Dynamic crossover and structure correlation

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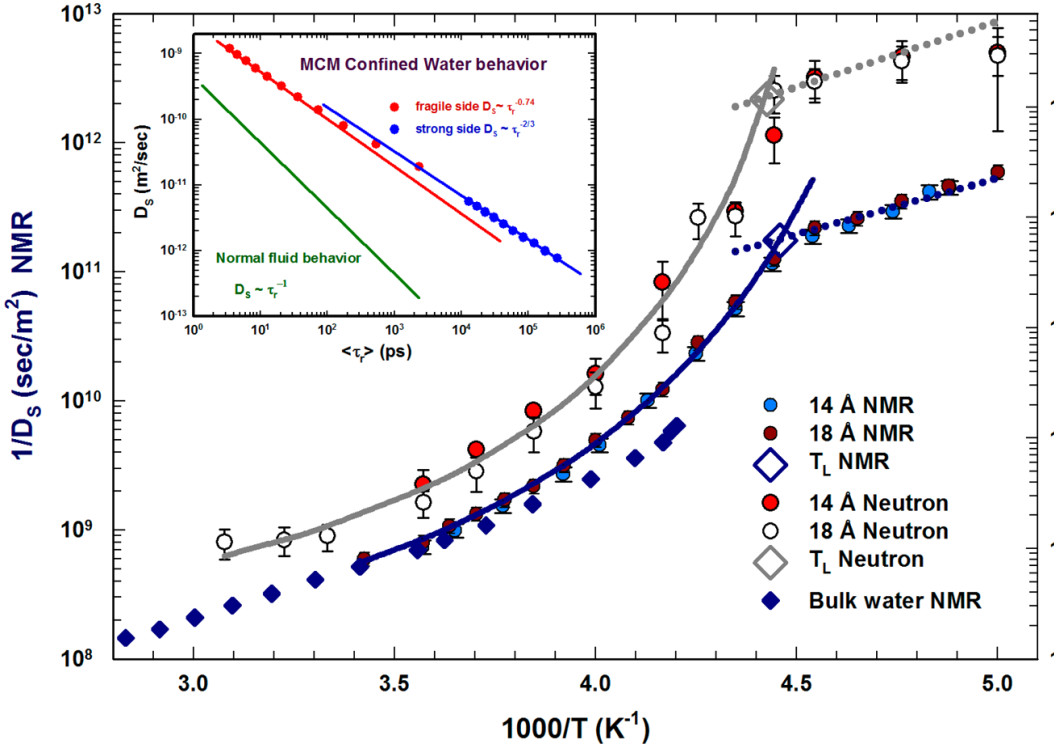
Course: Water and the water systems

Erice-Sicily, July 2016

Outline

- Different views on dynamic crossover
- Dynamic crossover & structural origin
- Dynamic crossover & potential energy landscape

Dynamic crossover in glass-forming liquids



Different views:

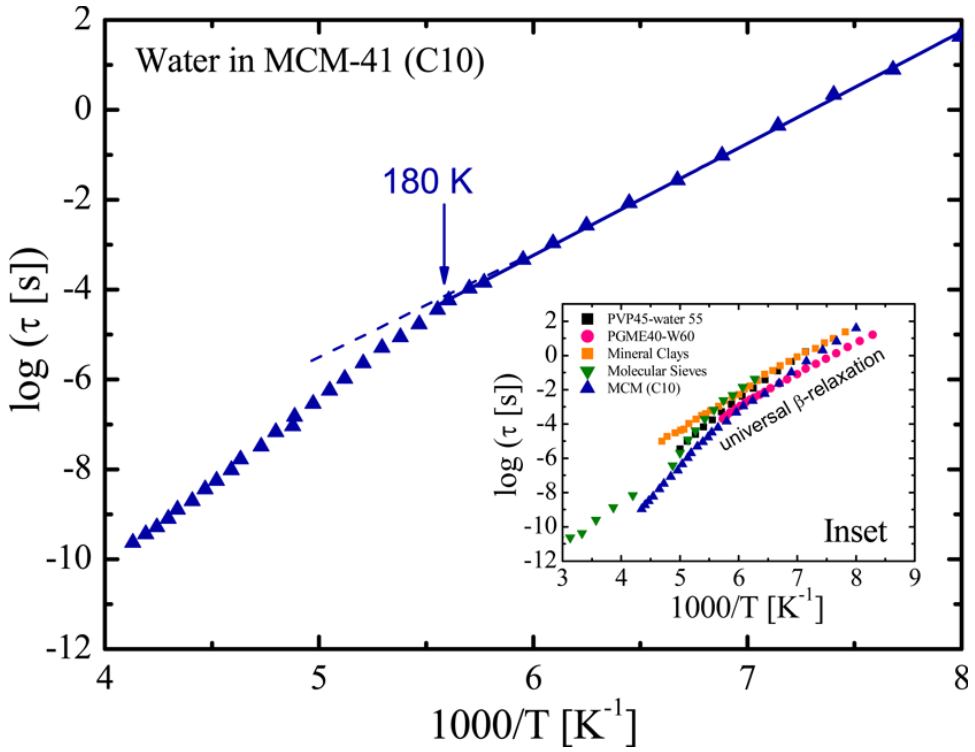
- ❑ Glass transition
- ❑ Phase transition
- ❑ Crystallization

Observed using different techniques (NMR, Neutron, BDS)

Observed in different systems (molecular, atomic, metallic)

Cerveny, Mallamace, Swenson, Vogel, Xu, Chemical Reviews (2016)

Dynamic crossover in glass-forming liquids



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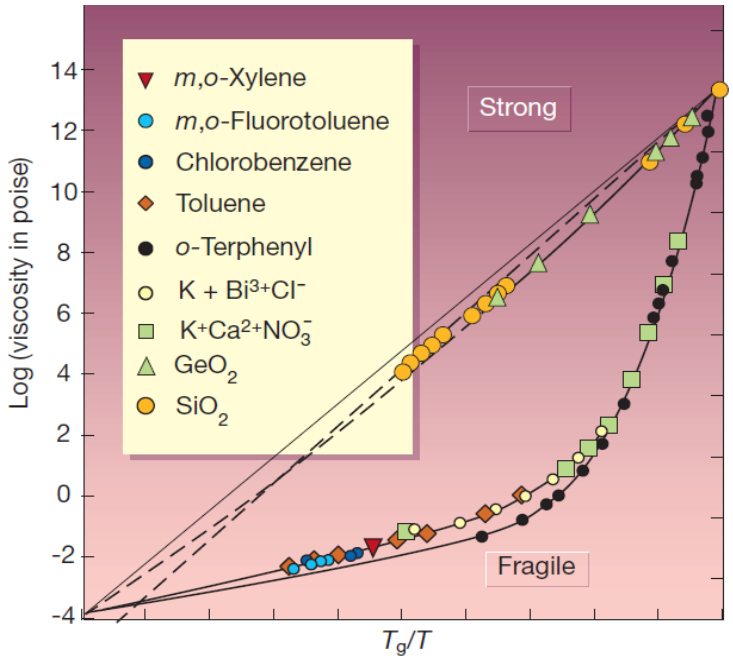
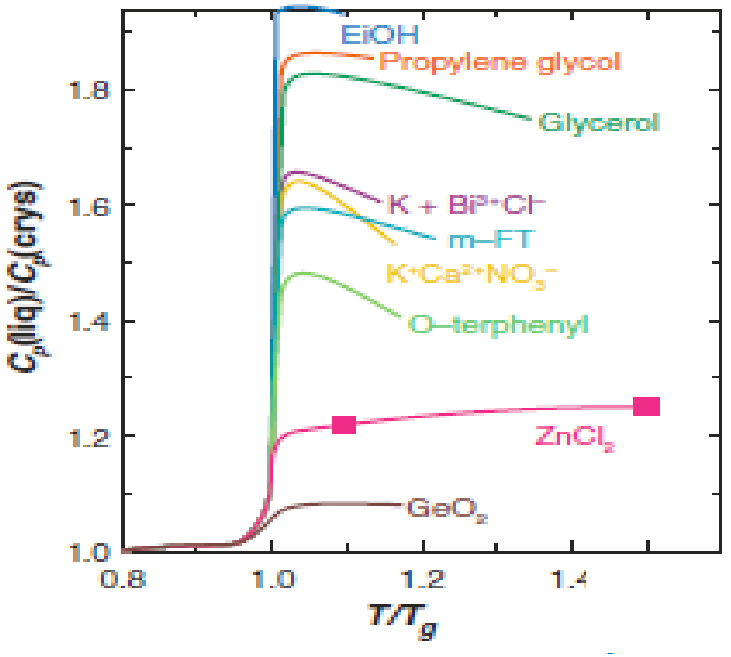
Dynamics and thermodynamic upon glass transition



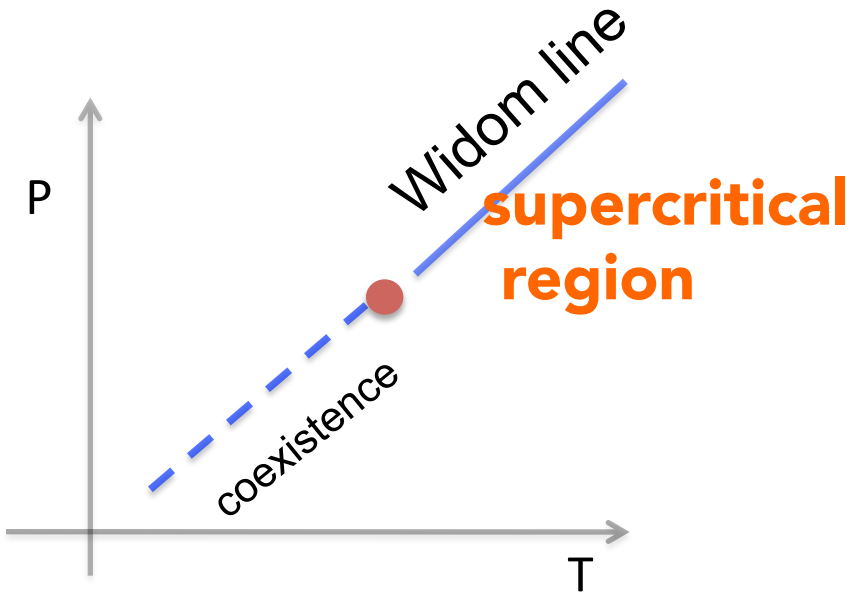
Debenedetti et al., *Nature* 2001

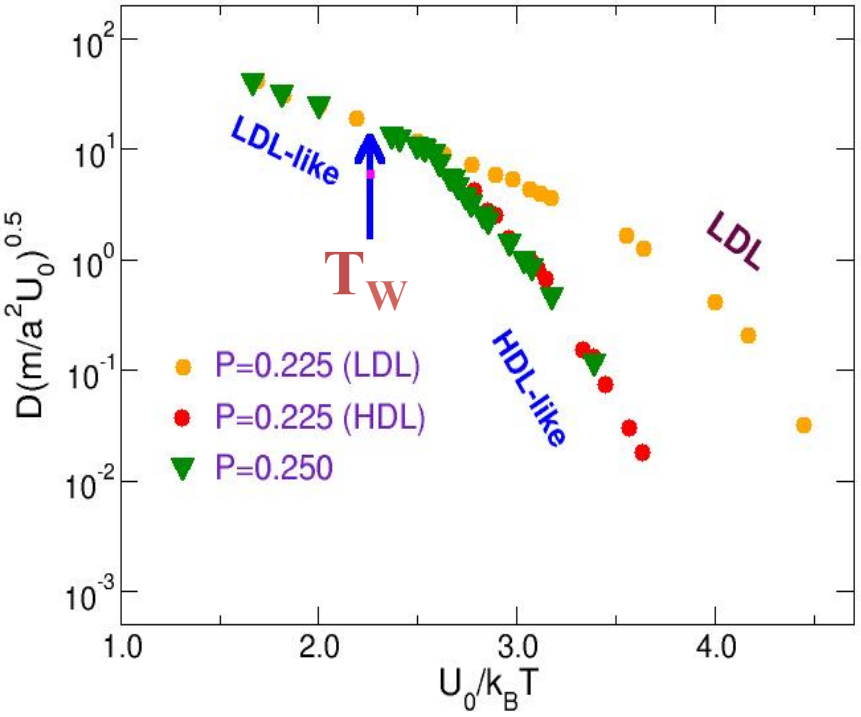


Characteristics near glass transition:

- ✓ Diverging of dynamics
- ✓ Continuous change in thermodynamics

Dynamic crossover & phase transition





Two phase coexistence region

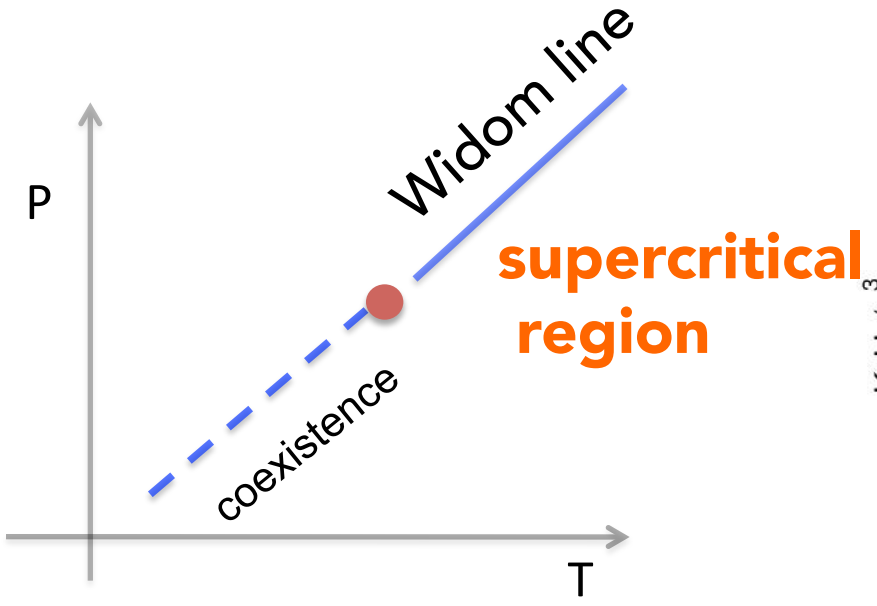
Critical point

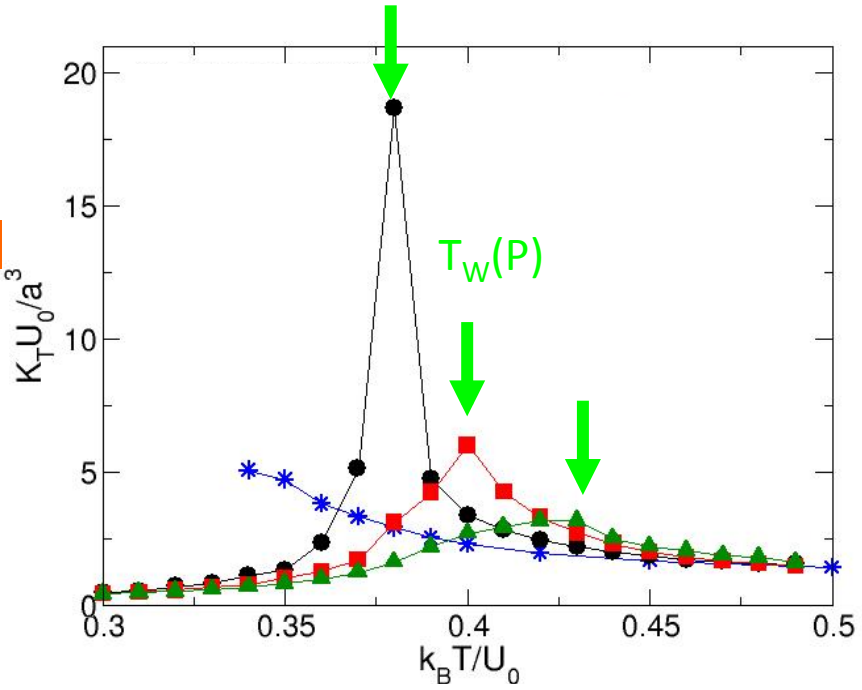
Two phase coexistence region

The Widom line

L. Xu et. al, PNAS (2005); Nature Physics (2009)

Phase transition: the Widom line





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Dynamic crossover & the Widom line

PHYSICAL REVIEW B **87**, 041101(R) (2013)

_c_-axis resistivity, pseudogap, superconductivity, and Widom line in doped Mott insulators

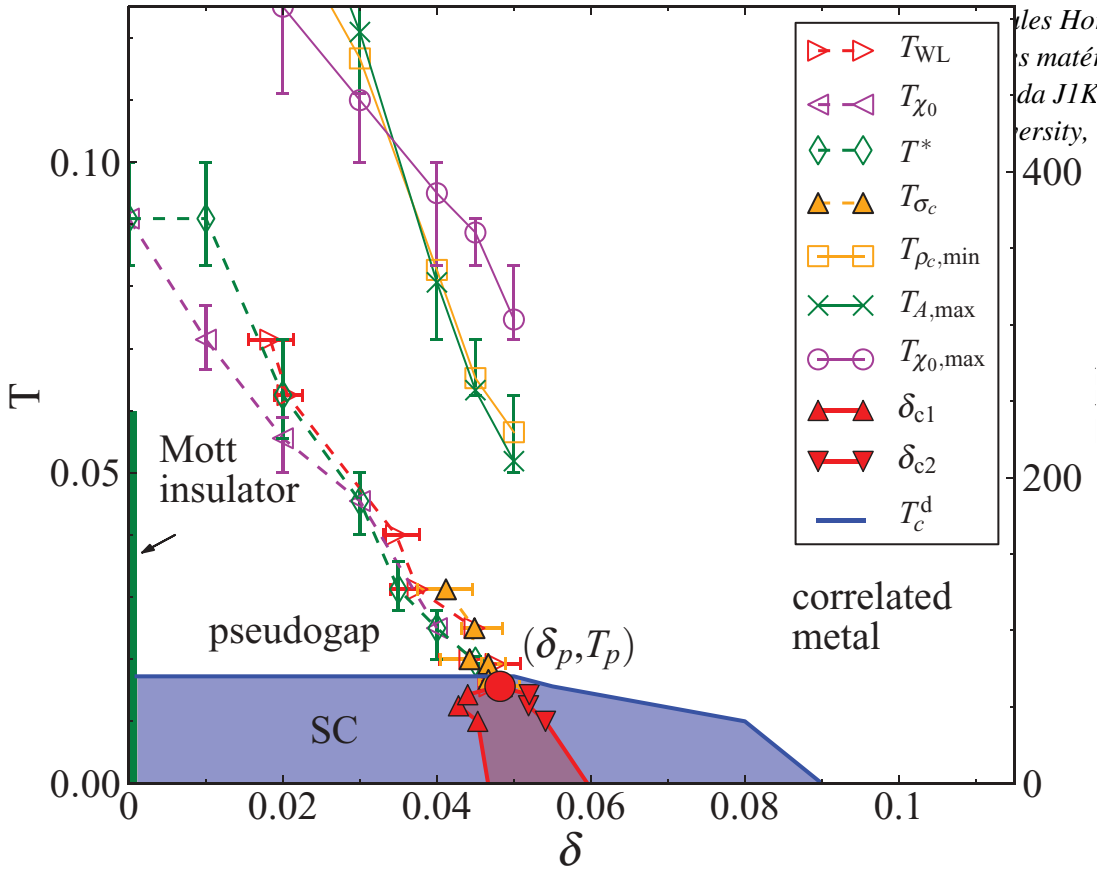
G. Sordi,[1] P. Sémon,[2] K. Haule,[3] and A.-M. S. Tremblay[2,4]

les Horowitz, 38042 Grenoble Cedex, France

s matériaux de pointe, Université de Sherbrooke, Sherbrooke,

da J1K 2R1

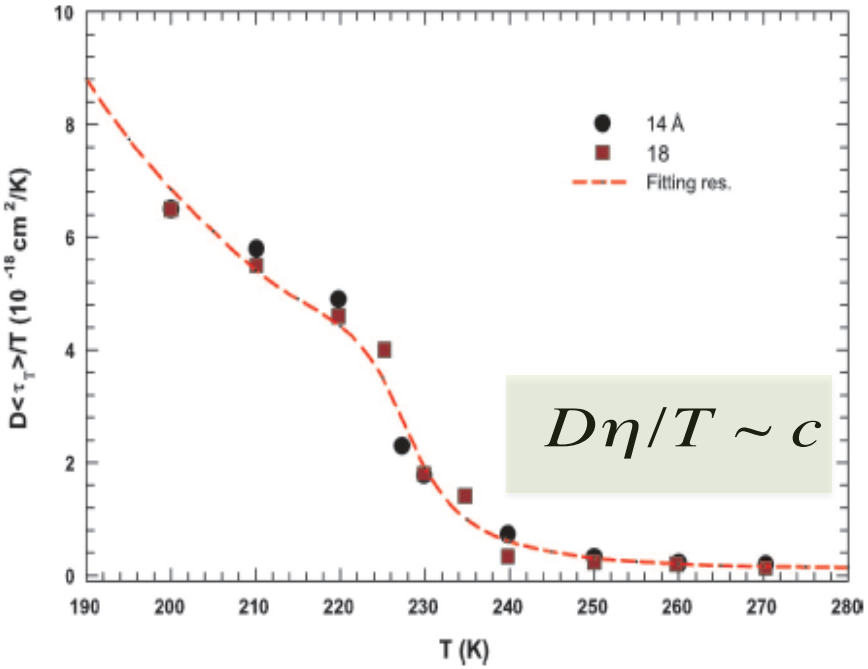
ersity,



Out-of-plane transport crossover:

- DC transport
- Dynamic crossover
- Thermodynamic crossover

Breakdown of SER associate with the Widom line

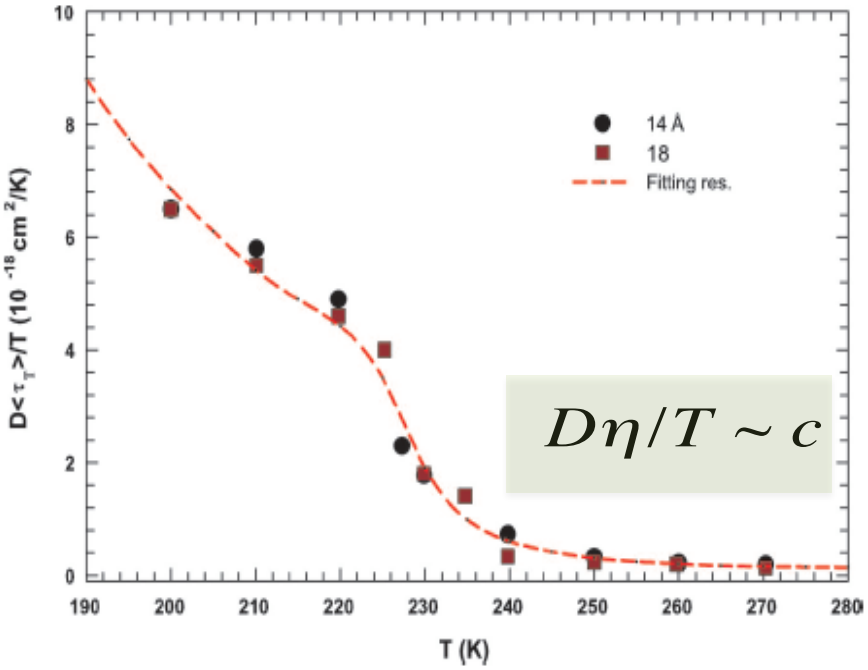


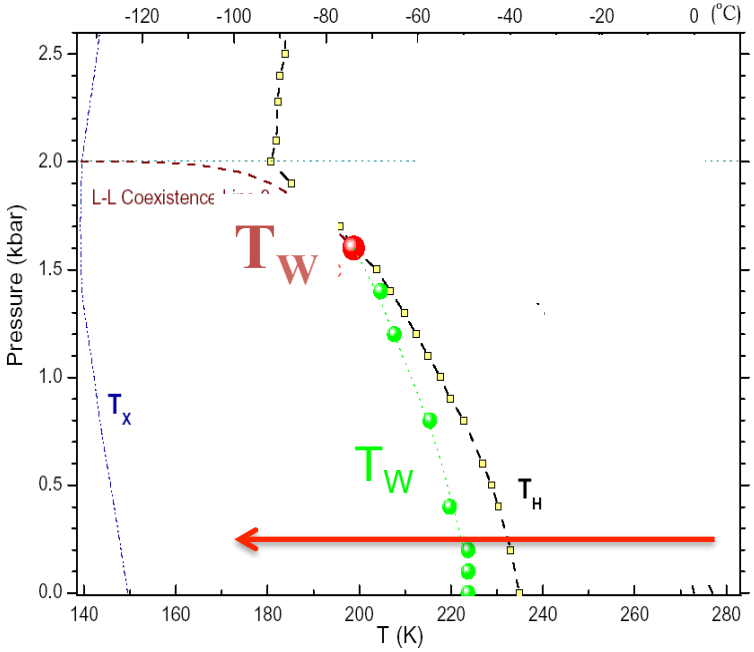
- Glass transition temperature for water: Tg ~ 135K—165K
- Breakdown for Stokes-Einstein relation: T～245K 》Tg

Breakdown is due to the crossing of the Widom line

S.-H Chen et al, PNAS (2006)

Breakdown of SER associate with the Widom line





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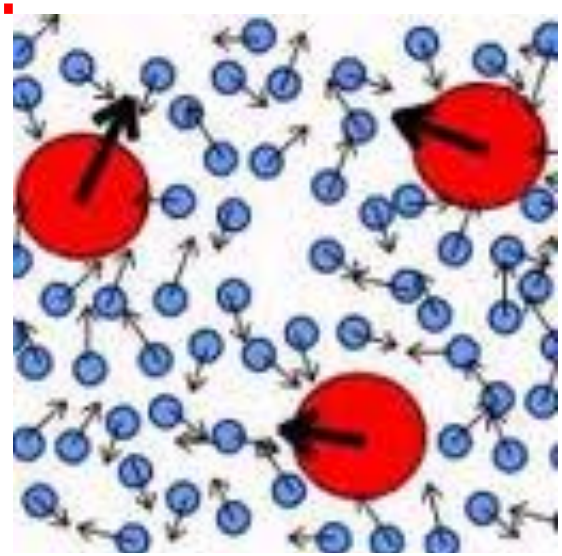
Characterization of dynamics: Stokes-Einstein relation

Stokes-Einstein relation (SER):

$$D = \frac{k_B T}{6\pi\eta R}$$



D: diffusivity

η : is the Viscosity

R: hydrodynamic radius

Characterization of dynamics for Brownian particles, but approximately true for molecule systems

Dynamics: Stokes-Einstein relation breakdown

Stokes-Einstein relation (SER):

$$D\eta/T \sim c \qquad \text{or} \qquad D \sim \left(\frac{\eta}{T}\right)^{-\gamma}$$

Breakdown of Stokes-Einstein relation:

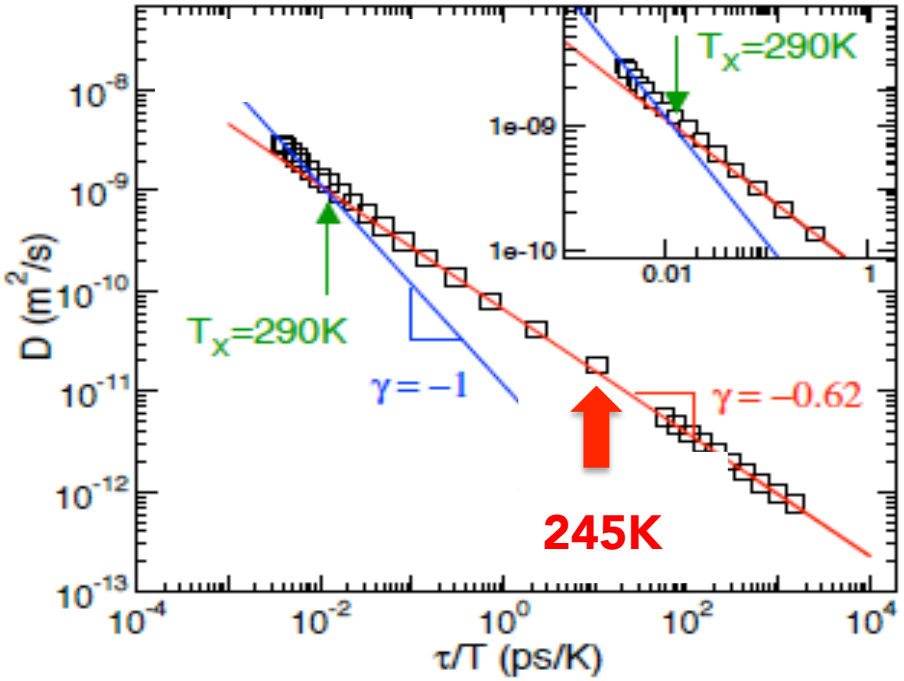
1) c is not a constant or becomes temperature dependent

OR

2) $\gamma \neq 1$ (fractional Stokes-Einstein relation)

Breakdown of Stokes-Einstein relation has been related to glass transition

Dynamic crossover in molecular system



Stokes-Einstein relation （SER）

$$D \sim \left(\frac{\eta}{T}\right)^{-\gamma}$$

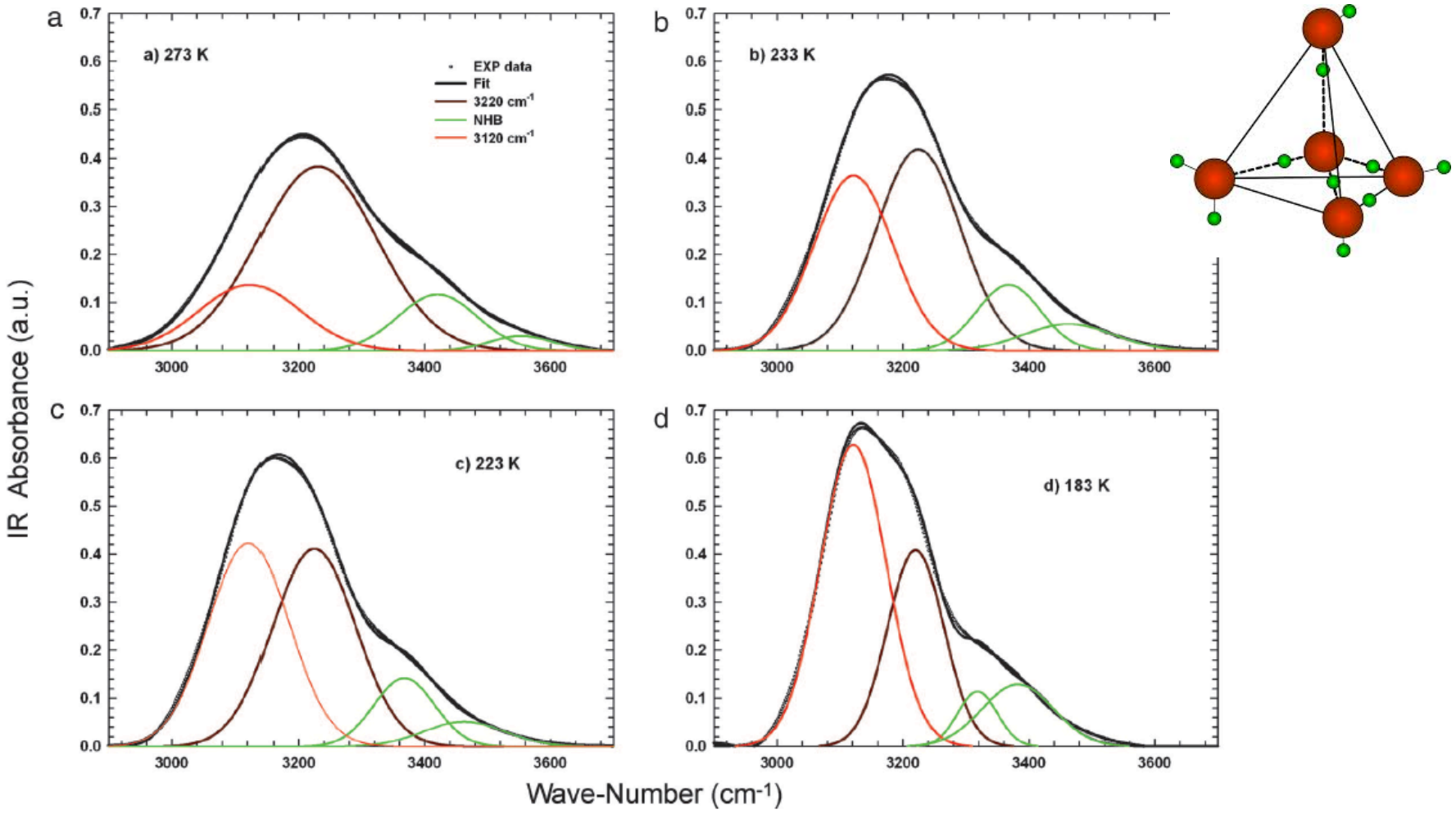
$\gamma = 1$ SER

$\gamma \neq 1$ fractional SER

- Dynamic crossover at 290 K>Tg=135~165K **(not due to glass transition)**
- Dynamic crossover temperature 290>Tw=245K **(not directly due to phase transition)**

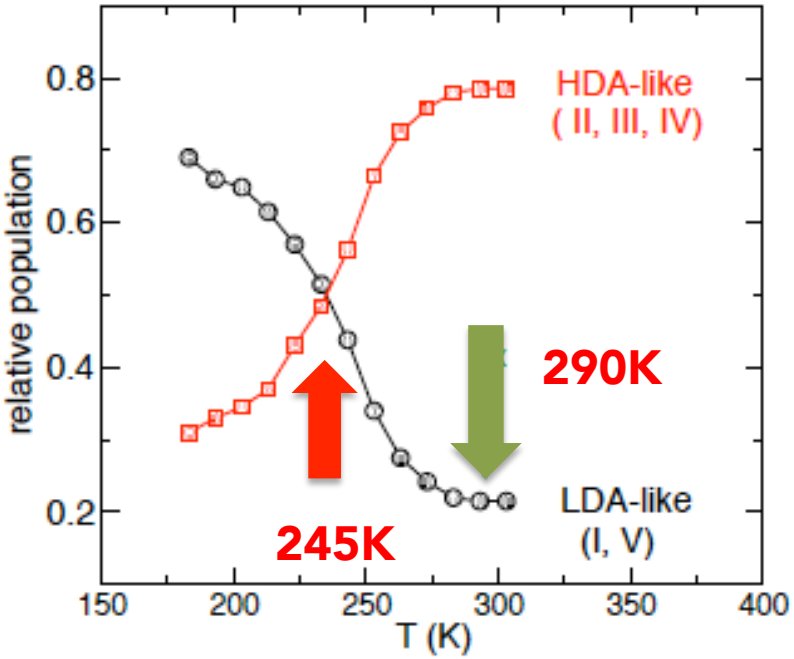
Xu et al, Nature Physics 2009

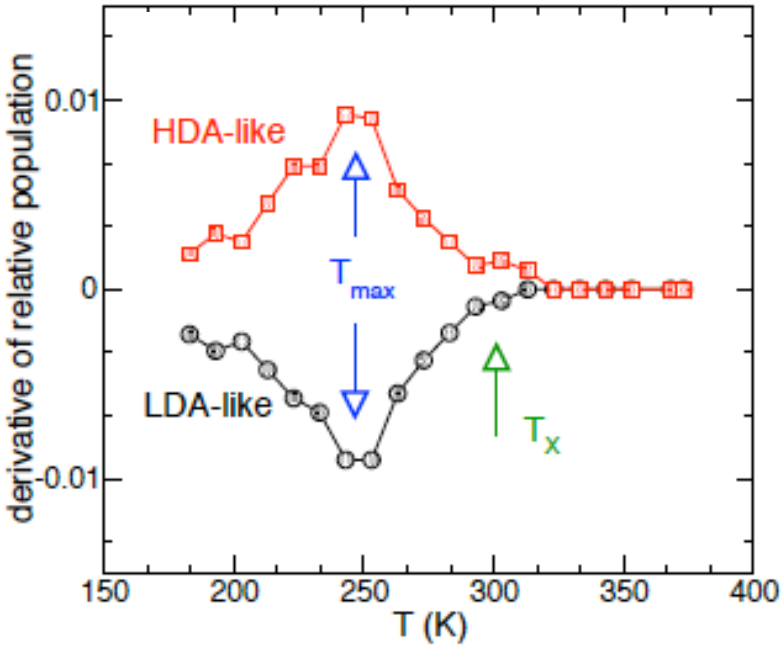
Local structure for Water—infrared spectroscopy



Xu et al, Nature Physics 2009

Correlation between structure and dynamics

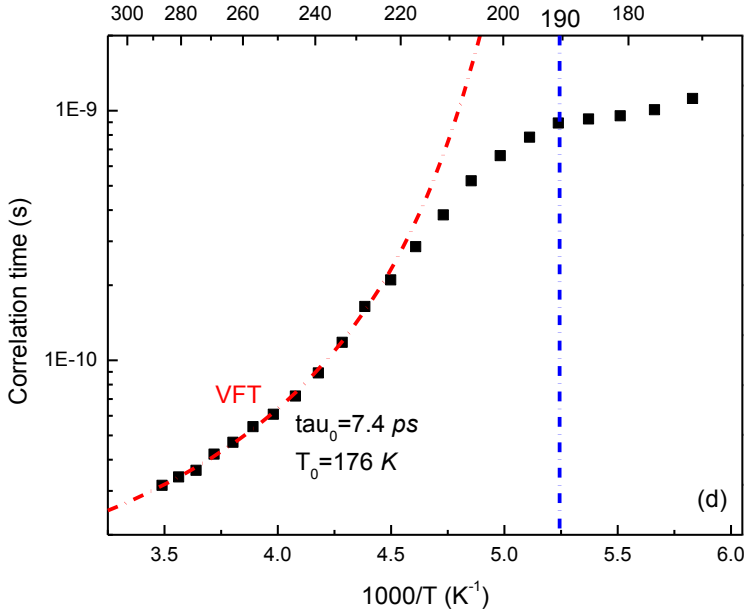


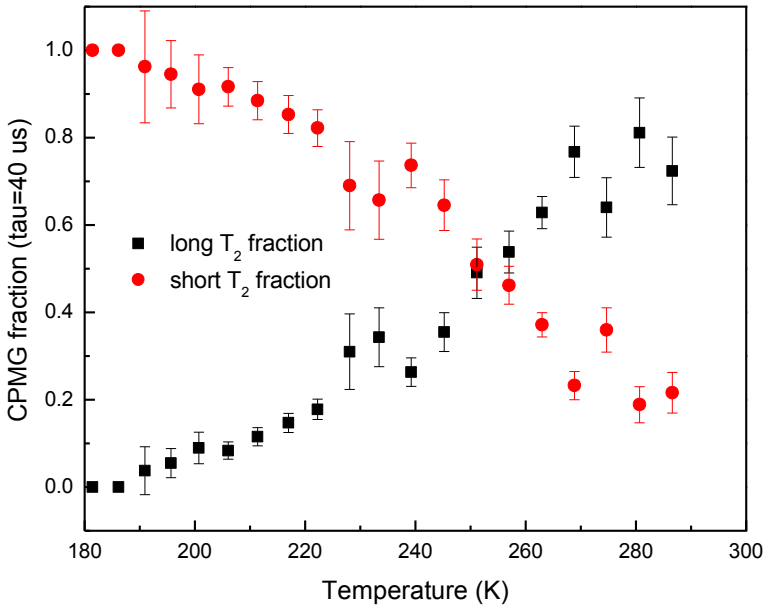


Dynamic crossover occurs at temperature where the local structure of water changes

Relation with phase transition: near the Widom line temperature, structure change is a maximum

Dynamic & structure correlation for hydrophobic confined water



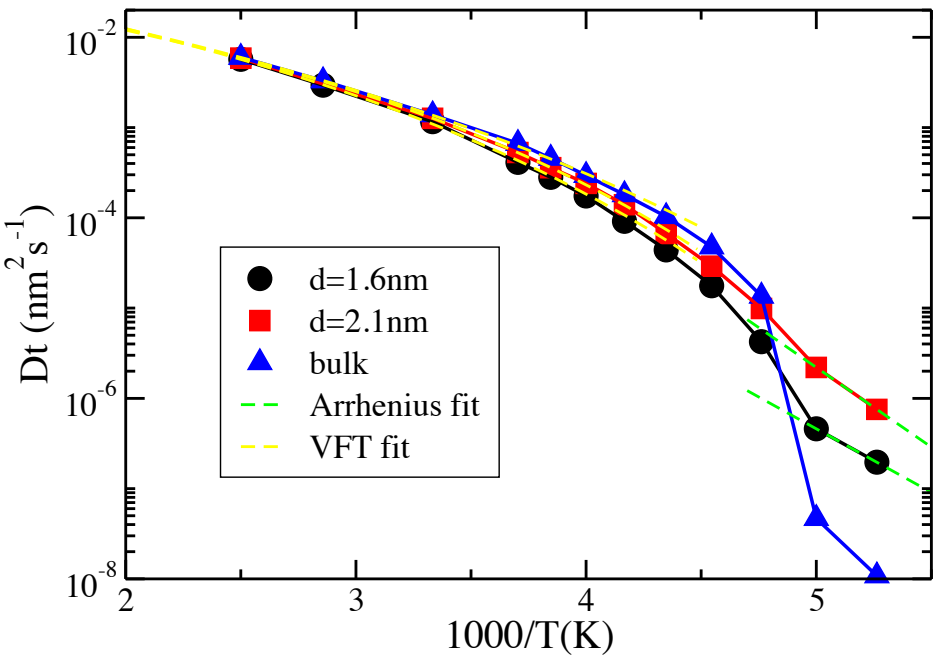


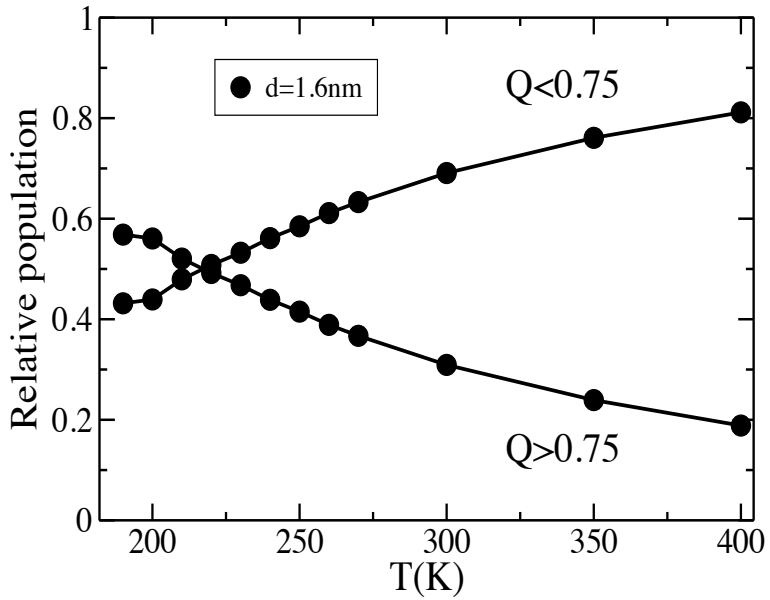
For water confined in less 2nm region, two local structural states are detected, HDL-like and LDL-like.

Below 200 K , LDL-like dominates the hydrophobic confined water

Ling, wang, Xu, Wu (unpublished)

Dynamic crossover of hydrophobic confined water

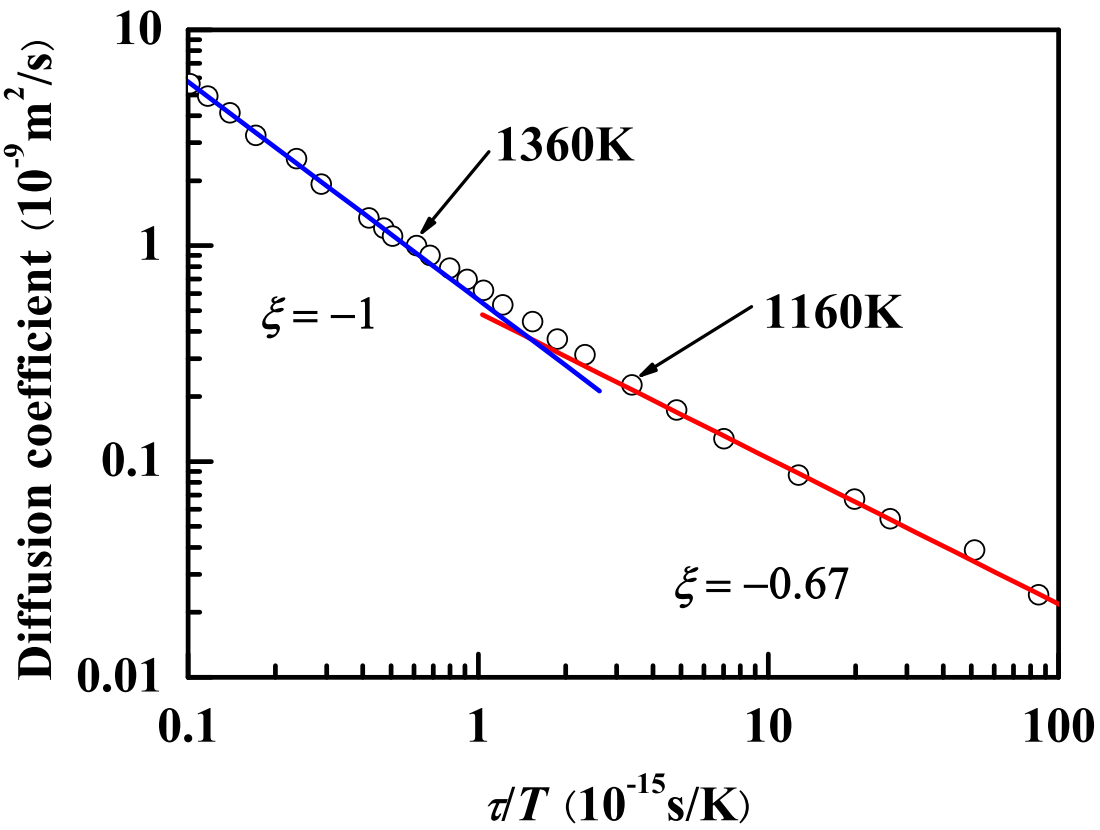




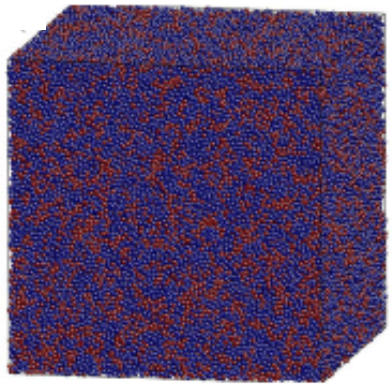
- Above 200 K the dynamical properties of confined water and bulk water (supercool without crystallization) are similar.
- A dynamic crossover occurs at temperature region 228-200 K, and it is correlated with the structural change in confined water.

Ling, wang, Xu, Wu (unpublished)

Dynamic crossover in metallic liquids



$Cu_{64}Zr_{36}$



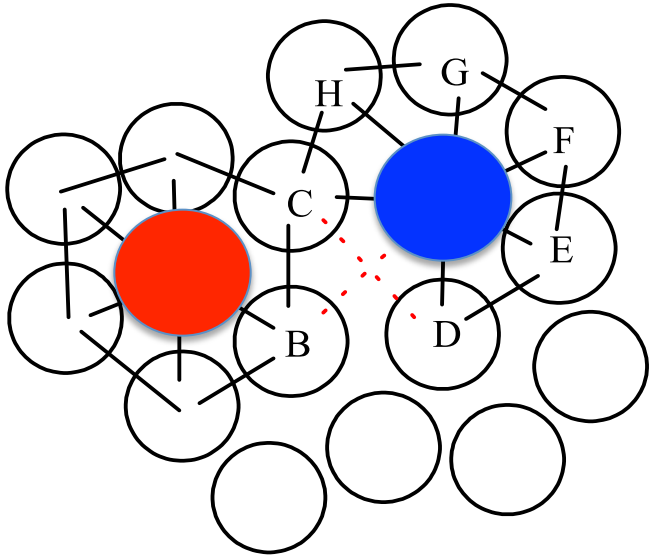
Dynamic crossover from SER to fractional SER is also observed in metallic system

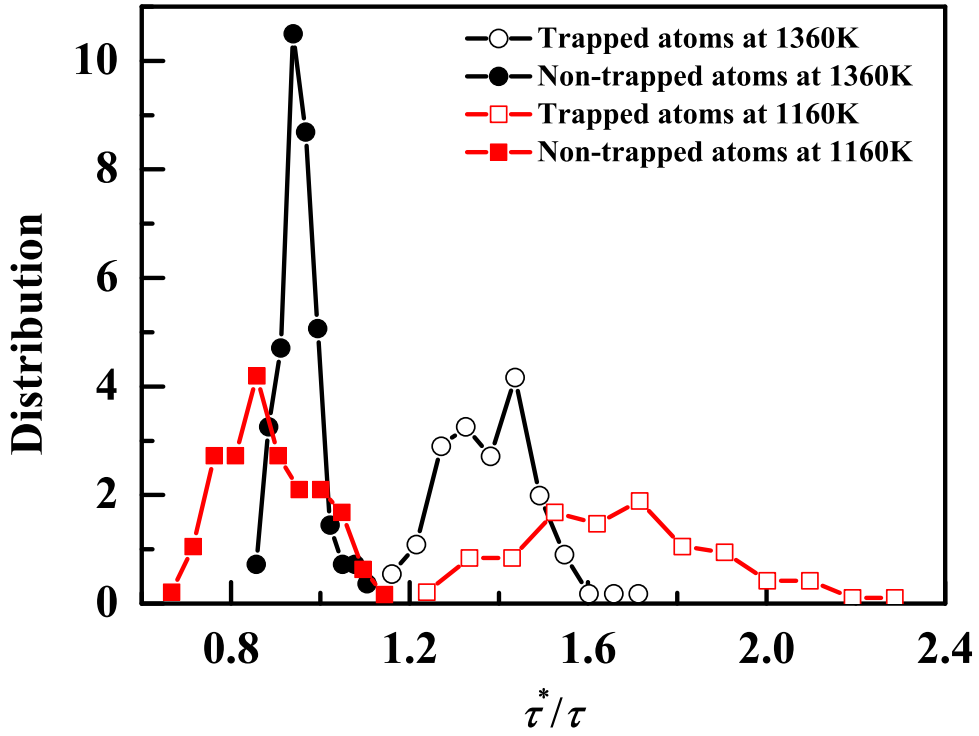
Pan, Wang, Li, Xu, submitted

Classification of atoms: trapped and non-trapped

Red: trapped atoms

Blue: non-trapped

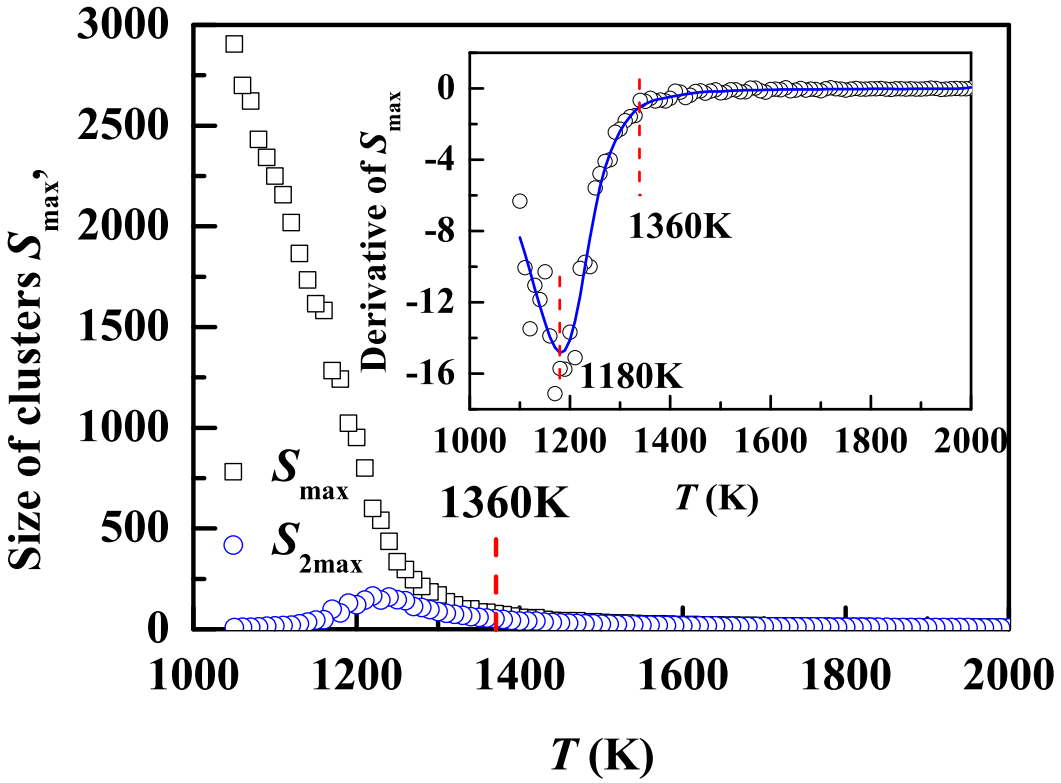




Trapped atoms has slow relaxation while non-trapped atoms are more mobile

Pan, Wang, Li, Xu

Change in the size of the largest cluster



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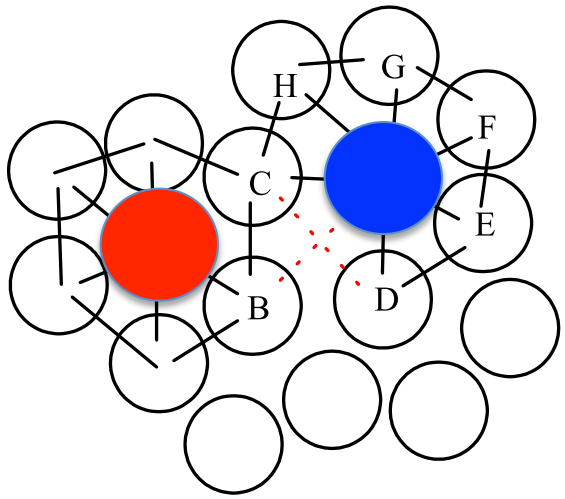
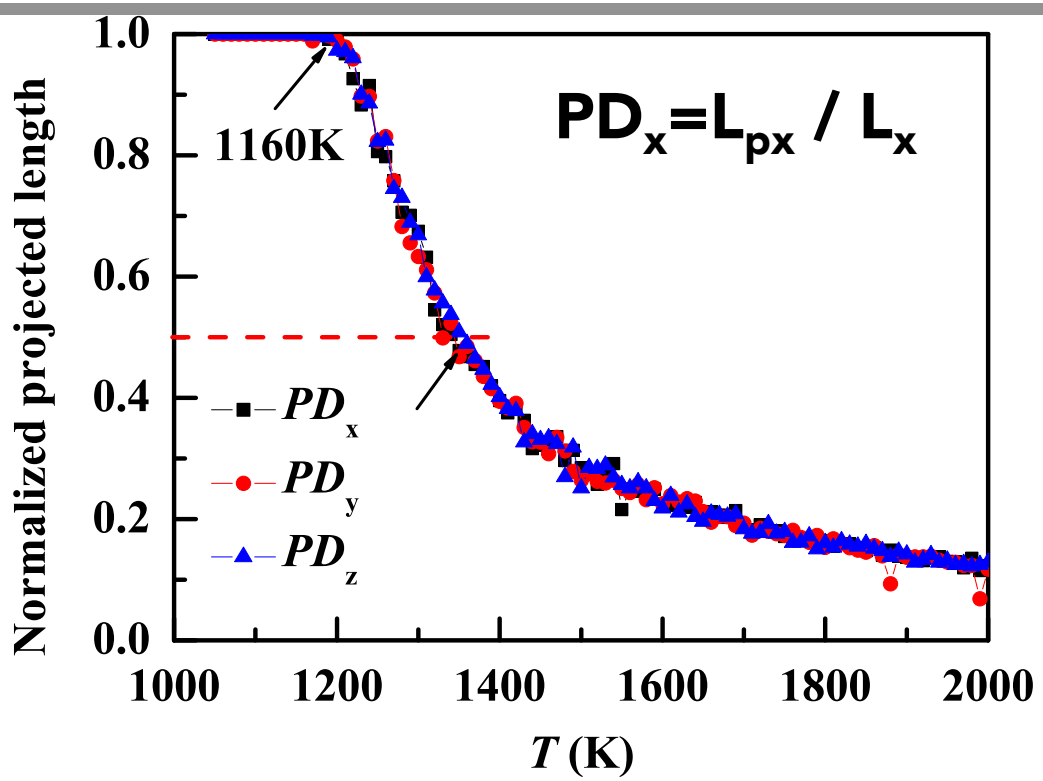
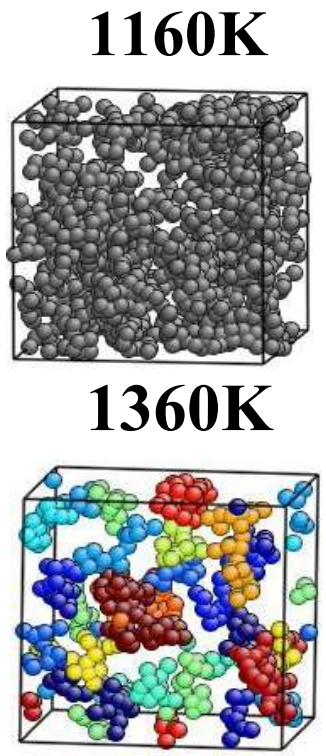


- Breakdown of SER occurs at T=1360K when the size of the largest cluster start to change dramatically
- Onset of fractional SER occurs at T~1180K where the change in the size of the largest cluster is a maximum

Pan, Wang, Li, Xu, submitted

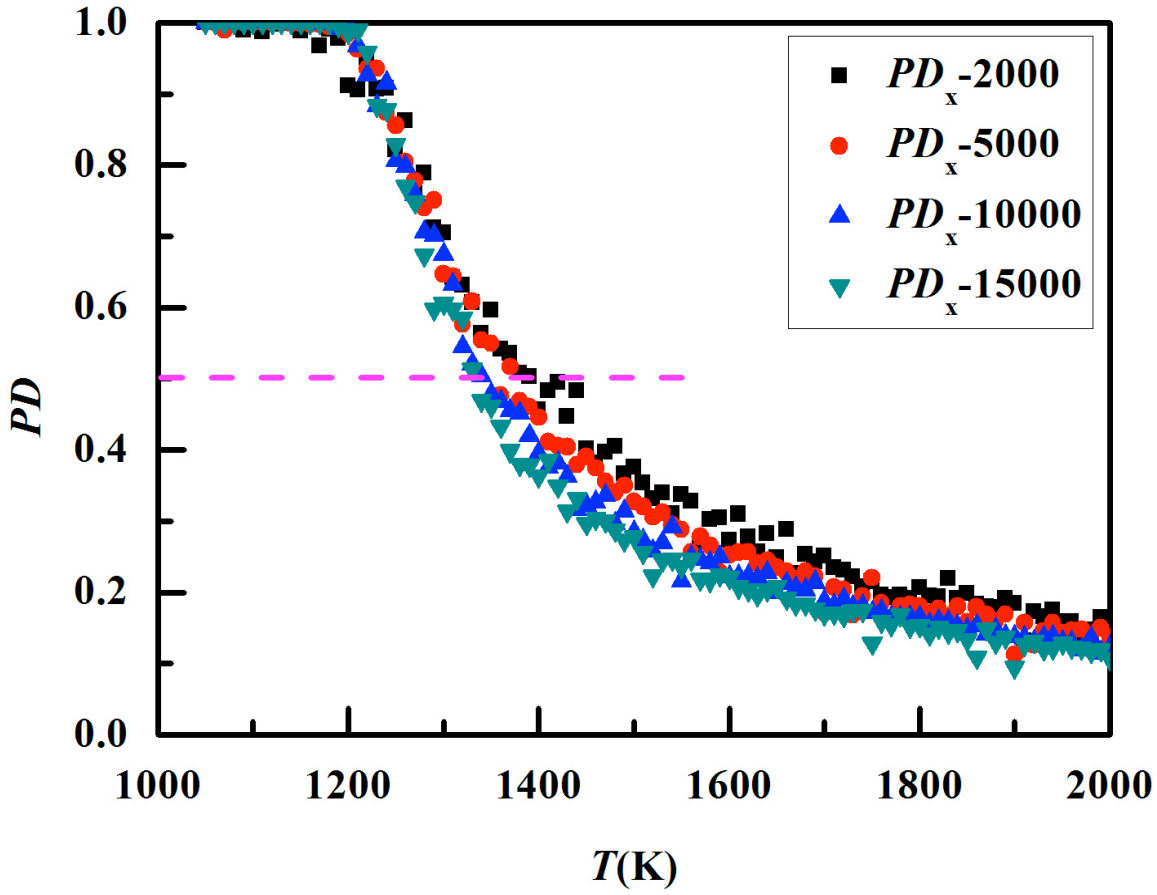
Association with the percolation dimension





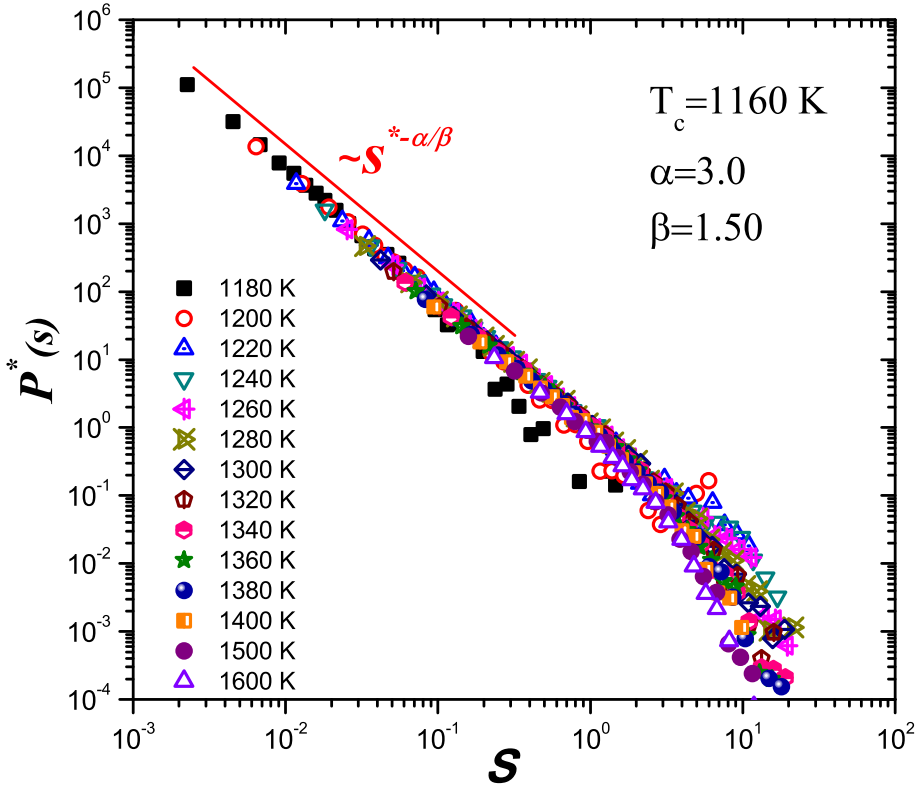
- At the breakdown temperature, 1360K, the largest cluster expands half of the system
- At the onset temperature of fractional SER, T~1160K, largest cluster percolates the entire system

Size effect?



Our system size is larger than 10000 atoms

Distribution of the size of clusters



$$P(S)$$

$$\sim \ [S/(T/T_c-1)^{-\beta}]^{*-\alpha/\beta} * (T/T_c-1)^{\alpha}$$

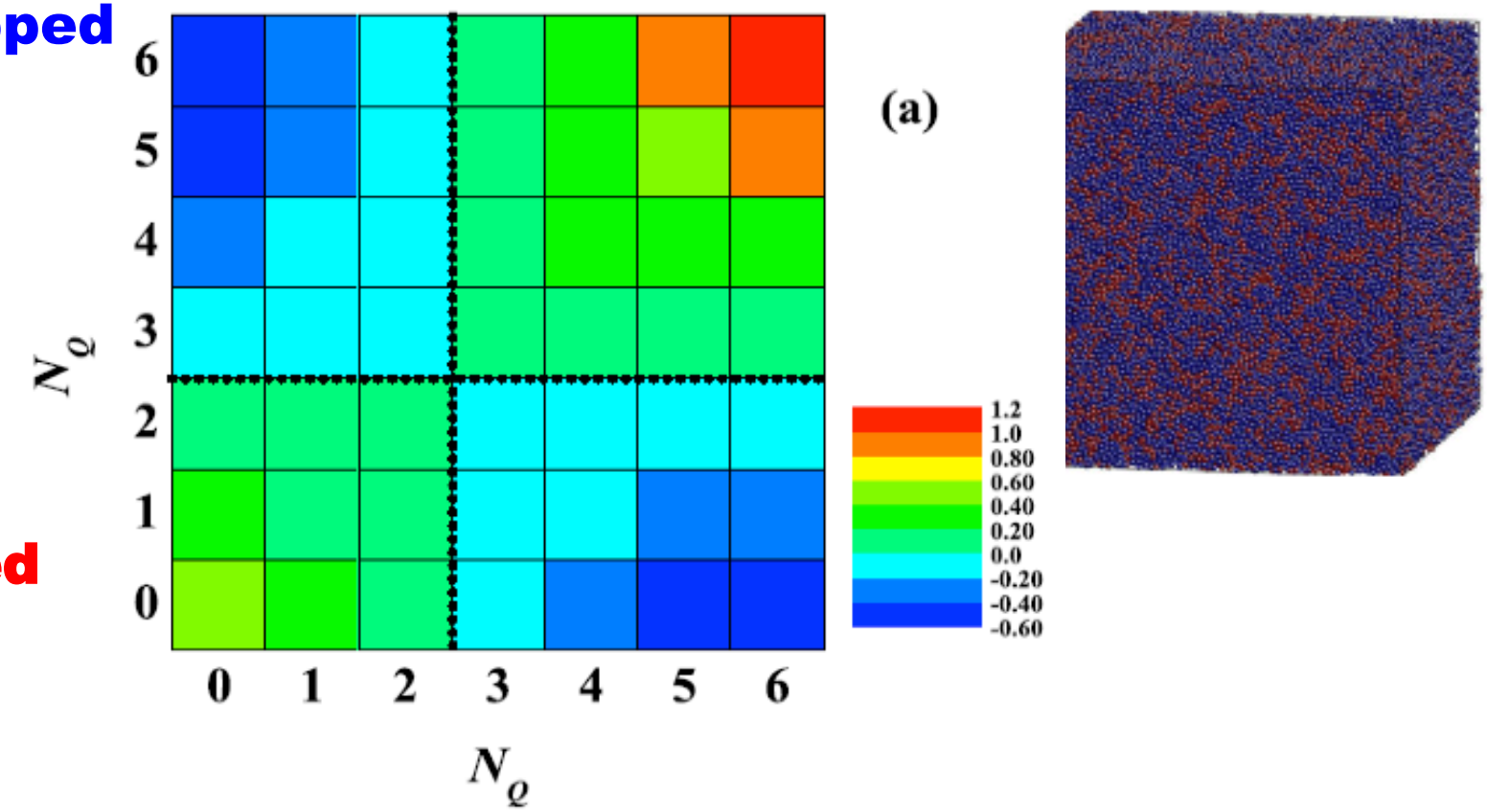
$$\sim S^{\alpha/\beta}$$

The size of clusters at T~1160K follows a power law behavior, indicating the percolation occurs at ~1160K at which fractional SER start to obey

Pan, Wang, Li, Xu (submitted)

Structure heterogeneity

non-trapped

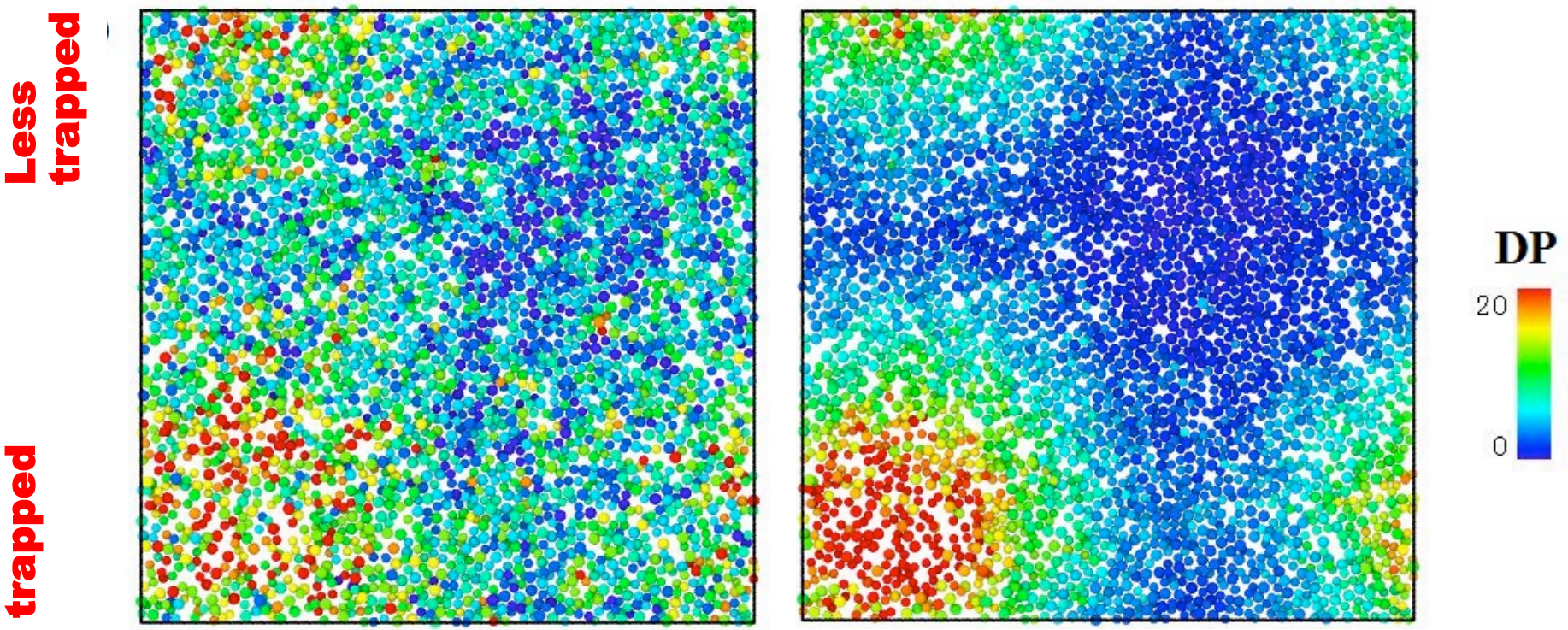


trapped atoms

Trapped atoms tend to be neighbors of trapped one while non-trapped ones tend to be neighbors of non-trapped

Structural heterogeneity

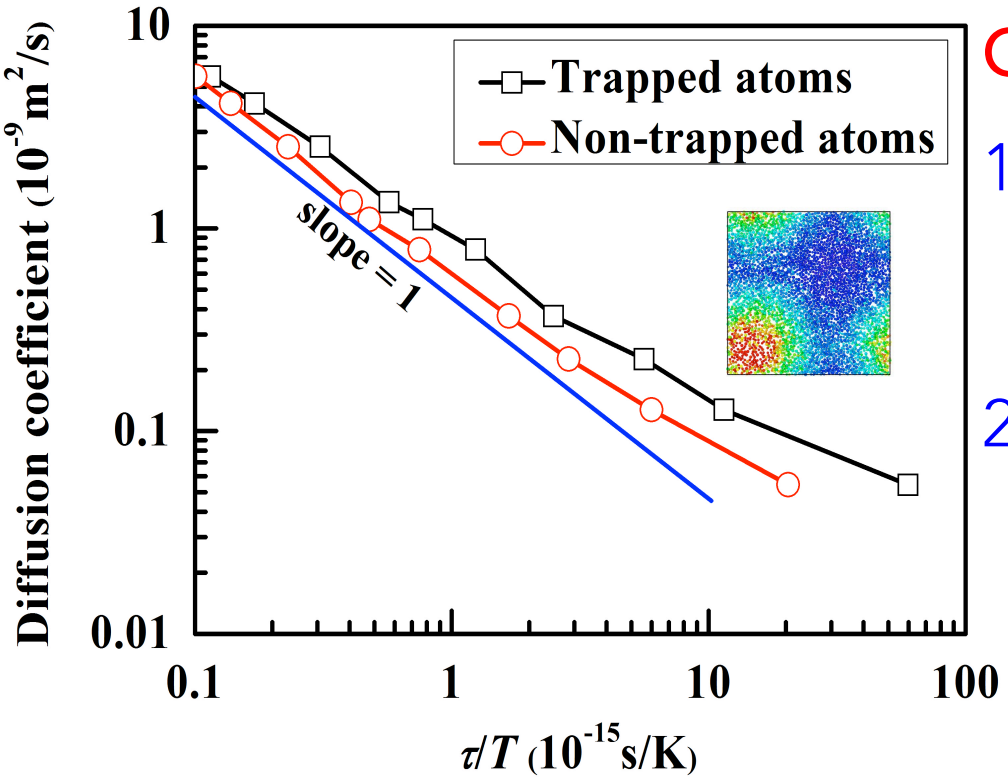
Structure heterogeneity and dynamic heterogeneity



Trapped atoms show low dynamic mobility while less trapped atoms show high dynamic mobility

Structural and dynamic heterogeneity are correlated

Breakdown of SER: fast and slow moving particles?



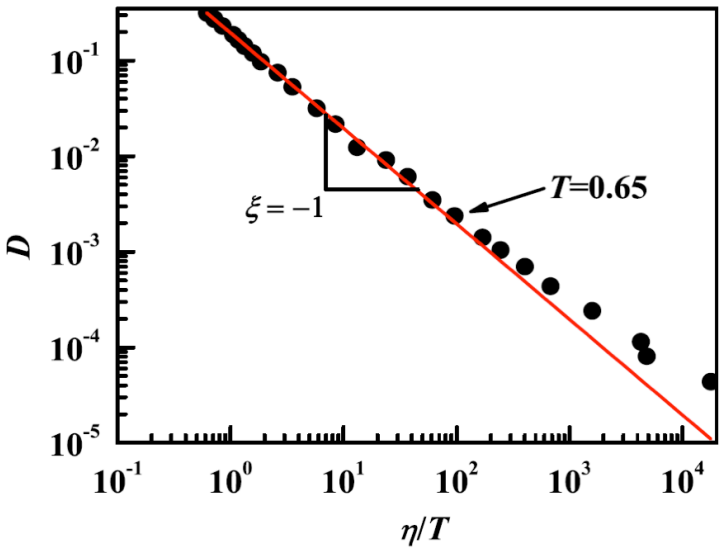
Opinions:

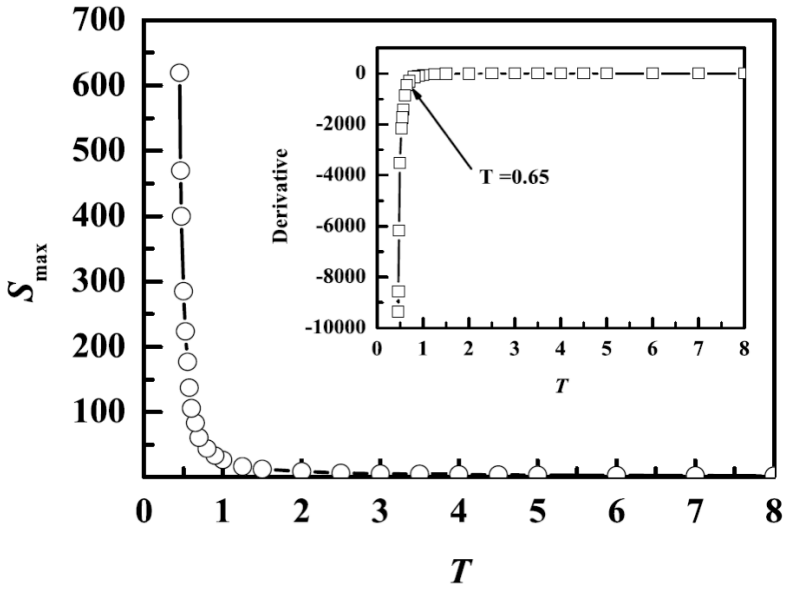
1) Mobile region violate the SE relation *[Kumar et. al, JCP. 124, 214501, 2006]*

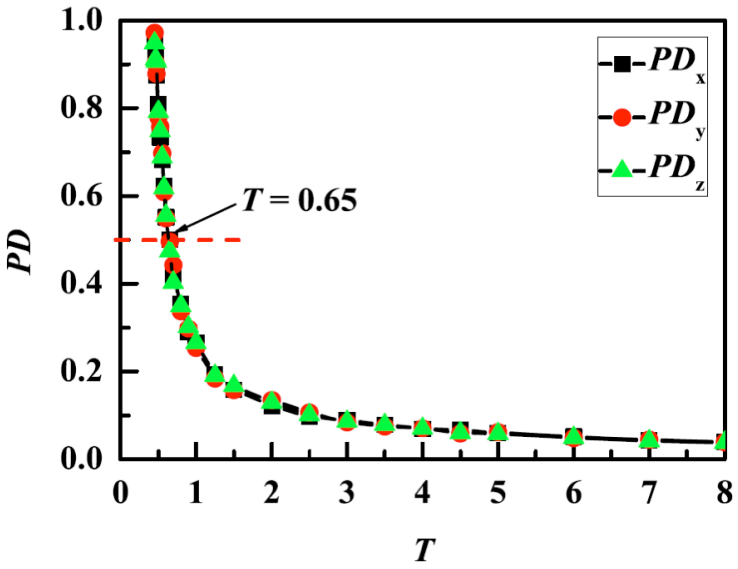
2) Both fast and slow regions violate the SE relation *[Becker, PRL 97, 055901, 2006]*

Both trapped and non-trapped atoms violate SER, thus our results are consistent with the latter

Similar features for general systems







Breakdown of SER ~T=0.65

Onset of structural change~T=0.65

Percolation length L/2~T=0.65

Dynamic and structural heterogeneities are correlated!

Outline

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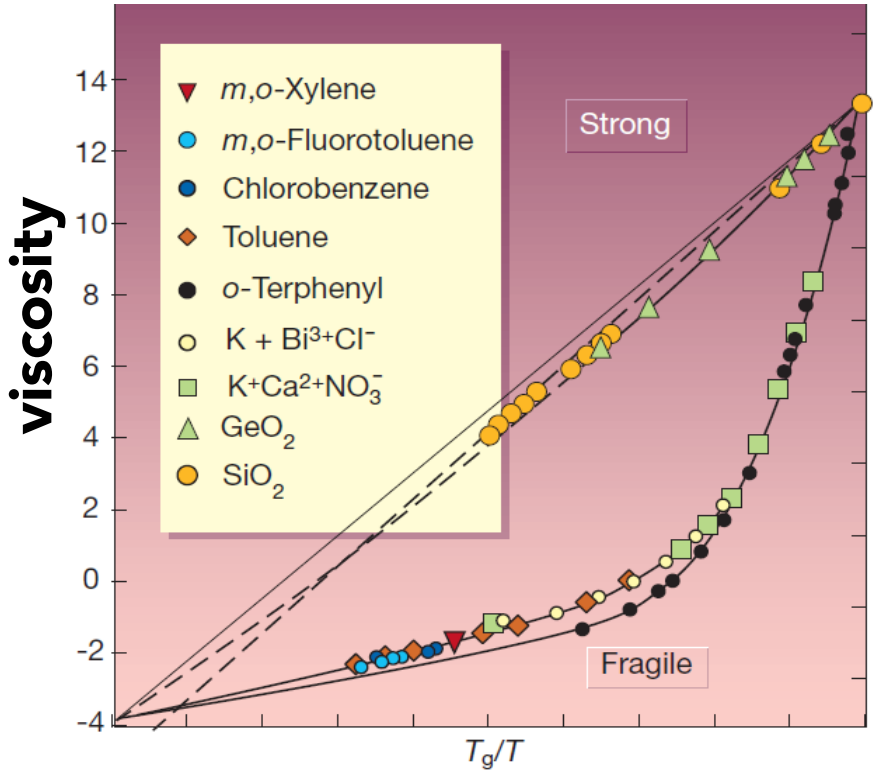
- Dynamic crossover & potential energy landscape

Dynamics near glass transition

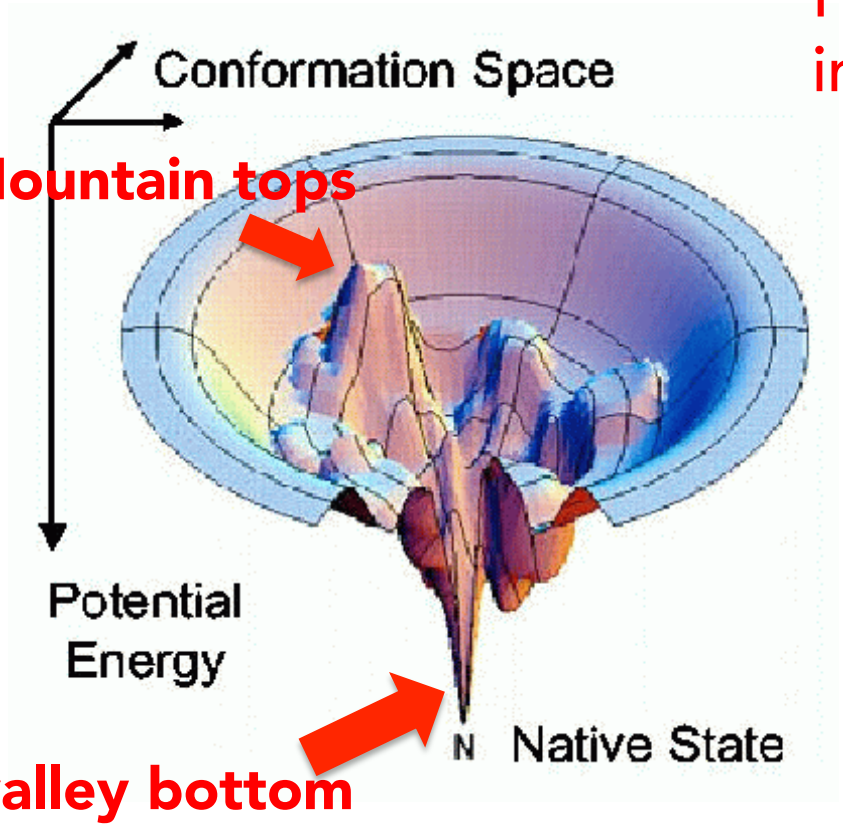


- Diverging of dynamics (ranging in an order of about 20 order)
- Continuous change in thermodynamics

Glass is far from equilibrium, thus obtaining thermodynamic and dynamic properties from configurations is helpful

Debenedetti et al., *Nature* 2001

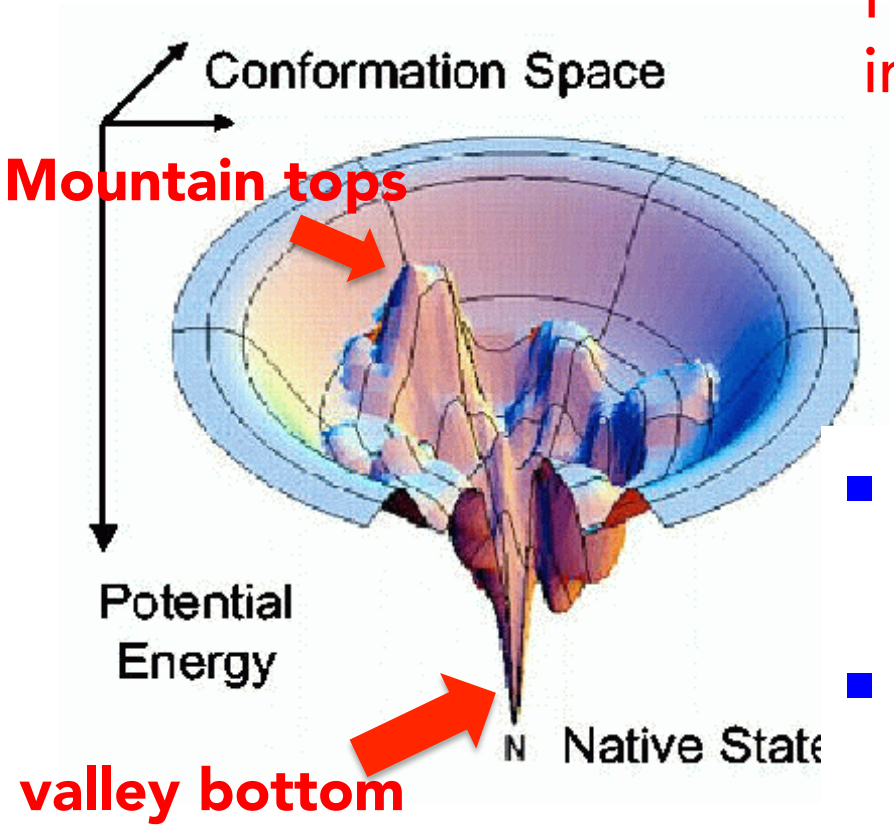
Potential energy landscape (PEL)



PEL: the potential energy function in conformation space

$V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$

Potential energy landscape



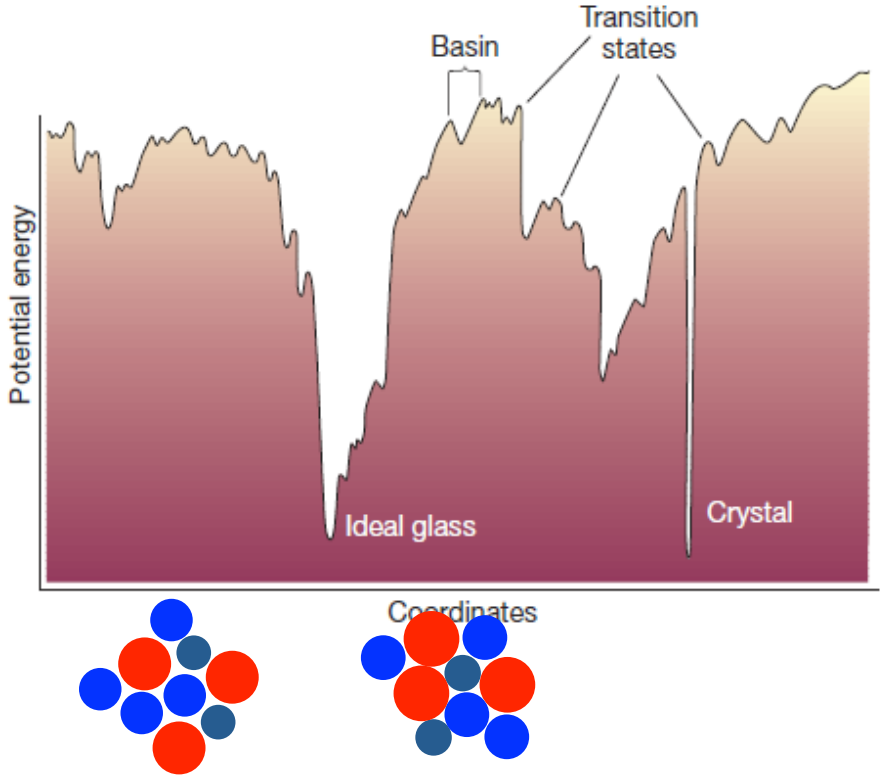
PEL: the potential energy function in conformation space

$$V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

- PEL does not depend on temperature
- the exploration of the PEL is strongly T dependent

i.e. which parts of the surface are explored

Potential energy landscape

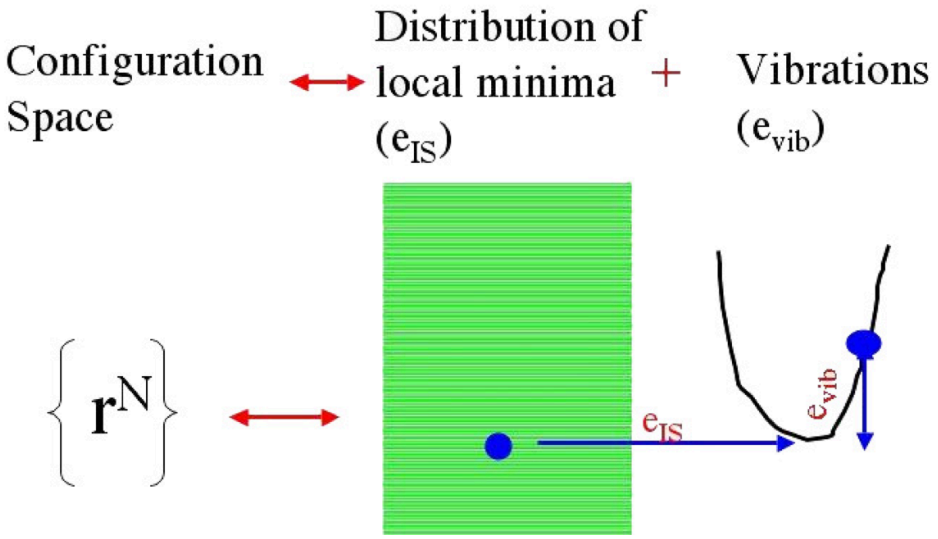


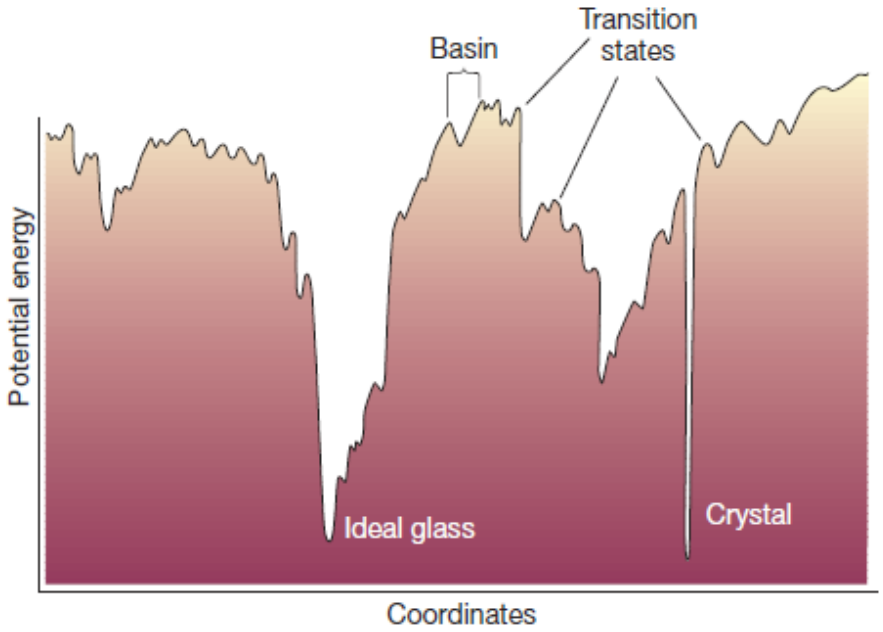
- Minima vary in depth
- Transition state between basins
- Equivalent minima attained by permutations of identical particles

- **Minima:** mechanically stable arrangements
- **Lowest lying minima:** perfect crystal
- **Higher lying minima:** amorphous particle packing

Franck H. Stillinger, Science 267, 1995

Free energy: decoupling of vibrational contribution



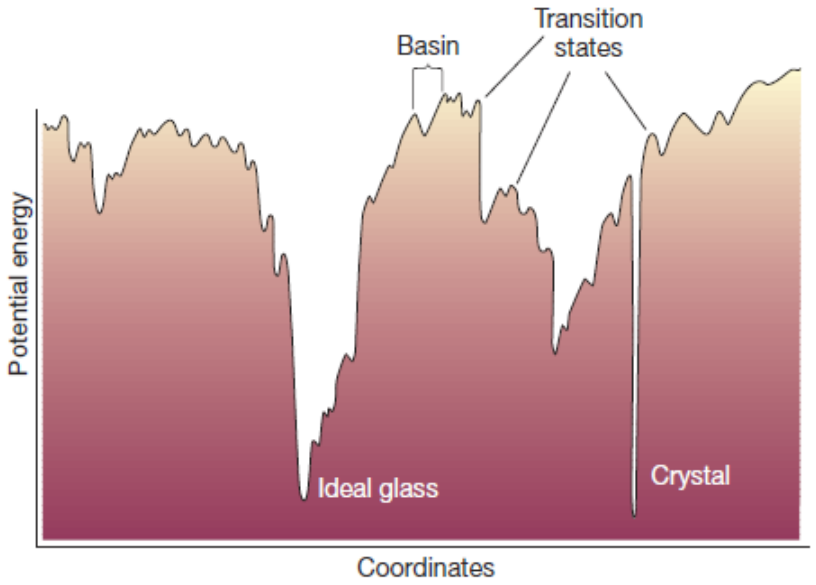


Potential energy: local minimum + vibrational contribution

$$V(r_1, \ldots, r_N) = e_{IS} + e_{vib}$$

Francesco Sciortino J.Stat. Mech. 2005

Important issues about potential energy landscape



1) Number of local minima:

$$\Omega(N) \sim N!\,\exp(\alpha N)$$

2) Shape of the surface around the local minimum:

parabolic shape

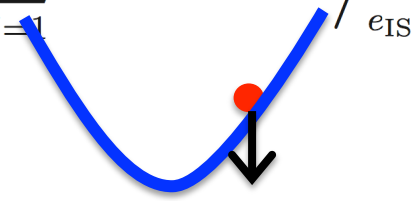
3) Distribution in energy:

$$\Omega(e_{\mathrm{IS}})de_{\mathrm{IS}} = e^{\alpha N}\frac{e^{-(e_{\mathrm{IS}}-E_0)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}}de_{\mathrm{IS}}$$

Inherent structure e_{is}:

Vibrational energy e_{vib}:

$$\beta f_{\mathrm{vib}}(e_{\mathrm{IS}},T,V) = -\left\langle \sum_{j=1}^{3N} \ln[\beta\hbar\omega_j(e_{\mathrm{IS}})] \right\rangle_{e_{\mathrm{IS}}}.$$



Franck H. Stillinger, Science 267, 1995

Potential energy landscape & equation of state

Partition function:

$$Z(T,V) = \sum_{e_{\mathrm{IS}}} \Omega(e_{\mathrm{IS}}) \mathrm{e}^{-\beta f_{\mathrm{basin}}(e_{\mathrm{IS}},T,V)}$$

Free energy:

$$F = -Nk_BT\,lnZ$$

Equation of state:

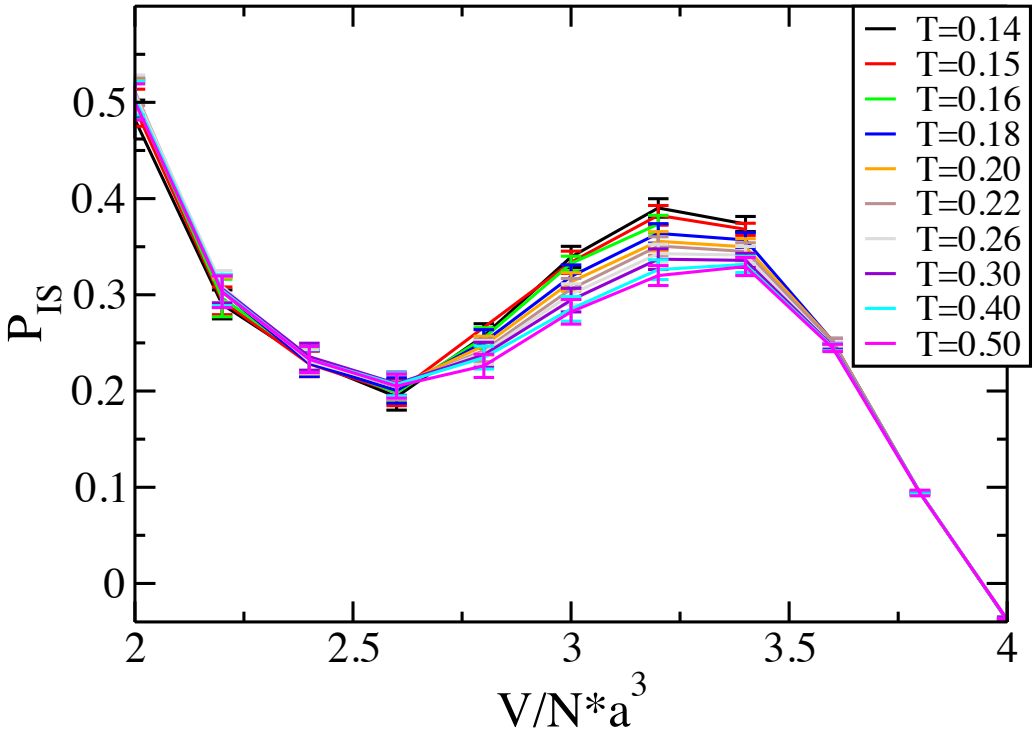
$$P(T,V) = -\left[\frac{\partial F(T,V)}{\partial V}\right]_T$$

Van de Waals loop of inherent pressure

According to harmonic approximation:

Pressure:

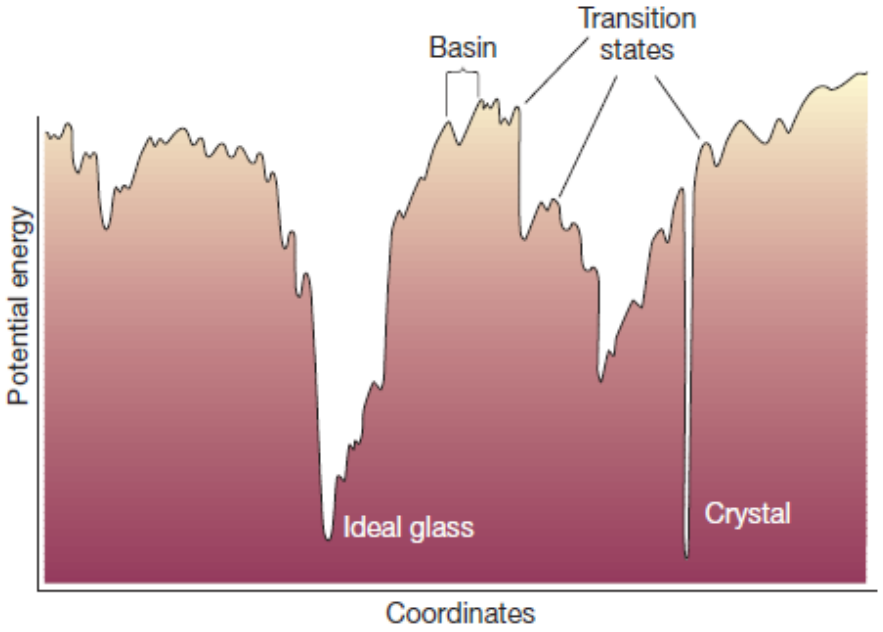
$$P=P_{IS}+P_{vib}$$

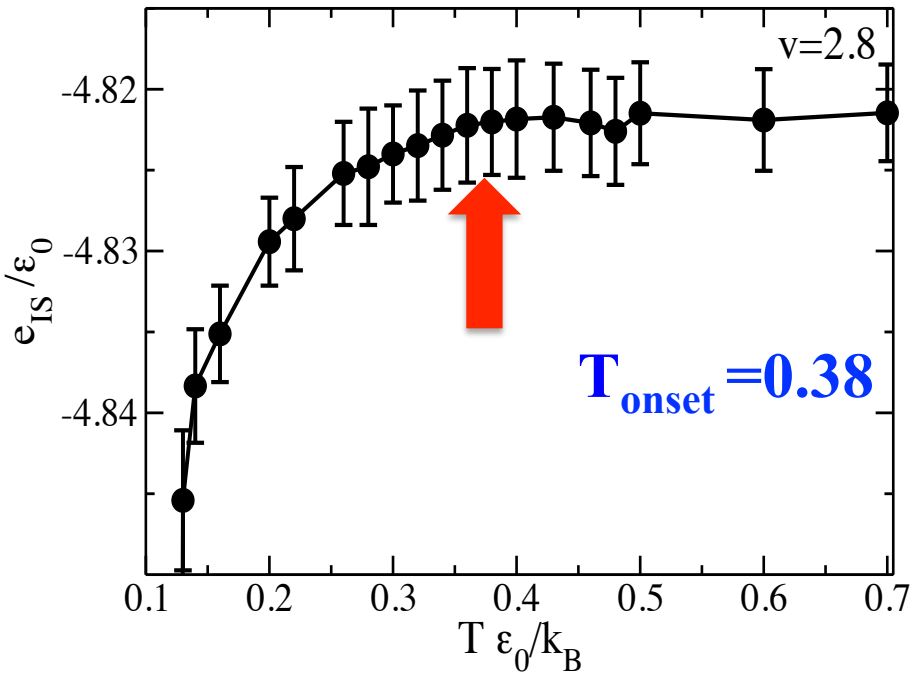


The inherent pressure shows Van der Waals loop, indicate of first-order phase transition

Sun, Giovambattista, Xu, submitted

Inherent energy as function of temperature

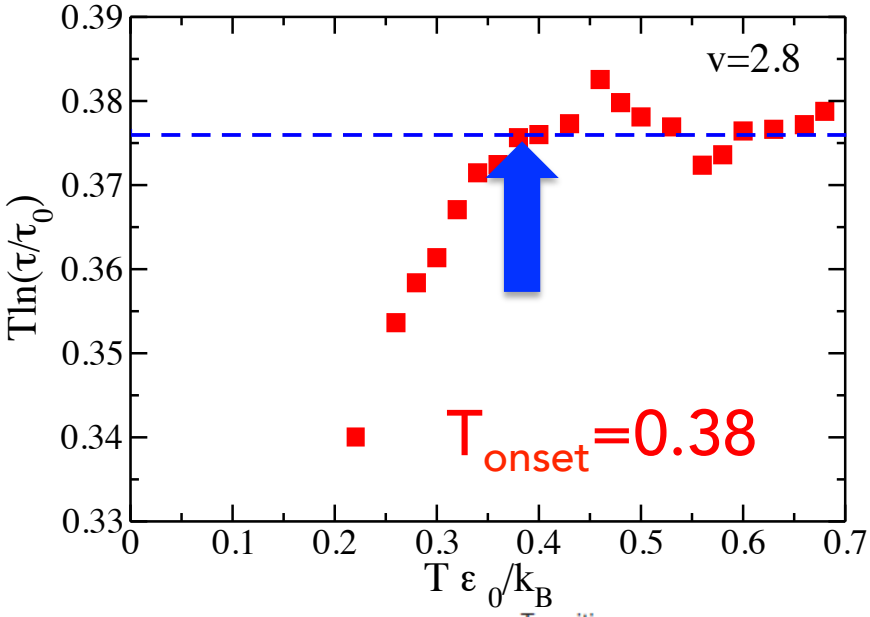




A change in the manner of the exploration of the inherent energy e_{is} indicates that above the transition temperature, all local states are visited

Sun, Giovambattista, Xu, submitted

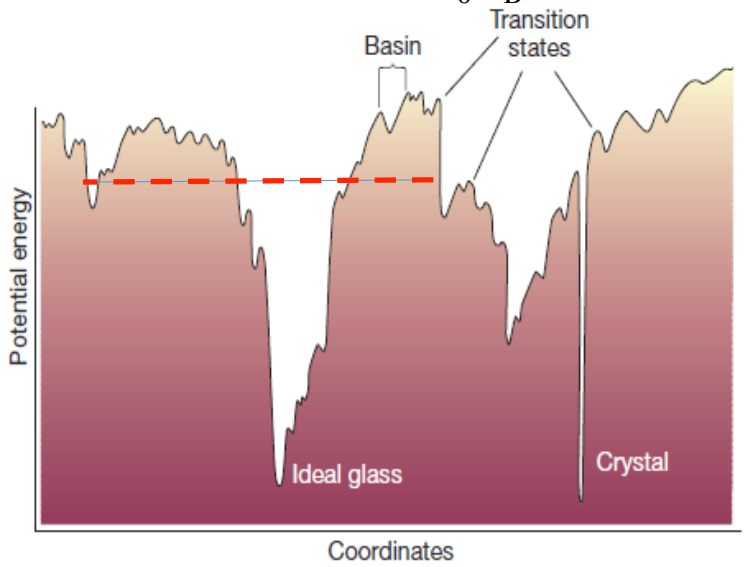
Change in dynamics



According to Adam-Gibbs theory, relaxation time τ_0:

$$\tau = \tau_0 \exp(E/k_B T)$$

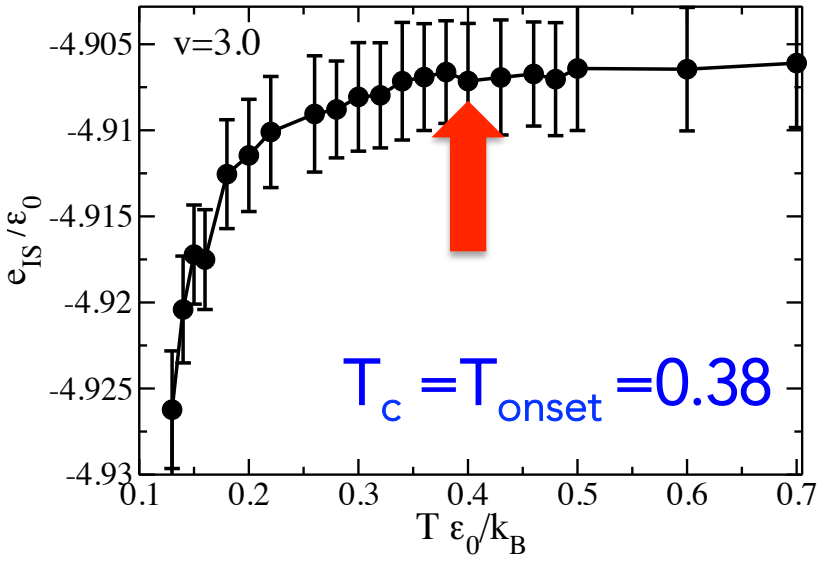
At high T: thermal energies comparable to barriers heights

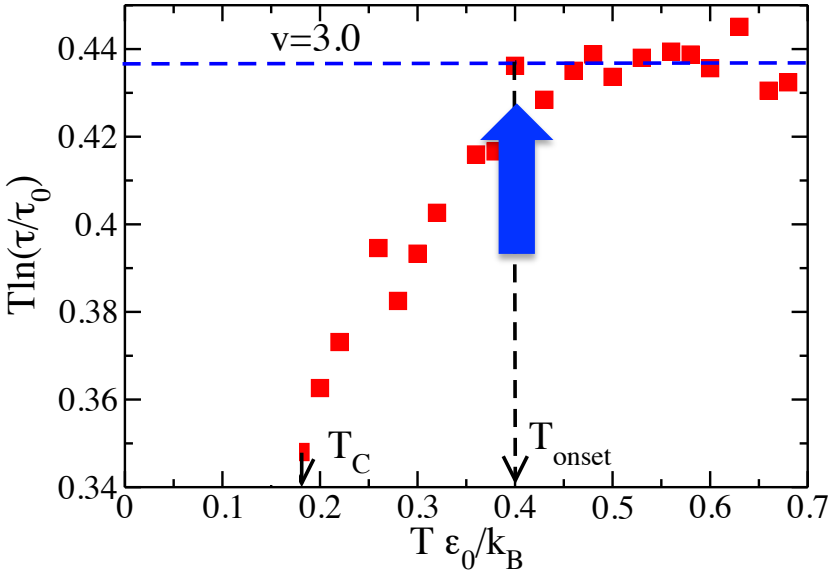


At low T: particles move by hopping between nearby basins

There exists a critical temperature Tc where dynamic crossover occurs

Connection between dynamics and inherent energy





Connection between the onset of dynamics and a change in the manner of exploration potential energy landscape

Sun, Giovambattista, Xu, submitted

Summary I

- ✓ **Glass transition & dynamic crossover**

  Dynamic crossover may occur above glass transition

- ✓ **Dynamic crossover & structure percolation**

  Dynamic crossover is correlated to structural heterogeneity

- ✓ **Dynamic crossover & potential energy landscape**

  Onset of dynamic crossover and a change in the manner of potential energy landscape exploration

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