“Water and Water Systems”

3rd Course of the ERICE School “NEUTRON SCIENCE AND INSTRUMENTATION” 22nd July– 31st July 2016, Erice (Italy)

Roles of local structural ordering in water anomalies and ice nucleation

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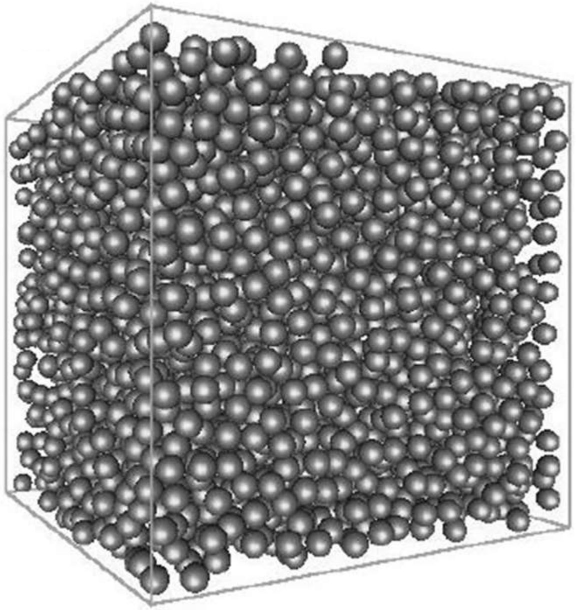
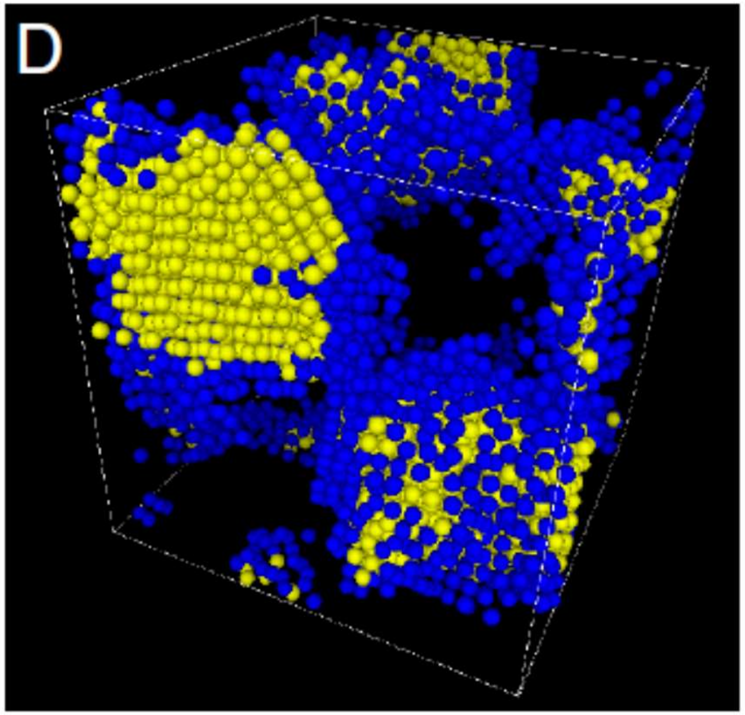
How is a crystal born in a supercooled liquid?

Question:

Is it a sudden event or any preparation for the birth?



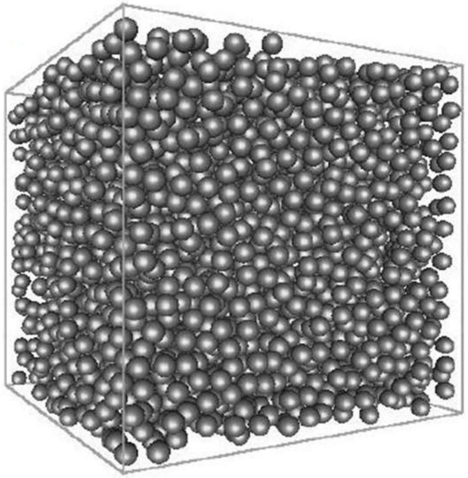
Liquid has a random structure?



Crystal has a periodic regular structure.

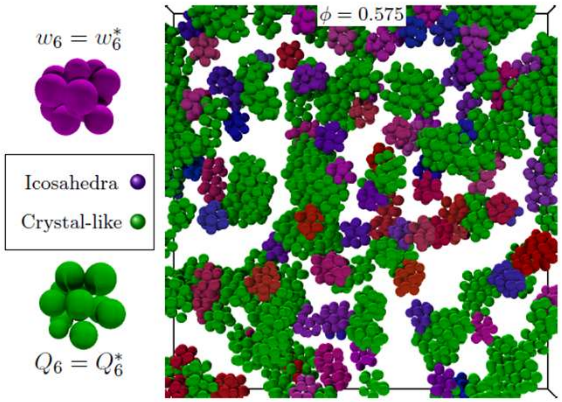
Our view

high-*T* liquid



little structural order

Supercooled liquid



glass

Growth of structural order=Slower dynamics

Preordering acts as precursor for crystal nucleation

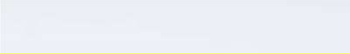
crystal

With an increase in the degree of supercooling, structural order *generally* develops in a liquid.

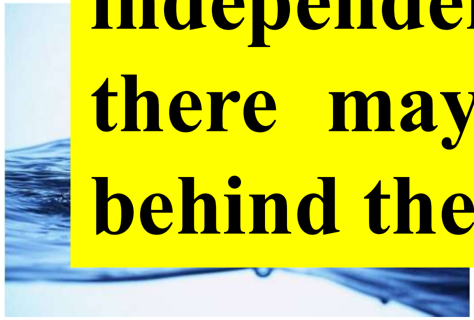
Here we consider link between slow glassy dynamics of a supercooled liquid and crystal nucleation.

Glass transition

glass



cooling

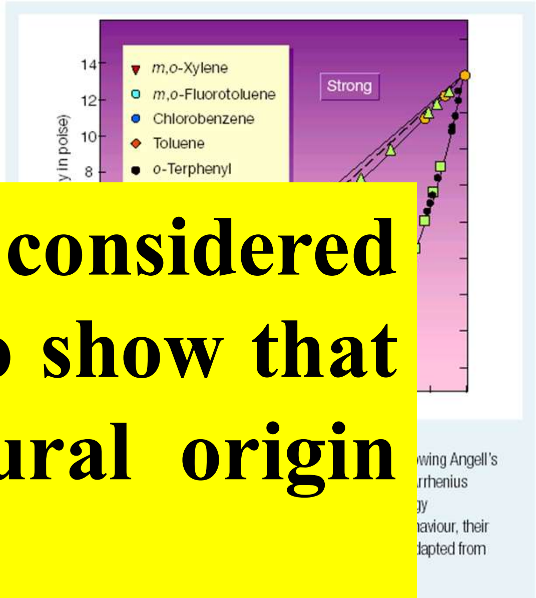


These problems have so far been considered independently, but we are going to show that there may be a common structural origin behind them!

*T*m

crystal

Crystallization



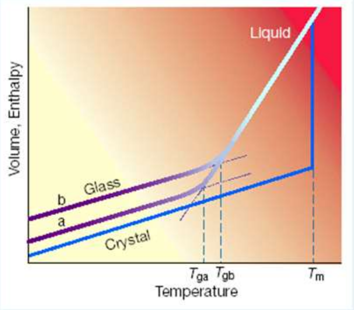
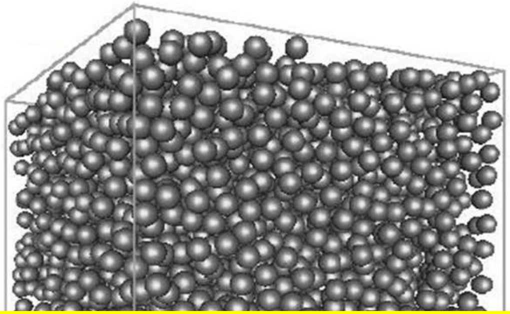
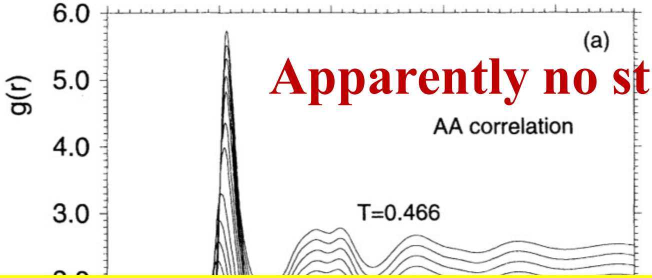


Figure 1 Temperature dependence of a liquid's volume *v* or enthalpy *h* at constant pressure. T_m is the melting temperature. A slow cooling rate produces a glass transition at T_{ga}; a faster cooling rate leads to a glass transition at T_{gb}. The thermal expansion coefficient $\alpha_p = (\partial \ln v/\partial T)_p$ and the isobaric heat capacity $c_p = (\partial h/\partial T)_p$ change abruptly but continuously at T_g.

Standard view on a supercooled liquid





Apparently no structural change!

We are going to show that this picture may not be true for a highly supercooled state.

In classical nucleation theory and density functional theory, $\rho(r)$ is the only order parameter.

In this framework, a perfect crystal is born suddenly in a disordered liquid.

Our view

glass

Liquid is more and more structured locally upon cooling. But this cannot be seen by probing translational order, e.g., g(r).

Liquid lowers the free energy by local structuring upon cooling and is preparing for future crystallization in a supercooled state.

crystal

This structural order cannot be seen by 2-body density correlator.

Density or translational order is not enough to describe structuring in liquid!

The key question:
What is the important structural order parameter beside density field?

Most analytical theories are based on the conventional liquid state theory, which is mainly described by two-body density correlators.

Popular theories of glass transition

- **Mode-coupling theory**
- **Random-first-order-transition (RFOT) theory**
- **….**

Standard theories of crystallization

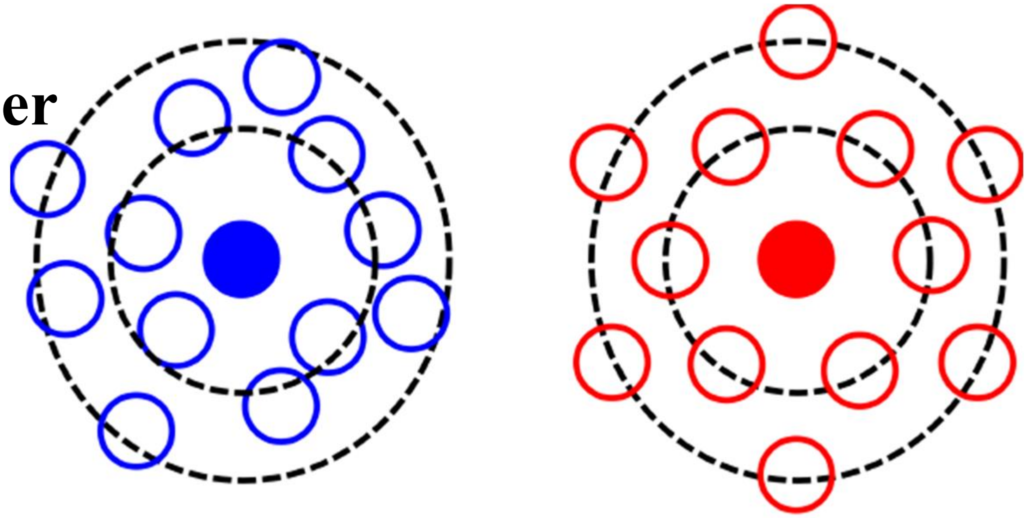
- **Density functional theory**

Q: It is not so sure whether the density field (two-point density correlator) is enough for the physical description of a supercooled liquid or not.

Two types of symmetries which are broken upon crystallization in a quasi-single component system

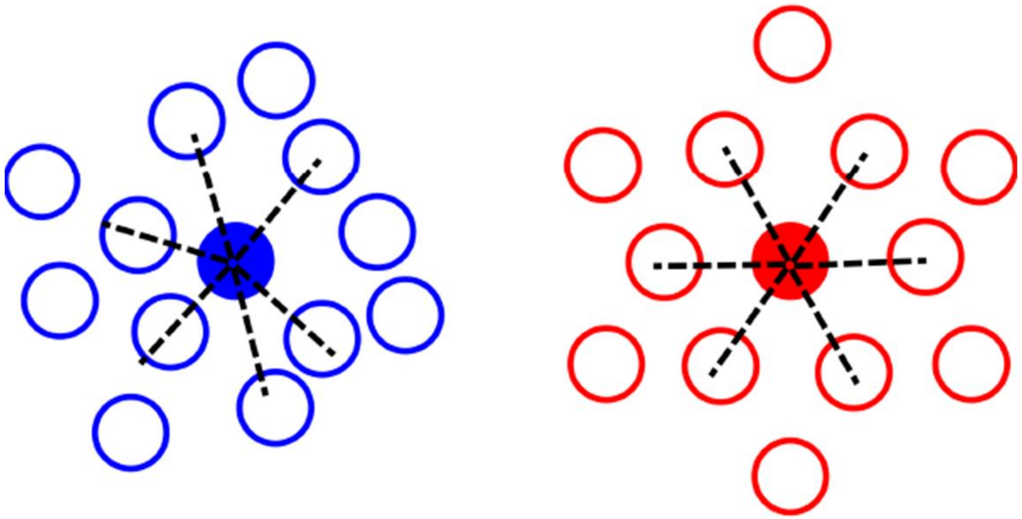
Translational Symmetry
(Translational Order):
It is associated with global order with spatial periodicity.

Translational order is fragile against disorder or frustration



Rotational Symmetry
(Bond Orientational Order):
It can be defined locally!

Bond orientational order is persistent even under disorder or frustration



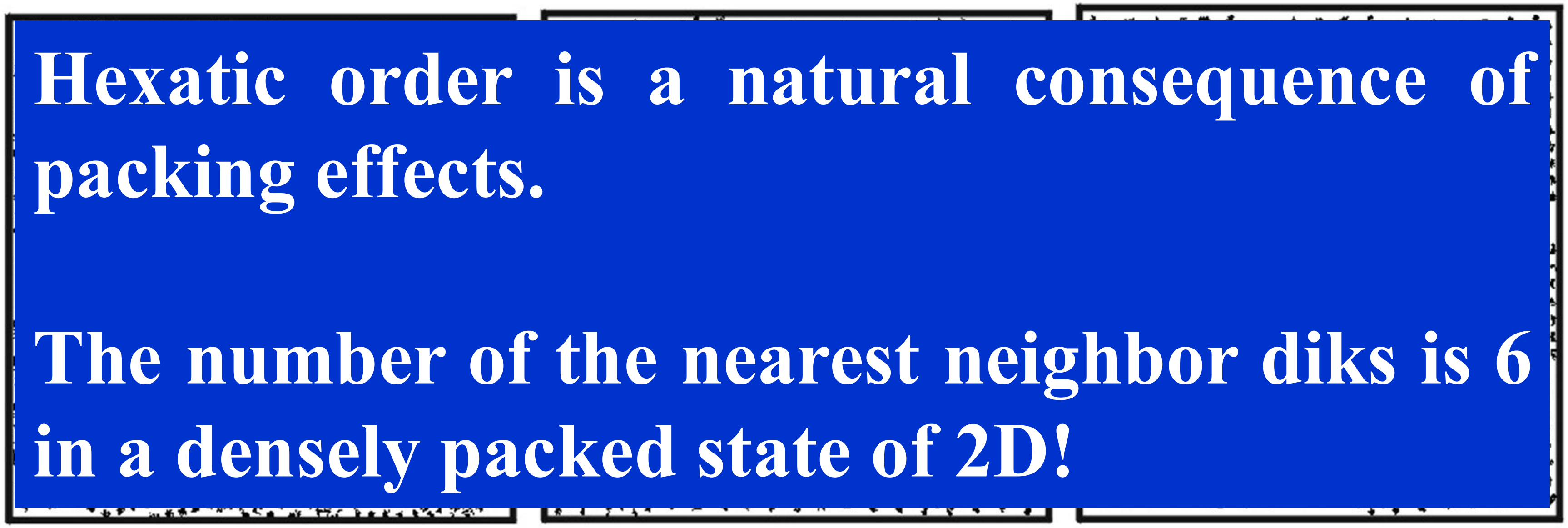
In 2D, it is widely accepted that orientaional order plays a crucial role in liquid-solid transition.

Two-step orderings:
Liquid-hexatic-crystal transition

Ordering of 2D hard disks

KTHNY scenario

density



Hexatic order is a natural consequence of packing effects.

The number of the nearest neighbor diks is 6 in a densely packed state of 2D!

liquid **hexatic** **crystal**

short-range positional order

quasi-long-range positional order

short-range orientaional order

quasi-long-range orientaional order

How are the two types of symmetries broken upon crystallization?

So far liquid-glass transition and crystallization in 3D liquids has been discussed on the basis of translational ordering.

Here we focus on roles of bond orientational ordering in these phenomena!
This ordering is a manifestation of non-trivial many-body effects!

breakdown of rotational symmetry, rotational ordering is hidden behind translational one!
If crystallization is avoided, hidden rotational ordering may appear in a supercooled state.

Here we consider two very important liquids: hard spheres and water.

1. **Hard spheres: the simplest liquid**
   Isotropic hard-core interaction
   Only entropy (or packing) matters.
   The density is a control parameter to induce crystallization.
2. **Water: the most important liquid on the earth**
   Directional interaction due to hydrogen bonding
   The temperature is a control parameter to induce crystallization.

Conventional view

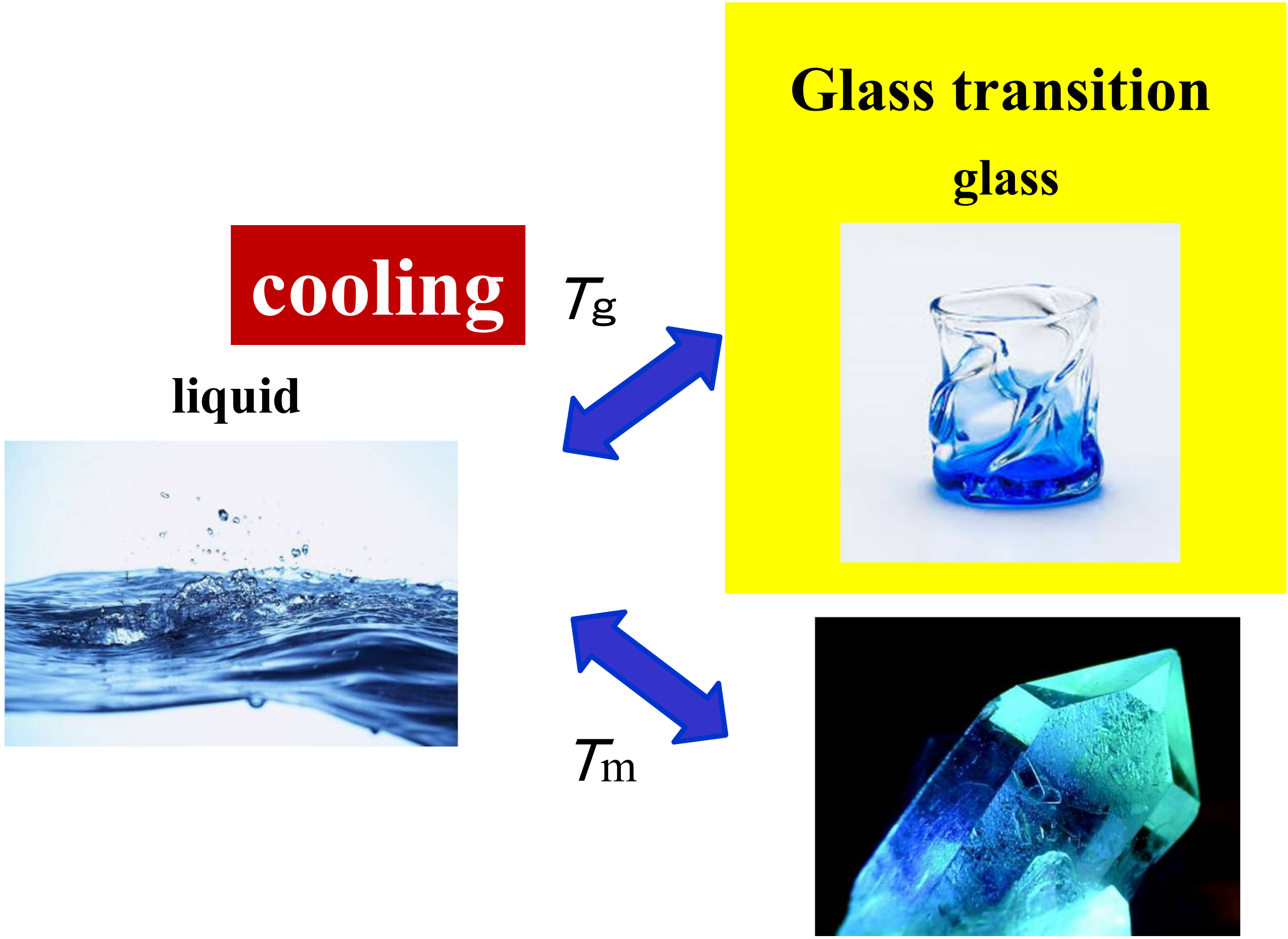
So far liquid-glass transition and crystallization have been discussed on the basis of translational ordering for 3D systems.

Our standpoint

For 2D, there is a consensus on the importance of bond orientational order. Why not in 3D?

Here we focus on roles of bond orientational ordering in these phenomena.
We note that this ordering is a manifestation of non-trivial many-body effects!

Vitrification



Glass transition

glass

cooling

T_g

liquid

T_m

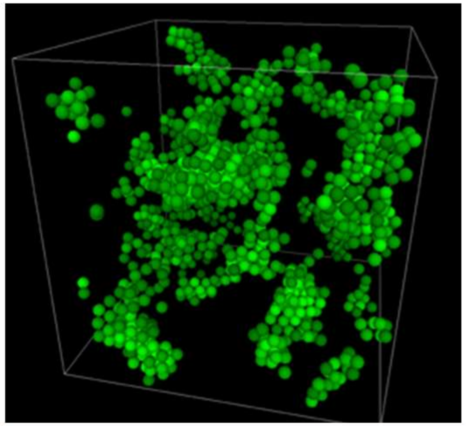
crystal

Crystallization

Next we discuss

Structural ordering and glassy behavior in 3D hard-sphere liquids

control parameter=volume fraction



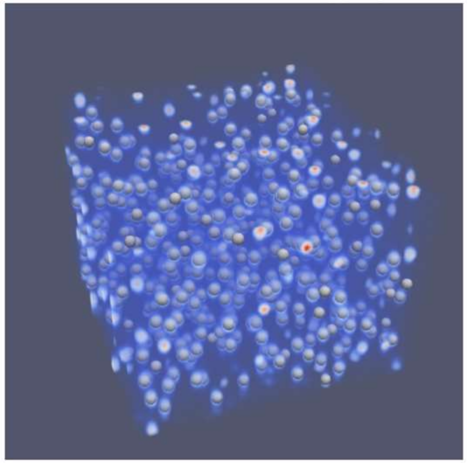
3D Brownian Dynamics Simulations

H. Tanaka, T. Kawasaki, H. Shintani, & T. Watanabe,

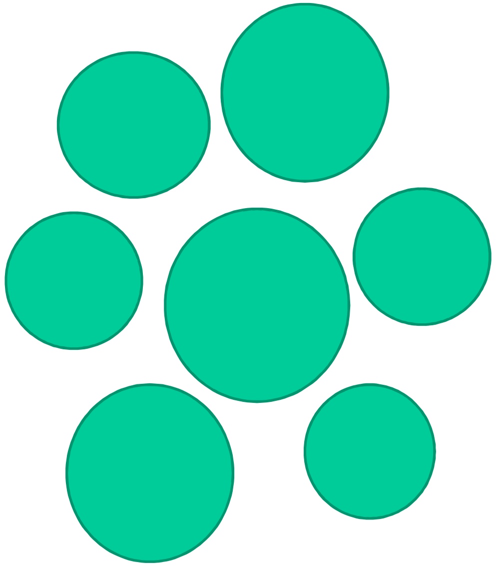
Nature Mater. 9, 324 (2010).

3D confocal microscopy experiments

M. Leocmach & H. Tanaka, Nature Comm. (2012)



We introduce the size polydispersity to induce frustration effects on crystallization and prevent crystallization.



Variance of size distribution= Δ

Questions:
How does the degree of frustration Δ affect the glass-forming ability and dynamical slowing down of liquid?

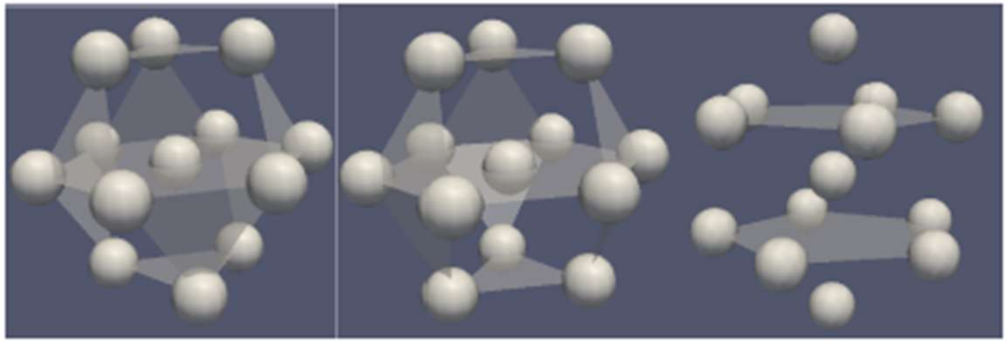
T. Kawasaki, T. Araki and H. Tanaka, *Phys. Rev. Lett.* 100, 099602 (2008)

H. Tanaka, T. Kawasaki, H. Shintani, & T. Watanabe, Nature Mater. 9, 324 (2010).

What are key structural ordering in 3D hard spheres?

The natural number of nearest neighbors in 3D is 12 under dense packing.

Local rotational symmetries selected under this constraint are

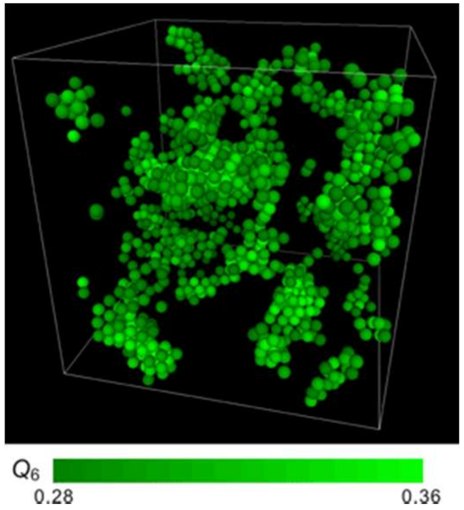


(a) FCC (b) HCP (c) Icosahedron

Steinhardt bond-orientational order parameter

$$\bar{Q}_l^k = \frac{1}{\tau_\alpha}\int_0^{\tau_\alpha} dt \left(\frac{4\pi}{2l+1}\sum_{m=-l}^{+l}|Q_{lm}^k|^2\right)^{1/2}$$

Q_6

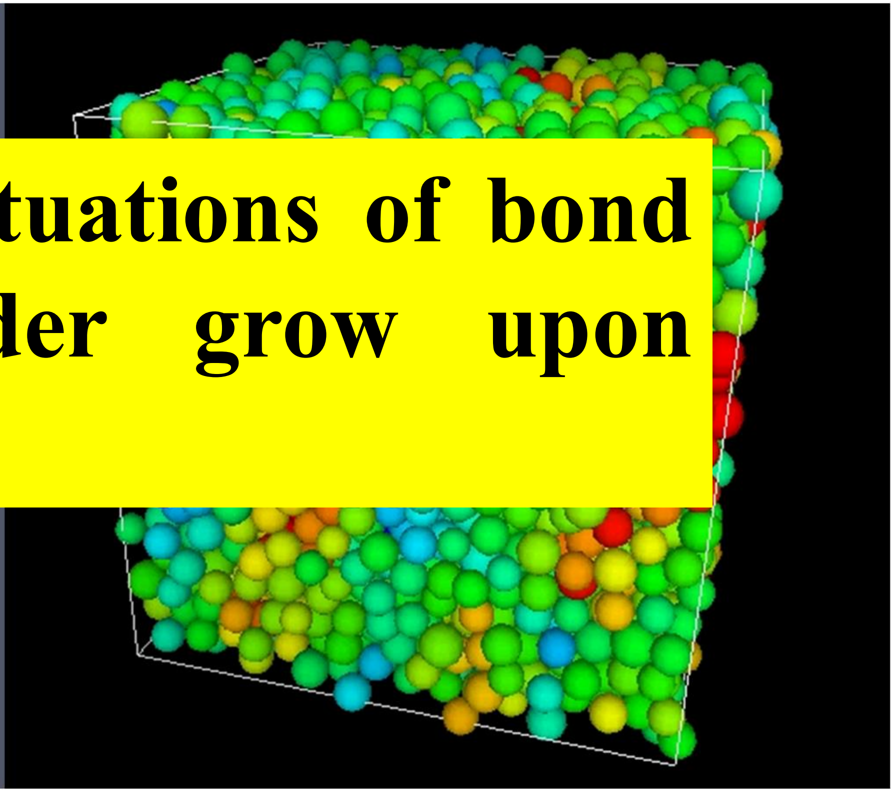


3D polydisperse hard spheres ($\Delta=6\%$)

Critical-like spatio-temporal fluctuations of crystal (fcc)-like bond orientational order (Q6)

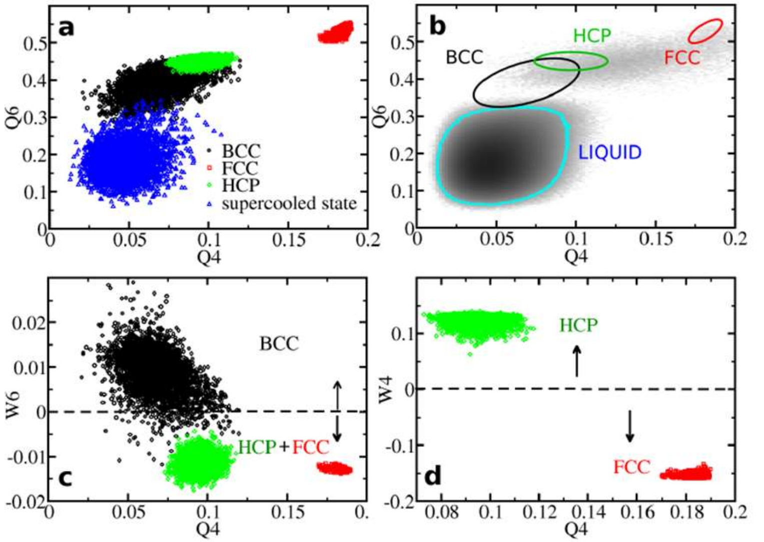
Critical-like fluctuations of bond orienational order grow upon densification.

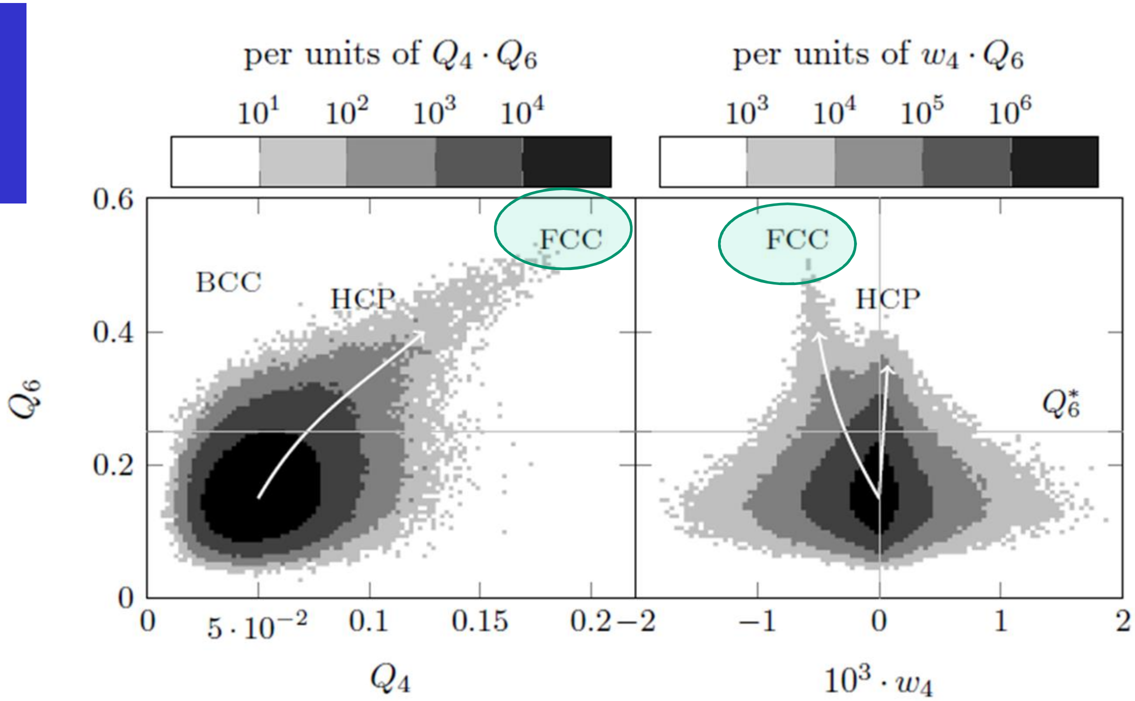
Confocal observation by M. Leocmach
Nature Comm. (2012)



BD simulation by T. Kawasaki
Nature Mater. 9, 324 (2010).

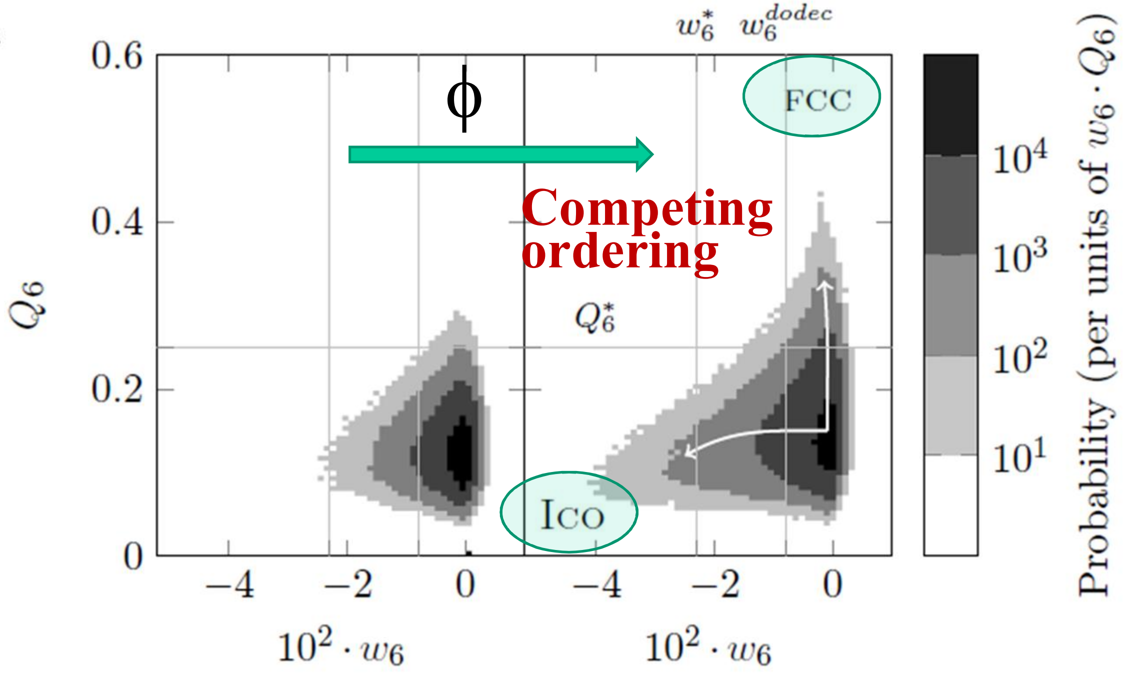
Order parameter maps for a supercooled liquid



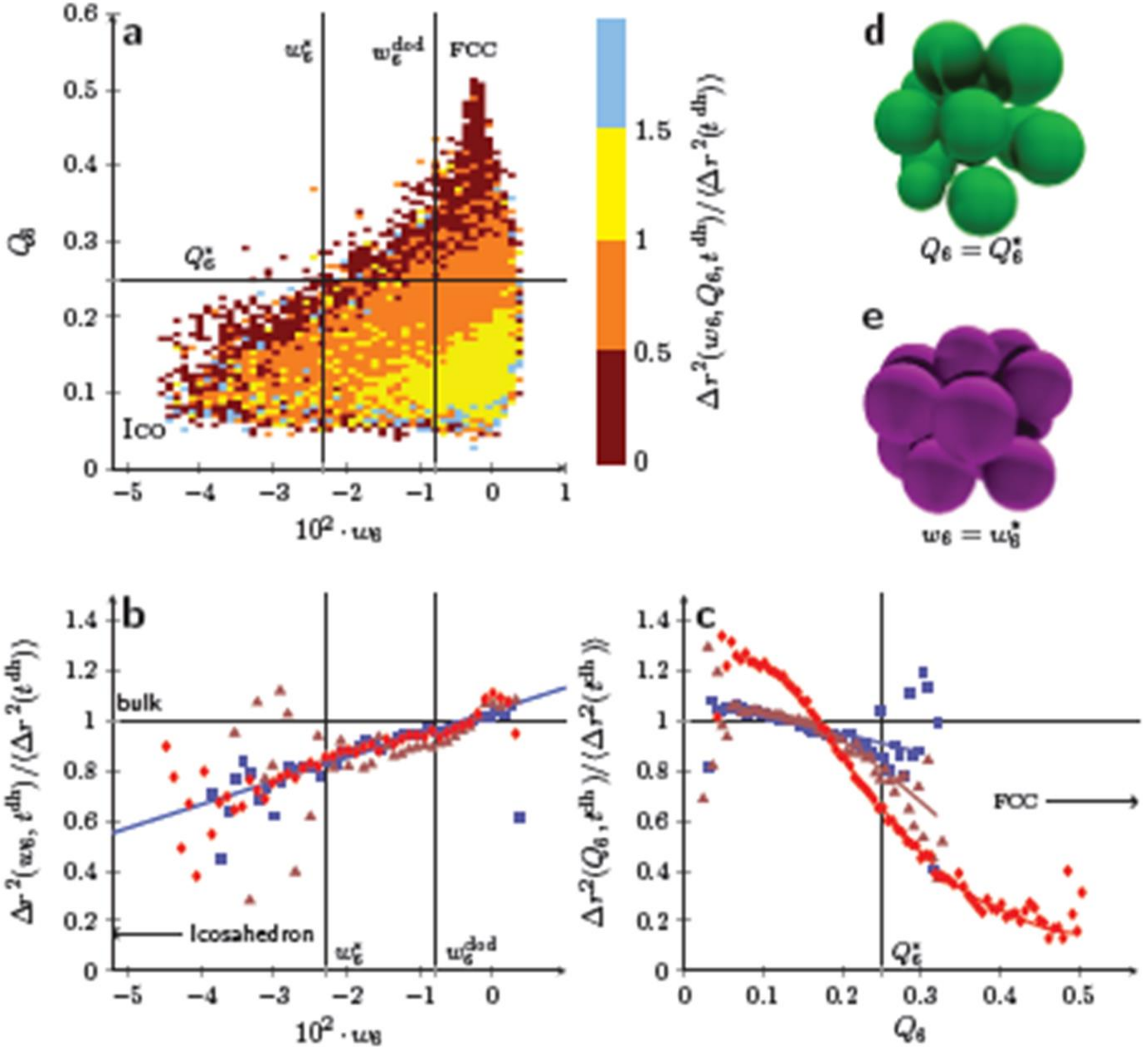


Here W_l is the third order invariant of Q_l.

$$W_l \equiv \sum_{\substack{m_1,m_2,m_3 \\ m_1+m_2+m_3=0}} \begin{bmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{bmatrix} \times \bar{Q}_{lm_1} \bar{Q}_{lm_2} \bar{Q}_{lm_3}$$



Bond order mobility



Only spatially extendable order can cause slow dynamics!

Growth of structural order in a supercooled liquid

Steinhardt bond-orientational order parameter

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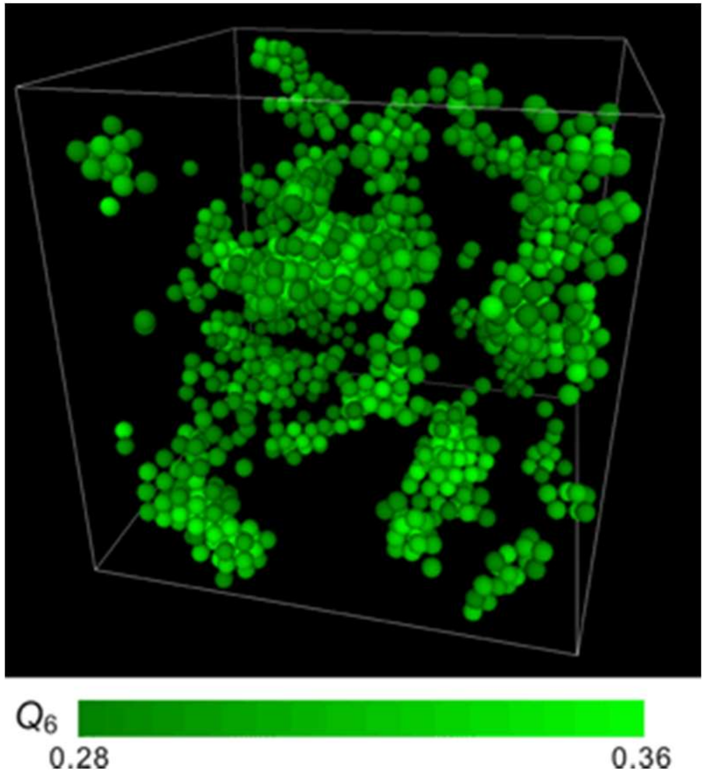
$$Q_{lm}^k = 1/N_b^k \sum_{j=1}^{N_b^k} q_{lm}(\vec{r}_{kj})$$

$$q_{lm}^k = 1/n_b^k \sum_{j=1}^{n_b^k} Y_{lm}(\vec{r}_{kj})$$

N_b^k: the number of the nearest neighbors of particle k (including k itself)

n_b^k: the number of the bonds of particle k

$Y_{lm}(\vec{r}_{kj})$: the spherical harmonics; degree of l-th



$$\Delta = 6\%$$

Spatio-temporal fluctuations of the orientational order parameter

↓

Clusters of high MRCO after black &white operation

More detailed characterization of structural order: 2D order-parameter maps

Coarse-graining

Q6-Q4 correlation map for classification of crystal structures:
W. Lechner and C. Dellago, J. Chem. Phys. 129, 114707 (2008)

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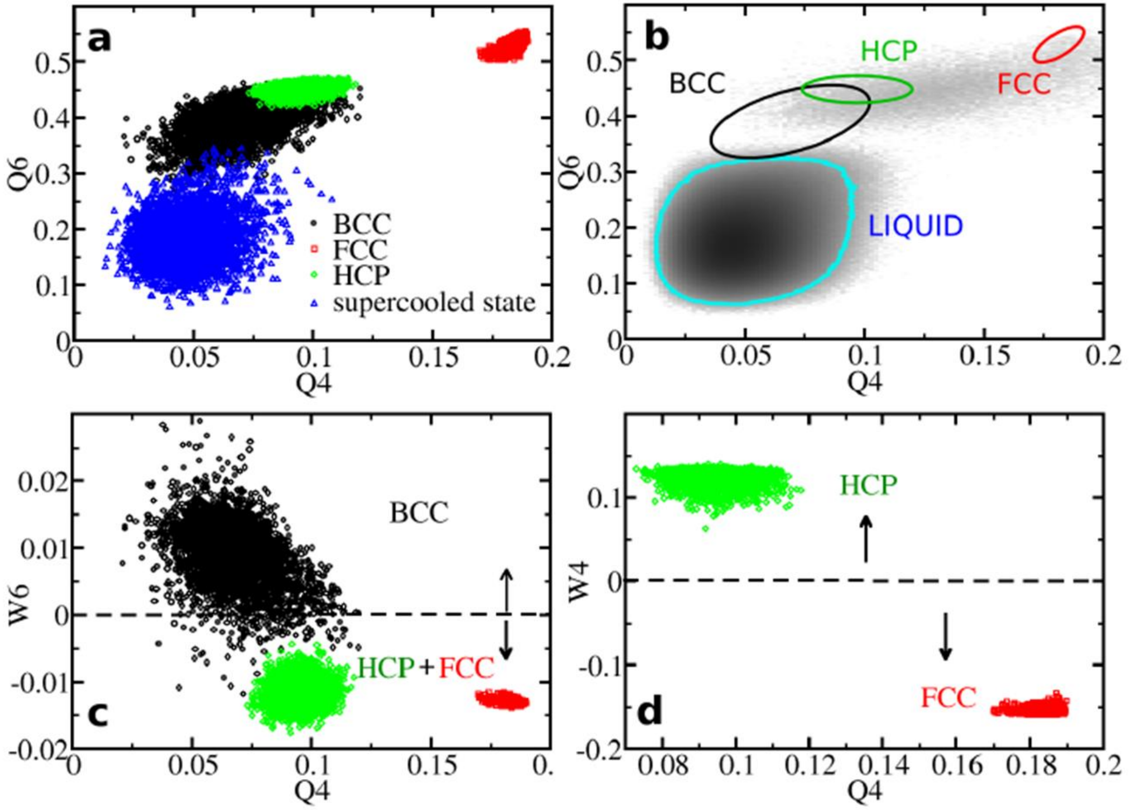

Order parameter maps for a supercooled liquid

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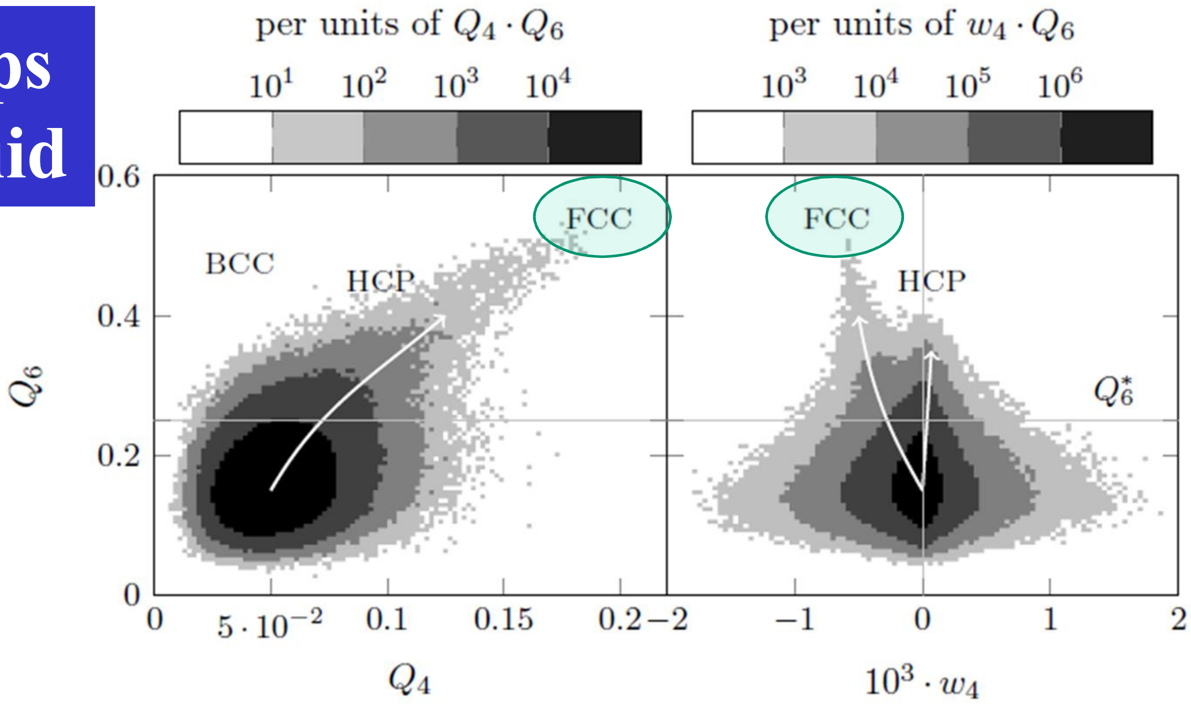

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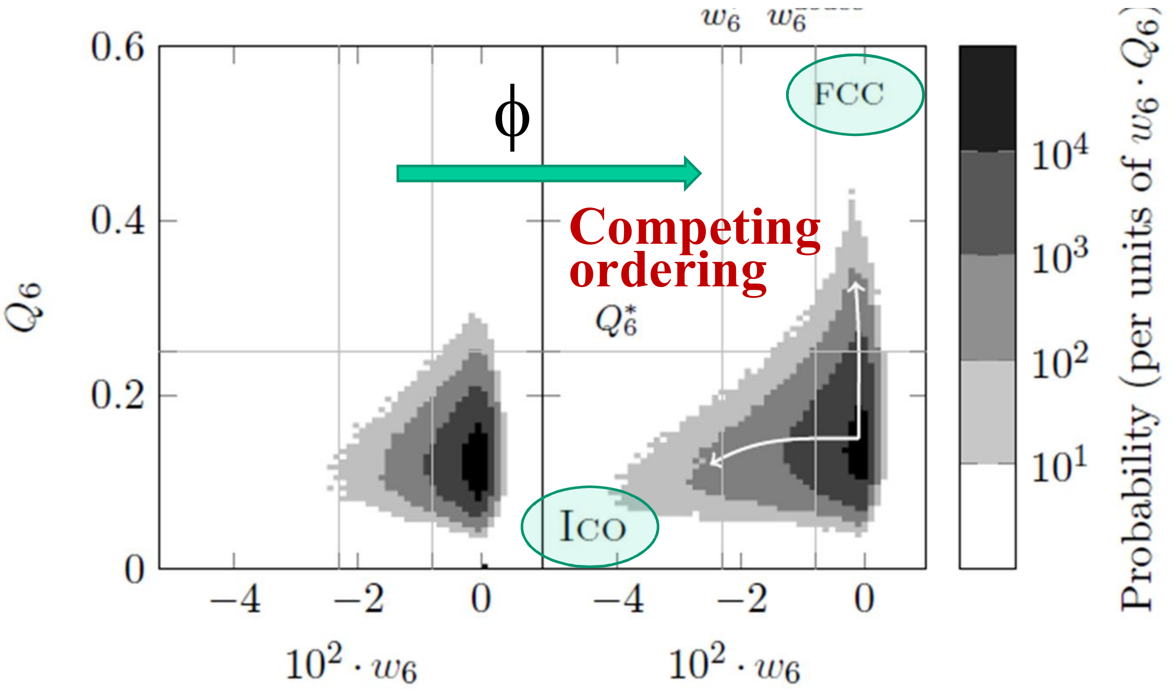
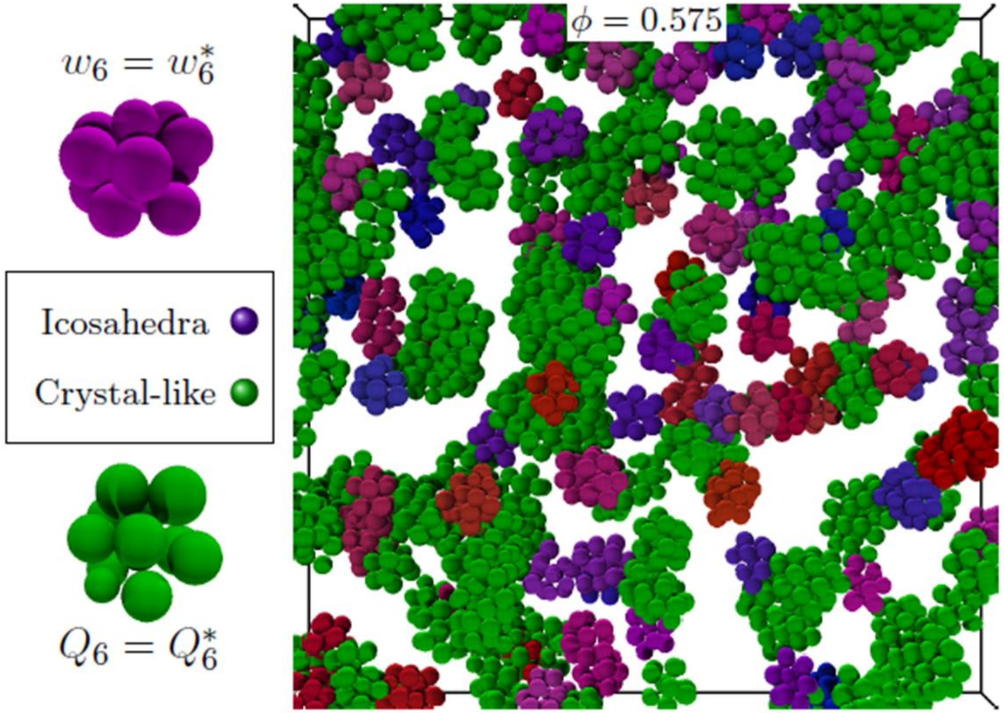
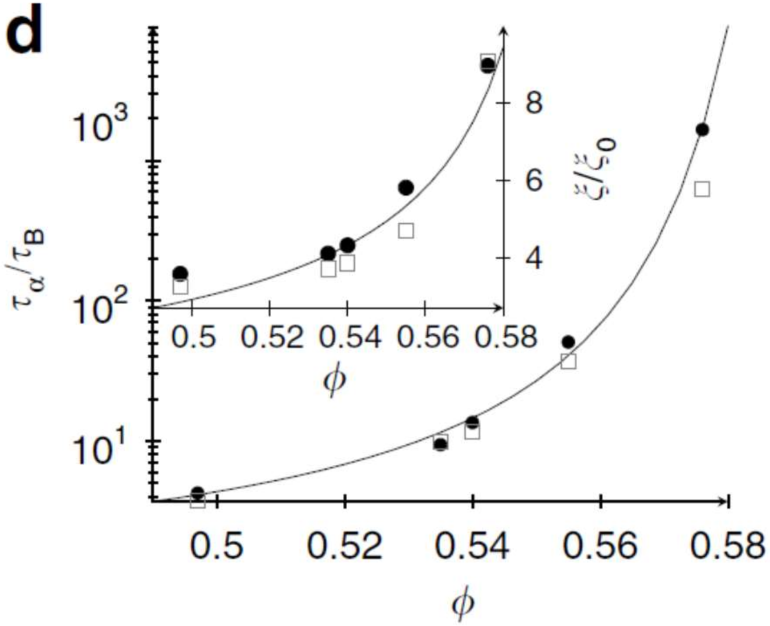


Growth of structural order of a supercooled colloidal liquid upon densification





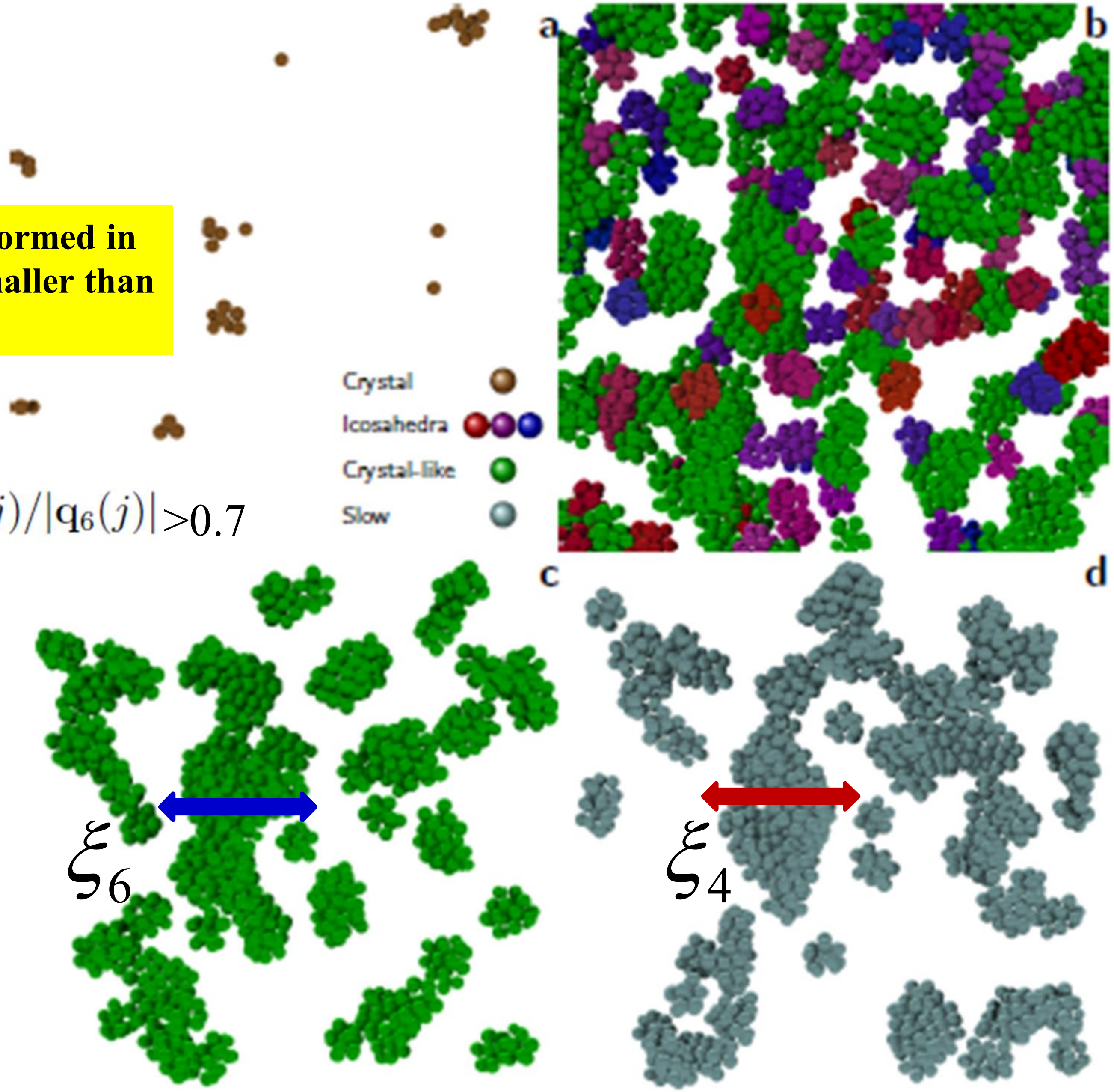
fcc-like vs icosahedral-like competing ordering

The correlation length grows upon densification and the dynamics slows down.

What is a link between them?

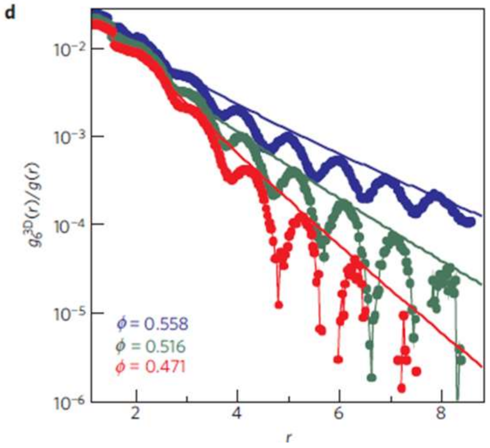
Structural order in a supercooled colloidal liquid

Crystal nuclei are always formed in preordered regions, but smaller than the critical size.



$$\mathbf{q}_6(i)/|\mathbf{q}_6(i)|\cdot\mathbf{q}_6(j)/|\mathbf{q}_6(j)|>0.7$$

Spatial correlation function



Relationship between structure and dynamics

a, Correlation length

- The size of highly ordered clusters → ξ
- The size of non-activated clusters → ξ_4

Both increase coherently toward

the gla

$\xi =$

b, Structural relaxation time and correlation length

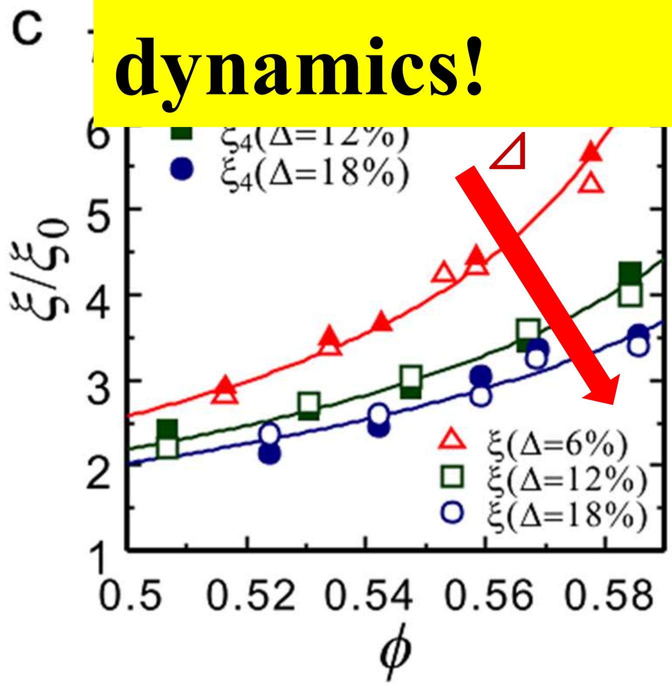
$$\tau_\alpha = \tau_0 \exp\left[D(\xi/\xi_0)^{d/2}\right]$$

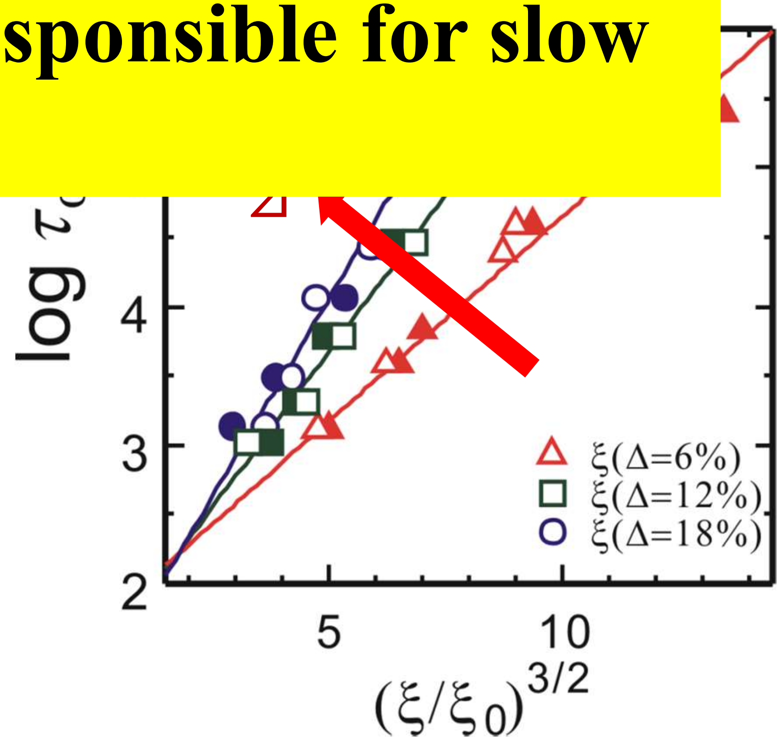
Increasing → *Increasing*

ion time

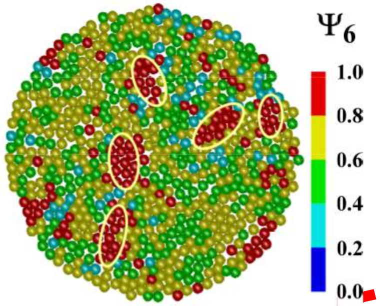
s

Growth of fcc-like bond-orientational fluctuations may be responsible for slow dynamics!

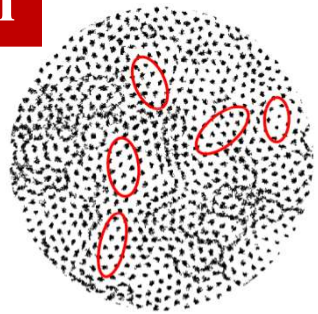


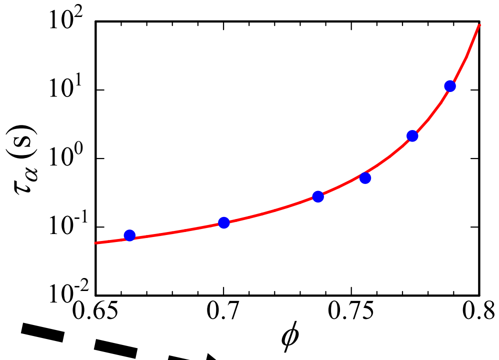


Summary of glass transition



High order=slow





Dynamic heterogeneity

Crystal-like order

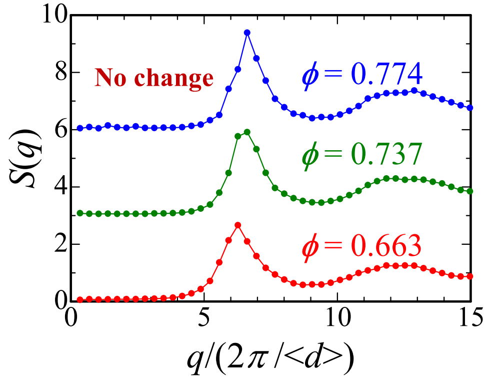
Slow dynamics

Not density, but BOO

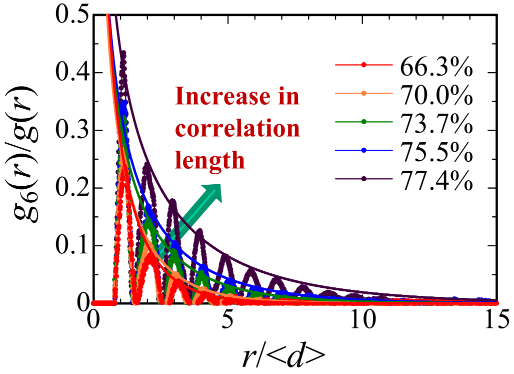
$$\tau_\alpha = \tau_0 \exp\left[D(\xi/\xi_0)^{d/2}\right]$$

Correlation length of BOO exhibits critical-like divergence.

Suggesting a link between structural ordering and slow dynamics

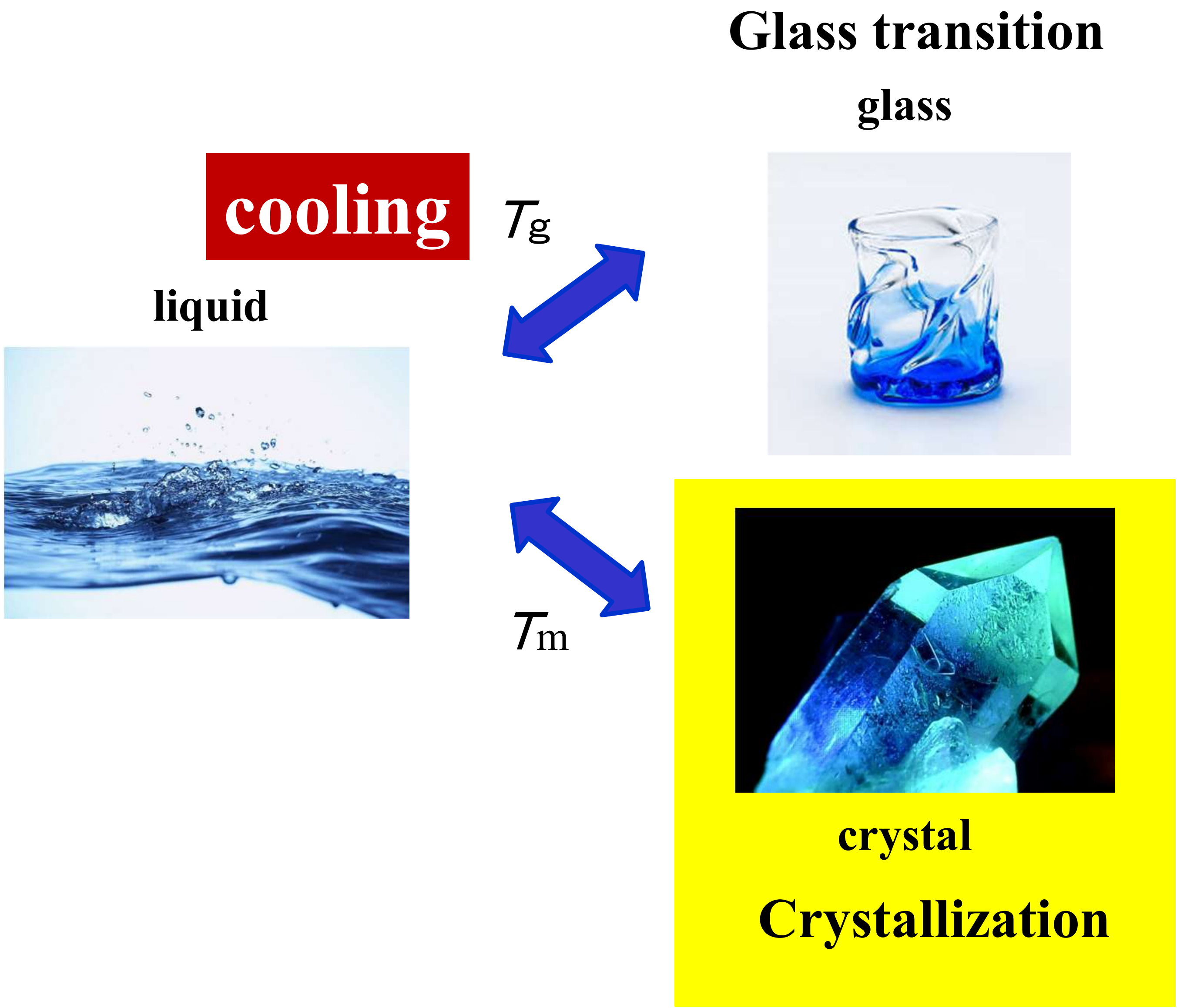


No medium-range correlation in 2-body density correlator



But there is a distinct static correlation, if we look the structure through a proper order parameter!!!

Crystallization



Glass transition

glass

cooling

T_g

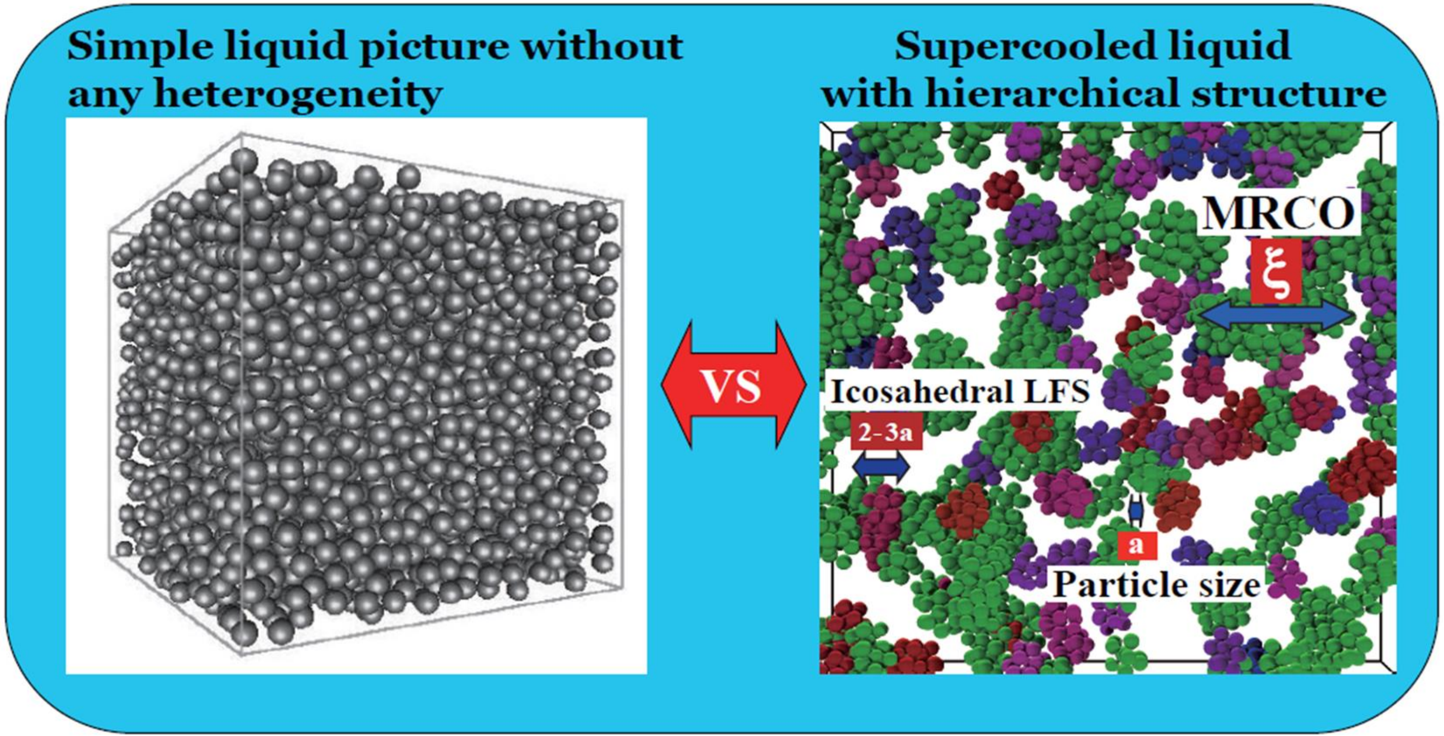
liquid

T_m

crystal

Crystallization

Previous theories such as classical nucleation theory and density functional theory assume that a supercooled liquid is in a homogeneous random state.



Our study clearly indicates that this is not the case.

Here we study the impact of pre-ordering on crystal nucleation.

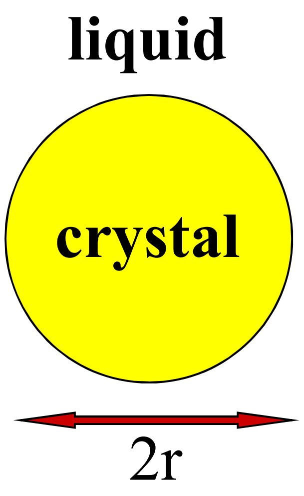
Crystal nucleation: Monodisperse hard spheres & water as examples

Previous theories such as classical nucleation theory and density functional theory assume that a supercooled liquid is in a homogeneous random state.

Our study clearly indicates that this is not the case.

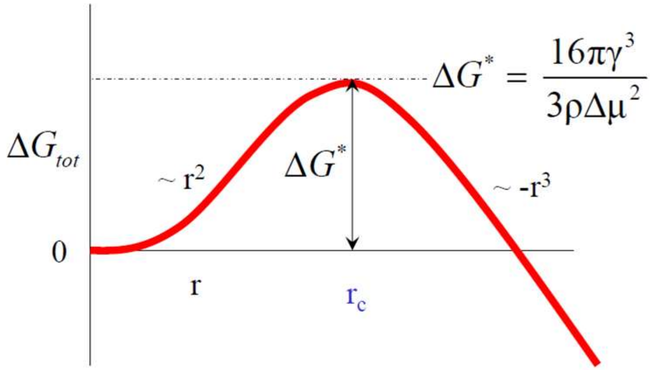
Classical Nucleation Theory (CNT)

Three key factors determining the nucleation rate
1. **Kinetic factor=translational diffusion constant *D***
2. **Thermodynamic driving force *Δμ***
3. **Interfacial tension *γ***

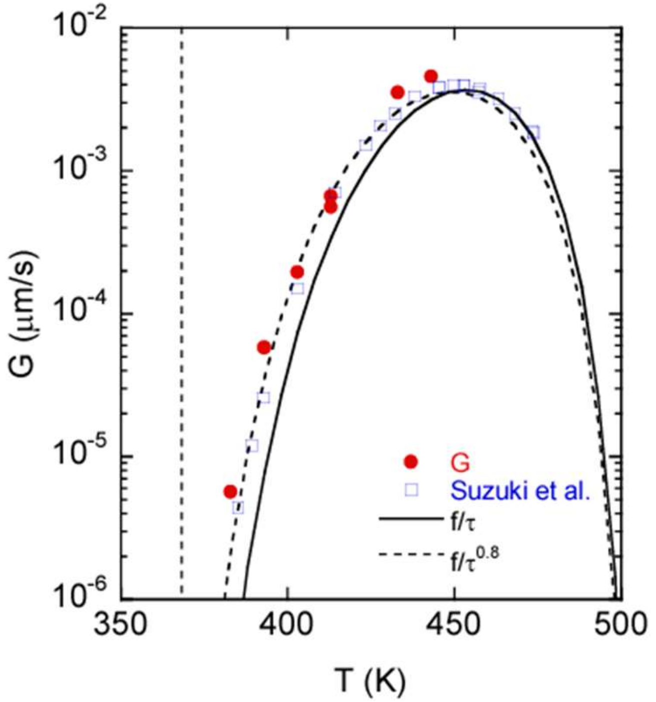


Nucleation Frequency

$$I = \frac{k_n}{\tau_t}\exp\left(-\frac{\Delta G^*}{k_B T}\right)$$



$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta\mu^2}$$



Free-energy gain $\quad \Delta G_{bulk} = \frac{4\pi}{3} r^3 \Delta\mu_{s,l} < 0$

Free-energy loss $\quad \Delta G_{\mathrm{int}} = 4\pi r^2 \gamma_{s,l} > 0$

Beyond classical nucleation theory (brief history)

Ostwald Step Rule (1887)

A crystal with the lowest free energy does not necessarily appear,
But a crystal having the free energy closest to a liquid should appear.

These approaches are all from the crystal side. We propose a new approach to crystal nucleation from the liquid side!

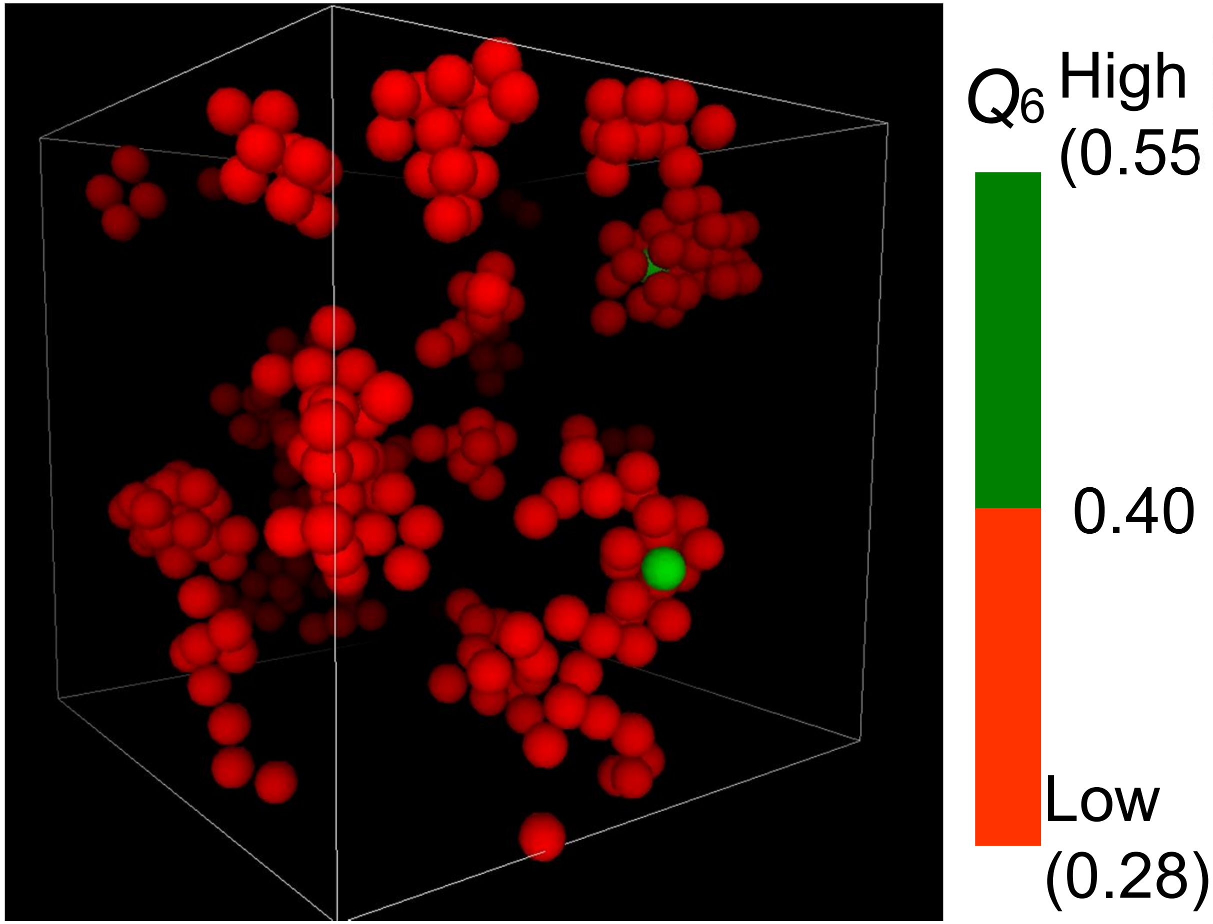
On the basis of the Landau theory, they showed that a bcc structure is generally favored in the early stage of crystallization.

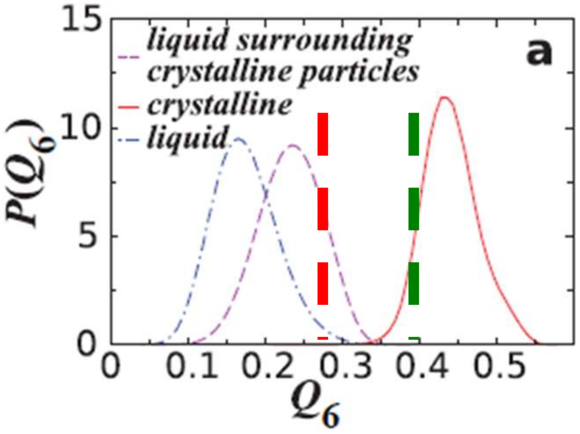
Ten Wolde, Montero&Frenkel (1995)

Nuclei initially formed have a bcc structure, but later transform to an fcc structure, but bcc structure remains around the growth interface.

Nucleation process: structural evolution

Temporal change in Q_6 ($\Delta=0$, $\phi=0.537$)



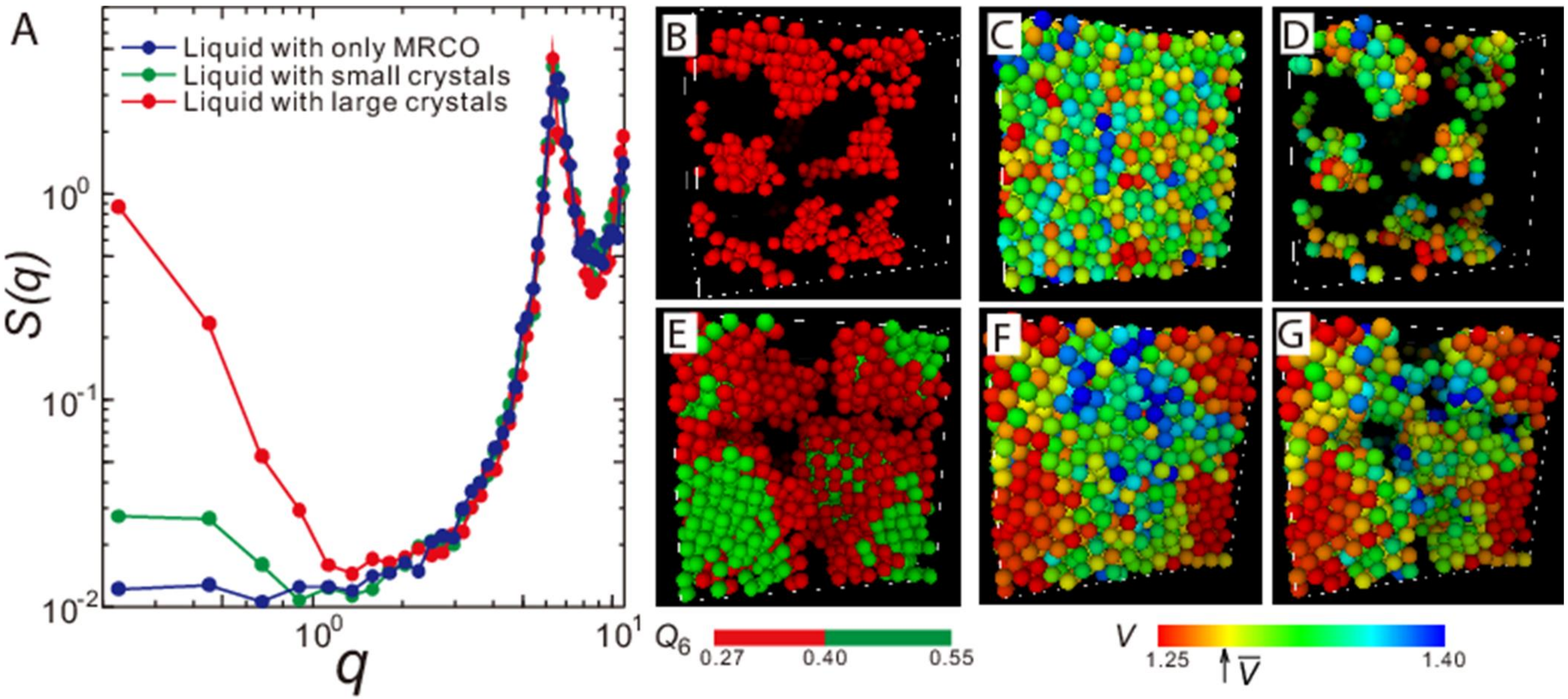


- Central parts of crystals have fcc-like structure, which matches the surrounding MRCO with fcc-like order.

- Crystal nuclei are always formed in high MRCO regions because of the lower interfacial energy.
- MRCO fluctuations are pinned by crystal nuclei due to wetting effects

Difference between MRCO and crystalline order

Static structure factor S(*q*)



MRCO has the same density as the liquid on average, although locally higher density regions (precursors) exist due to fluctuations!

Crystal nuclei have a higher density than the average density of liquid.

Microscopic Mechanism of Crystal Nucleation

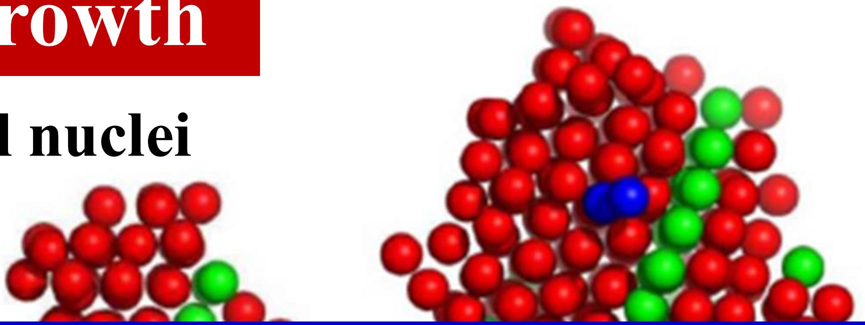
J. Russo & H. Tanaka,
Soft matter (2012);
Sci. Rep. (2012)

Crystal nucleation and growth

Fraction of polymorphs in crystal nuclei

Fcc is dominant and bcc is rare.

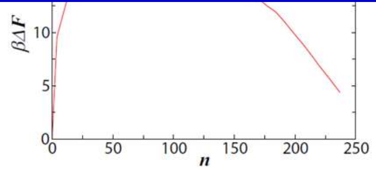
fcc:hcp=3:1 not 1:1!



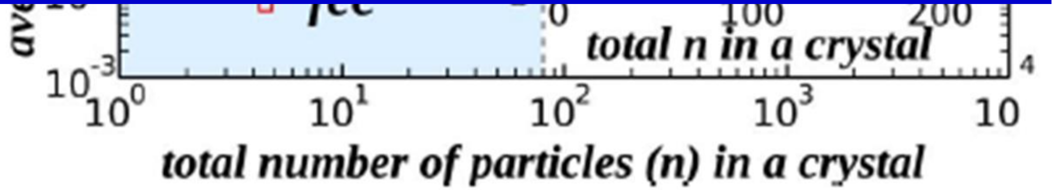
Question:

The fcc and hcp crystals have almost the same free energy for hard spheres!

Why is fcc more abundant than hcp in the nucleation stage?

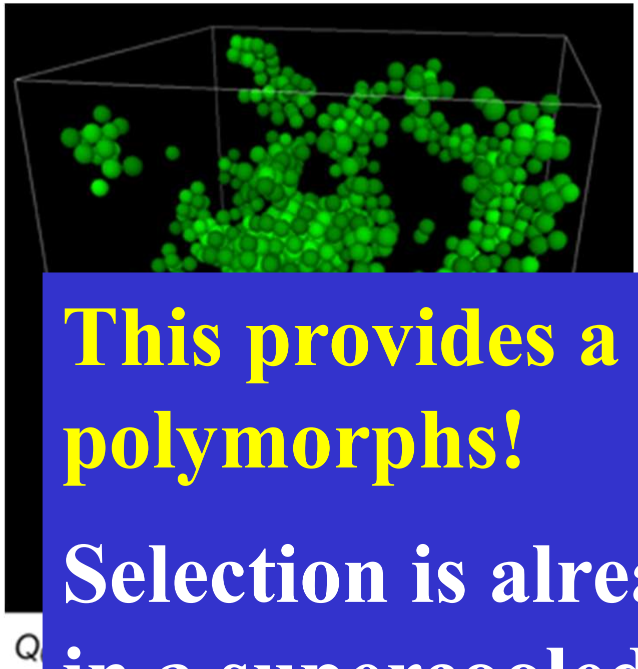


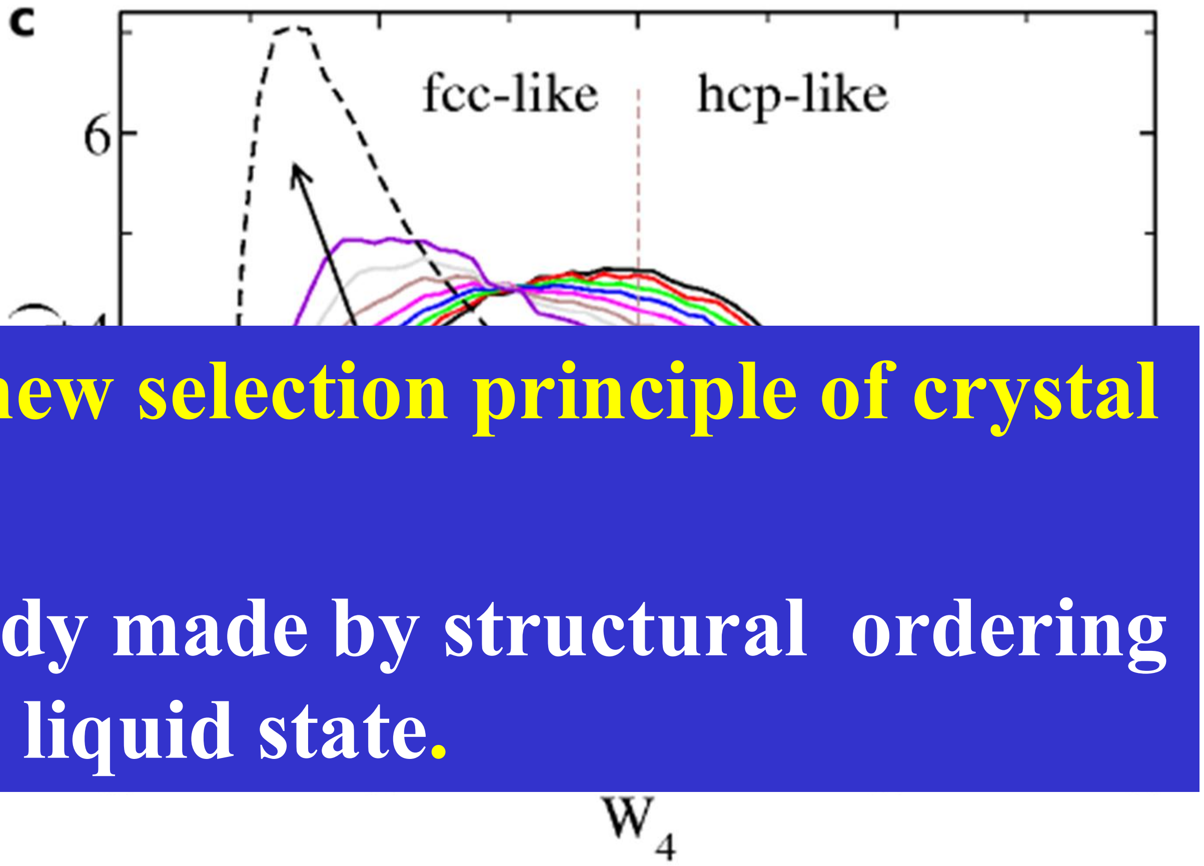
SFigure 1: Free energy barrier for the system at $\beta p\sigma^3 = 17.0$, obtained from Umbrella Sampling simulations.



Selection of crystal polymorphs upon nucleation

Fcc-like BOO





This provides a new selection principle of crystal polymorphs!

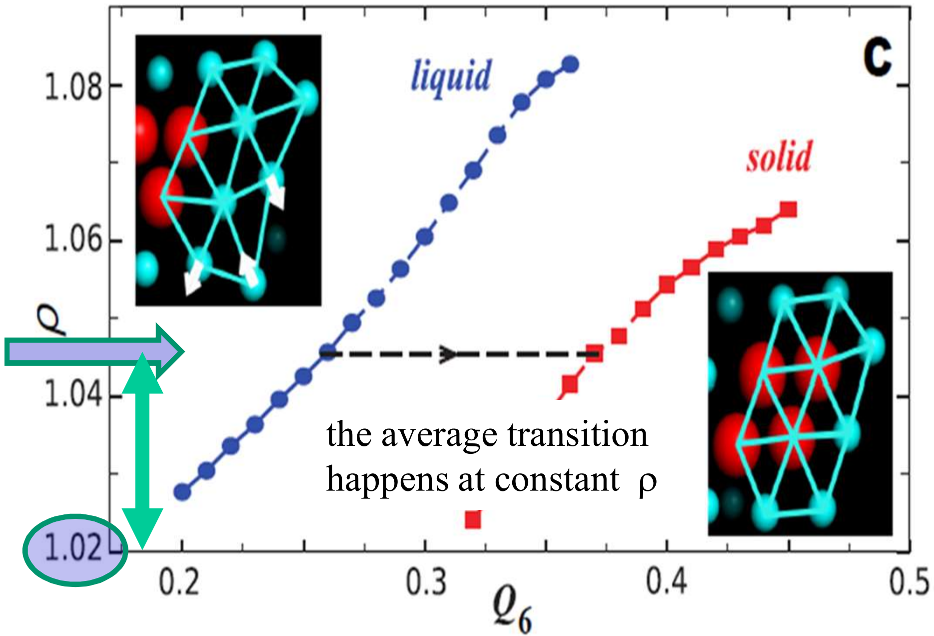
Selection is already made by structural ordering in a supercooled liquid state.

It is local symmetry in preordered regions in a supercooled liquid that selects crystal polymorphs!!

Roles of density and bond orientational order fluctuatsions in crystal nucleation

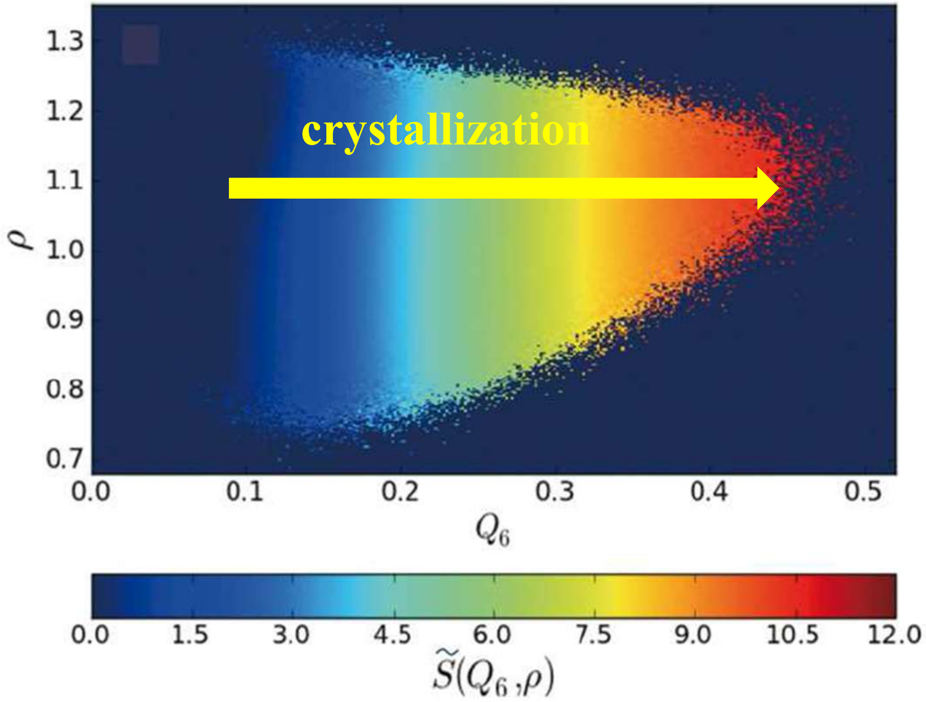
Microscopic pathway of nucleation

Microscopic pathway of crystallization



the average transition happens at constant ρ

Average density of liquid

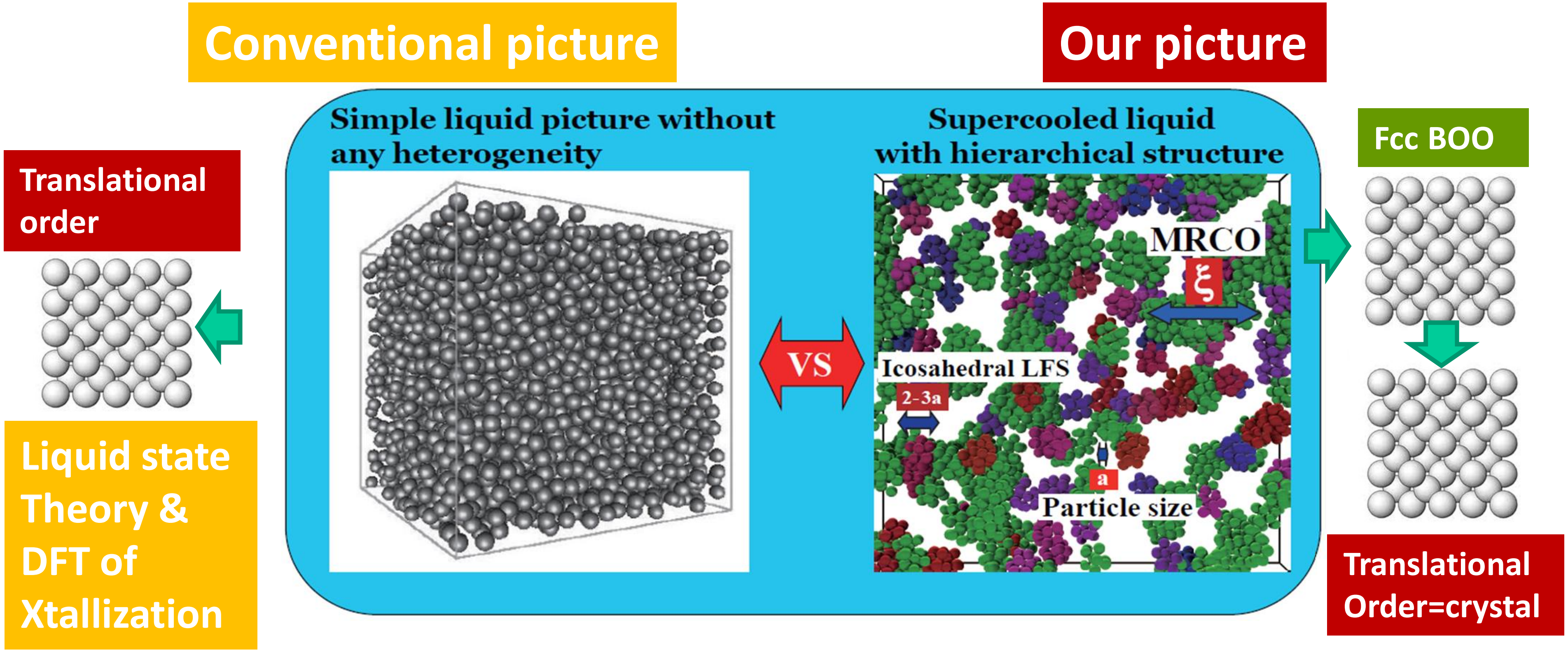


Early stage of crystal nucleation is the enhancement of the coherency of BOO with little density change. Only in the late stage, translational order comes into play.

No sharp Fourier component

Summary of Crystal Nucleation

- In a supercooled state, rotational symmetry is already broken locally, which promotes not only slow dynamics but crystal nucleation.
- Crystal polymorph to be nucleated is already selected in a supercooled state.
- Crystal nucleation starts from the enhancement of spatial coherency of bond orientational order and translational ordering comes later.



Conventional picture

Our picture

Translational order

Liquid state Theory & DFT of Xtallization

Simple liquid picture without any heterogeneity

VS

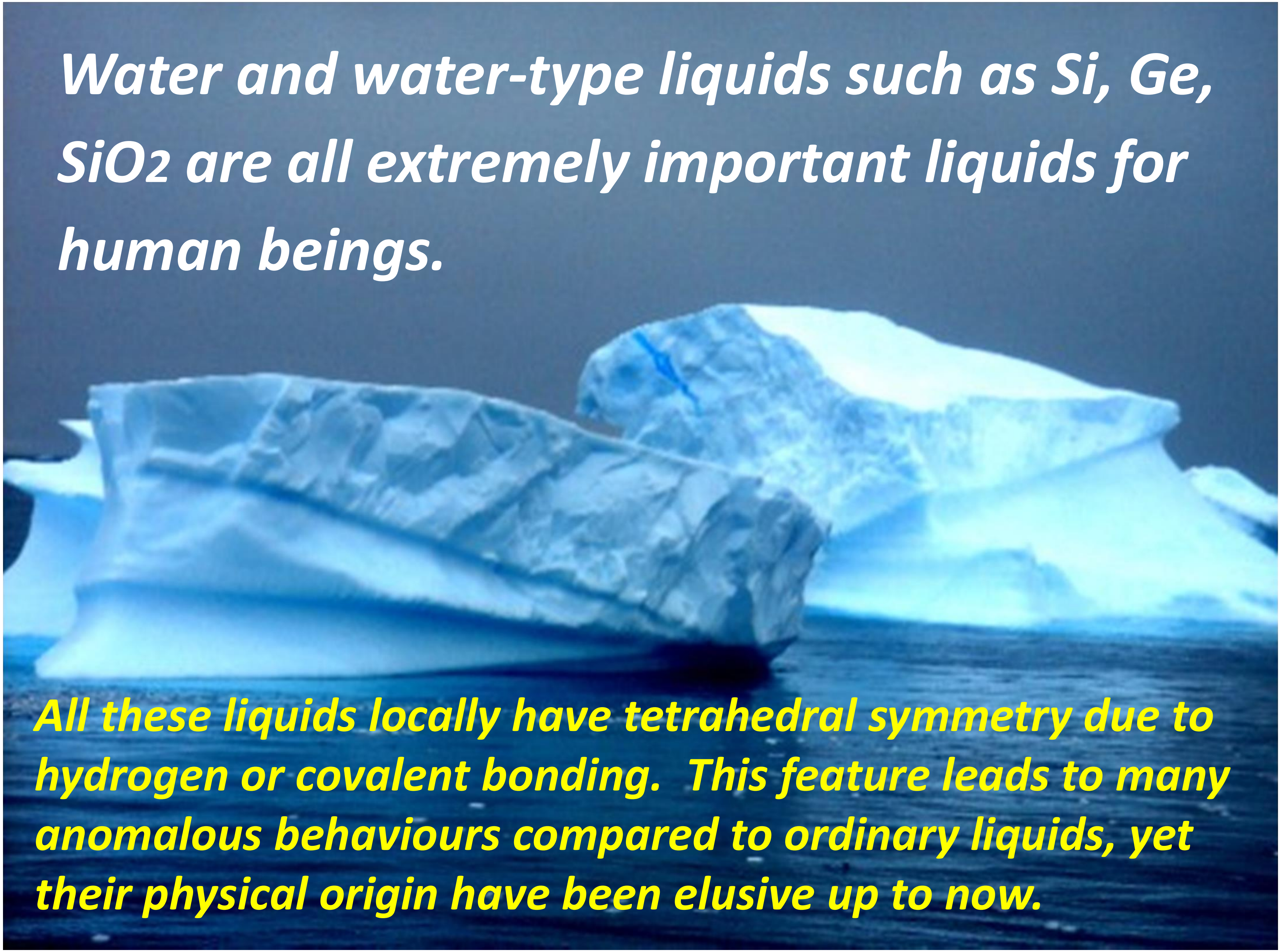
Supercooled liquid with hierarchical structure

Fcc BOO

Translational Order=crystal

Such behavior may be generic to any liquids!

H. Tanaka, Eur. Phys. J. E 35, 113 (2012).

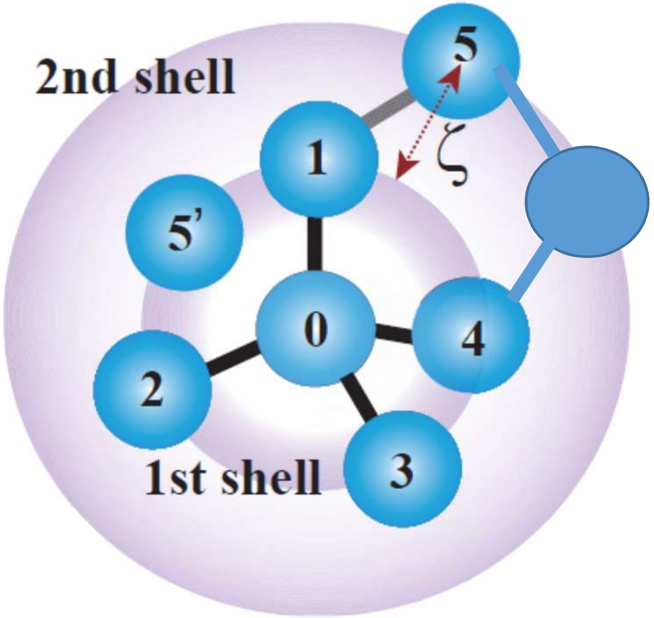


Water and water-type liquids such as Si, Ge, SiO_2 are all extremely important liquids for human beings.

All these liquids locally have tetrahedral symmetry due to hydrogen or covalent bonding. This feature leads to many anomalous behaviours compared to ordinary liquids, yet their physical origin have been elusive up to now.

Structural characterization of or locally favored structures in water

Tendency to form a closed pentagonal ring!



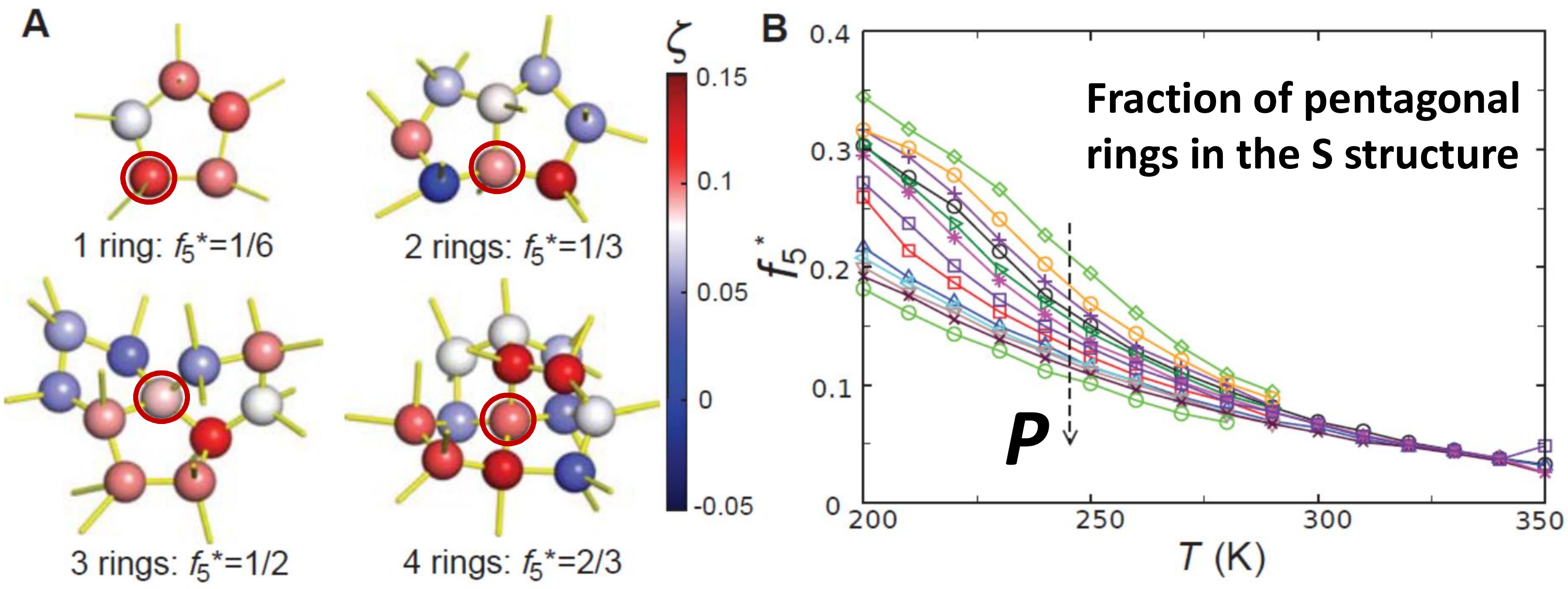
Why pentagonal rings?

Although the formation of a pentagonal ring accompanies the distortion of tetrahedral symmetry, the entropy loss is much smaller compared to the formation of a hexagonal ring!

4-member ring: too much distortion

6-member ring: too much entropy loss

Importance of pentagonal rings in water structures: Frustration against crystallization



Fraction of pentagonal rings in the S structure

Locally favored structures include more pentagonal rings upon cooling, which leads to frustration against crystallization into ice I, which is made of only hexagonal rings.

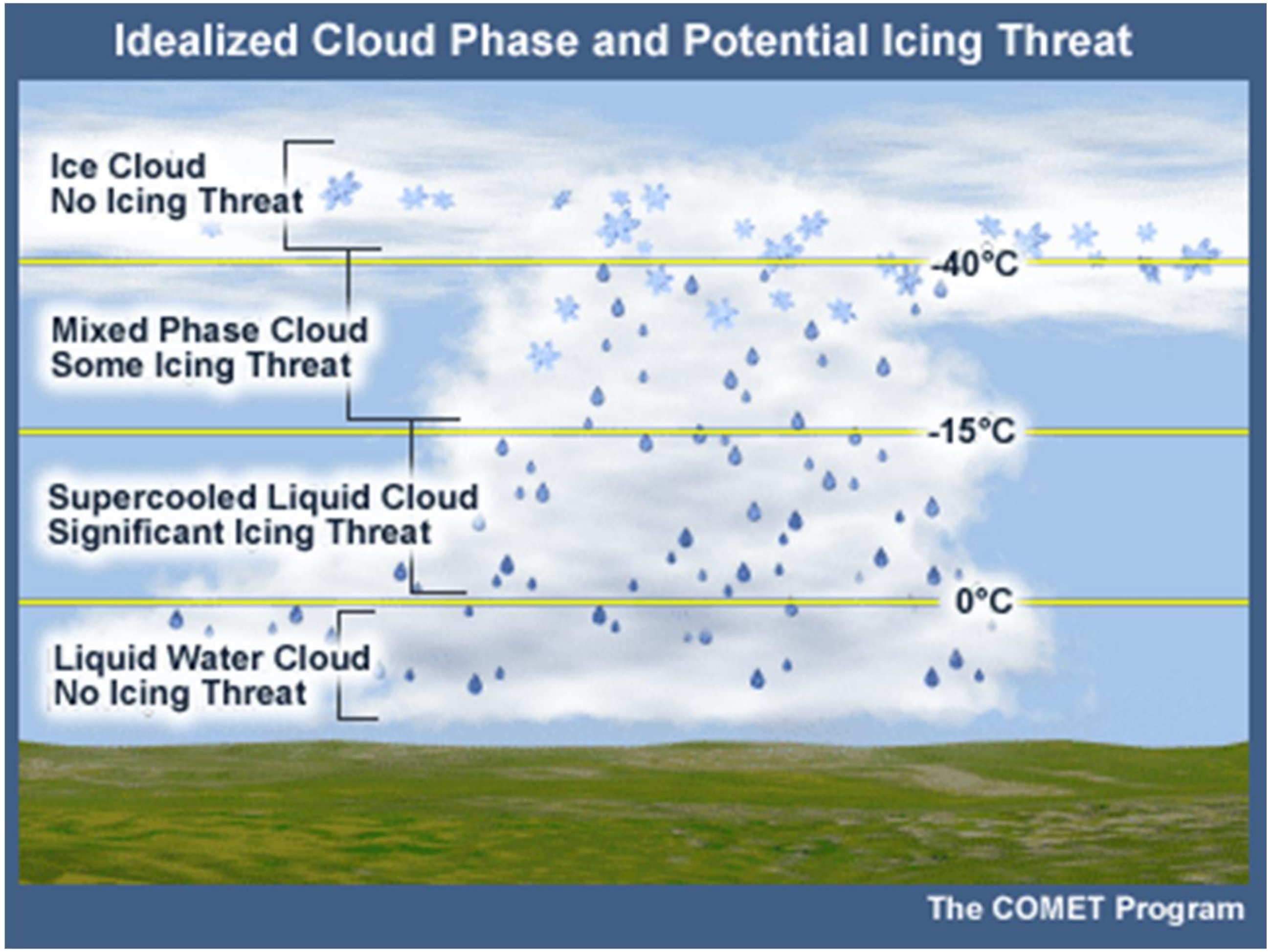
But we are going to show that the locally favored structures act as precursors for nucleation of a new metastable form of ice (Ice 0).

How are ice crystals formed from supercooled water?

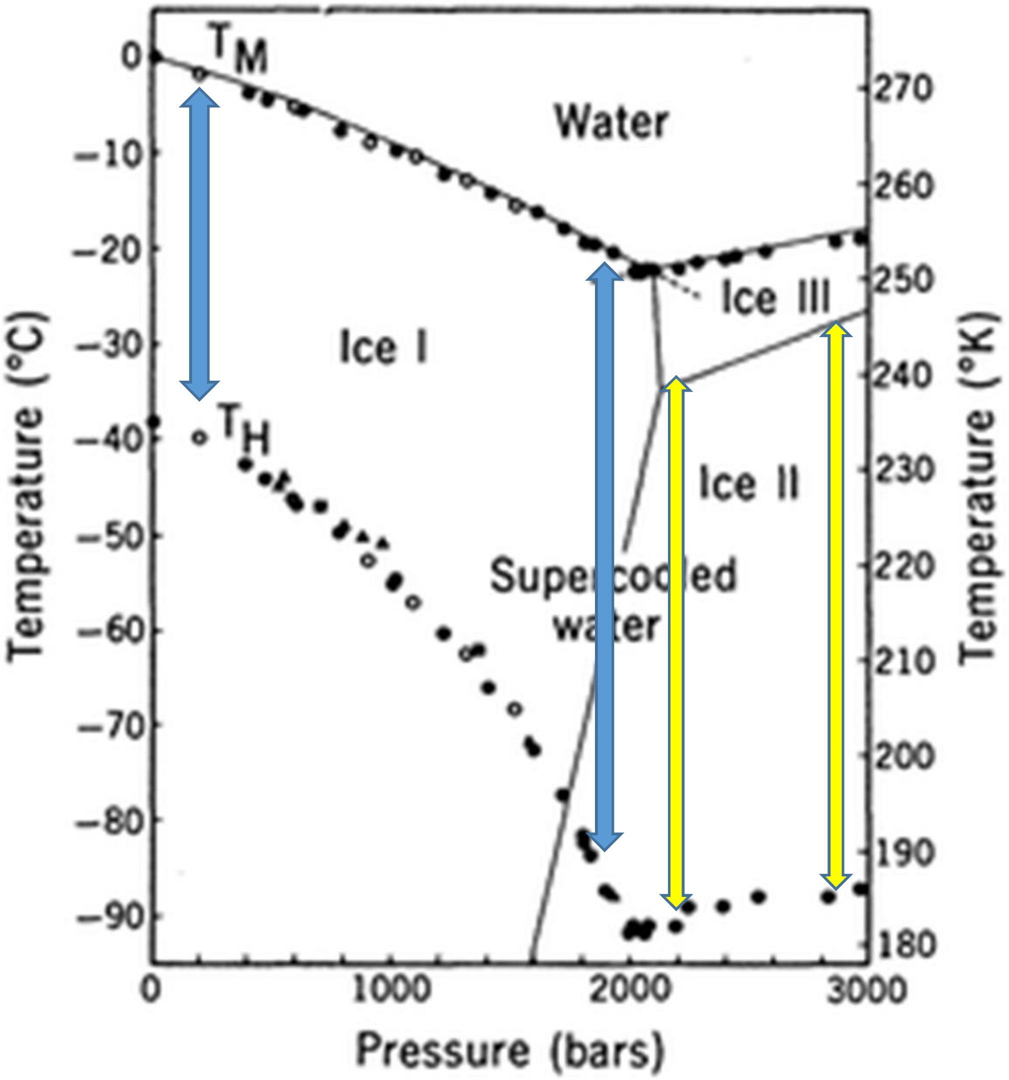
with John Russo & Flavio Romano

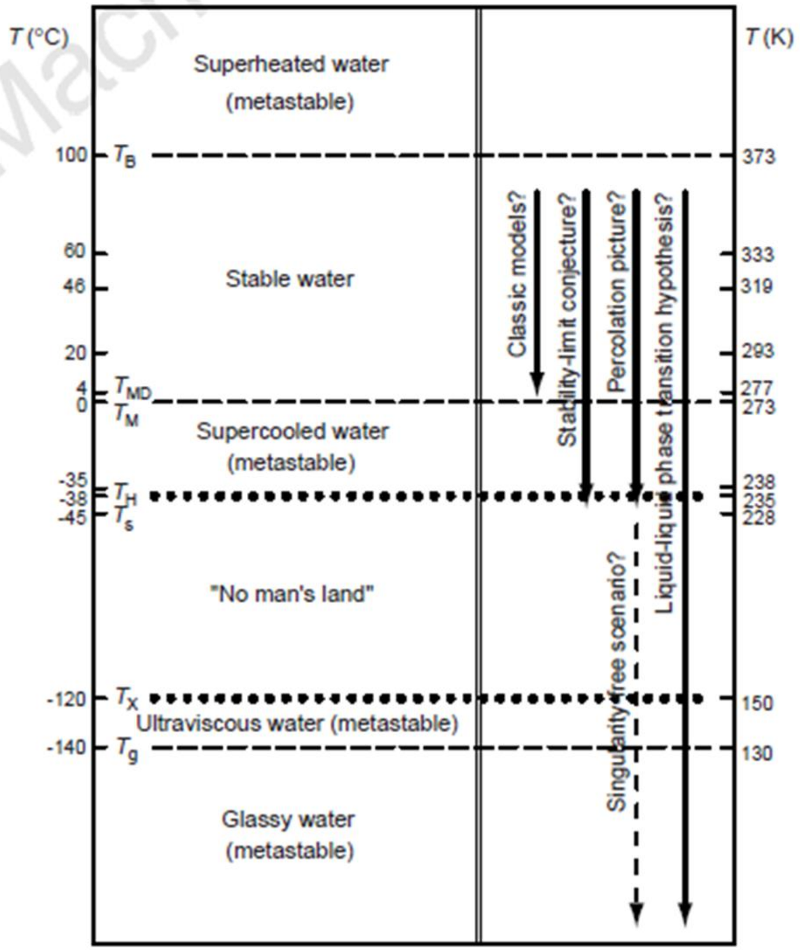
Water can be supercooled rather deeply if we can avoid heterogeneous nucleation!

- **Homogeneous ice nucleation takes place below -40 C!**
- **This may be due to frustration effects of locally favored structures with pentagonal rings on the formation of Ice Ih.**



Homogeneous nucleation line is not parallel to the melting point of hexagonal ice! Why?





Kanno&Angell

Water models we employed

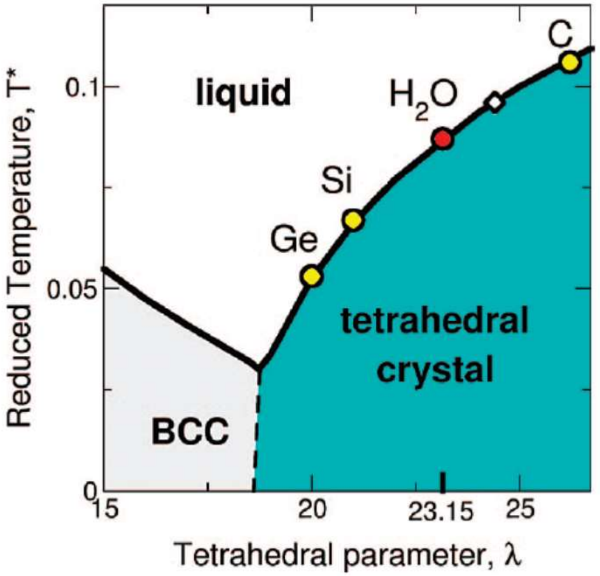
Monoatomic water model (modification of Stillinger-Weber potential)

mW water Molinero&Moore *J. Phys. Chem. B* **2009**, *113*, 4008–4016

$$E = \sum_i \sum_{j>i} \varphi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \varphi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\varphi_2(r) = A\varepsilon\left[B\left(\frac{\sigma}{r}\right)^p - \left(\frac{\sigma}{r}\right)^q\right]\exp\left(\frac{\sigma}{r - a\sigma}\right)$$

$$\varphi_3(r, s, \theta) = \lambda\varepsilon[\cos\theta - \cos\theta_0]^2 \exp\left(\frac{\gamma\sigma}{r - a\sigma}\right)\exp\left(\frac{\gamma\sigma}{s - a\sigma}\right)$$

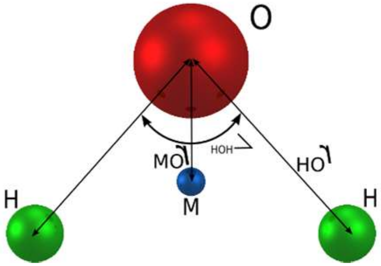


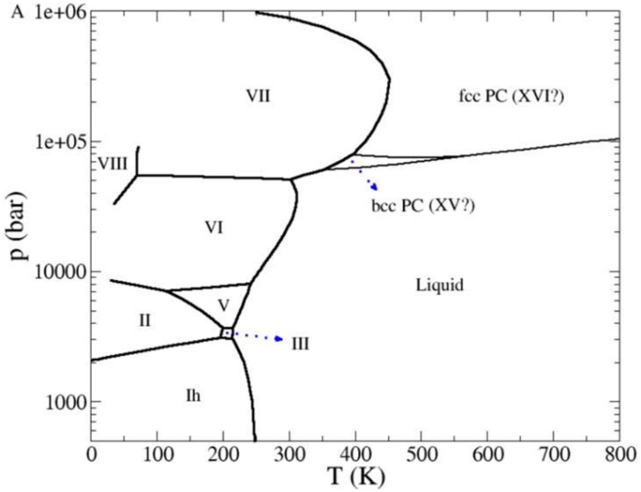
Computationally efficient: we can directly study crystal nucleation process!!

TIP4P/2005

Abascala&Vega, JCP 123, 234505 (2005)

a rigid four site model which consists of three fixed point charges and one Lennard-Jones center





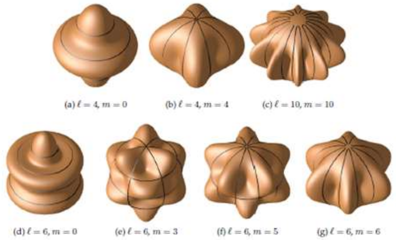
Atomistic model, which gives the most accurate representation of water at supercooled conditions and thermodynamic predictions across the whole phase diagram!!

OP for searching tetrahedral crystals

Previous order parameters are targeted to detect only the stable crystals at ambient pressure , i.e., Ice Ih and Ice Ic.

It is crucial to search a good order parameter to pick up all the relevant crystal structures of local tetrahedral order.

We find that a new order parameter Q12 is best for this purpose.



Steinhardt bond orientational order parameter
We find *l*=12 is the best!

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\mathbf{\hat{r}_{ij}})$$

Its coarse-grained version (sum over *N*b(*i*)=16)

$$Q_{lm}(i) = \frac{1}{N_b(i)} \sum_{k=0}^{N_b(i)} q_{lm}(k)$$

**The sum runs over 16 neighboring particles.
This choice accounts for the first two coordination shells in tetrahedral crystals.**

1. Detection of all types of ice crystals

Steinhardt bond orientational order parameter
We find *l*=12 is the best!

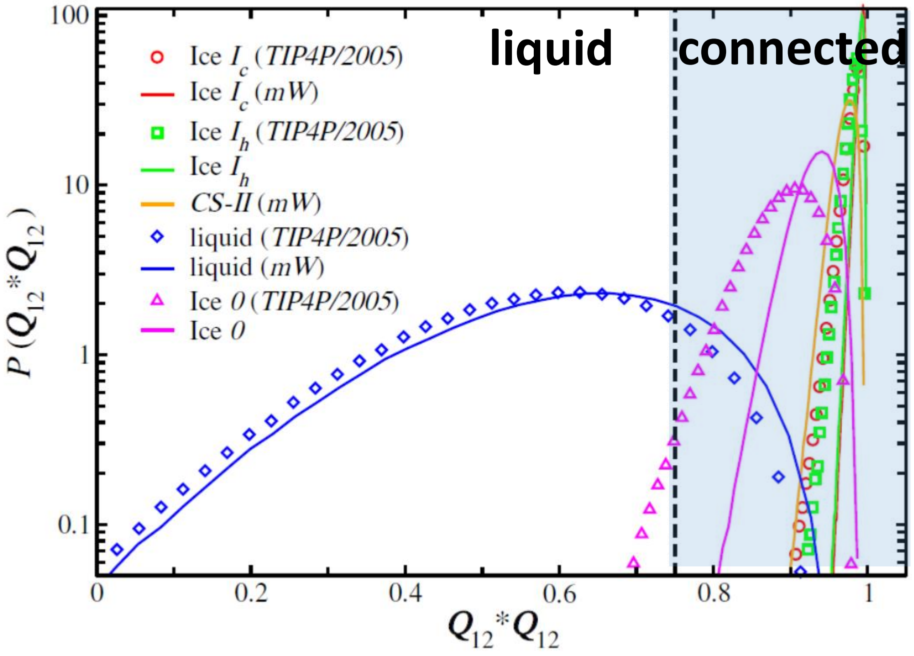
$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{\mathbf{ij}})$$

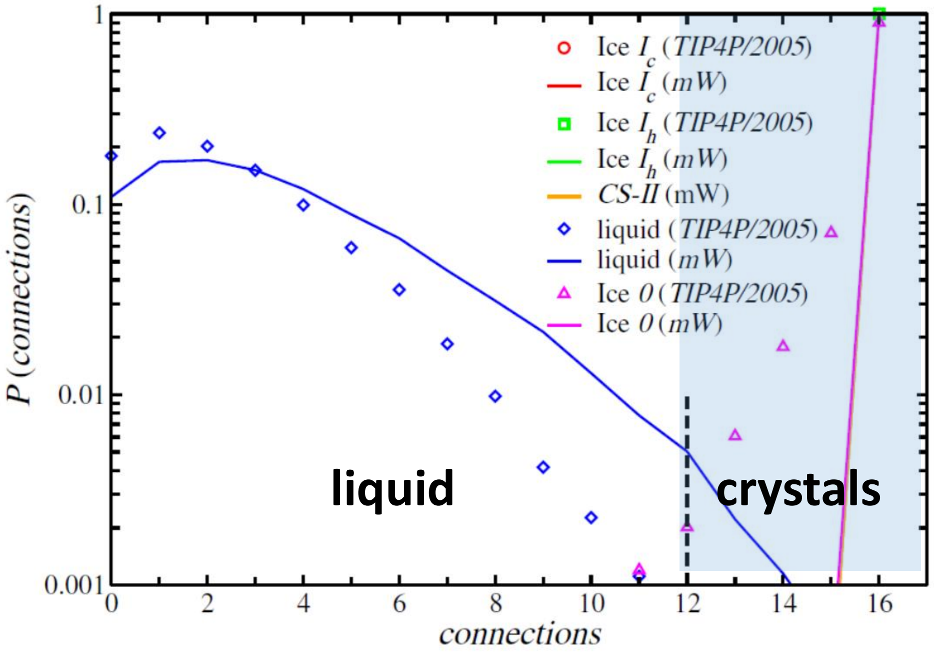
Its coarse-grained version (sum over *N*b(*i*)=16)

$$Q_{lm}(i) = \frac{1}{N_b(i)} \sum_{k=0}^{N_b(i)} q_{lm}(k)$$

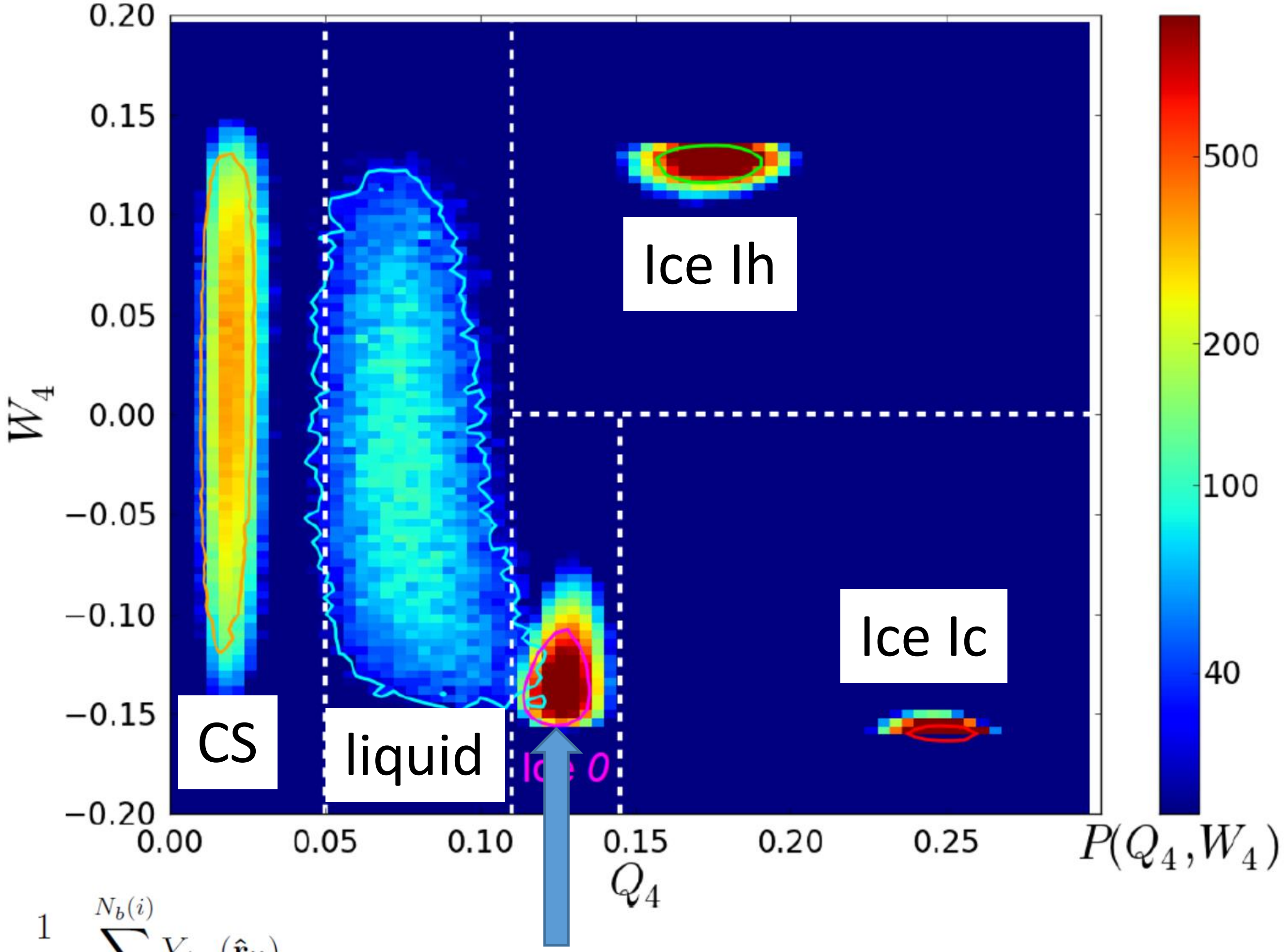
With this OP, we can detect all crystal forms.

$$\mathbf{Q}_{12} * \mathbf{Q}_{12} = (\mathbf{Q}_{12}(i)/|\mathbf{Q}_{12}(i)|) \cdot (\mathbf{Q}_{12}(j)/|\mathbf{Q}_{12}(j)|)$$





2. Classification of ice crystals on the Q_4-W_4 map



New Ice! =Ice 0

$$\mathbf{q_4} \equiv q_{4,m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{4m}(\hat{\mathbf{r}}_{\mathbf{ij}})$$

$$\mathbf{Q_4} \equiv Q_{4,m}(i) = \frac{1}{N_b(i)} \sum_{k=0}^{N_b(i)} q_{4,m}(k)$$

$$Q_4(i) = \sqrt{4\pi/(2*4+1)}|\mathbf{Q}_4(i)|$$

$$W_4(i) = \sum_{m_1,m_2,m_3=0}^{l} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \frac{Q_{4,m_1}(i)Q_{4,m_2}(i)Q_{4,m_3}(i)}{|\mathbf{Q}_4(i)|^3}$$

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Tetragonal Allotrope of Group 14 Elements

Zhisheng Zhao,[†] Fei Tian,[‡] Xiao Dong,[‡] Quan Li,[§] Qianqian Wang,[†] Hui Wang,[§] Xin Zhong,[§] Bo Xu,[†] Dongli Yu,[†] Julong He,[†] Hui-Tian Wang,[‡] Yanming Ma,*[,§] and Yongjun Tian*[,†]

J. Am. Chem. Soc. 2012, 134, 12362−12365

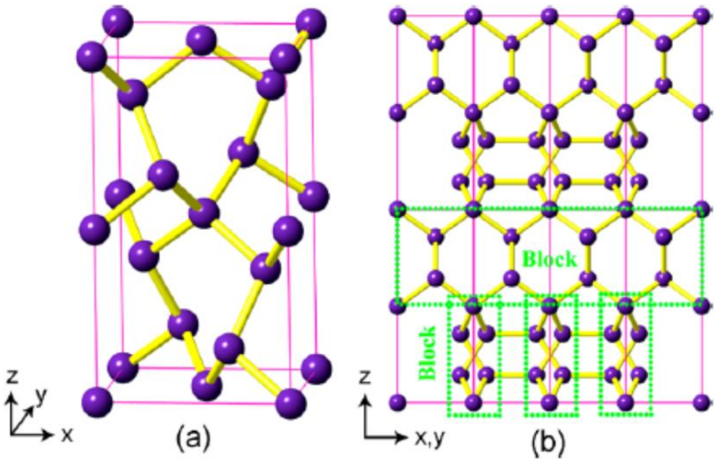
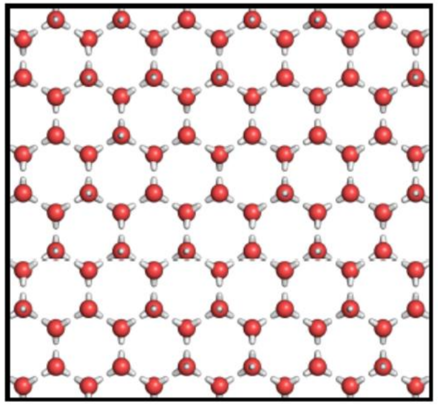
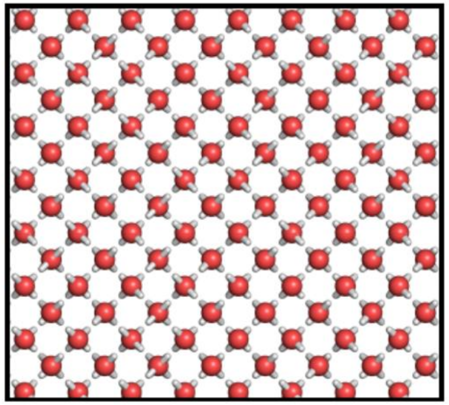


Figure 1. Crystal structure of the T12 phase: (a) 3D view; (b) view along the (110) crystal plane. The T12 structure adopts a *P*42/*ncm* space group (No. 138) and contains 12 atoms/cell, wherein atoms occupy the 4*b* (0, 1, 0.5) and 8*i* (−0.164, 0.336, 0.357) positions. At ambient pressure, the optimized structural parameters are a = 3.388 Å and c = 6.011 Å for C, a = 5.135 Å and c = 9.167 Å for Si, and a = 5.292 Å and c = 9.346 Å for Ge. The green blocks indicate the wrinkled six-membered rings.

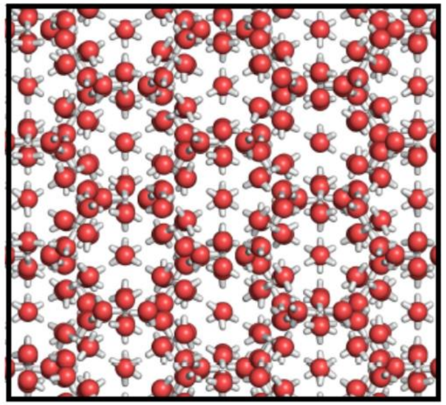
Discovery of a new metastable form of ice!



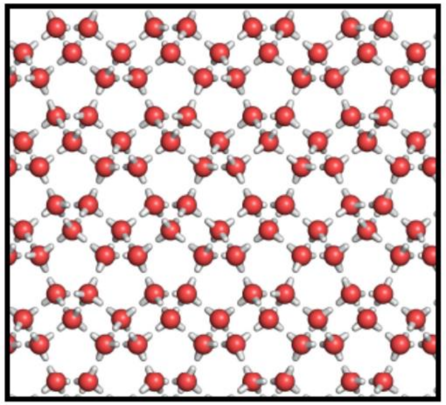
Ice I_h



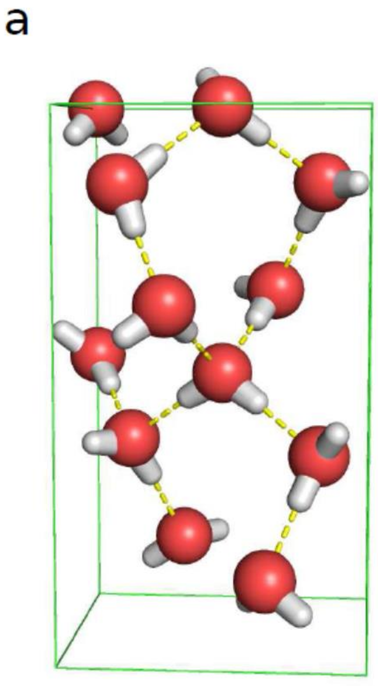
Ice I_c



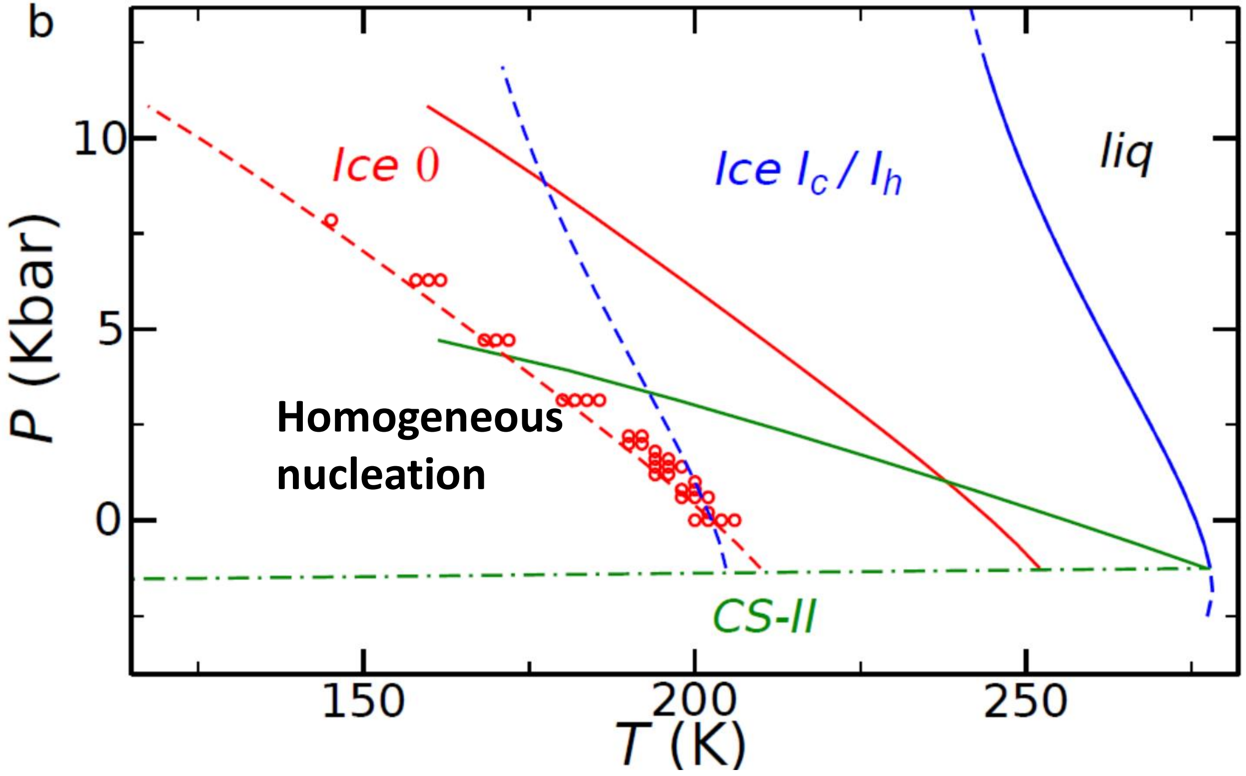
clathrate



Ice 0



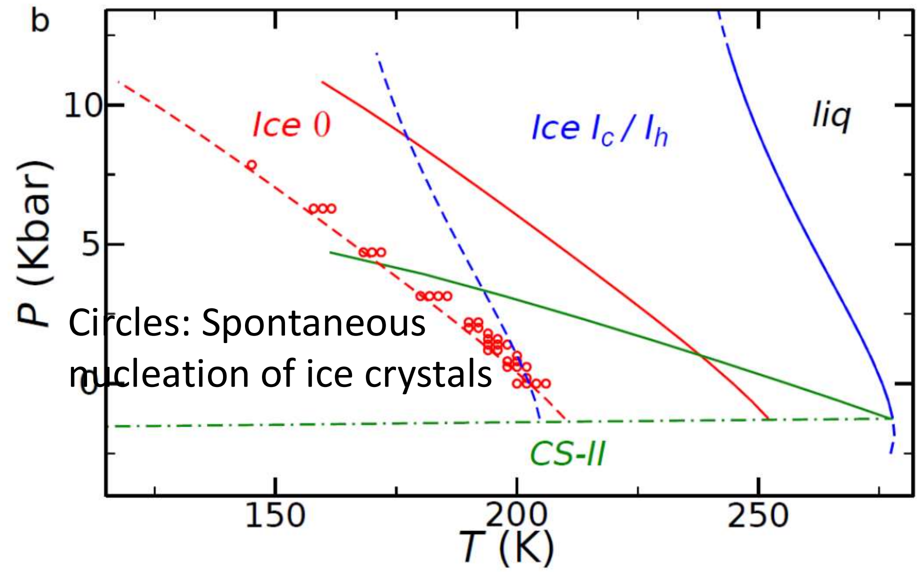
Ice 0 unit cell



Homogeneous nucleation

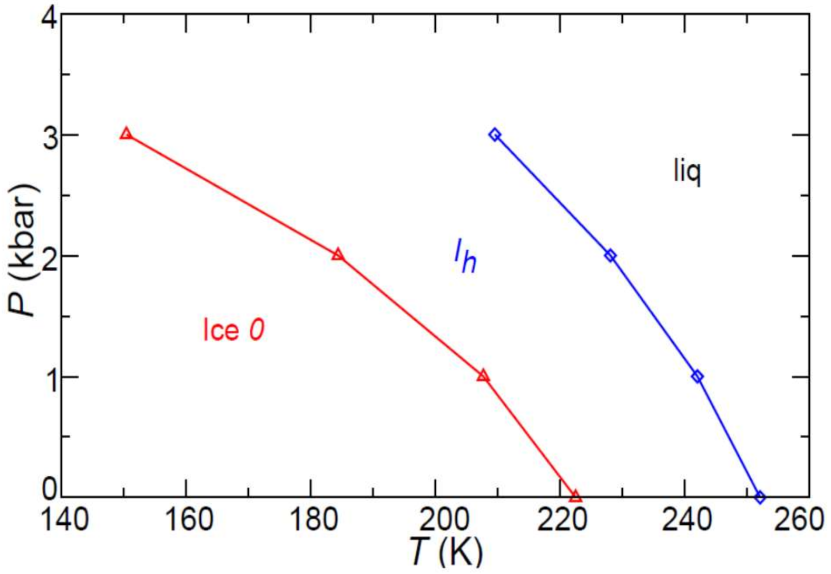
New phase diagram of water in a low pressure region

mW water



Circles: Spontaneous nucleation of ice crystals

TIP4P/2005

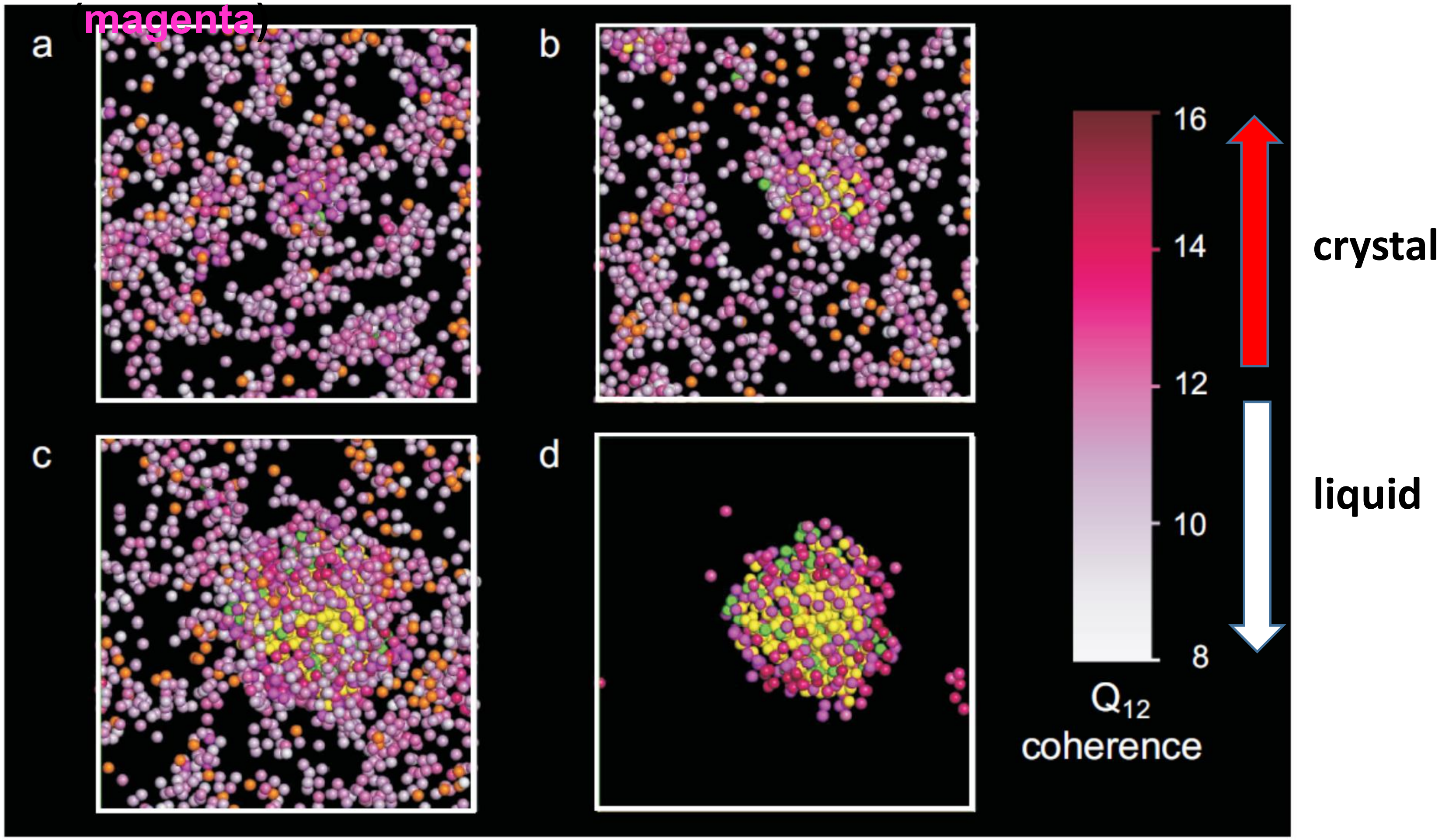


1. Presence of a new metastable form of ice=Ice 0
2. It acts as a precursor upon homogeneous nucleation.
3. Its meting line has a slope steeper than that of Ice I and is almost parallel to the homogeneous nucleation line.

Roles of Ice 0 in ice crystal nucleation
I: Metastable Ice 0 acts as precursors for crystal nucleation

Direct homogeneous nucleation processes of ice crystals in 10,000 mW water at 206K

Ice I_c (yellow), Ice I_h (green), clathrate (orange) and Ice 0 (magenta)

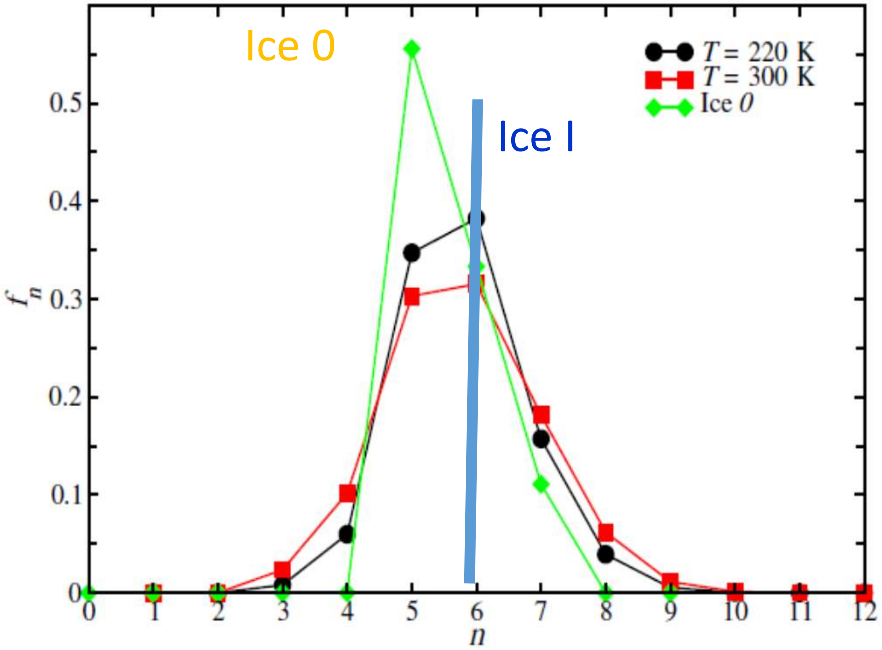


Polymorph selection is already made in a supercooled liquid state!

Ostwald step rule

$$\mu_{liq} > \mu_0 > \mu_{I_c} \simeq \mu_{I_h}$$

the degree of distortion of local tetrahedral symmetry

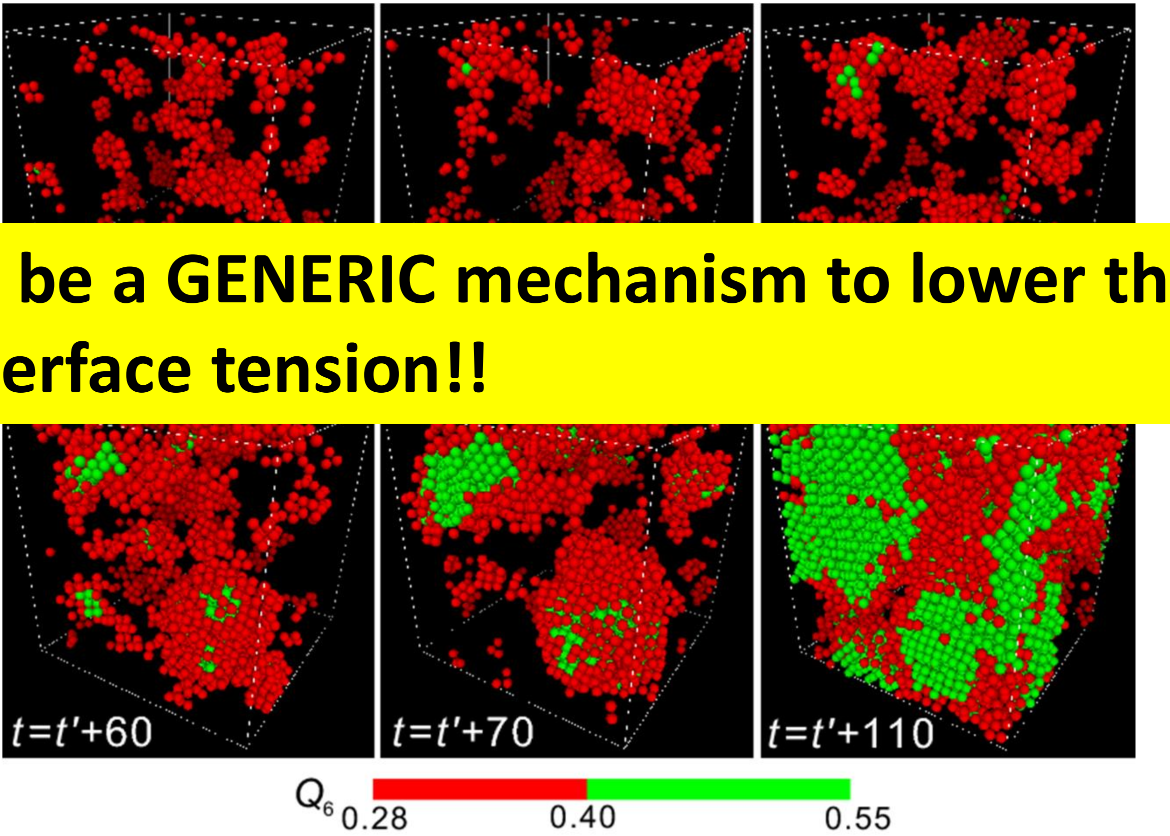


- Liquid water has a rather broad distribution of hydrogen bond rings. The stable Ice Ic and Ih forms contain only six-membered rings. This mismatch in the structure between liquid and crystal leads to a large interfacial energy and thus to a large nucleation barrier for Ice Ih/Ic.
- On the other hand, the structure of Ice 0 is much more friendly to that of liquid water, lowering the surface free-energy cost for the homogeneous nucleation of ice.
- We may say that a crystal whose structure is closest to local structural order in the liquid acts as a precursor for crystal nucleation.
- This scenario looks similar to that found recently for hard spheres.

The behavior is basically the same as what we found in hard and soft spheres!

Kawasaki&Tanaka, PNAS (2010); J. Russo & H. Tanaka, Soft matter (2012); Sci. Rep. (2012)

Process of crystal nucleation from a supercooled hard-sphere liquid



Fcc-like MRCO

Fcc(+hcp) crystals

This may be a GENERIC mechanism to lower the crystal-liquid interface tension!!

Crystals are always formed in preordered regions (or, precursors) of a supercooled liquid and polymorph Is already selected there before nucleation takes place.

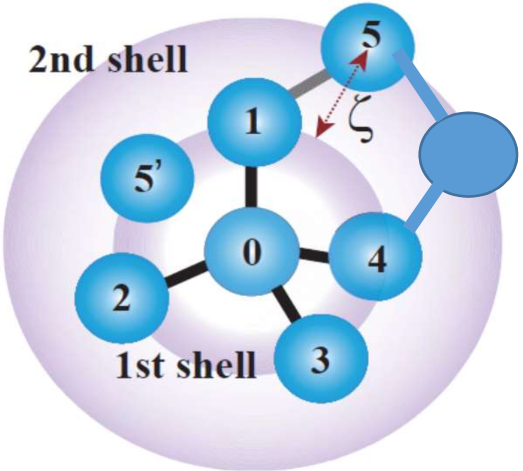
New scenario of homogeneous ice nucleation

- There is a novel metastable crystal form of ice, which we name Ice 0 (tetragonal t12 crystal).
- Although metastable Ice 0 is hidden behind stable Ice I crystals, it plays a crucial role in crystal nucleation.
- It is the local order of the Ice 0 phase that triggers the birth of ice crystals, and upon its growth gradually transforms into stacking of Ice Ic and Ice Ih. The key is the friendliness to the water structure.
- This can be seen as a manifestation of the Ostwald step rule.
- Locally favored structures of water has a connection to the local order of Ice 0. Both are characterized by high translational order in the second shell and inclusion of pentagonal rings.
- Our study shows that metastable crystalline phases of water play a crucial role, which has been largely overlooked, a result that might extend to crystallization of other supercooled liquids.

Glass transition

Local structural ordering in liquid plays key roles in both!

Beyond the first shell
of tetrahedral order



- **Locally favored structures act as precursors for both hard sphere and ice nucleation. For water, it lead to the formation of ice 0 upon crystal nucleation at low temperatures.**
- **Polymorph which is to be formed upon nucleation is already selected in a supercooled state. The symmetry is locally broken already in a supercooled state.**
- **The friendliness of the liquid structure to the crystal one is the key to the ease of nucleation!**

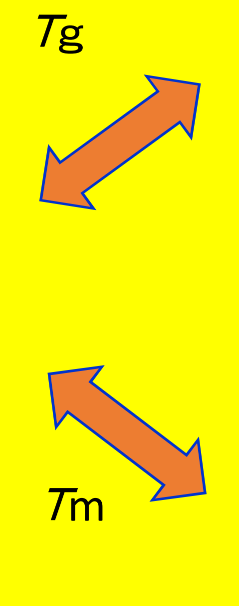
Crystallization of hard spheres and water

Glass-forming ability

cooling

liquid

bifurcation



Glass transition

glass

crystal

Crystallization

Glass forming ability of water-type liquids

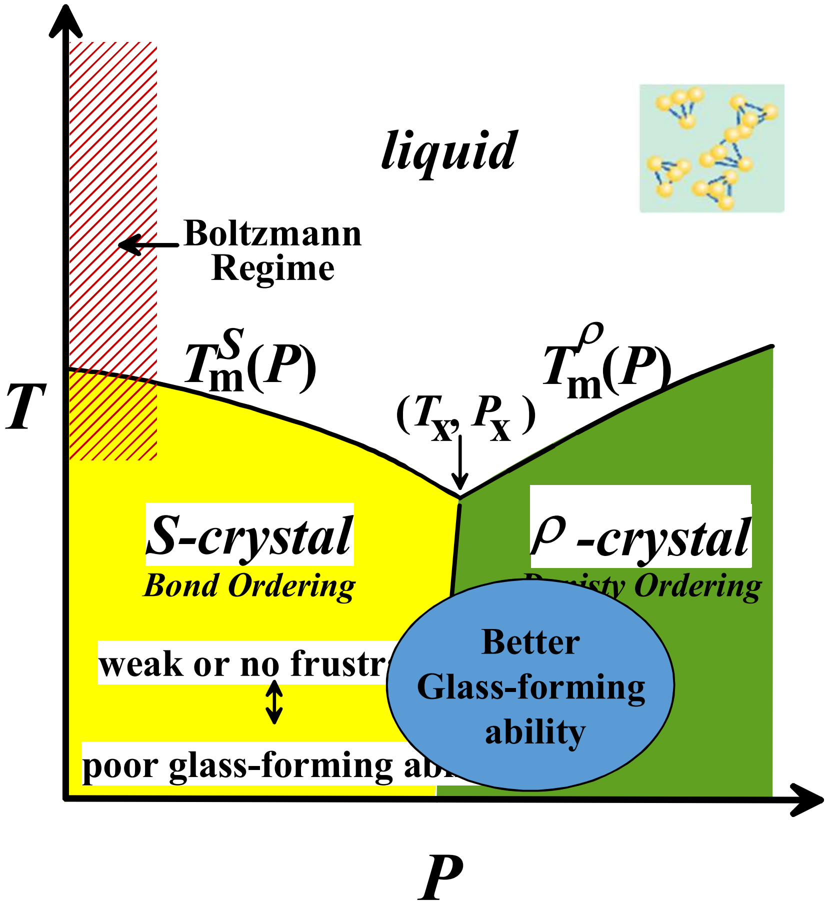
At ambient pressure, water-type liquids (water, Si, Ge, ..) are extremely difficult to vitrify. Vapor deposition on a cold substrate is the only way. This may be because the liquid structure is so friendly to the crystal structure.

What happens at high pressure?

We argued that there is a close relationship between phase diagram and thermodynamic anomaly&glass-forming ability

H. Tanaka, **Simple view of waterlike anomalies of atomic liquids with directional bonding**. ***Phys. Rev. B*** **66**, 064202 (**2002**)

Water-type atomic liquids: Si, Ge, Bi, Sb, & Ga



Water-like Phase Diagram

Water : $P_x \approx 0.2$ GPa
Si : $P_x \approx 14$ GPa
Ge : $P_x \approx 10.5$ GPa
Bi : $P_x \approx 2.4$ GPa
Sb : $P_x \approx 6$ GPa
Ga : $P_x \approx 1$ GPa

Long-range bond ordering at low *P*!

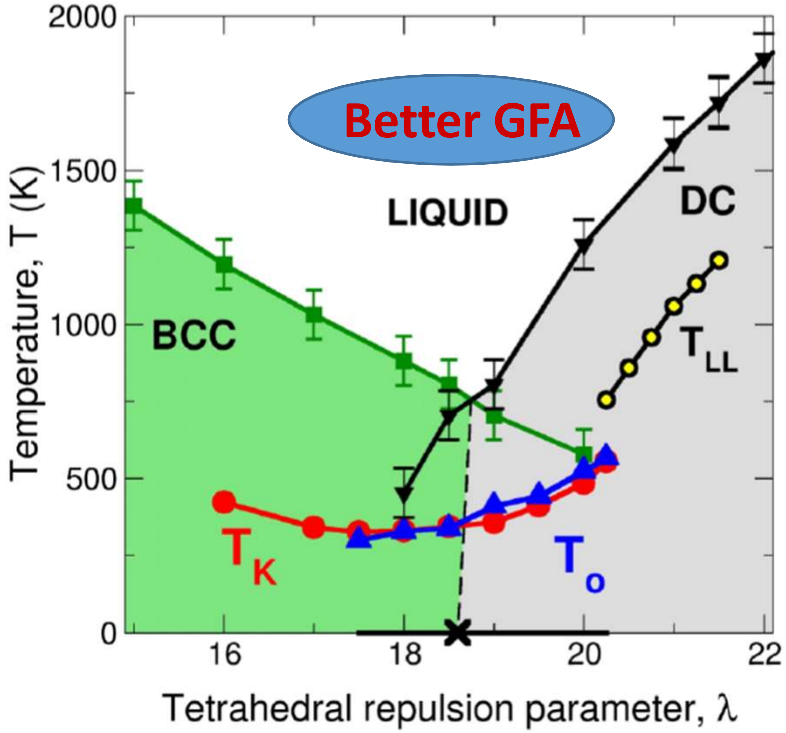
H. Tanaka, *Phys. Rev. B* **66**, 064202 (**2002**)

Water-type atomic liquids : Poor glass formers at ambient pressure!
Consistent with the prediction of our two-order-parameter model

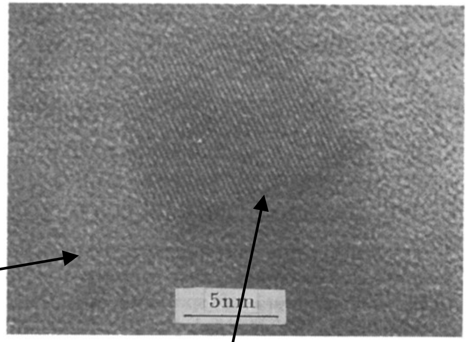
Competing orderings should lead to high glass forming ability!

Tuning of tetrahedrality in a Stillinger-Weber potential yields a series of monatomic (metal-like) glassformers of very high fragility.

V. Molinero, S. Sastry, and C. A. Angell, PRL (2006)



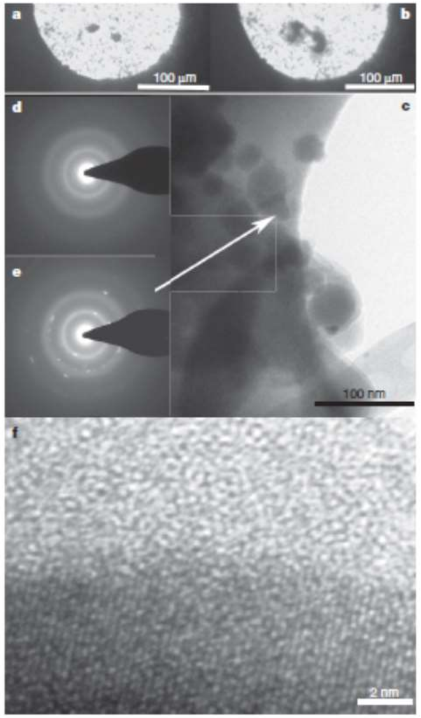
Zhang & Wang, Appl. Phys. Lett. 67, 617 (1995)



Amorphous Ge

FIG. 2. High resolution image of Ge quenched from the melt at 3 GPa with undercooling of 126 K.

First crystallized into a metallic, high-pressure form of crystal, Ge-II

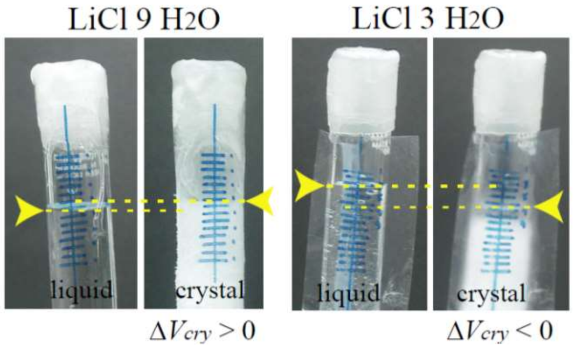


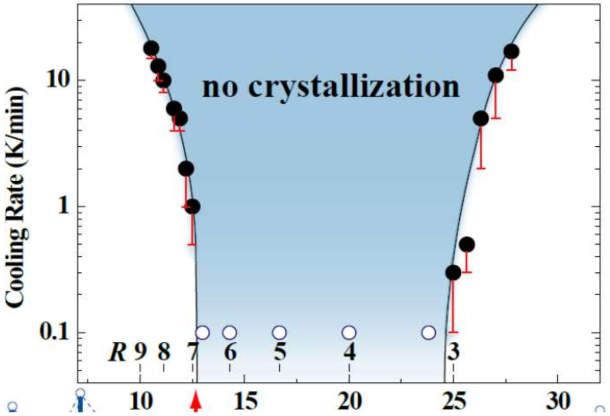
Vitrification of a monoatomic metallic liquid
Bhat et al., Nature 448, 787 (2007)

7.9 GPa

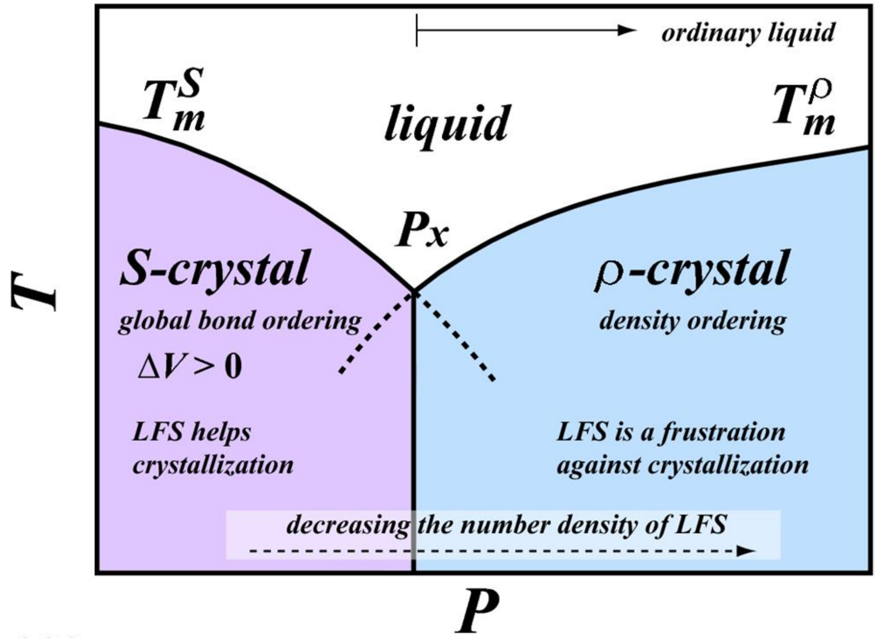
Link between phase diagram, glass-forming ability and fragility

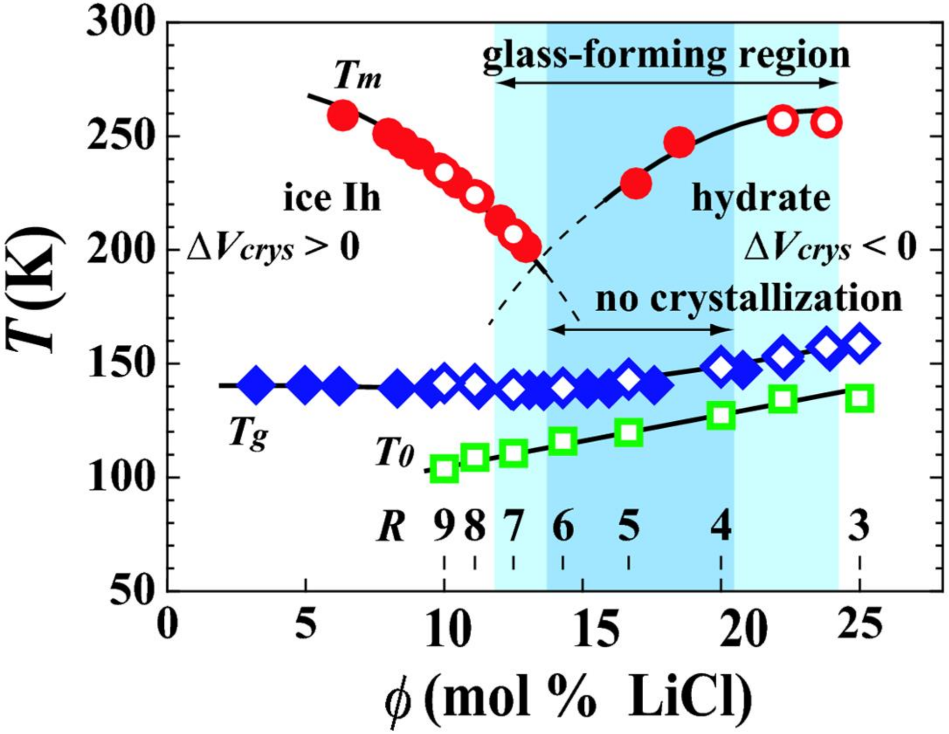
hinted by Angell&Sare's work (JCP, 1968)





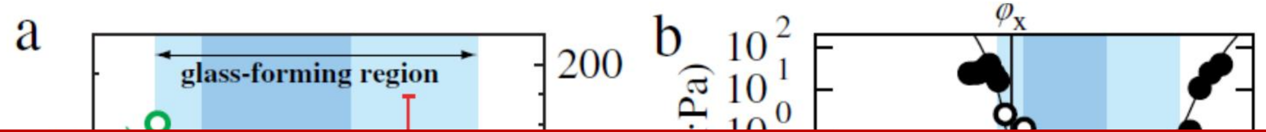
R: Number of water molecules per LiCl





Kobayashi&Tanaka, PRL(2011)

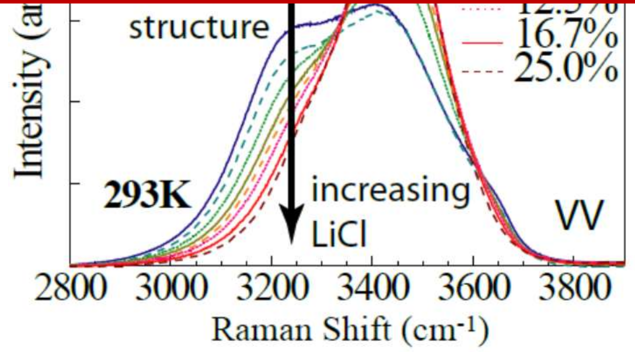
Dependence of fragility on the LiCl concentration

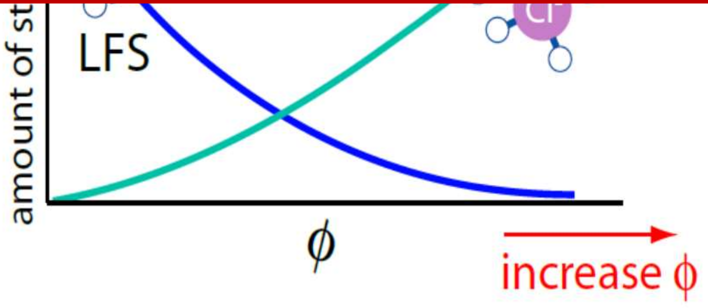


These results are consistent with our prediction that competing orderings lead to high glass forming ability, but its microscopic origin is still elusive!

We study this problem by using numerical simulations to seek the physical origin.

Be
Na
Bu





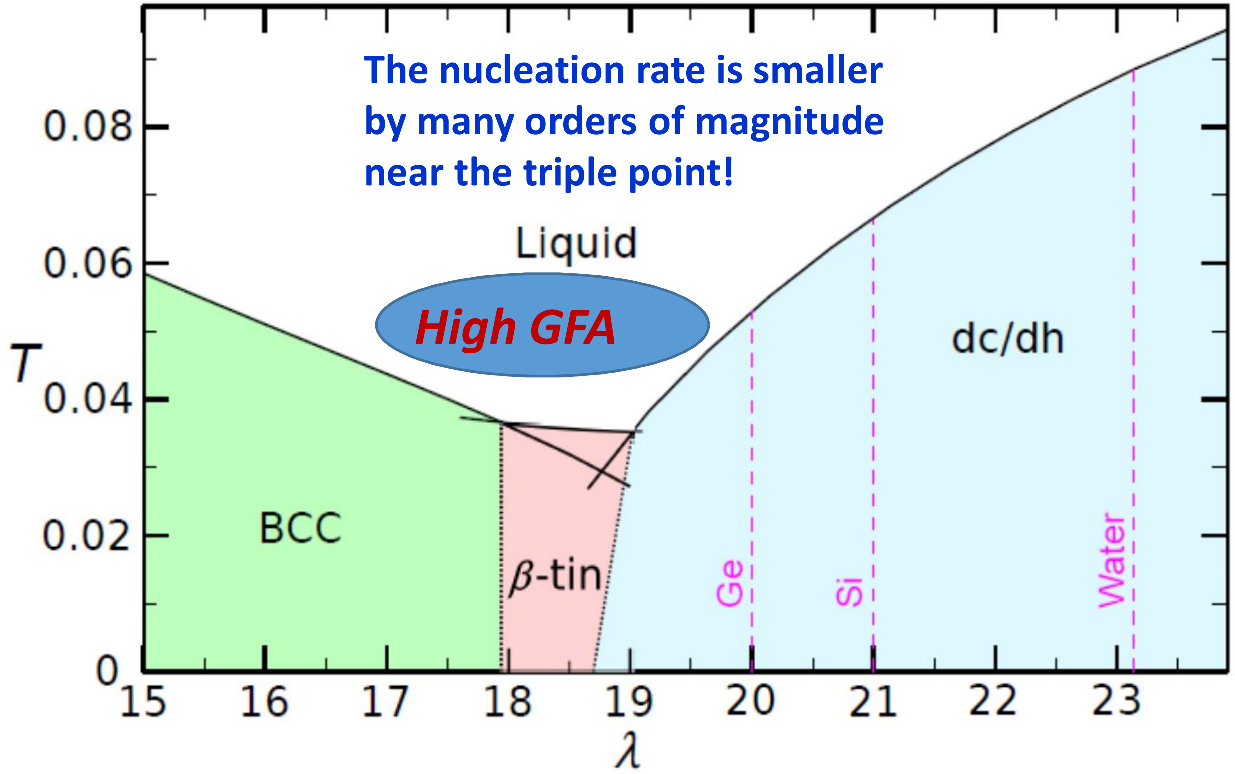
Generalized Stillinger-Weber potential

V. Molinero, S. Sastry, and C. A. Angell, PRL (2006)

Control parameter

$$U = \sum_i \sum_{j>i} U_2(\mathbf{r}_{ij}) + \lambda \sum_i \sum_{j\neq i} \sum_{k>j} U_3(\mathbf{r}_{ij}, \mathbf{r}_{ik})$$

Two-body interaction **Three-body interaction favoring tetrahedrality**


The nucleation rate is smaller by many orders of magnitude near the triple point!

High GFA

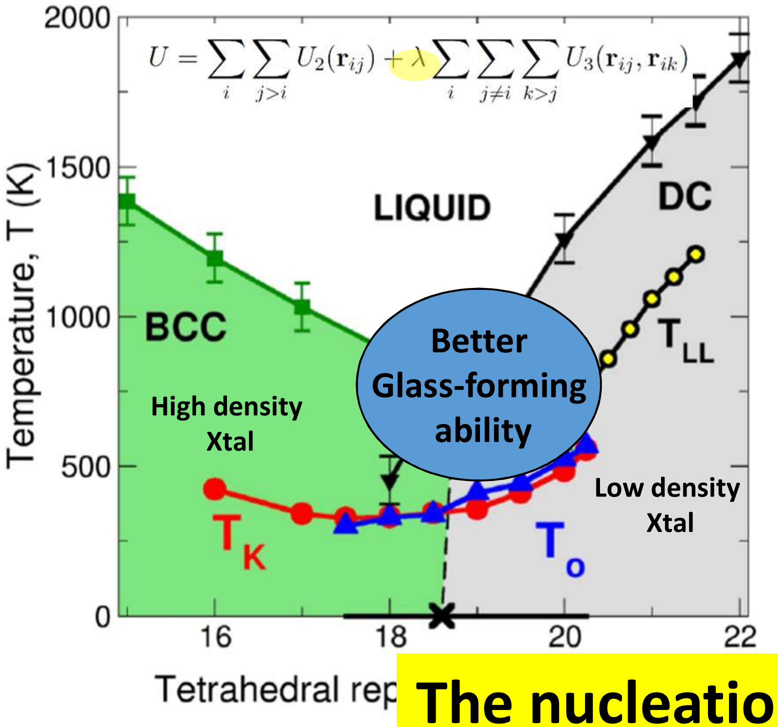
What is the physical factor controlling glass-forming ability?

Our answer: Competing orderings or frustration lead to the avoidance of crystallization!?

Competition between different crystal orderings

Size disparity+Random mixing

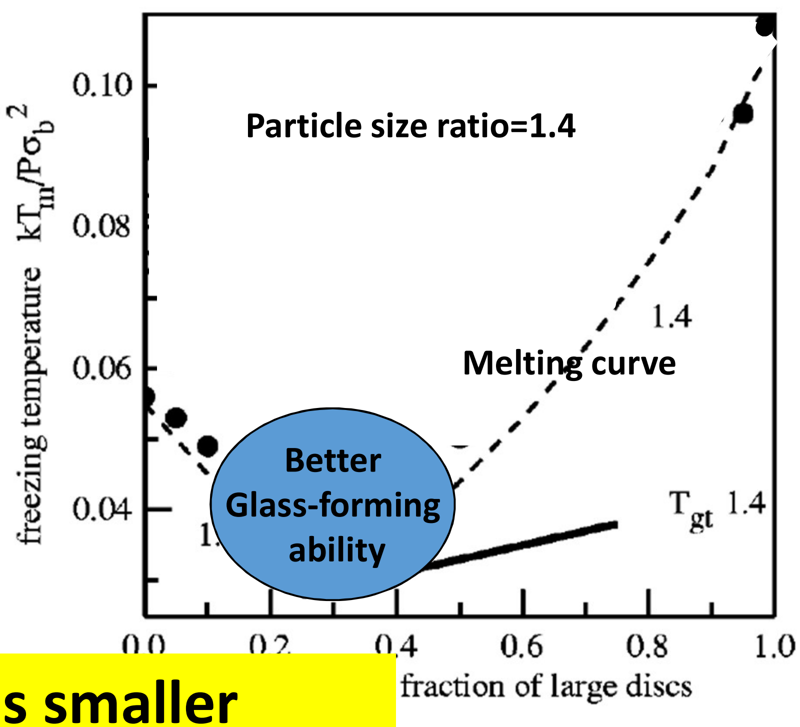
Generalized Stillinger-Weber potential



$$U=\sum_{i}\sum_{j>i}U_2(\mathbf{r}_{ij})+\lambda\sum_{i}\sum_{j\neq i}\sum_{k>j}U_3(\mathbf{r}_{ij},\mathbf{r}_{ik})$$

Better Glass-forming ability

Binary hard disk mixtures



Particle size ratio=1.4

Better Glass-forming ability

The nucleation rate is smaller by many orders of magnitude near the melting point minimum!

Triple points of W

nt of metallic alloy

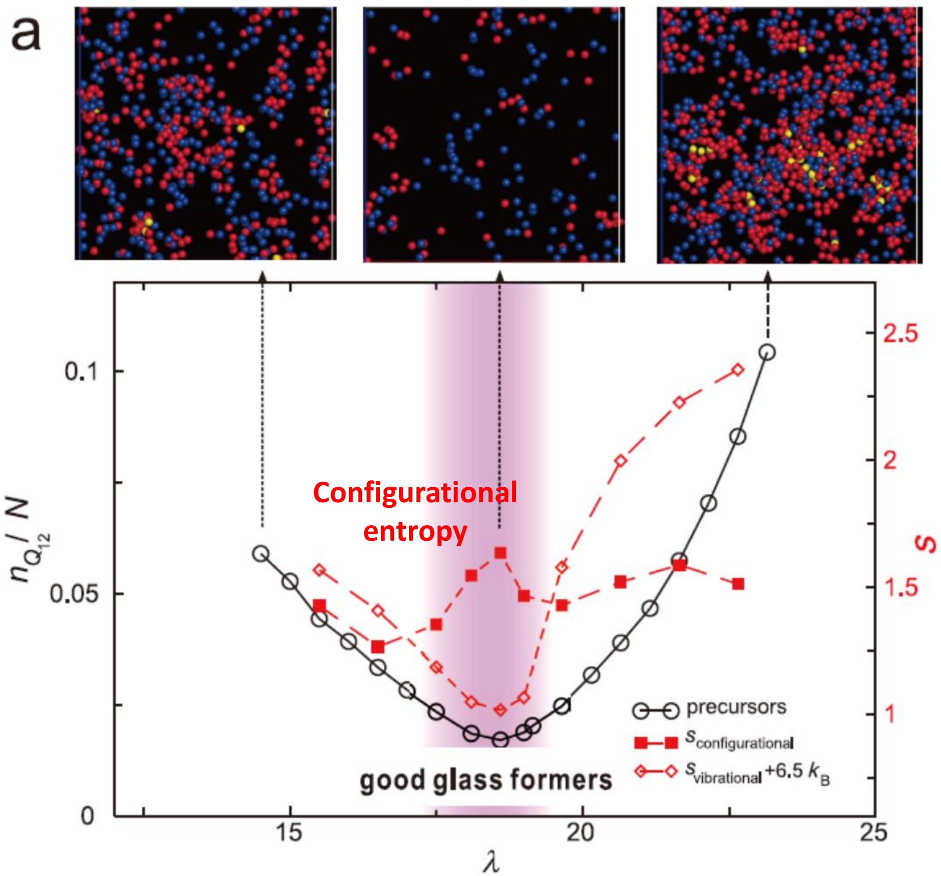
H. Tanaka, Phys. Rev

hys. 110, 4559 (1999).

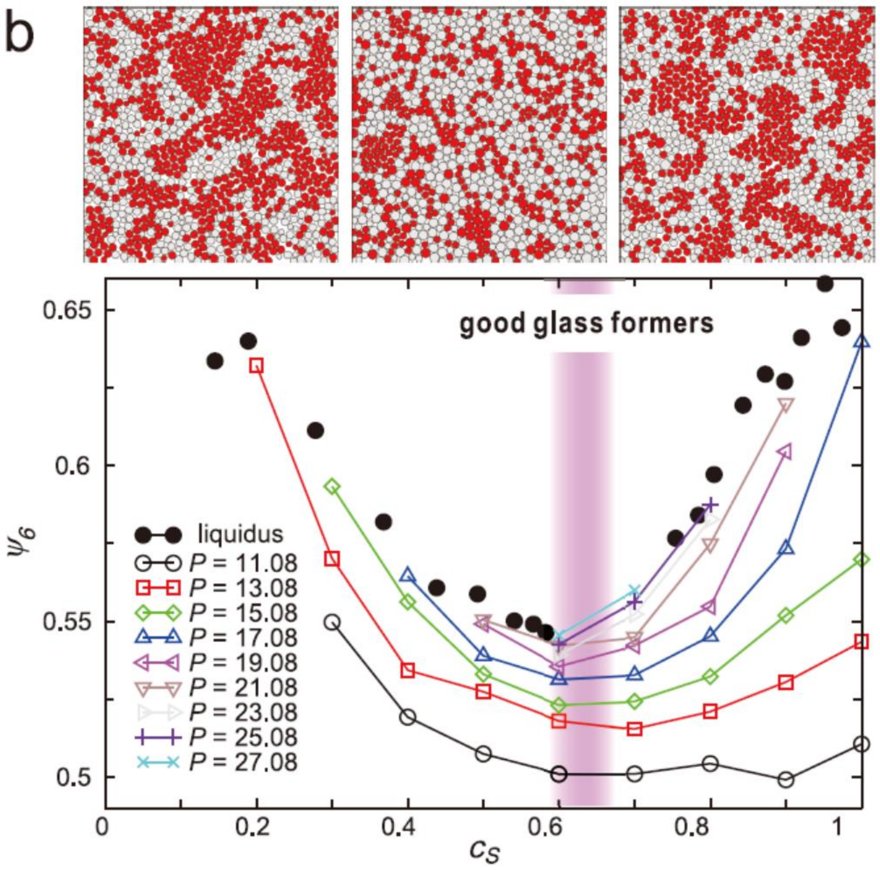
V. Molinero, S. Sastry, and C. A. Angell,
Phys. Rev. Lett. 97, 075701 (2006)

The cause of λ&cs-dependence of the interface tension: λ&cs-dependence of precursors for state points with constant $\beta\Delta\mu$

Q_{12} (bcc,β-tin,dc,dh)



ψ_6 (haxatic)

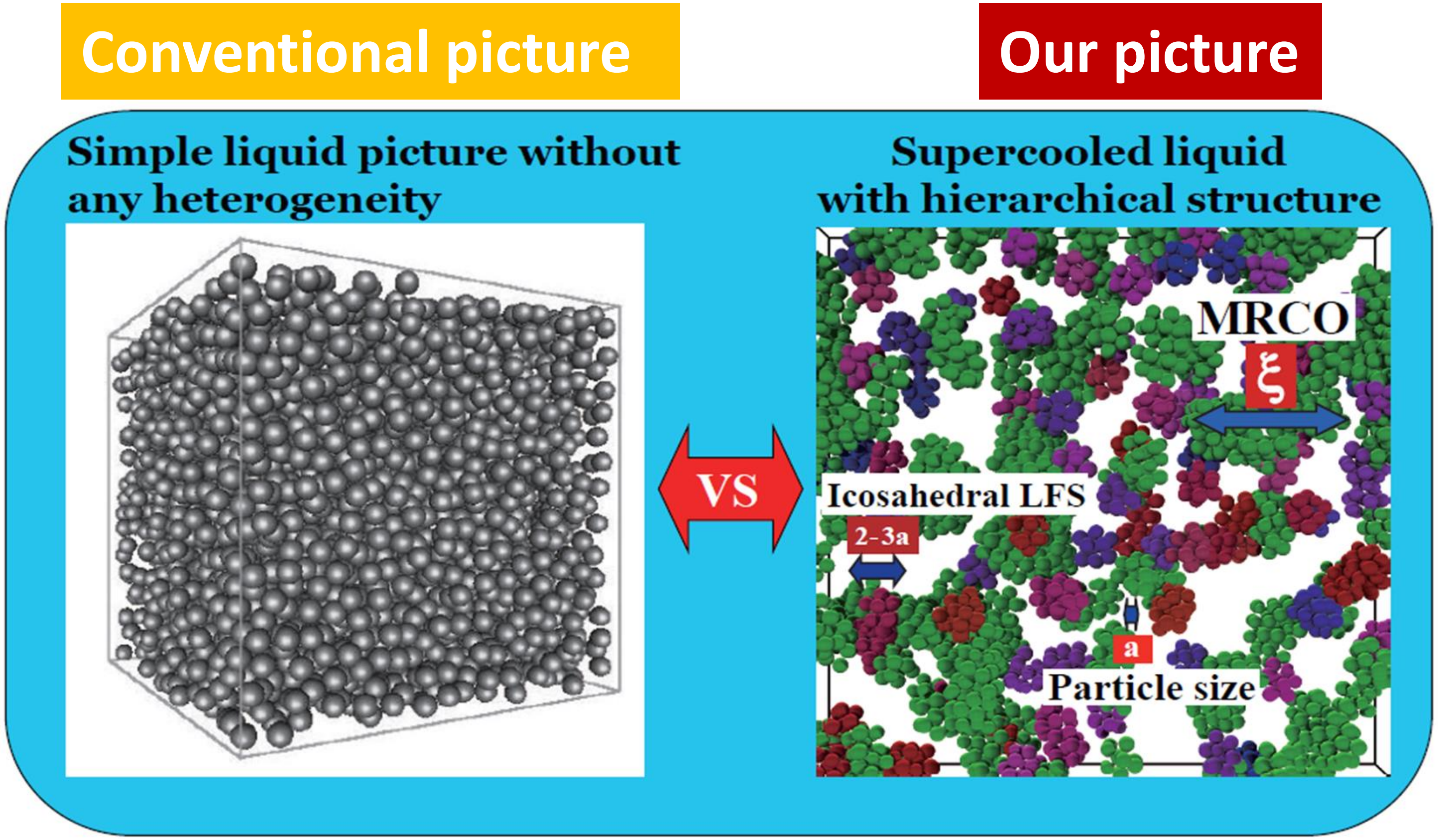


The glass forming region is around the minimum of the number of precursors. This provides an extremely simple, but appealing scenario for the ease of crystallization: the presence of well-developed crystal precursors in a supercooled liquid helps crystal nucleation and its absence due to frustration or competing orderings prevents it.

Summary of glass forming ability

- **The friendliness of the local symmetry of the liquid structure to the crystal one is the key to a low interface tension and thus to the ease of crystallization.**
- **Increase in frustration against crystallization suppresses preordering and results in high glass-forming ability.**
- **Due to strong frustration, a liquid in the glass-forming region has high structural complexity, i.e., high configurational entropy, which is a thermodynamic signature of large surface tension there.**

Key messages of this talk



Conventional picture

Simple liquid picture without any heterogeneity

Our picture

Supercooled liquid with hierarchical structure

Supercooled liquid is not a simple liquid, but soft-matter-like in the sense that there is spatio-temporal hierarchy!

This is a consequence of non-trivial many-body effects due to local symmetry selection under dense packing.

Structural ordering is not only responsible for slow glassy dynamics, but also triggers crystal nucleation!

A supercooled liquid is preparing for future crystallization!

Thank you!