The Growth of Dynamic Heterogeneities in Supercooled Water

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Boston University

Outline

- Introduction and motivation

- The TIP5P model

- Simulation results
  - Molecular mobility
  - Clustering of mobile molecules
  - Effect of orientational order

- Discussion and conclusions

Water

Is anomalous thermodynamically...

Density maximum

Fluctuations grow upon cooling

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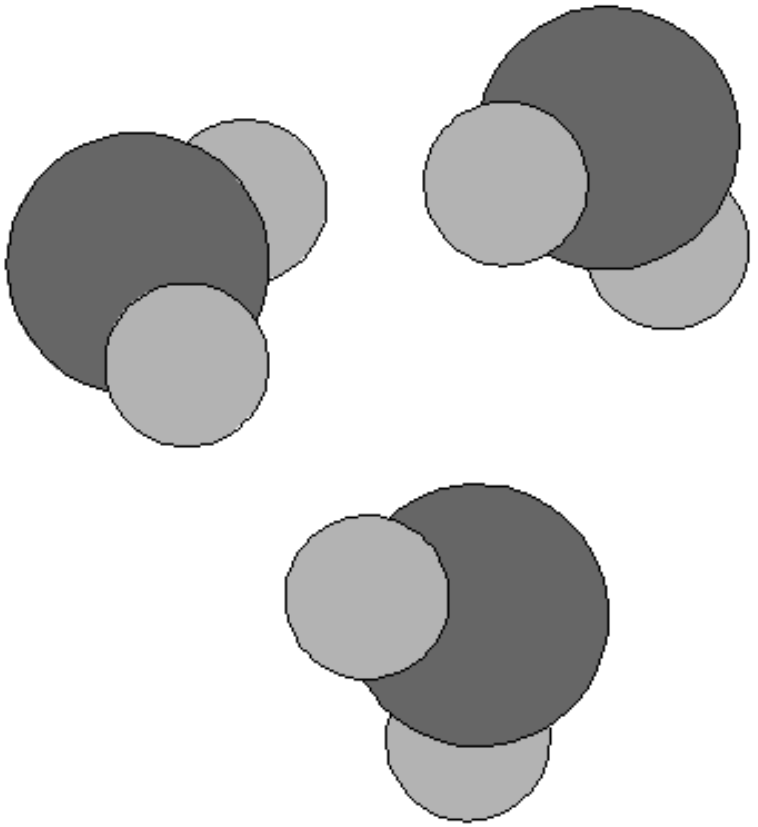
These effects are enhanced upon supercooling.

Hydrogen Bonds



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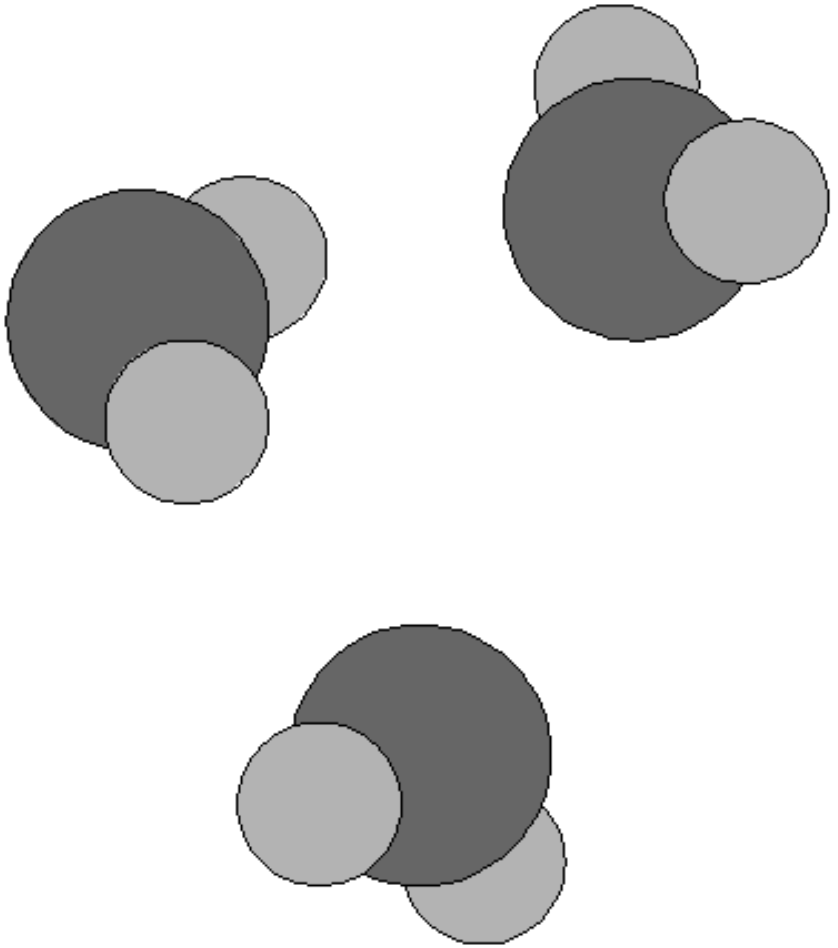
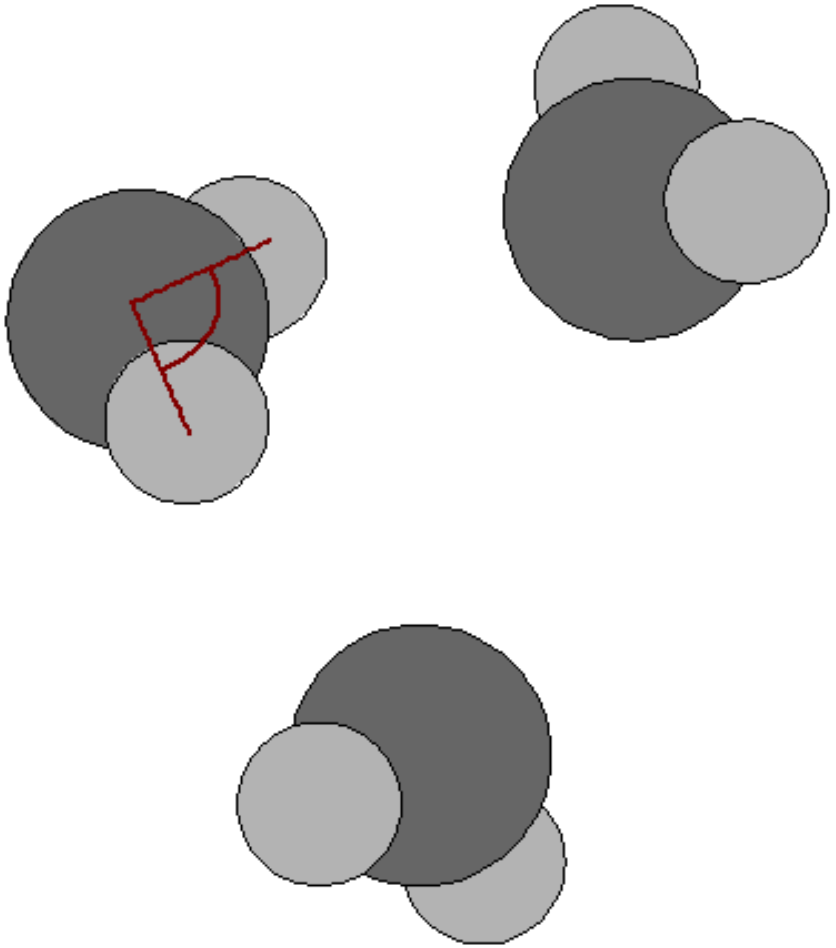


Energy decrease

vs

Entropy decrease

Hydrogen Bonds



H-O-H angle: 104.5°

Tetrahedral angle: 109.5°

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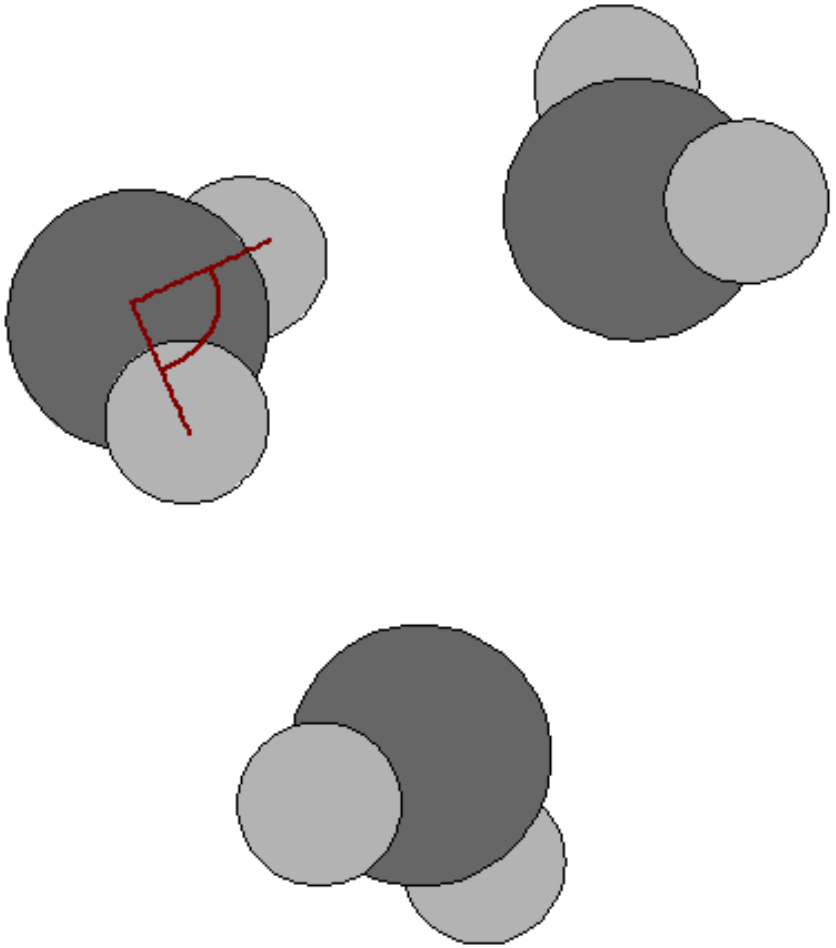

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Bonding leads to an open network
with 4 nearest neighbors

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Traditional liquid:

- homogeneous
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In equilibrium:

- over very short times, molecules appear identical
- over very long times, molecules appear identical

Heterogeneity in dynamics implies an intermediate timescale

Questions

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If so, what is its length scale?

What are the time scales involved?

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Experiments:

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We will look at a model and do simulations:

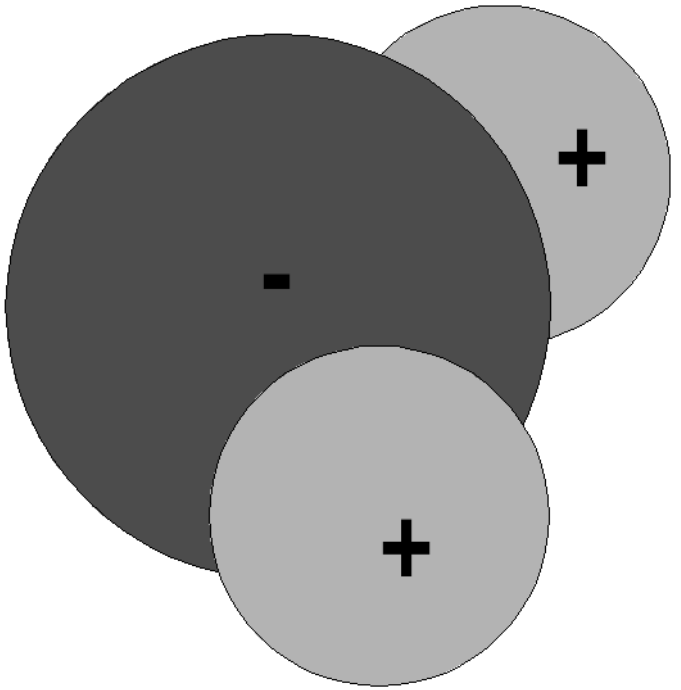
- Overcomes both experimental difficulties

Realistic Water Models

Primitive Model:

Hard sphere

Square well

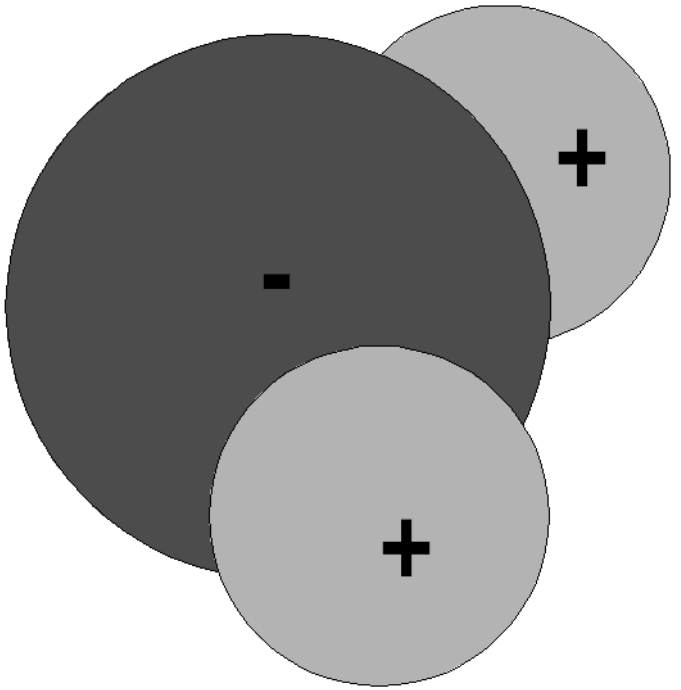


Realistic Water Models

3-Point Model:

Lennard-Jones

Coulombic

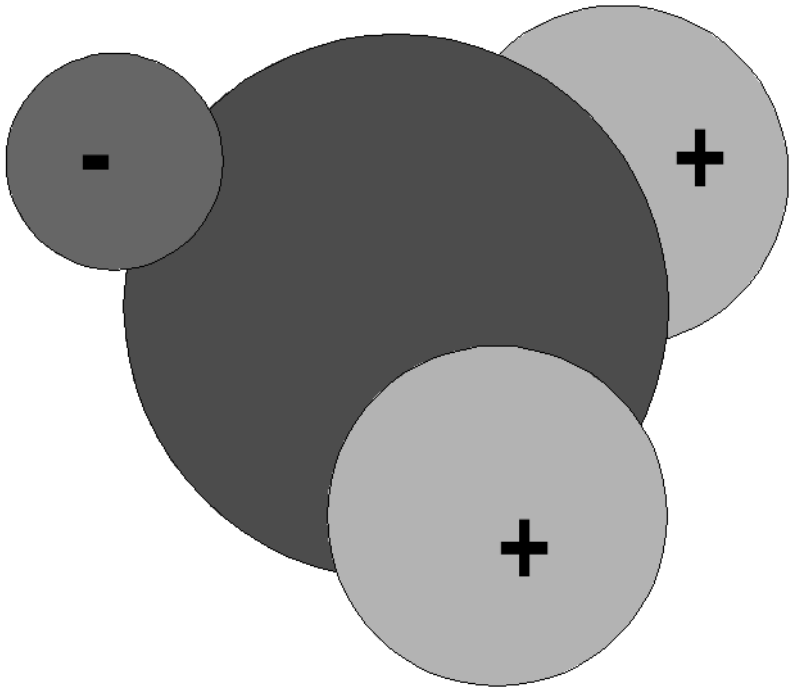


Realistic Water Models

4-Point Model:

Lennard-Jones

Coulombic

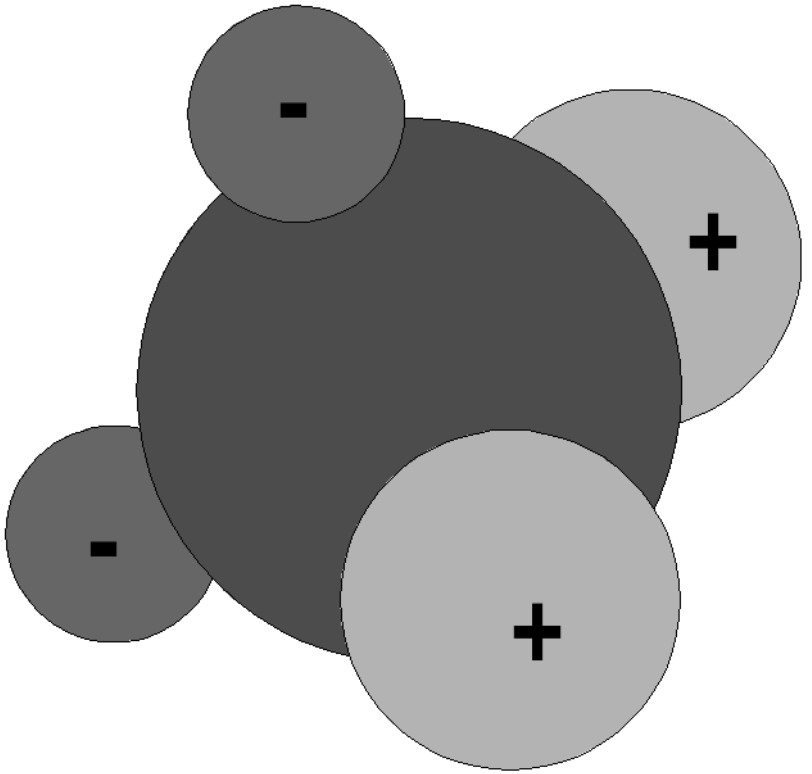


Realistic Water Models

5-Point Model:

Lennard-Jones

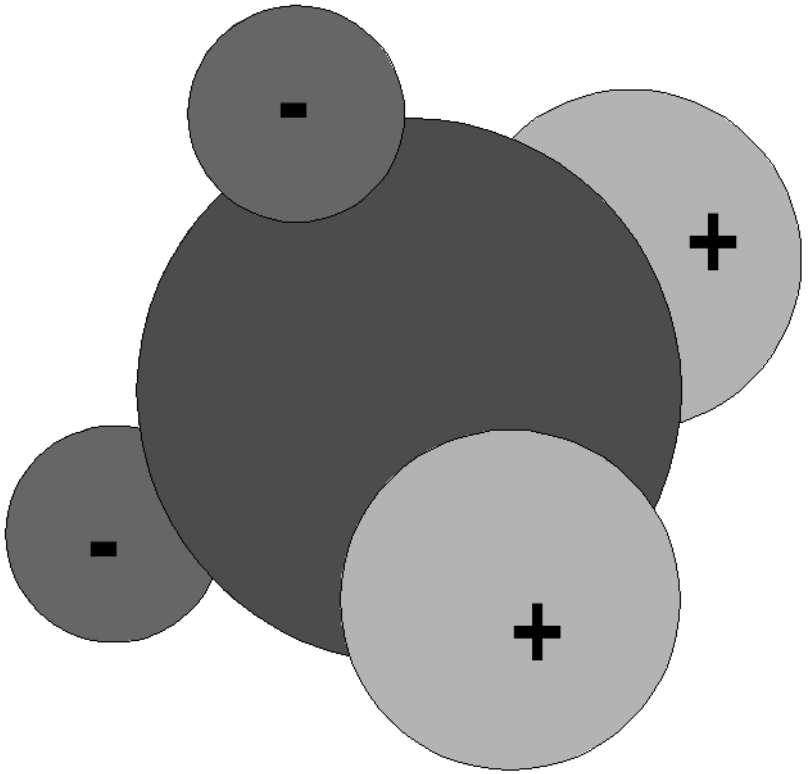
Coulombic



Realistic Water Models

TIP5P

LJ energy	0.16 kcal/mol
LJ distance	3.12 A
H charge	0.241 e
LP charge	0.241 e
O-H distance	0.9572 A
O-LP distance	0.7000 A
H-O-H angle	104.52°
LP-O-LP angle	109.47°



Fit to reproduce density from -37.5 K – 62.5 K

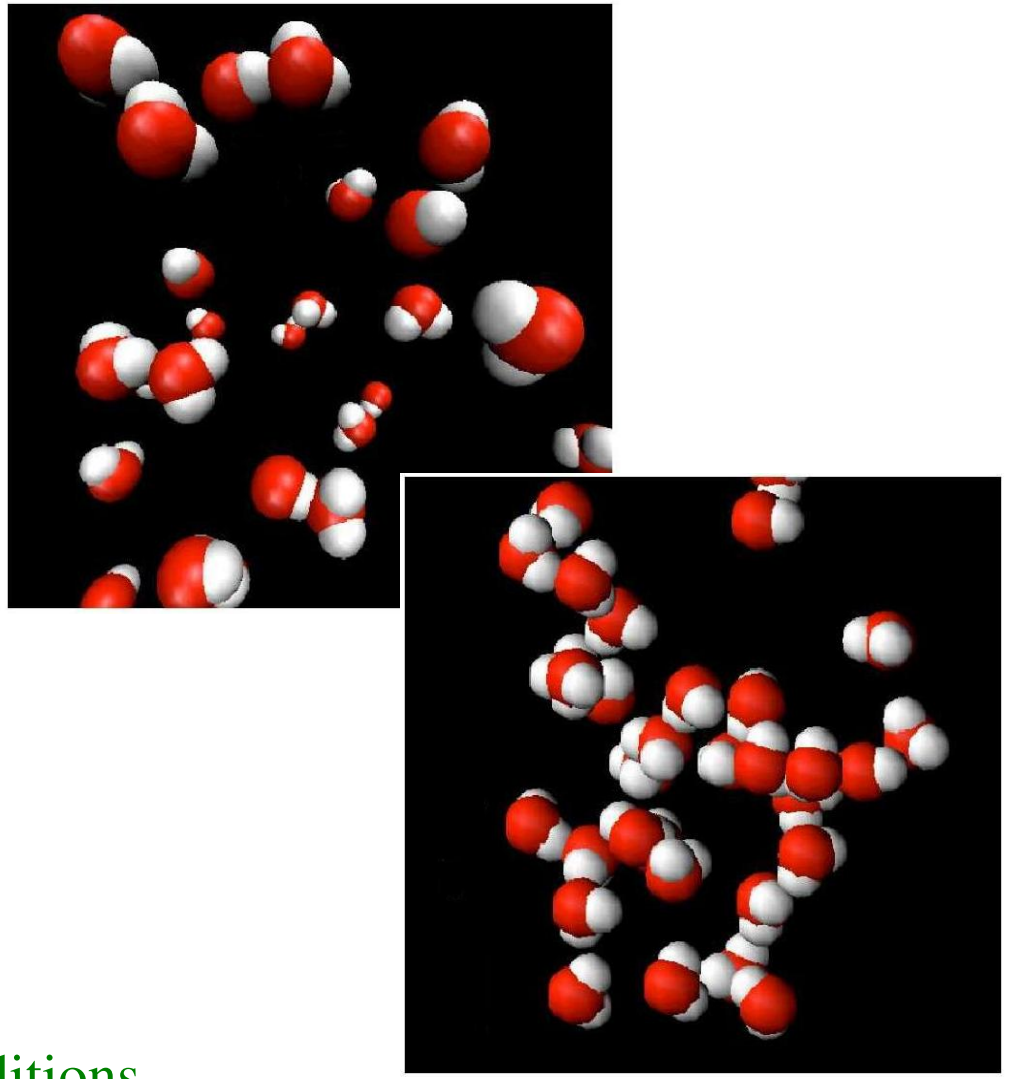
Mahoney MW and Jorgensen WL, J Chem Phys 112, 8910 (2000).

We Do Simulations

N = 512 water-like molecules

P = 0.01 Mpa

T = 235K – 300 K

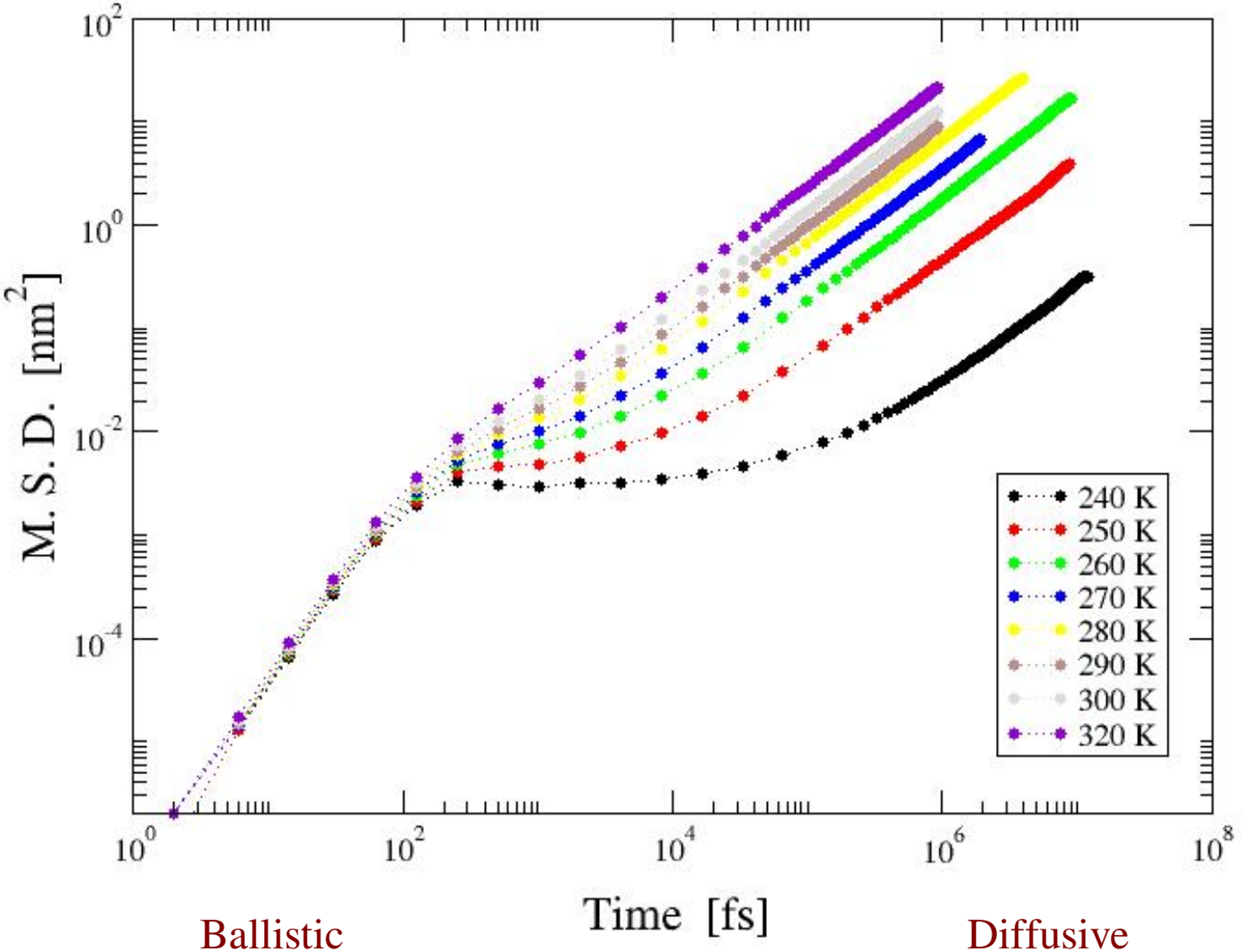


Boxsize is ~2.5 nm

We utilize periodic boundary conditions

Positions of all molecules saved in logarithmic steps

Mean Squared Displacement



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$\langle x^2 \rangle \sim \langle v^2 \rangle t^2$

Diffusive

$\langle x^2 \rangle \sim Dt$

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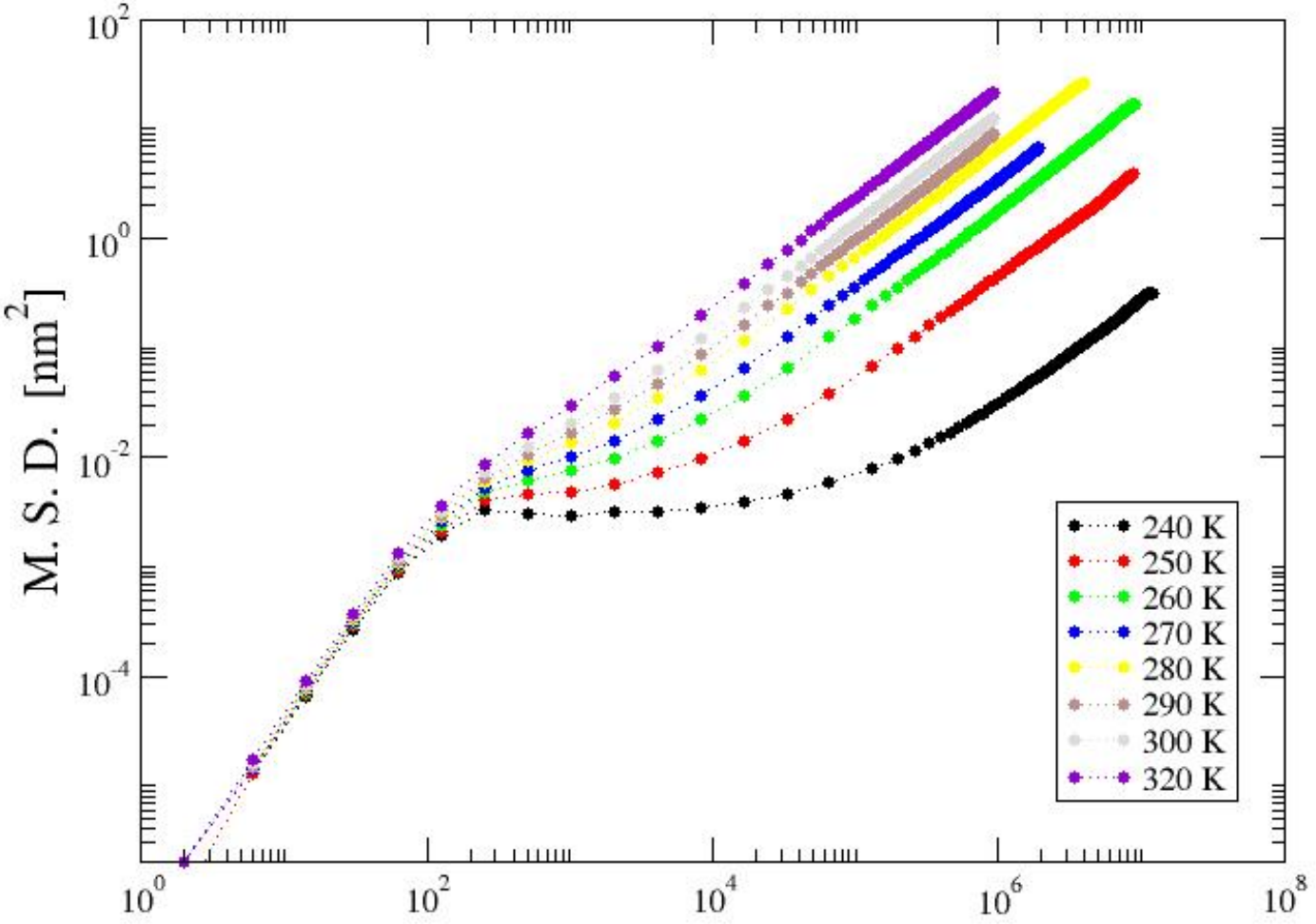

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Caging often reflects non-Gaussian distribution of mobilities

Non-Gaussian Parameter

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

Quantifies deviations from
Gaussian distribution of displacements

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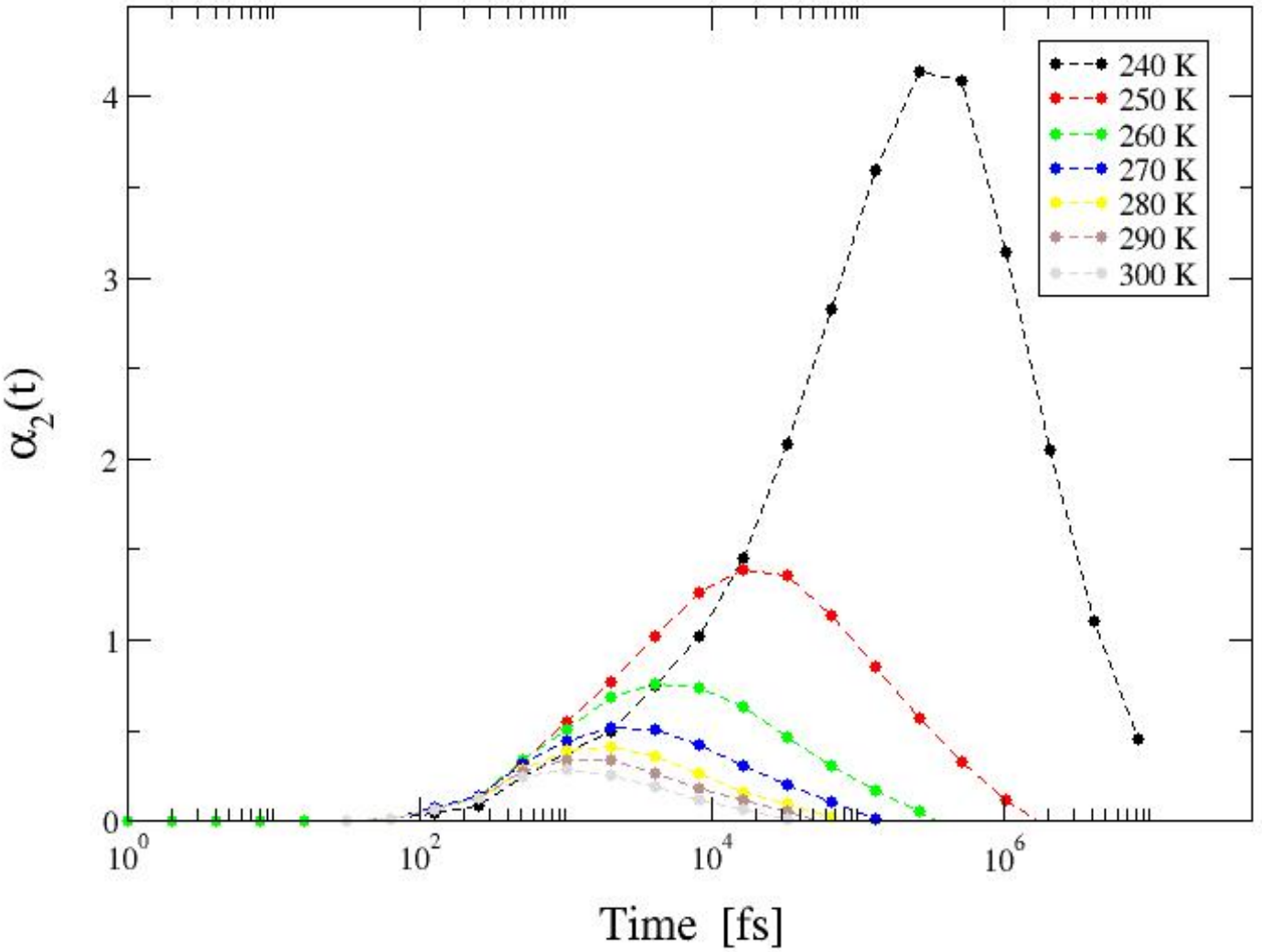

Mobile Clusters

Choose the 7% most mobile molecules over each time t

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$$\langle n(t) \rangle_{\mathrm{w}} = \langle n^2(t) \rangle \; / \; \langle n(t) \rangle$$

unity for isolated molecules

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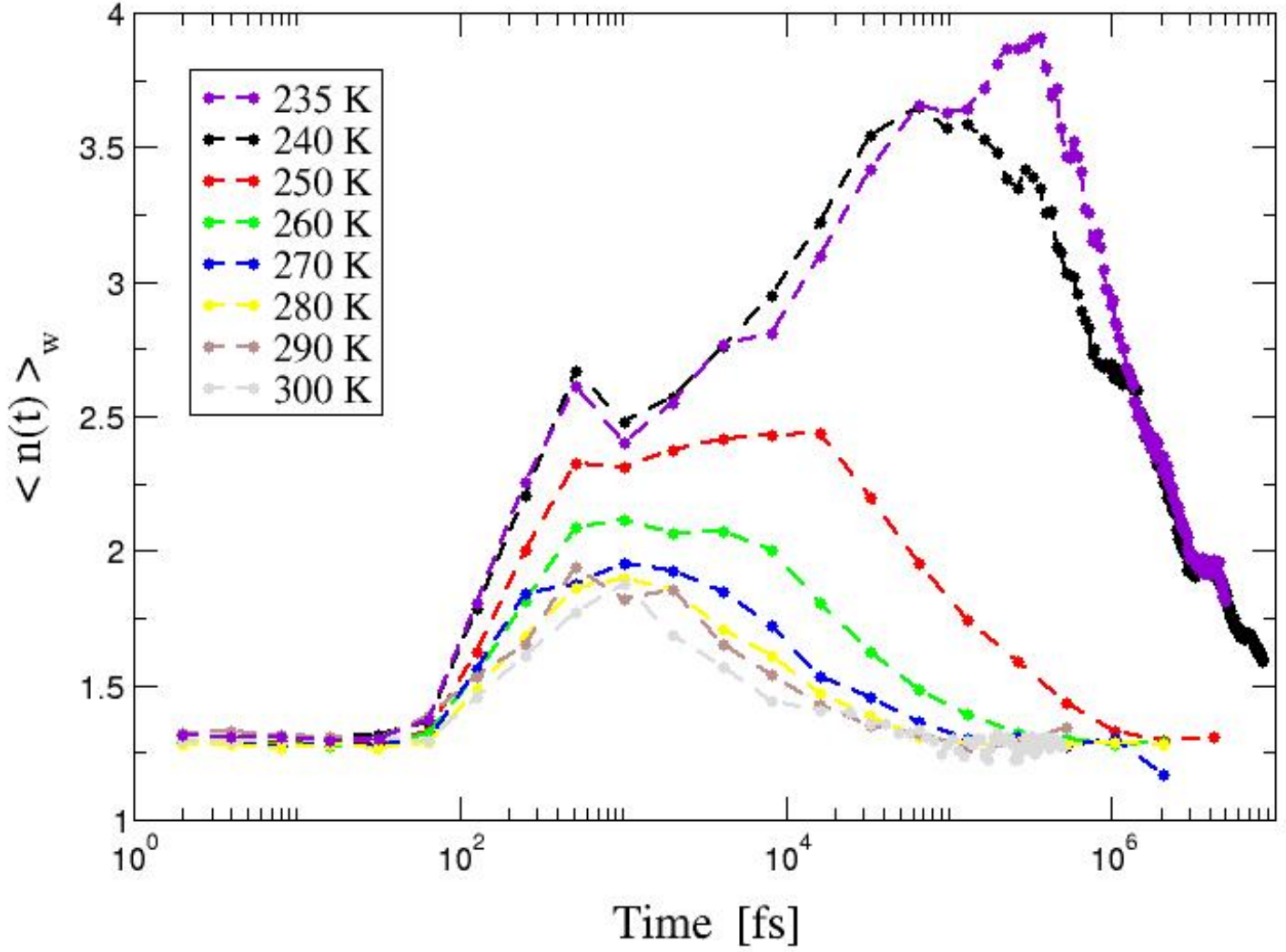
Gives a length scale to dynamic heterogeneity

Size of Mobile Clusters

$$\langle n(t) \rangle_w = \langle n^2(t) \rangle \, / \, \langle n(t) \rangle$$



Orientational Order

Quantify the degree of tetrahedrality:

$$Q_k = 1 - \frac{3}{8}\sum_{i}^{3}\sum_{j=i+1}^{4}[cos(\psi_{ikj}) + \frac{1}{3}]^2$$

$-3 < Q_k < 1$

$Q_k = 0$ for random arrangement

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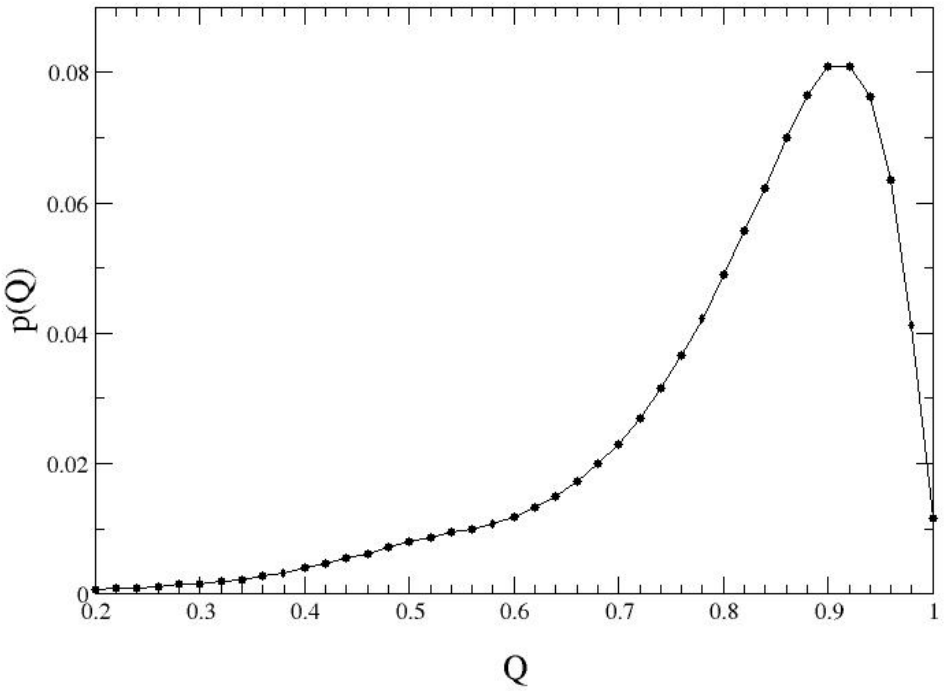
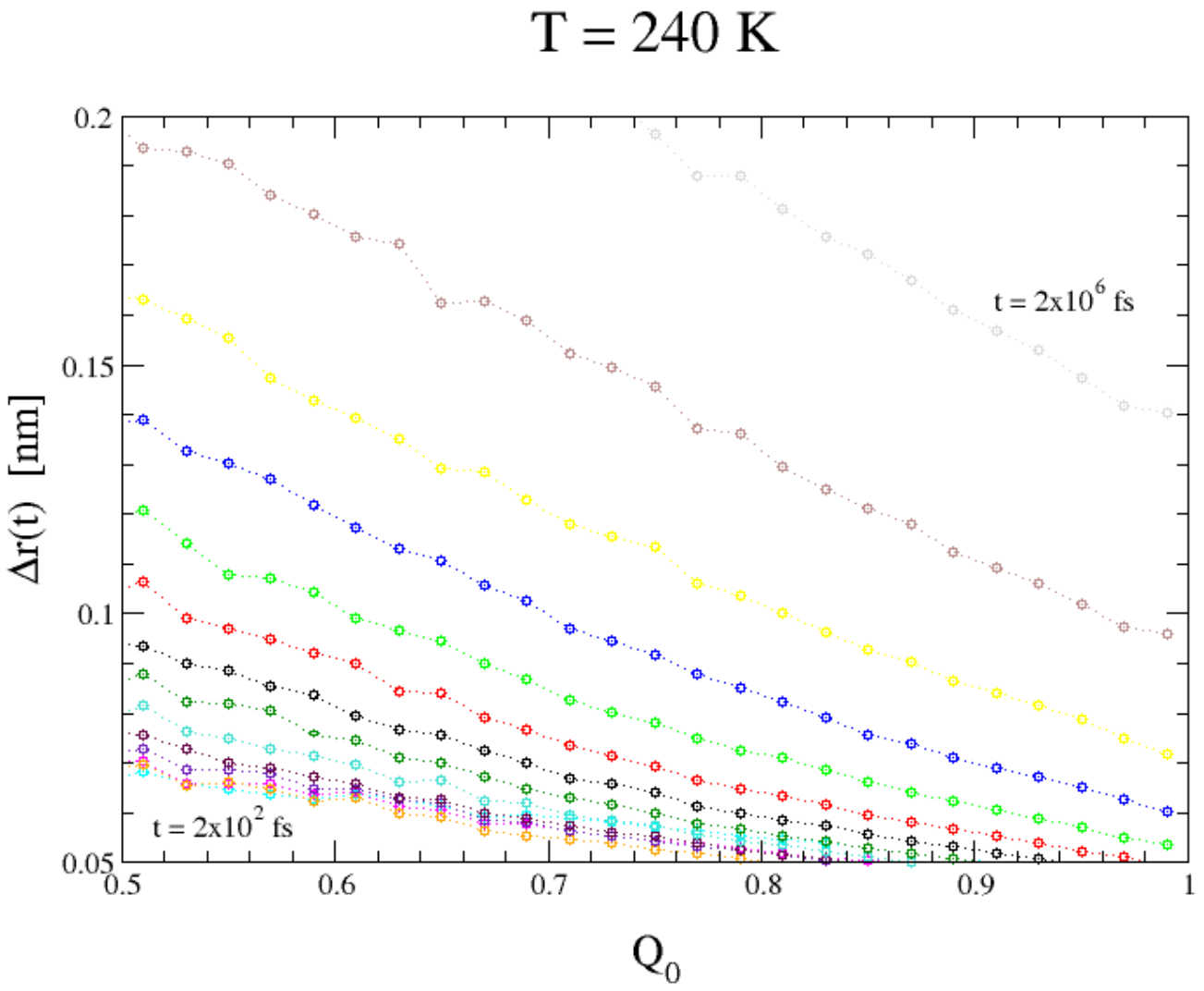
T = 240K



Effect of Initial Order



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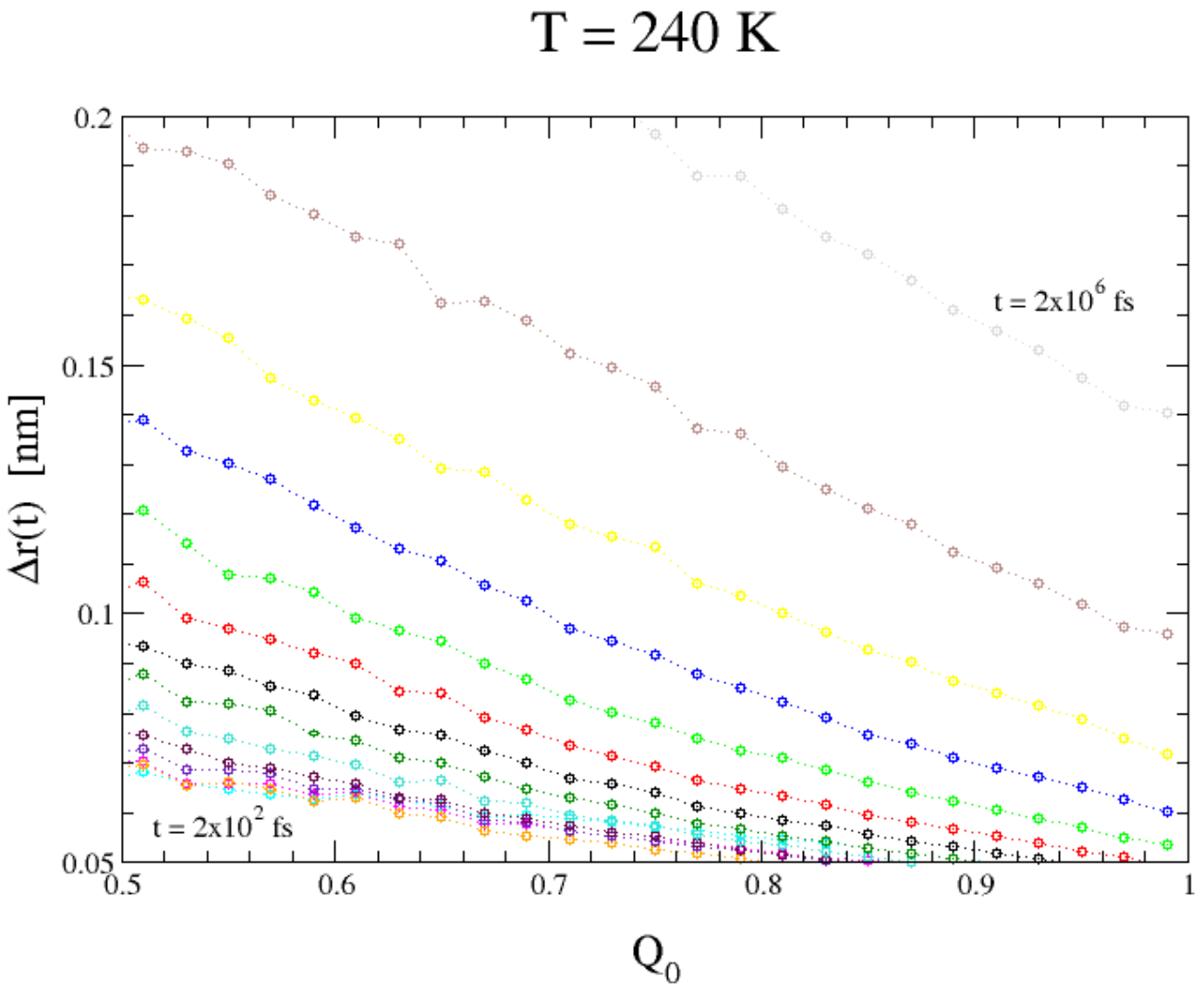

Increased order means decreased mobility

Order of Mobile Molecules

$$Q_{\mathrm{DH}}(t) = \frac{1}{N_{\mathrm{fast}}} \sum_{k=1}^{N_{\mathrm{fast}}} Q_k$$

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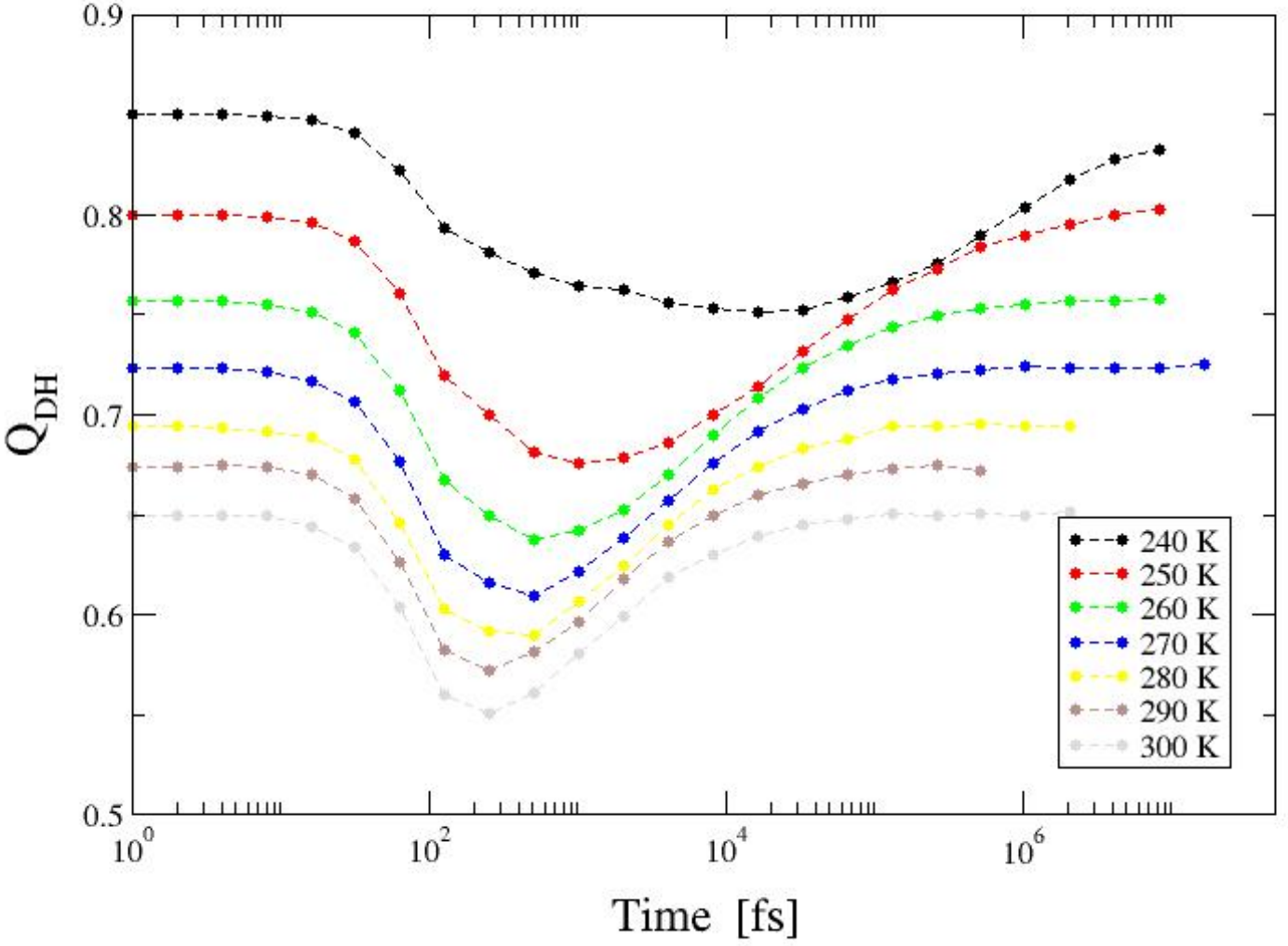
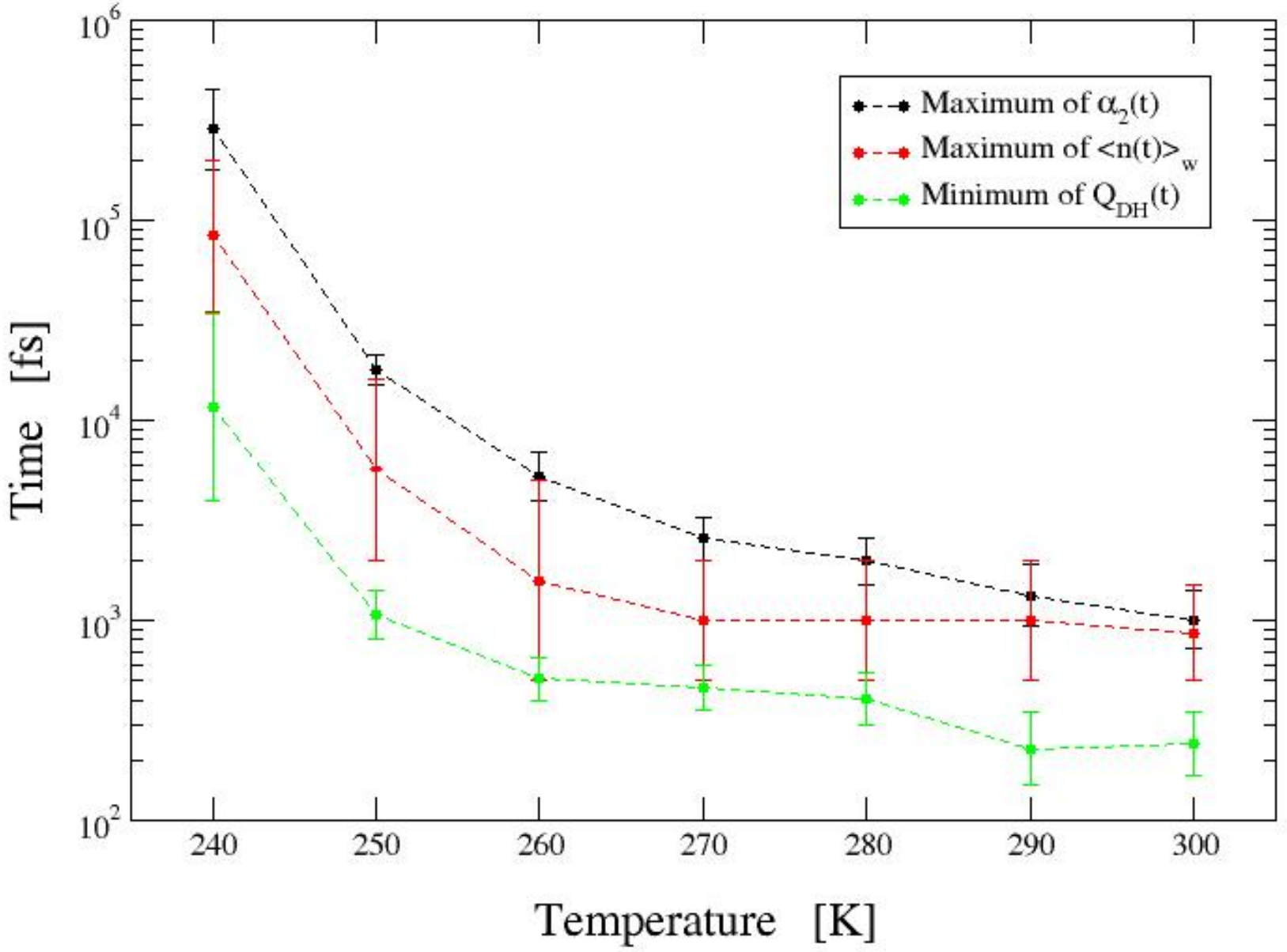


Time Scales


Maximum of $\alpha_2(t)$
Maximum of $\langle n(t) \rangle_w$
Minimum of $Q_{DH}(t)$
Time [fs]
10^6
10^5
10^4
10^3
10^2
240
250
260
270
280
290
300
Temperature [K]

Physical Picture

Fluctuations lead to molecules with less-than-average order.

This facilitates mobility among these molecules.

Those molecules which are able to stay mobile over longer periods of time are those whose neighbors are also mobile.

The resulting heterogeneities create a separation between 'fast' and 'slow' molecules, leading to a distribution of displacements which broadens with time.

This continues until the time of cage-breaking, after which even the 'slow' molecules have had enough time to break free of their environment.

Conclusions

We identify dynamic heterogeneity in TIP5P water, and an associated length scale.

We identify three time scales characteristic to the dynamic heterogeneity, which occur in a set order:

- The average order of the fastest molecules is a minimum
- The clustering of the fastest molecules is largest
- The distribution of displacements is broadest

These length and time scales grow upon cooling.

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