

Hydrophobic and Hydrophilic Surfaces and Interfaces

Water: One simple molecule, two interaction demands

One molecule, two ways of love

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LIQUID WATER

*“Laudato si, mi Signore, per sor’aqua,
la quale è molto utile et humilde
et pretiosa et casta.”*

Francesco d'Assisi

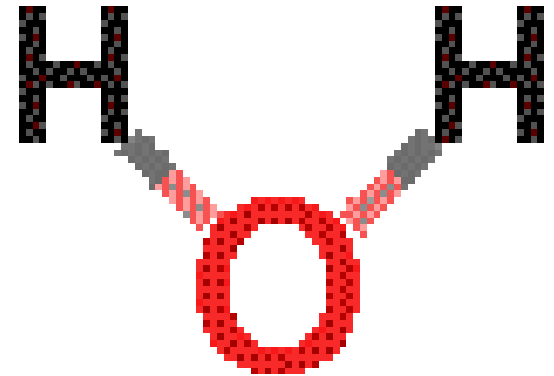
*(“Praised be You, my Lord, for **sister water**, who is very
useful and **humble** and precious and pure.”)*

Just one Oxygen and two Hydrogens.

In science, austerity is a sign of beauty.

Such **simplicity** in its molecular formula,
however, does not prevent water from
presenting quite a **complex behavior**.

*Temas de Biofísicoquímica,
J. Raul Grigera, Ed. Eudeba*



In fact, water presents several structural, thermodynamic and dynamic anomalies.

And anomalies make water relevant for hydration and nanoconfinement contexts; irreplaceable in Biology.

***Physics: Simplicity out of complexity.
How to bring complexity out of a simple molecular structure?***

Interactions: Hydrogen bonds (HB).

HB network / rearrangements.

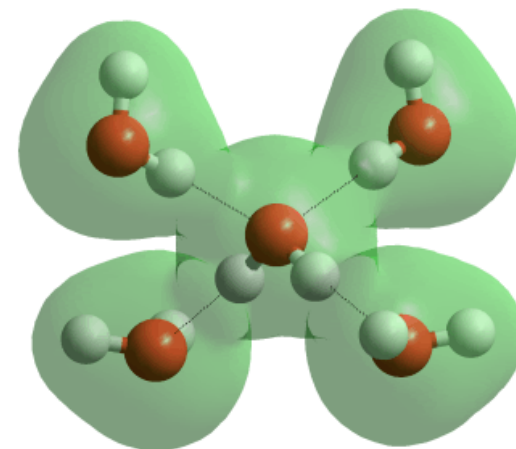
P. Gallo, et al. Chem. Rev. 116, 7463 (2016).

P. Gallo, et al. Eur. Phys. J. E 44, 143 (2021).

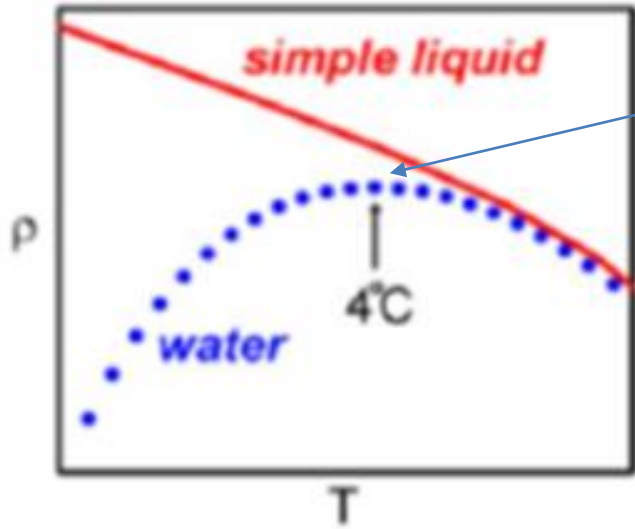
H. R. Corti, et al. Eur. Phys. J. E 44, 136 (2021)

(Workshop in Buenos Aires with Marcia and Paola)

Detailed description of water structure, properties and behavior: see Martin Chaplin's website



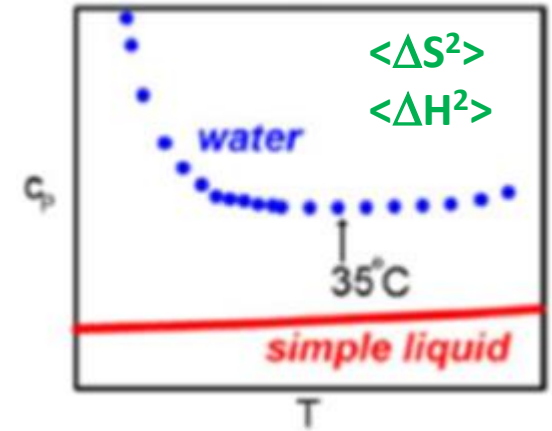
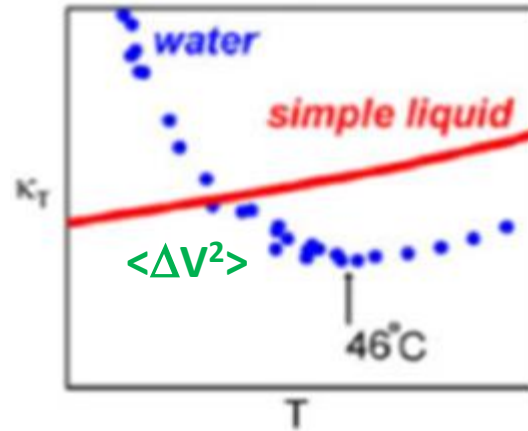
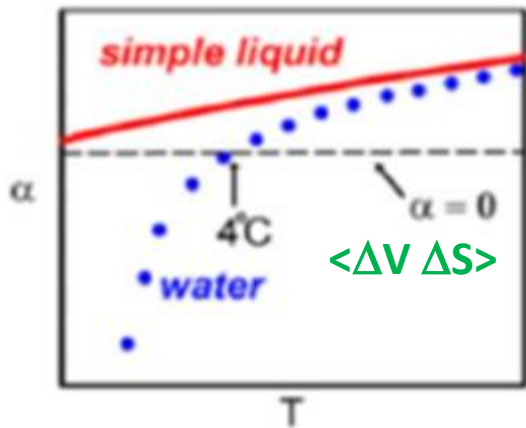
Why is it relevant to study water's supercooled regime?



Density anomaly (maximum)

Thermodynamic anomalies: More conspicuous as temperature is lowered below melting (T_m) \rightarrow Supercooled regime

Response functions. Supercooling enhances fluctuations:



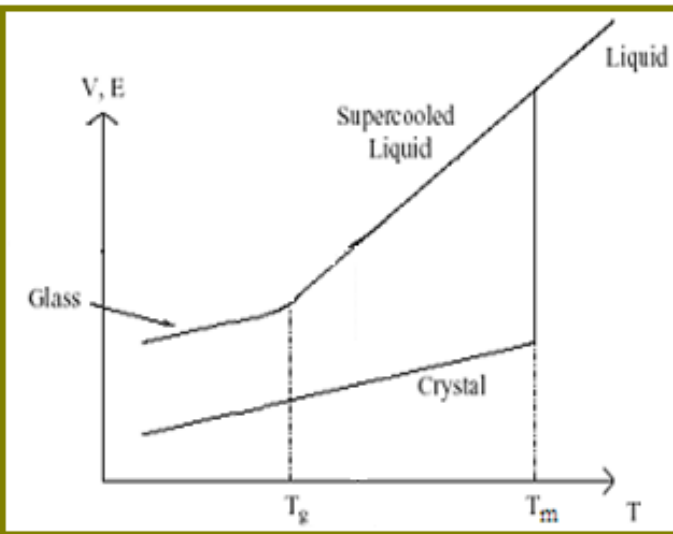
But, homogeneous nucleation interferes.
No man's land \rightarrow Computer simulations

SUPERCOOLED LIQUIDS AND GLASSES

Cooling a liquid below T_m fast enough to avoid crystallization.

Supercooled liquid: No long-range order, metastable, t_{relax} increases drastically with supercooling (dynamic slowing down).

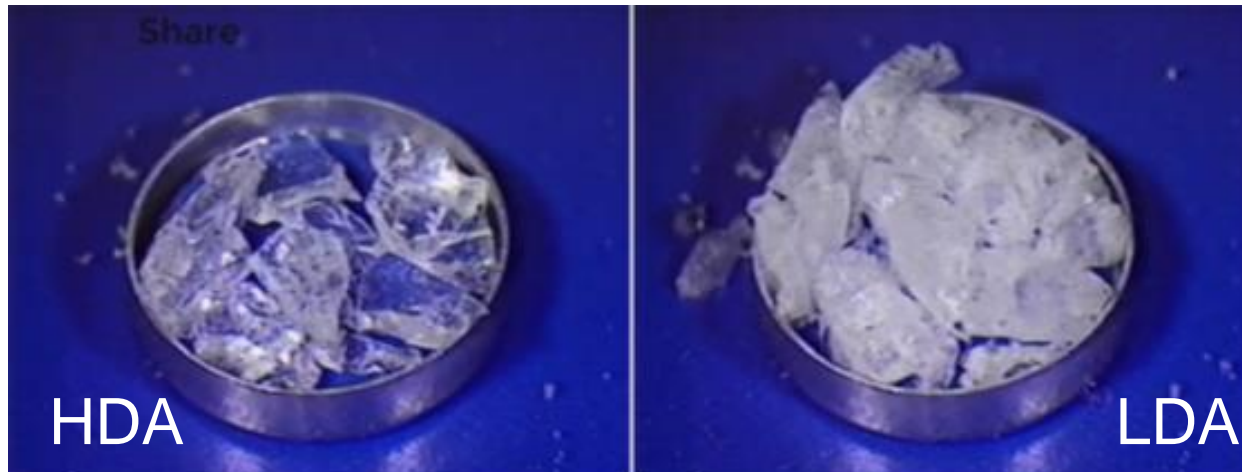
T_g : Glass transition temperature. Out of equilibrium (amorphous) solid.



GLASSY WATER:

Water presents different disordered solids (amorphous ices or glasses):

- High Density Amorphous ice, HDA
- Low Density Amorphous ice, LDA (also VHDA)



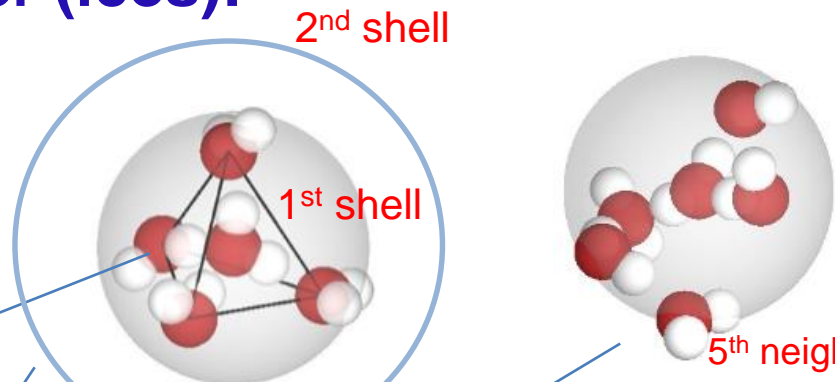
Mishima, O., Calvert, L. D. & Whalley, E. Nature **310**, 393 (1984), *Nature* **314**, 76 (1985).

Structure of amorphous water (ices):

LDA: Low local density. Tetrahedrally well-ordered first shell. Inter-shell gap.

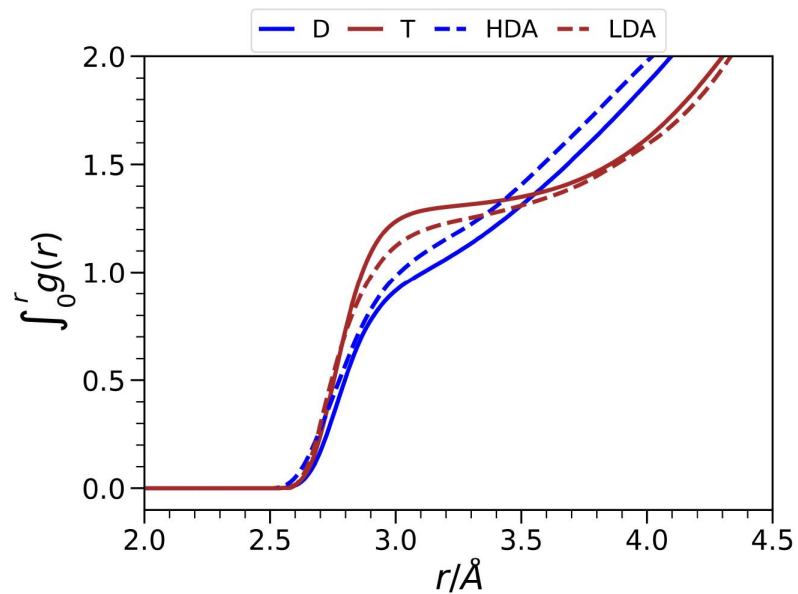
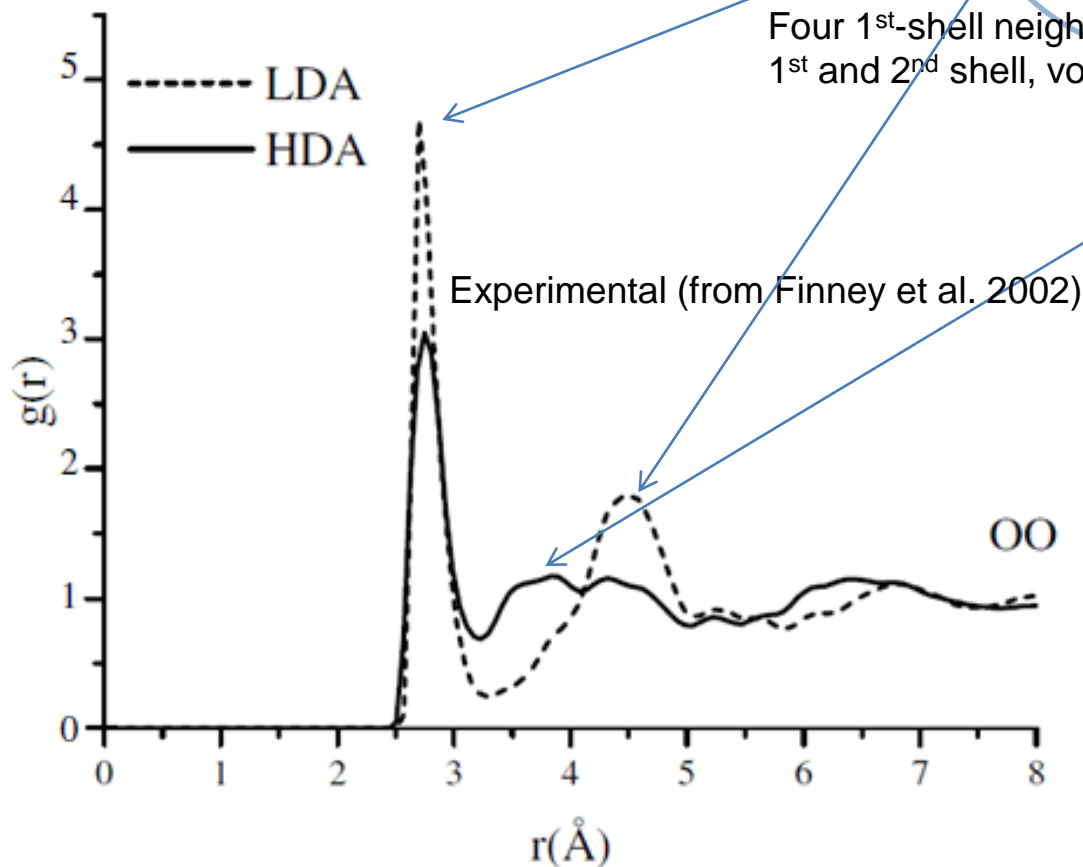
HDA: High local density. Distorted.

“Interstitial” molecules/ 2nd shell collapse.



Four 1st-shell neighbors. Gap between 1st and 2nd shell, volume expansion.

Collapse of part of 2nd shell over first one. Interstitials.



SUPERCOOLED WATER

Supercooling water (experimental situation):

Wild increase of isothermal compressibility while supercooling water below -20°C . Large fluctuations of density at the molecular level. Physical transformation? But water readily crystallizes.

*R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).*

Theory: Two-liquids scenario

Water's second critical point: Two liquid phases of different density. Density fluctuations arise from the competition between the two phases (sign of a L-L critical point).

*P. H. Poole, F. Sciortino, U. Essmann and H. E. Stanley, Nature **360**, 324 (1992).*

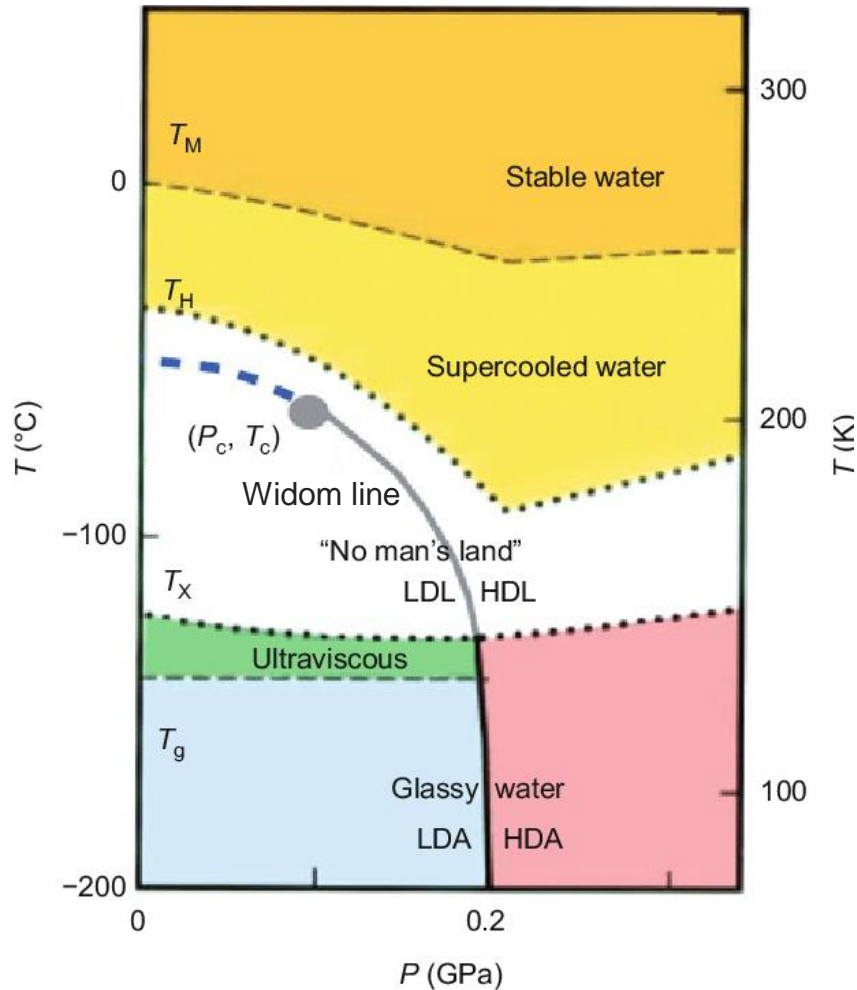
*K. H. Kim, et al., Science **370**, 978 (2020) (experimental)*

*P. G. Debenedetti, F. Sciortino and G. H. Zerbe, Science **369**, 289 (2020).*

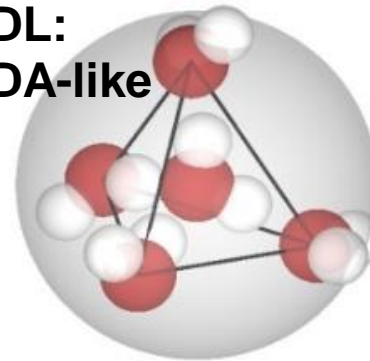
Two-liquids picture:

- High-density liquid.
- Low-density liquid.

Continuation of HDA-LDA coexistence line terminating at a critical point?

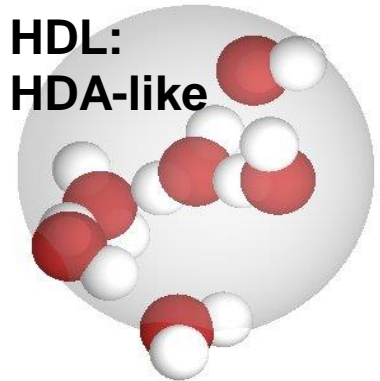


**LDL:
LDA-like**



Low entropy
Large volume
Tetrahedral, linear HBs

**HDL:
HDA-like**



Large entropy
Small volume
Distorted

Order parameter capable of producing clear two-peak distributions, even far from location of the L-L critical point.

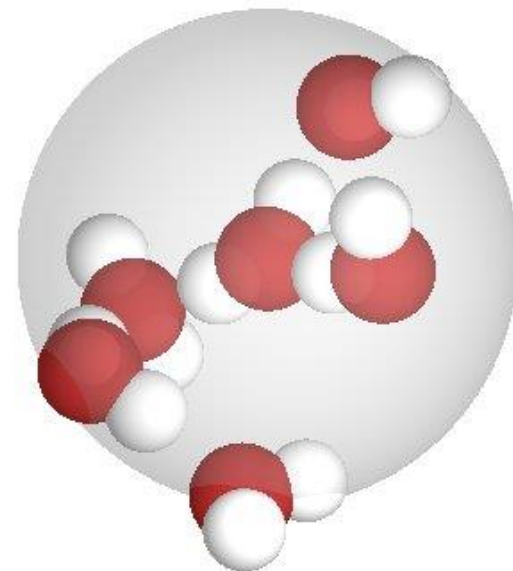
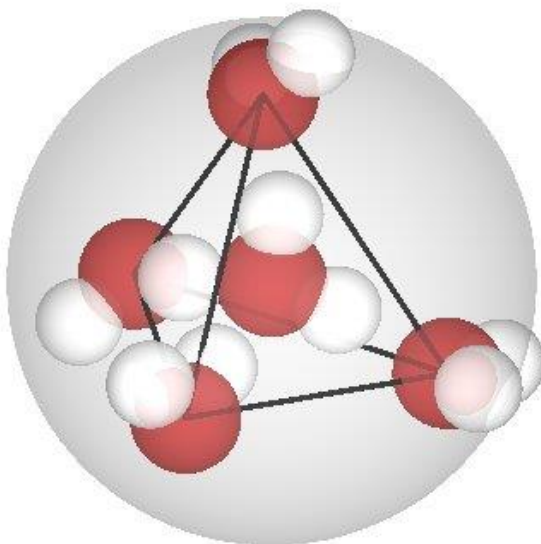
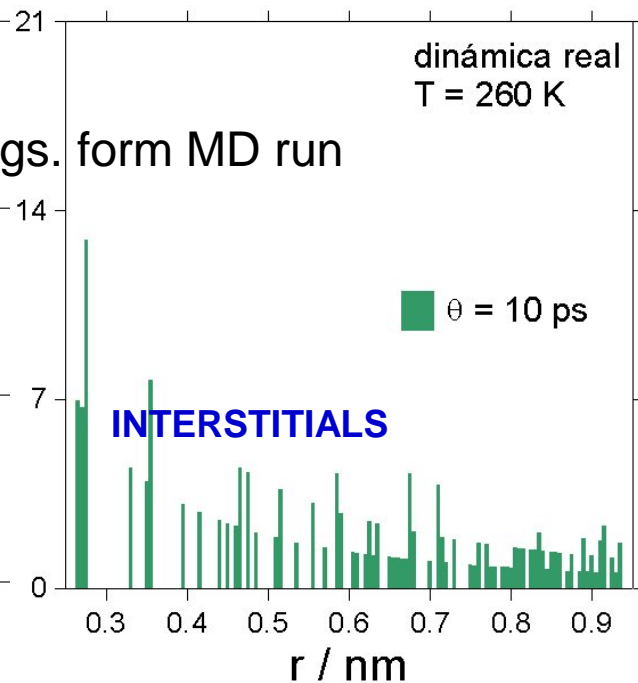
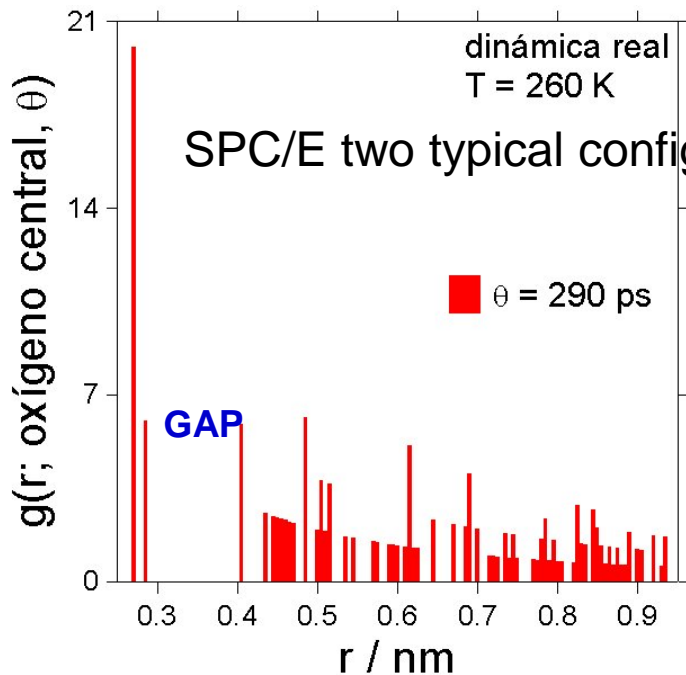
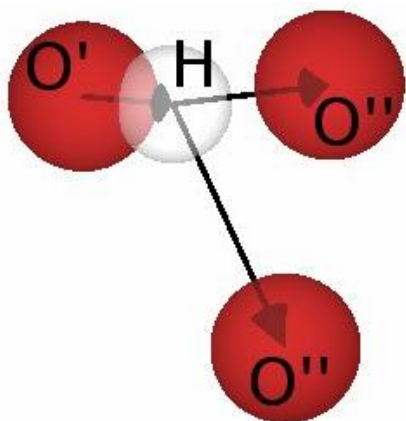
INTERSHELL GAP

Shiratani & Sasai:

Gap in $g(r)$.

- Low local density molecules, structured, slow (inusual).
- High local density molecules, unstructured, fast.

5° neighbor. Bifurcated HB, lower barrier (Stanley- Sciortino).



STRUCTURAL INDICATORS

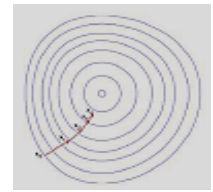
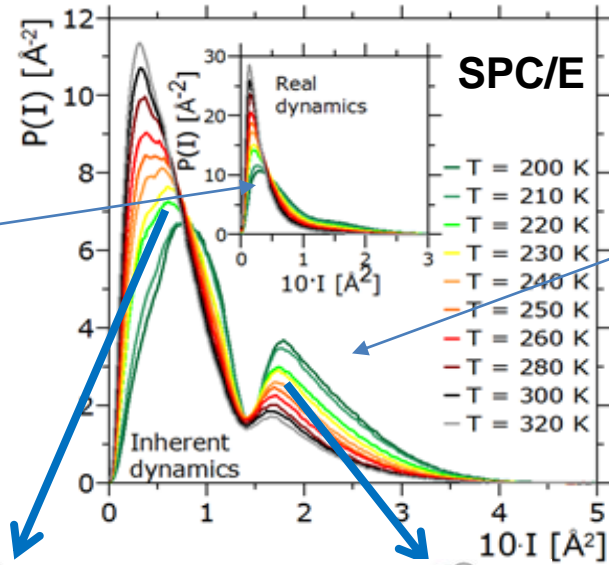
(There are several; we shall see two ones based on translational order up to 2nd shell)

Local structure index, LSI

$$I(\mu, t) = \frac{1}{n(\mu, t)} \sum_{i=1}^{n(\mu, t)} [\Delta(i; \mu, t) - \bar{\Delta}(\mu, t)]^2$$

where $\Delta(j; i, t) = r_{j+1} - r_j$ and $\Delta(i, t)$ is the average over all molecules of $\Delta(j; i, t)$ (molecules closest than 3.7 Å).

Shiratani & Sasai, *J. Chem. Phys.* **104**, 7671 (1996). (Real dynamics)

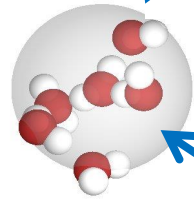


Inherent Structures (energy minimiz.)

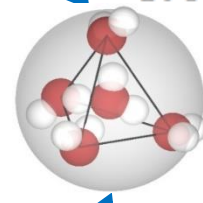
G. A. Appignanesi, J. A. R. Fris and F. Sciortino, *Eur. Phys. J. E* **29**, 305 (2009).

For first time: NEAT BIMODALITY!

Unstructured HDL-like

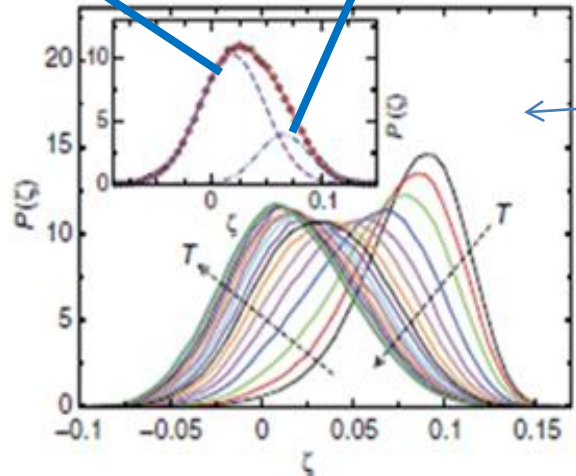
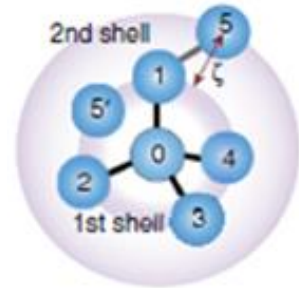


Structured LDL-like



ζ index

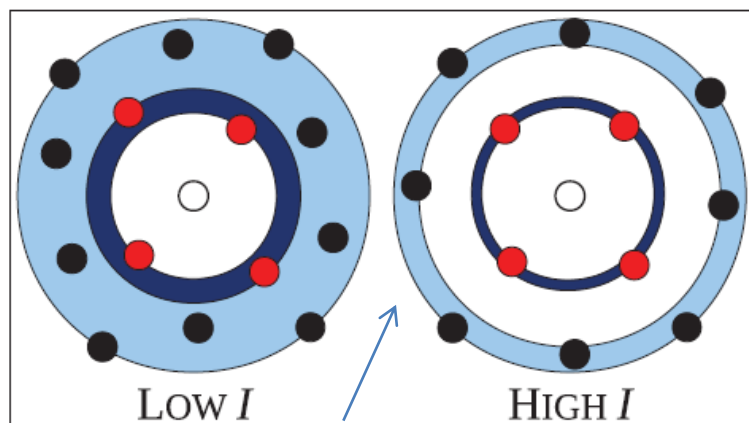
Difference between the distances of the central molecule to its first non H-bonded molecule and to its last H-bonded one.



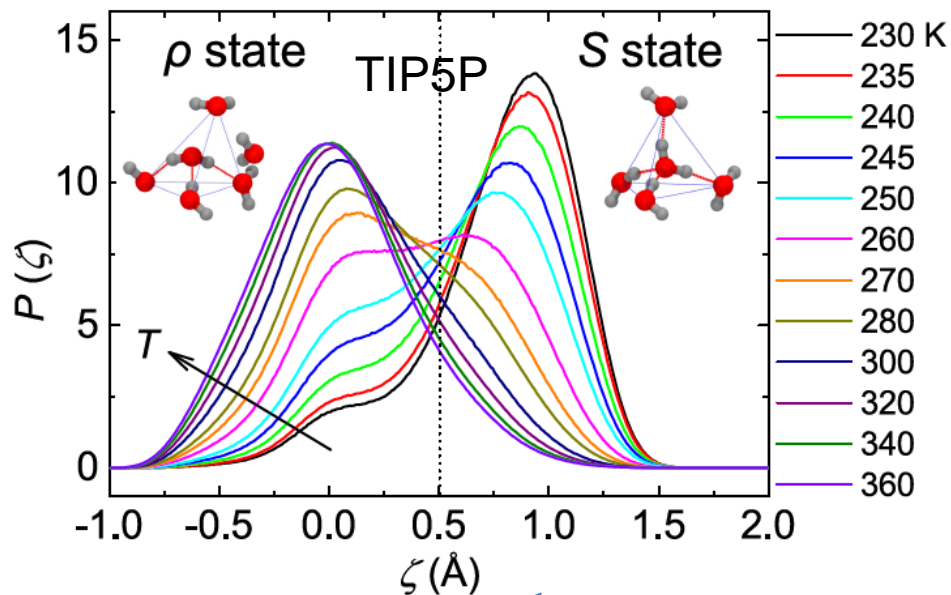
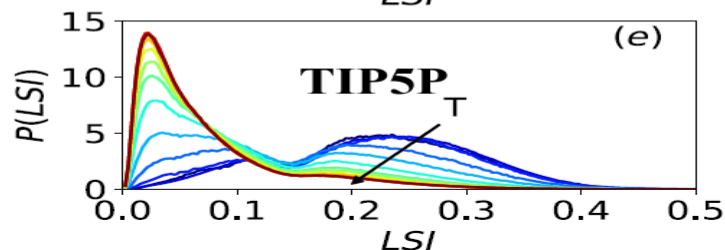
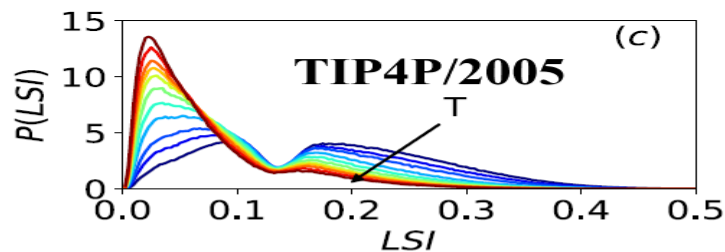
TIP4P-2005

J. Russo and H. Tanaka, *Nat. Commun.* **5**, 3556 (2014).

Both indices focus ***almost exclusively*** on the structured state and sense the translational order up to the second shell (inter-shell gap or collapse of the second shell; interstitial molecules). But the impact of that disorder on the first shell might be what really matters, since the HB network and its rearrangement is what furnishes water most of its distinctive behavior.



From R. Car's group: $I = LSI$



From H. Tanaka's group

Conceptual advance: consider HB

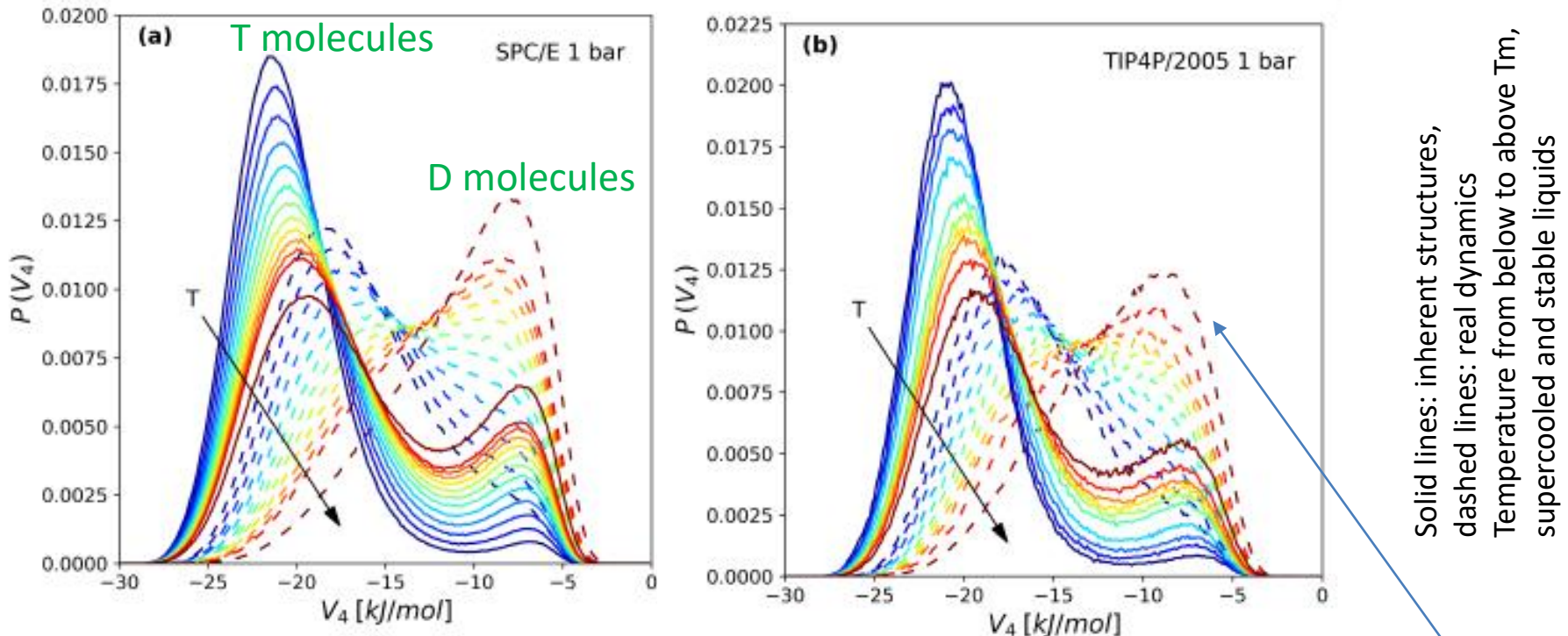
Inspiration for a brand new index; minimization. *But focusing explicitly on interactions.*

New parameter-free structural index for water, V_4 :

For each water molecule i , we evaluate all pair-wise interactions V_{ij} , $j \neq i$, and sort them according to their intensity, from the smallest to the largest value. We then define $V_4(i)$ as the fourth V_{ij} .

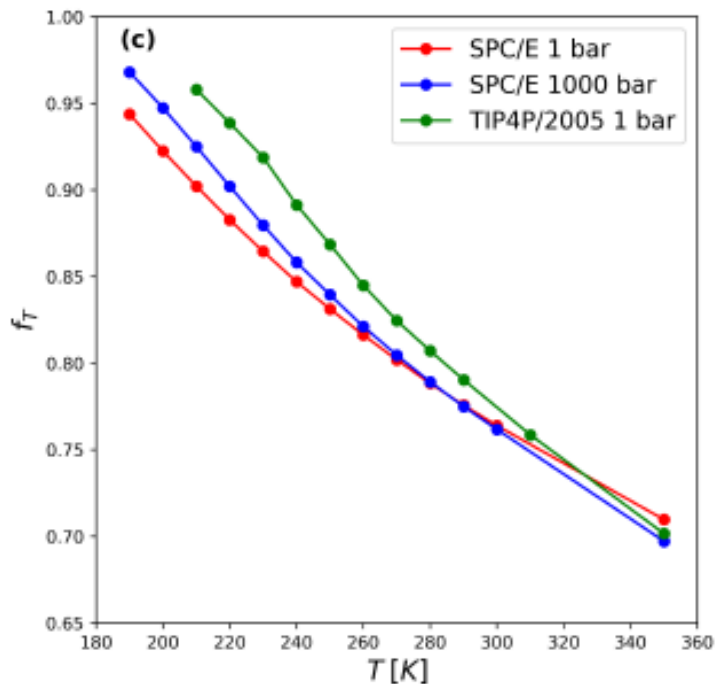
“A structural indicator for water built upon potential energy considerations”, *J. M. Montes de Oca, F. Sciortino and G. A. Appignanesi J. Chem. Phys. 152, 244503 (2020)*

Bimodal distributions both at the real dynamics (RD) and inherent structures (IS)



T molecules: $V_4(i) \leq -12$ kJ/mol (at IS), four strong linear HBs, $V_4(i) \approx$ linear HB energy.

D molecules: Larger $V_4(i)$, distortion of at least one HB, perturbation of the tetrahedral shell by insertion of 2nd-shell neighbors. Temperature-invariant peak. RD \rightarrow IS: Many molecules move to T peak (distorted by thermal energy but still structured; IS basin)

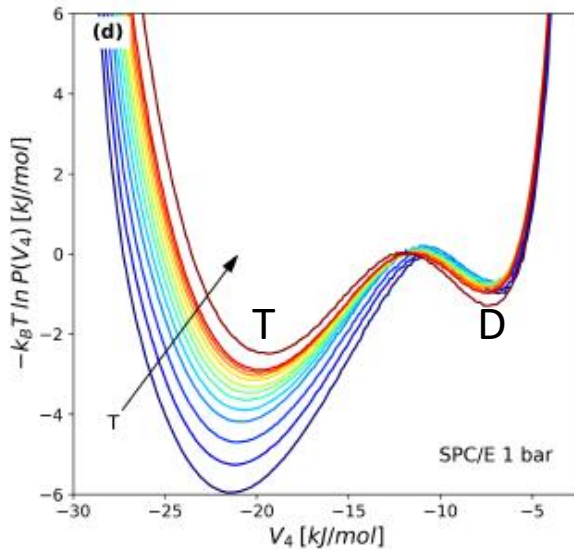


Temperature-dependence of fraction of T molecules:

T: dominate even at high temperatures; tetrahedral network.

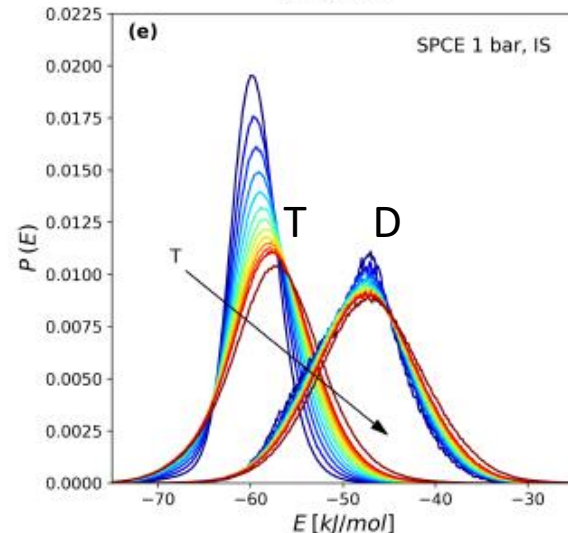
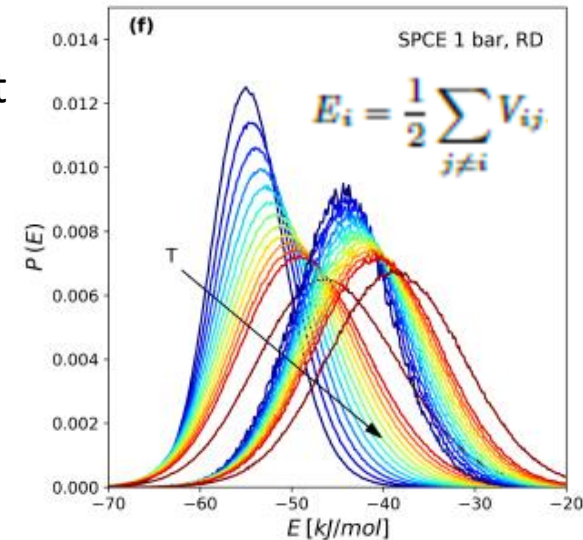
D: minority component (defects); different from other indices, like LSI, that overestimate the fraction of “unstructured” molecules.

Free energy profile:



Stability of T molecules increases with supercooling. D molecules do not change significantly.

Total potential energy:

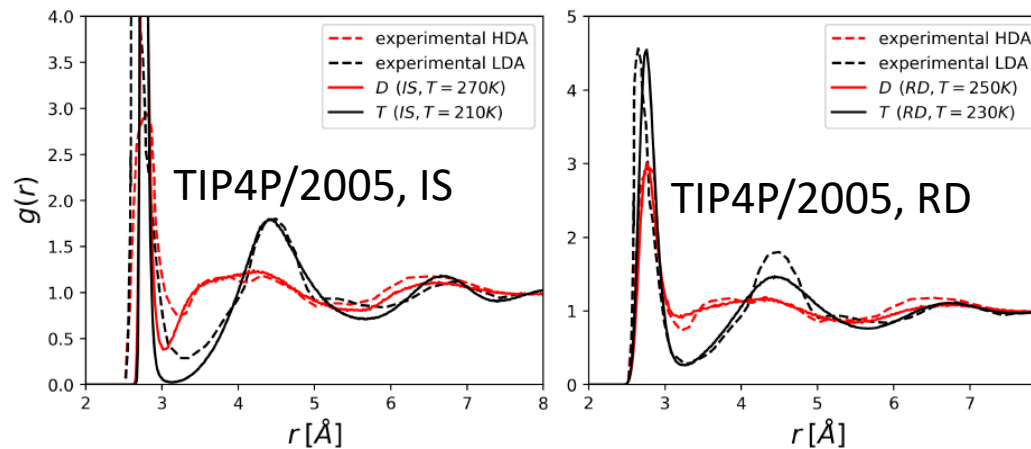
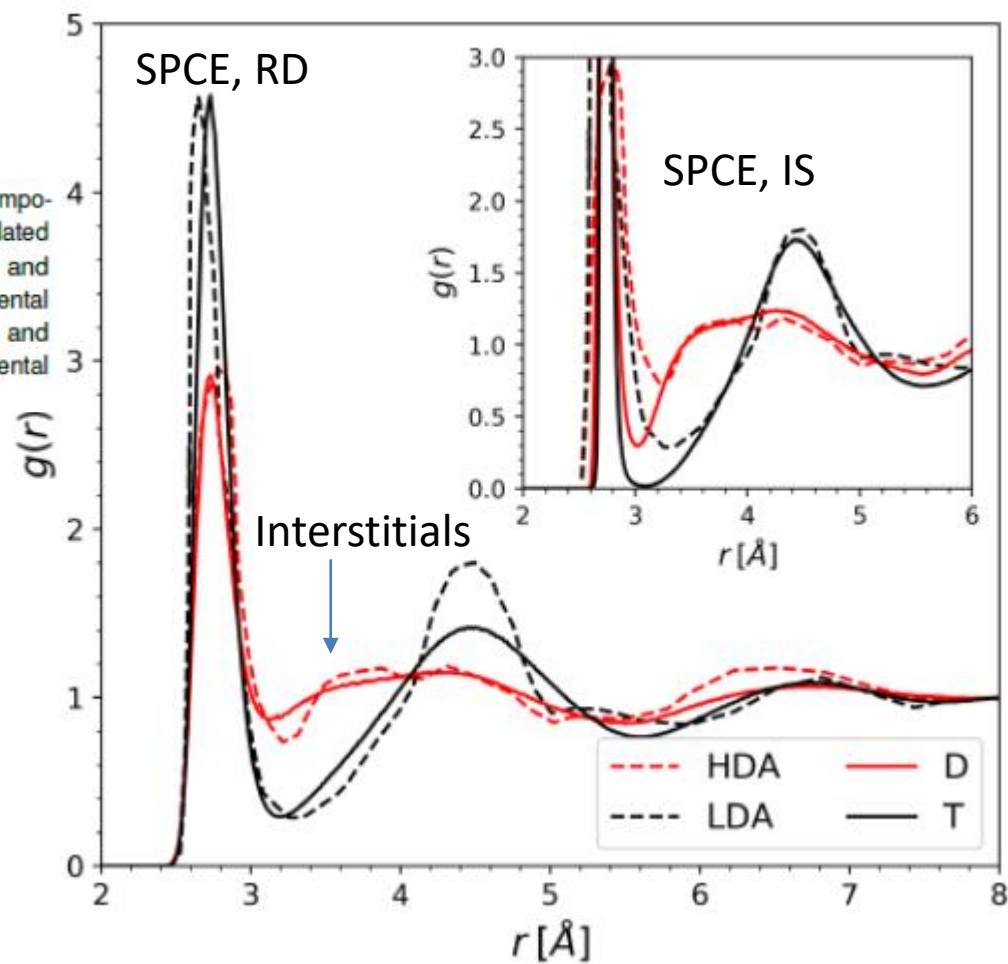


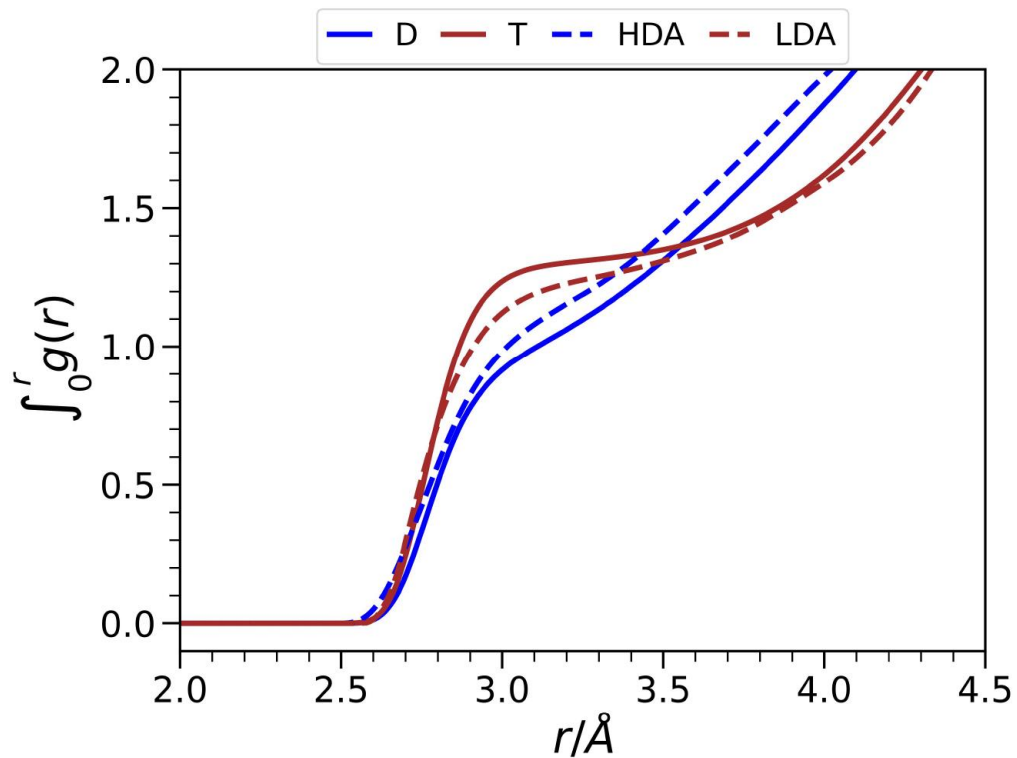
Structure (O-O RDF):

Fig. 2. Oxygen-oxygen radial distribution functions (RDF) separated into two components according to the identity (T or D) of the molecule located at the origin calculated for SPC/E model (see SI for TIP4P-2005 model) in the real dynamic (main) and Inherent Structures (inset). Temperature was chosen to best match the experimental RDF from Finney et al while pressure was always 1 bar. (42). Temperature and pressure were 210K and 1 bar for T-RDF and 240K and 1 bar for D-RDF. Experimental HDA and LDA was reported to be 80K.

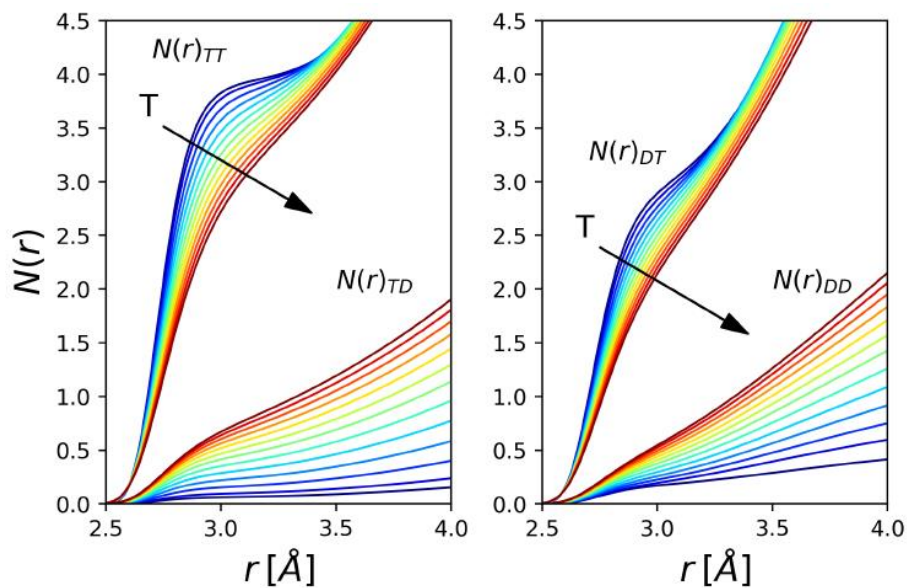
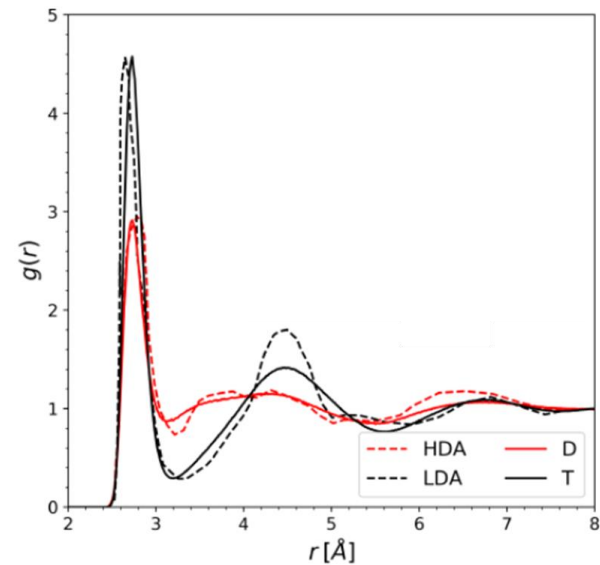
T molecules: LDA-like
D molecules: HDA-like

- Such a remarkable resemblance with experimental results has not been obtained so far.
- Liquid configurations as thermally deformed relatives of corresponding solid amorphous structures.
- HDL-LDL equilibrium as a thermally distorted version of the HDA-LDA equilibrium.

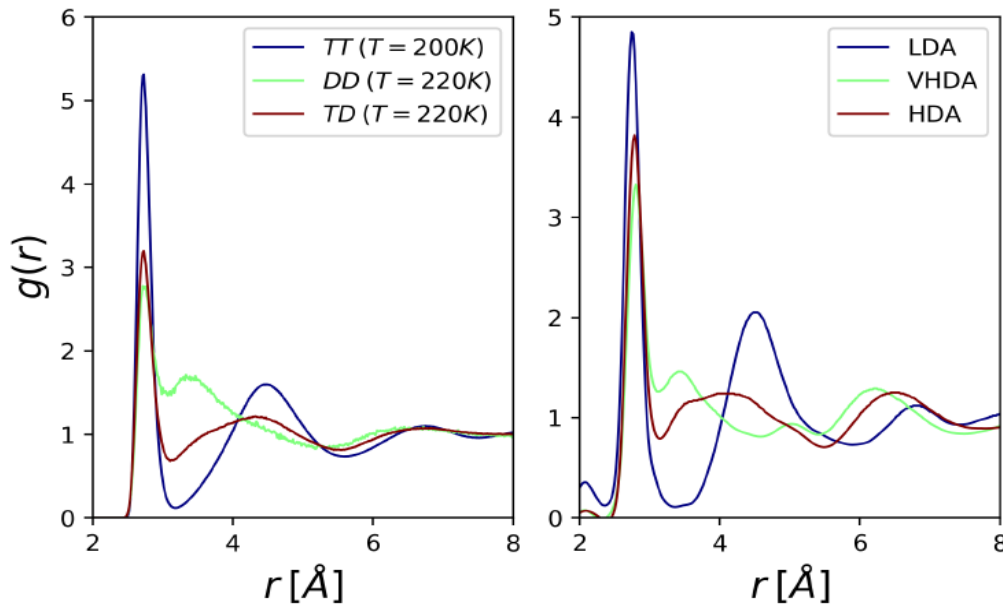




Local density:
Integration of $g(r)$.



Number of neighbors:



Partial RDFs:

Experimental
Winkel et al.

T is dominant even above T_m :

T molecules surrounded mostly by T molecules (almost pure state at low temperature), while D molecules surrounded by three T molecules (HB) and T and D further away.

LEADS TO REVISIT THE TWO-STATE PICTURE:

Properly description based **not on single-molecule properties** but on **two different local multi-molecule network environments**:

Instead of two pure states, as usually assumed: One almost purely tetrahedral phase (only T) and another mixed one (mixture of T and D).

Total correlation function: $h_{DD}(r) \equiv g_{DD}(r) - 1$

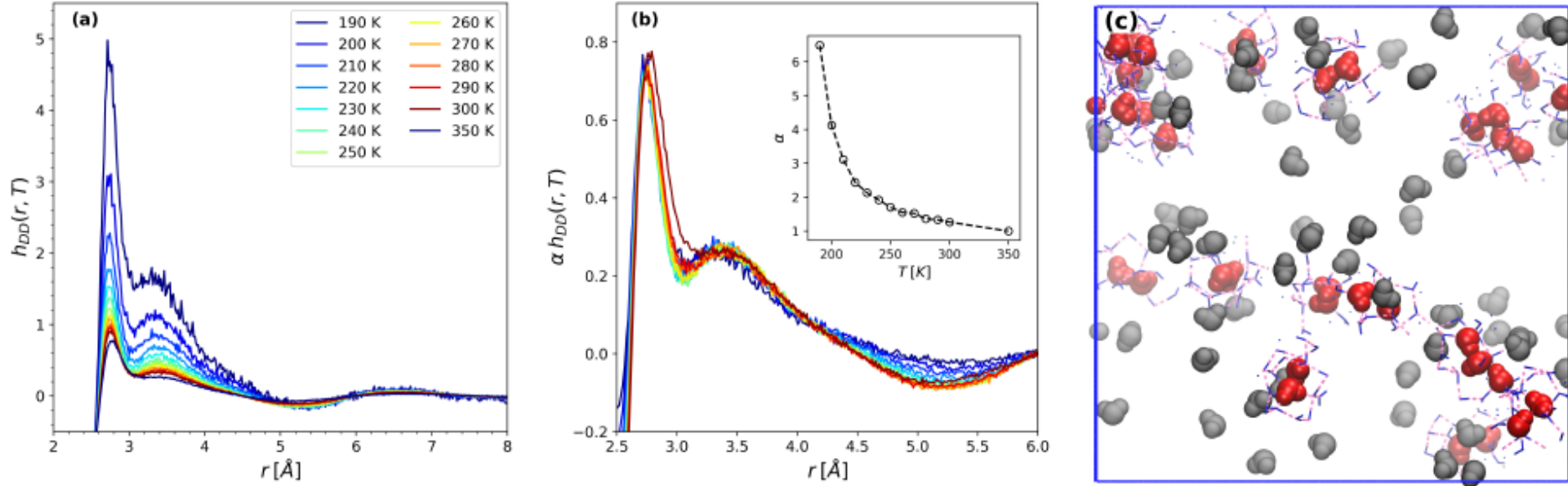


Fig. 3. (a) Total correlation function $h_{DD}(r, T)$. (b) Scaled total correlation function $\alpha(T)h_{DD}^C(r)$, with the resultant scaling factor with temperature (inset). (c) Representation of a typical configuration of SPC/E water at 180 K and ambient pressure, showing the clustering of the D molecules. Red molecules are D molecules with at least one other D molecule within 4Å, while grey molecules are isolated D molecules (the next D molecule is further than 4Å away).

Below 4.5 Å, $h(r) > 0$, thus **D molecules are spatially correlated.**

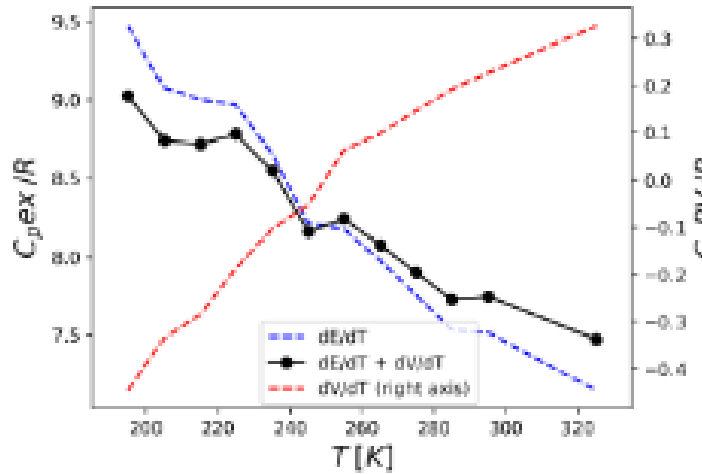
Separating the spatial dependence, $h(r)$, from the temperature dependence (scaling with $\alpha(T)$) show that, up to $\approx 4\text{Å}$, **the r dependence of h_{DD} is identical for all temperatures.**

Most D molecules are isolated and randomly dispersed in space but there also exist a non-negligible fraction of clusters.

Anomalies in thermodynamic response functions: Specific heat

$$C_p^{ex} \approx \frac{\partial E}{\partial T} = \frac{\partial [f_T E_T + (1 - f_T) E_D]}{\partial T}$$

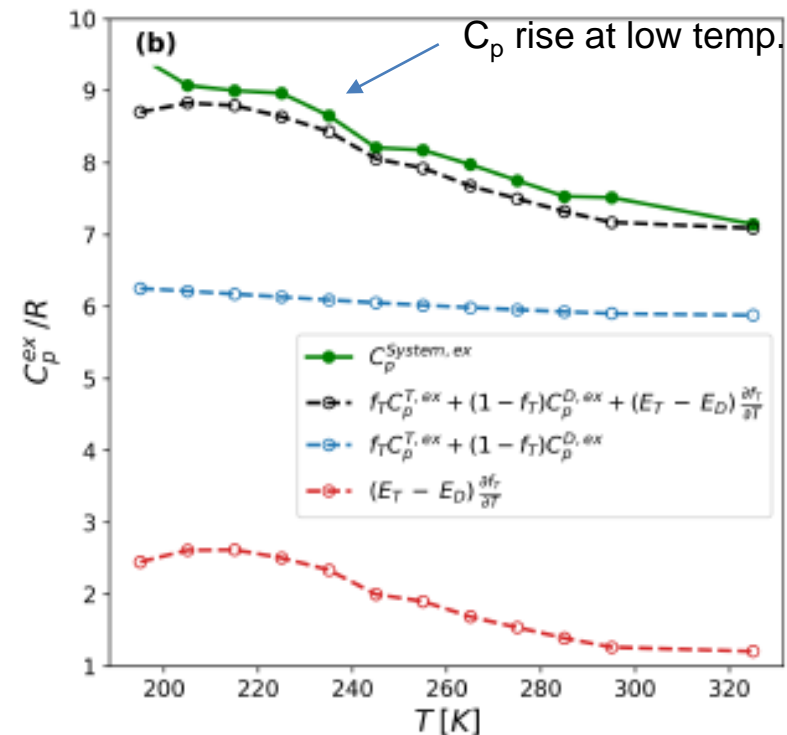
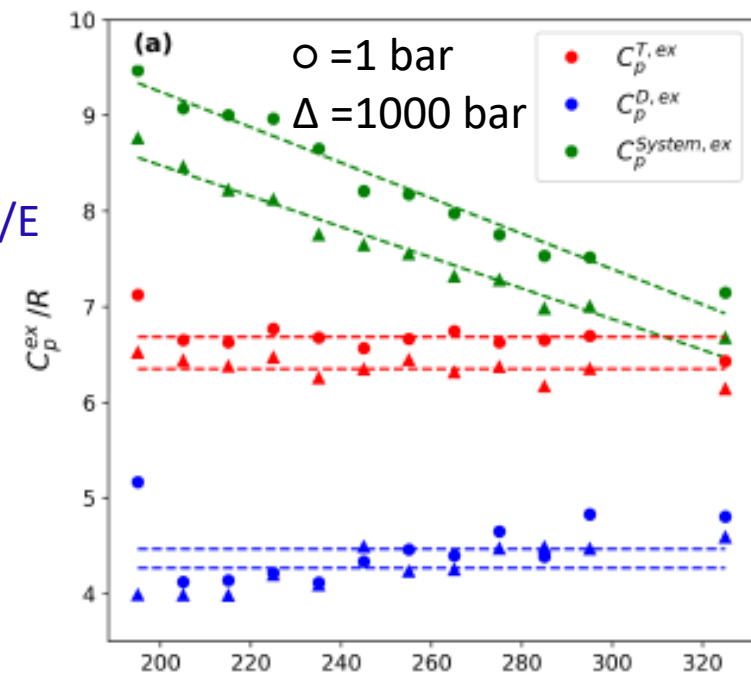
SPC/E

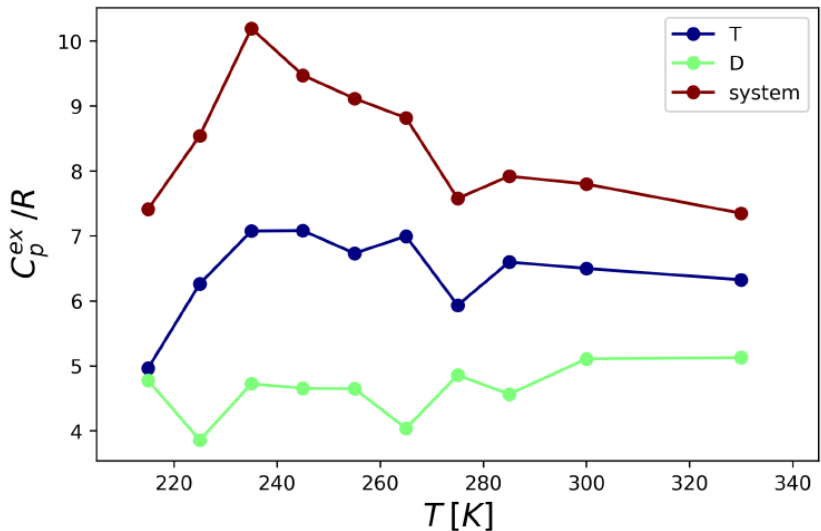


$$C_p^{ex} \approx f_T C_p^{T,ex} + (1 - f_T) C_p^{D,ex} + (E_T - E_D) \frac{\partial f_T}{\partial T}$$

where $C_p^{T,ex} \equiv \frac{\partial E_T}{\partial T}$ and $C_p^{D,ex} \equiv \frac{\partial E_D}{\partial T}$.

Isolated contributions of T and D molecules are small and basically temperature independent. The strength and temperature dependence of the Cp arises mostly from the inter-conversion between T and D molecules, $\frac{\partial f_T}{\partial T}$





Similar results for TIP4P/2005

But, classifying molecules with the LSI index or with V_4 but at real dynamics fail to give the C_p^{ex} independent of temperature for each kind of molecule. In both cases, the classification overestimates the fraction of “unstructured” molecules, which almost match the behavior of the complete system.

Fig. S2. Excess C_p^{ex} for TIP4P-2005 water model at $P = 1$ bar for molecules classified as T and D, and for the entire system.

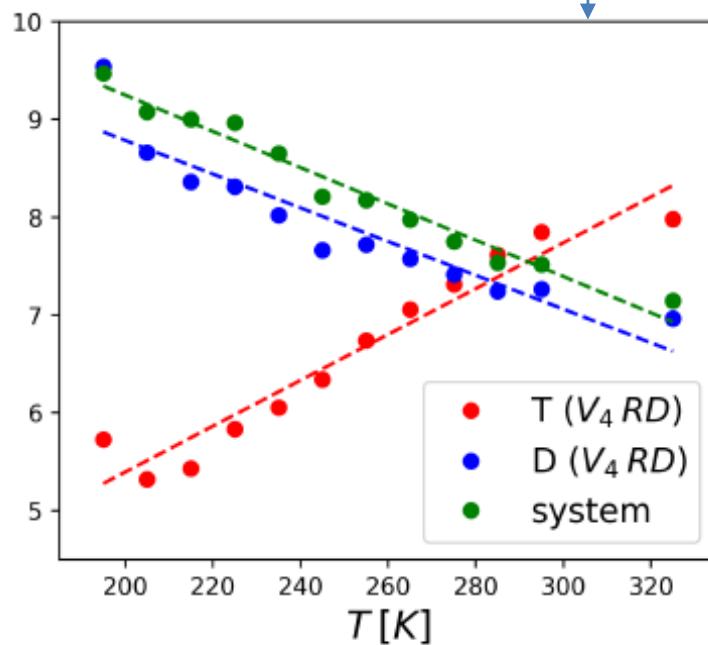
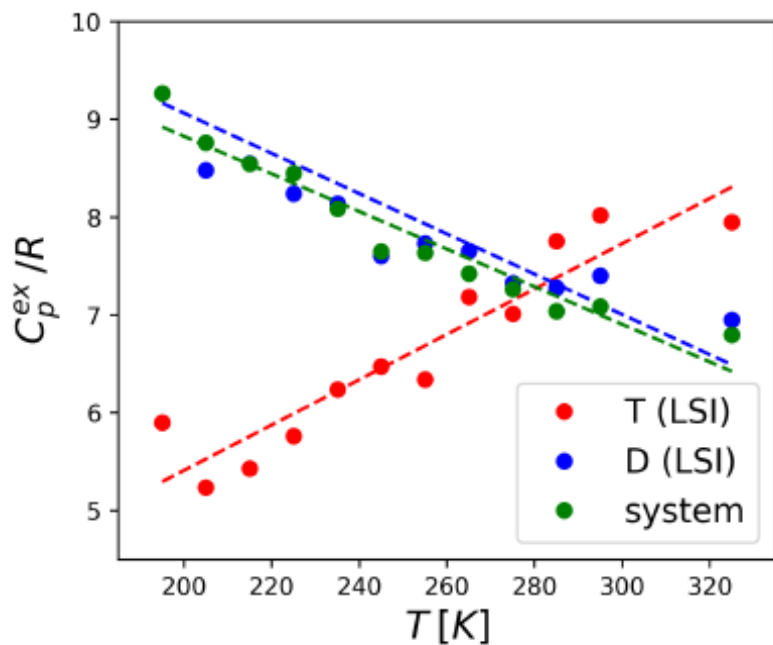
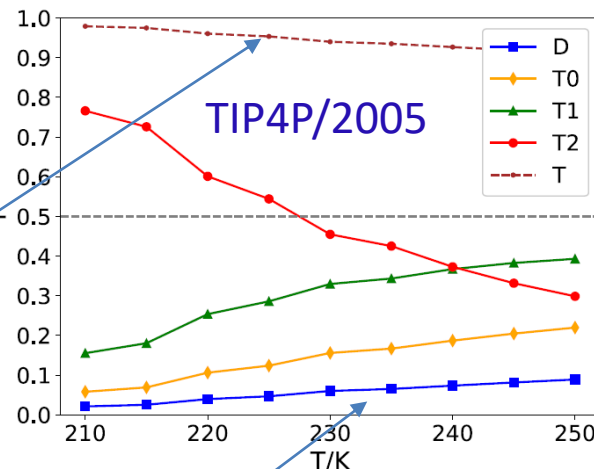
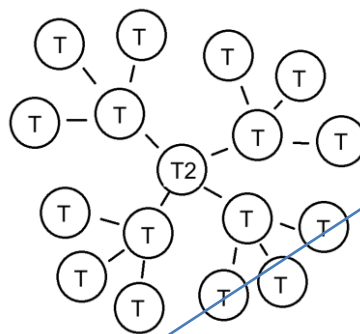
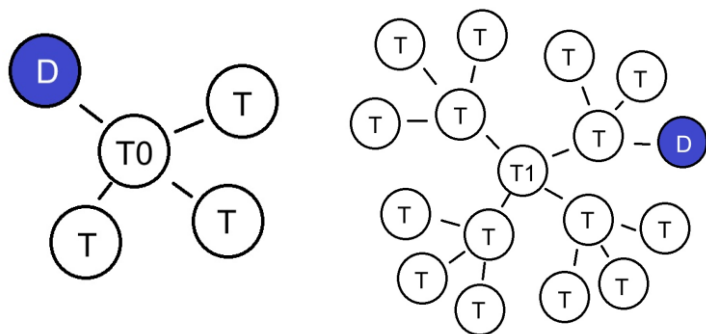


Fig. S3. Excess specific heat C_p^{ex} for SPCE water model at $P = 1$ bar, calculated for molecules classified either by V_4 in the RD, or by LSI in the IS scheme. As mentioned in the main article, when molecules are classified in this way, C_p^{ex} of each species does not remain temperature invariant. In fact, the C_p^{ex} of D-molecules, almost exactly matches the C_p^{ex} of the entire system, a clear indication of an overestimation of the “unstructured” molecules fraction.

From the single-molecule level to a multi-molecular index



T mainly surrounded by T, but D (defect) is very minority, mostly surrounded by T.

Defect correlation functions : How different molecular classes reach (or surpass) the mean defect fraction.

t^* : end of caging regime. Local cage-relaxation events.

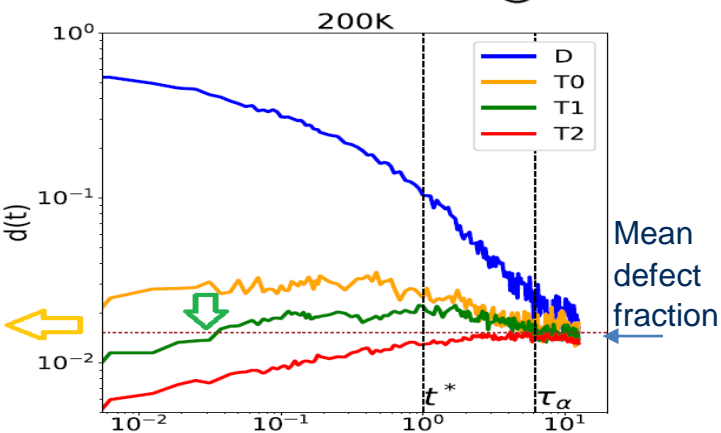
τ_α : structural relaxation time. Long range relaxation (all molecules moved on average one intermolecular distance)

T2 molecules “frozen” for long times (demand long range non-local events to relax)

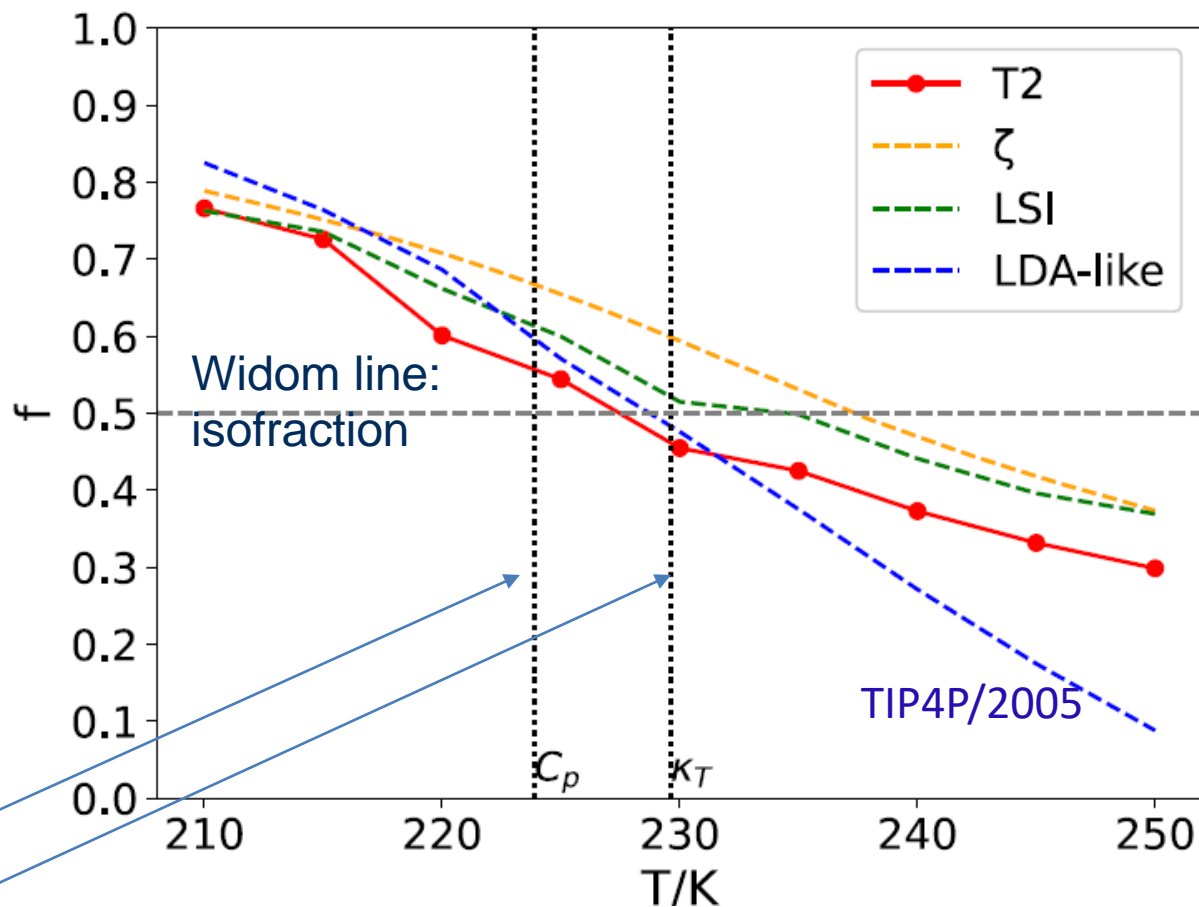
D, T0 and T1 quickly interconvert (defective). Short-range, local events.

T2: LDA-like.

D, T0 and T1: HDA-like.



From the single-molecule level to a multi-molecular index



LDA-like from machine learning, Martelli and Sciortino

C_p and K_T maxima at 1 bar: Signature of Widom line: isofraction, maximum competition, fluctuations are maxima (diverge at the end of Widom's line, the critical point; (T_C, P_C))

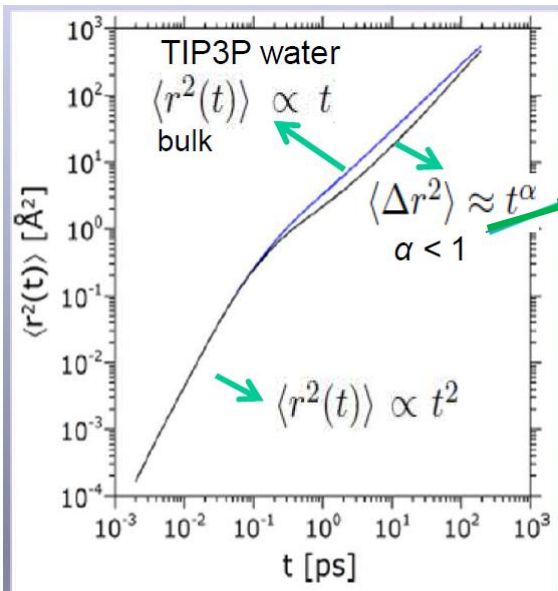
*"Turning a defect detector into an accurate water structural indicator": N.A. Loubet A.R. Verde, J.A. Lockhart, GA Appignanesi, J. Chem. Phys. **159**, 064512 (2023)*

However: Only valid for bulk water. Thus, we will move to a more generic index!

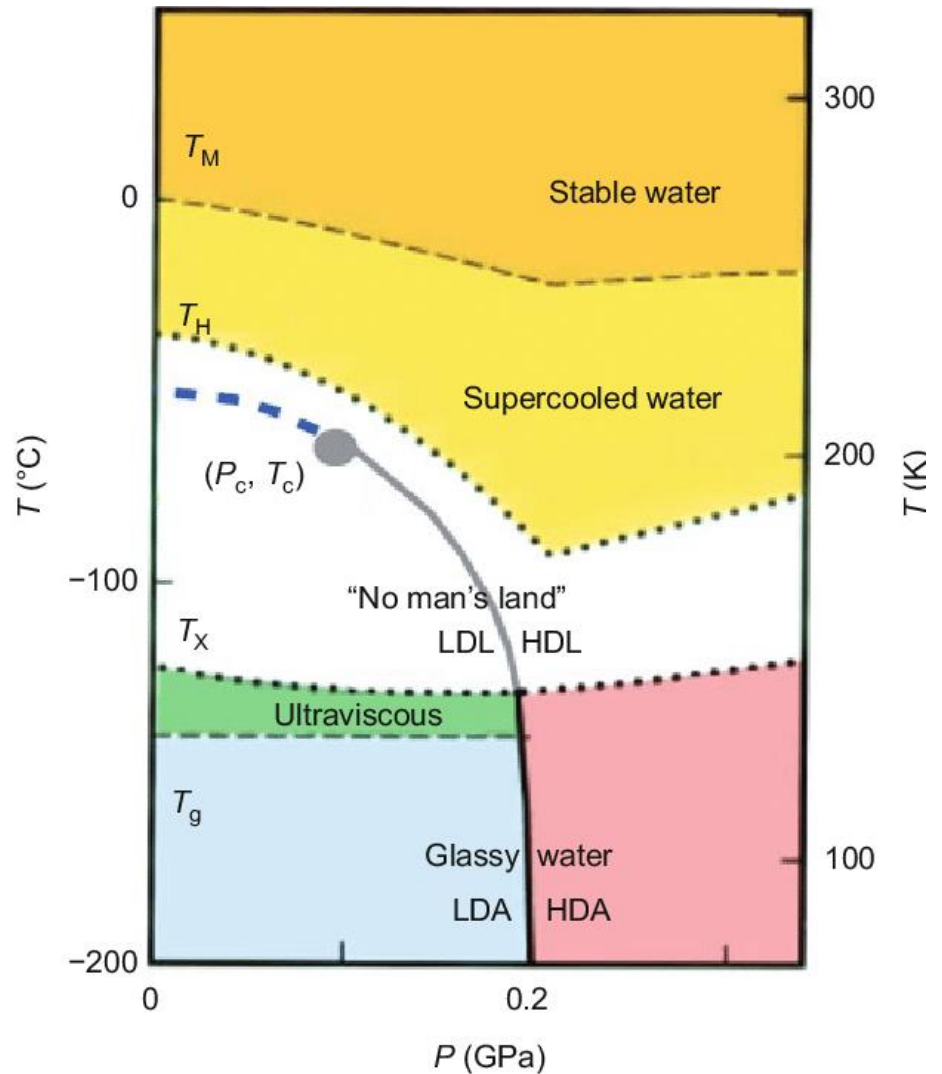
Supercooled / glassy water:

(Sorry for a rather longish disgression)

Close to critical point: critical fluctuations dominate,
But far from it: typical glassy relaxation



Hydration water at short times and short distances. Subdiffusive, slower than bulk



Protein hydration water: Reminiscence of glassy behavior (at ambient temperature)

62 proteins, 400 MD runs each

COMPLEX SYSTEMS

- Many strongly interacting units
- Wide range of intrinsic relaxation timescales
- Diversity: Significantly different states
- Examples: glasses, spin glasses, biopolymers.

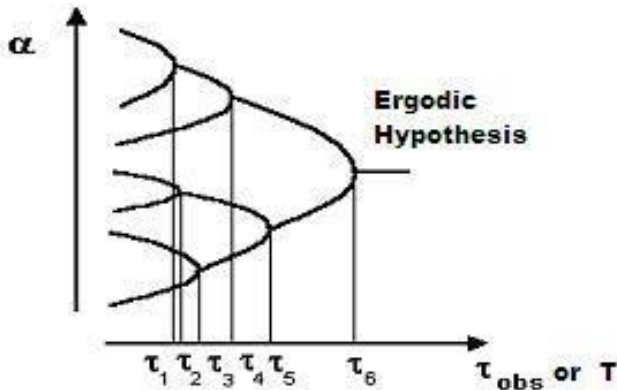
RELAXATION BEHAVIOR:

- Simple systems: One activation barrier → Exponential law (Debye)
- Complex systems: Many barriers. Stretched exponential (Kohlrausch). Slower. Ubiquitous.

$$q(t) = q(0) \exp[-(t/\tau)^\beta]; 0 < \beta < 1$$

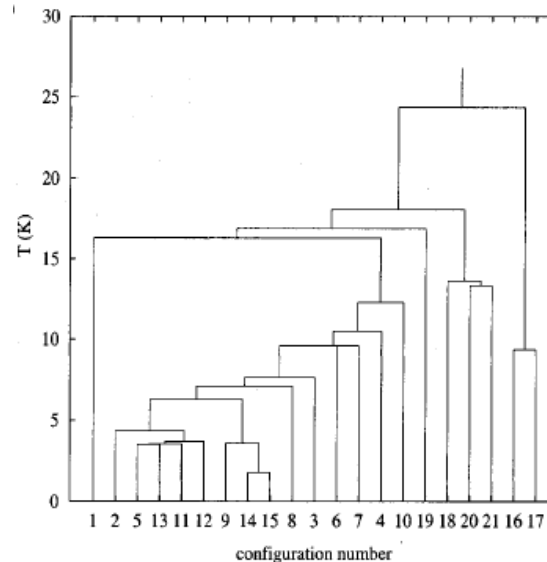
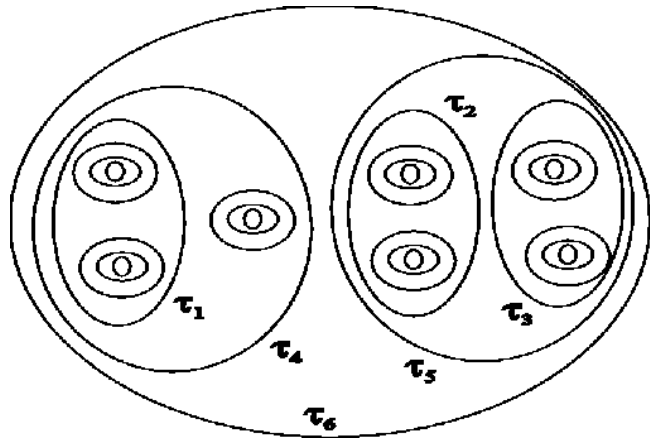
BROKEN ERGODICITY - HIERARCHICAL SYSTEMS –
ULTRAMETRIC SYSTEMS – SPIN GLASS THEORY (random coupling between spins,
frustration) ...

BROKEN ERGODICITY - HIERARCHICAL SYSTEMS: PHENOMENOLOGICAL PICTURE



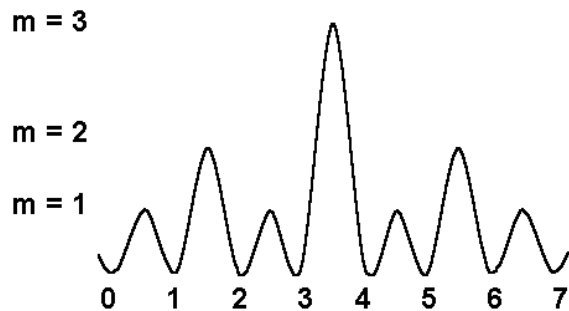
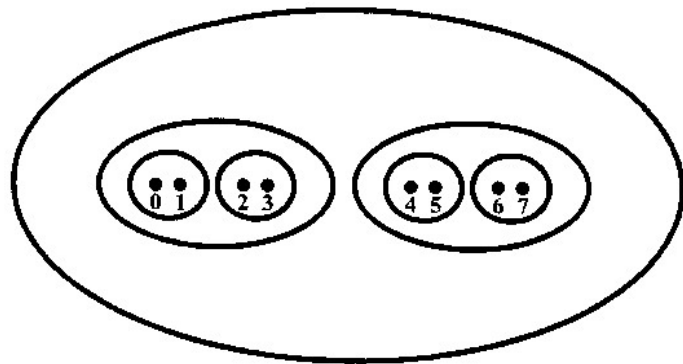
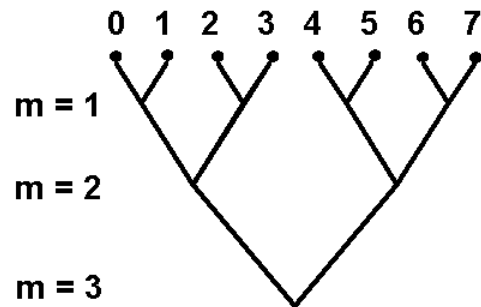
- Broken ergodicity (PALMER - STEIN)
- Ergodic decomposition of Γ_E

$$P_{\text{esc}} = \tau_{\text{obs}} w_0 \exp(-B/RT)$$
- Components (α): Disjoint. Internally ergodic. Confine τ_{obs} . Merge hierarchically.
- Irreversibility (T)
- Metastability
- Small clusters (Berry, Wales), simple proteins (Karplus, Becker).



Small Ar clusters (Ar_9).
Change T (or merging
rate constants)
(Ball & Berry)

ULTRAMETRIC SYSTEMS



- Sherrington-Kirkpatrick (SK) Spin glass solution (Parisi-Mezard-Virasoro). Palmer, Anderson et. al.: Spin constrained system (dynamic facc.).

- $d(x,y) \leq \max(d(x,y),d(y,z))$; $s = 2^m$

Dynamics: $B = B(m)$ (ad hoc)

- $B = \Delta \ln m$; $m \sim t^\beta$; $\mathbf{P}_0(t) \sim \exp(-c t^\beta)$

$\beta = RT/\Delta \leq 1$ Limit of convergence of the dynamics – Debye / Kohlrausch

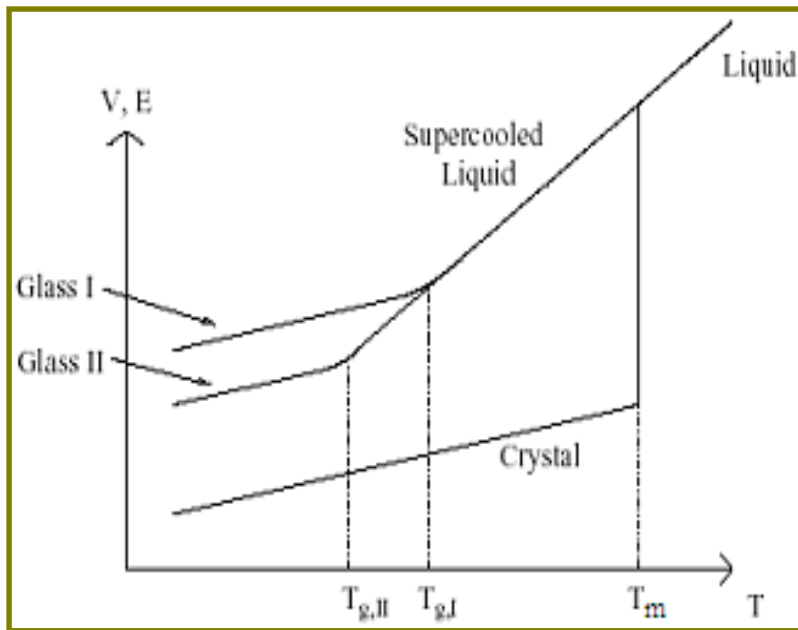
- $B = \Delta m$; $m \sim \gamma \ln t$; $\mathbf{P}_0(t) \sim t^{-\gamma}$

$\gamma = RT/\Delta \leq 1$ Limit of compact exploration - Power decay law (fractals). More than internally ergodic.

Robust respect to addition of ruggedness beyond ultrametricity (dynamic Glauber MC simul.). Most disordered: hierarchical structure. Variational principle (least action), brachistochrone curve (least time)

A. Fernández and G. Appignanesi, *Phys. Rev. Lett.* **78**, 2668 (1997);
 A. Fernández and G. Appignanesi, *Physica A* **256**, 359 (1998);
 G. A. Appignanesi, *Physica A* **272**, 188 (1999); **276**, 413 (2000).

SUPERCOOLED LIQUIDS AND GLASSES



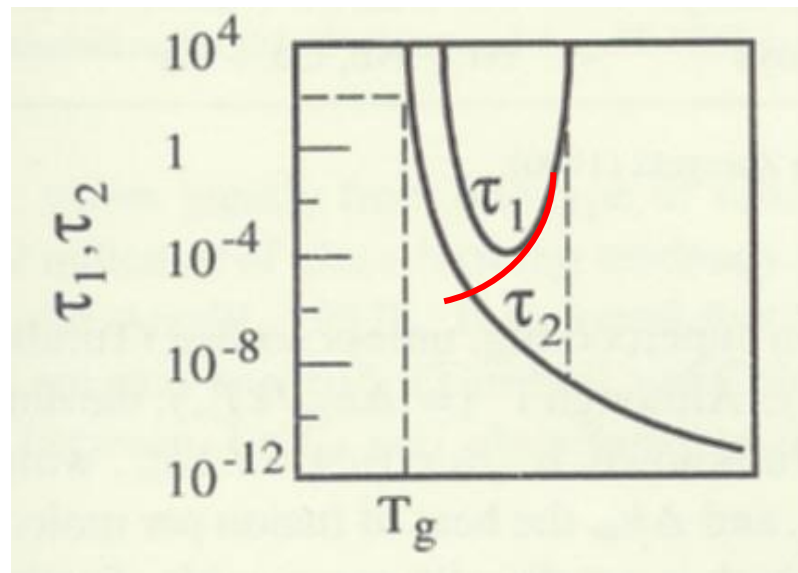
“Quenching” below T_m . Supercooled liquid.
 T_g : metastable solid (no long-range order).

Static vs. dynamic parameters:

$$t_{\text{relax}} = \tau \propto \exp(A/(T - T_0)); \text{ VFT}$$

(Vogel–Fulcher–Tammann equation).

Metastable liquids, Pablo Debenedetti, Princeton University Press



Internal relax. time τ_2 vs. crystalliz. time. τ_1
 Viscous slowdown (controls τ_1) at low T.

Dynamic slowing down.

Nonexponential relaxation (slow). Kohlrausch.

➤ Supercooled liquids are **Dynamically Heterogeneous**. Dynamics vary orders of magnitude from one region to another.

➤ Transition to rigidity involves the occurrence of relaxation domains whose dimensions and lifetimes increase upon supercooling.

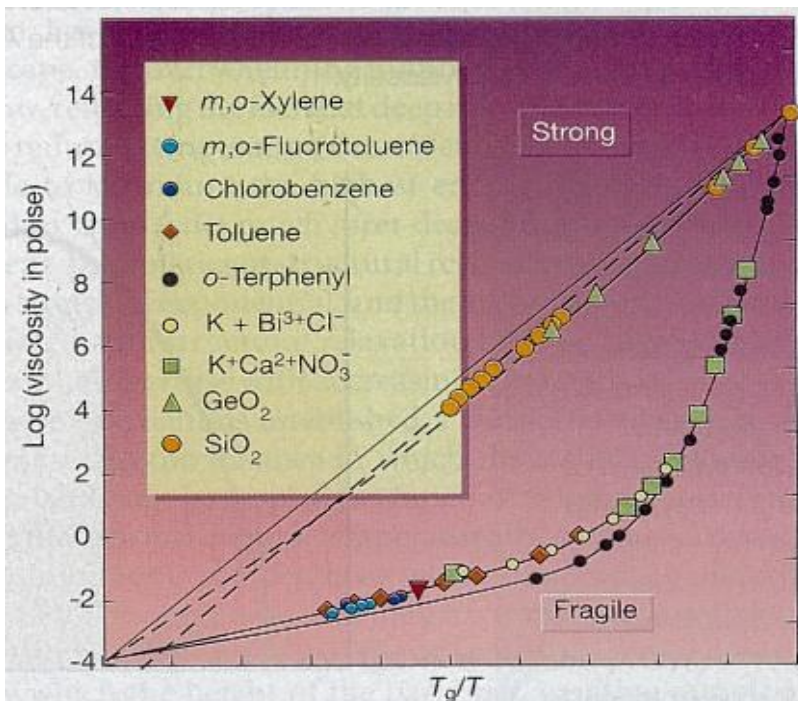
Adam&Gibbs theory: Thermodynamic-kinetic.

Cooperative rearranging regions (CRR), $T \downarrow \Rightarrow$ size of CRR $\uparrow \Rightarrow S_{\text{conf}} \downarrow \Rightarrow \tau \uparrow$

$$\tau = A \exp(B/k_B T S_{\text{conf}}), S_{\text{conf}} \propto T - T_0 \rightarrow \text{VFT}; \text{CRR} \propto 1/S_{\text{conf}}$$

CRR: Cooperatively rearranging regions (CRR). Their size increases with cooling as S_{conf} decreases and τ increases. No characterization criterion (nor size) ? Inhomogeneous relaxation scenario \rightarrow Kohlrausch law.

Dynamical heterogeneities: Transition to rigidity = slowly relaxing domains whose dimensions and lifetimes grow with supercooling.



FRAGILITY OF VITREOUS SYSTEMS (C. Austen Angell's classification)

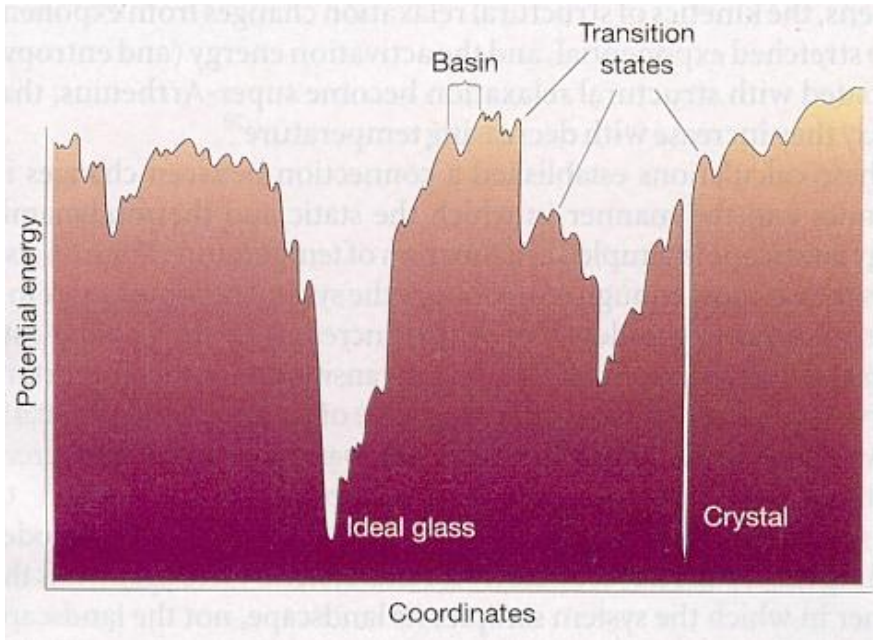
- Quenching below T_m
Out of equilibrium solid. No long range order. Metastable.
- Cooling velocity: rearrangements – τ
config. exploration $\rightarrow T_g$
- Angell's Classification:

Strong (Arrhenius behavior)

Fragile (non Arrhenius, $E_a \uparrow$ if $T \downarrow$)

Water fragile/strong

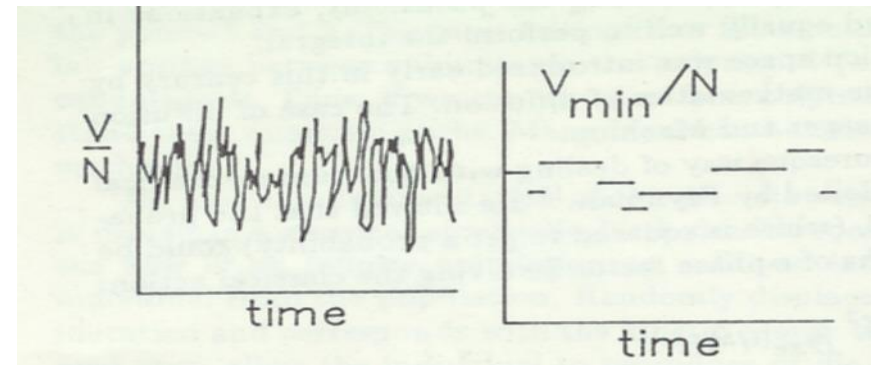
TOPOGRAPHIC APPROACH



Landscape paradigm
Potential energy surface, PES)
(Goldstein – Stillinger&Weber)

Ideal glass: Kauzmann temperature,
relaxation divergence.

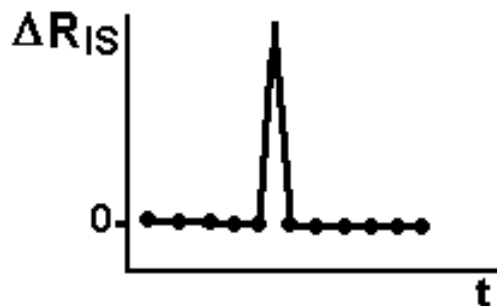
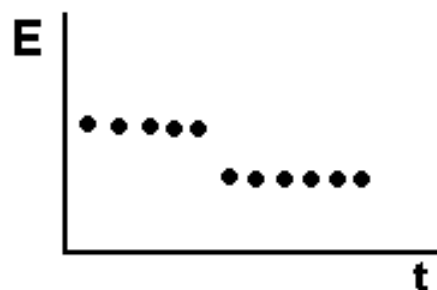
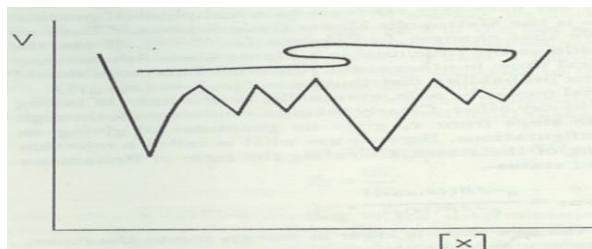
Exploration method: Distinguish rare events that would be masked by thermal fluctuations



TOPOGRAPHIC APPROACH

(Landscape paradigm, potential energy surface, PES)

Exploration method: Distinguish rare events that would be masked by thermal fluctuations (Goldstein – Stillinger&Weber)



- PES (N particles, 3N Dimensions)
- Low T: *Timescale separation* (vibrat. around local minima vs. transitions between minima).

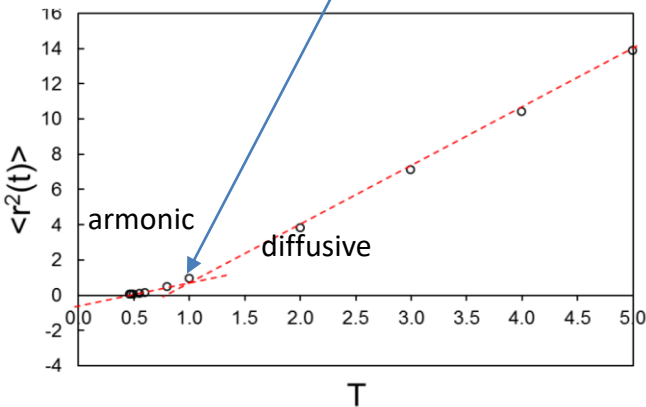
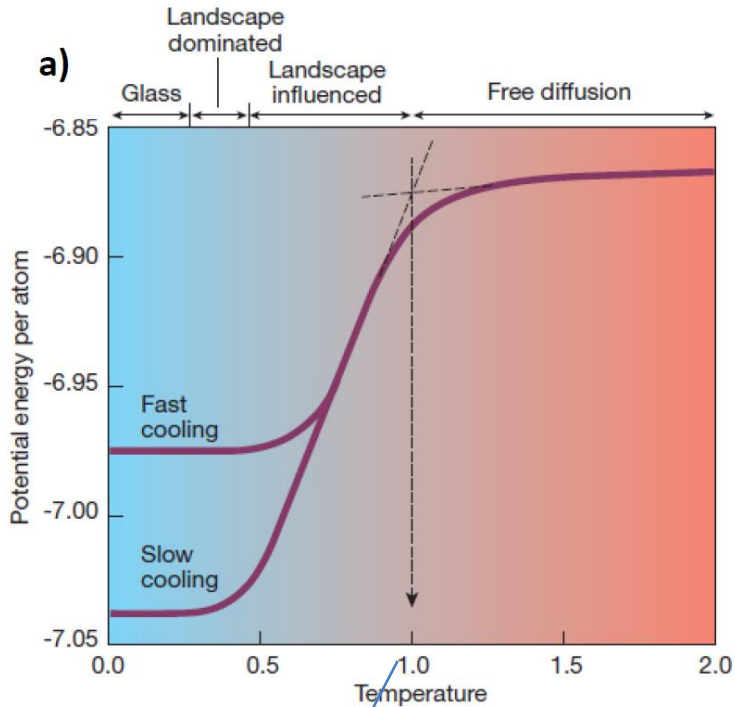
Mapping by local minimization of potential energy $V \rightarrow V_{\min} = E$, (conjugate gradient or steepest descent; or extraction of kinetic energy, quenching).

Partitions configuration space into basins, Inherent Structures (IS).

Dynamics at the IS level: *Inherent dynamics vs. real (instantaneous) dynamics.*

$$\Delta R_{IS} = (\sum (r_i^{IS}(n) - r_i^{IS}(n+1))^2)^{1/2}$$

LANDSCAPE EXPLORATION



Binay LJ: fragile glass former (Kob&Andersen)
 MD Simulations (quench \rightarrow IS)
 (Sastry-Stillinger&Debenedeti)

3 exploration regimes:

(Debye - Kohlrausch - Power decay law?)

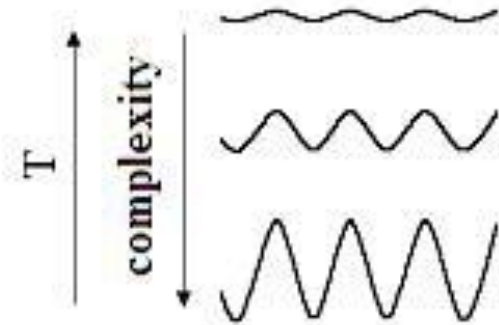
*Free Diffusion – Landscape Influenced –
 Landscape Dominated*

Exploration: T-dependent (Angell) ruggedness

$A = E - TS$; $S = k_B \ln W$
 Crystal (min. E). Fusion ($\uparrow TS$)

High T: Explores whole PES.
 Majority of minima are shallow.
 Low T (close to T_c): minima are scarce (high barriers \rightarrow confinement)

T_c = mode coupling T,
 relax. divergence.



Theoretical approaches

Free-volume theories (Cohen-Grest).

Adams&Gibbs: Kinetics-thermodynamics. Inhomogeneous scenario for relaxation.

$$\tau = A \exp(B/k_B T S_{\text{conf}}) \rightarrow \text{VFT law}$$

Mode-Coupling Theory

Dynamics of simple dense fluids (Götze et al.)

$T = T_c$ divergence of relax. timescales (power law divergence). Ergodic-nonergodic transition. No relaxation below T_c (ideal MCT)

Hopping terms. Restore ergodicity/relaxation below T_c .

If weak: power law divergence below T_c but Arrhenius above T_c .

$$\tau(T) \propto D^{-1} \propto (T - T_c)^{-\gamma}$$

BINARY LENNARD-JONES SYSTEM (Computer simulations)

Model glass-former. Fragile. Binary: Circumvents crystallization (as in single component LJ). (Kob & Andersen) 80% A and 20% B, B smaller than A. 3-Dimensional system.

$$V_{\alpha\beta} = 4\epsilon_{\alpha\beta} \left\{ \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right\} \quad \epsilon_{AA} = 1.0, \sigma_{AA} = 1.0, \epsilon_{AB} = 1.5, \sigma_{AB} = 0.8, \epsilon_{BB} = 0.5 \text{ and } \sigma_{BB} = 0.88.$$

Interaction potential was truncated at $r = 2.5 \sigma_{AA}$

Molecular Dynamics (MD) NVE or NPT; $T_c = 0.435$ (Mode coupling temperature)

Reduced units (Argon): r in σ_{AA} , T in ϵ_{AA}/k_B and t in $\sqrt{\sigma_{AA}^2 m / \epsilon_{AA}}$ units.

Don't crystallize, "fragile" glass formers (Angell's classification).

No real system. Why to study such simple kind of systems?

Glassy phenomenology common to many different systems (underlying physics. Universal features)

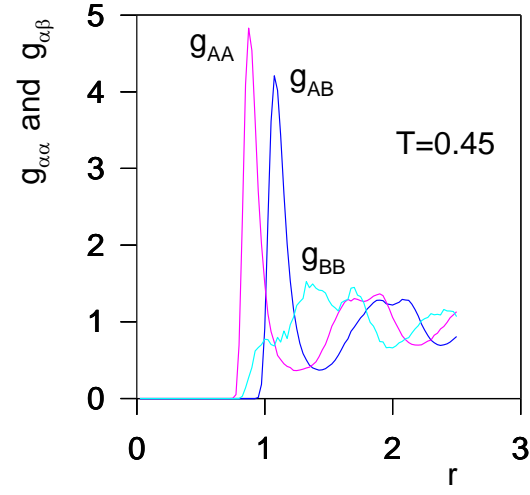
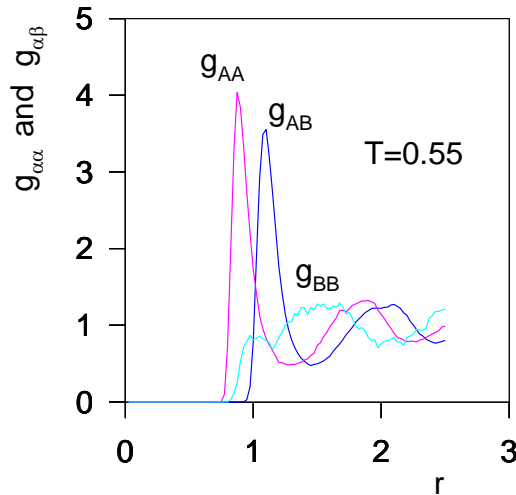
Theories lack specific details (MCT).

Molecular Dynamics simulations: systems not necessarily very large. Parameters (full detailed inf.) not accessible experimentally. Relatively long times (ns), longer than experimental (neutron scattering)

Computer simulations of supercooled liquids and glasses,
Walter Kob, *J. Phys.: Condens. Matter* **11** R85 (1999)

Static Quantities

Pair correlation functions



$$g_{\alpha\beta}(\mathbf{r}) = \frac{V}{N_{\alpha}N_{\beta}} \left\langle \sum_{\substack{i \in \alpha \\ j \in \beta}} \delta(\mathbf{r} + \mathbf{r}_j - \mathbf{r}_i) \right\rangle$$

$$g_{\alpha\alpha}(\mathbf{r}) = \frac{V}{N_{\alpha}(N_{\alpha} - 1)} \left\langle \sum_{i,j \in \alpha} \delta(\mathbf{r} + \mathbf{r}_j - \mathbf{r}_i) \right\rangle$$

r in σ_{AA} units. First peak sharp. Second peak rounded.

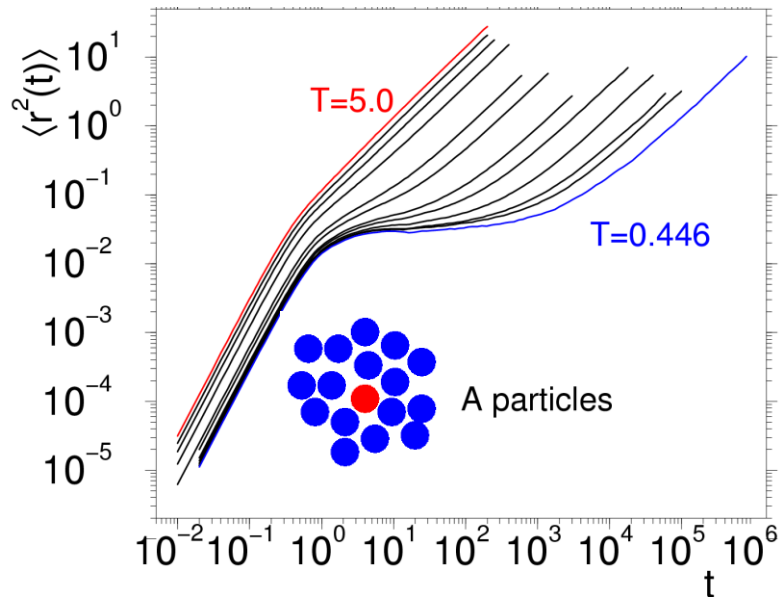
No dramatic change: As $T \downarrow$ the first peak sharpens and the second one splits into two peaks.

Time dependent correlation functions.

Transport coefficients

Mean squared displacement, MSD

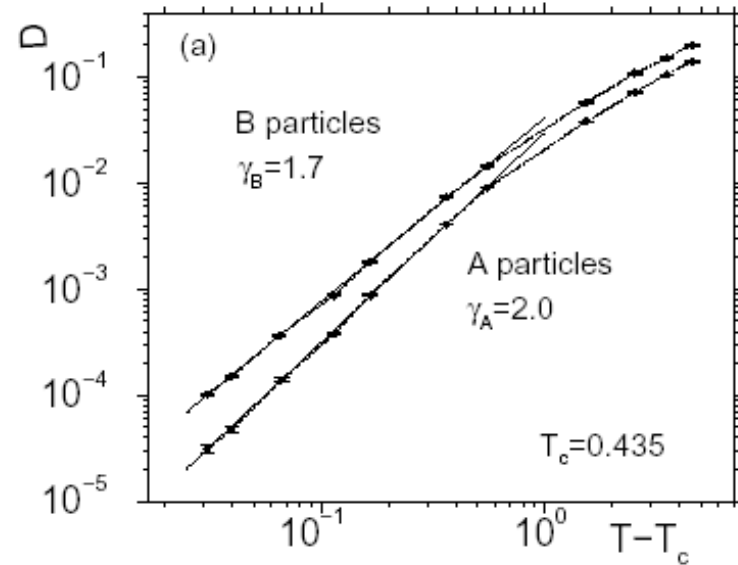
$$\langle r_\alpha^2(t) \rangle = N_\alpha^{-1} \sum_{i=1}^{N_\alpha} \langle |r_i^\alpha(t) - r_i^\alpha(0)|^2 \rangle$$



Diffusion constant, D

Using the Einstein relation

$$D = \lim_{t \rightarrow \infty} \langle r^2(t) \rangle / 6t$$



MSD: Three regimes: Ballistic (slope 2), “caging” (plateau) β -relaxation, α (structural)-relaxation (diffusive, slope 1). Picture of particle motion: caging and cage breaking.

α / β relaxation. Transition at the end of the plateau

D: Well fitted by MCT in the low T regime. $D \propto (T - T_c)^\gamma$

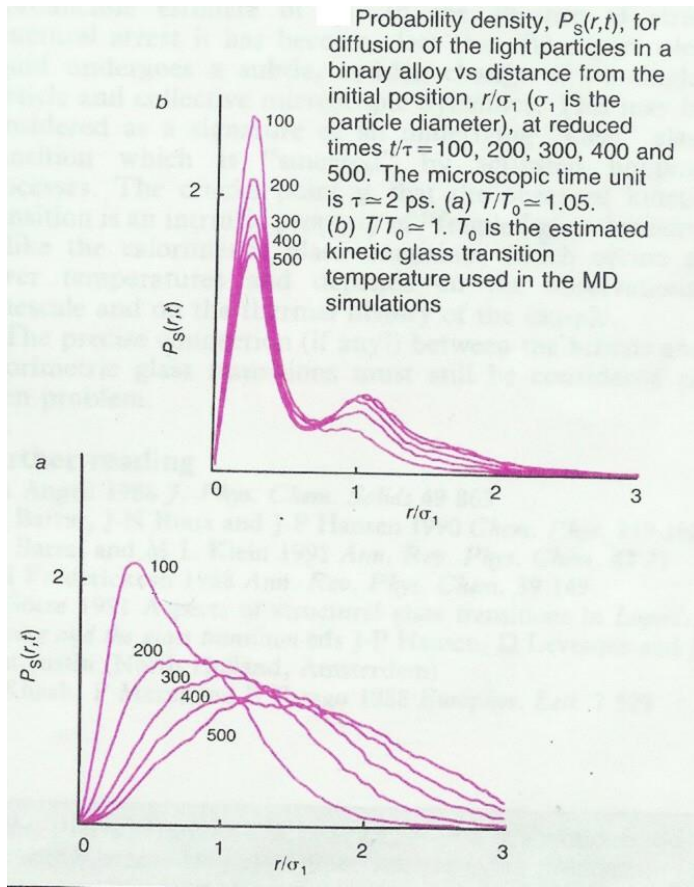
Van Hove correlation function

$$G_s(\mathbf{r}, t) = \frac{1}{N_\alpha} \left\langle \sum_i \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)) \right\rangle$$

(self part) = probability to find a particle at time t at a distance r from its position at $t = 0$

$$P_s(r, t) = 4\pi r^2 G_s(r, t)$$

of particles located at time t at distance r from their initial position



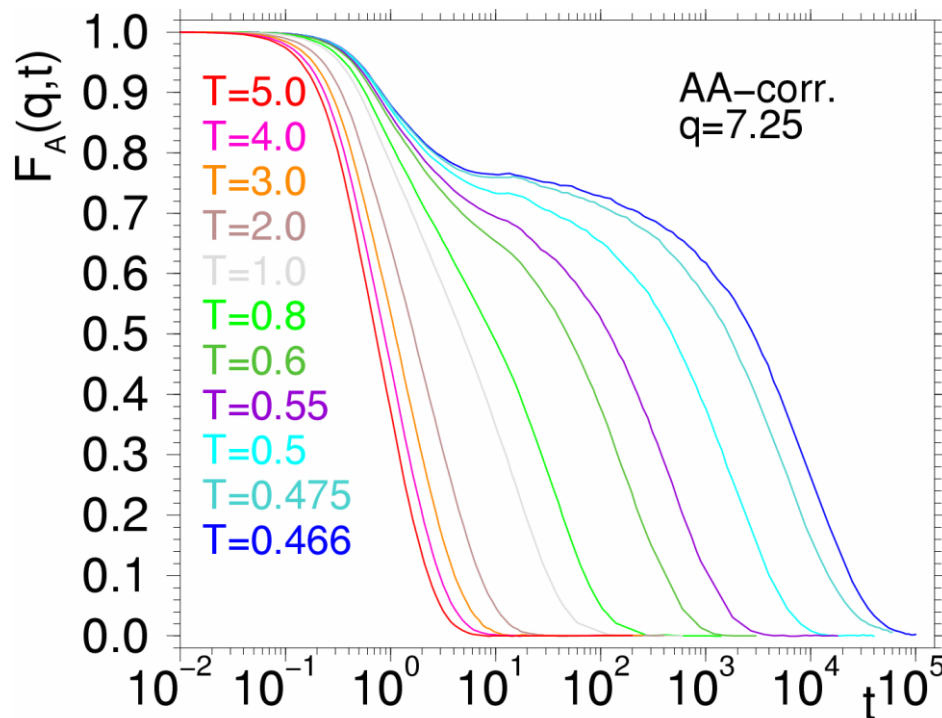
$T > T_c$ (but very close) single maximum. Moves with r following $t^{1/2}$ (Brownian motion)
 At $T \leq T_c$ second peak at $r = 1 \sigma_{AA}$. No ideal MCT. **HOPPING**

(J-L Barrat, J-N Roux & J-P Hansen, for other Binary LJ system)

RELAXATION DYNAMICS:

Experimentally (neutron and light scattering experiments): Fourier transform of $G_s(r,t)$, self part of the intermediate scattering function, $F_s(q,t)$ (for wave vector q)

$$F_s(q, t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \langle \exp(iq \cdot [r_j^\alpha(t) - r_j^\alpha(0)]) \rangle$$



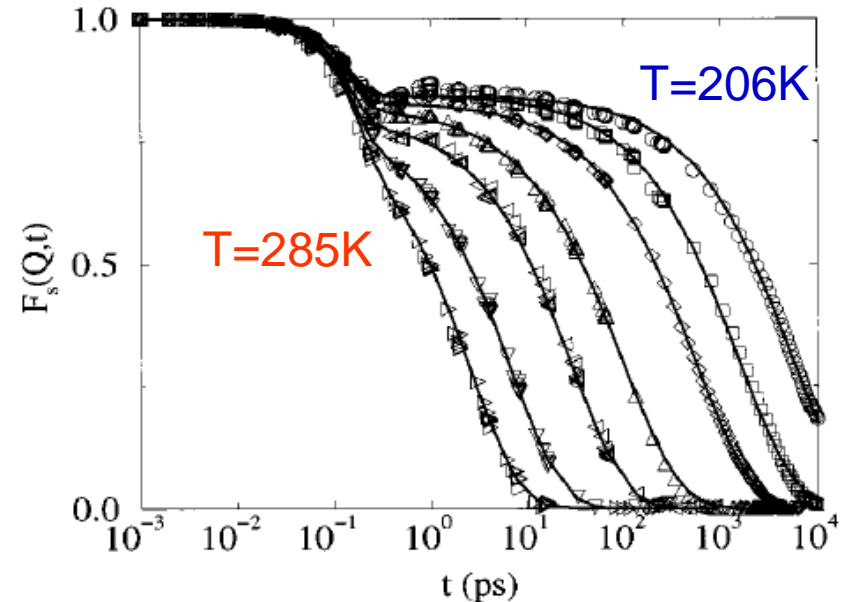
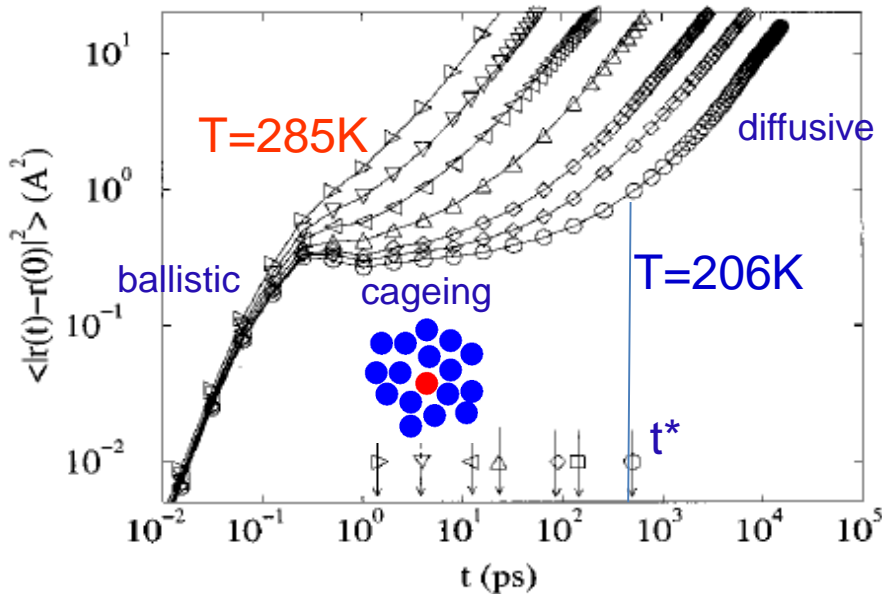
Two-step relaxation (similar to MSD).

Non Debye.

α -relaxation fits to Kohlrausch law (slow dynamics).

τ_α = structural relaxation time. Decay of $(F_s(Q,t))$ to certain value ($1/e$ molecules moved on average one intermolecular distance)

SUPERCOOLED WATER



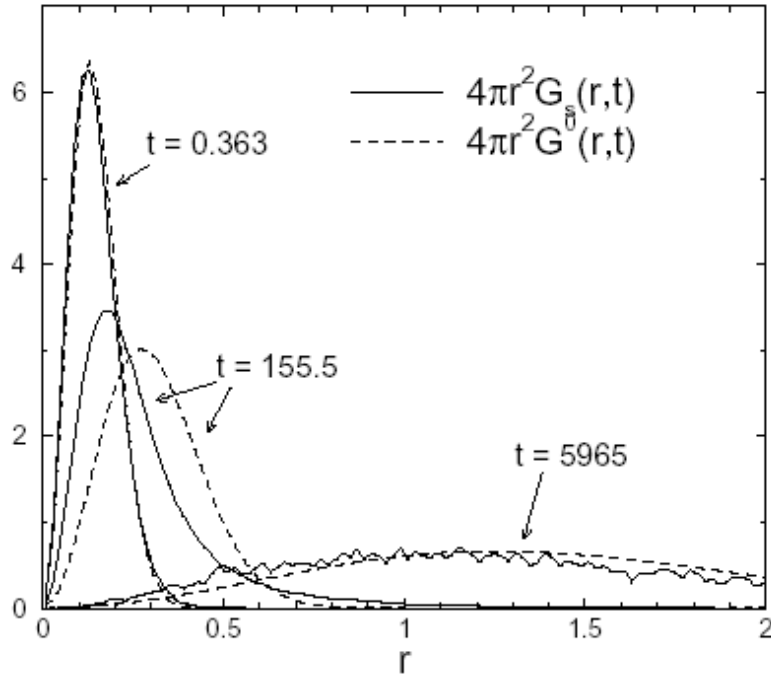
SPC/E water, supercooled regime; from F. Sciortino, P. Gallo, P. Tartaglia and S. -H. Chen, Phys. Rev. E (1996).

At t^* less than 10% of the system has relaxed (the rest of the molecules have not moved considerably). **Dynamical heterogeneities:** dynamics vary orders of magnitude from one region of the system to another. This leads to slow subdiffusive dynamics. t^* is when the system is most dynamically heterogeneous.

Structural α -relaxation (τ_α) the whole system has structurally relaxed since all the molecules have moved on average one intermolecular distance. Diffusive regime.

Kob_Andersen LJ mixture:

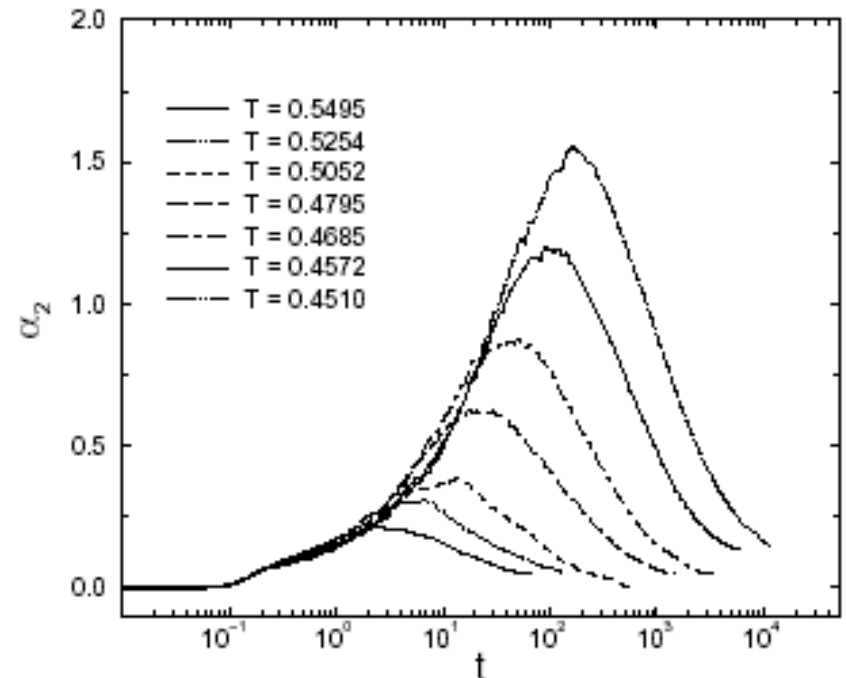
Van Hove correlation function vs Gaussian approximation (Brownian motion; not valid at intermediate times, plateau) ($T=0.451 > T_C$)



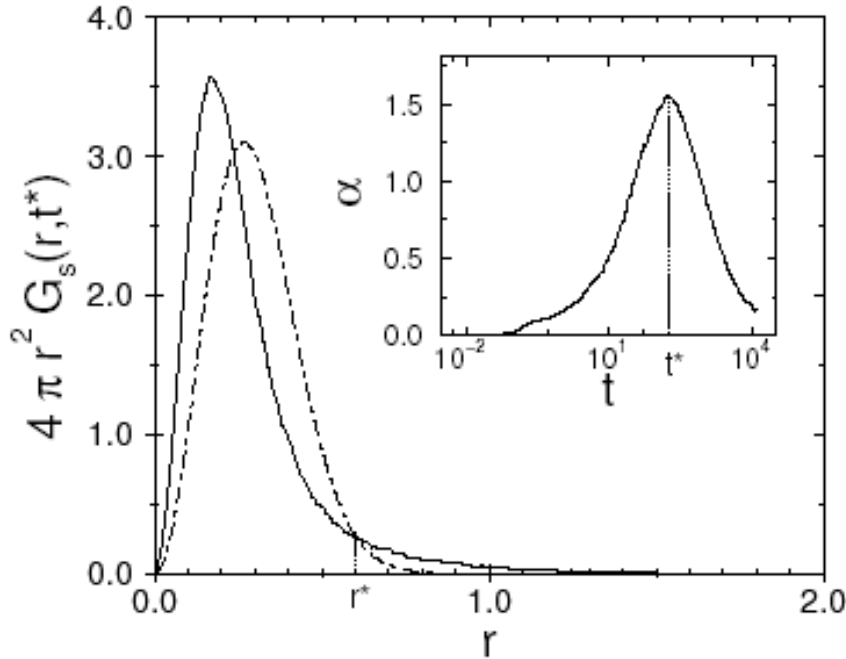
$$G^0(r, t) = \left(\frac{3}{2\pi \langle r^2(t) \rangle} \right)^{\frac{3}{2}} \exp \left(-\frac{3r^2}{2 \langle r^2(t) \rangle} \right)$$

Non-gaussian parameter

$$\alpha_2(t) = \frac{3 \langle r^4(t) \rangle}{5 \langle r^2(t) \rangle^2} - 1$$



DEVIATION FROM BROWNIAN BEHAVIOR



non-gaussian parameter:
 $\alpha(t) = 3\langle r^4(t) \rangle / (5\langle r^2(t) \rangle^2) - 1$

t^* : time of maximum inhomogeneous behavior (curve collapse for $\alpha_2(t)$).
 Characteristic time. Located at late β -early α relaxation

$G_s(r,t)$: Self van Hove function = Prob. finding part. at distance r from origin.

$G^0_s(r,t) = (3/(2\pi\langle r^2(t) \rangle))^{3/2} \exp(-3r^2/2 \langle r^2(t) \rangle)$
 Brownian Motion

DYNAMICAL HETEROGENEITY

(C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. 1998)

also experimentally and amorphous silica (W. Kob) and water (H. E. Stanley).

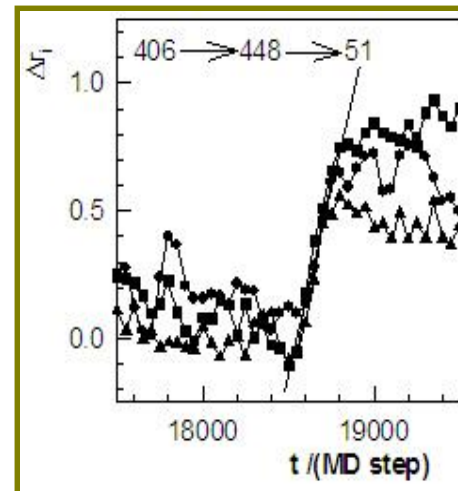
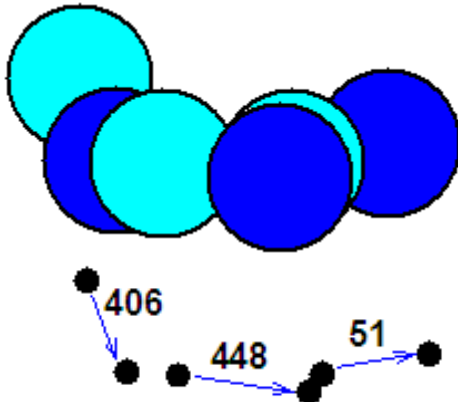
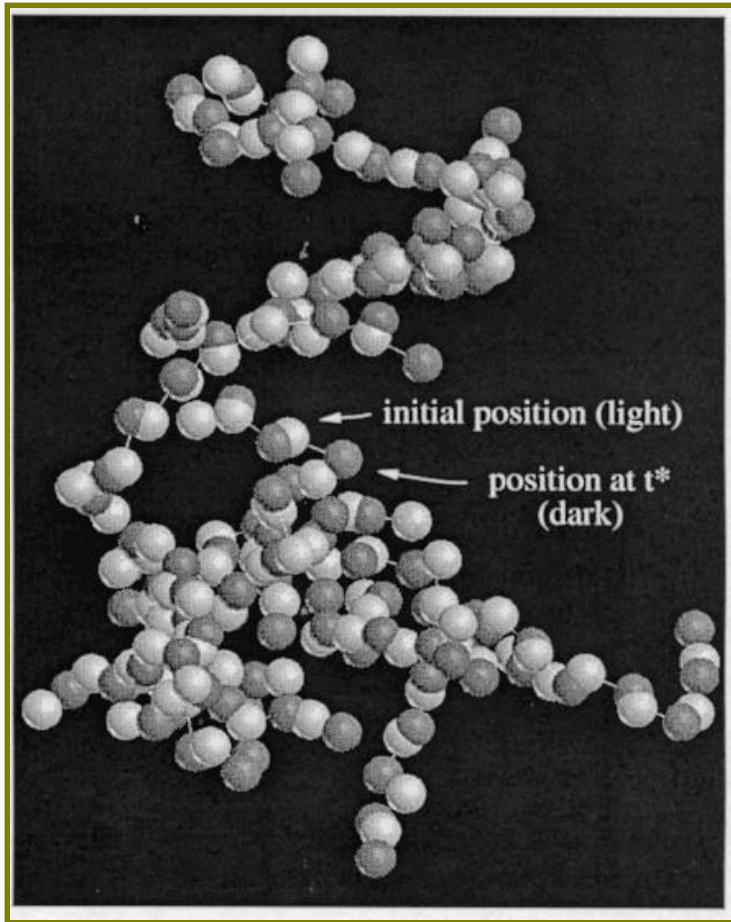
“Mobile” particles: $r \geq r^*$

DYNAMICAL HETEROGENEITIES

$[0, t^*]$. Mobile particles: ($\sim 5-10\%$). Not uniformly distributed but organized in CLUSTERS.

Global Clusters ($\tau = t^*$) decompose in “STRING-LIKE” MOVEMENTS. (Donati, Glotzer, Kob et al.).

$$\Delta r_{ij}(t^*) = r_i(t^*) - r_j(0) < 0.6 \sigma_{AA}$$

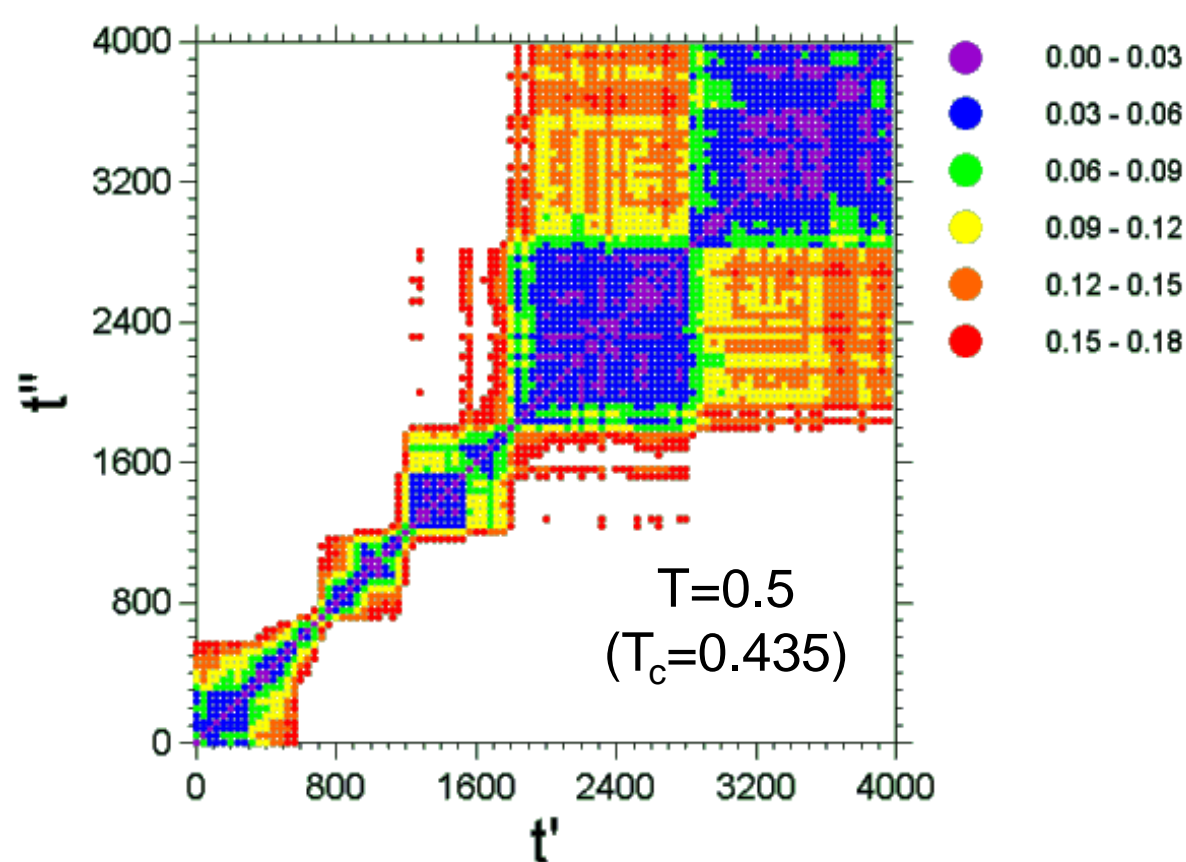


Ballistic substring motions
(Appignanesi et al. *Physica A* (2004))

LOOKING FOR RELEVANT RELAXATION EVENTS: METABASIN (MB) TRANSITIONS (in real or inherent dynamics)

Distance Matrix (DM): $G_s(r, t', t'') = 1/N \sum_i (r_i(t') - r_i(t''))^2$; $r_i(t)$ = position of particle i at time t

Kob&Andersen Binary Lennard-Jones, 80% A and 20% B particles, $r_A = 1.1 r_B$.
Small system ($N=150$) or small sub-system immersed within a large one (single out individual cooperative events). Time intervals 1% τ_α ; $\tau_\alpha \sim 4 \times 10^3$. (I. Ohmine)



Potential Energy

Landscape. Set of similar structures grouped in MBs and separated from others mutually similar.

- MB = Islands

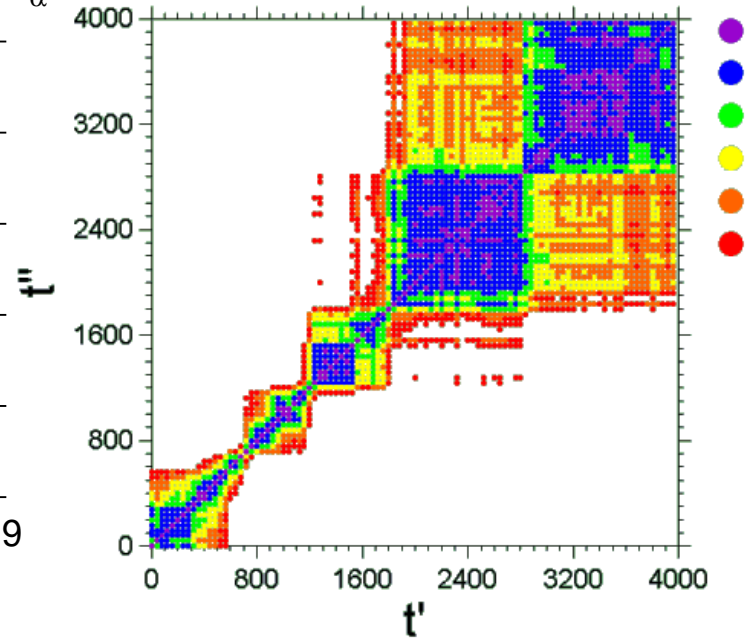
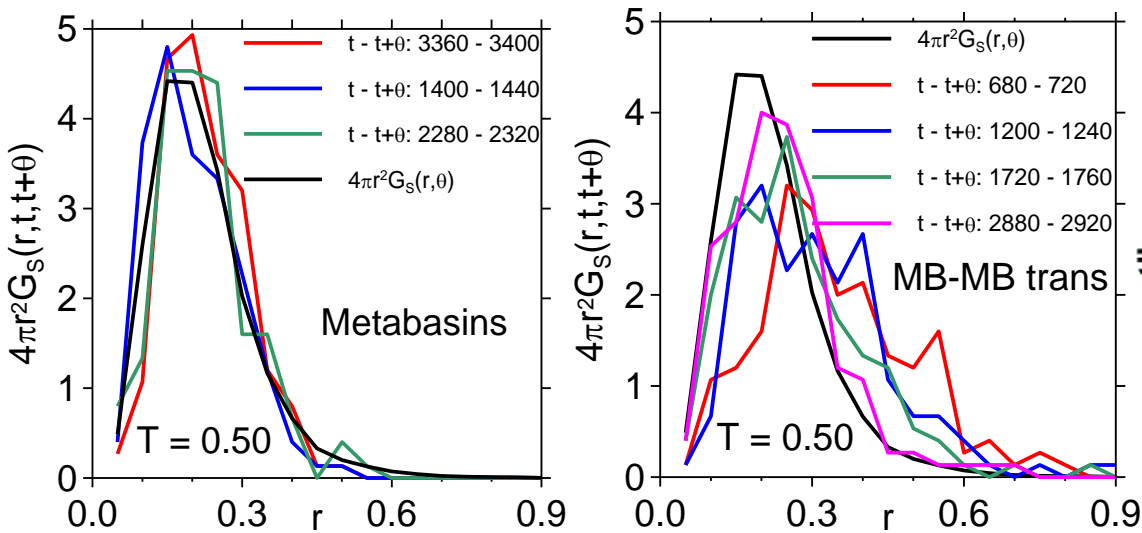
$\tau_{MB} \sim 10\% \tau_\alpha$

- Transitions between MBs: Fast. Small series (5-10) \Rightarrow α -relaxation.

- $\downarrow T$, MB residence time grows quickly.

D-CLUSTERS (relaxation heter. in space *but also in time, intermittent*)

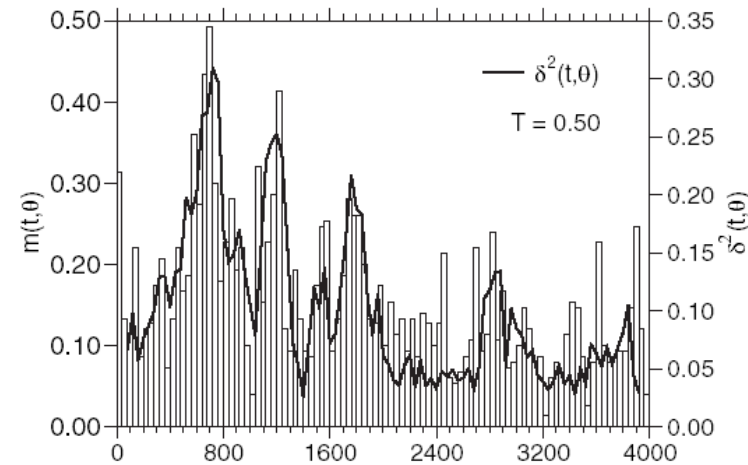
$$G_S(r, t', t'+\theta) = 1/N \sum_i (r_i(t') - r_i(t'+\theta))^2, \theta = 40 = 1\% \tau_\alpha$$



MB Transitions: Increase in displacements (all lengths.)

- Define “mobile particles” as those that move more than $0.3 \sigma_{AA}$ in a θ time interval.
- ¿How is such fraction $m(t, \theta)$? See Bars.

- **A substantial fraction of particles move collectively in a MB transition. ($\geq 20-40\%$, 30-60 particles).**

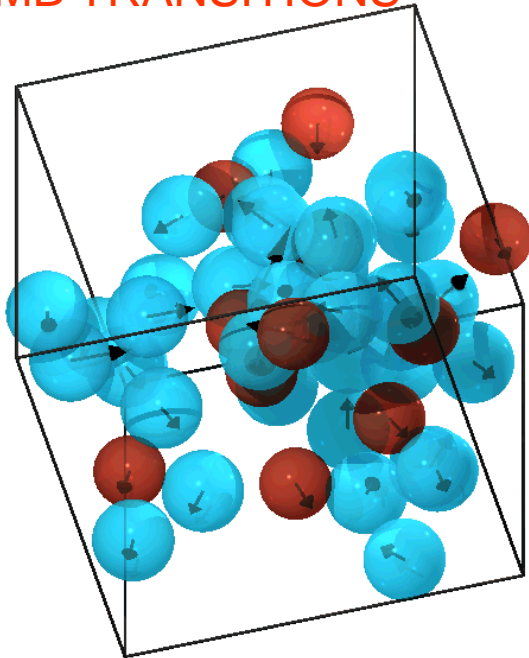


$\delta^2(t, \theta)$ = Average squared displacement in $[t-\theta/2, t+\theta/2]$ (along main diagonal of DM)

NATURE OF D-CLUSTER EVENTS

(relaxation heter. in space *but also in time, intermittent*)

MB TRANSITIONS

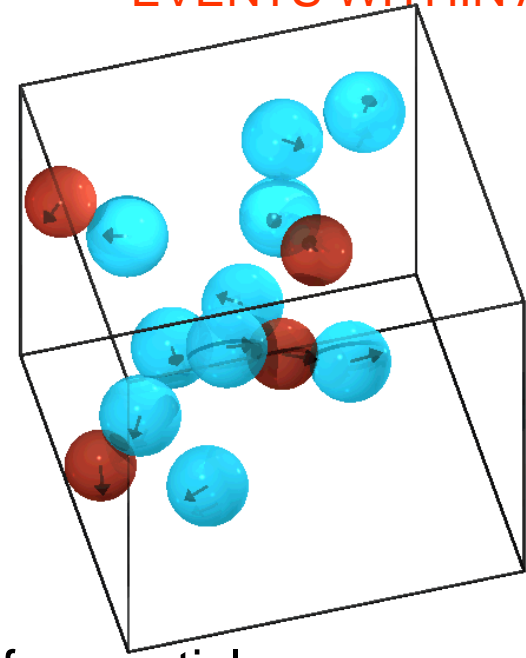


Many particles move collectively (30-60) organized in compact clusters: d-clusters

G.A. Appignanesi,
J.A.Rodríguez Fris, R.A.
Montani and W. Kob,
Phys. Rev. Lett. **96**,
057801 (2006).

G.A. Appignanesi,
J.A.Rodríguez Fris and
M.A. Frechero,
Phys. Rev. Lett. **96**,
237803 (2006).

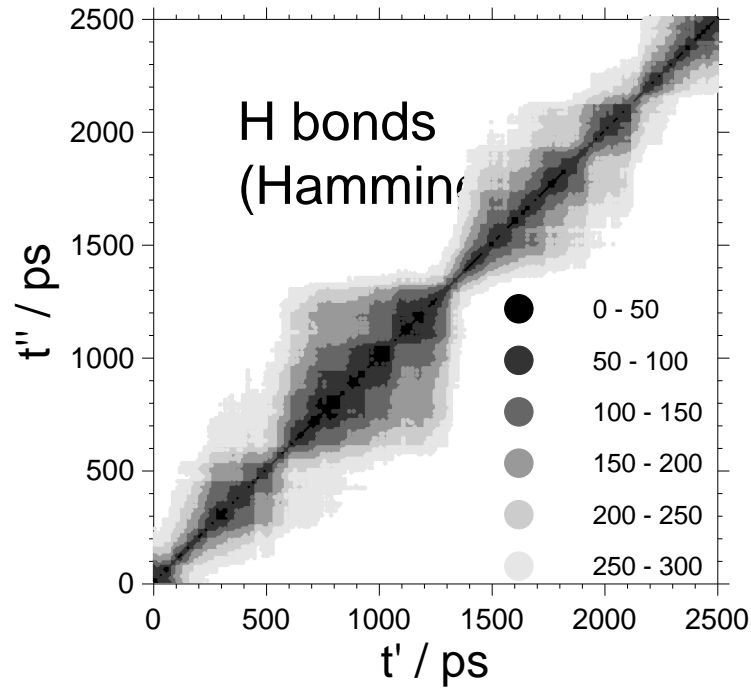
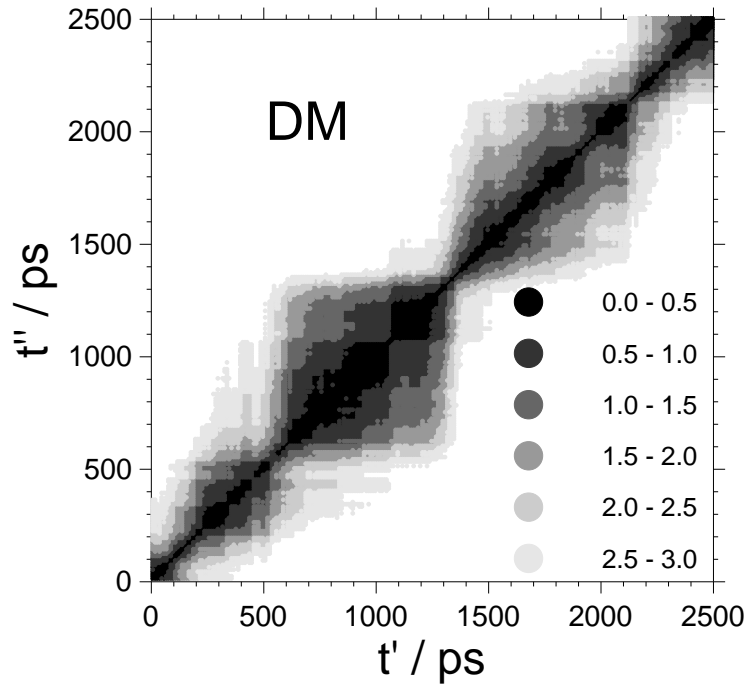
EVENTS WITHIN A MB



A few particles move collectively

- The trajectory spends large periods of “inactivity” and suffers rare fast events (dynamical “hot spots”) when a significant portion of the system becomes “active” or mobile: d-clusters.
- A series of a few of these events accomplish the α -relaxation.
- Potential candidates for the CRRs of Adam&Gibbs.

SUPERCOOLED WATER

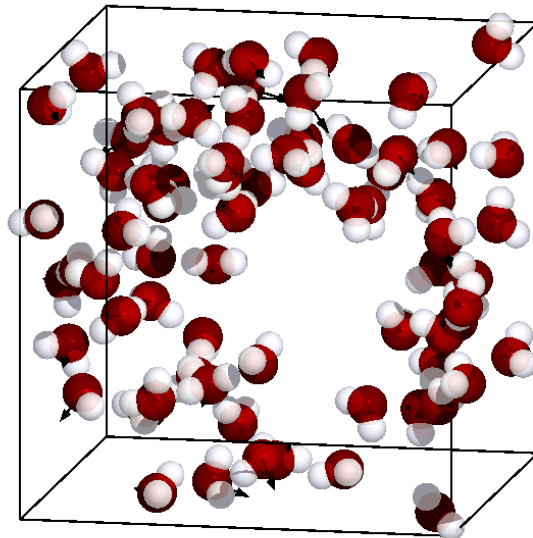


H₂O (SPCE,
T=210K)

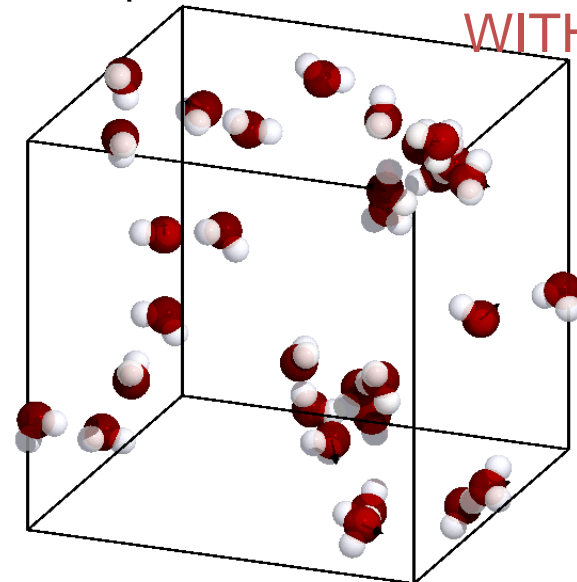
J.A. Rodríguez
Fris, G.A.
Appignanesi, E.
La Nave
and F. Sciortino,
Phys. Rev. E **75**,
041501 (2007).

MB TRANSITION

Mobile particles in regions with defects (distorted tetrahedral order, coordination greater than four and bifurcated H-bonds).



WITHIN A MB

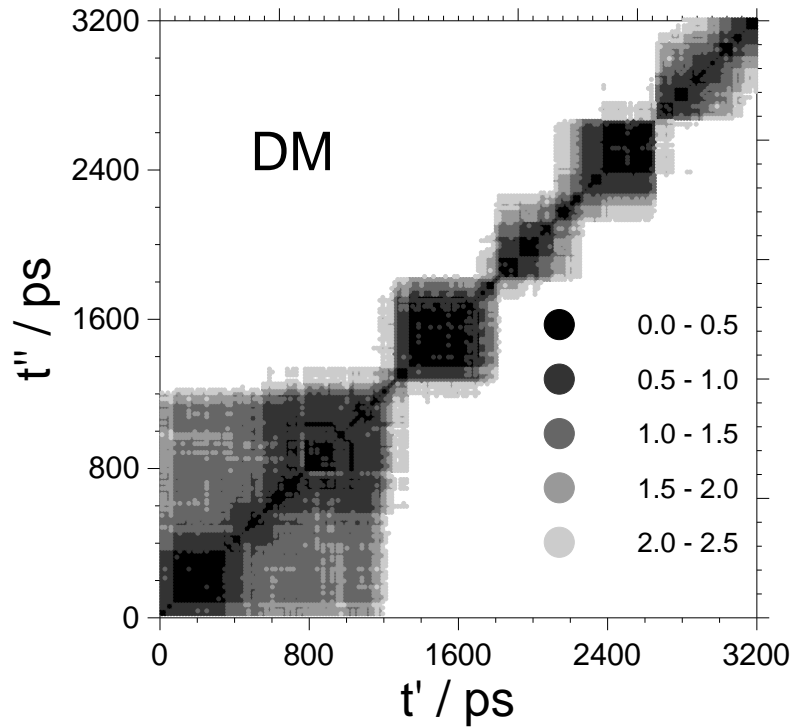


AMORPHOUS SILICA

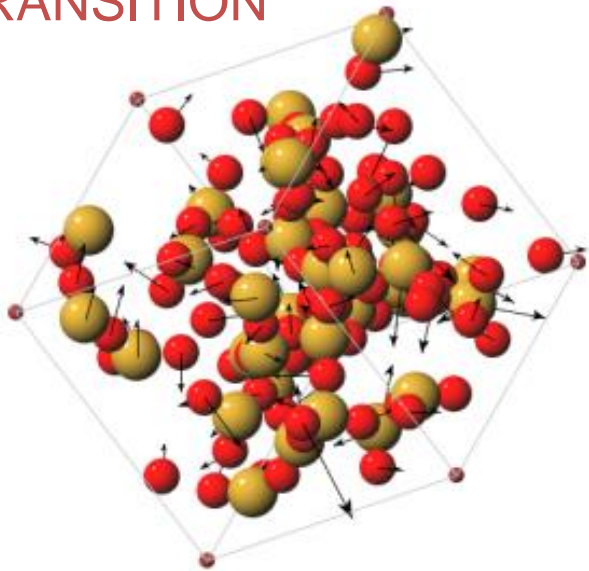
SiO_2 T=3000K

J.A. Rodríguez Fris,
G.A. Appignanesi
and W. Kob

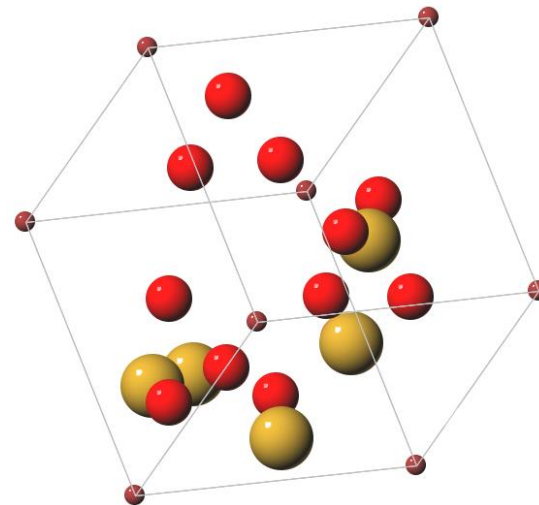
J.A. Rodríguez Fris, PhD
Thesis



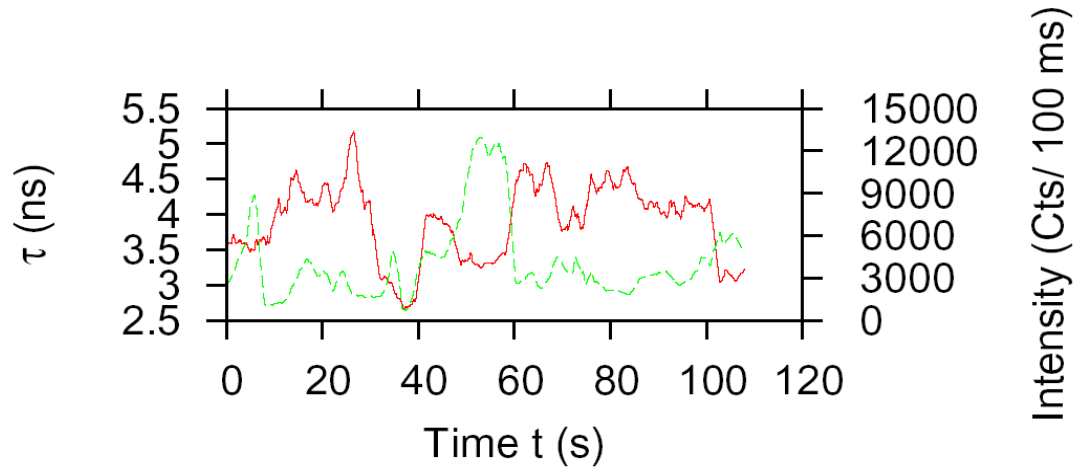
MB TRANSITION



WITHIN A MB



EXPERIMENTAL (GLASSY POLIMER)



*Single-molecule Fluorescence
Oligoestirene + probe*

R.A.L. Vallée, M. Van der Auweraer,
W. Paul and K. Binder.

Phys. Rev. Lett. **97** 217801 (2006)

FIG. 1: Fluorescence lifetime (full curve) and intensity (dashed) trajectories of a single BODIPY[®] molecule embedded in the OS matrix.

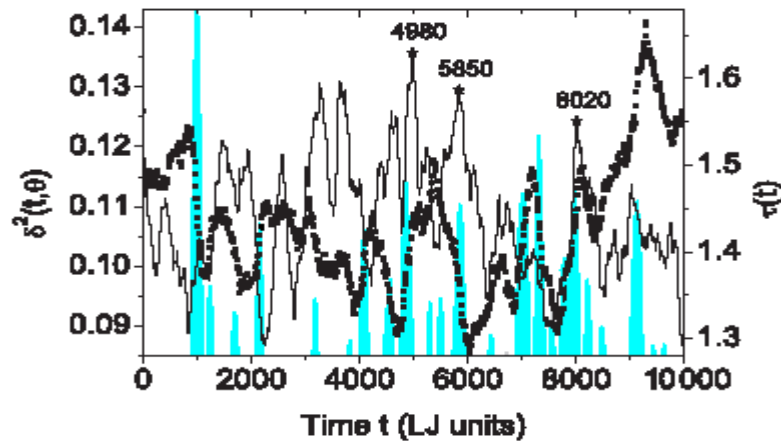


FIG. 3: Fluorescence lifetime τ (symbols, right ordinate) and average square displacement between t and $t + \theta$, $\delta^2(t, \theta)$ (line, left ordinate), trajectories calculated for a fluorophore embedded in the OS matrix at a temperature $T = 0.48$. The value of θ is 20. The gray shaded peaks represent the absolute derivatives of the fluorescence lifetime.

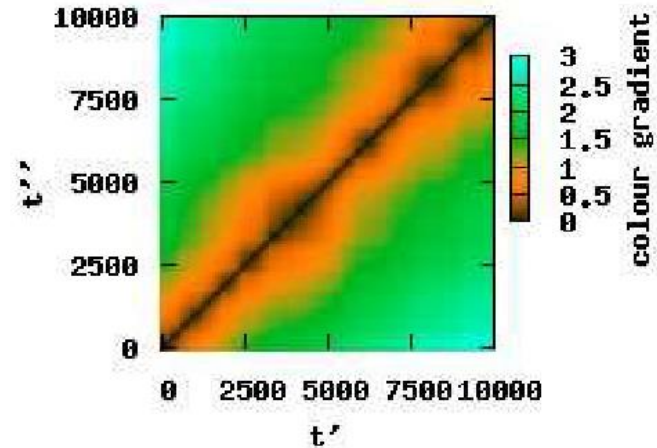


FIG. 4: Distance matrix $\Delta^2(t', t'')$ of the system used already in figure 3 for $T = 0.48$. The color levels correspond to values of $\Delta^2(t', t'')$ that are given in the color gradient on the right of the figure.

COLLOIDAL SUSPENSIONS (experimental):

Confocal microscopy data (particle tracking) (Eric Weeks)

Experimental model of glass: Order parameter is not T , but packing fraction, ϕ . Glassy behavior at large ϕ

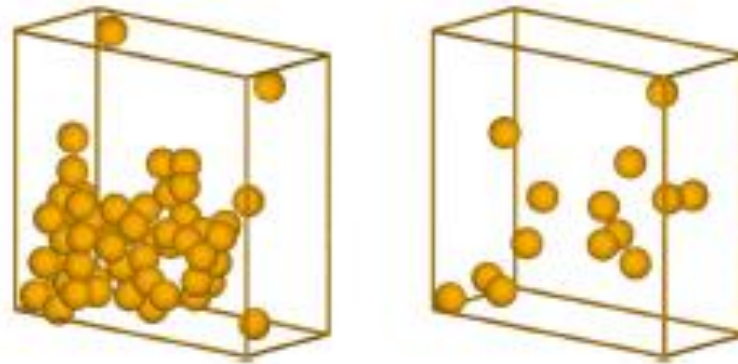
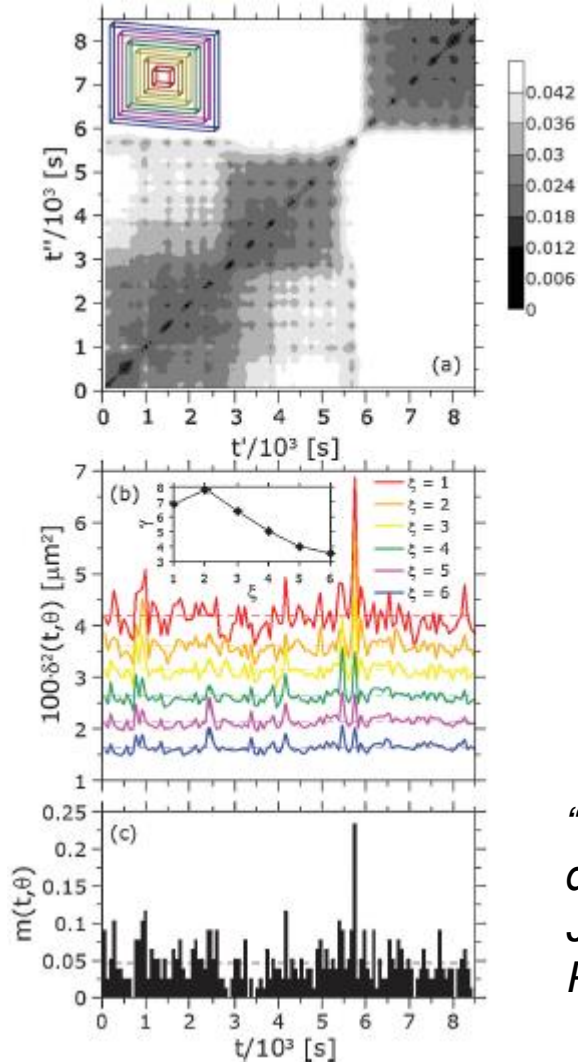


FIG. 4 (color online). Position of democratic particles for: (left) a MB-MB transition from $t = 5706$ s to $t + \theta$ and (right) $t = 7290$ s to $t + \theta$ inside a MB. The data are for $\xi = 2$, $\theta = 72$ s, $\phi = 0.56$.

*“Experimental verification of rapid, sporadic particle motions by direct imaging of glassy colloidal systems”,
J. A. Rodríguez Fris, G. A. Appignanesi and E. R. Weeks,
Physical Review Letters **107**, 065704 (2011).*

STRUCTURE-DYNAMICS

¿Is there anything in the local structure responsible for this behavior?

“At present, it is an article of faith that something in the structure is responsible for dynamics that can vary by orders of magnitude from one region of the sample to another, at T_g .” (Ediger, 2000).

Inverse question: ¿Which aspect of dynamical heterogeneity depends on structure? (Widmer-Cooper & Harrowell, Phys. Rev. Lett. 2004)

Isoconfigurational ensemble, IC (many trajectories from the same initial configuration -positions- but different momenta chosen from the appropriate Boltzmann distribution).

2D model Glass Former.

Mobile particles and dynamical heterogeneity differ from run to run (not reproducible).

DYNAMIC PROPENSITY

$$\langle \Delta r_i^2 \rangle_{IC} = \langle (r_i(\Delta t) - r_i(0))^2 \rangle_{IC}$$

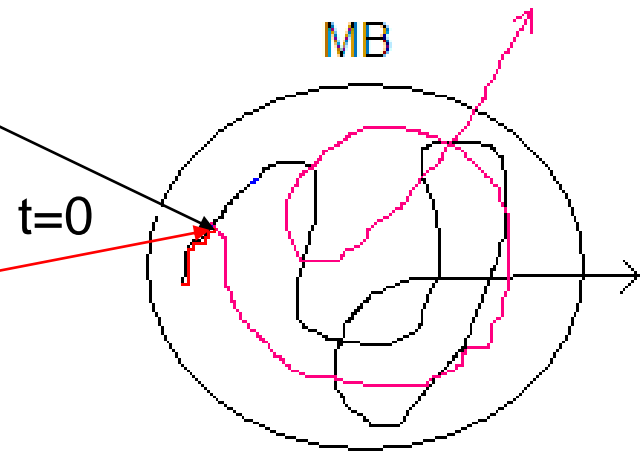
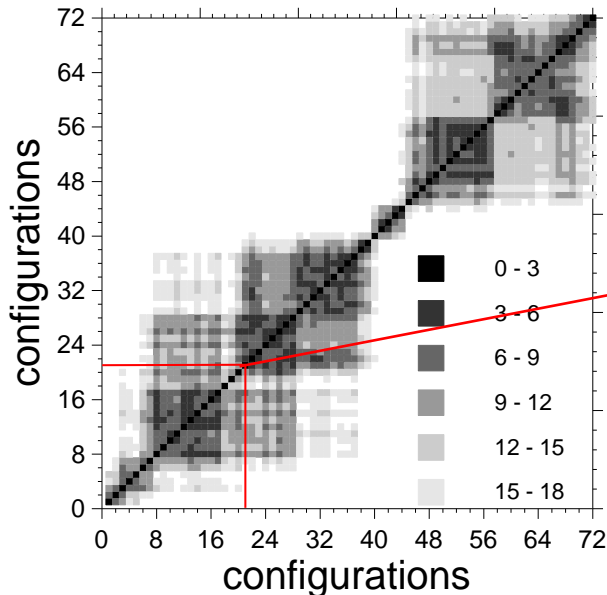
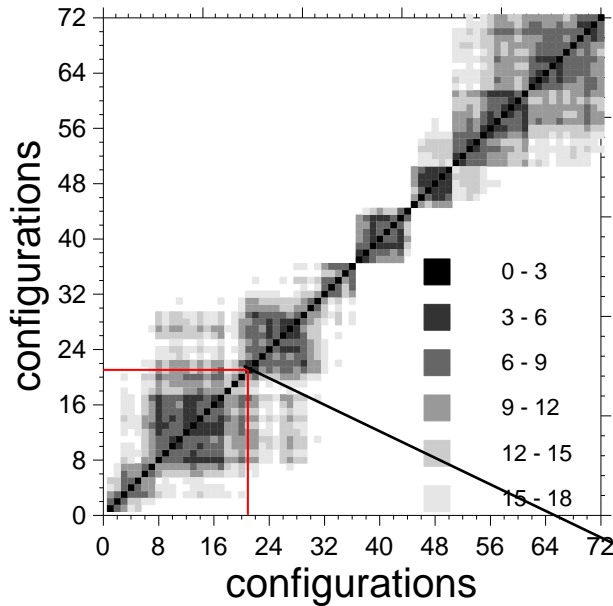
Tendency to be mobile (averaged over many IC runs).

Spatial distribution of propensity determined by initial configuration.

Regions of high propensity (compact) = “un-jammed”, “active” or “hot”.

STATISTICAL TOOL FOR MB EXPLORATION (IC METHOD)

The structure locally dictates the MB. Both trajectories confined at first to the same MB and performing transitions to different MBs. Metabasin dynamics not reproducible. Long time dynamics = Random walk on MBs. (~1% prob. to go to the same 2nd MB).



Binary Lennard-Jones 3D

LIFETIME OF INFLUENCE OF LOCAL STRUCTURE

Time-dependent Propensity:

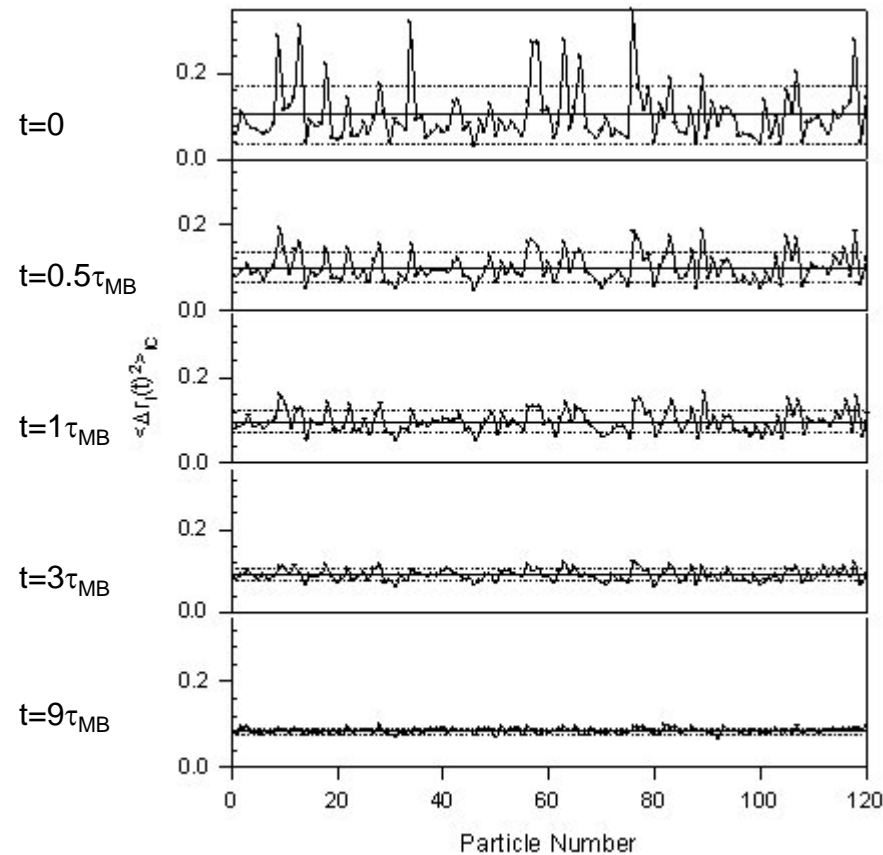
3D Binary LJ

$$\langle \Delta r_i(t)^2 \rangle_{IC} = \langle (r_i(t+\Delta t) - r_i(t))^2 \rangle_{IC}$$

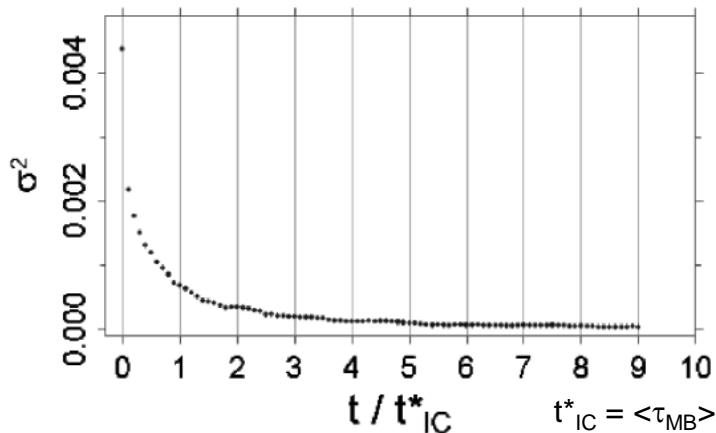
The influence of structure on dynamics is only local: Affects β but not α -relaxation.

Fades beyond the metabasin residence time ($\langle \tau_{MB} \rangle$) since it does not survive a MB transition, a d-cluster.

Propensities relax significantly (become uniform) once a d-cluster occurs.



IC: 1200 trajectories



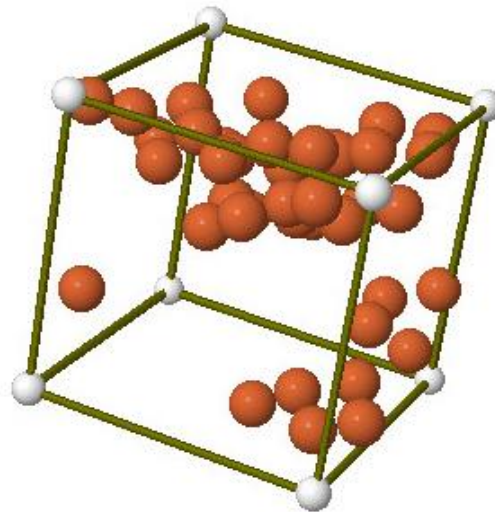
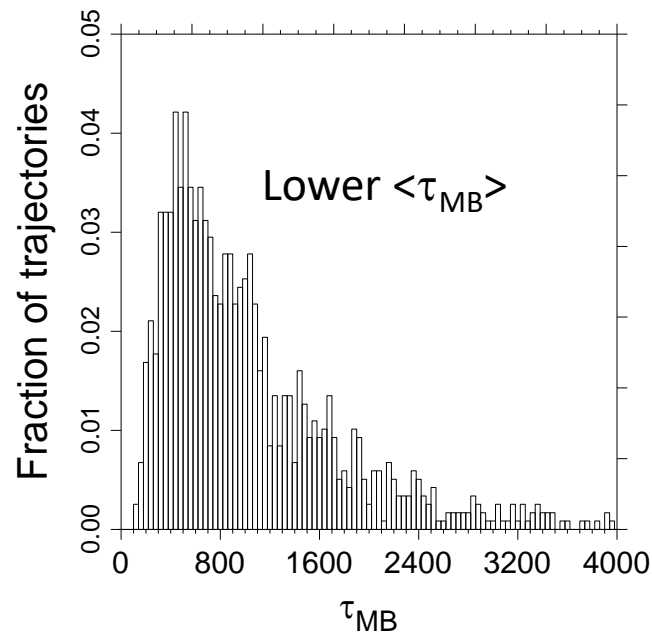
“ACTIVE” REGIONS AND DEGREE OF JAMMING

MB residence time (τ_{MB}) for trajectories of the IC

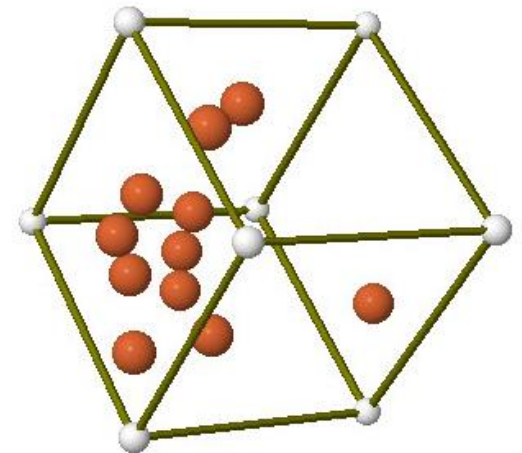
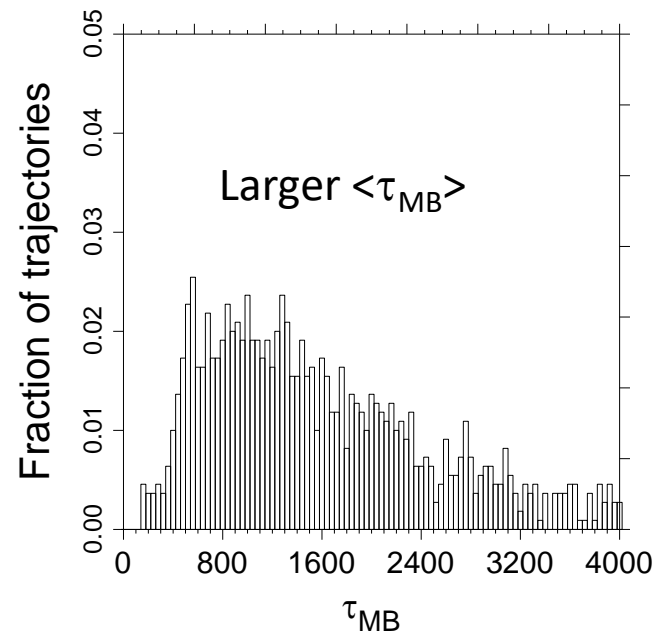
G.A. Appignanesi,
J.A. Rodríguez Fris
and M.A. Frechero
Phys. Rev. Lett. **96**,
237803 (2006).

High propensity
Un-jammed regions

Ensemble IC 1



Ensemble IC 2

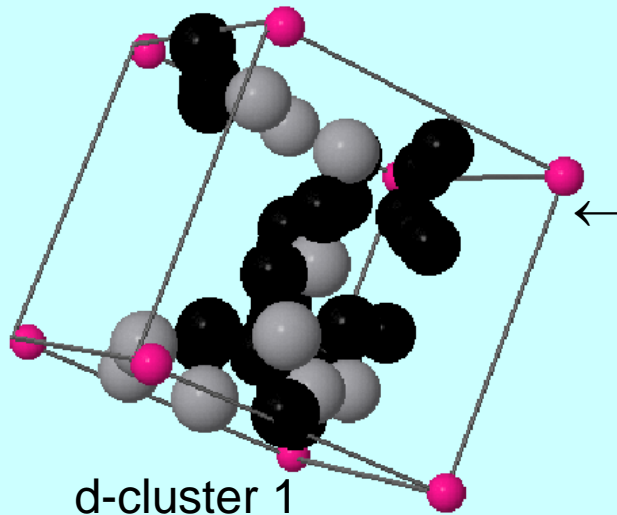
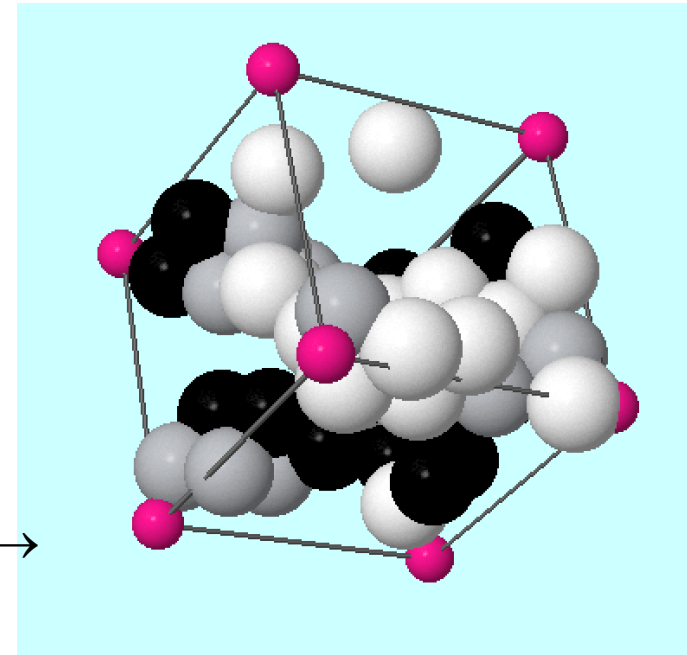


“HOT” REGIONS

High propensity (HP) regions and d-clusters are compact (at variance from “string” clusters).

Each trajectory of the IC escapes from the MB by means of a different d-cluster, relaxing the HP region.

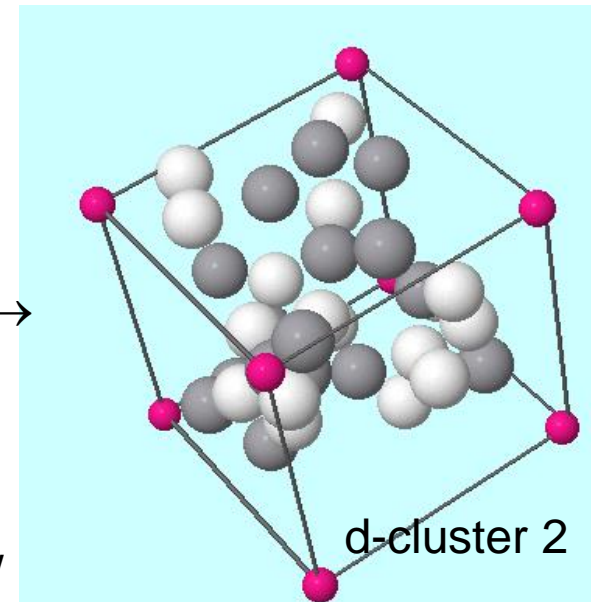
HP particles (in black or white, respectively: the ones which shall take part of a d-cluster in two different trajectories of the same IC). →



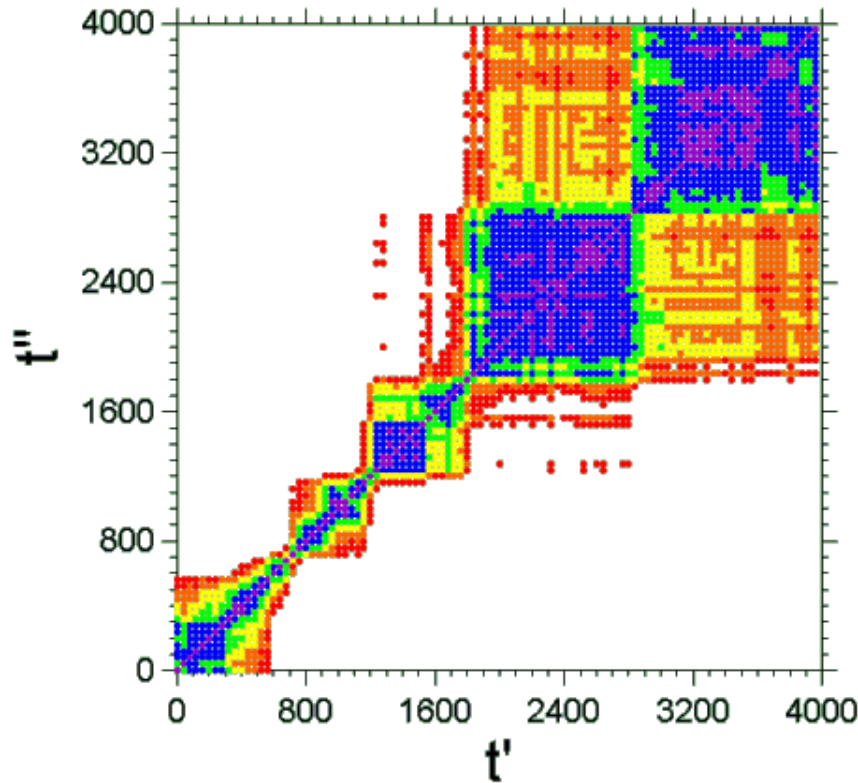
Full d-clusters (first MB transition) for the two trajectories.

We indicate in gray the particles that are also HP particles. →

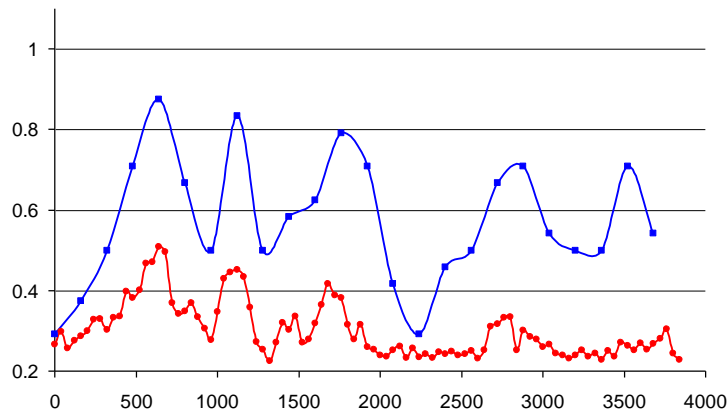
M. A. Frechero, L. M. Alarcón,
E. P. Schulz and G. A.
Appignanesi, Physical Review
E (2006).



INTERPLAY BETWEEN STRUCTURE AND DYNAMICS

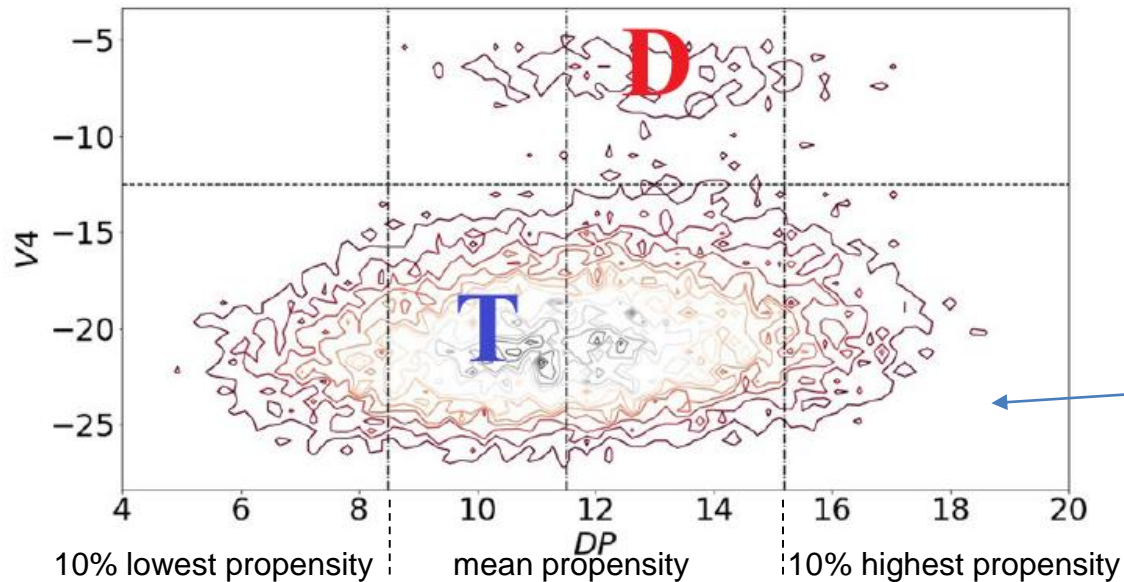


- IC ensembles at different times from structures *over a given trajectory*.
- Bottom graph: Fraction of changes in the 20% highest HP particles between consecutive ICs (blue line). Peaks coincide with that of $\delta^2(t, \theta)$ (red line) which marks MB transitions (d-clusters). **d-clusters reformulate jamming.**



Interplay between structure and dynamics (“hot” structurally un-jammed regions and dynamical “hot spots”):

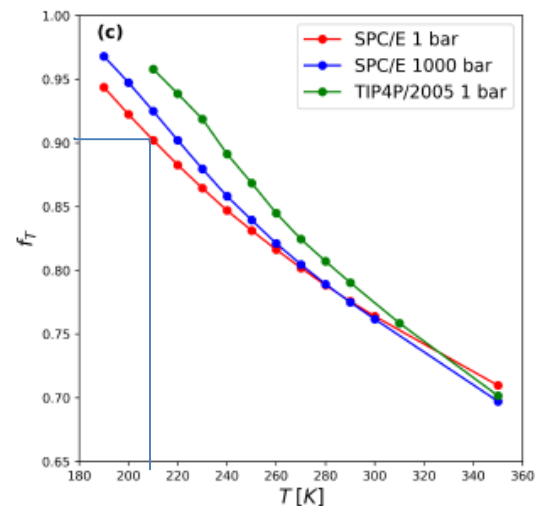
HP regions promote d-clusters within them and d-clusters relax HP regions to generate new distinct un-jammed domains.



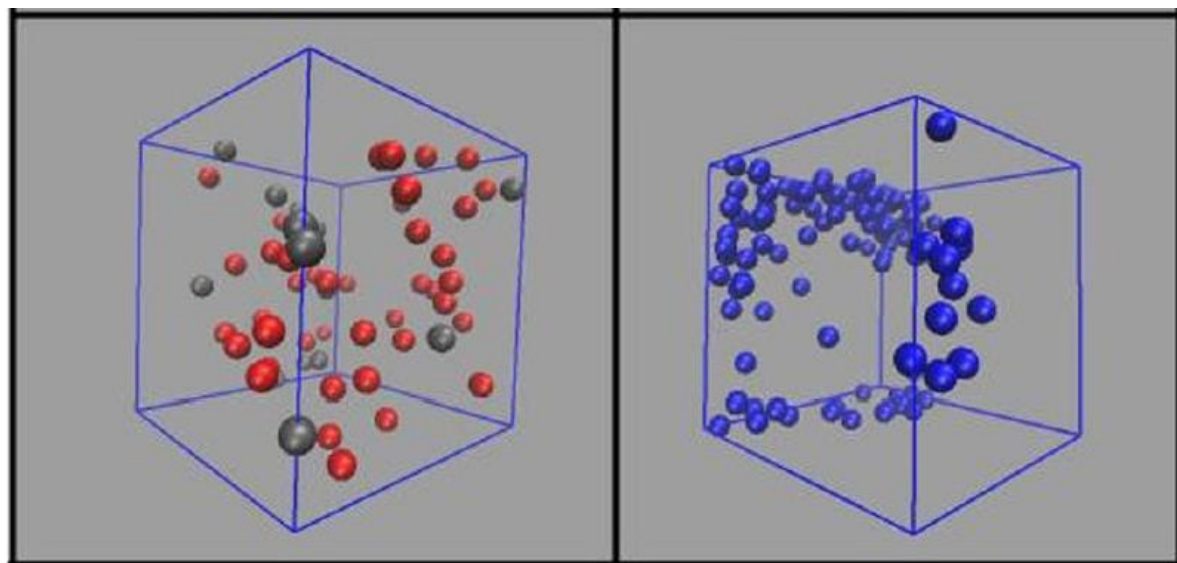
SPC/E WATER Supercooled (T=210K)

T and D from V_4 classification

Correlation v_4 - DP (dynamic propensity)



D ~10%, T ~90%



Spatial distribution correlation

D molecules: Propensity highest than mean value (red), otherwise (grey)

10% lowest propensity molecules: T molecules (blue), no D molecules in this config.