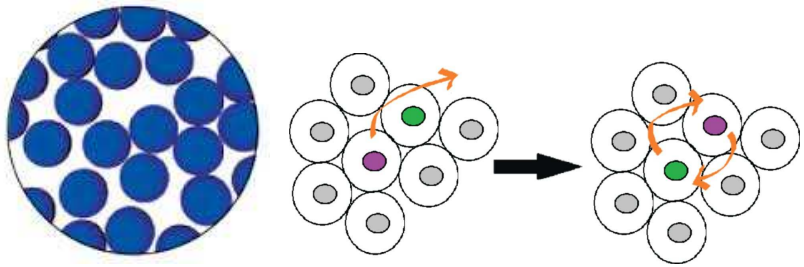
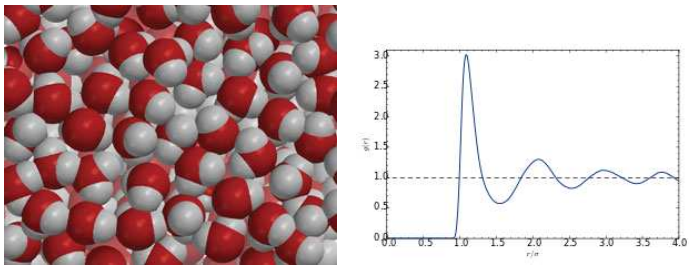
Observing the Dynamics of Molecules at Their Own Scale : A Continuous Time Random Walk Approach

Biswaroop Mukherjee,

Thematic Unit of Excellence
Computational Materials Science
S. N. Bose National Centre for Basic Sciences
Kolkata

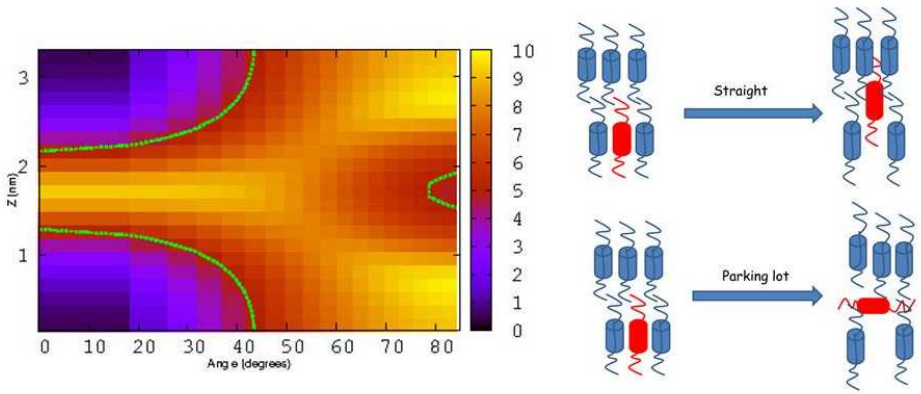
Liquids

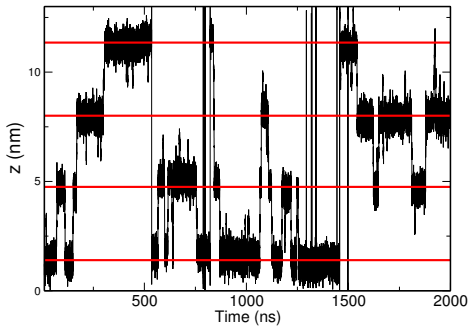




- Liquids posess short-ranged positional order.
- This induces caging and cage breaking events.
- Give rise to intermittencies. Thermally accessible barriers.
- True for both translation and rotation.

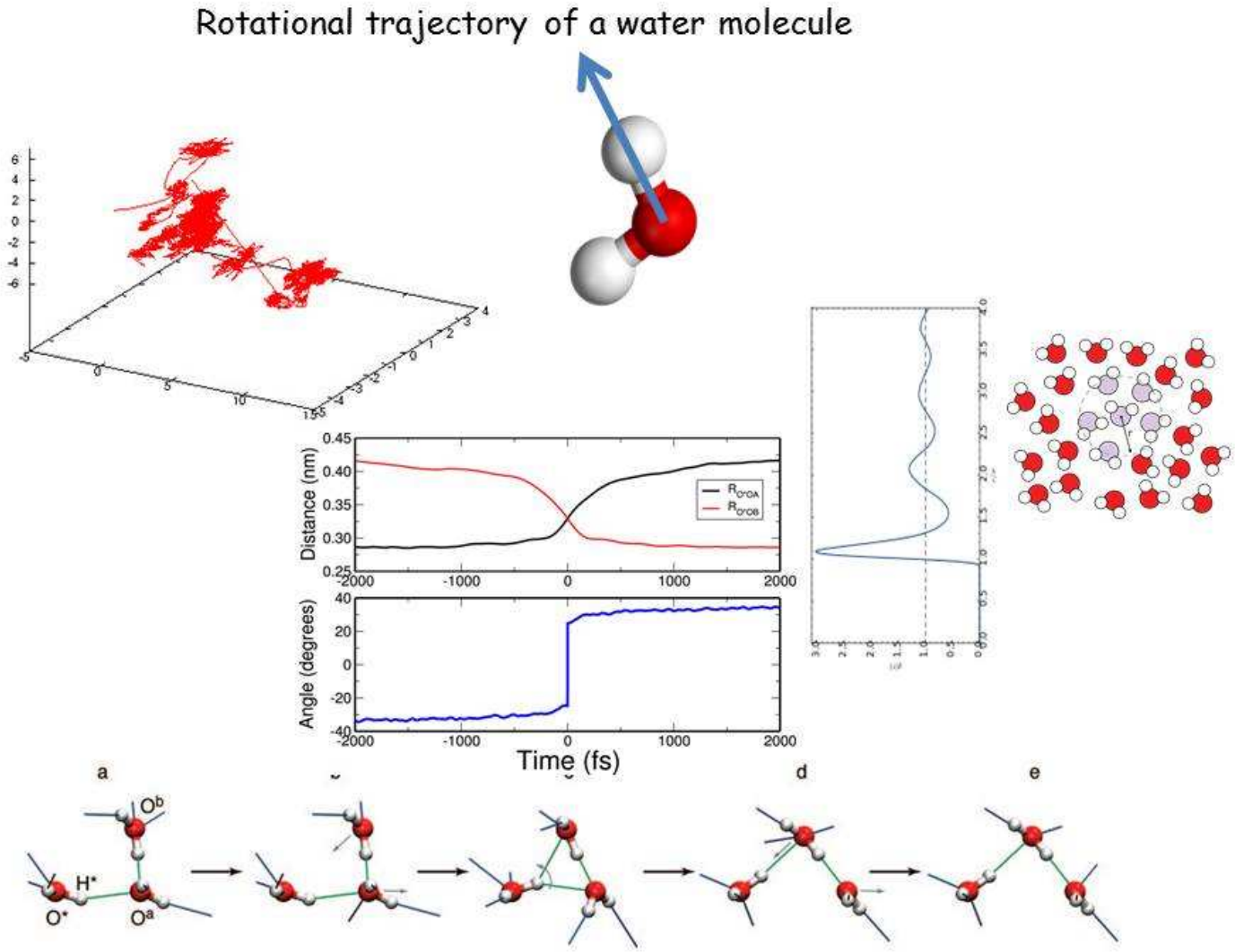
Single Molecule Transport in Smectics





- Liquid crystalline smectic phase.
- Translocation between adjacent layers.
- Free energy landscape with barriers $\sim$ 5 to 10 k_BT.

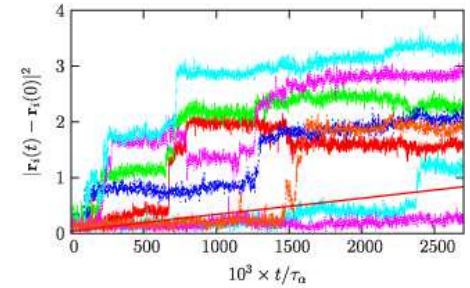
Single Molecule Rotation in H-Bonded Liquids

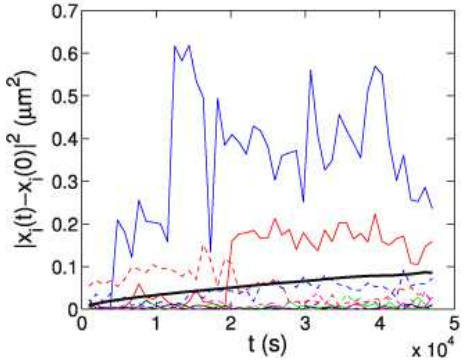


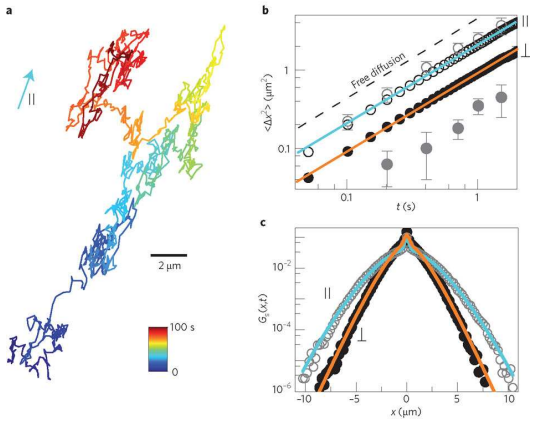
Basic Plan and Motivation

- Detection of microscopic dynamical events from MD trajectories.
- Continuous time random walk formalism used to relate properties of microscopic dynamical events to macroscopic transport properties.
- Diffusion constant (ensemble averaged).
- As liquids are supercooled, dynamics is dominated by fluctuations, not the mean.
- Statistical properties of these basic dynamical events (temporal statistics).
- Relate these to other typical measures of dynamical heterogeneities.

Dynamical Heterogeneities are Ubiquitous



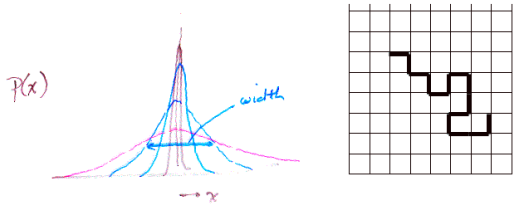




- Observed in colloidal fluids, foams, gels, fiber networks, cell tissues etc.
- Van hove function exhibits a Gaussian centre with broader, exponential tails.
- Emergence of exponential tails explained via a continuous time random walk analyses.
- Fickian but non-Gaussian diffusion.
- Possible to de-convolute the van-Hove function to obtain a bimodal density distribution.

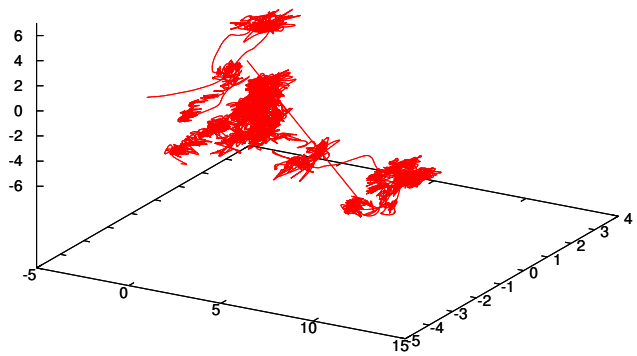
Chaudhuri *et al.* J. Phys. Cond. Mat. 2008, Wang *et al.* Nat. Mat. 2012,

Continuous Time Random Walks



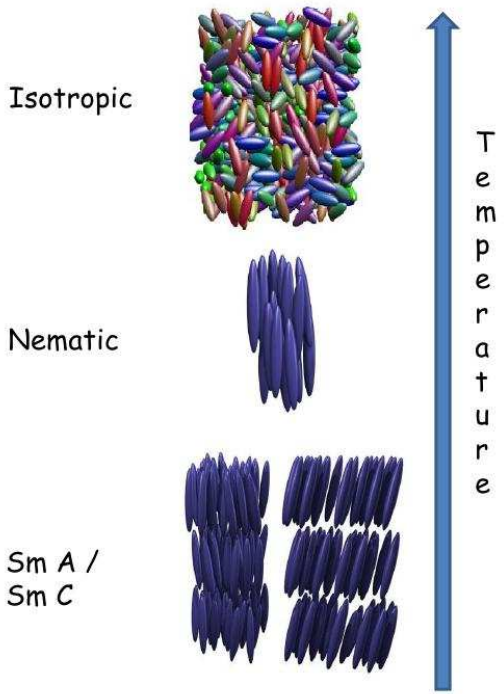
$$< r^2 > = 6Dt$$

- Jumps from one site to next at random times
- R(t) : Waiting / Residence time distribution.
- $\phi(\mathbf{r})$: Distribution of jump amplitudes.
- Conditions under which a CTRW description is viable : no correlations between jump amplitudes and waiting times.
- $< \tau_{wait} > \ll < \tau_{jump} >$
- CTRW approach used for understanding glassy dynamics in colloids.



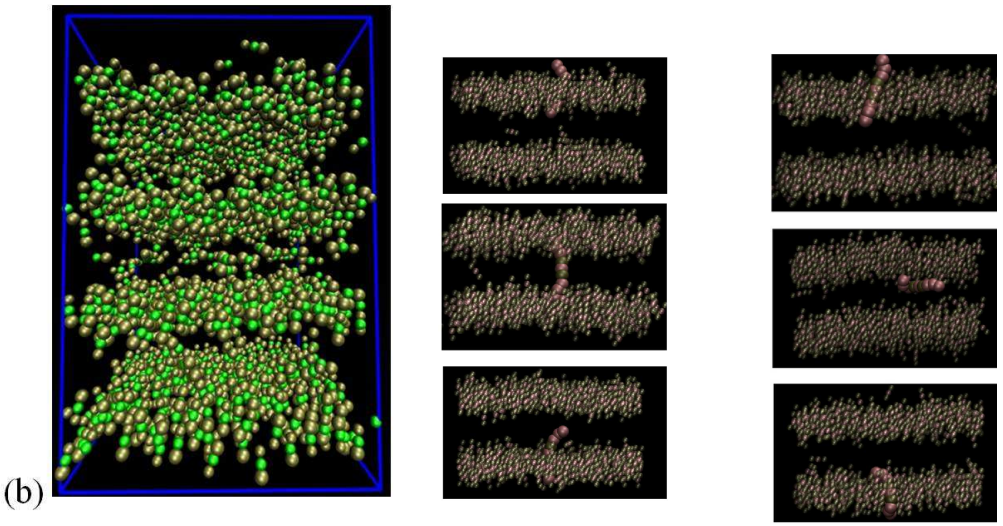
Chaudhuri *et al.* Phys. Rev. Lett. 2007

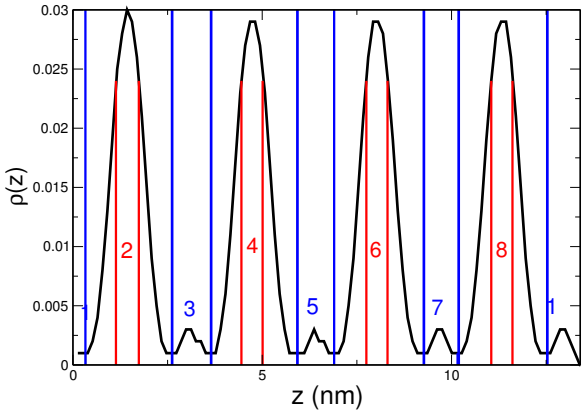
Liquid Crystalline Phases

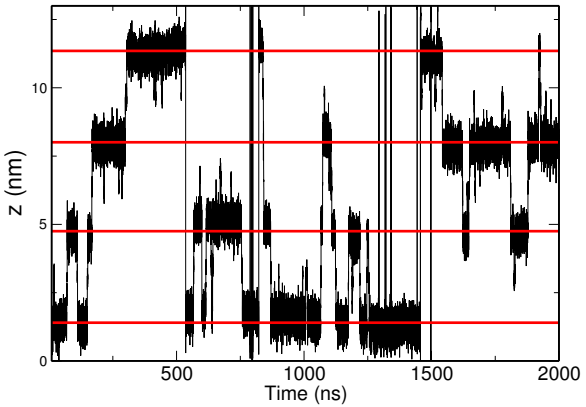


- Anisotropic interactions stabilise these phases.
- Isotropic phase at high temeperatures. Rotational and translationally symmetric.
- Nematic phase : Loss of orientational symmetry.
- Smectic phase : Loss of orientational symmetry and one dimensional translational periodicity.
- Smectic phase : 2D liquids stacked on top of each other.

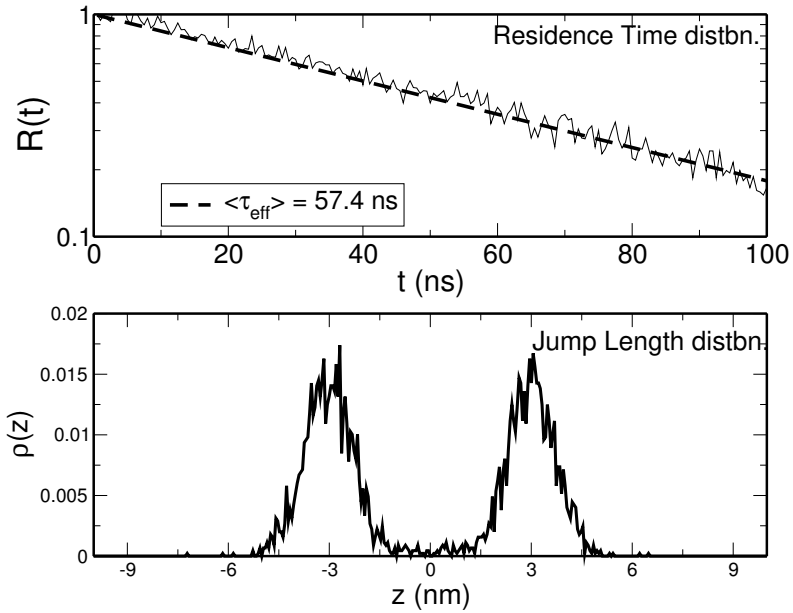
Smectic LC's : Out-of-plane dynamics

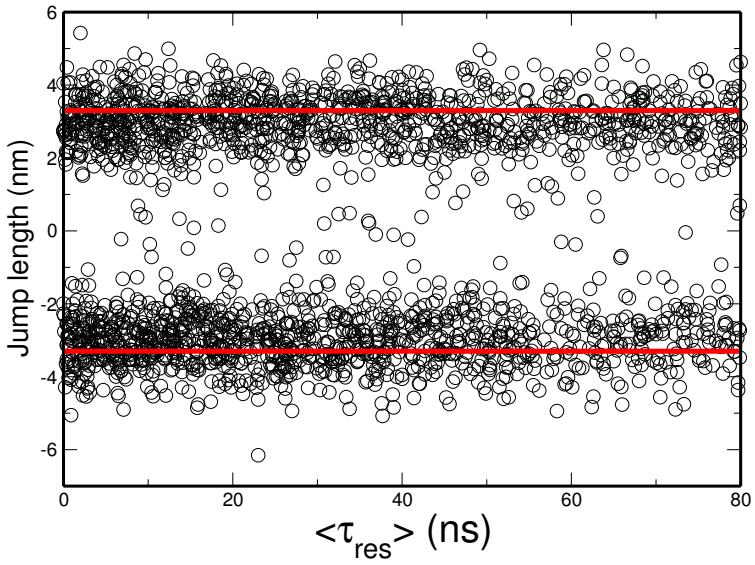






Smectic LC's : Out-of-plane dynamics

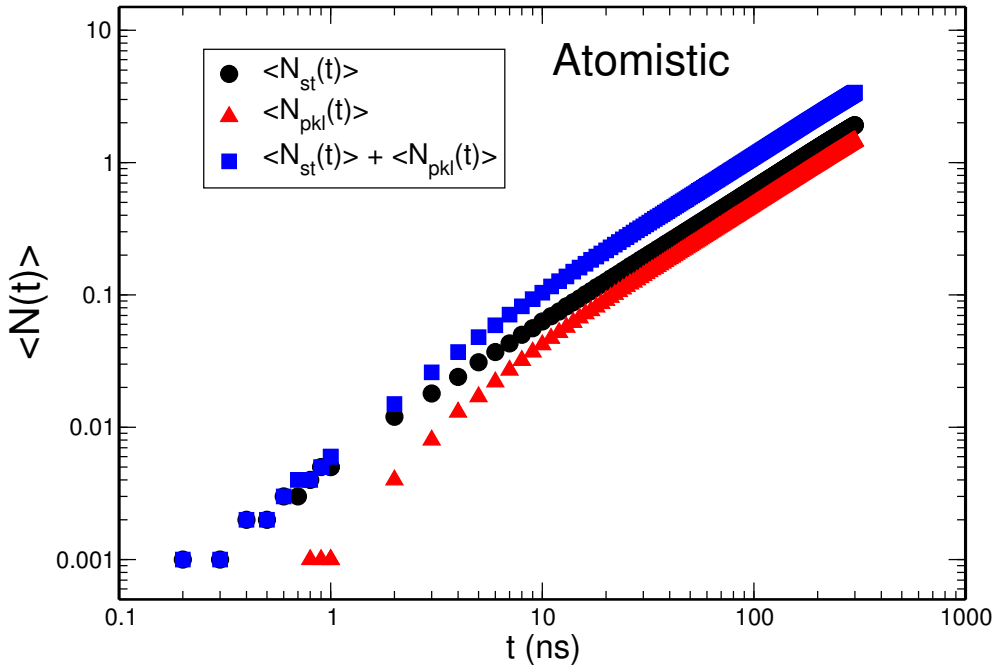




- Uncorrelated jump length and waiting times
- Dynamics can be described by a continuous time random walk description

Smectic LC's : Out-of-plane dynamics

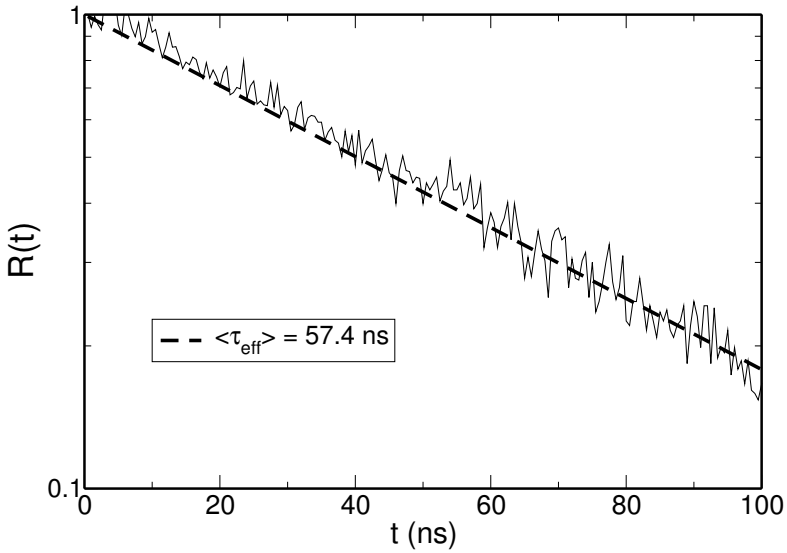
- (Assumption) Transport comprises of two independent translocation processes. Neglect the correlations.

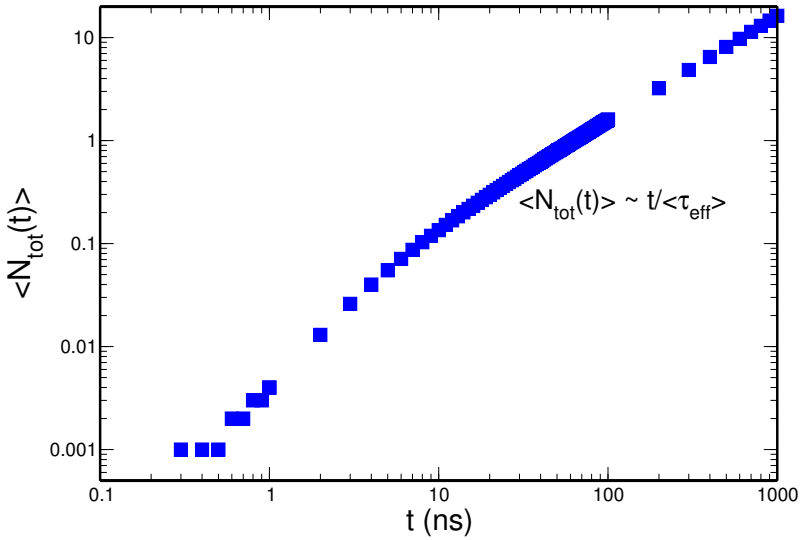


- $\langle N_{tot}(t)\rangle = \langle N_{st}(t)\rangle + \langle N_{pkl}(t)\rangle$
- $\langle N_{tot}(t)\rangle \sim t/\langle \tau_{eff}\rangle$
- $\langle N_{st}(t)\rangle \sim t/\langle \tau_{st}\rangle$
- $\langle N_{pkl}(t)\rangle \sim t/\langle \tau_{pkl}\rangle$
- $\frac{1}{\langle \tau_{eff}\rangle} = \frac{1}{\langle \tau_{st}\rangle} + \frac{1}{\langle \tau_{pkl}\rangle}$

- Similarity to parallel electrical resistances.

Smectic LC's : Out-of-plane dynamics

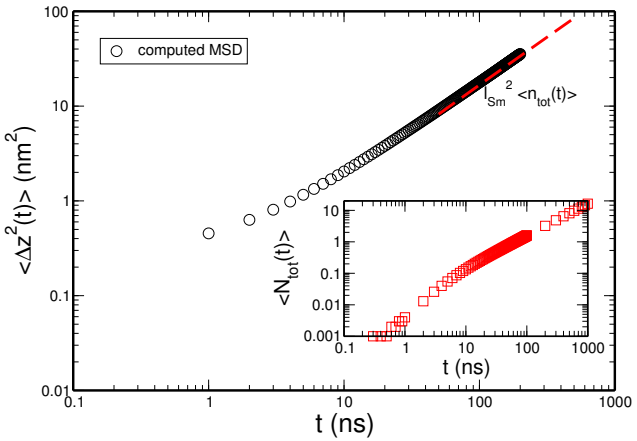


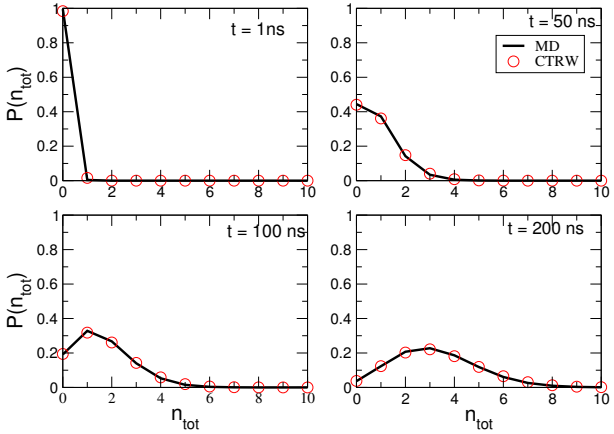


- Exponential residence time distribution
- $\langle N_{tot}(t) \rangle \sim \frac{t}{\langle \tau_{eff} \rangle}$
- $\frac{1}{\tau_{eff}}$ is the average rate of translocations.

Mukherjee et al. (under review)

Smectic LC's : Out-of-plane dynamics



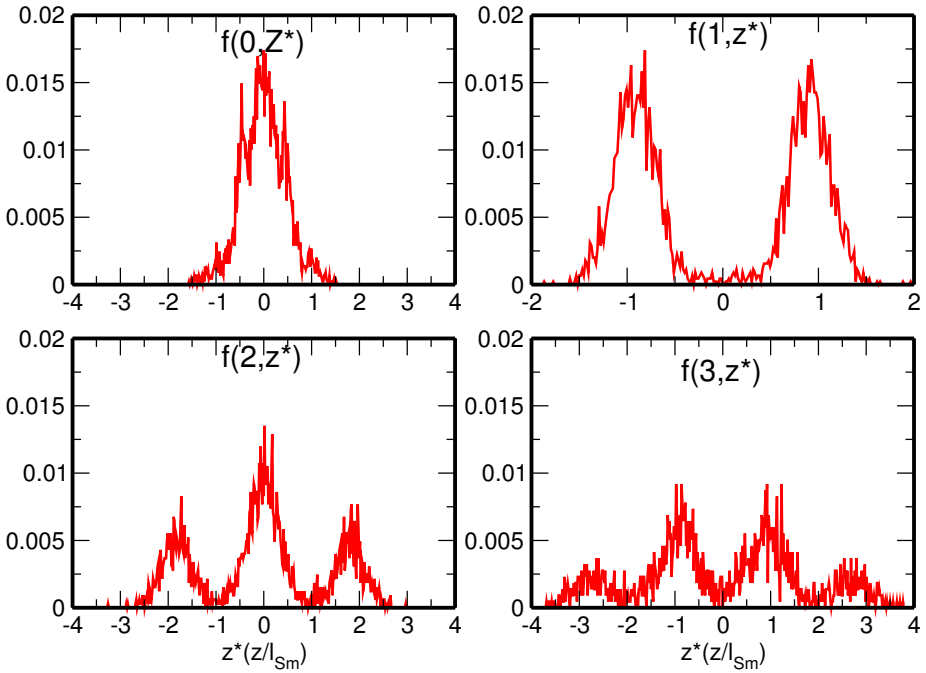


- $\langle \Delta z^2(t) \rangle = \langle N_{tot}(t) \rangle l_{sm}^2 \sim \frac{t}{\langle \tau_{res} \rangle} l_{sm}^2$
- $P(N_{tot}, t) = \frac{(t/\langle \tau_{res} \rangle)^{N_{tot}} e^{-t/\langle \tau_{res} \rangle}}{N_{tot}!}$
- A Poisson distribution expresses the probability of a given number of events occurring in a fixed interval of time if these events occur with a known average rate and independently of the time since the last event.

Mukherjee et al. (under review)

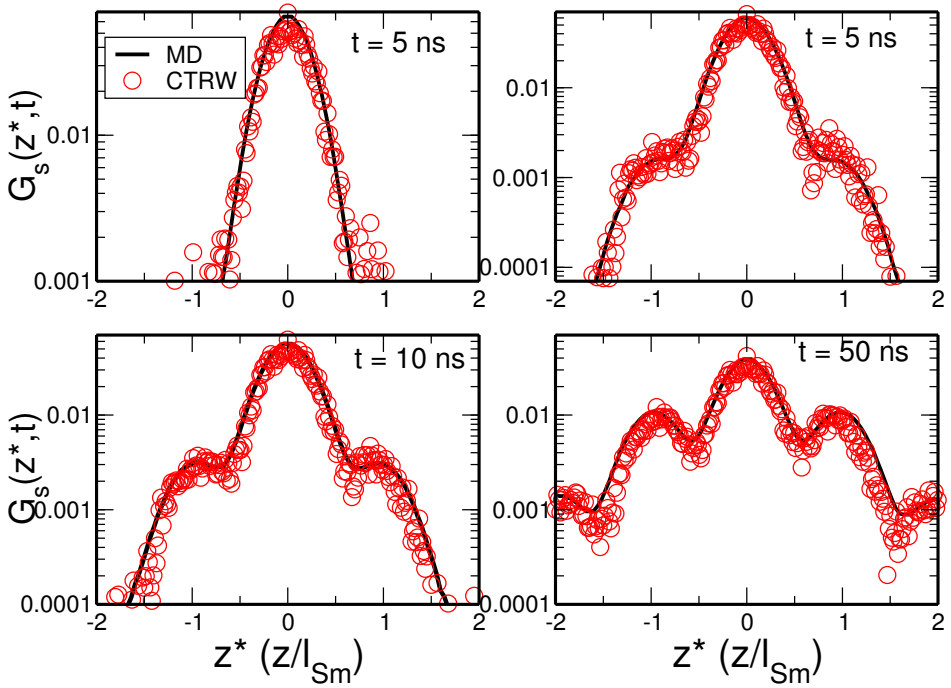
Smectic LC's : Out-of-plane dynamics

$$G_s(z,t) = \sum_{N_{tot}=0}^{\infty} f(N_{tot}, z) P(N_{tot}, t)$$



Mukherjee et al. (under review)

Smectic LC's : Out-of-plane dynamics



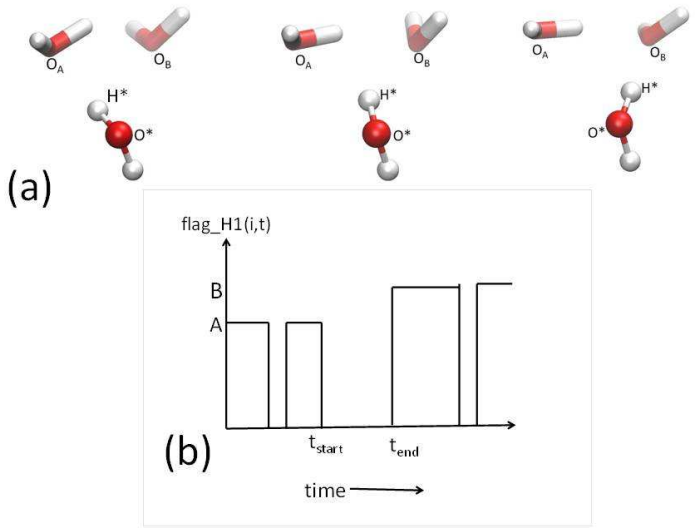
$$\mathrm{G}_s(\mathbf{r},t) = \frac{1}{N}\langle\sum_{i=1}^{N}\delta(\mathbf{r}-[\mathbf{r_i}(t_0+t)-\mathbf{r_i}(t_0)])\rangle_{t_0}$$

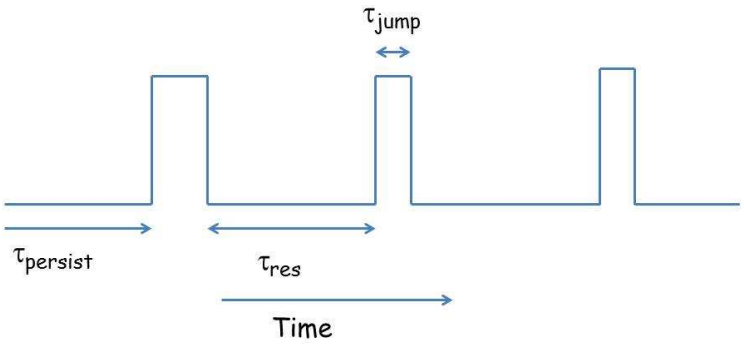
$$\mathrm{G}_s(\mathrm{z},\mathrm{t}) = \sum_{N_{tot}=0}^{\infty} f(N_{tot},z)P(N_{tot},t)$$

Mukherjee et al.(under review)

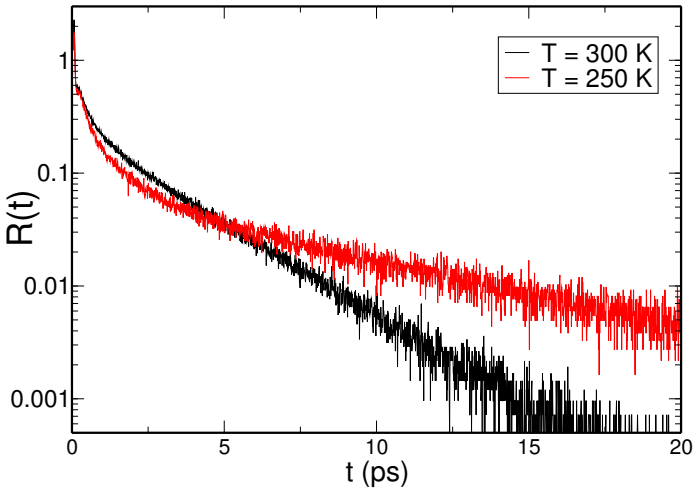
Molecular Rotation in Hydrogen-Bonded Fluids

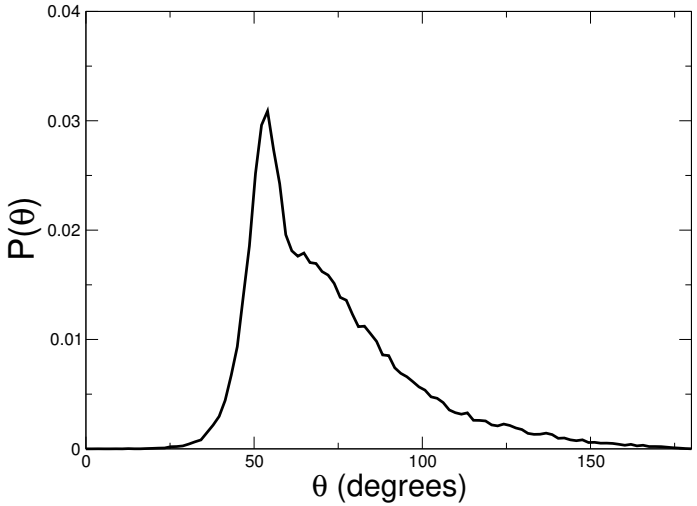
- Result of H-bond coordination fluctuations.
- Typical energy barrier $\sim$ few $k_B T$'s
- $\langle \tau_{wait} \rangle \sim 10 \langle \tau_{jump} \rangle$ (instantaneous rotation events).
- Universal rotation mechanism for supercooled water, confined water, aqueous binary mixtures, liquid acetamide, deep-eutectic mixtures and ionic liquids.





Molecular Rotation in Hydrogen-Bonded Fluids

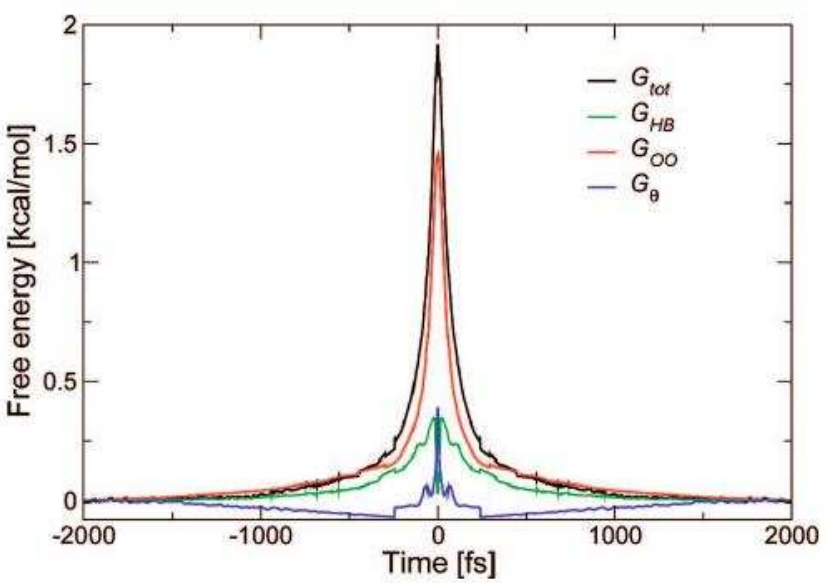


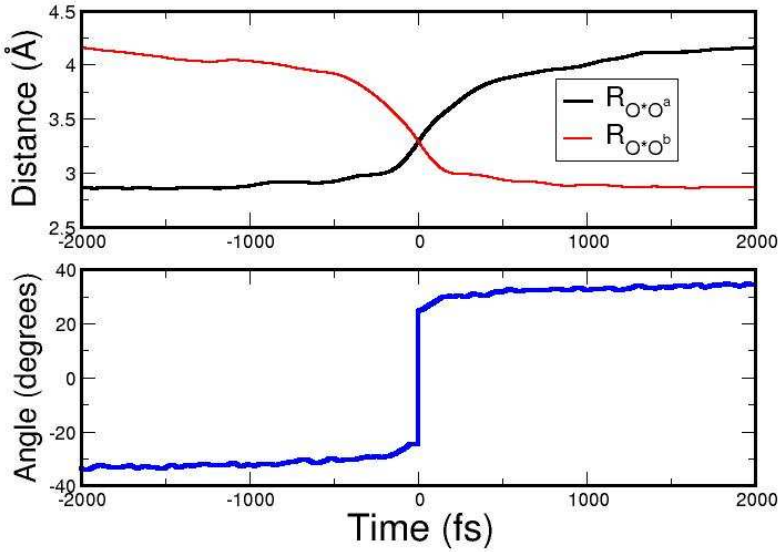


- Multi-exponential waiting time distributions.
- Large amplitude angular jumps, $\Delta\theta_{jump} \geq 60$ degrees.
- Also observed for water confined inside narrow carbon nanotubes.

D. Laage, J.T. Hynes, J. Chem. Phys. B, 2008, B. Mukherjee, P. K. Maiti, C. Dasgupta, A. K. Sood, J. Phys. Chem B, 2009, B. Mukherjee, J. Chem. Phys., 2015

Molecular Rotation in Hydrogen-Bonded Fluids





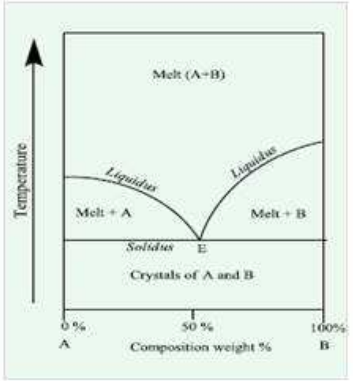
- Most of the rotational free energy barrier arises due to translation of oxygen molecules.
- Underlines the microscopic rotation-translation coupling.

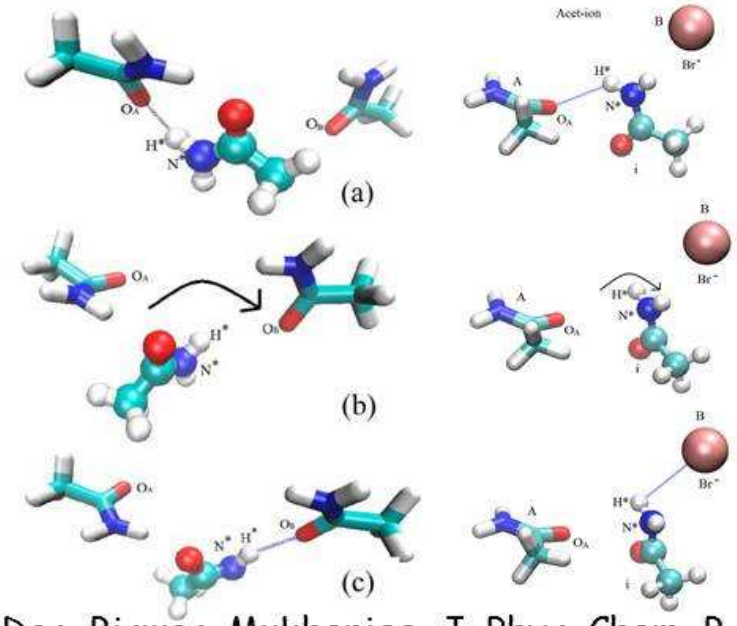
D. Laage, J.T. Hynes, J. Chem. Phys. B, 2008 and B. Mukherjee, J. Chem. Phys., 2015

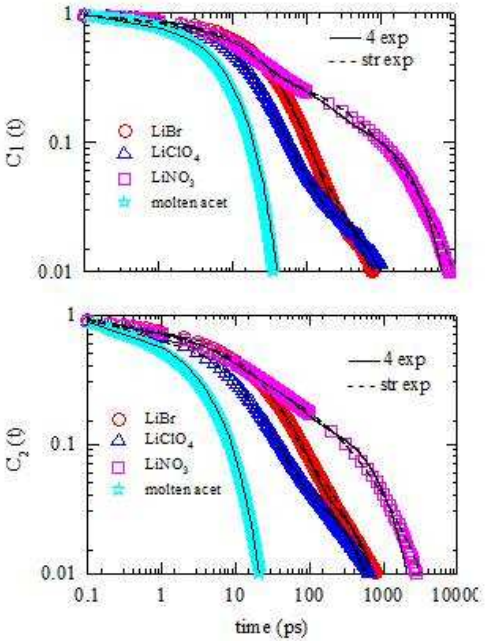
Molecular Rotation in Hydrogen-Bonded Fluids

Deep Eutectic Solvents

- Mixture of two (or more) compounds that form liquid at a temperature much lower than individual melting points of constituents.
- Show characteristics of super-cooled liquids





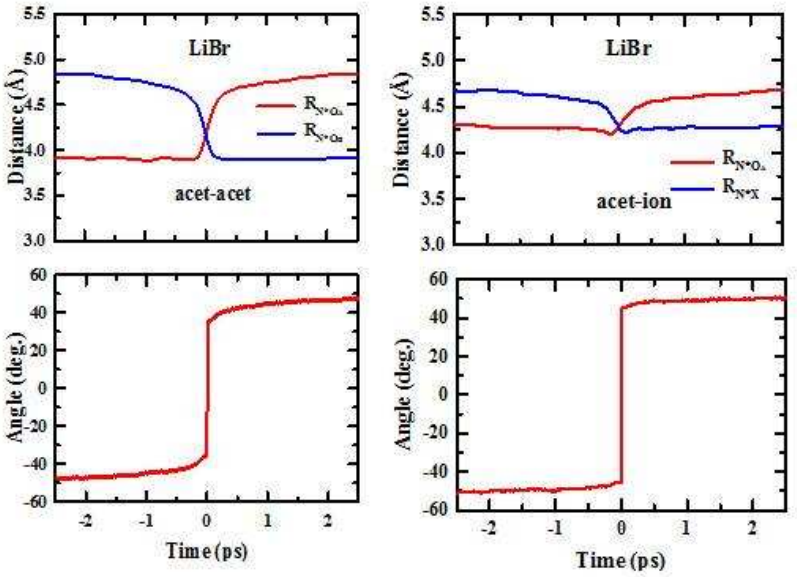


Das, Biswas, Mukherjee, J. Phys. Chem. B, 2014.
Das, Biswas, Mukherjee, J. Phys. Chem. B, 2015.

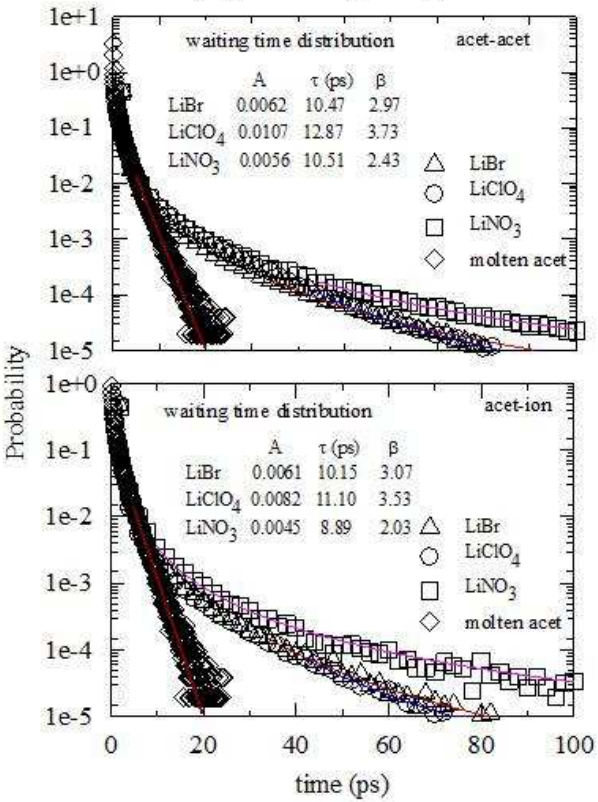
Molecular Rotation in Hydrogen-Bonded Fluids

Distribution of waiting times between orientational jumps

$$P(t) \propto \mathrm{A}(\mathrm{t}/\tau)^{-\beta}$$



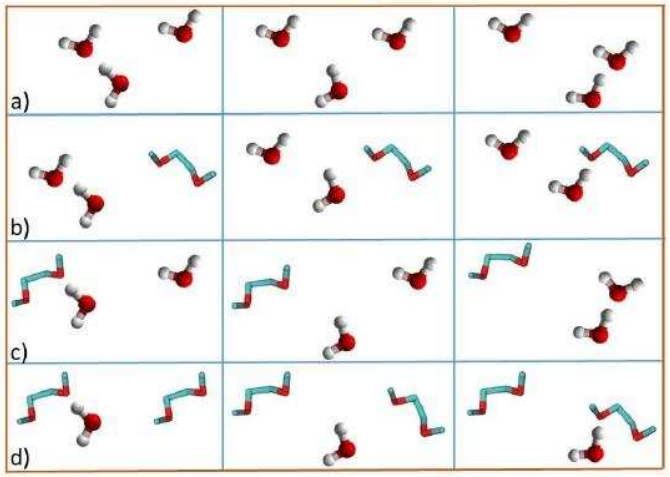
Time evolution of geometric parameters associated with rotational jumps

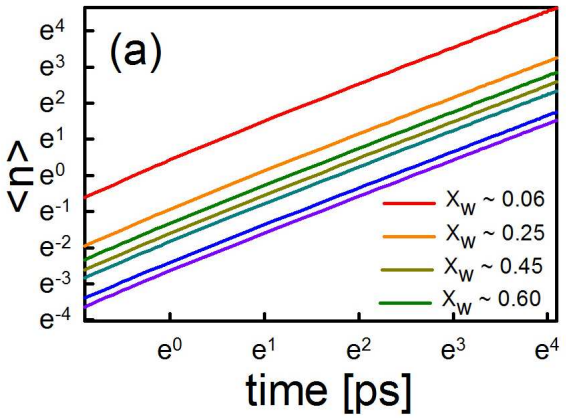


Power law waiting time distribution

Das, Biswas, Mukherjee, J. Chem. Phys., 2016.

Water-DME binary mixture

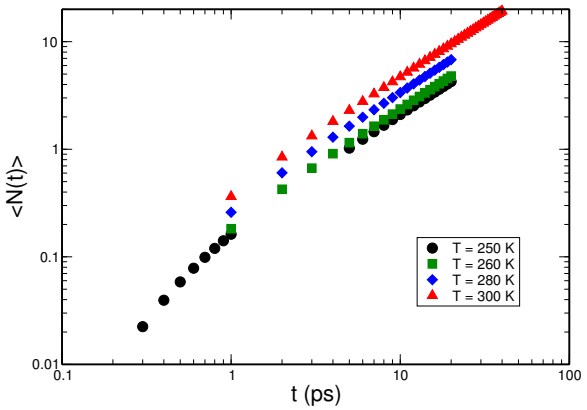


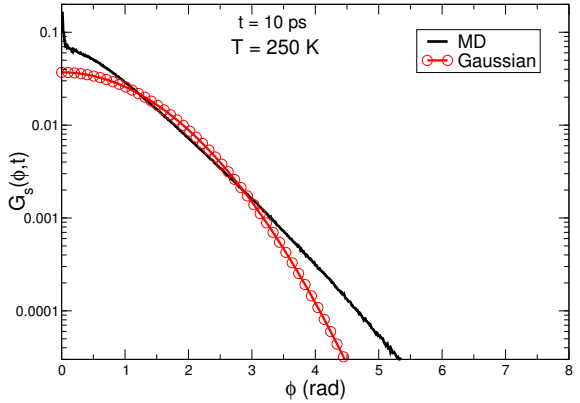


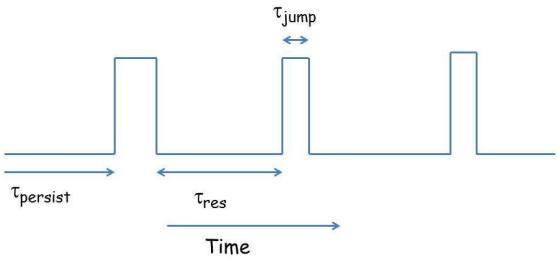
- Binary mixture of water and DME simulated at various concentrations.
- Water molecules exhibit rotational jumps
- Linear time-dependence of $\langle N(t) \rangle$.
- Heterogeneity in rotational dynamics increases at low water concentrations.

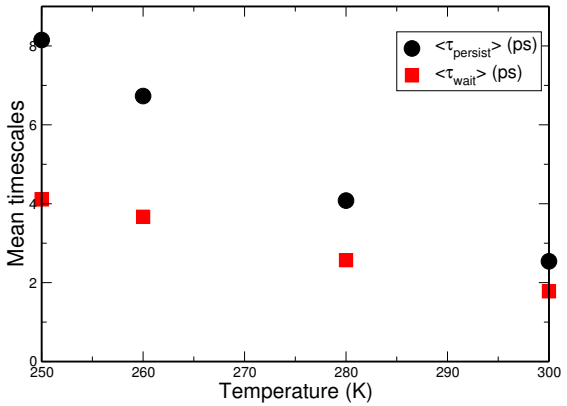
D. Das Mahanta, A. Patra, N. Samanta, T. Luong, B. Mukherjee, R. K. Mitra, J. Chem. Phys., 2016

Molecular Rotation in Supercooled Water



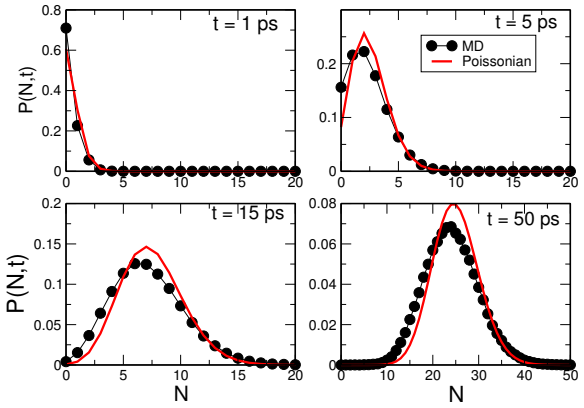


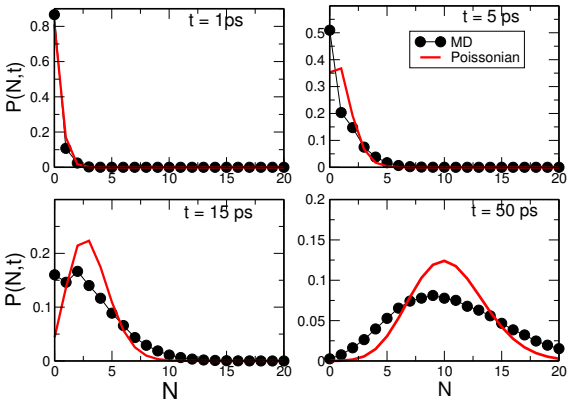




B. Mukherjee (under preparation)

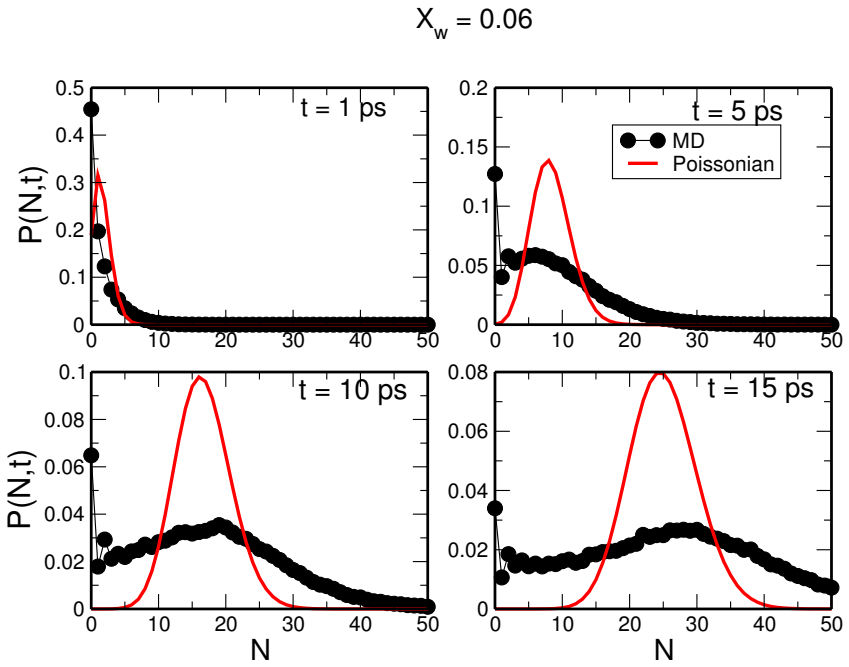
Molecular Rotation in Supercooled Water





- Single molecule rotational diffusivity proportional to number of rotational jumps.
- P(N,t) : probability of a molecule undergoing "N" jumps within time duration "t".
- P(N,t) is Poissonian at high temperatures, 300 K (left).
- The distribution P(N,t) is not Poissonian at 250 K (right). Presence of facilitated dynamics ?

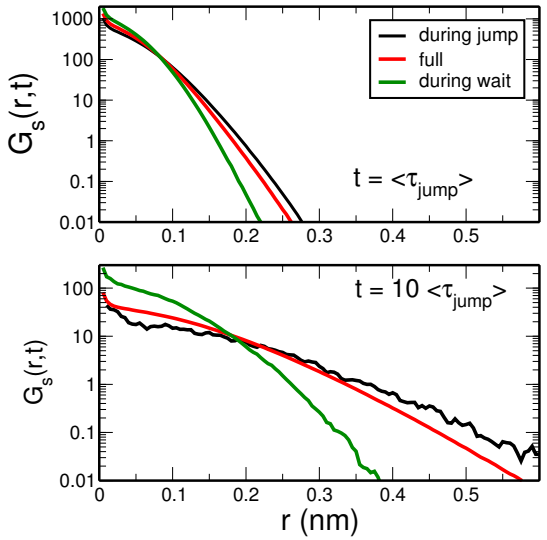
Molecular Rotation in a Binary Mixture



- Exhibits transient bimodality. Co-existence of mobile and immobile molecules.
- To be compared to diffusivity distribution obtained via de-convoluting van-Hove function.

S. Sengupta, S. Karmakar, J. Chem. Phys., 2014

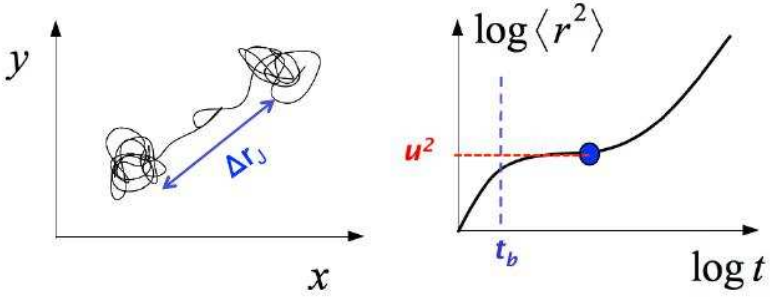
Molecular Rotation in Hydrogen-Bonded Fluids



- Translational dynamics coupled to rotational jump events.
- Translational dynamics probed separately during rotational jump (black) and rotational waiting (green) periods.
- Explains the origin of temporal heterogeneity in the translational dynamics of liquid water @ 300 K and below.
- Heterogeneity increases upon supercooling.

B. Mukherjee, J. Chem. Phys., 2015

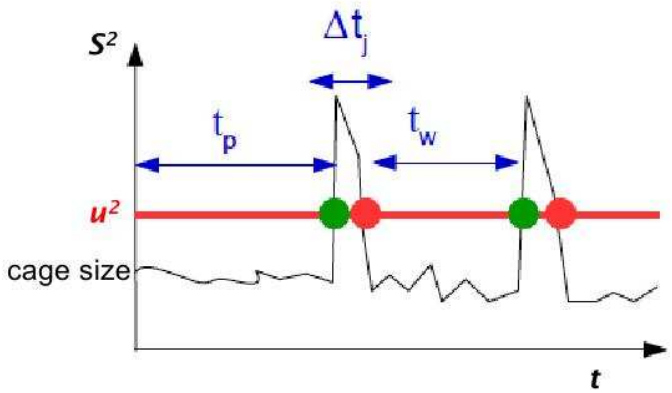
CTRW from a Trajectory



- u^2 = Debye-Waller factor
- t_b = ballistic time
- $\delta \cong 20\ t_b$

• Fluctuation of the position of the i[th] particle : $S_i^2(t) = \left\langle \left(r_i(t) - \langle r_i(t) \rangle_\delta \right)^2 \right\rangle_\delta$

- $< u^2$ → caged
- $> u^2$ → jumping



- Δr_J = jump length
- Δt_J = jump duration
- t_p = persistence time
- t_w = waiting time
- Cage size

Conclusions and Future Directions

- Single molecule translational and rotational dynamics can be understood as a CTRW.
- Similarity with models exhibiting facilitated dynamics.
- Finding a microscopic measure of translation rotation coupling.

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Thanks For the Attention !!