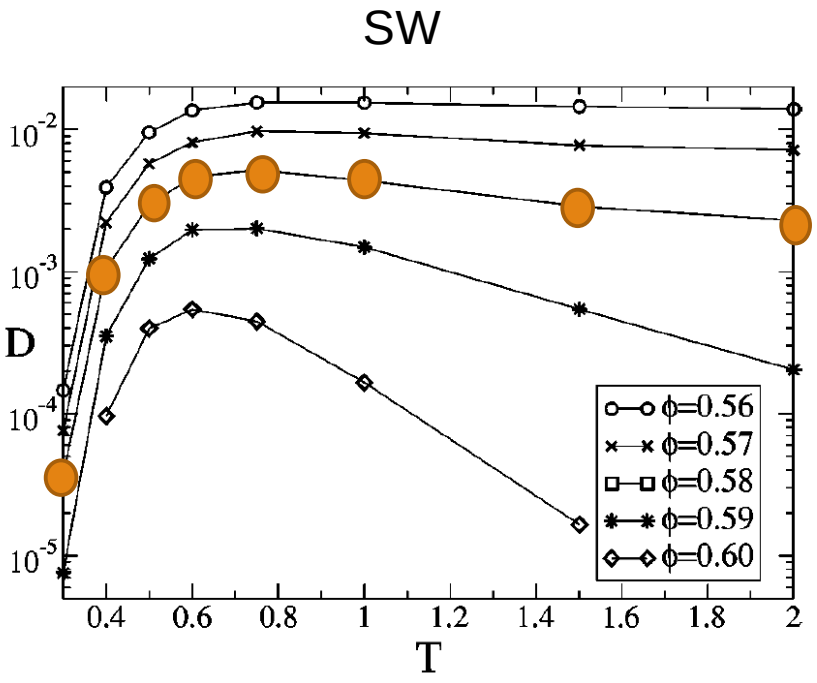

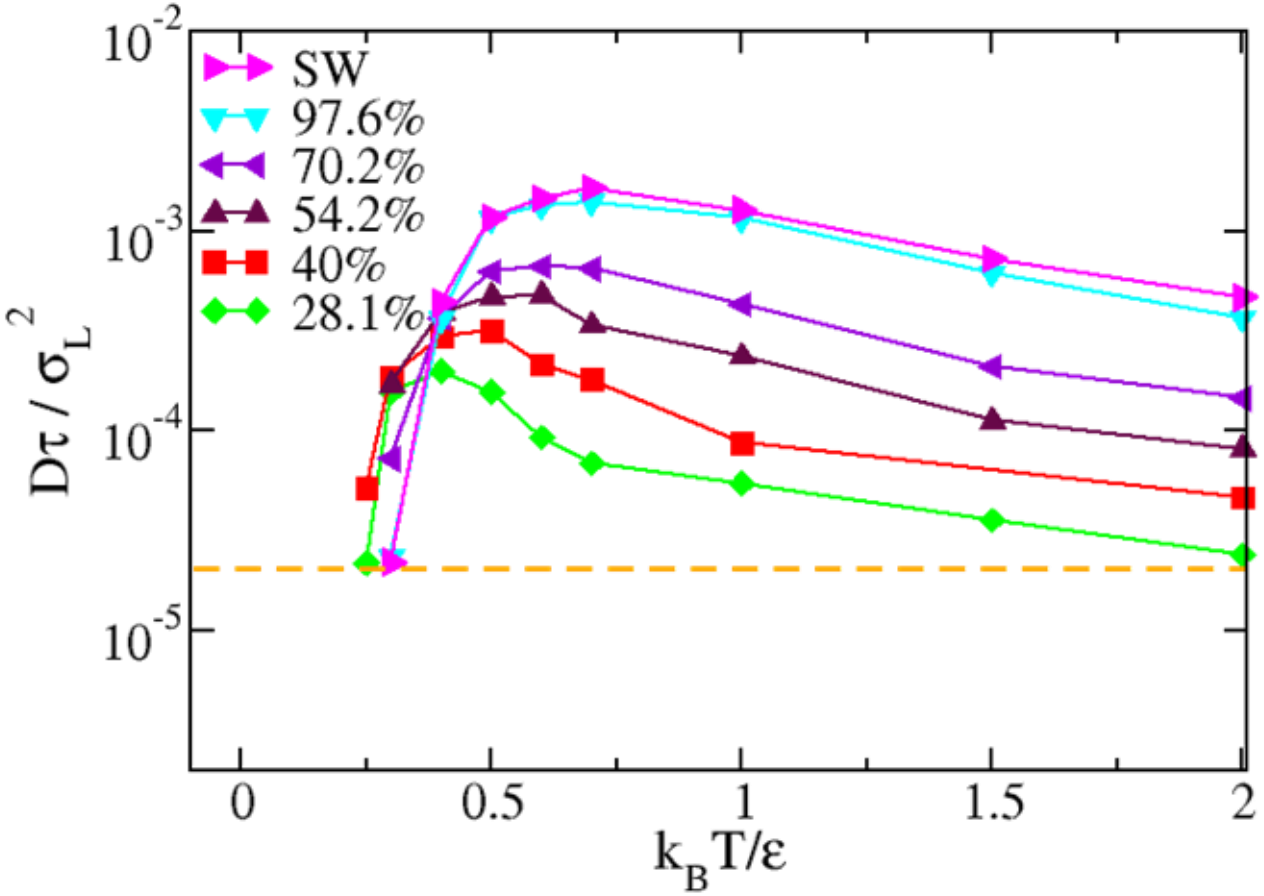

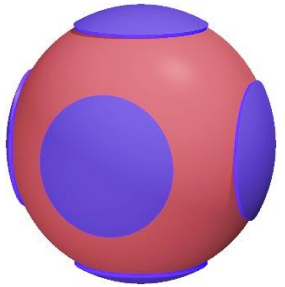

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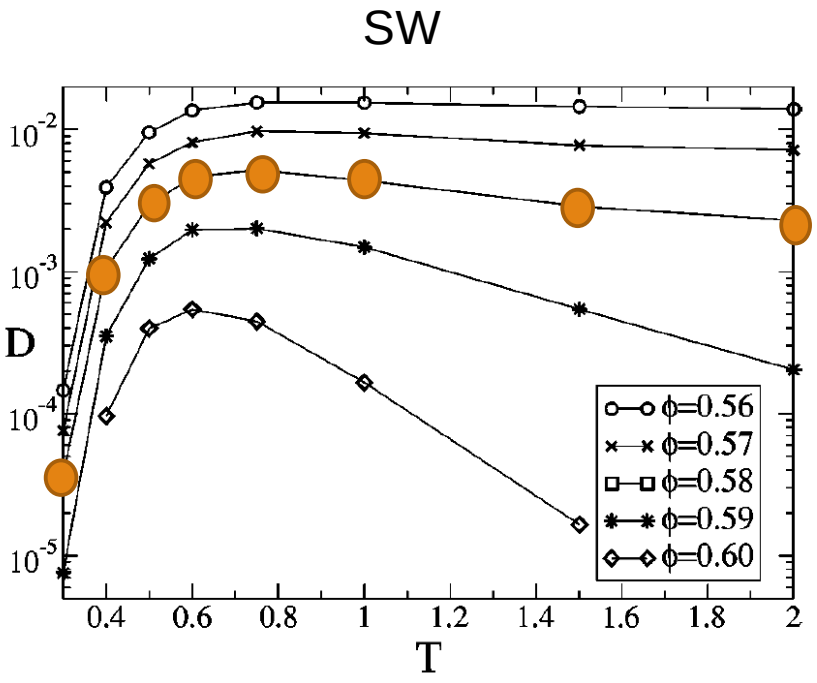

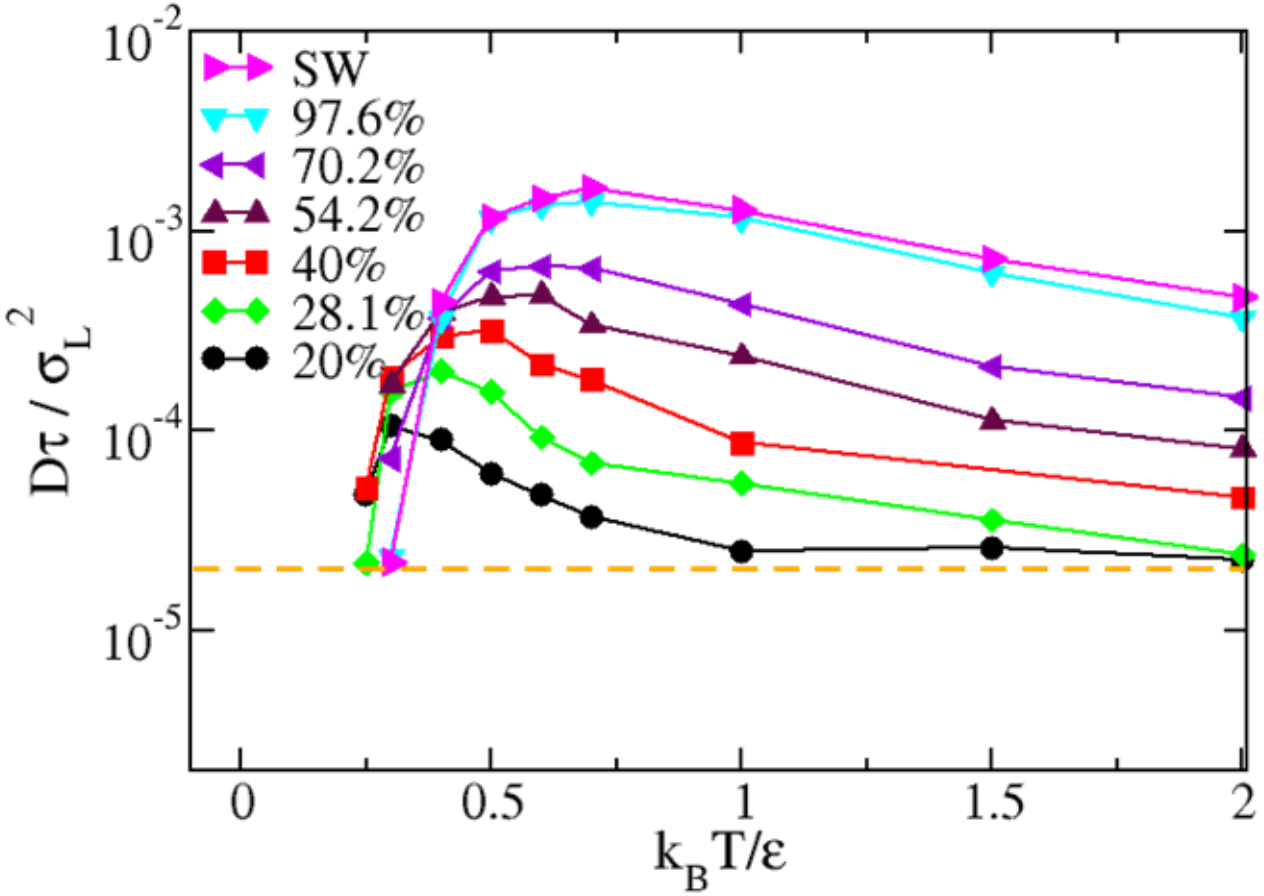

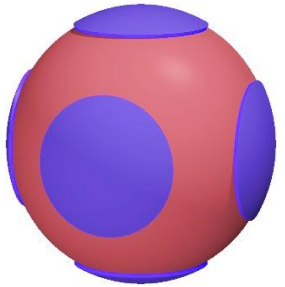

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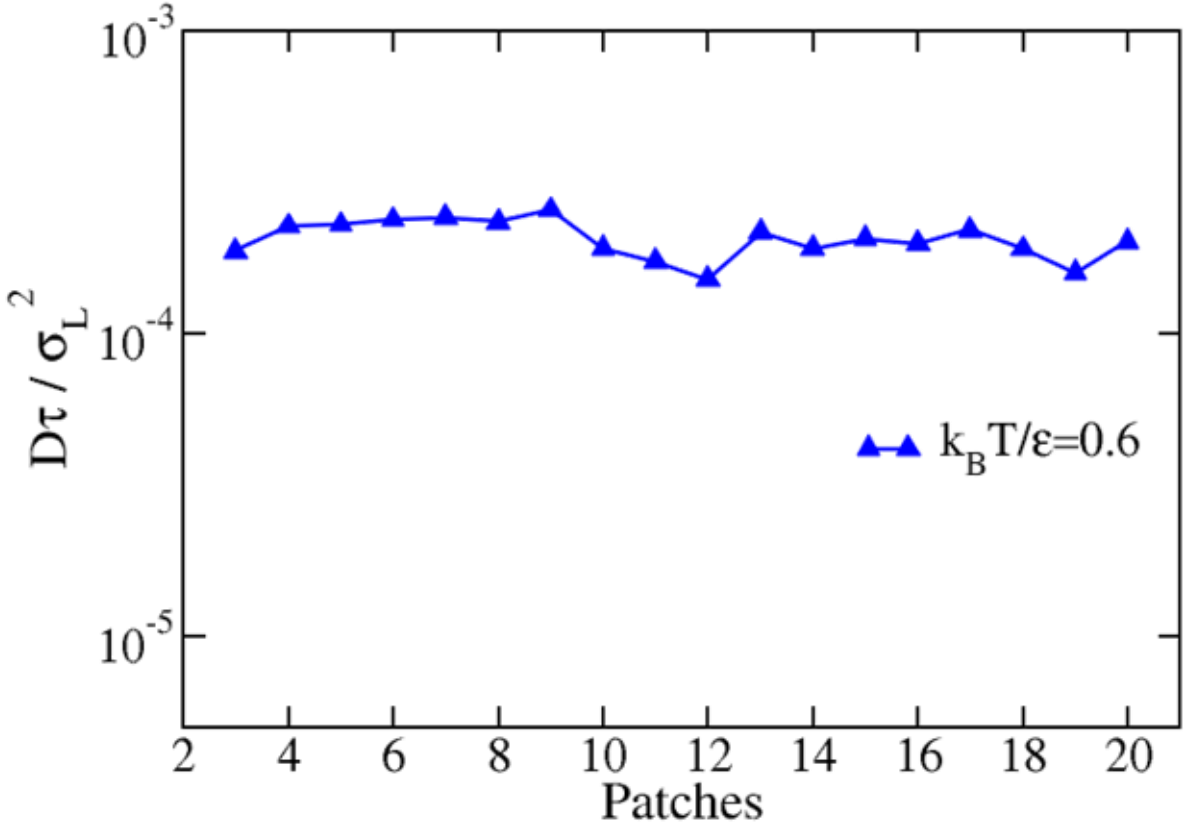
(Octahedron)

What is the behavior with different geometries?

Fixed surface coverage of 40%



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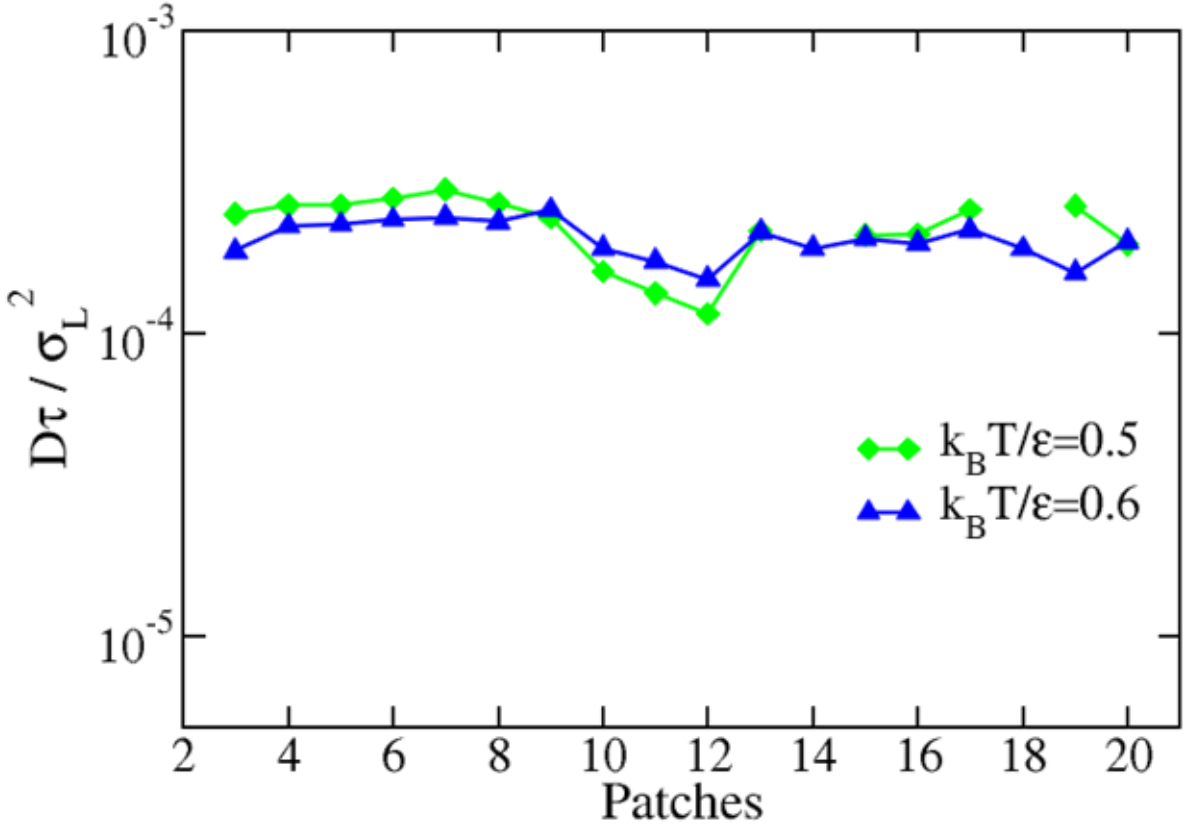

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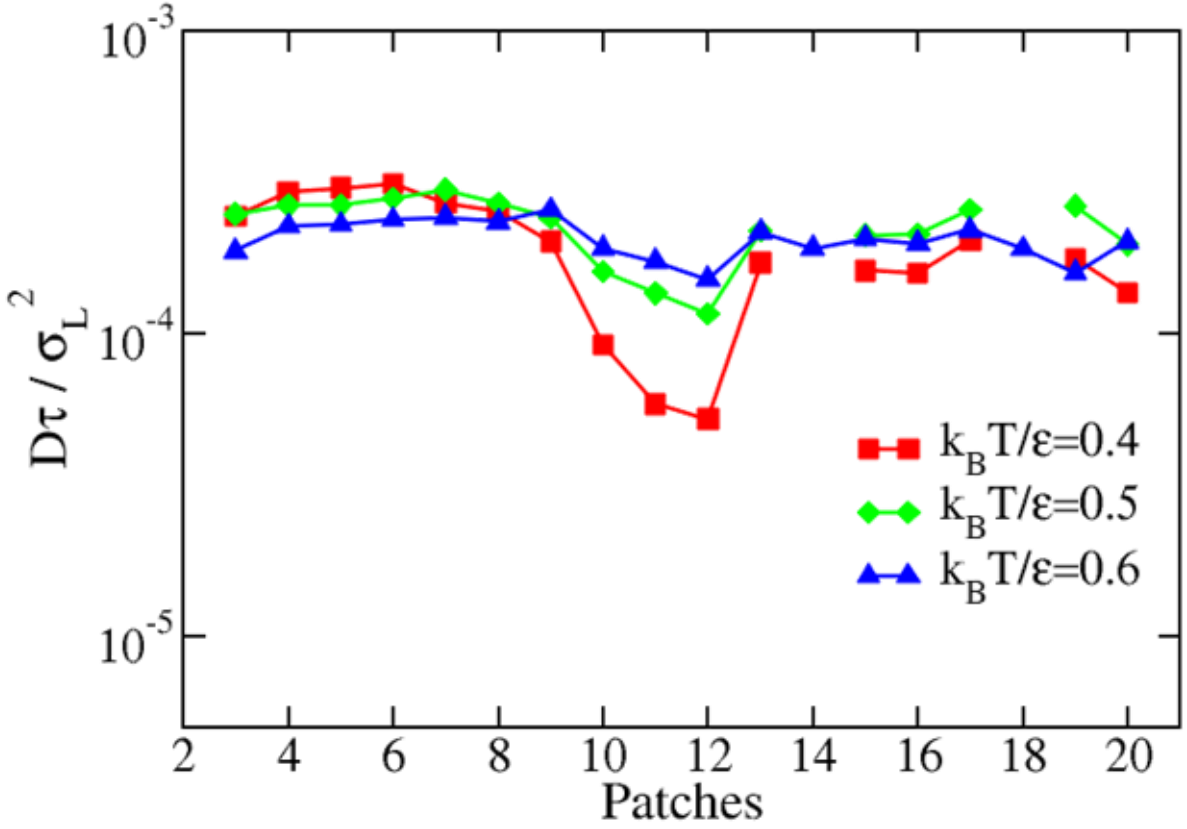

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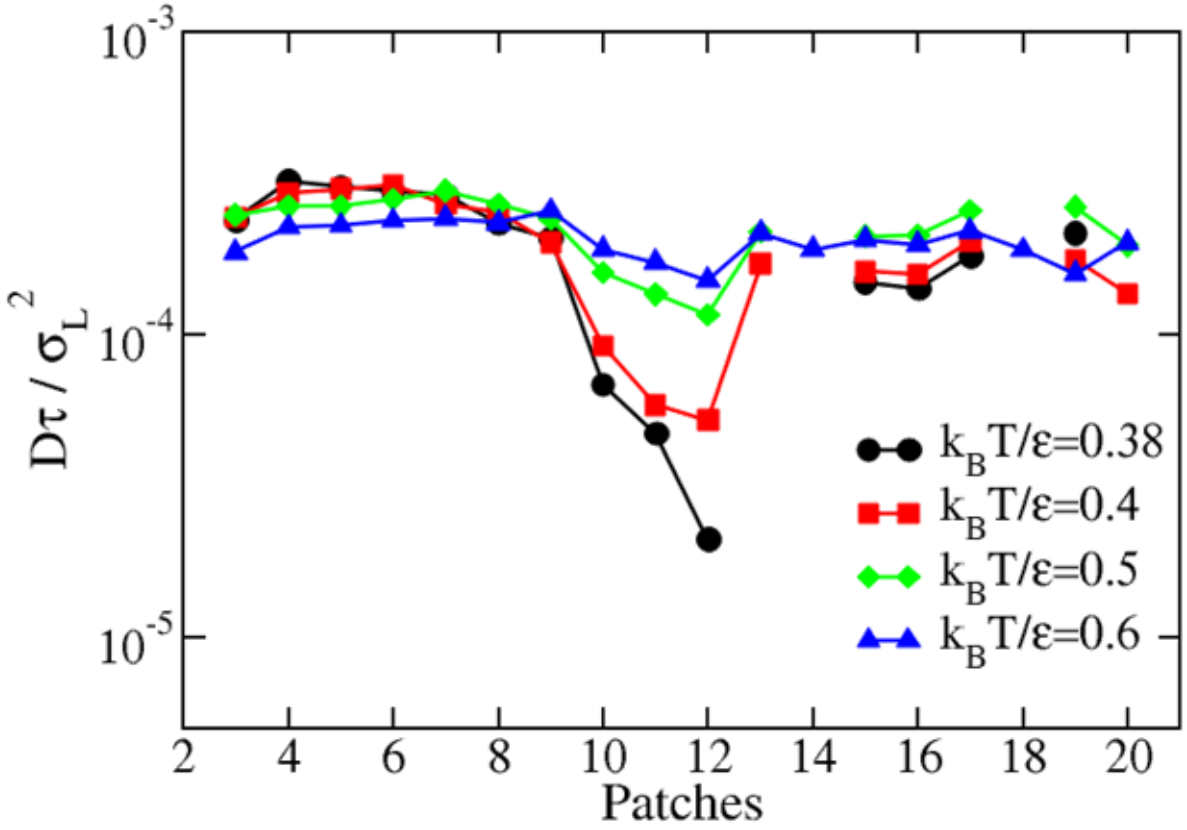
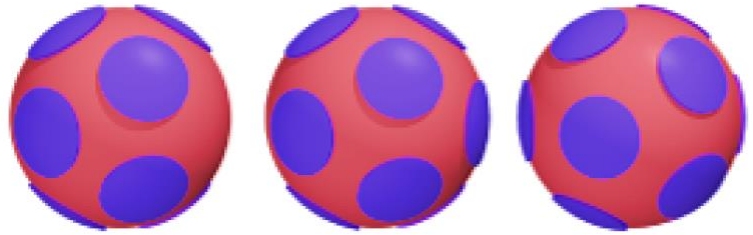


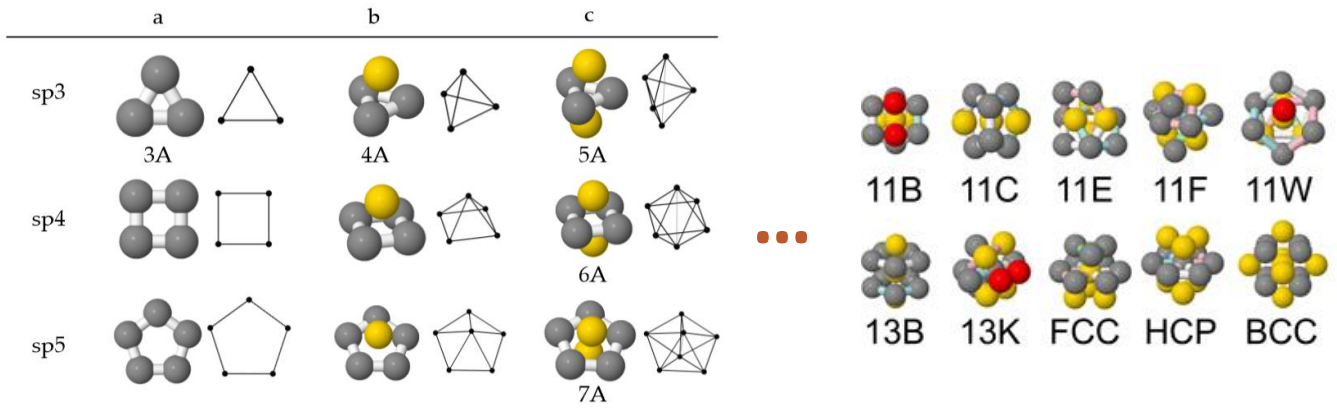
Drastic slowdown for
10, 11, and 12 patches.

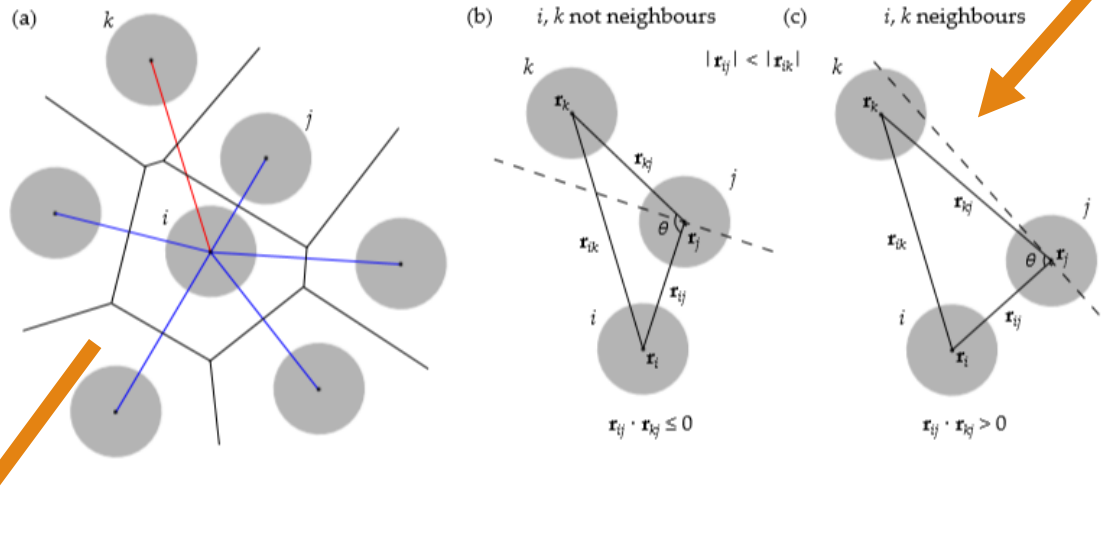


$n = 10$ $n = 11$ $n = 12$

What about the local structure?

Topological Cluster Classification

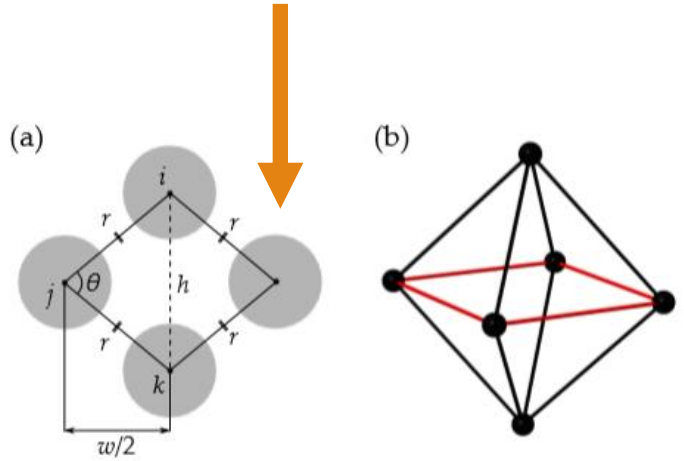




"Direct neighbours "

Modified Voronoi construction that:

- Prevents counting the particles in the second shell.
- Allows distorted 4 ring members.



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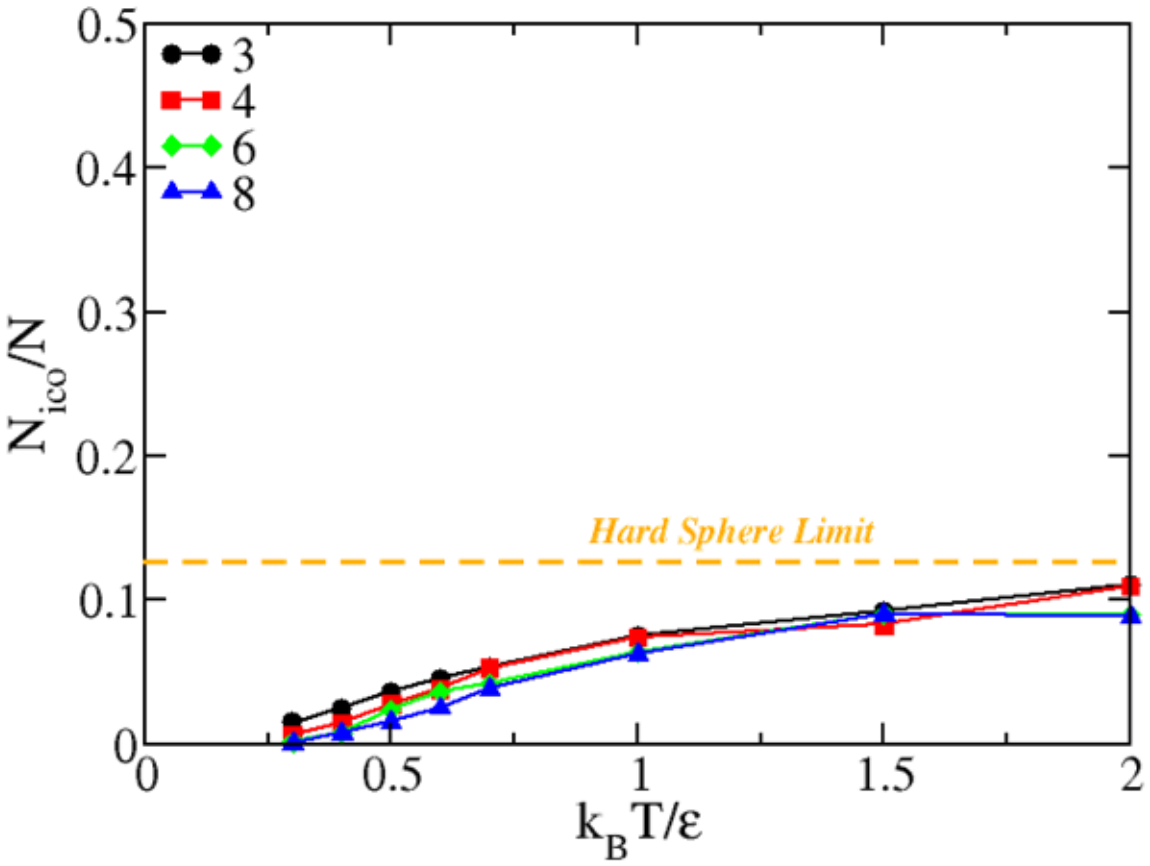
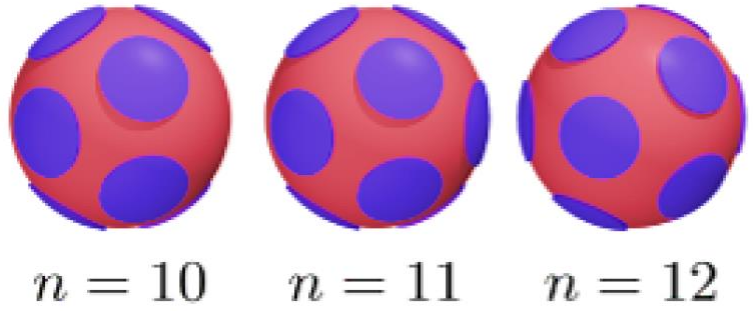
Why 10, 11 and 12 patches are so special ?

Fraction of particles involved in an icosahedral cage.





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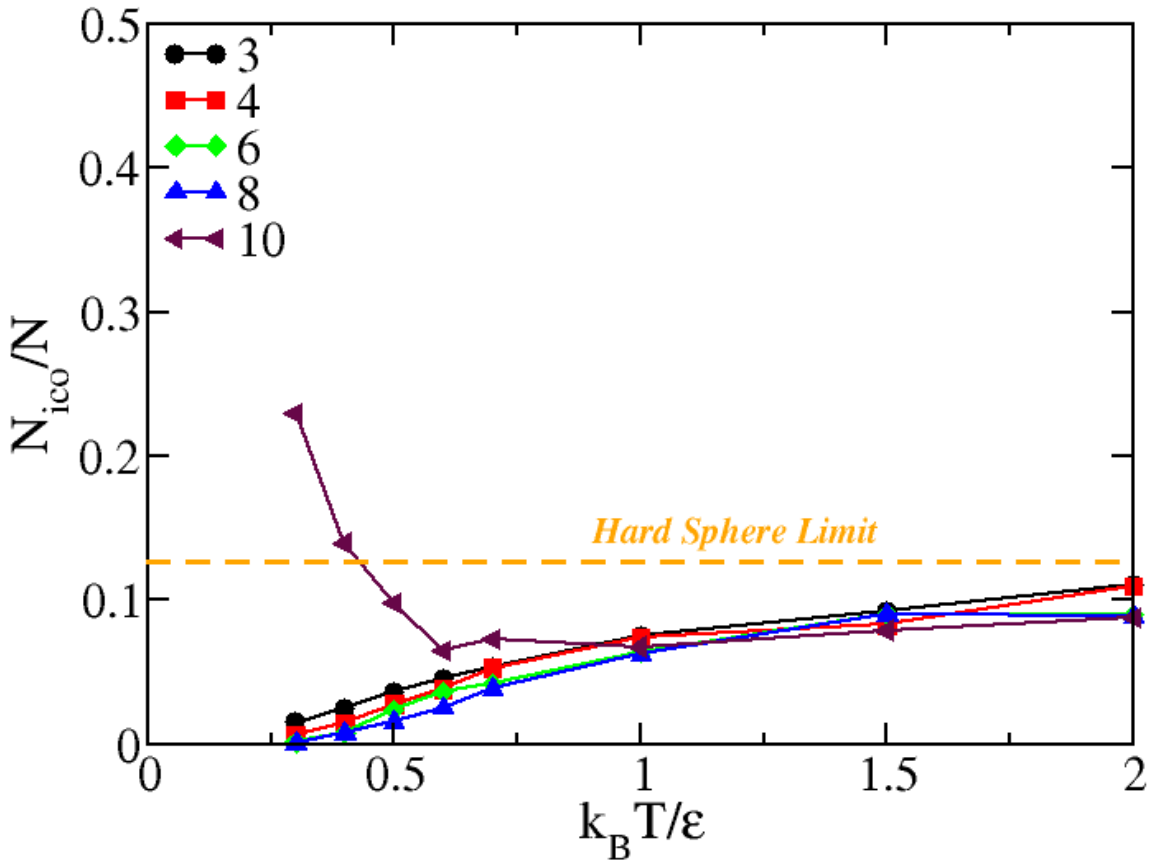

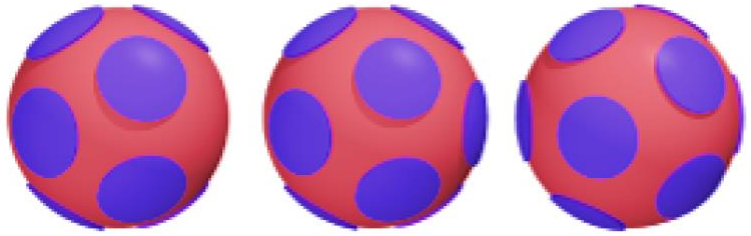

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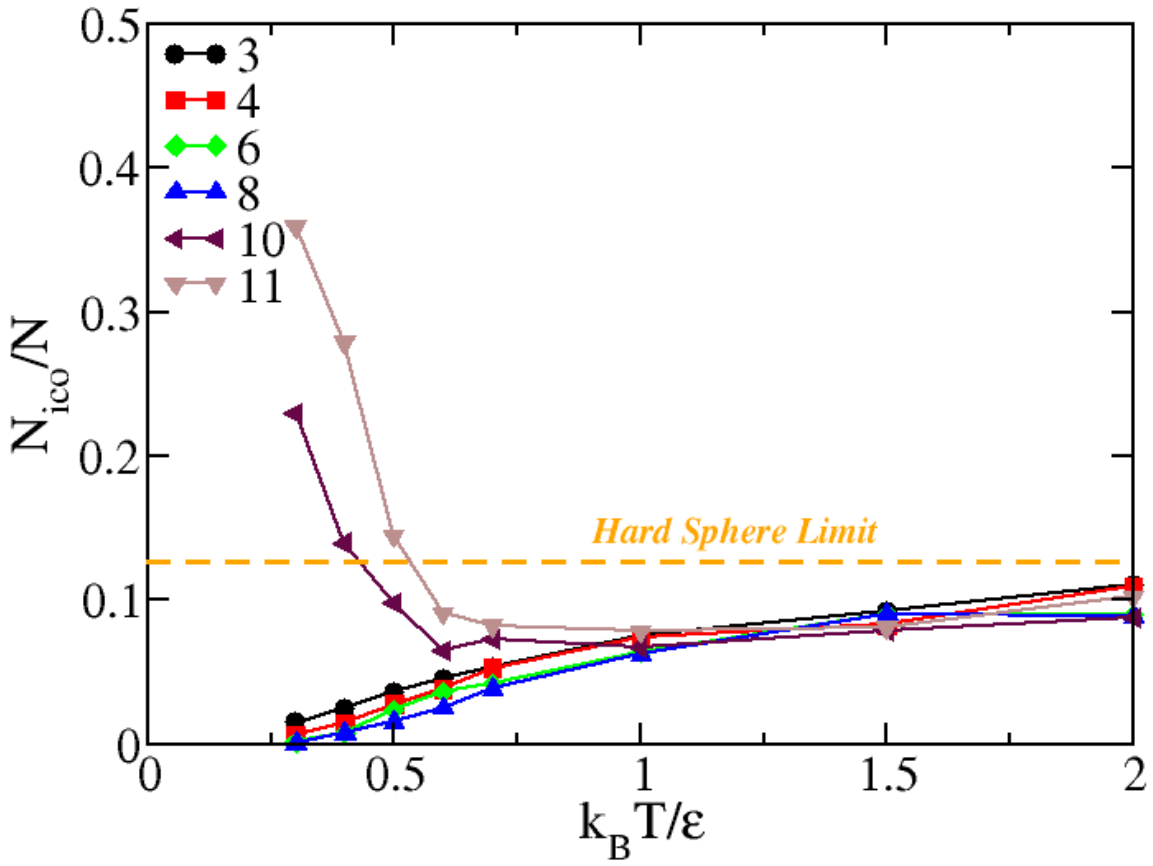
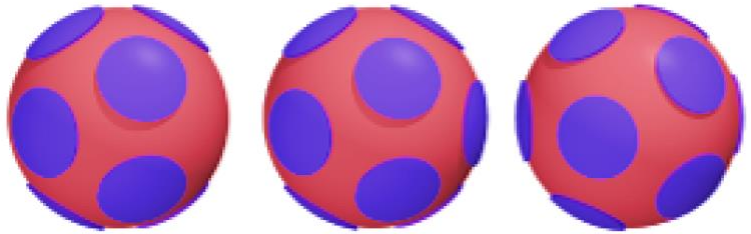
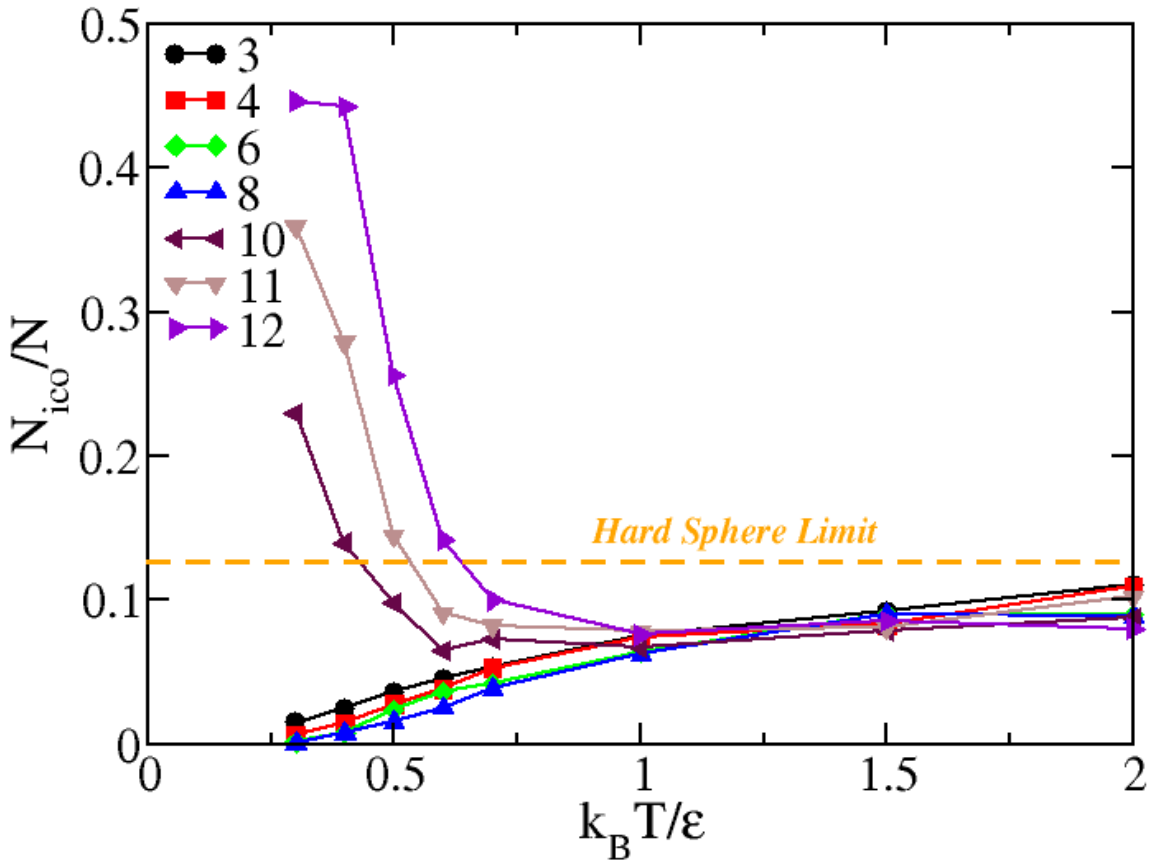


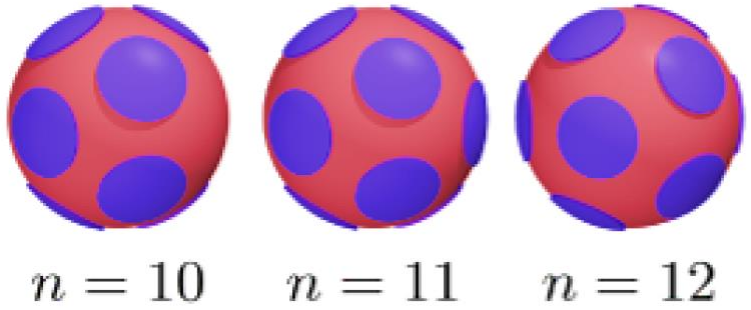


$n = 10$ $n = 11$ $n = 12$

Why 10, 11 and 12 patches are so special ?

Fraction of particles involved in an icosahedral cage.





Why 10, 11 and 12 patches are so special ?

10, 11 and 12 patch case reinforce icosahedral order at low temperature

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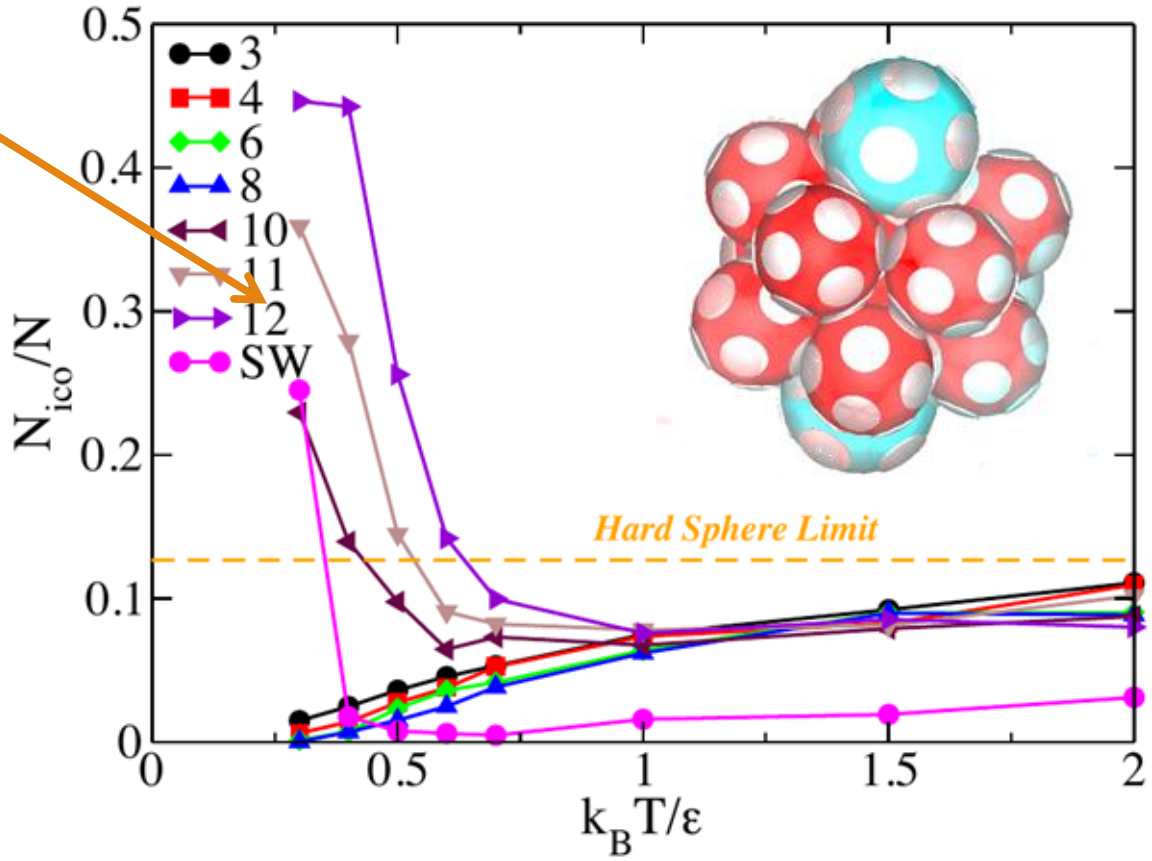

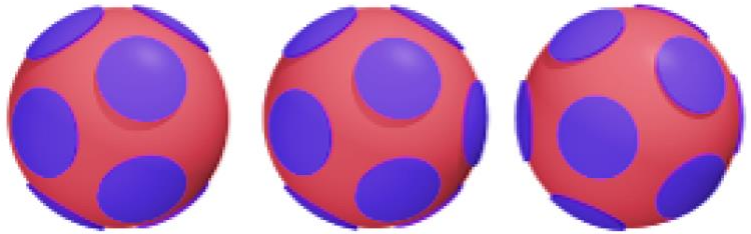

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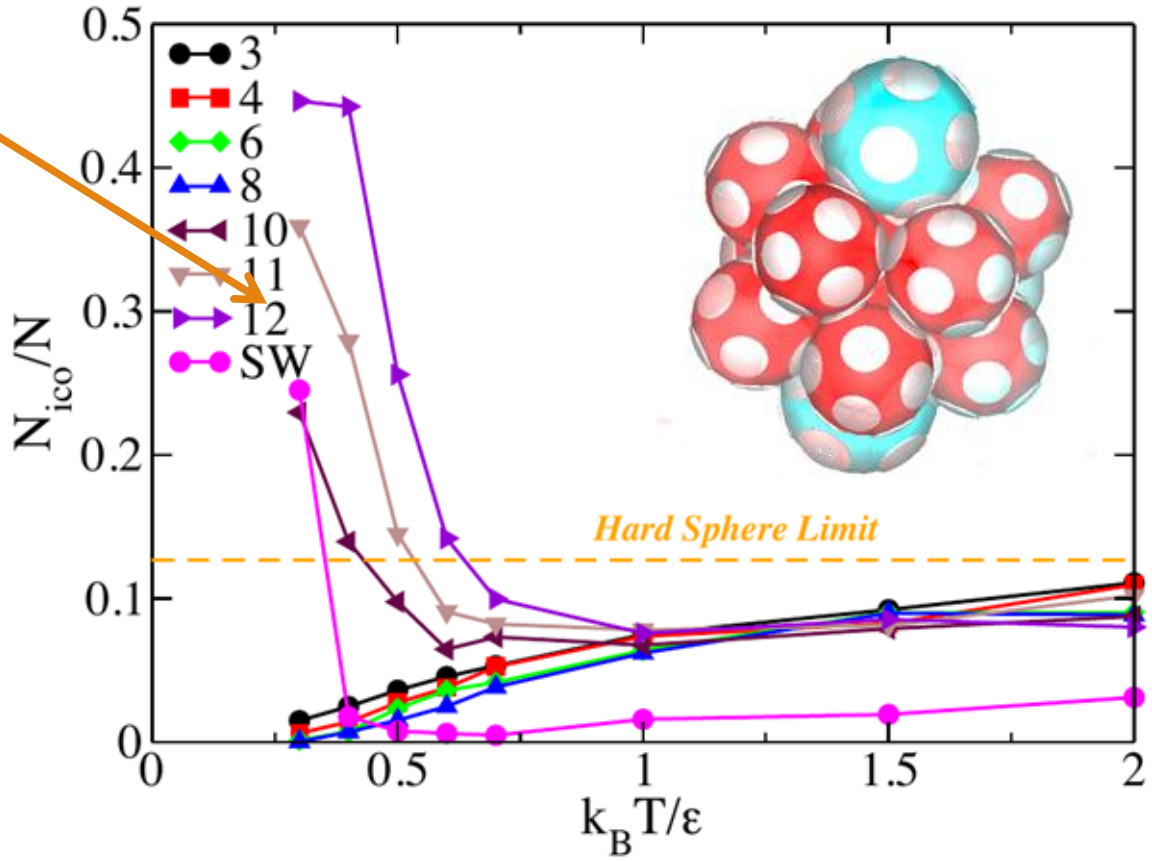
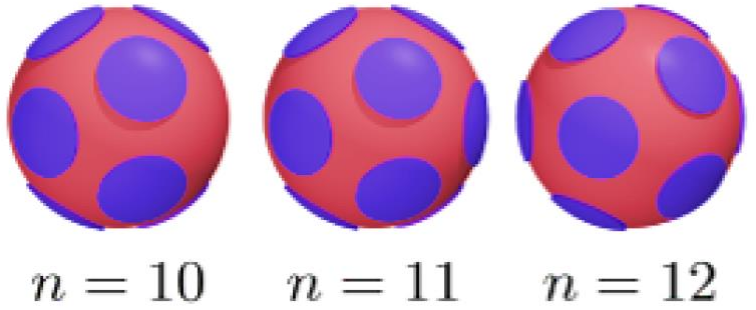
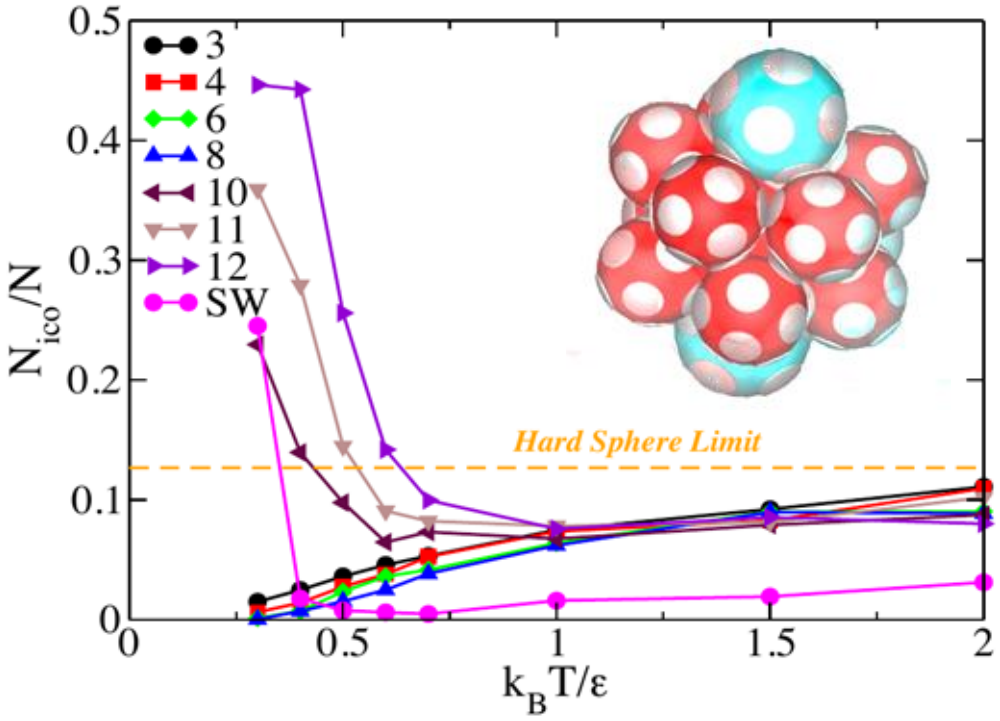


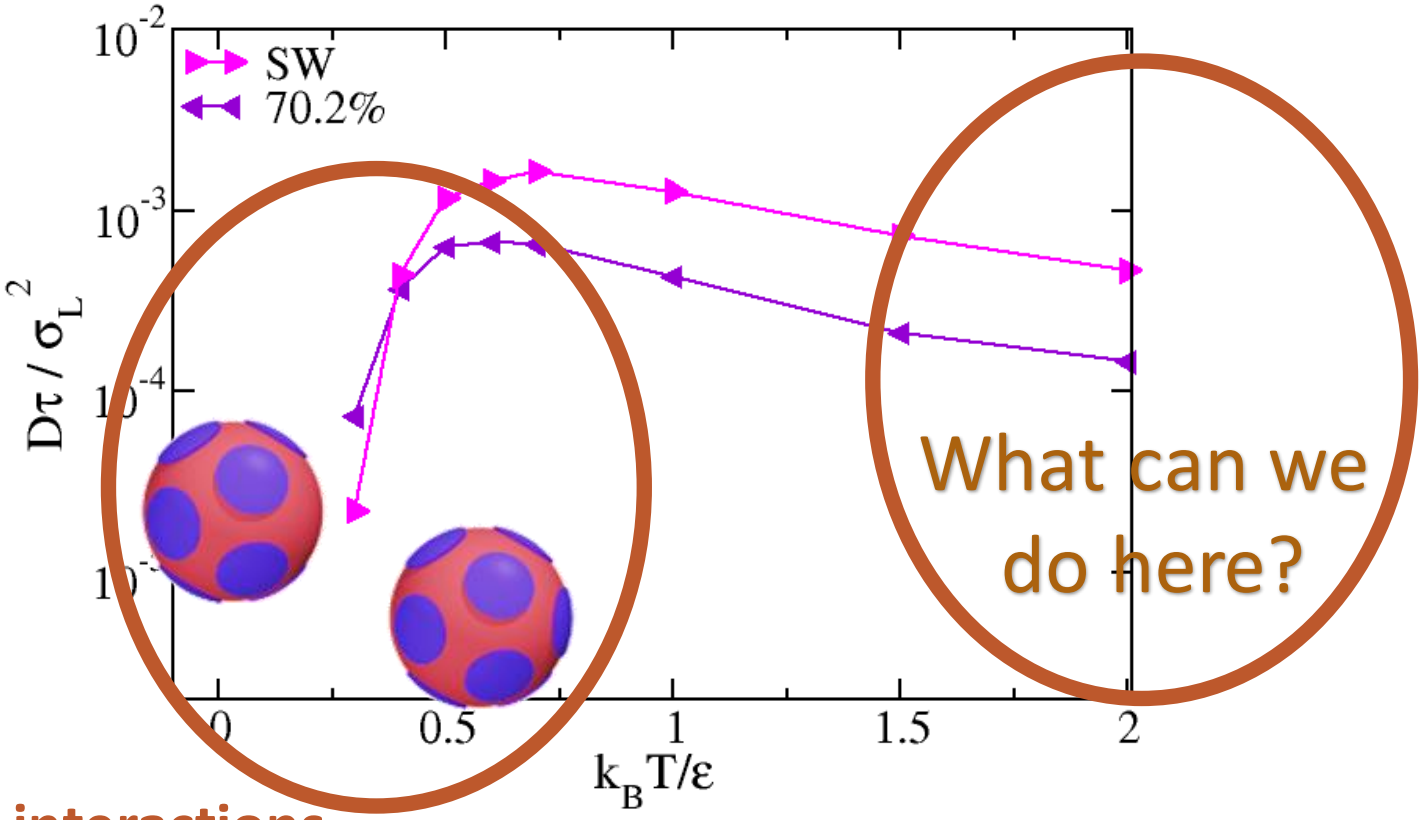


By adding directionality to interactions, there is a way of changing the structure of the cages by reinforcing the geometries that match with long-lived structures.

Why 10, 11 and 12 patches are so special ?

Fraction of particles involved in an icosahedral cage.

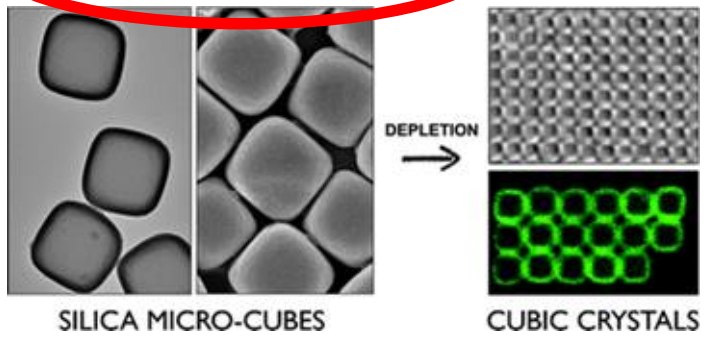




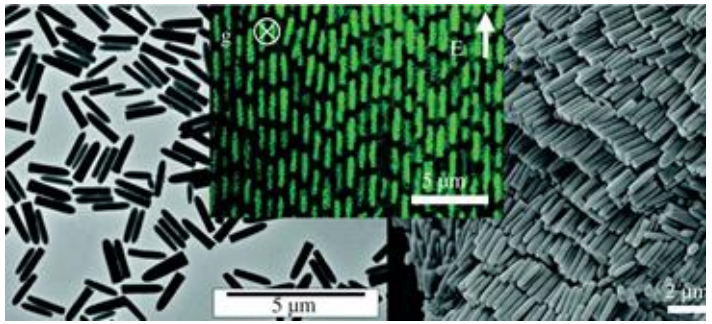
Patchy interactions play a major role

Colloidal glasses and how to model them?

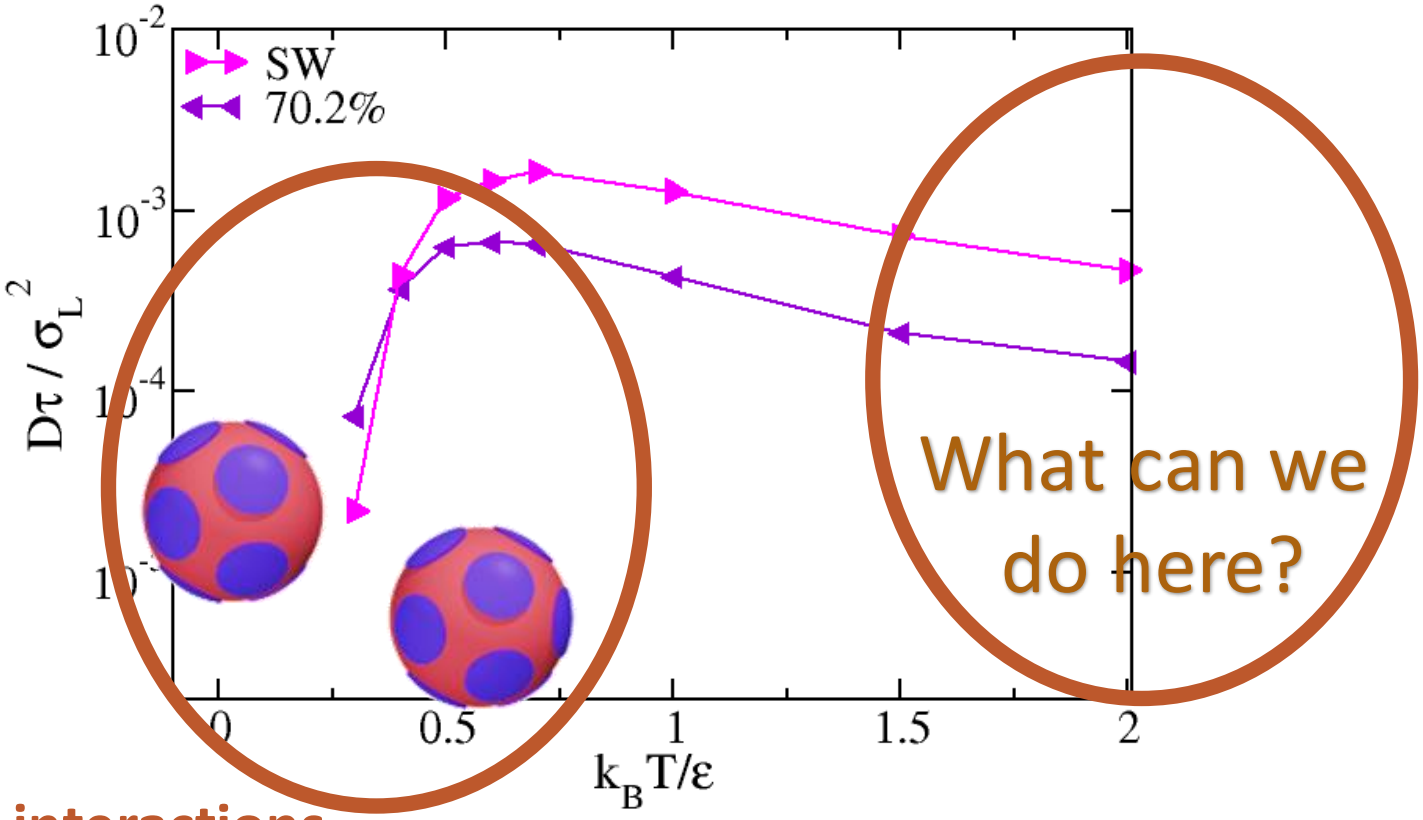
Shape



Rossi *et al.*, Soft Matter **7**, 4139 (2011)



Kuijk *et al.*, J. Am. Chem. Soc. **133**, 2346 (2011)



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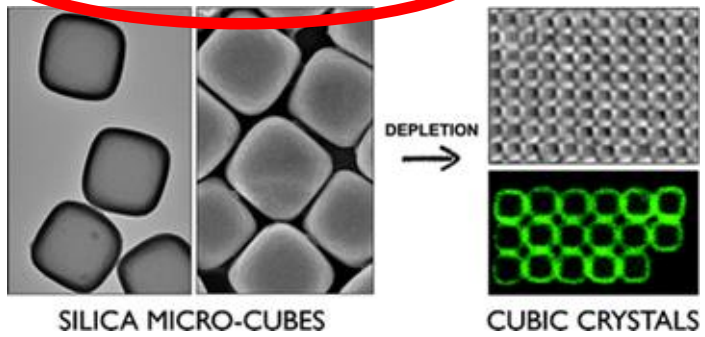

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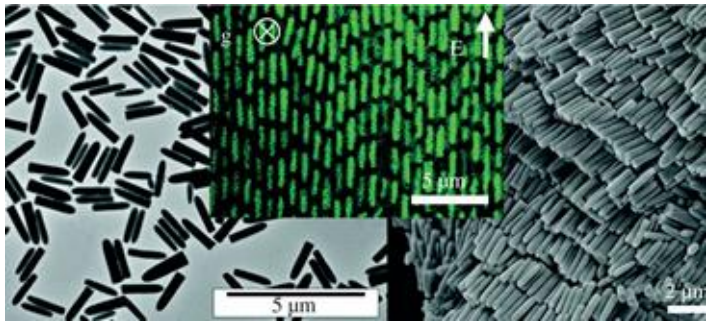
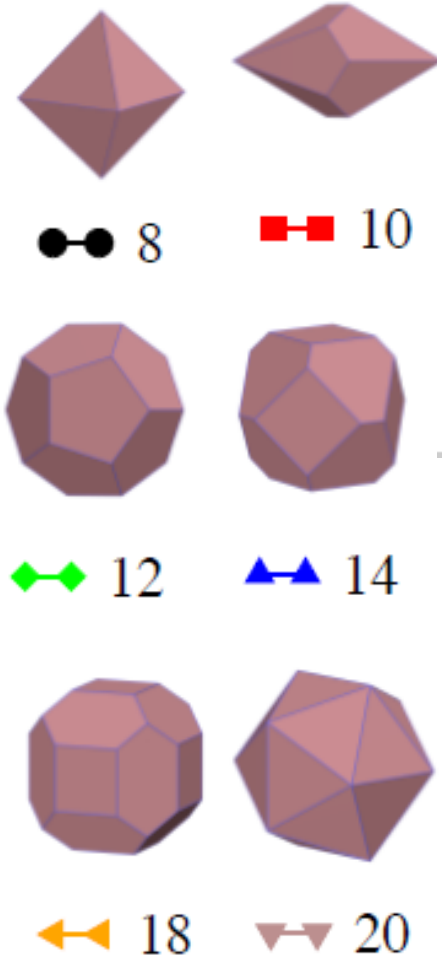
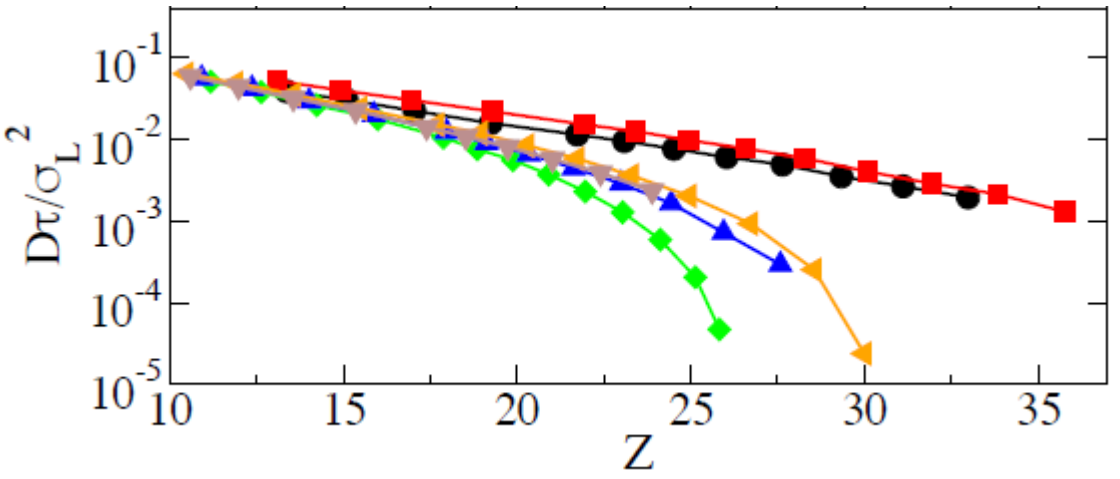
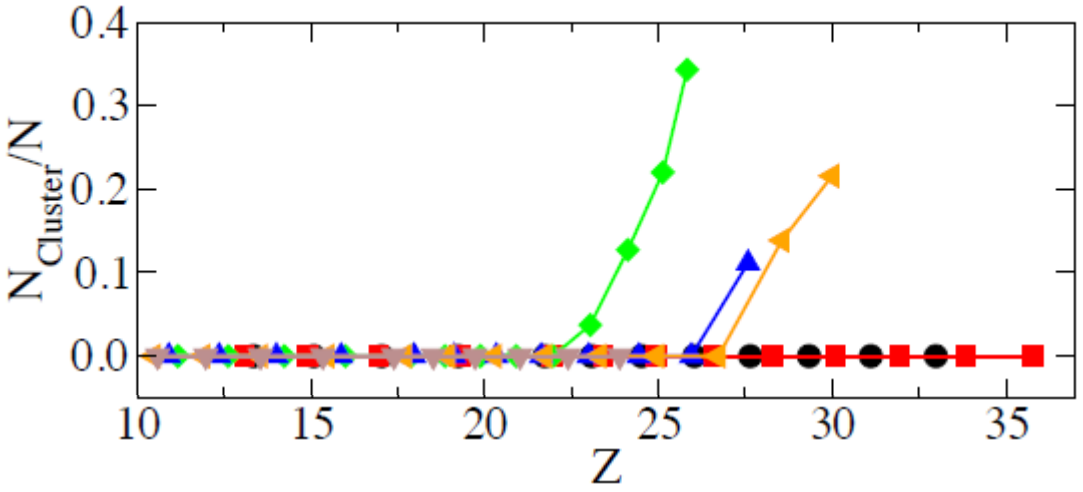


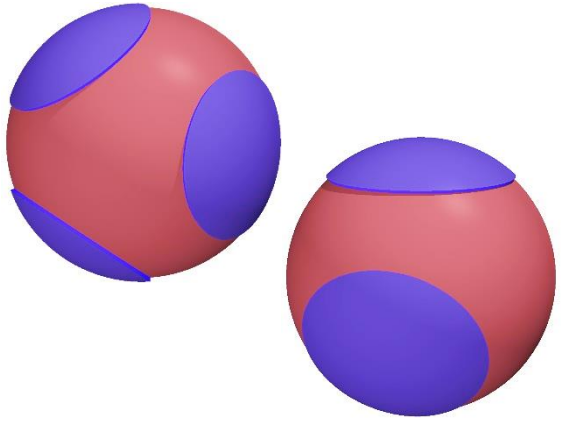
Kuijk *et al.*, J. Am. Chem. Soc. **133**, 2346 (2011)



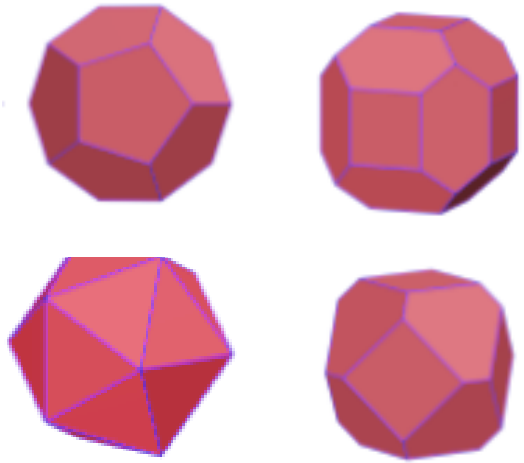




Surface chemistry



Shape



- Directional interactions can induce changes in the local structure.
- The enhancement of icosahedral clusters promotes a slowing down on dynamics in patchy particles and polyhedral repulsive particles.
- The reentrance is conserved in systems of patchy particles.
- Systems with same coverage behave the same excepting for the ones that enhance specific local structures.

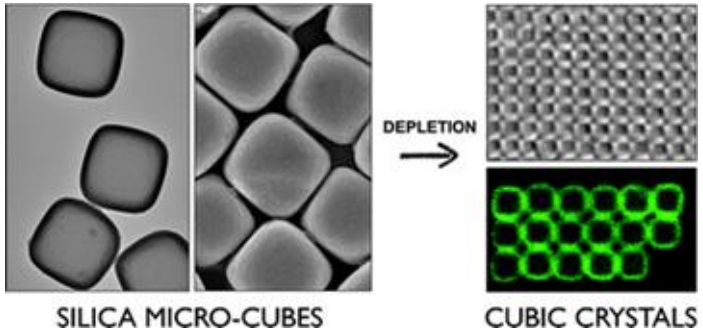
Slowing down supercooled liquids by manipulating their local structures

arXiv:1812.00764

Colloidal glasses and how to model them?

Colloids: ideal playground for studying glasses.

Shape



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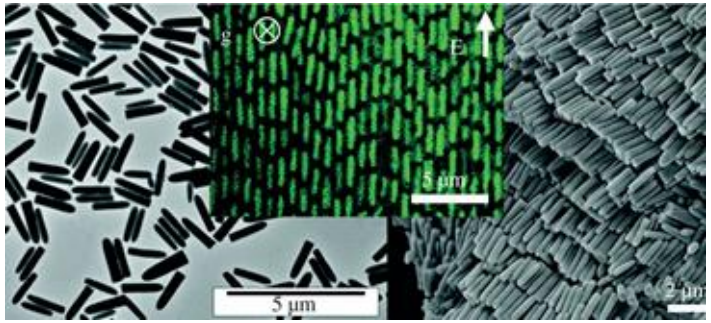

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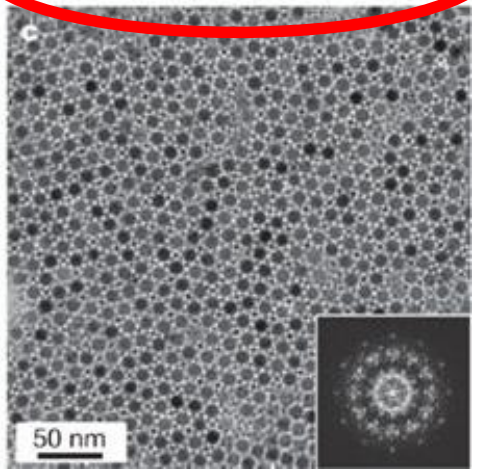
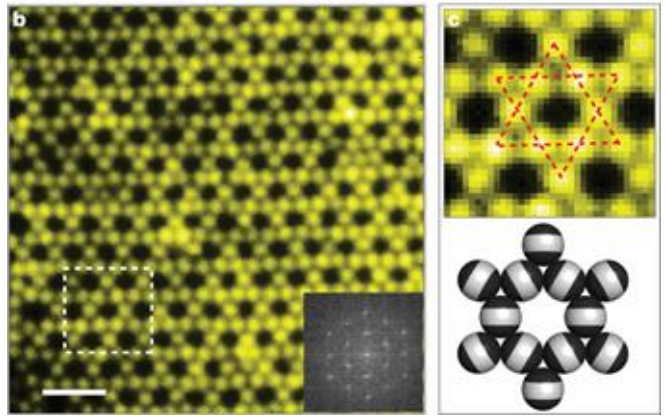
Size distribution

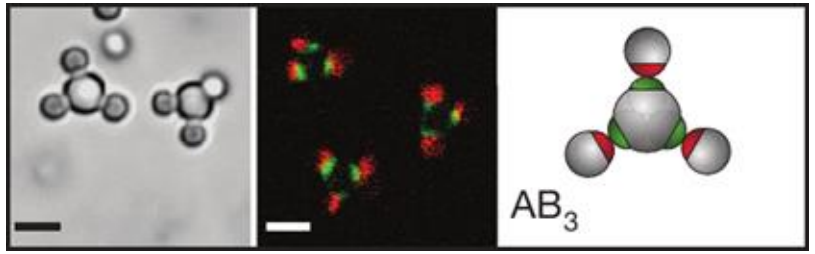


Talapin *et al.*,
Nature **461**,
964 (2009)

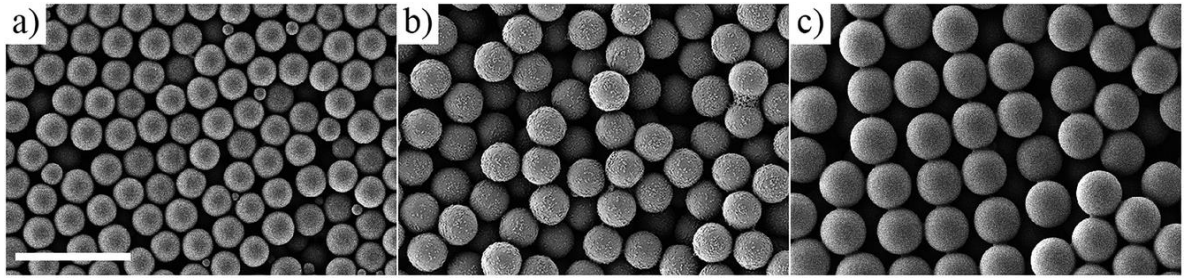
Surface chemistry



Chen *et al.*, Nature **469**, 381 (2011)

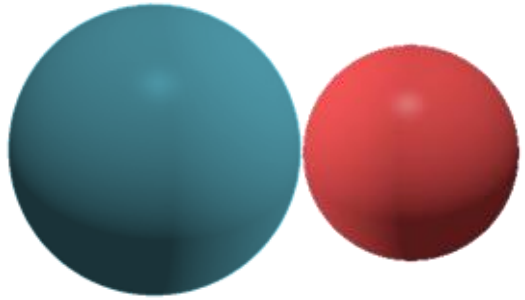


Y. Wang *et al.*, Nature **491**, 51 (2012)

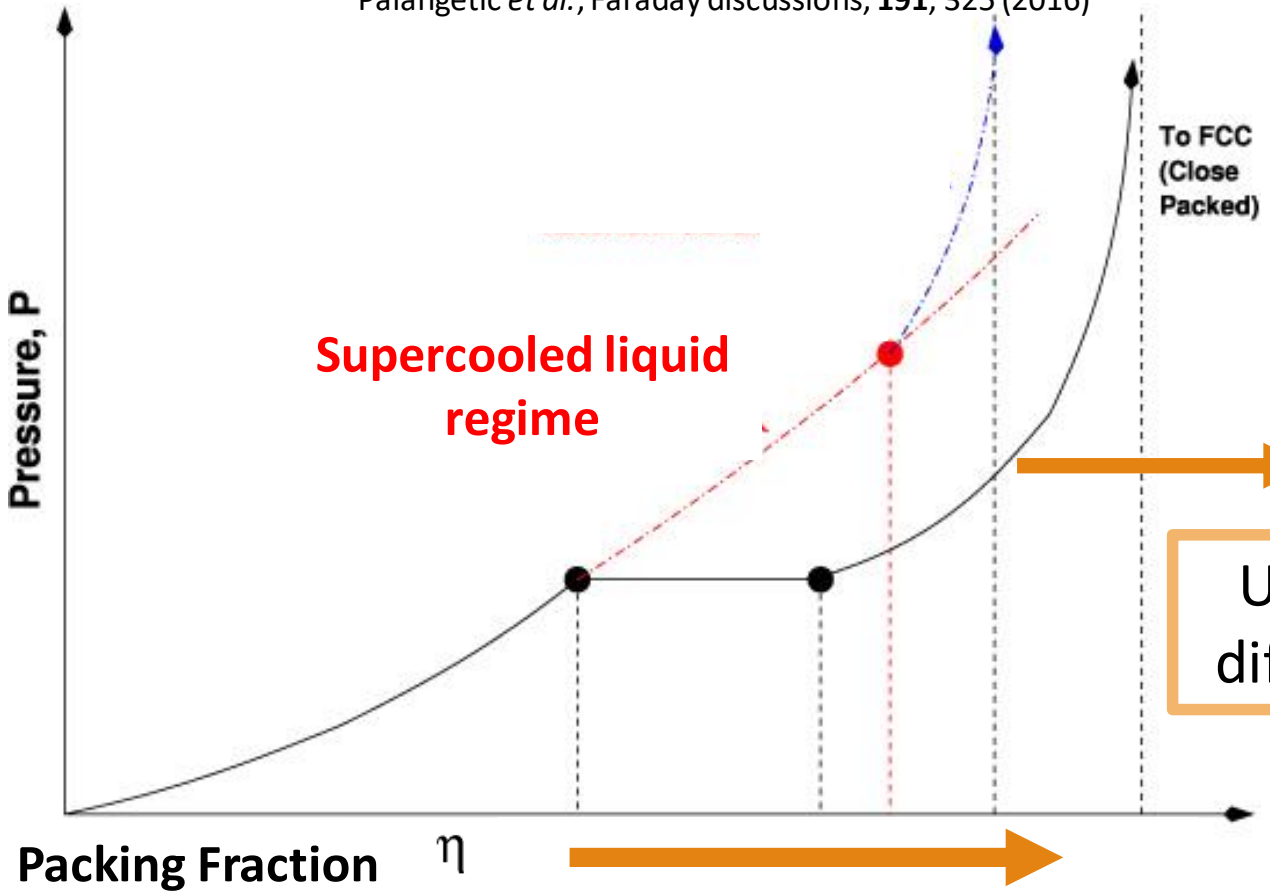


Palangetic *et al.*, Faraday discussions, **191**, 325 (2016)

Hard Sphere Systems



- Purely repulsive interactions
- Capture changes on dynamics towards the glass regime



How to avoid?

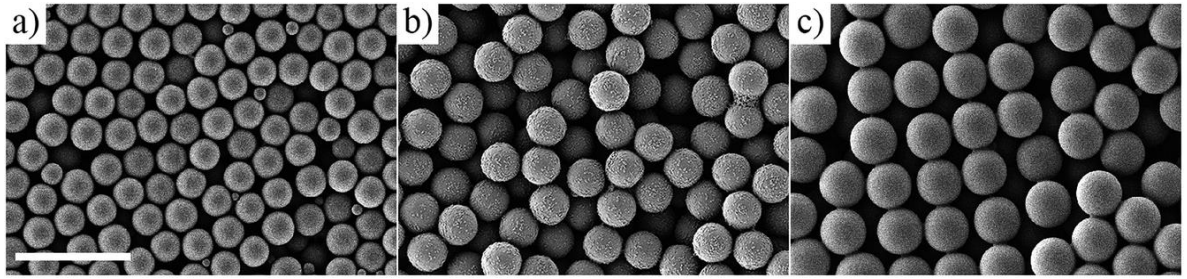
Using mixtures of different size ratios

Experiments

Simulations

Theory

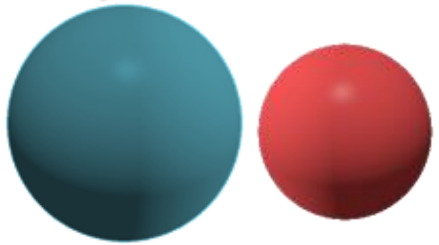
Parisi *et al.*, JSTAT, **2009**, 03 (2009)



Palangetic *et al.*, Faraday discussions, **191**, 325 (2016)

Hard Sphere Systems

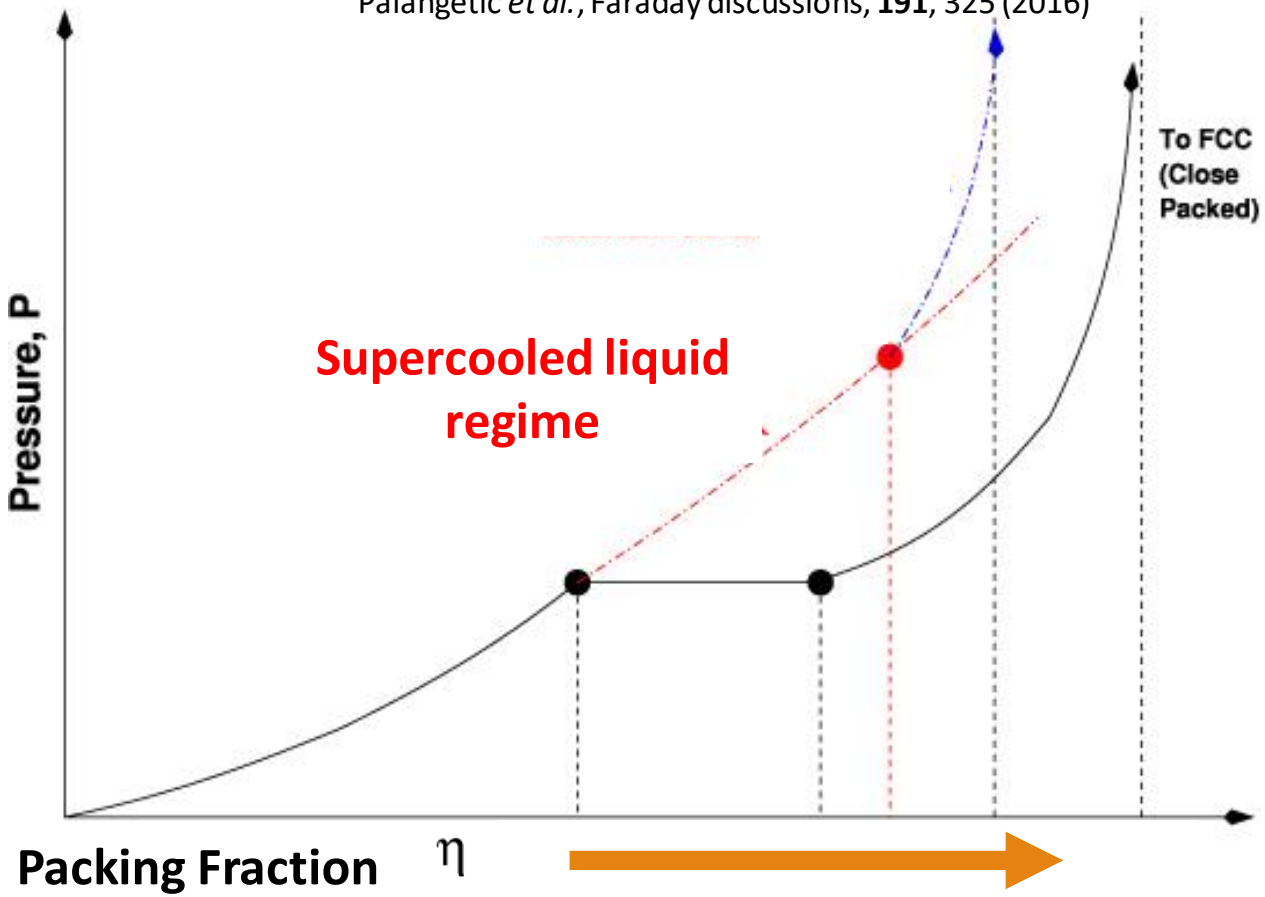
Binary Mixtures



Change size ratio q (from 0.6 to 0.8)
Change in composition x_L (from 0.2 to 0.65

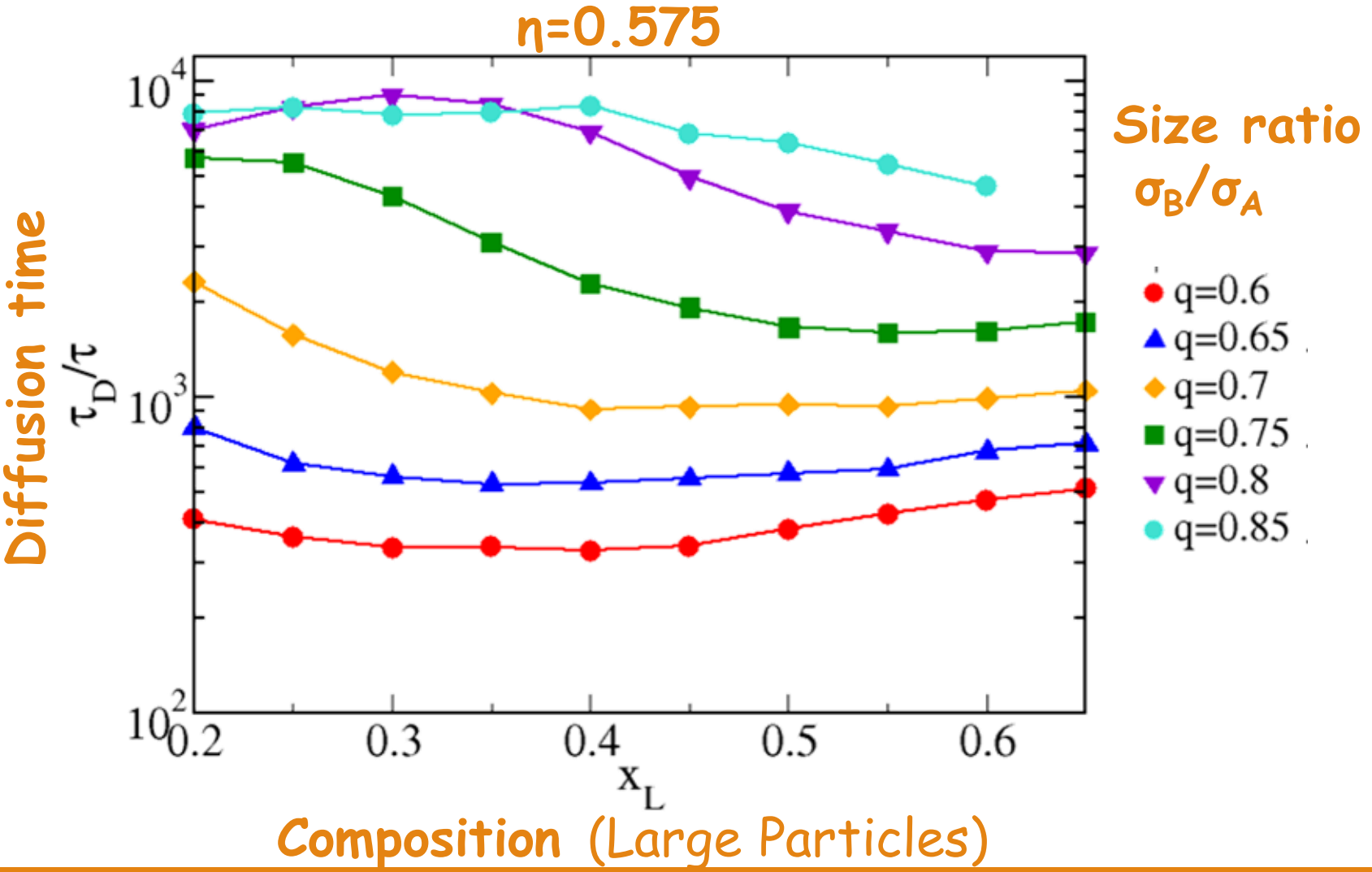
Polydisperse Systems

Change polydispersity from 2% - 8%



Parisi *et al.*, JSTAT, **2009**, 03 (2009)

Dynamics (Binary Mixtures)



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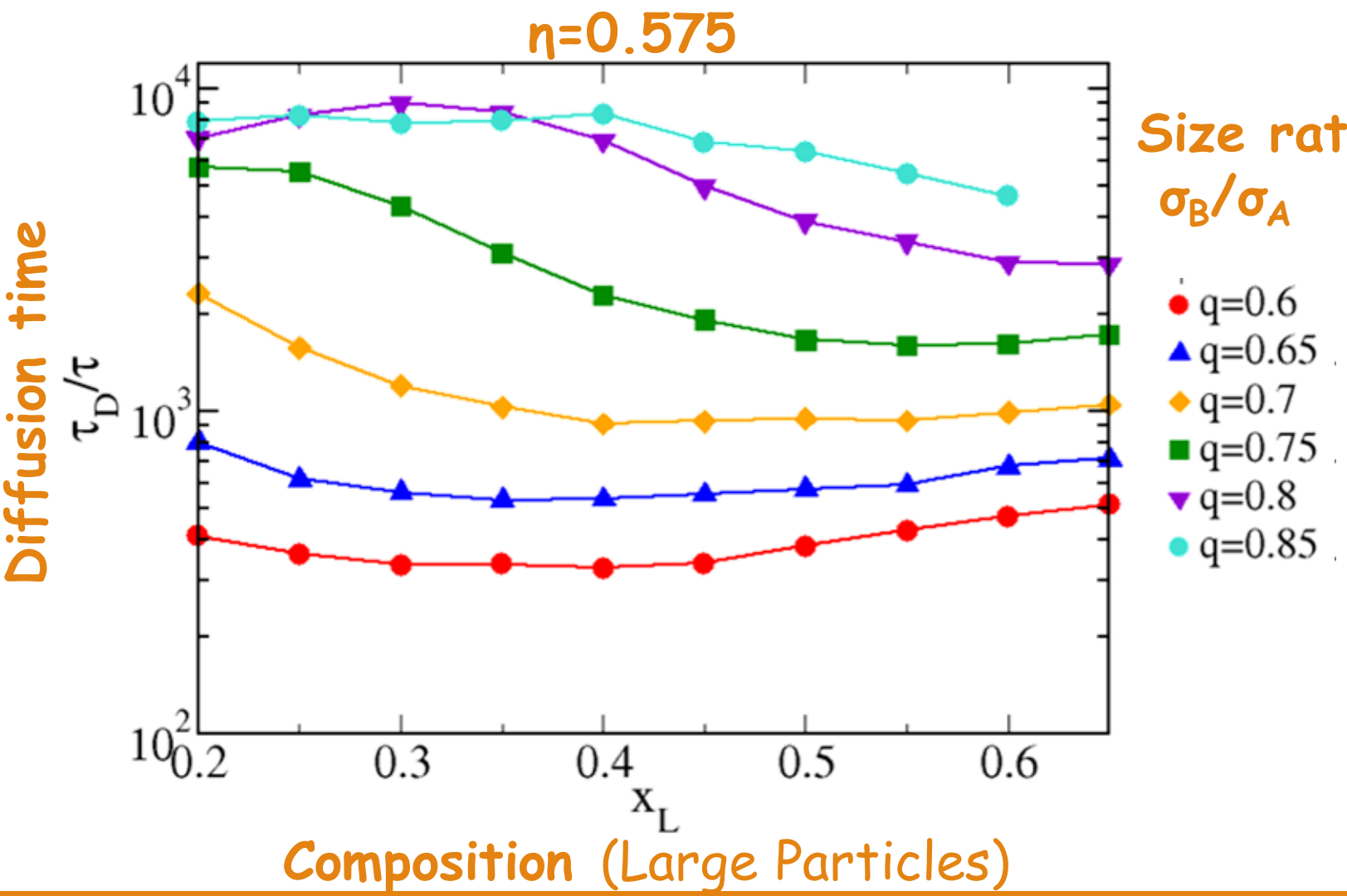
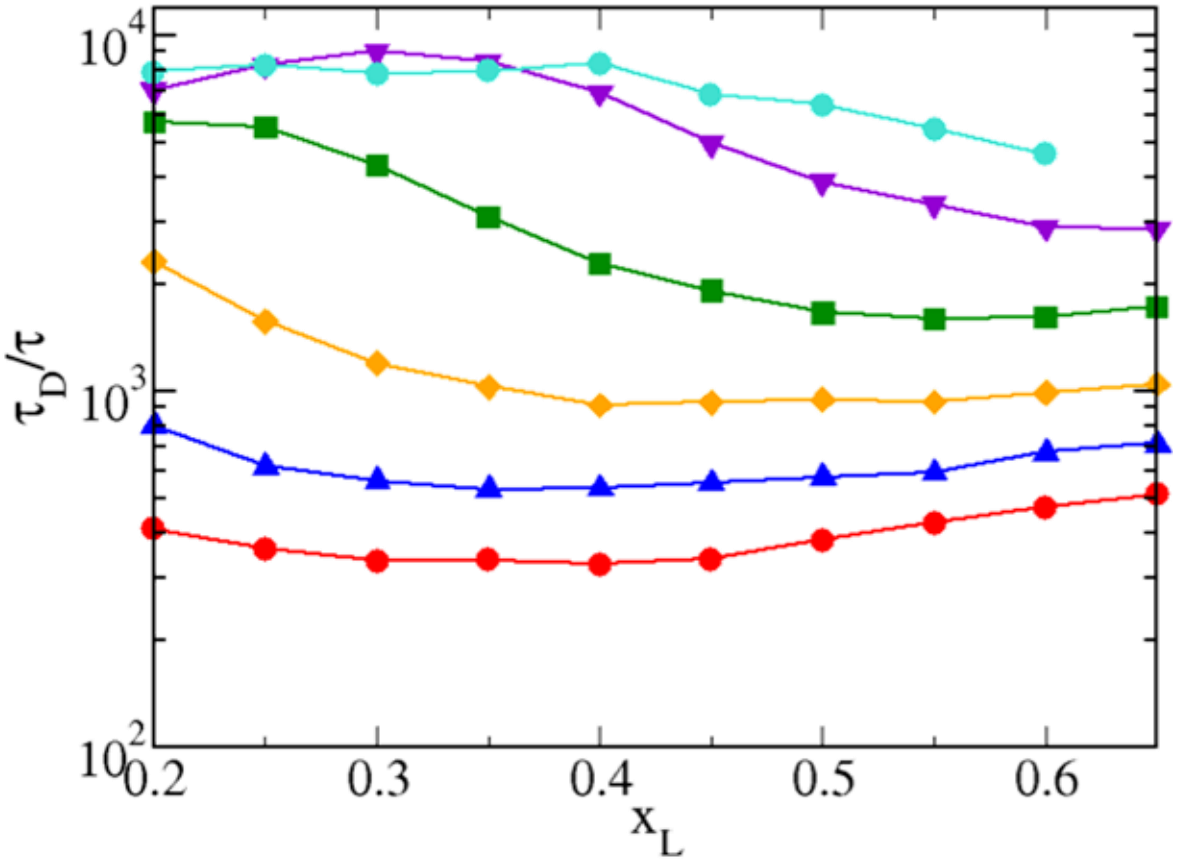


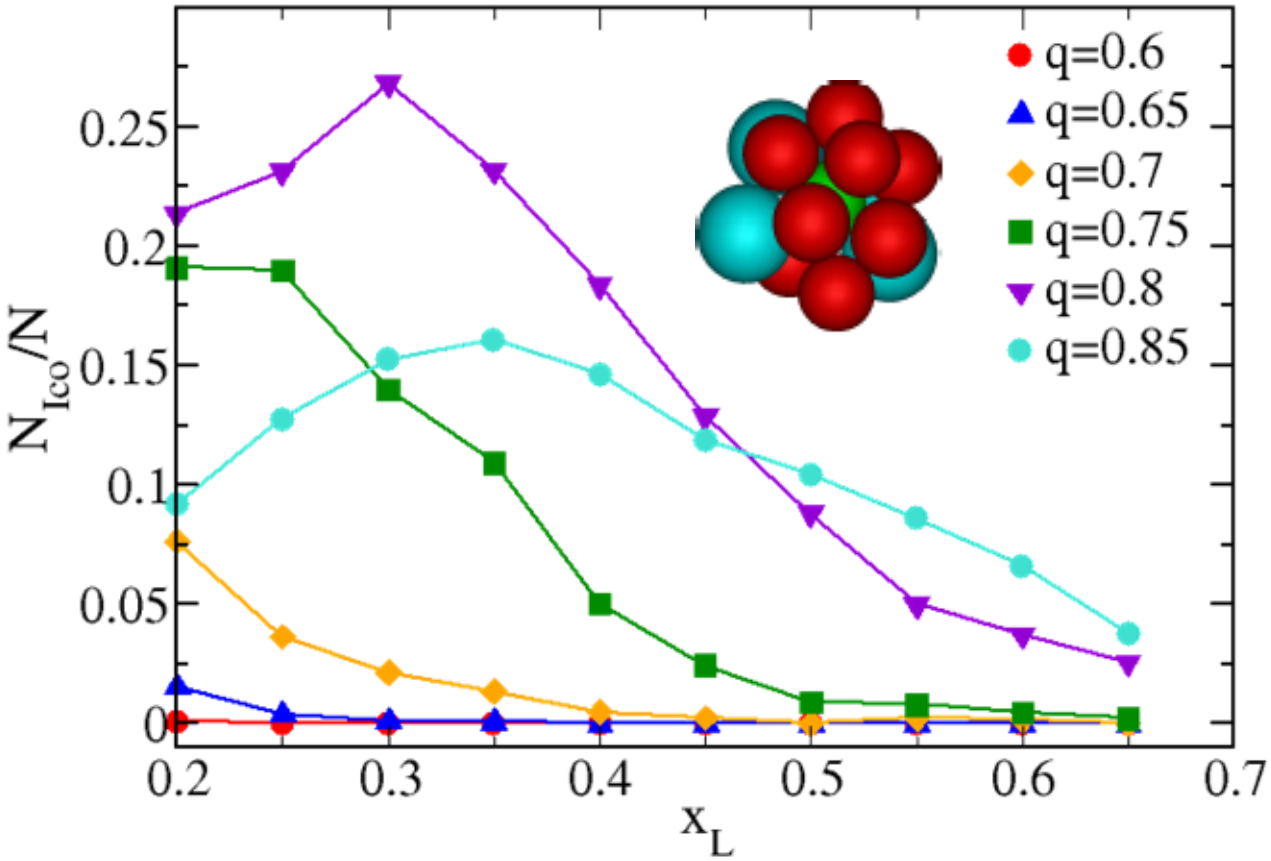
- Non monotonous behaviour on dynamics by changing size ratio and composition.

Dynamics and Structure

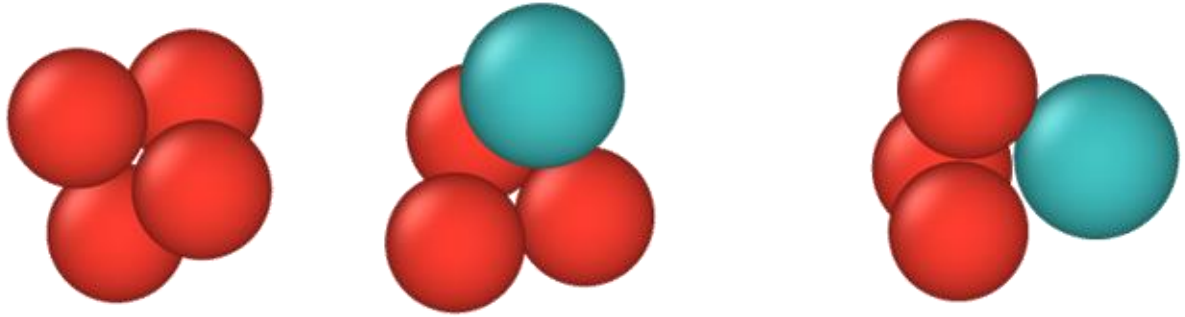
η=0.575

Number of particles in Icosahedral Clusters





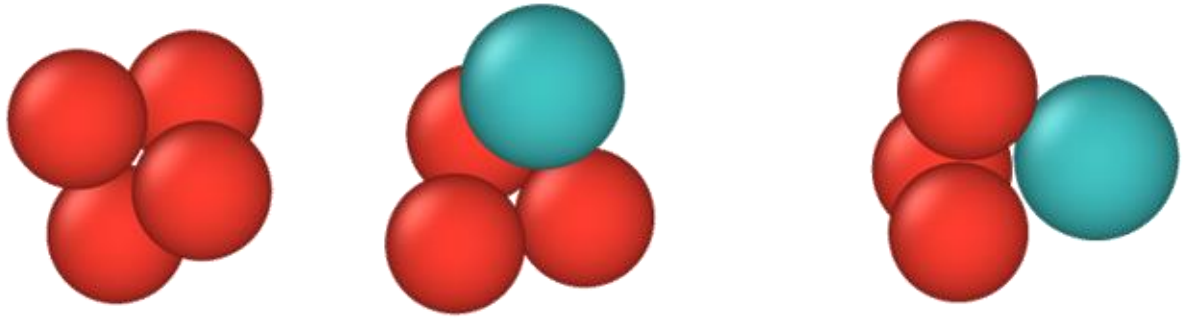
Tetrahedrality



Tetrahedron: smallest cluster in 3 dimensions.

Tetrahedral cluster: 4 neighbour particles linked all together by distance.

Tetrahedrality



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Quantify the **tetrahedrality of the local structure**:

Counting the number of tetrahedron that one particle is involved in.

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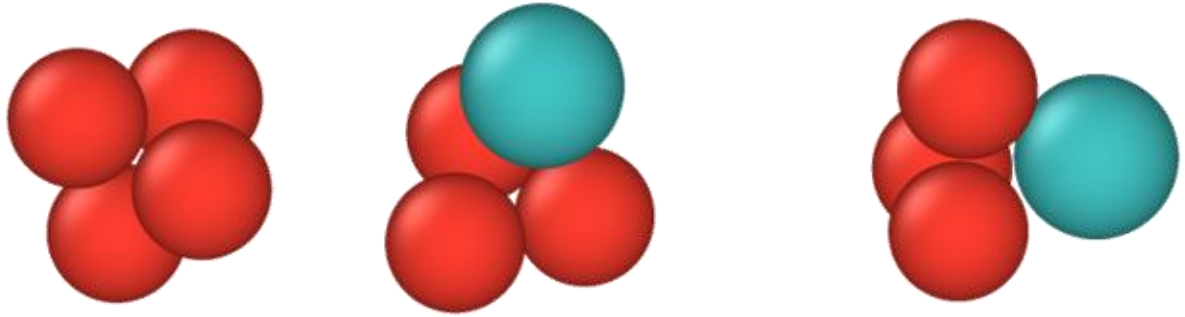

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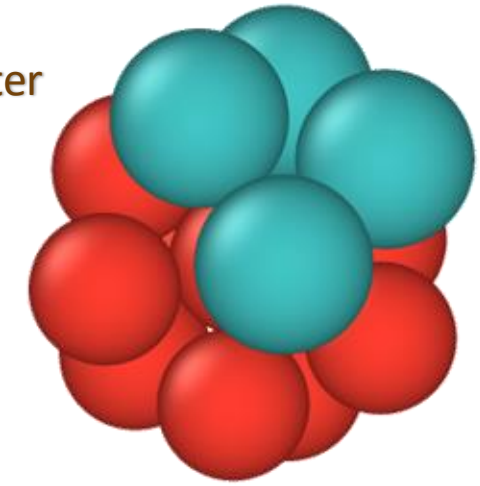

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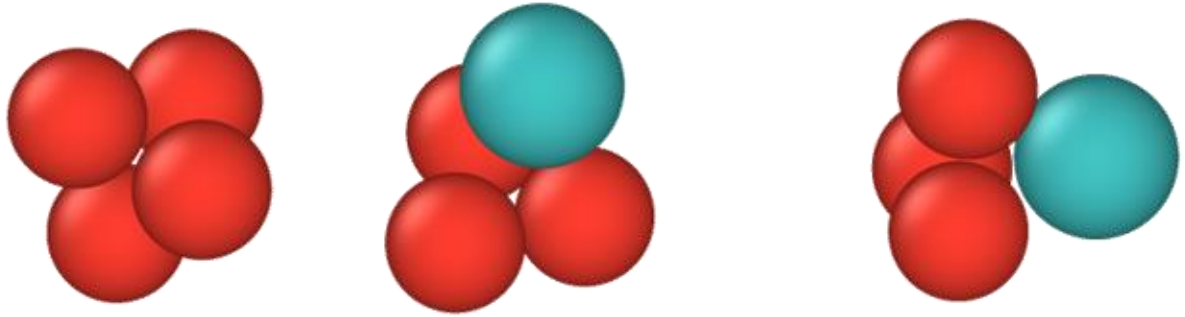

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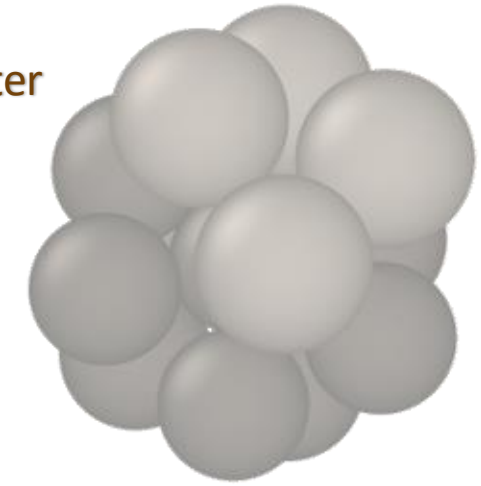

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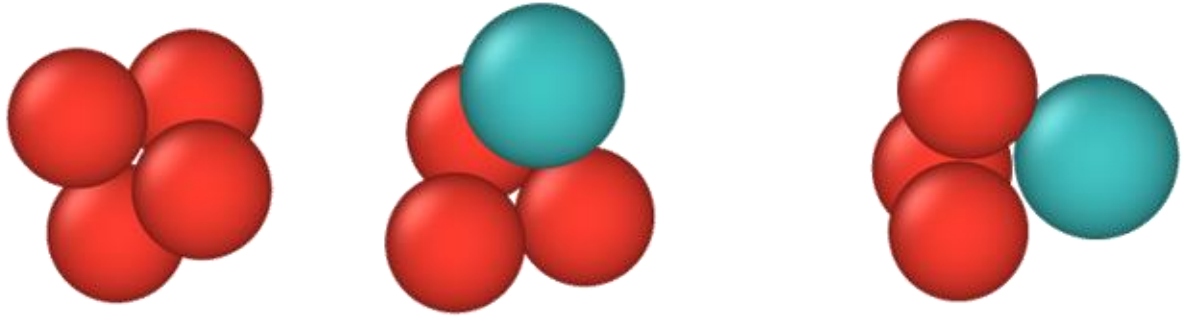

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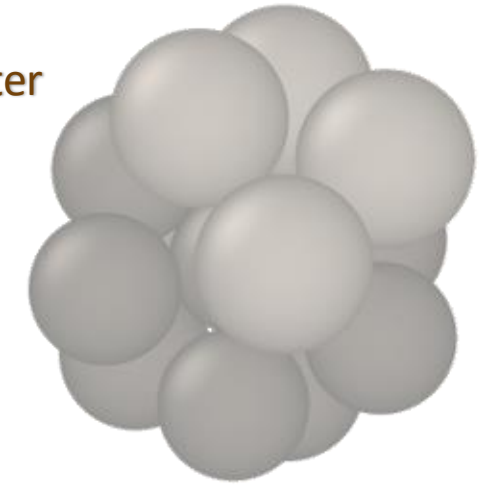

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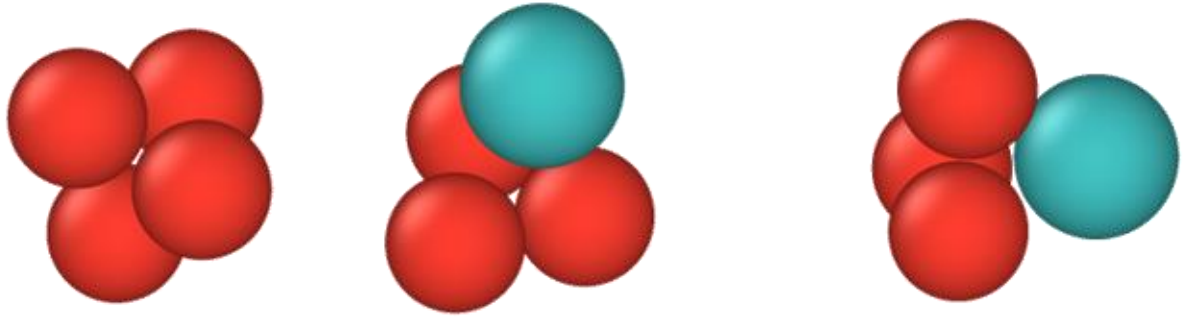

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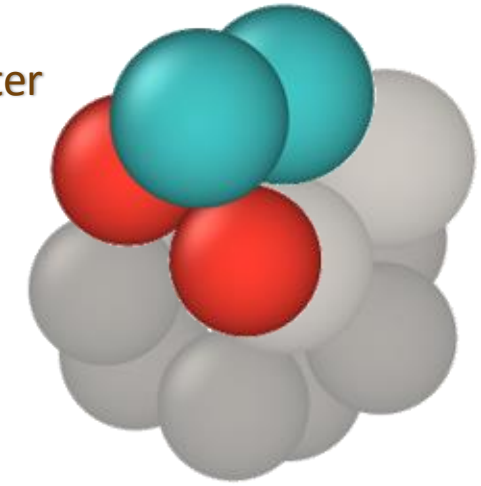

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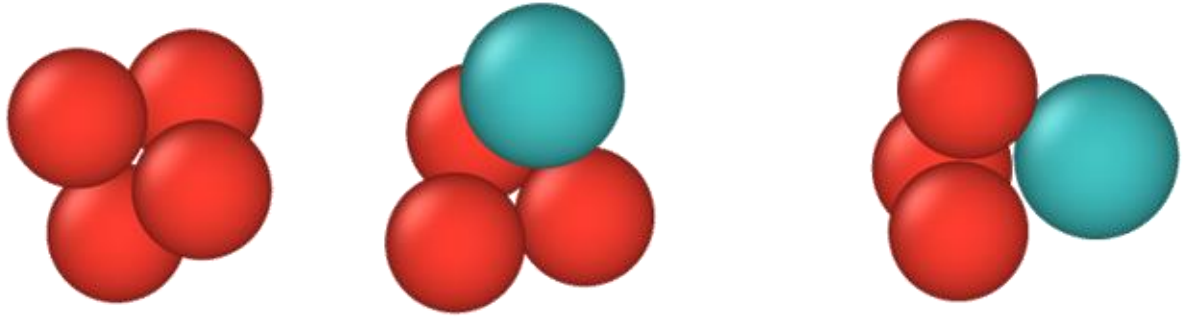

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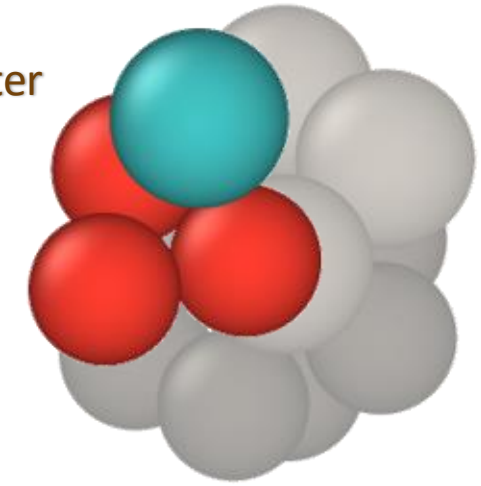

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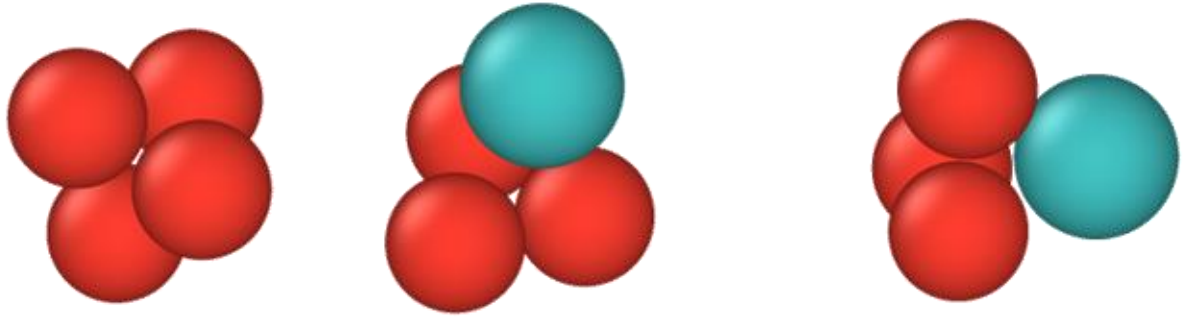

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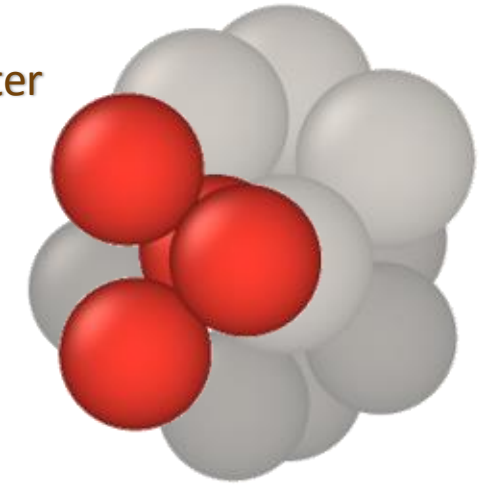

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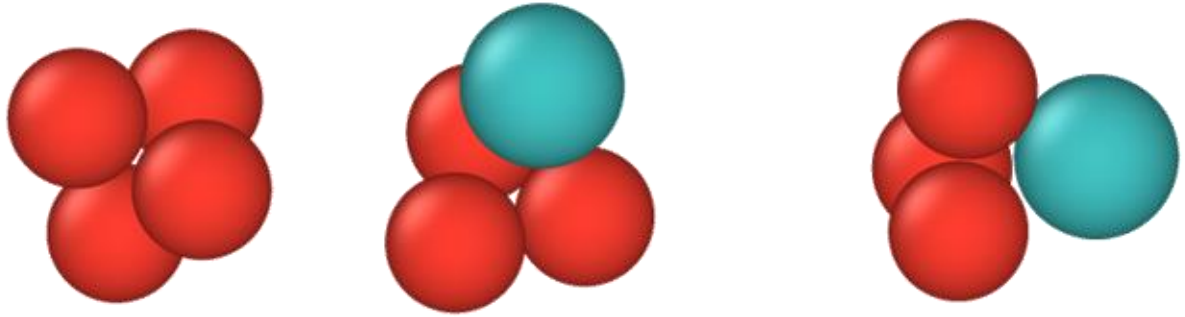

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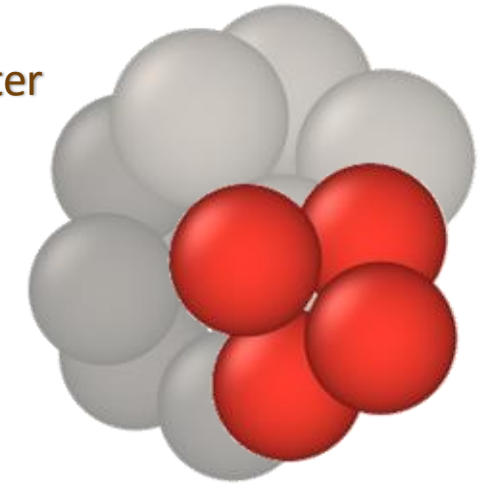

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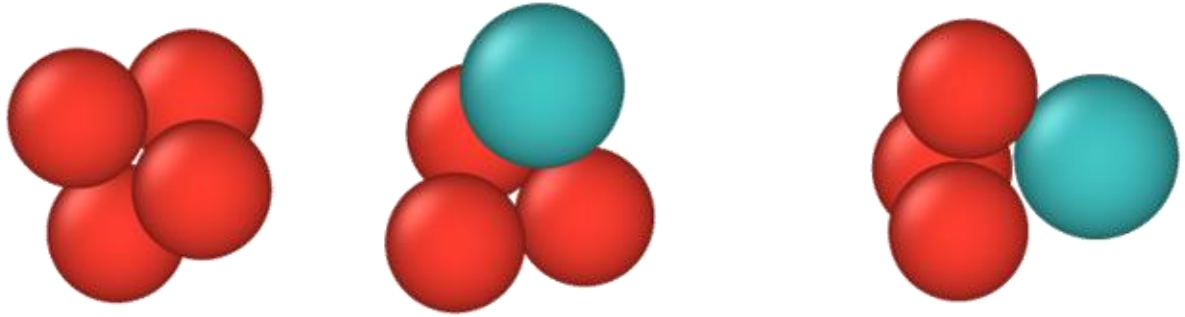

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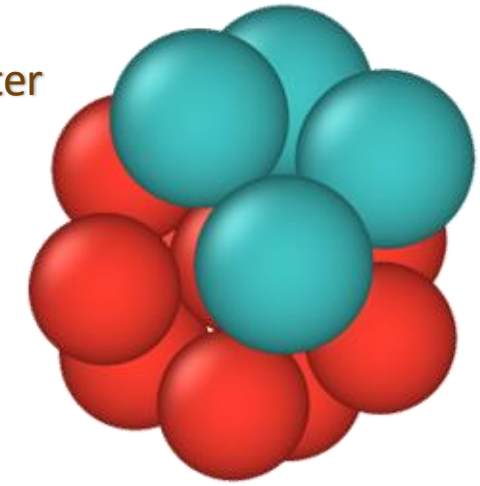
Tetrahedral cluster: 4 neighbour particles linked all together by distance.

Quantify the **tetrahedrality of the local structure**:

Counting the number of tetrahedron that one particle is involved in.

Icosahedral Cluster



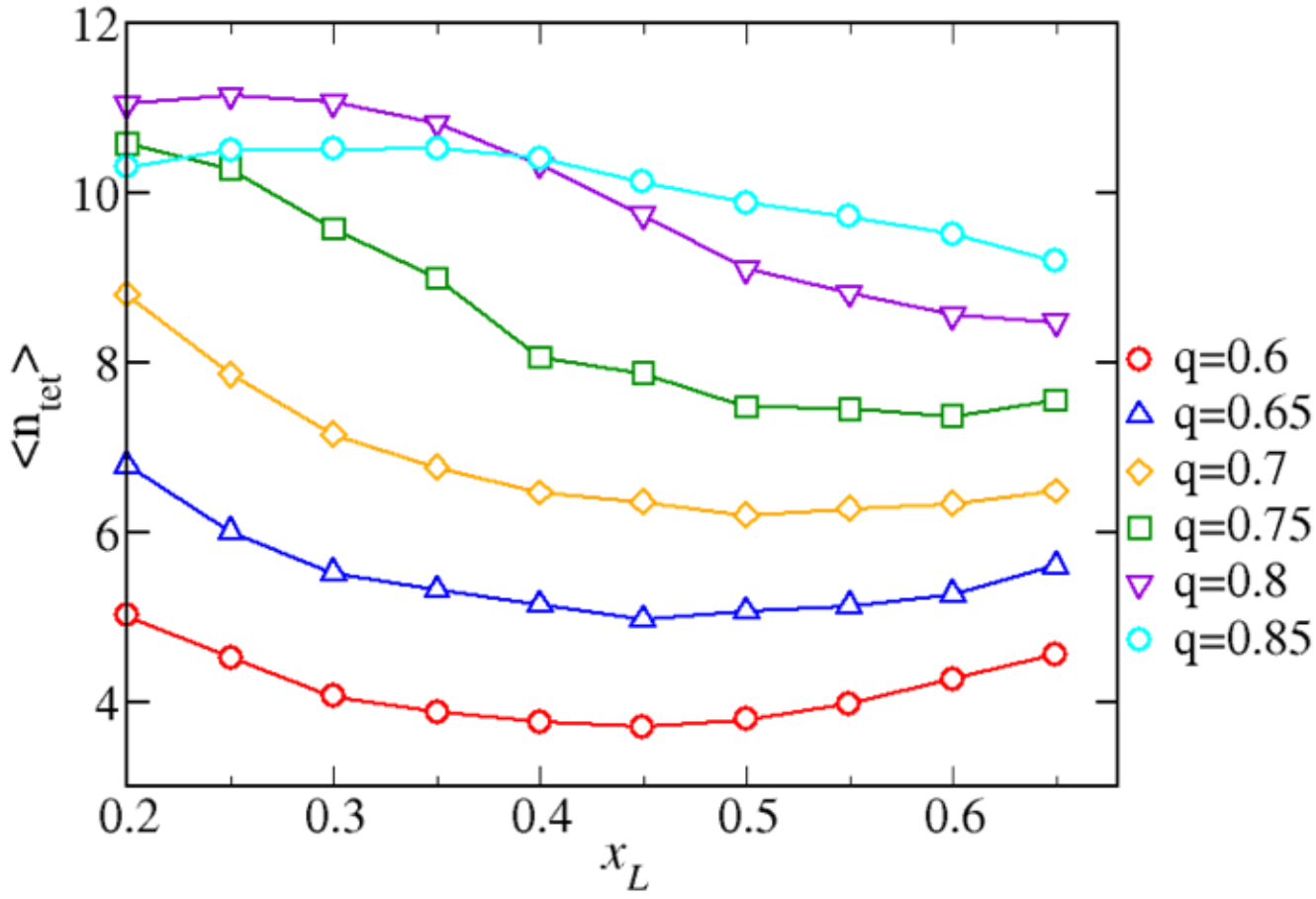
The central particle will be involved in 20 tetrahedrons

Dynamics and Structure

η=0.575

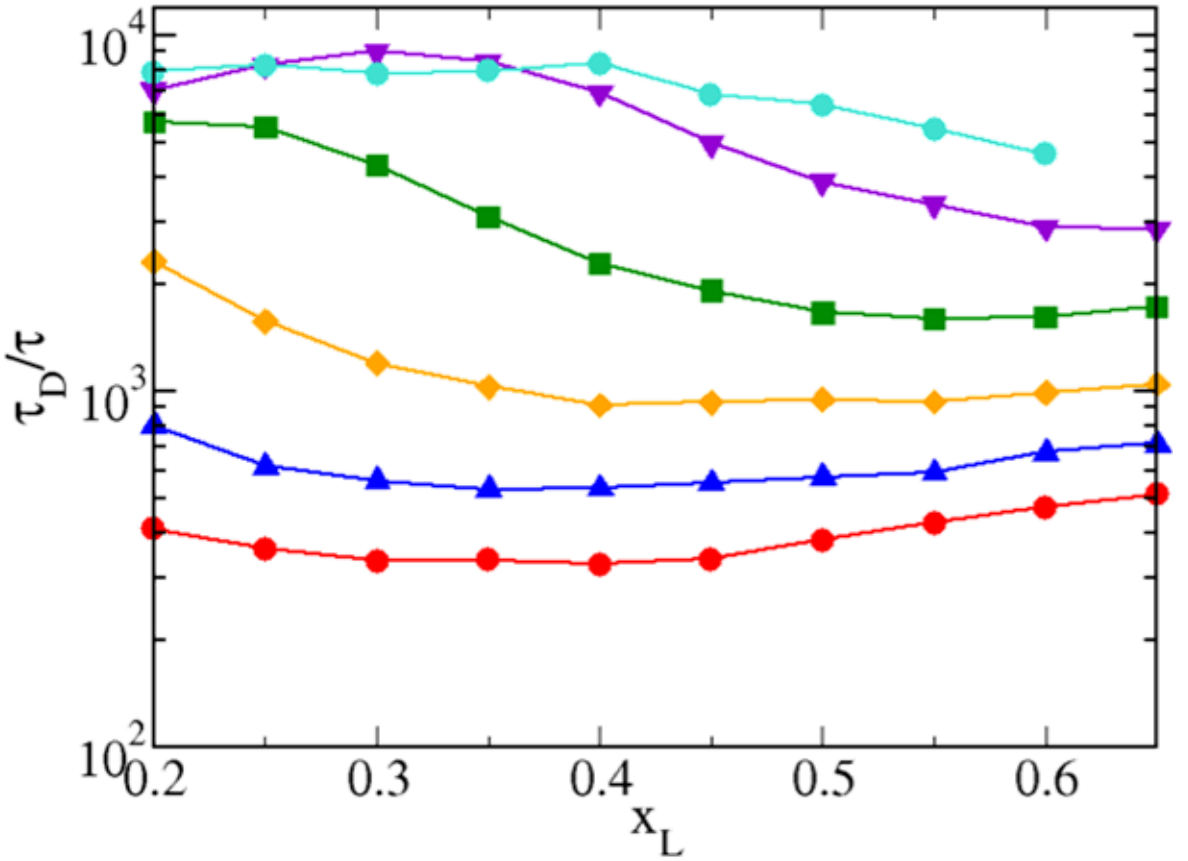
- Non monotonous behaviour on average number of tetrahedron per particle.
- Sensitive parameter to the changes of q and X_L

Number of tetrahedron per particle

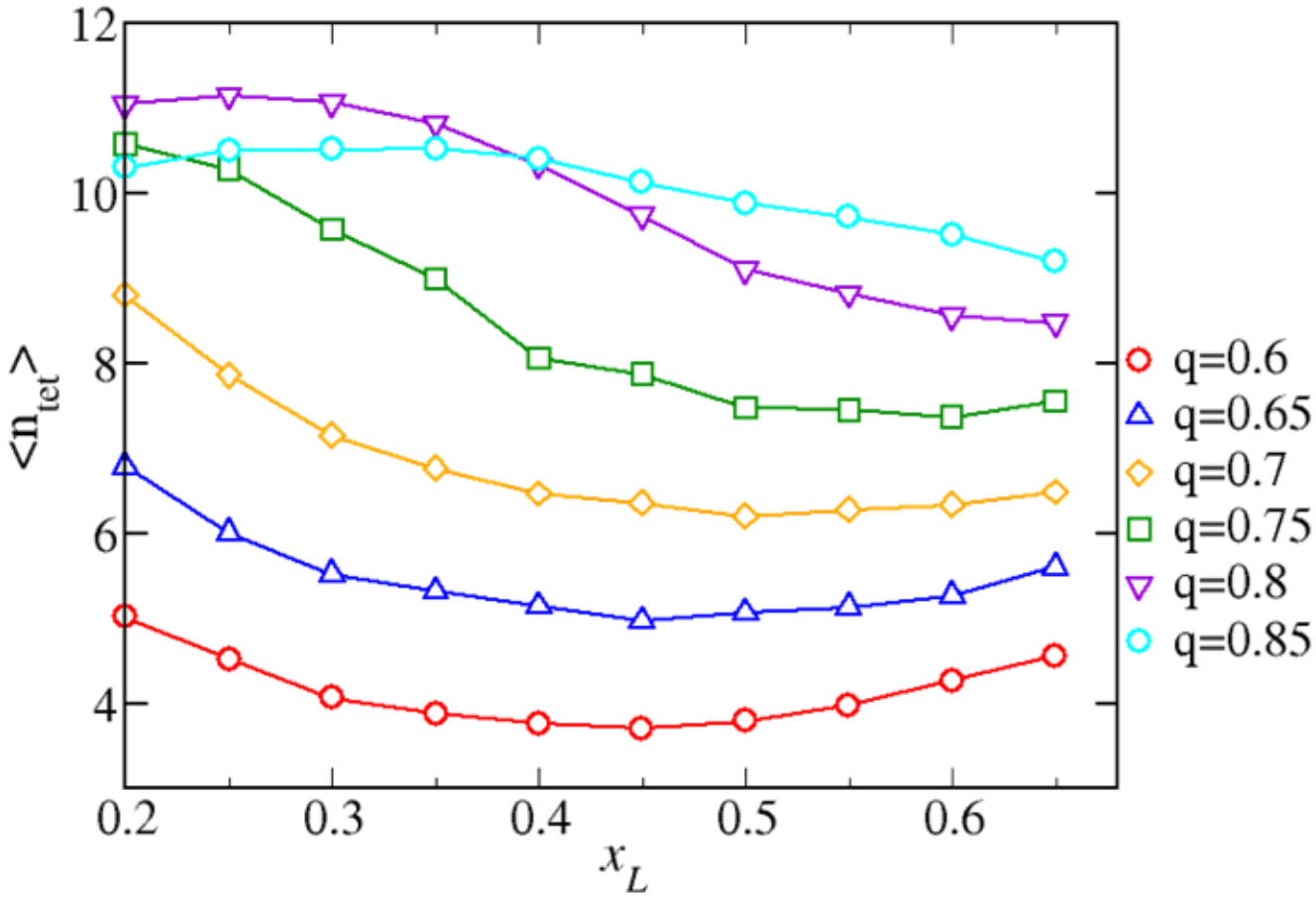


Dynamics and Structure

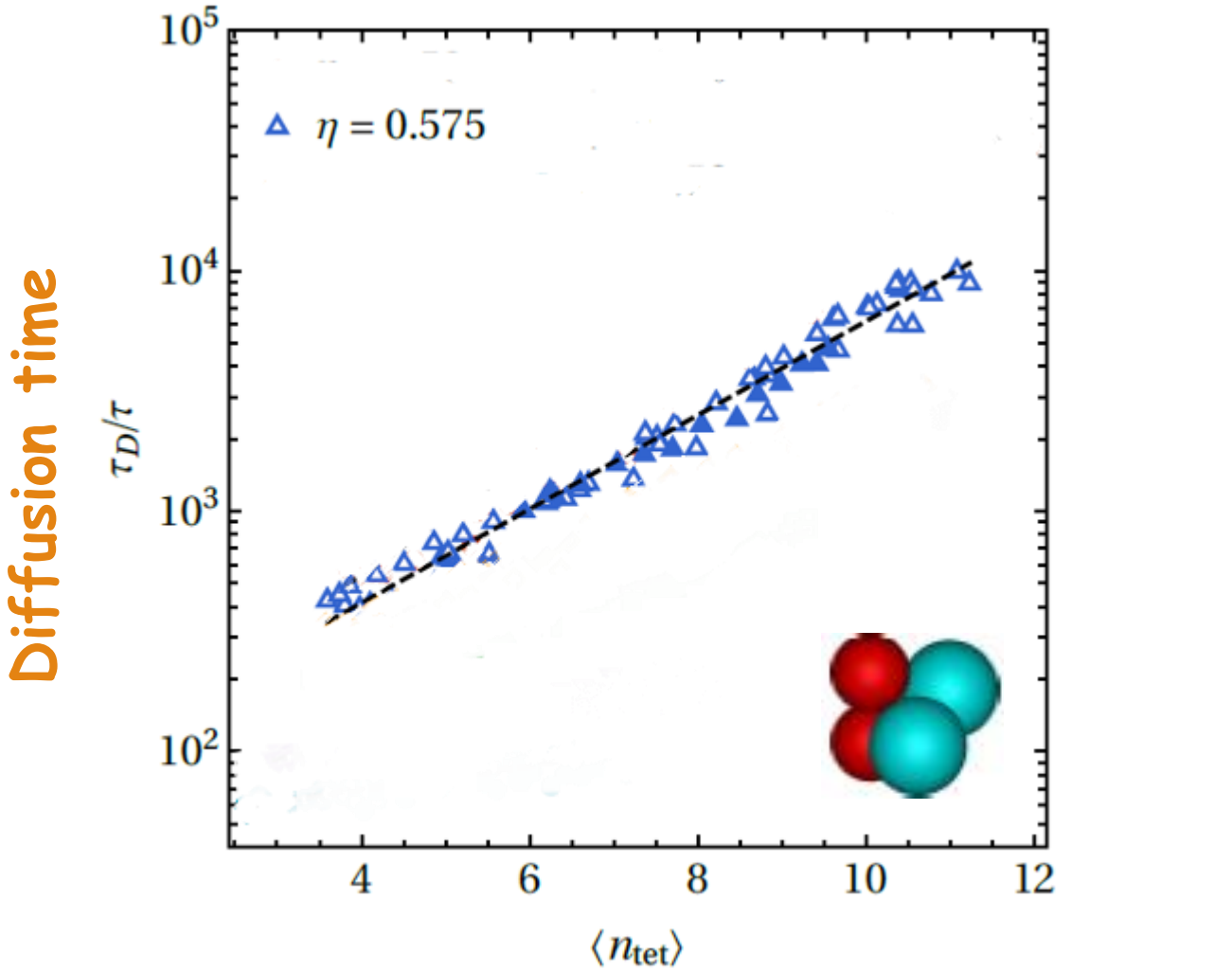
η=0.575



Number of tetrahedron per particle

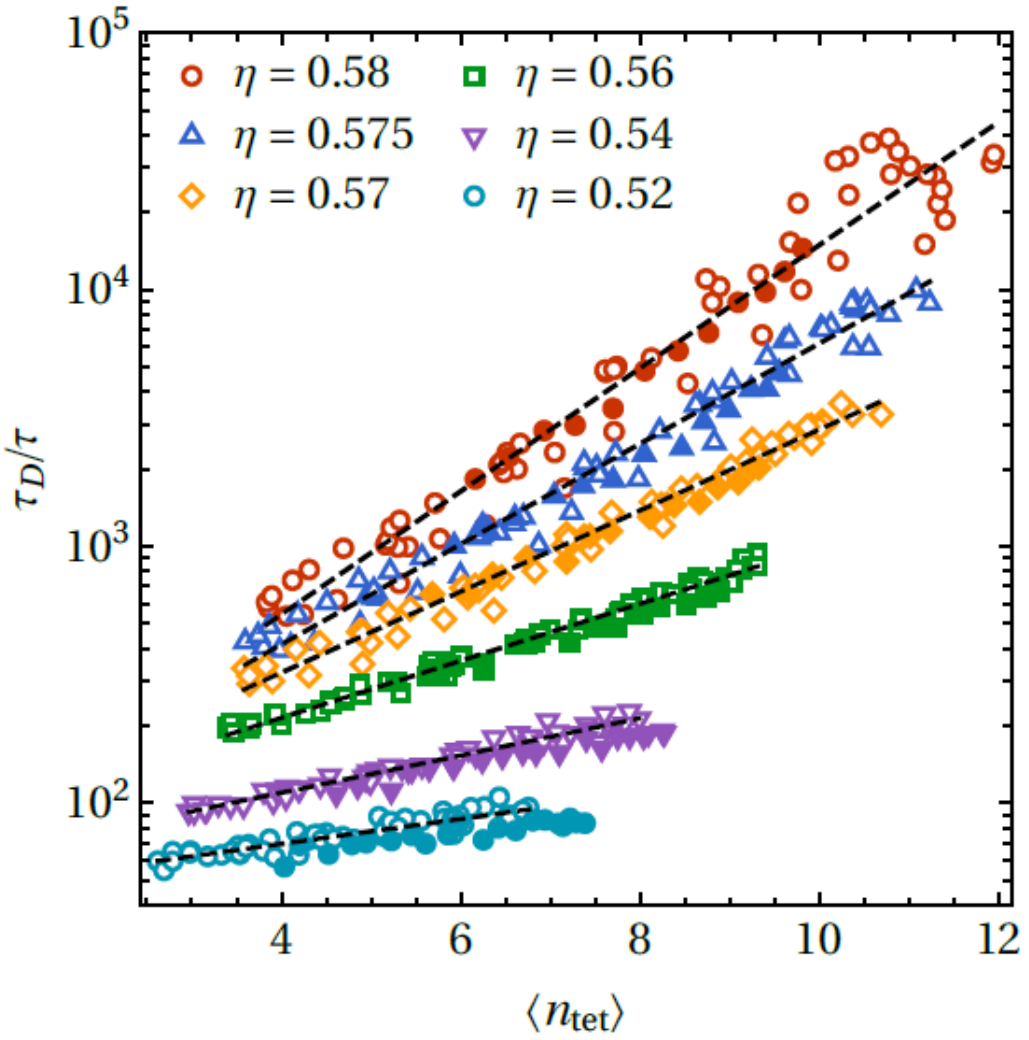


Hard Sphere Systems



Hard Sphere Systems

Different packing fractions follow the same relation between the number of tetrahedra and the diffusion time.



Hard Sphere Systems

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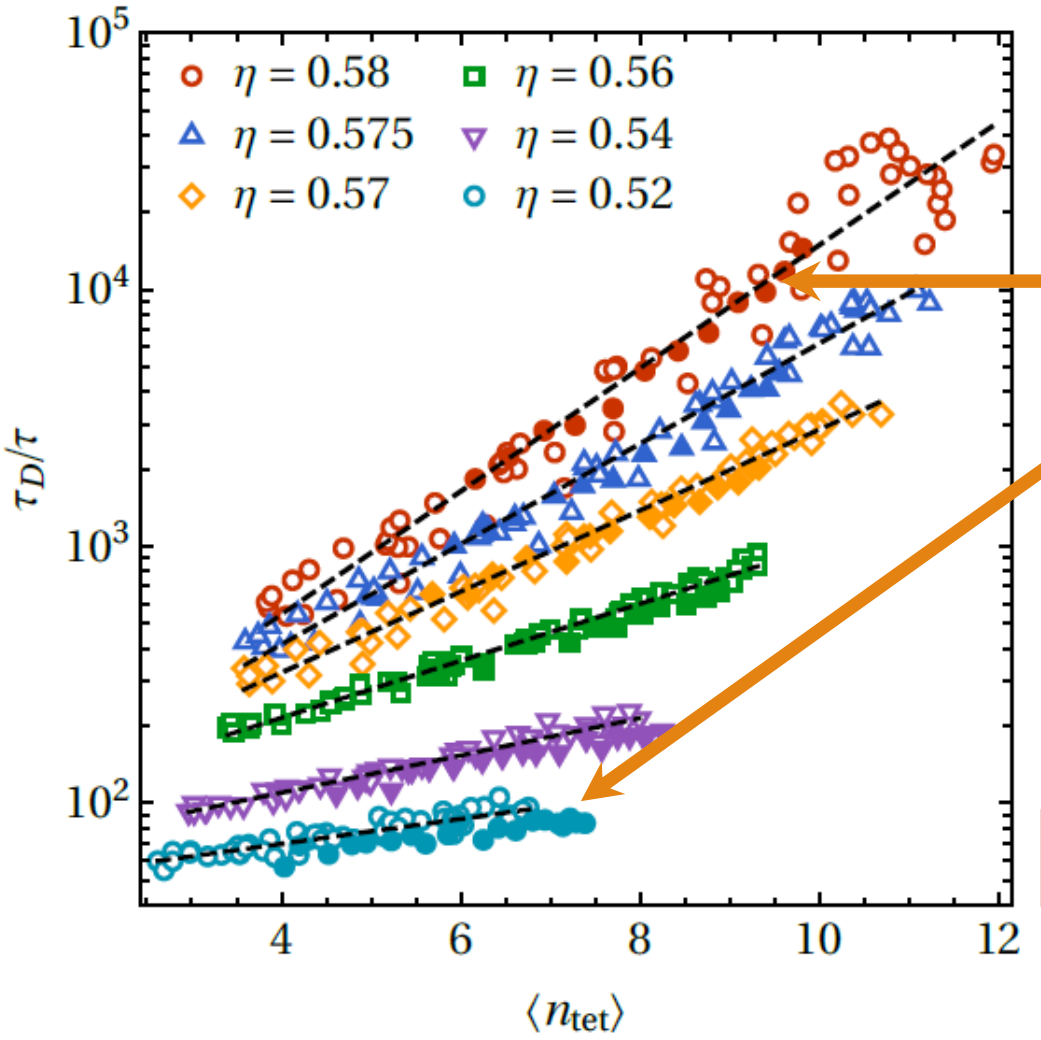
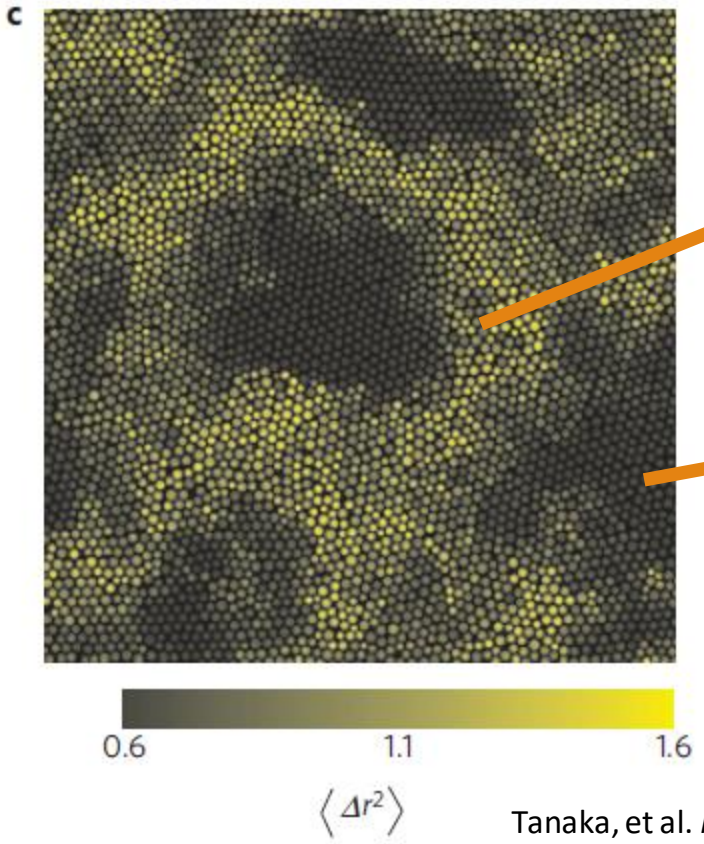


The polydisperse systems follow the same trend.

General Behavior

Heterogeinity

Local Behavior



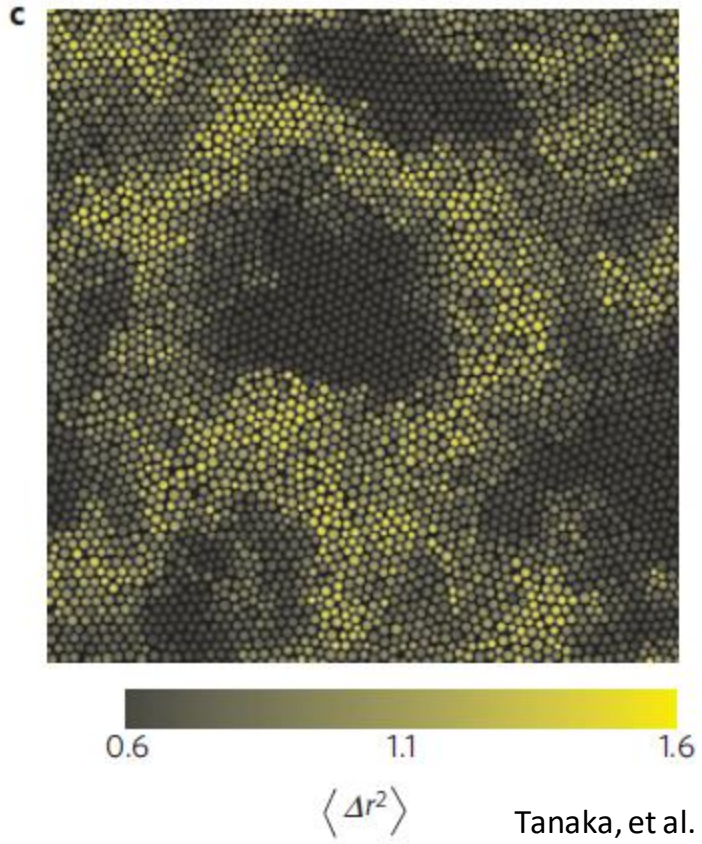
Regions of high mobility

Regions of low mobility

Tanaka, et al. *Nat. mater*, **9**, 4, (2010)

Heterogeinity

Local Behavior



How the tetrahedrality of the system affects local mobility?

Characterize:

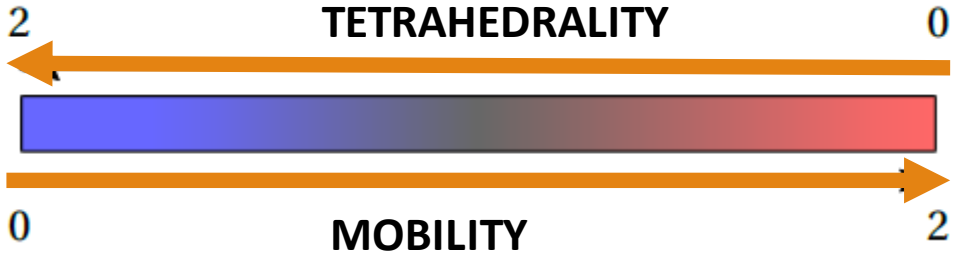
- Local mobility (Propensity)
- Local tetrahedrality

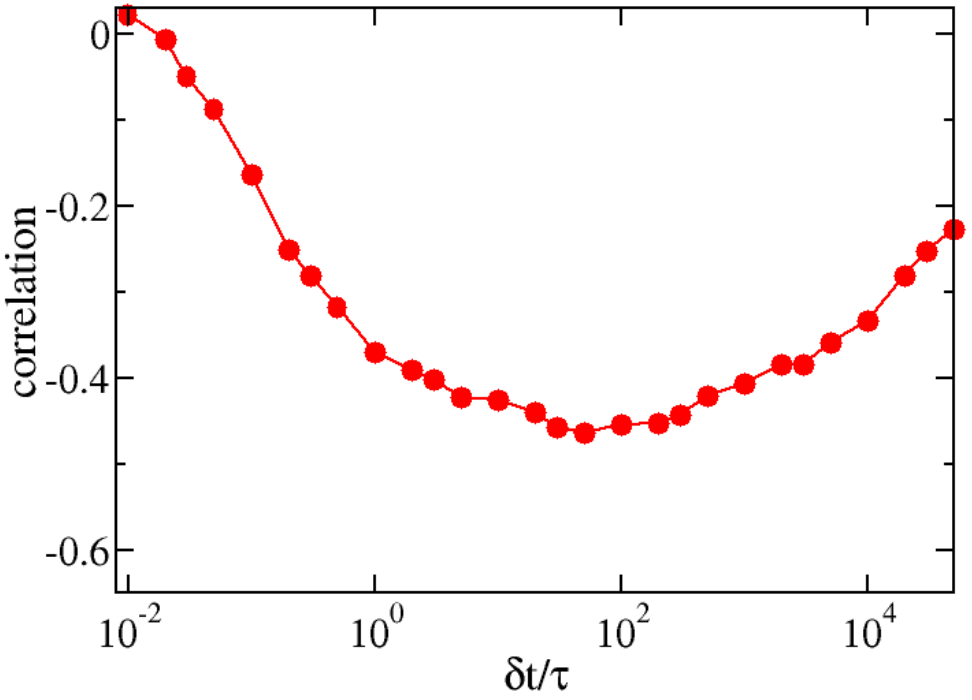
} Correlation

Tanaka, et al. *Nat. mater*, **9**, 4, (2010)

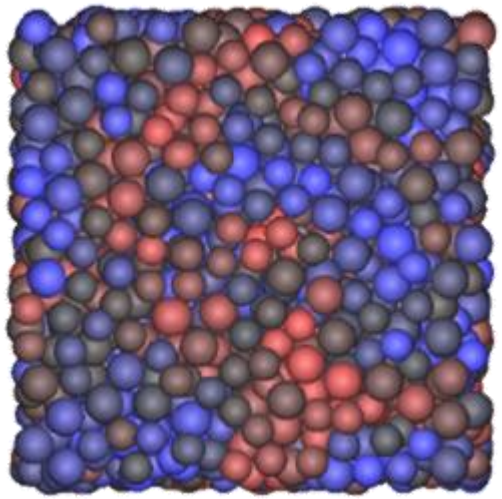
Hard Sphere Systems

How well correlated are those two quantities in time?





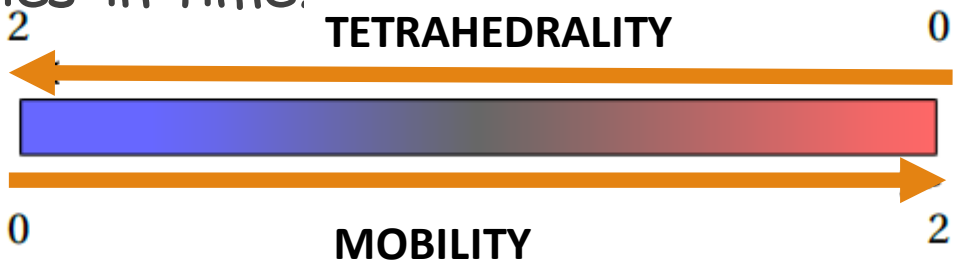
Anticorrelation

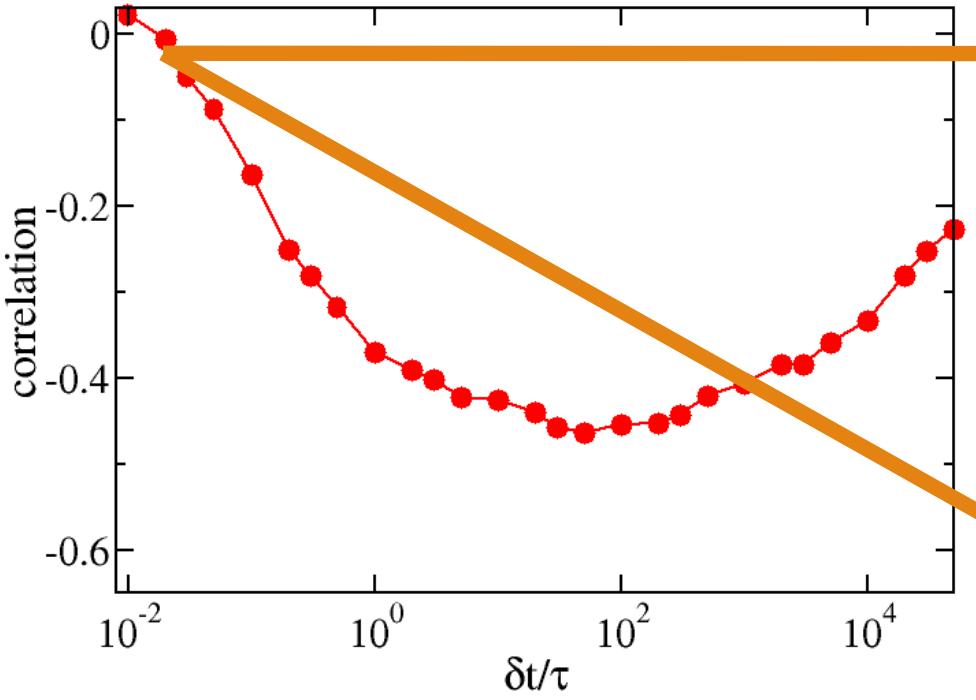


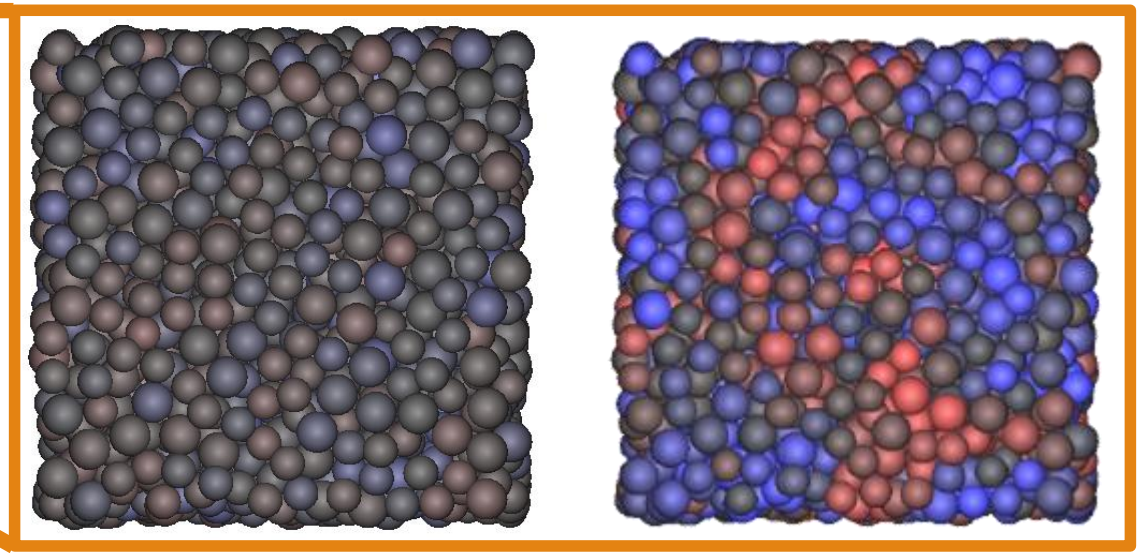
Number of tetrahedra

Hard Sphere Systems

How well correlated are those two quantities in time?





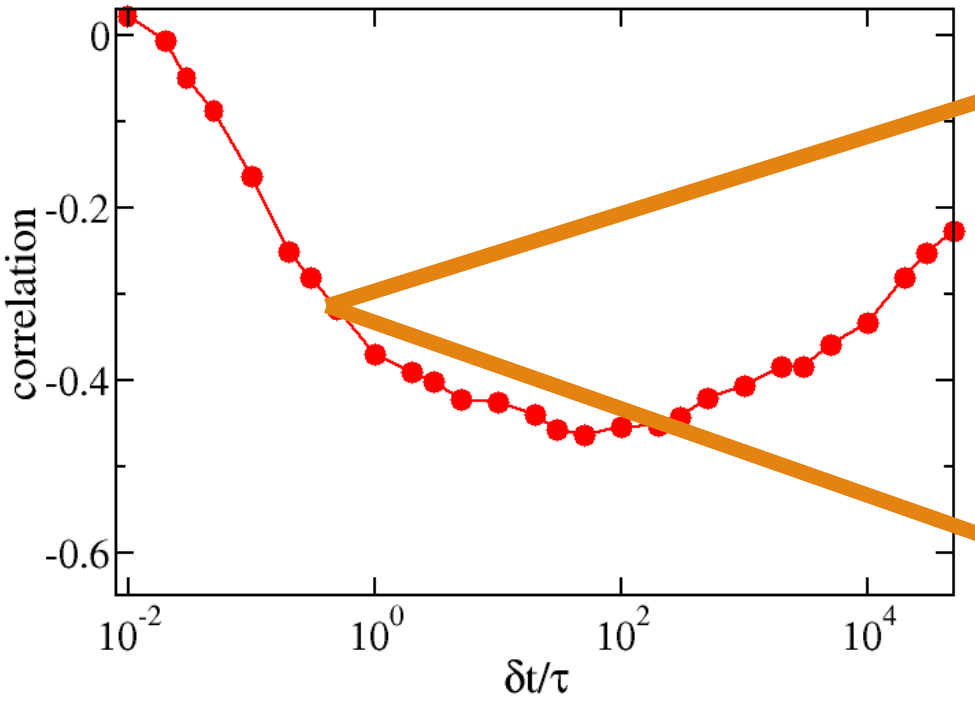


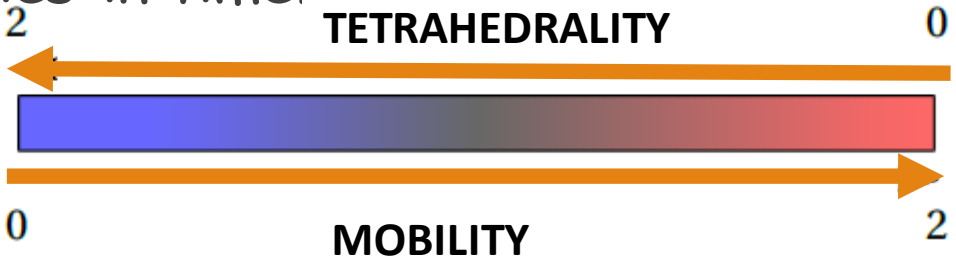
Propensity

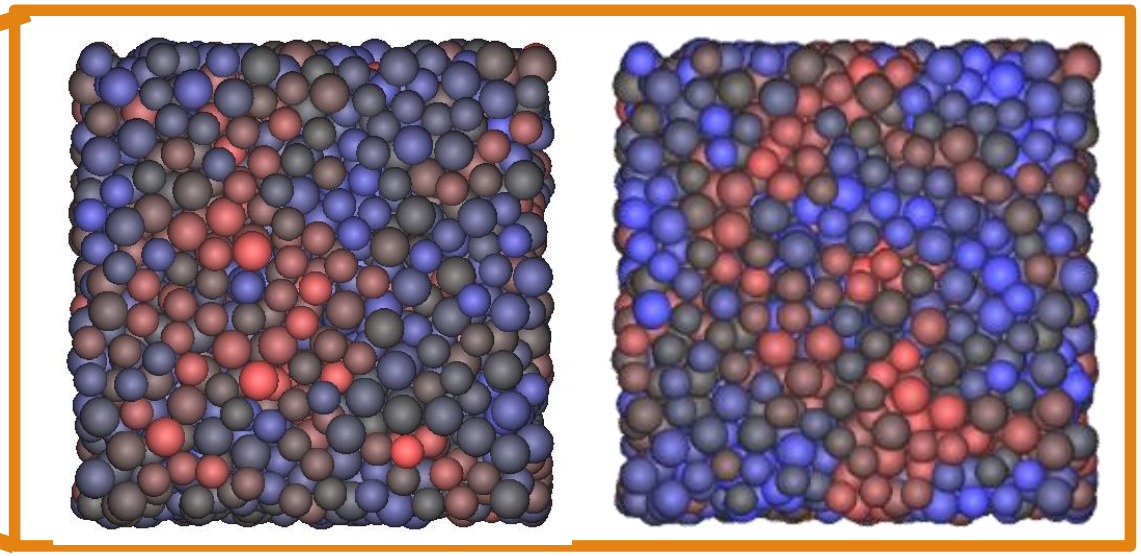
Number of tetrahedra

Hard Sphere Systems

How well correlated are those two quantities in time?







Propensity

Number of tetrahedra

Hard Sphere Systems

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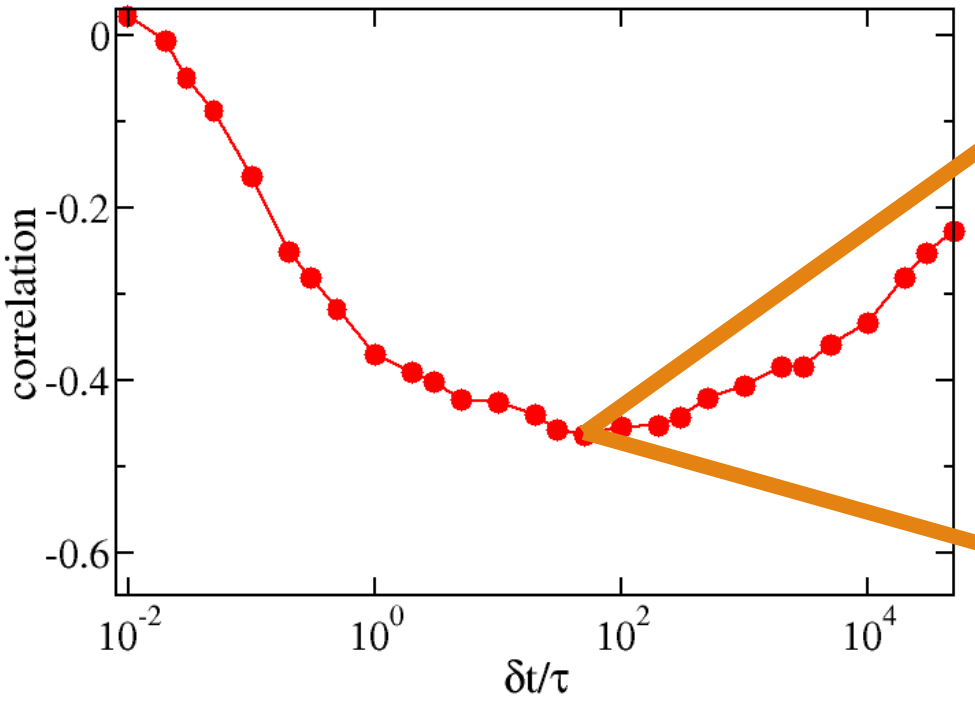
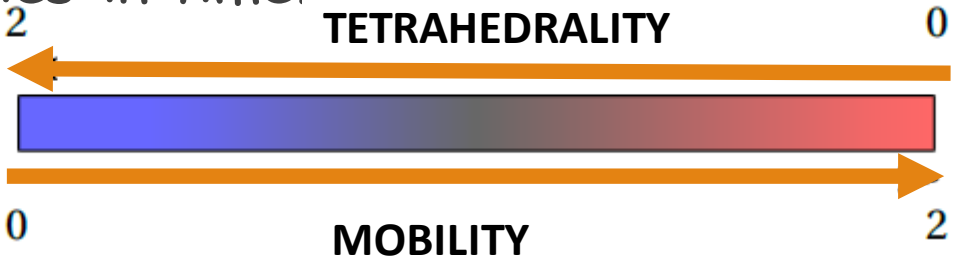
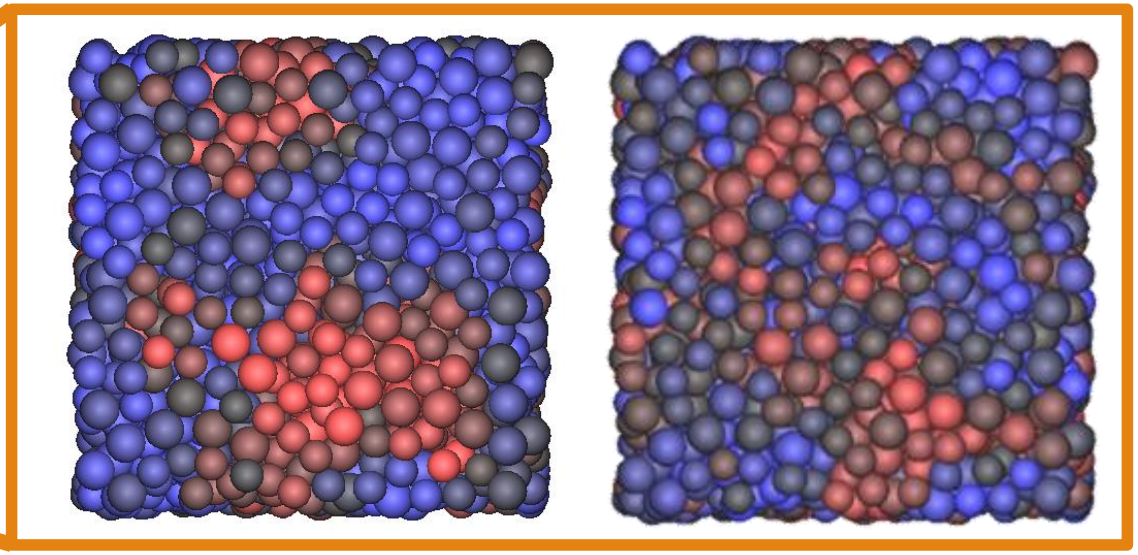




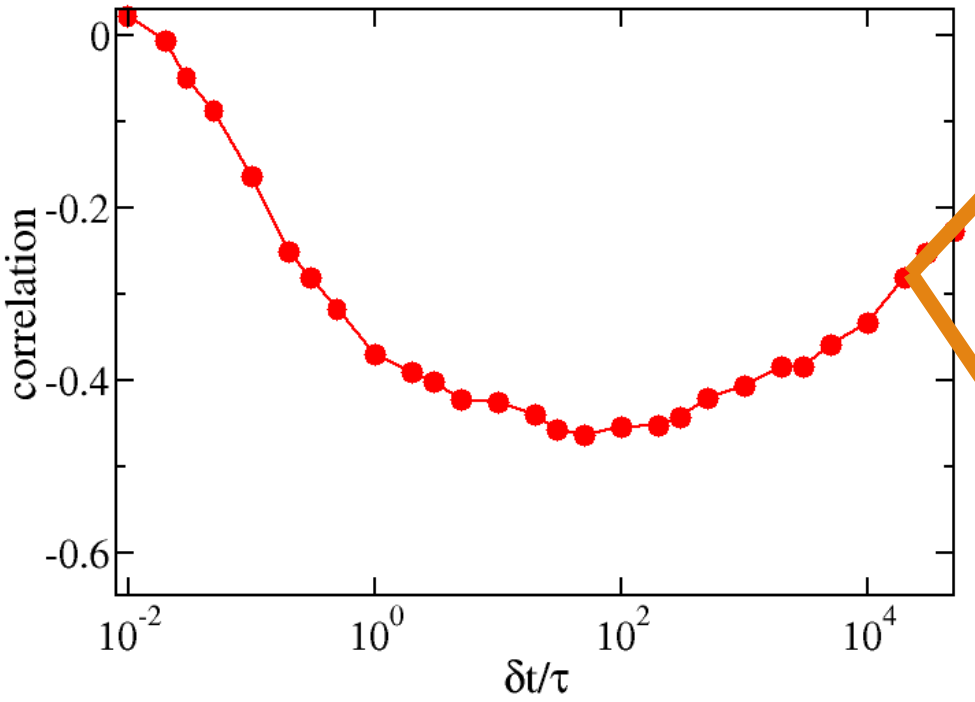


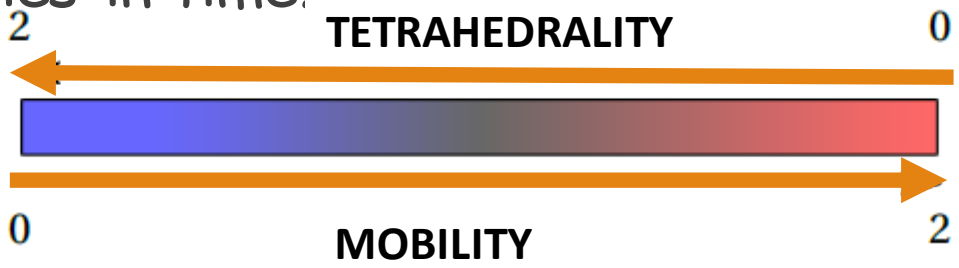
Propensity

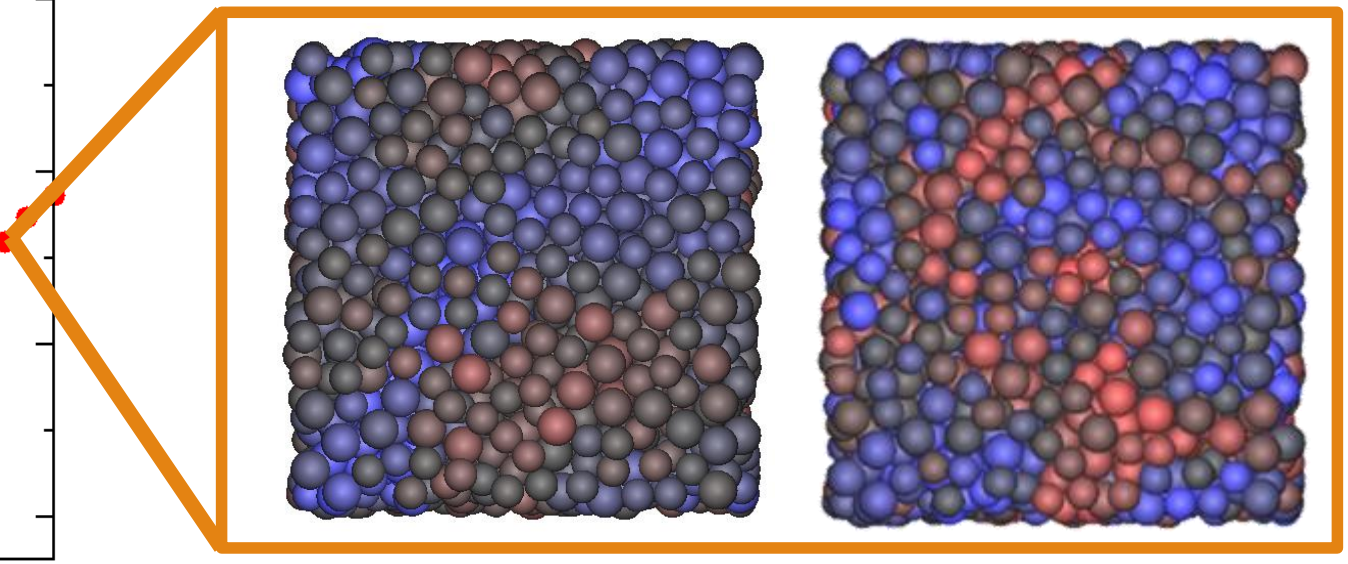
Number of tetrahedra

Hard Sphere Systems

How well correlated are those two quantities in time?



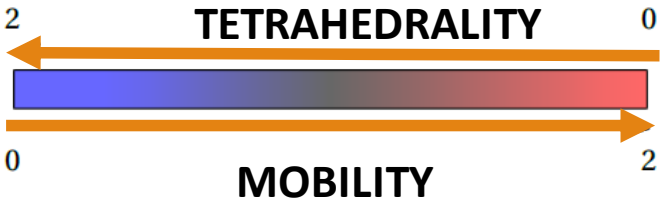


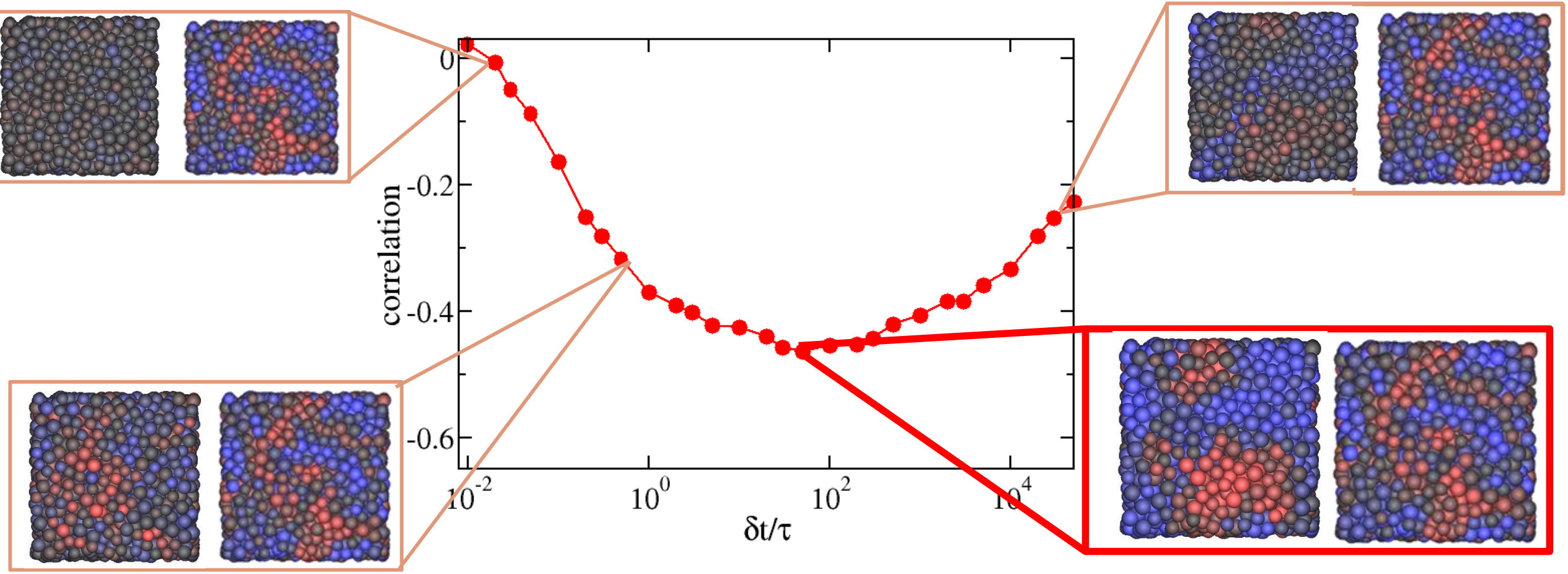


Propensity

Number of tetrahedra

Hard Sphere Systems





Summary (second part)

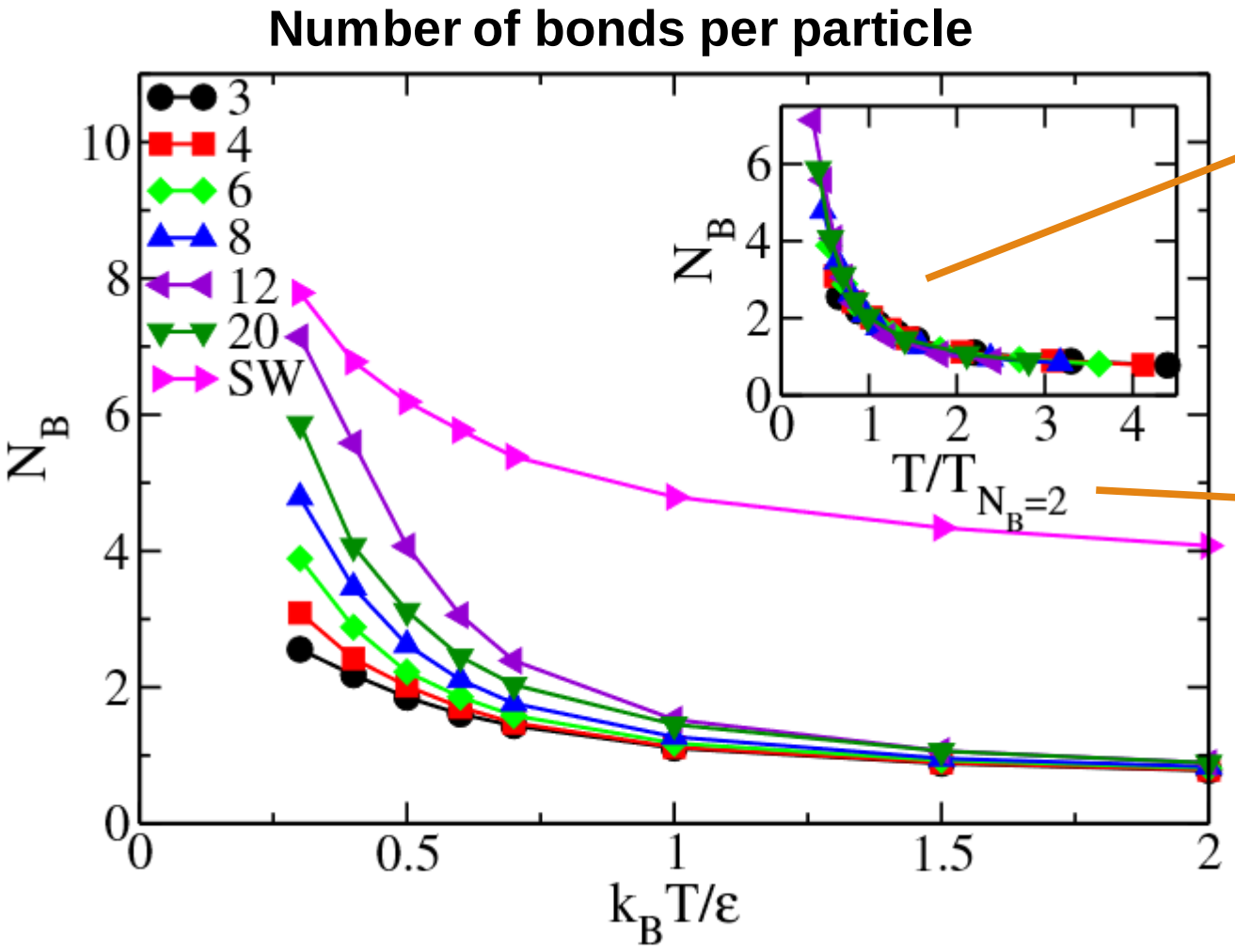
- Changing the size ratio and the composition induces changes in the local structure and the dynamics.
- Tetrahedrality is a good parameter that can be used to predict global dynamical properties.
- At a local level, regions with high tetrahedrality are less mobile.

Tetrahedrality dictates dynamics in hard spheres

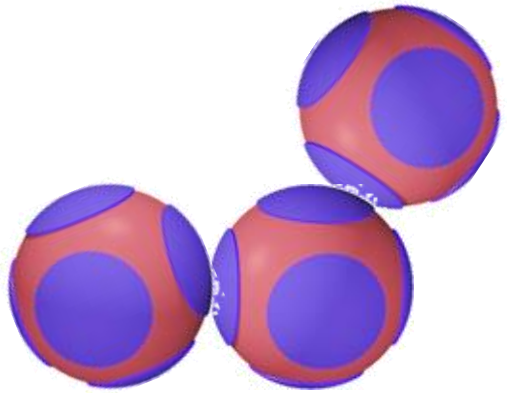
arXiv:1908.00425

Thank you!

Different Patch Geometries

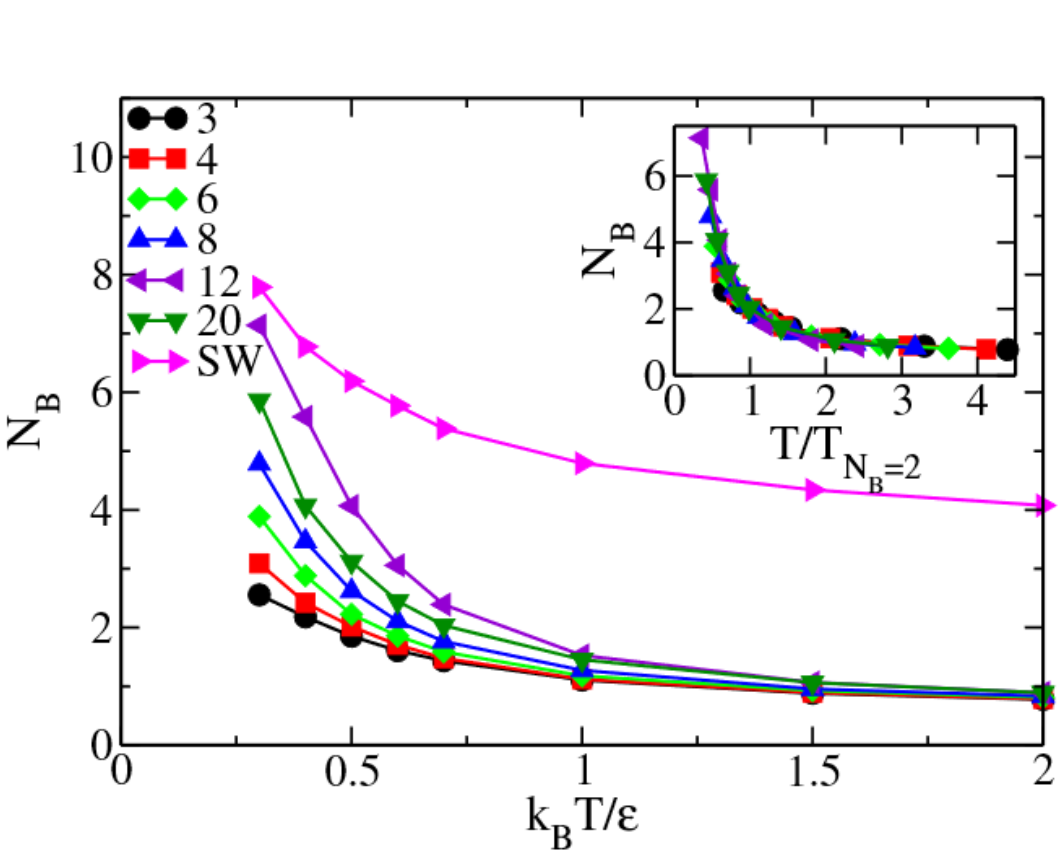


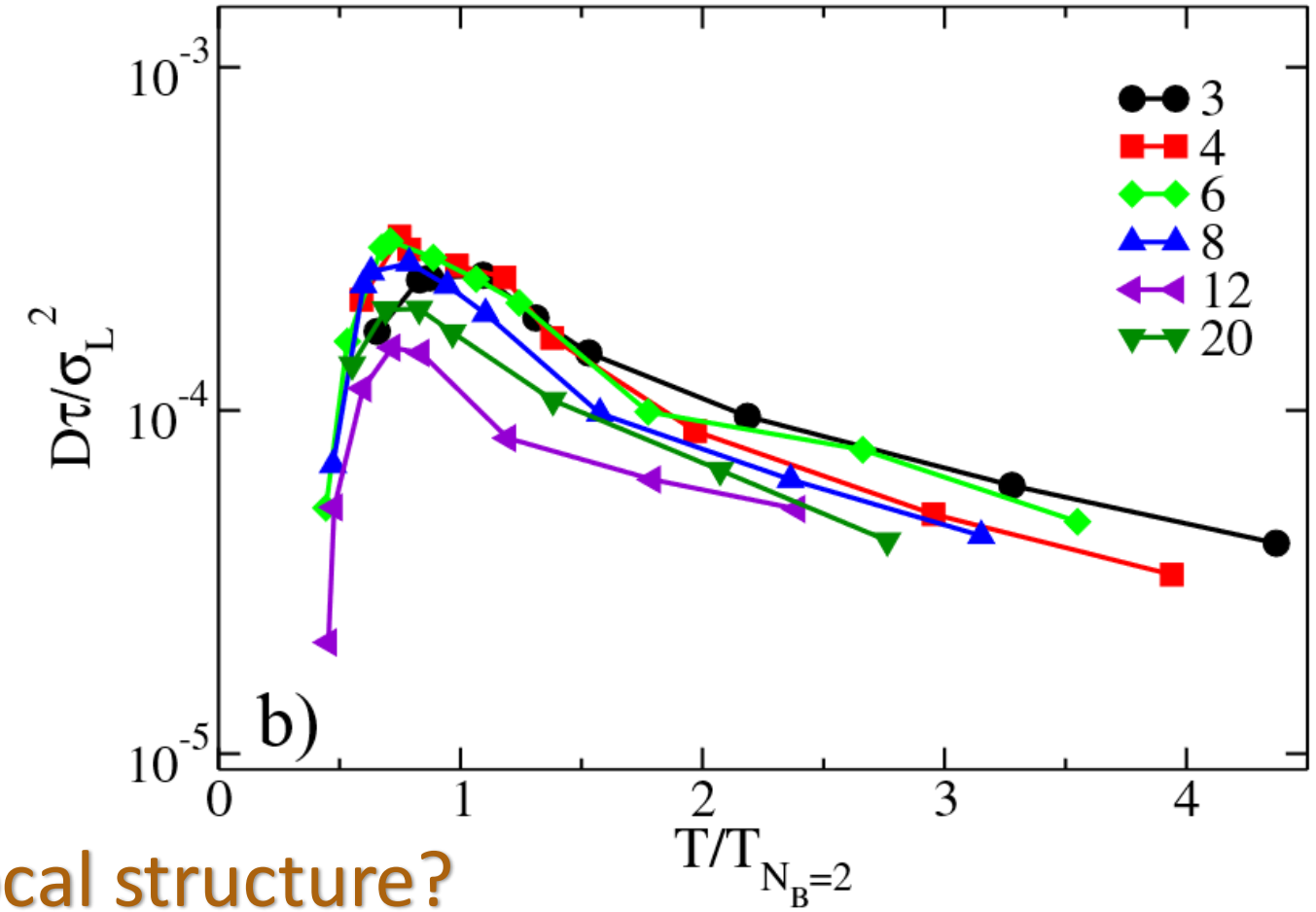
The number of bonds obeys a master curve, when the temperature is normalized.



Different Patch Geometries

Number of bonds per particle





Then… what about the local structure?