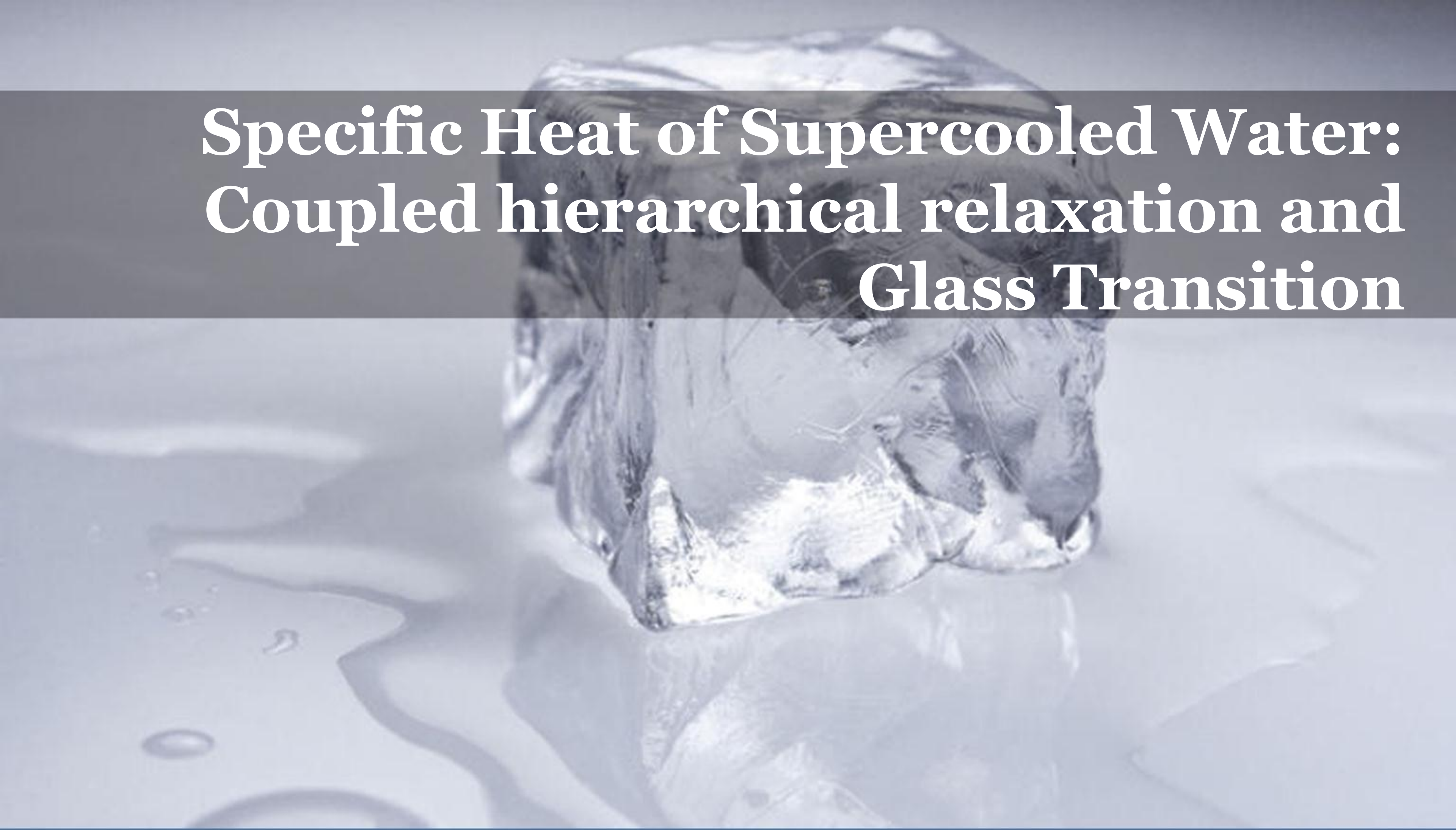
Specific Heat of Supercooled Water: Coupled hierarchical relaxation and Glass Transition



Biman Bagchi
Solid State and Structural Chemistry Unit
Indian Institute of Science

Difference between Isobaric (C_p) and Isochoric (C_v) specific heats

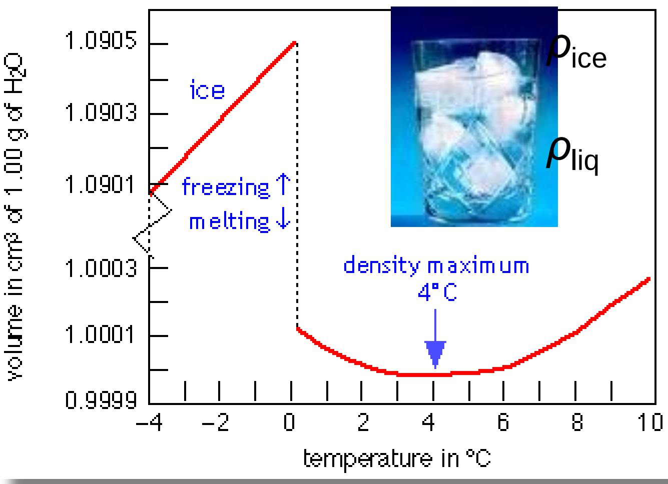
For normal liquids, $C_p = C_v$ at all Temperatures (in the liquid state)

NOT FOR WATER in the SUPERCOOLED STATE!

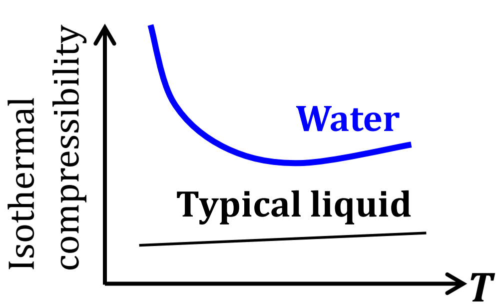
Why?
Role of volume fluctuations !
Speedy and Angell (1975)

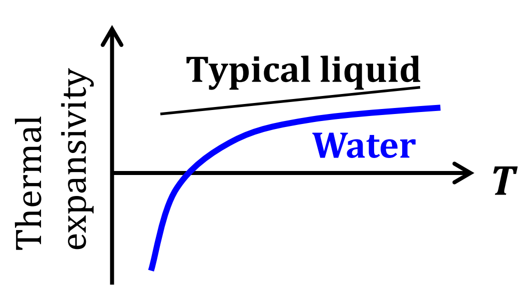
Thermodynamics of liquid water

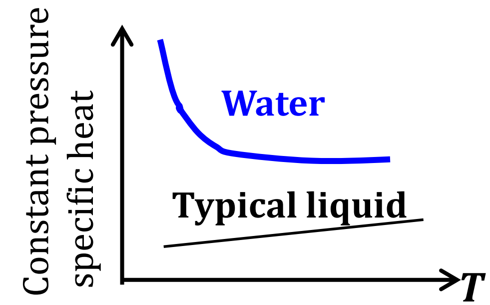
- ✓ **Anomalous thermodynamic properties:**
  - high melting and freezing points, density maximum at 4 ˚C, . . .
- ✓ **Three-dimensional (tetrahedral and strong) hydrogen bond network**



- ✓ **Enhancement of anomalies in supercooled state**
  - decrease in density down to ~ -40 ˚C
  - significant changes (look like diverge) in κ_T, α_P, and C_P





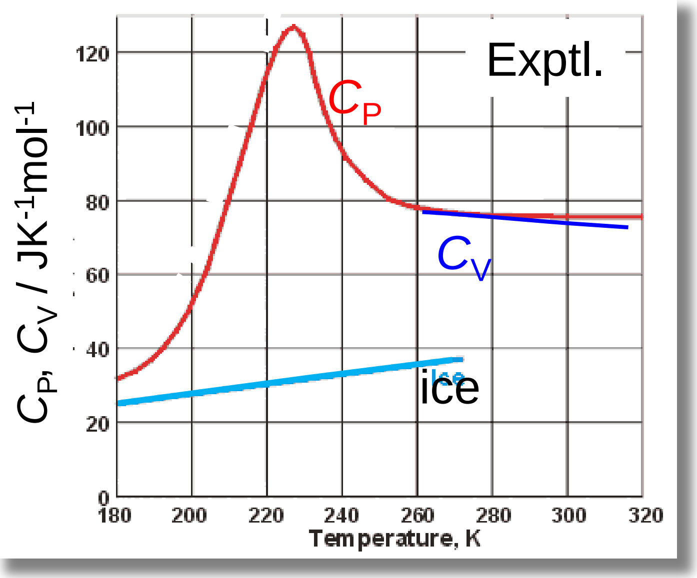


No consensus about what causes thermodynamic anomalies

Limited our understanding of molecular origin of anomalies

Spectroscopic analyses by Chen, Righini, Tokomakoff, Hamm, . . .

Anomalous temperature dependence of C_P of water



Sharp increase in C_P in supercooled state

- **The absence of a sharp increase in C_V in water (is considered)**
- **The absence of an increase in C_P in simple liquids and alcohols**

Molecular origin of increase in C_P of supercooled water

- **Difference between liquid structure and dynamics under two, i.e. constant pressure and volume, conditions**
- **Time- and length-scales of motions involved in anomalous temperature dependence of C_P**

Expression for frequency dependent specific heat

The temperature fluctuation time correlation function given by

$$K(t) = N <\delta T(0)\, \delta T(t)/T^2$$

By using the Fourier-Laplace transform of the time derivative of *K(t), ˙K(t), the specific heat is expressed as*

$$C = [\ 1/N_f \quad + K(0)]^{-1}$$

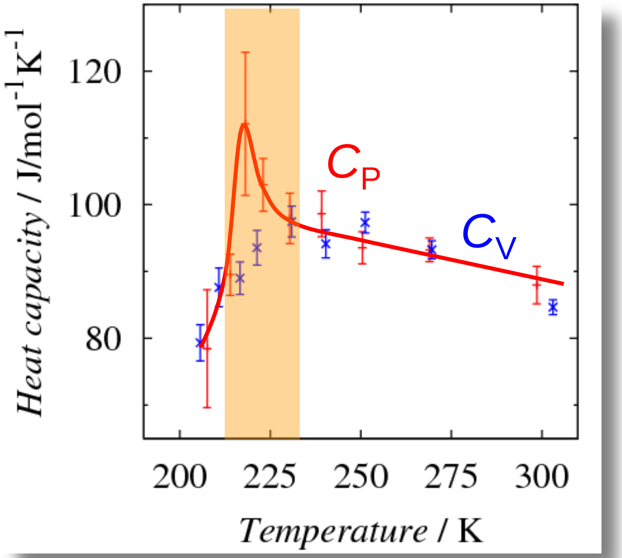
.

By generalizing the static specific heat given i to the frequency dependent specific heat,

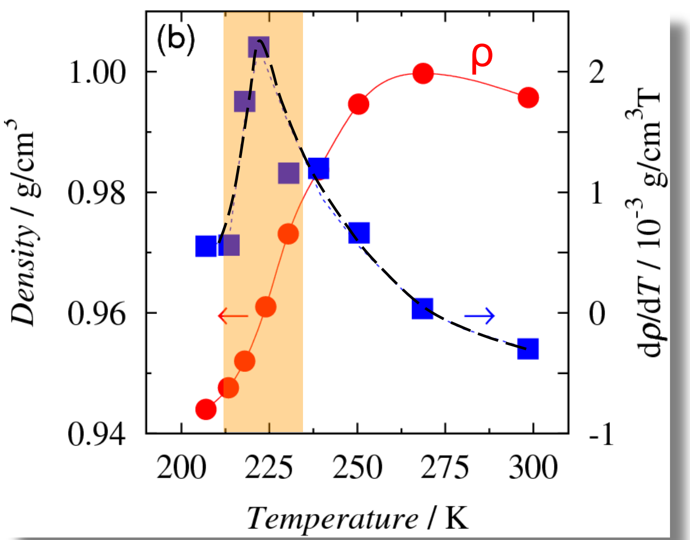
$$C(\omega) = [1/N_f \ + K(\omega)]^{-1}$$

Results of MD simulations

Temp. dep. of calculated C_P and C_V



Temp. dep. of calculated ρ and $d\rho/dT$



- $C_P \sim C_V$ at $T > 230$ K
- **Sharp increase in C_P at ~ 230 K**
- **Maximum of C_P at ~ 220 K**
- **Decrease in C_V at $T \sim 230$ K**

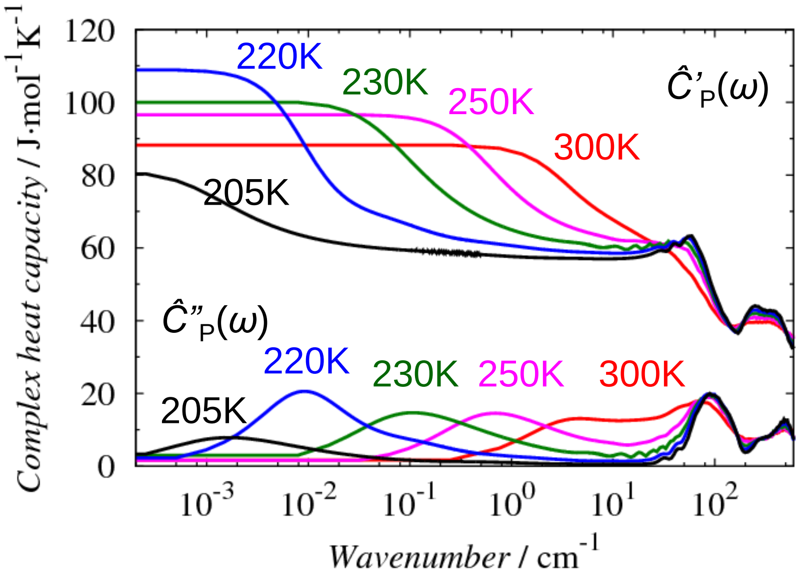
Model for water: TIP4P-2005

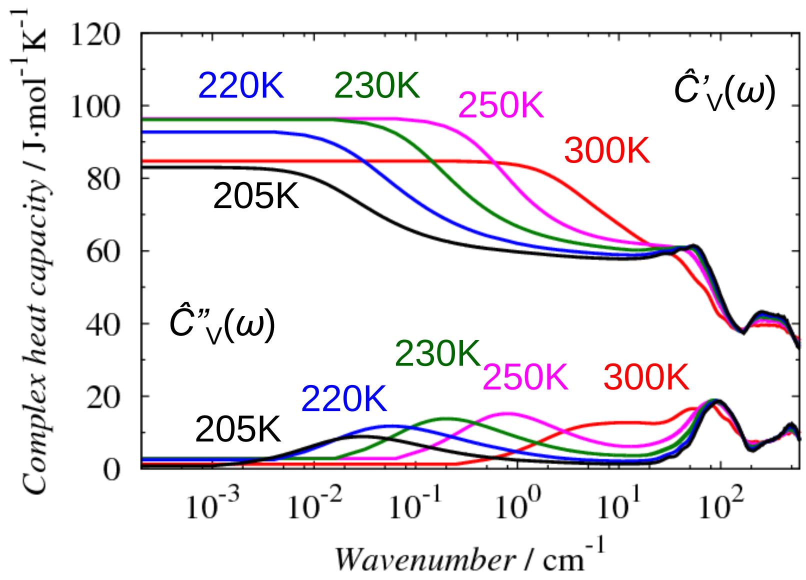
Saito, Ohmine, & Bagchi, JCP **138**, 094503 (2013).

- **Sharp decrease in density**
  $210 \text{ K} < T < 230 \text{ K}$
- **$T_{\text{Max of } d\rho/dT} \sim T_{\text{Max of Cp}}$**

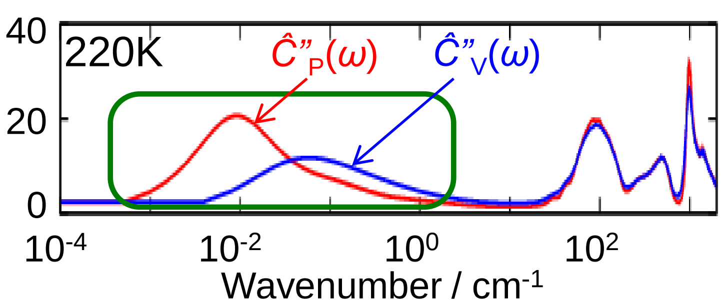
Change in dynamics caused by decrease in density is involved in change in C_P.

Complex specific heat: ‘Specific heat spectroscopy’





- $\hat{C}_P(\omega) \sim \hat{C}_V(\omega)$ for all ω at $T > 230$ K
- Difference between $\hat{C}_P(\omega)$ and $\hat{C}_V(\omega)$ for $\omega < 1$ cm^{-1}, i.e. HB network dynamics, at $T < 230$ K

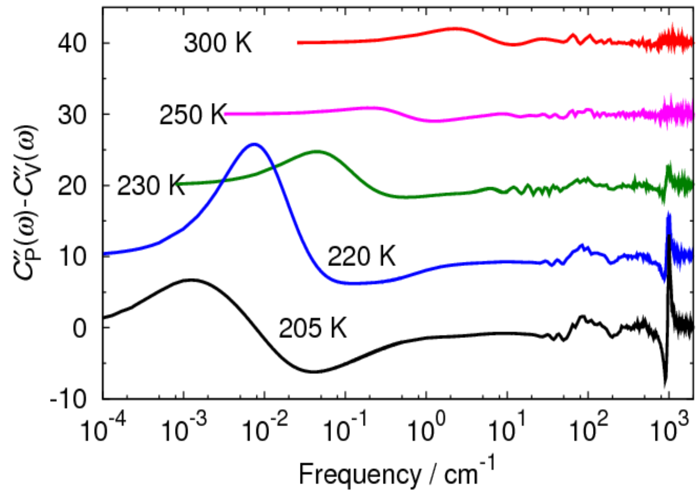


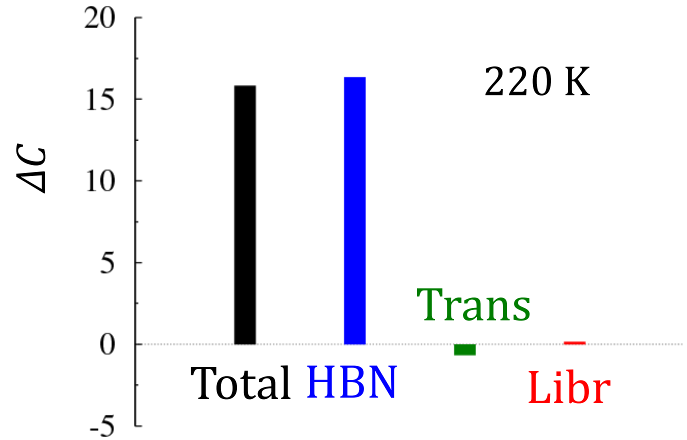
Two differences between $\hat{C}''_P(\omega)$ and $\hat{C}''_V(\omega)$

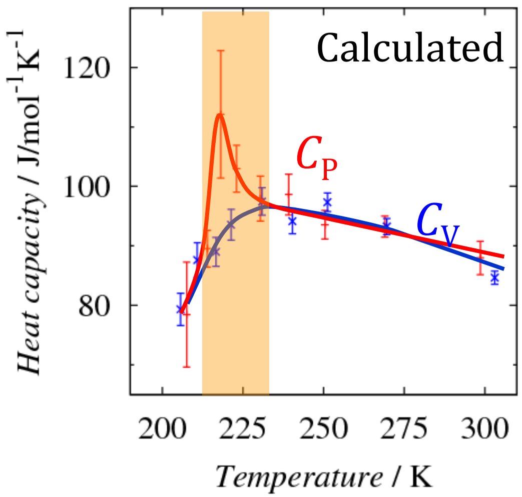
- **Peak frequency: $\omega_{HBN} < \omega_{HBN}$**
- **Peak intensity: $\hat{C}''_P(\omega_{HBN}) > \hat{C}''_V(\omega_{HBN})$**

Saito, Ohmine, & Bagchi, JCP **138**, 094503 (2013).

Quantification of contribution of motions to ΔC ($\equiv C_P - C_V$)







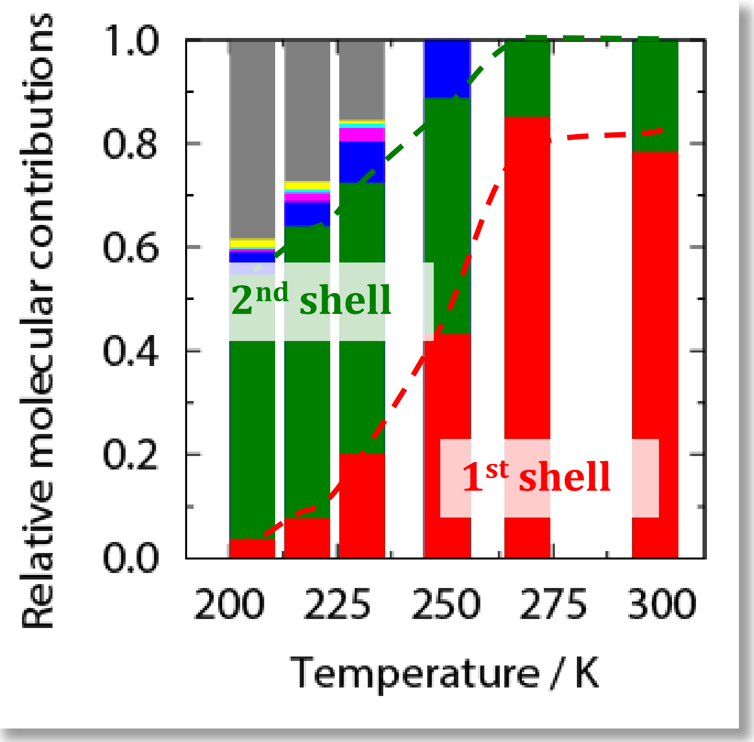
$$C_P - C_V = \hat{C}'_P(0) - C'_V(0)$$

$$= \frac{2}{\pi}\int_0^\infty \left(\frac{\hat{C}''_P(\omega)}{\omega} - \frac{\hat{C}''_V(\omega)}{\omega}\right) d\omega$$

$$\sim \frac{2}{\pi}\int_{HBN} \left(\frac{\hat{C}''_P(\omega)}{\omega} - \frac{\hat{C}''_V(\omega)}{\omega}\right) d\omega$$

- **Difference between C_P and C_V**
- **Difference between HB network dynamics under two conditions**

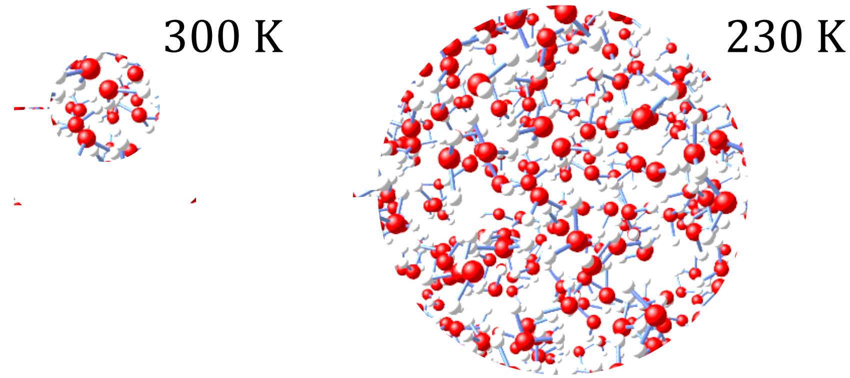
Length-scale of temperature fluctuation in C_P



Relative shell-wise contribution to temperature fluctuation caused by HB network dynamics

At 300 K, ~80 % from the 1st shell

At 230 K, only 20 % from the 1st shell



Growth of spatially correlated dynamics

Temperature dependence of liquid structure

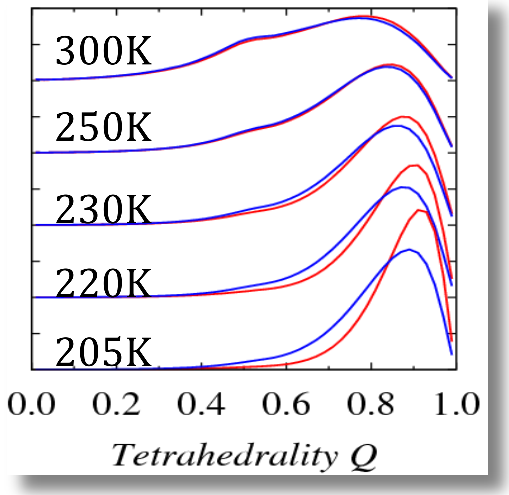
Tetrahedrality

$$Q = \frac{1}{N}\sum_{i=1}^{N}\left(1-\frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\theta_{jik}+\frac{1}{3}\right)^2\right)$$

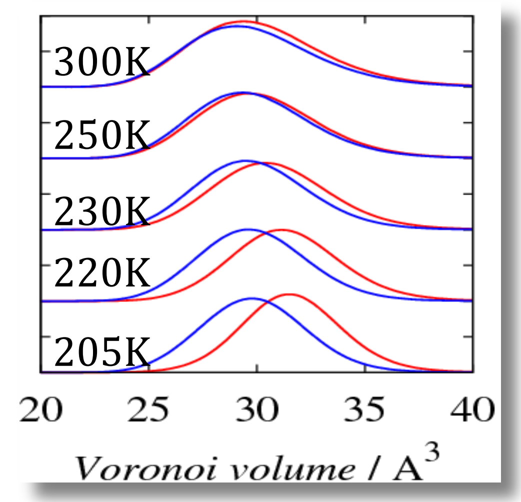
Q=1:Td structure, Q=0: Random structure

const. P. condition
const. V. condition
(ρ=1g/cc)

Tetrahedrality

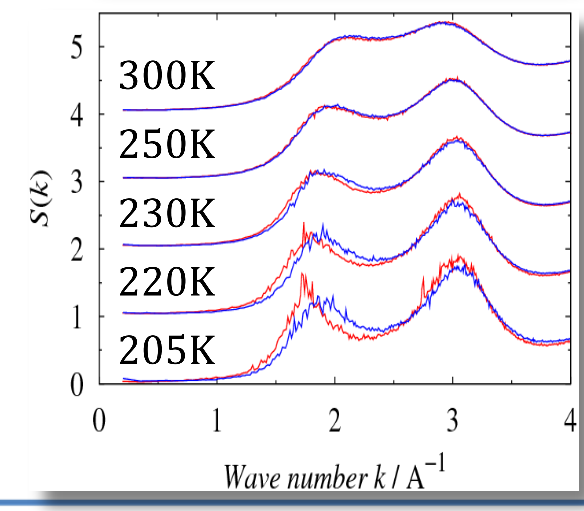


Volume of Voronoi polyhedra



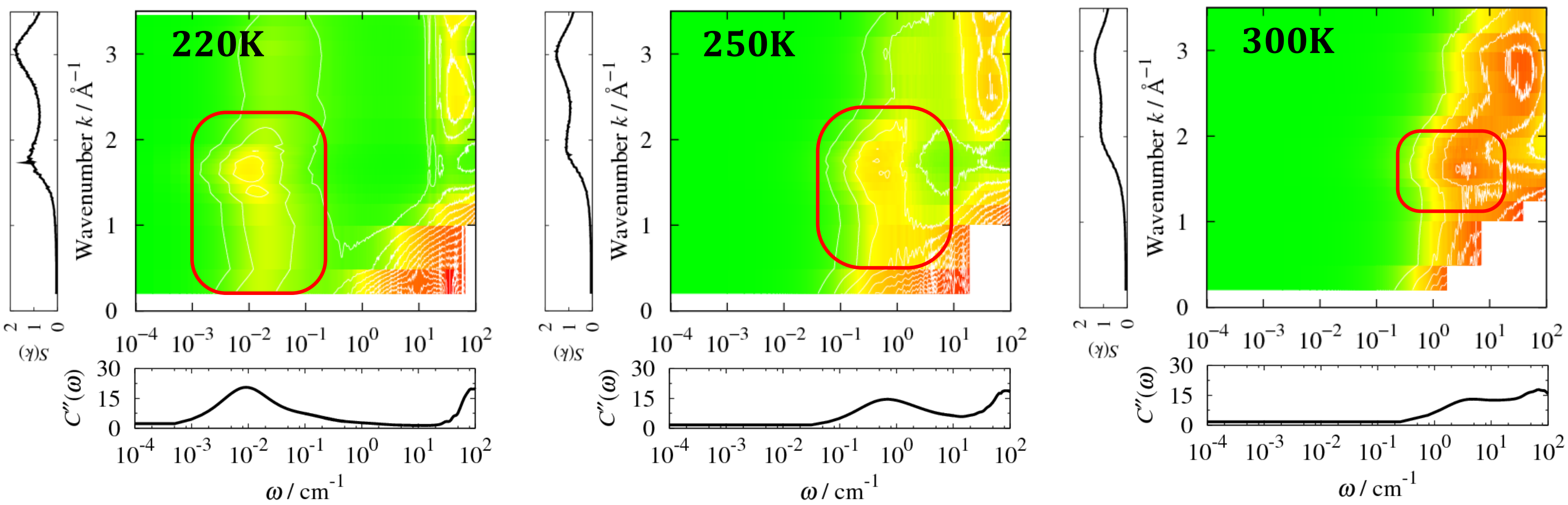
- **No large difference at *T* > 230 K**
- **Clear difference at *T* < 230 K**
  - Growth of tetrahedral structure caused by decrease in density under constant pressure condition

Static structure factor



Spatio-temporal scales of temperature fluctuation in C_P

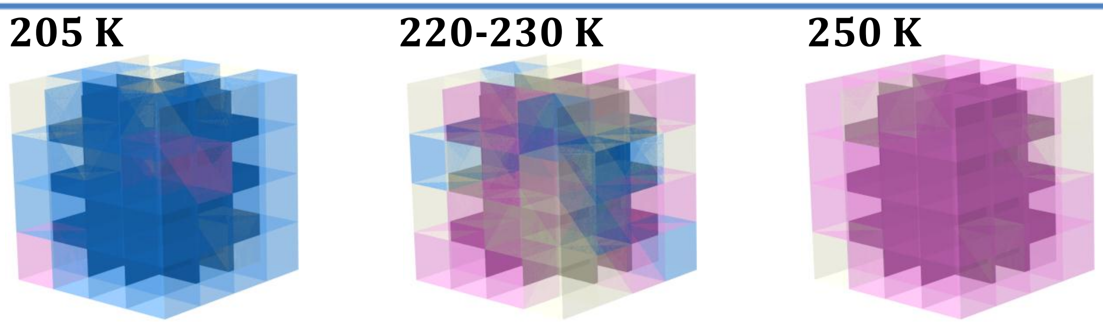
$$|\hat{K}(\omega,k)|^2 / S(k)$$



- Decoupling between intermolecular motions and HB network dynamics
- Contribution of 1st shell to temp. fluct. at ω_{HBN} ~10%
- Increase in contribution of outer-shells
- Emergence of correlated HB dynamics

- Strong coupling between intermolecular motions and HB network dynamics
- Fast energy dissipation
- Contribution of 1st shell to temp. fluct. at ω_{HBN} ~80 %

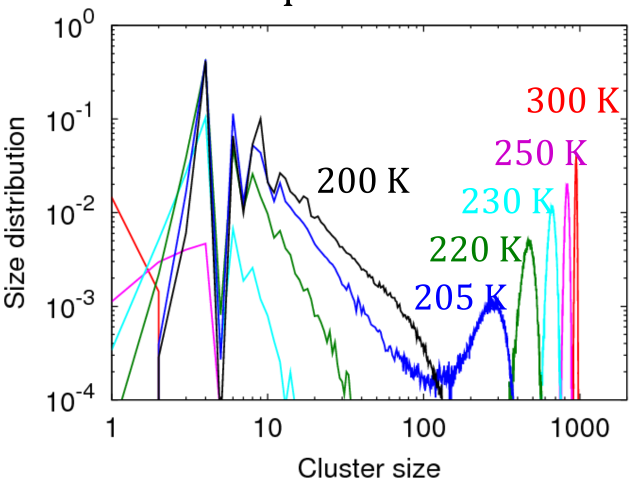
Temperature dependence of local density fluctuation



Red (blue) cubic : a region with high ratio of liquid-like (ice-like) molecule

Percolation of ice-like molecules | **Large local density fluctuation** | **Percolation of liquid-like molecules**

Temp.-dep. of size-distribution of clusters of liquid-like molecules



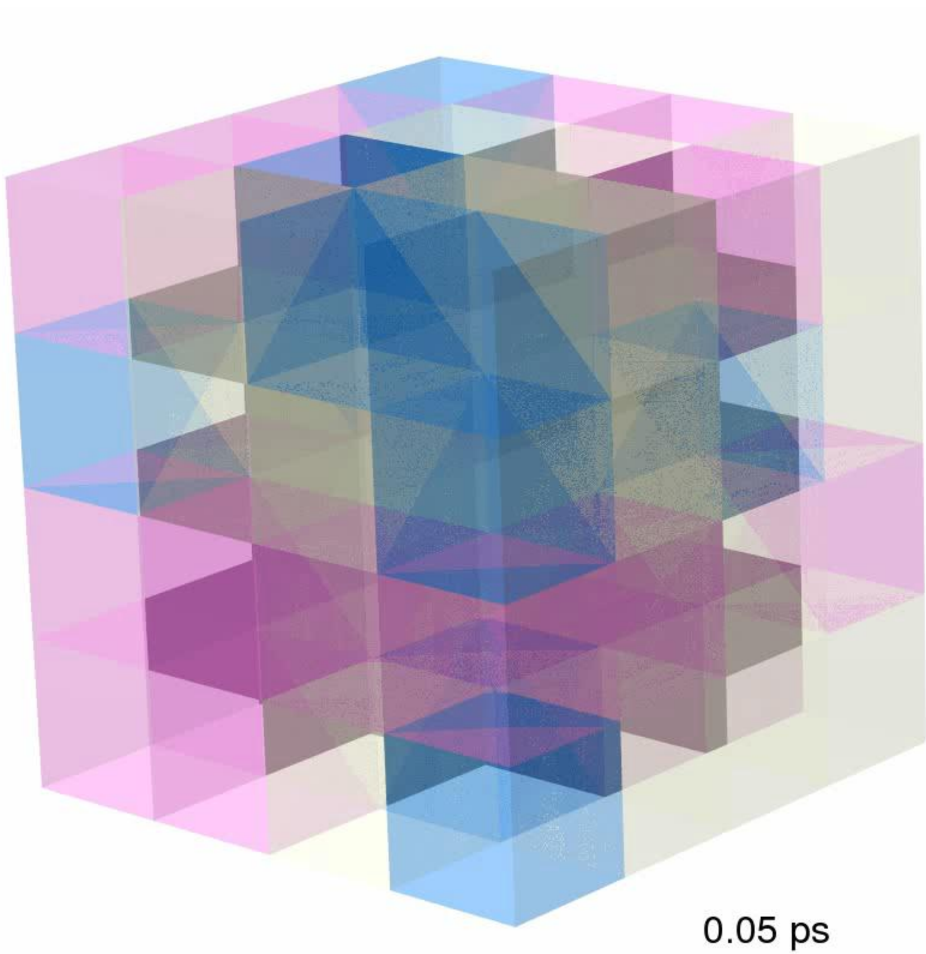
Ice-like molecule: A 4-coordinated molecule which is coordinated to four 4-coordinated molecules

Liquid-like molecule: otherwise

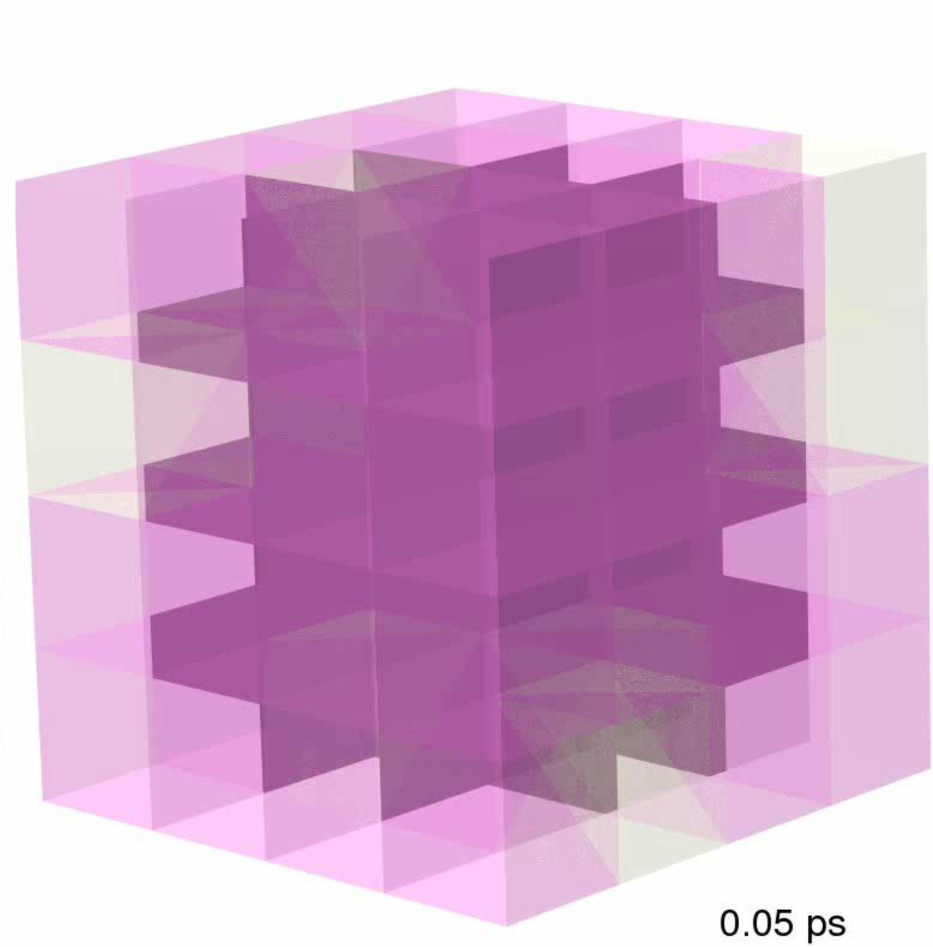
- ✓ **Large clusters of liquid-like molecules at *T* > 250 K**
- ✓ **Percolation transition of clusters of liquid-like molecules at ~ 220 K**
- ✓ **Emergence of large clusters of ice-like molecules at *T* < 220 K**

Movie

230K

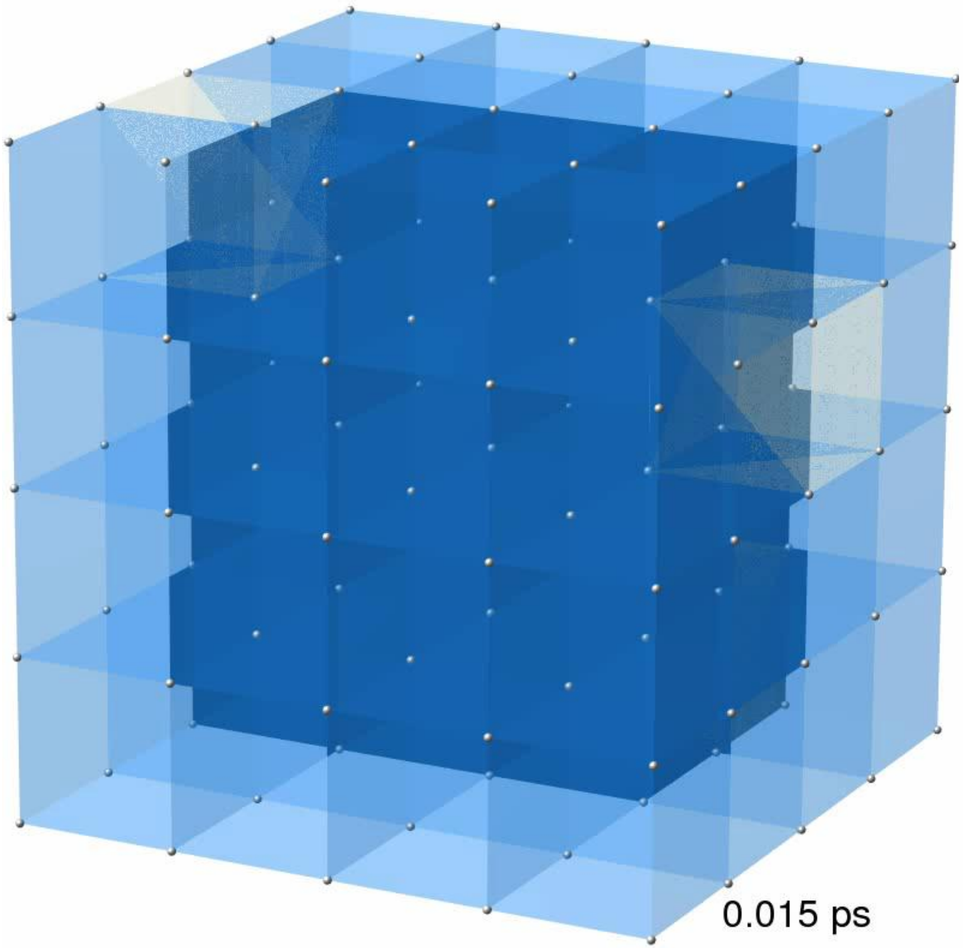


250K

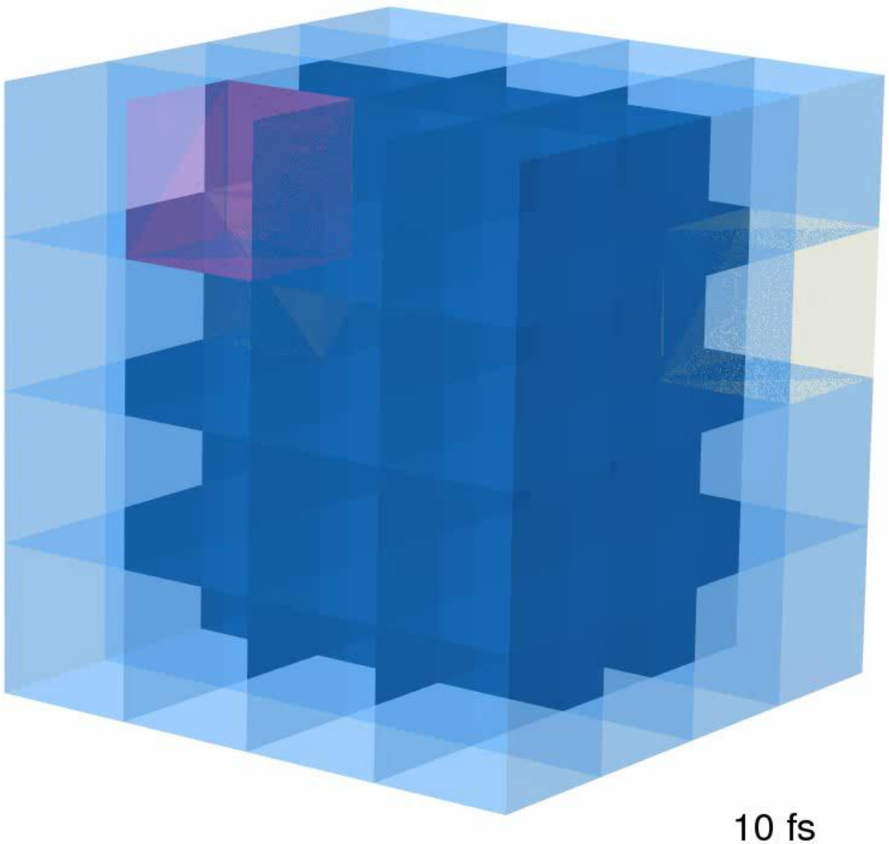


Movie

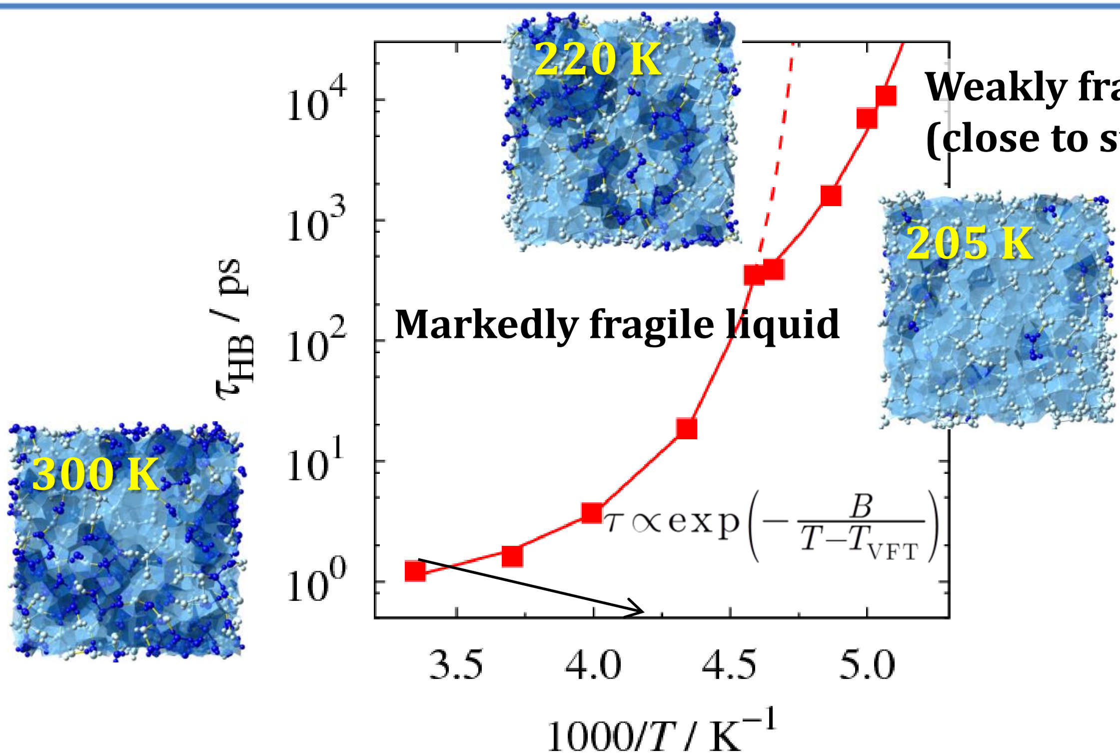
170K



190K



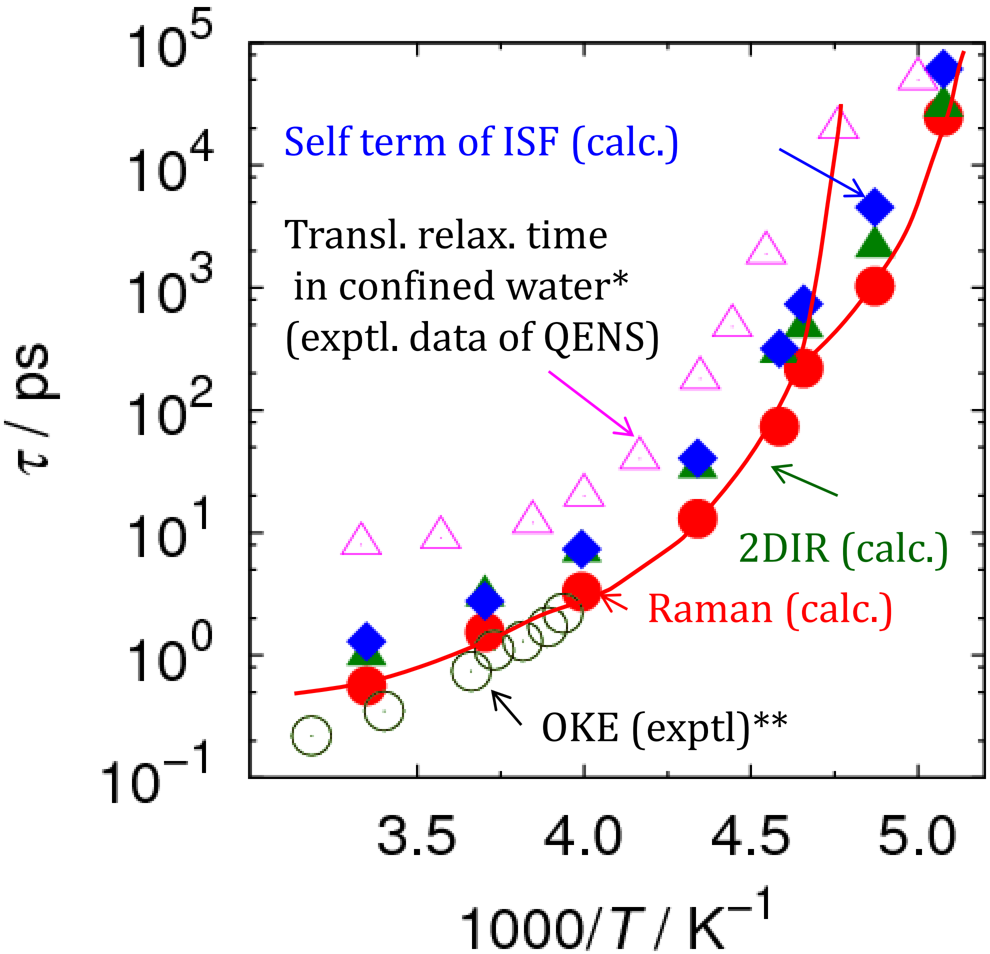
FRAGILITY CROSS-OVER IN C_P



*Velikov et al. Science **294**, 2335 (2001).

- **Non-Arrhenius behavior (= fragile liquid)**
- **Two Vogel-Fulcher-Tamermann equations (markedly and weakly fragile liquids)**
- **Transition from a fragile liquid to a weakly fragile (or strong) liquid at ~220 K**
- **Significant differences in structure, dynamics, and thermodynamics between two fragile liquids**
- **T_{VFT} = 173 K (in weakly fragile liquid) ~ $T_{glass\ trans.}$ proposed by Angell***

Temperature dependence of relaxation times



Similar to temp-dep. of HB network dynamics involved in C_P

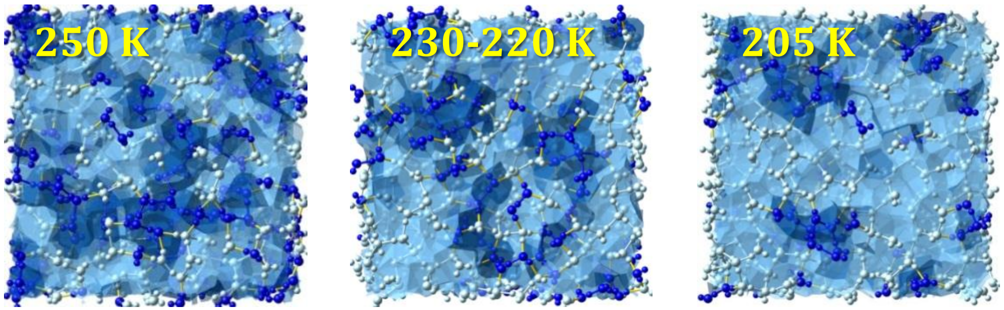
- Non-Arrhenius behaviors
- 'Fragile-strong' transition at ~ 220K

*Zhang et al, PRE **79**, 040201(R) (2009).

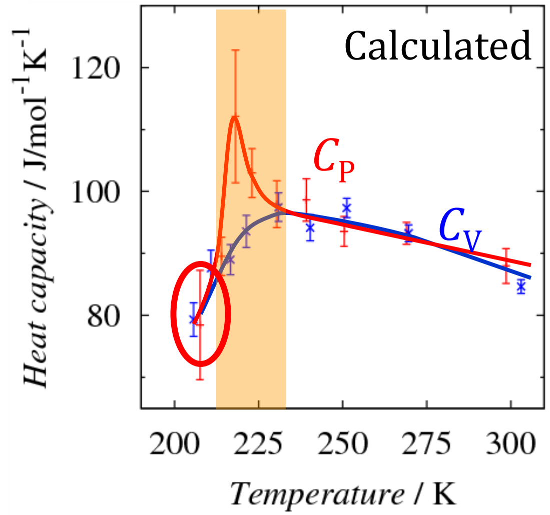
Torre et al., Nature **428, 296 (2004).

Local density fluctuations under two conditions

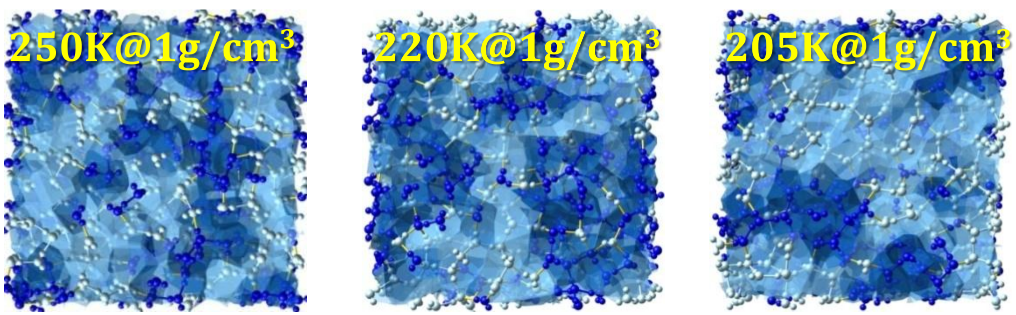
Constant pressure condition



Percolated liquid-like molecules | **Large local density fluctuation** | **Percolated ice-like molecules**



Constant volume condition

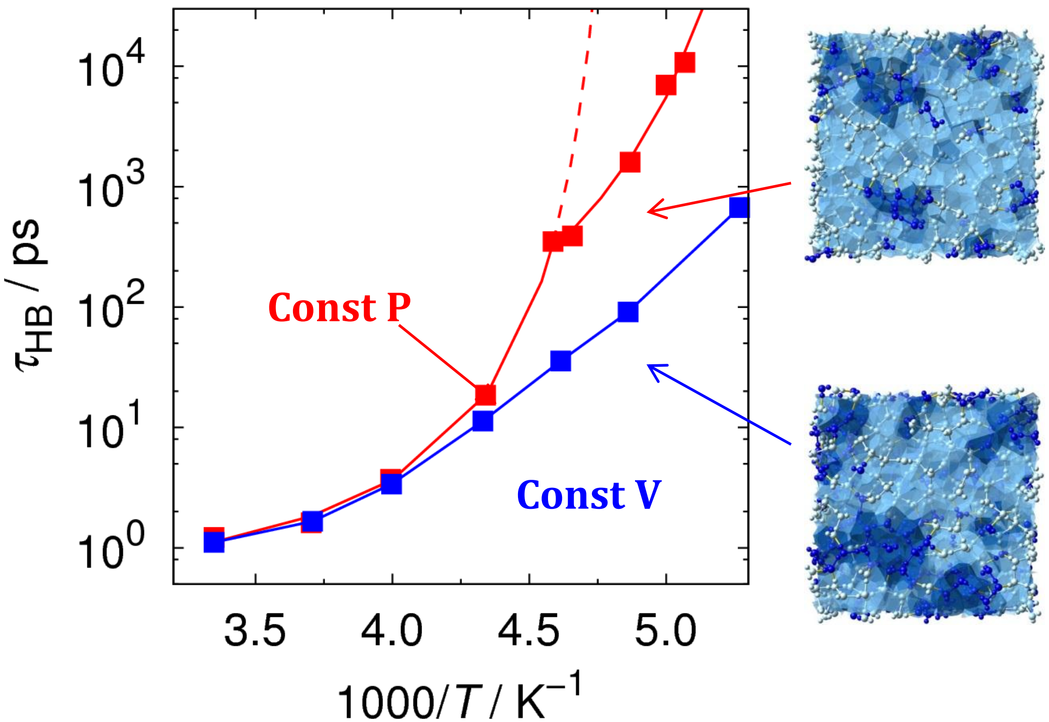


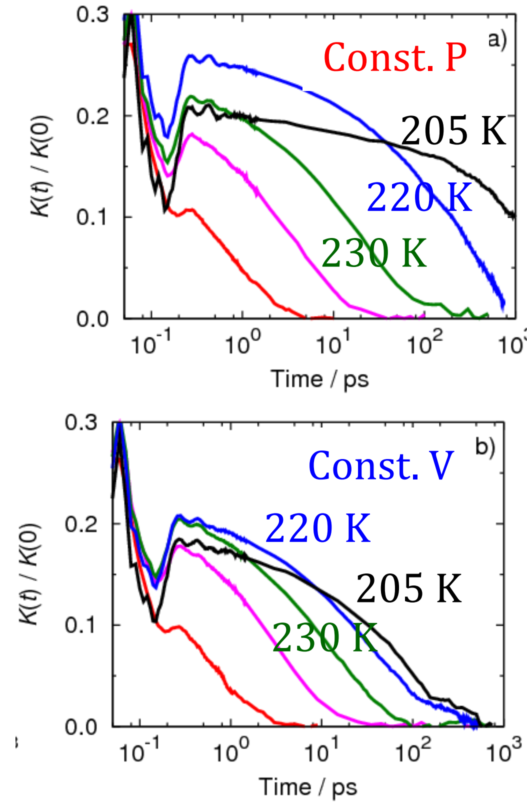
The presence of clusters of liquid-like molecules (locally disorder high density region) even at very low temperatures

Percolation transition of cluster of locally high density molecules at ~ 220 K

Significant difference in structure between two conditions, though C_P ~ C_V at very low temp.

Large difference between HB network dynamics involved in C_P and C_V

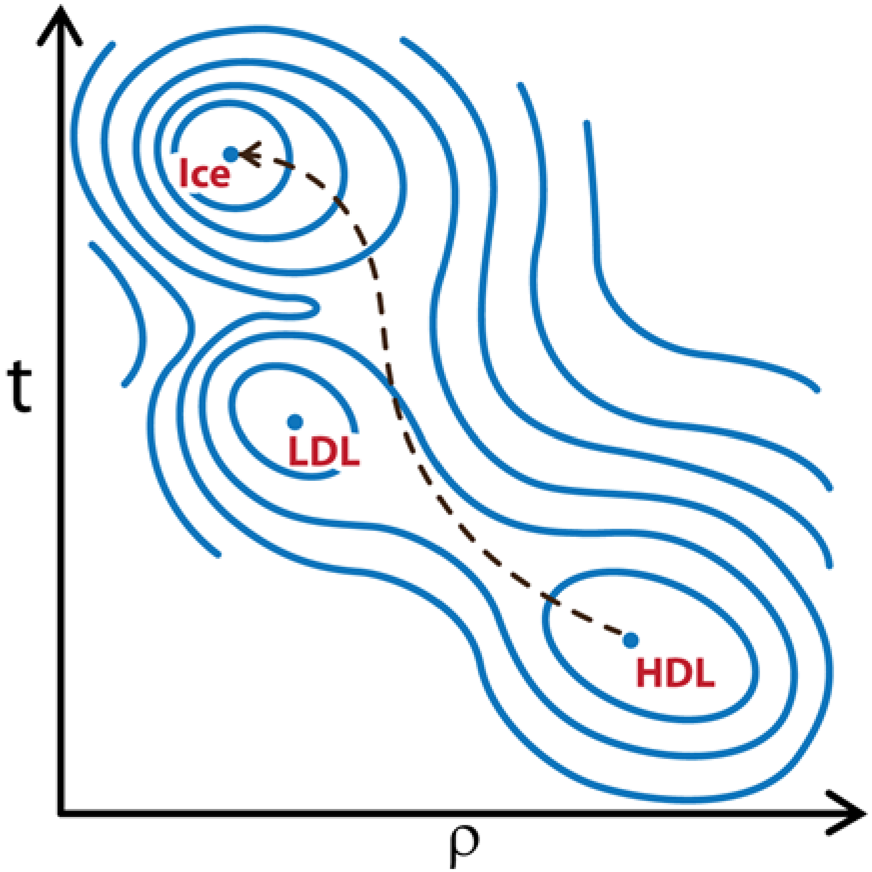




- **Unclear ‘fragile-strong’ transition under constant volume condition**
- **Difference in structure, dynamics, and thermodynamics of HB network dynamics between constant P. and constant V conditions**
- **Difference in energy landscape between two conditions**

Water Freezes at 232K!

- **LDL-HDL critical point suspected 220-230K!**

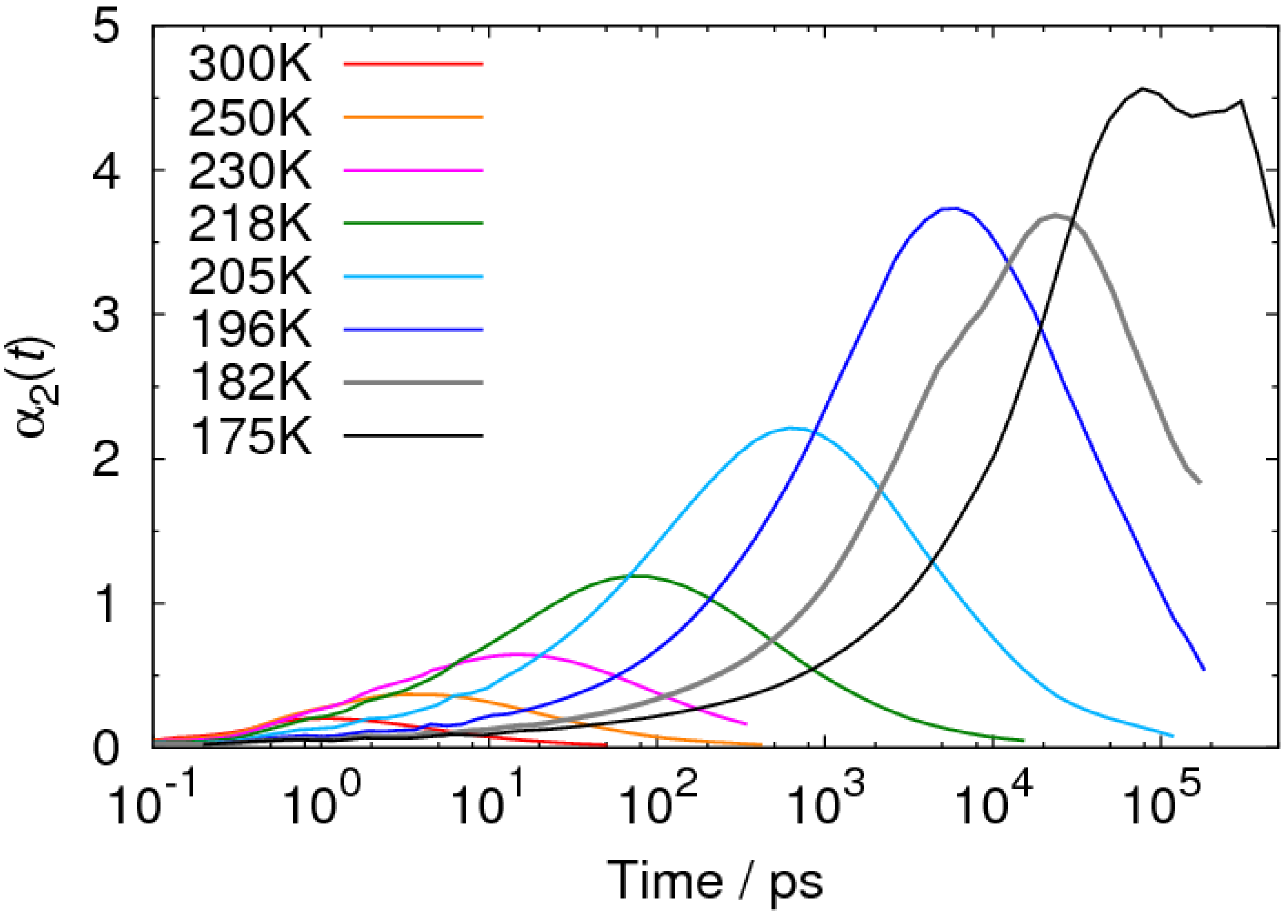


In the Search for a Glass Transition

- There are several outstanding controversies about the temperature of glass transition, if any

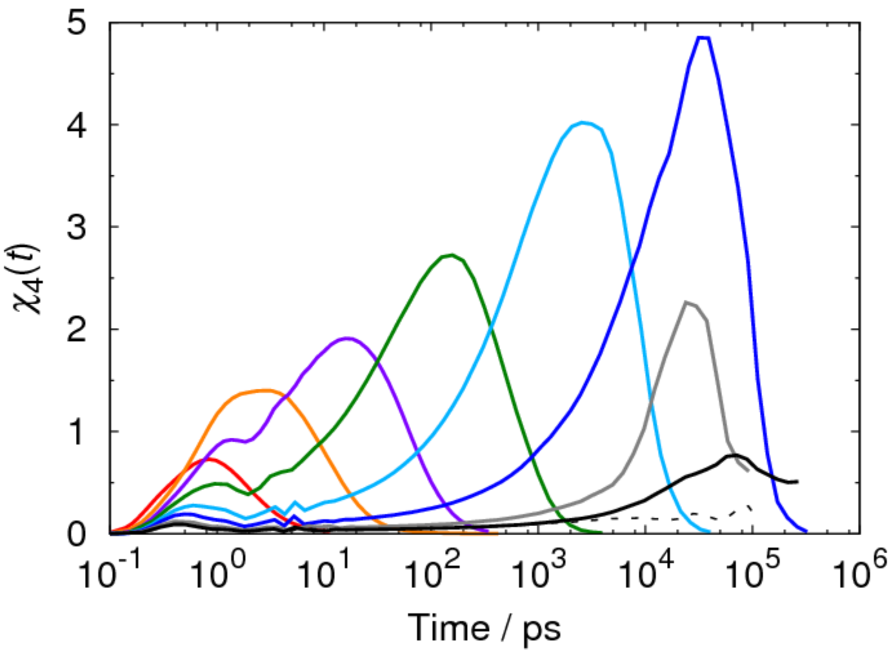
- Amorphous ice is stable up to 155K beyond which it is known to undergo crystallization

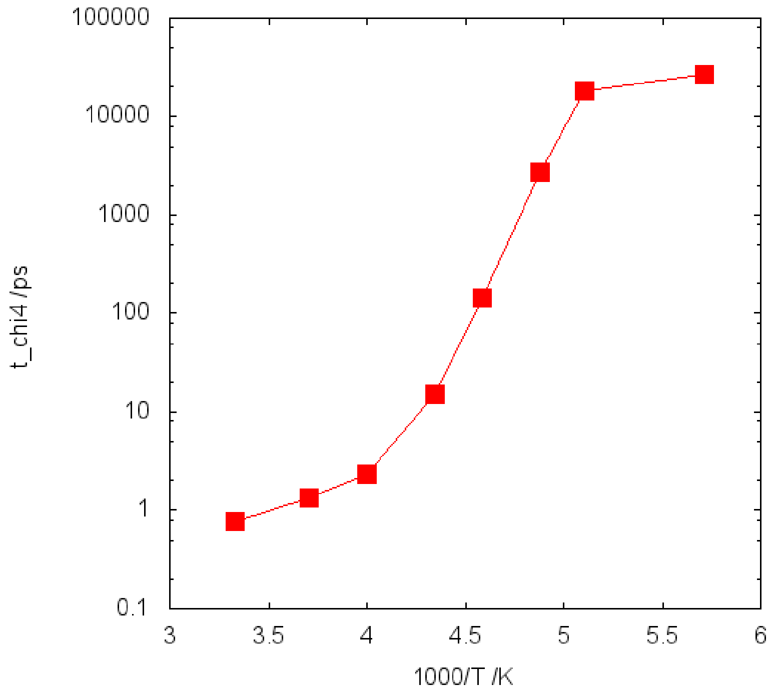
Static/dynamic heterogeneity



Jana, Singh and Bagchi, PCCP (2012)

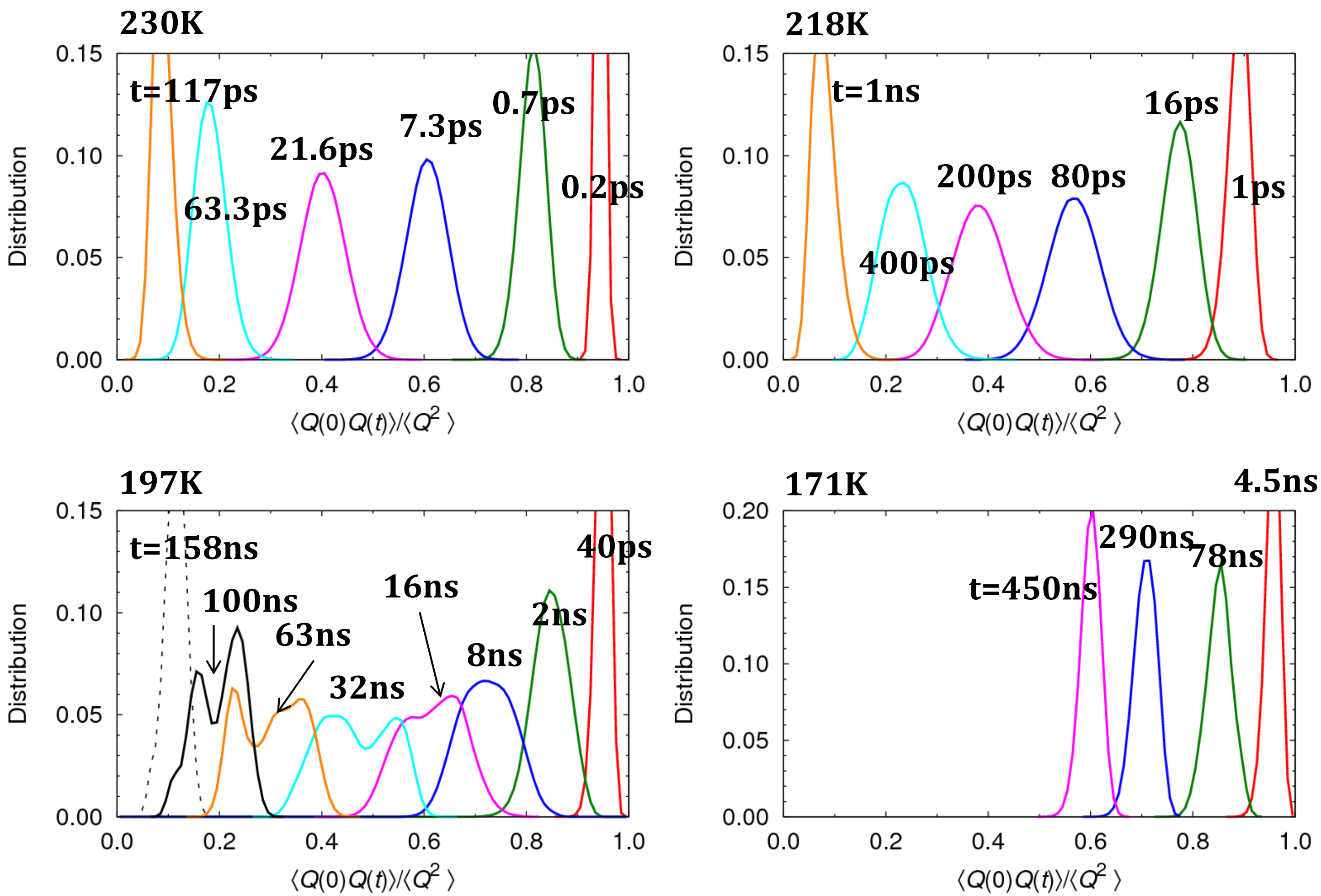
Dynamic Heterogeneity : Non-linear response function, χ_4 (t)



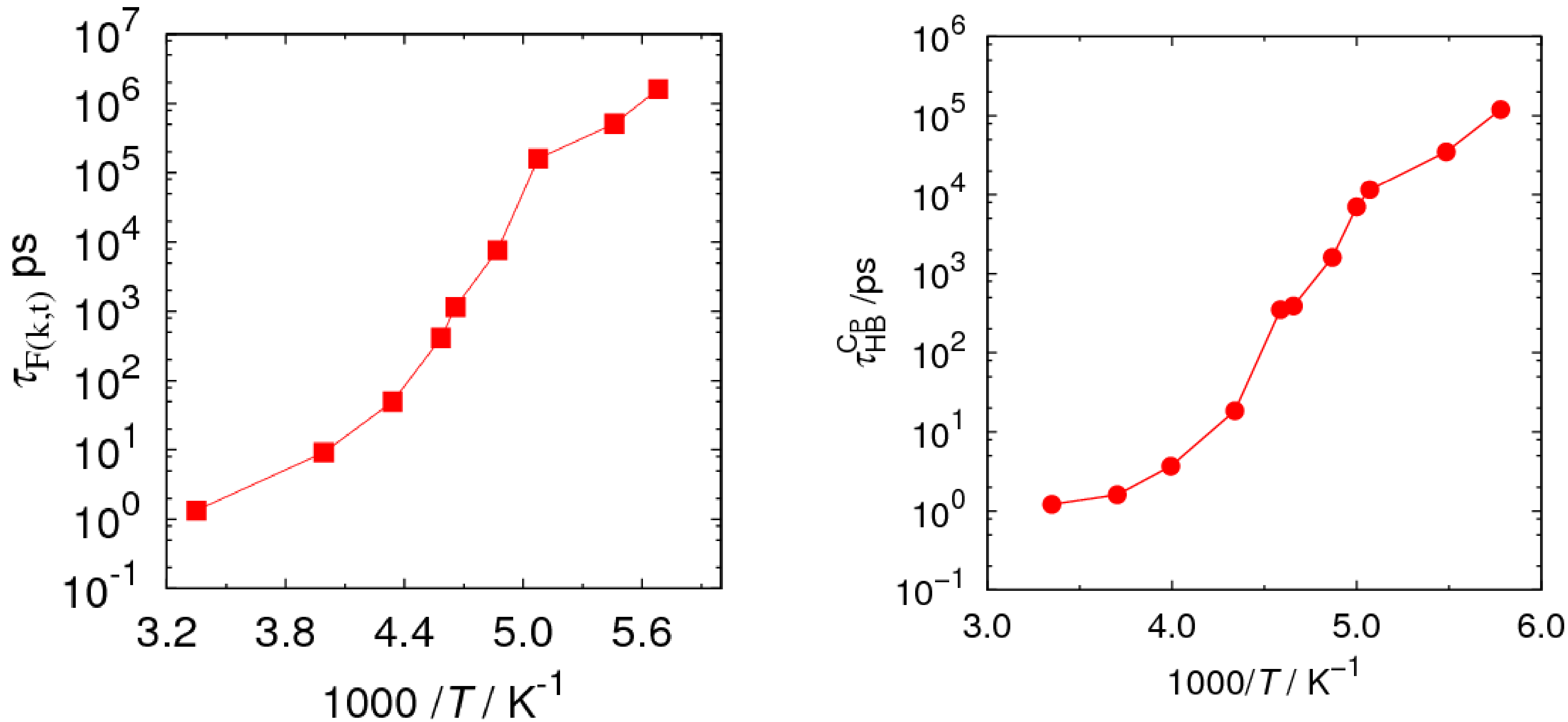


Distribution of Q(t)

Distribution of TCF of Q(t)



Temperature vs. relaxation time

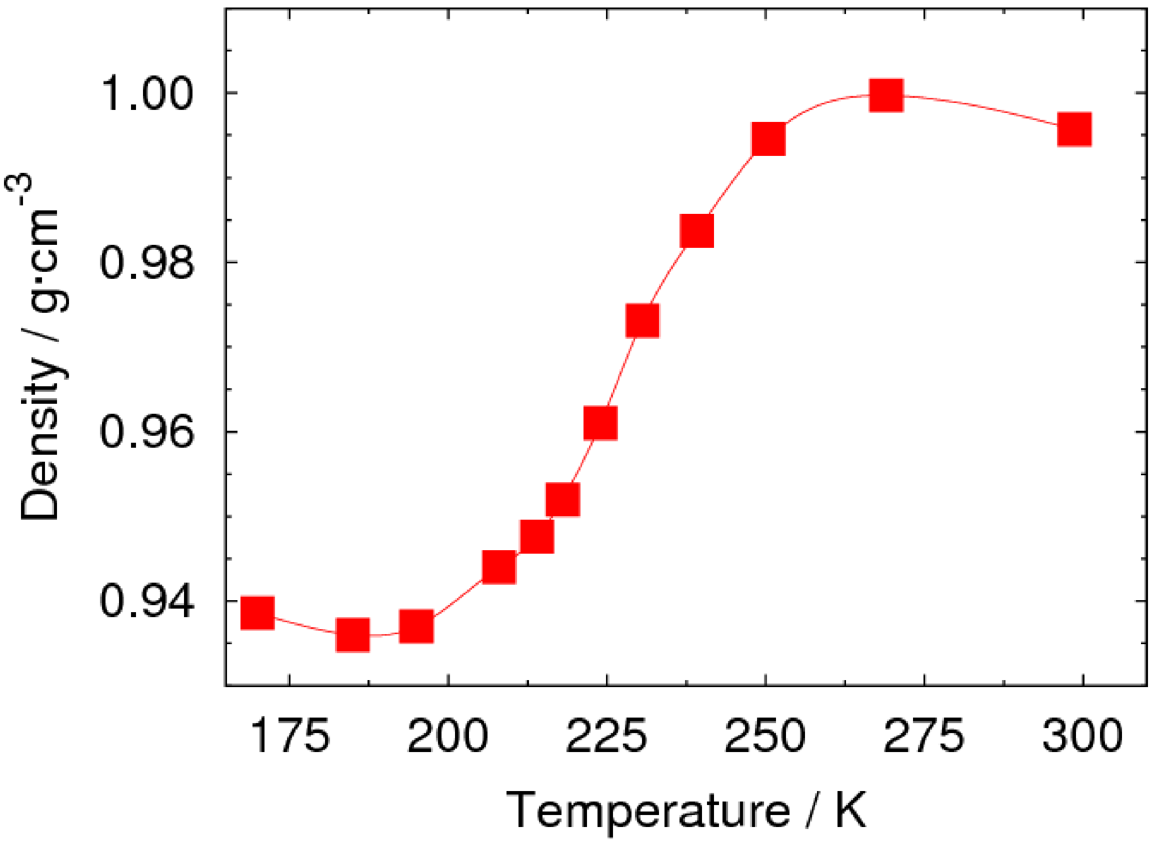


Relaxation time of intermediate scattering function

Relaxation time of temperature fluctuation

✓**Two inflection points and three domains**

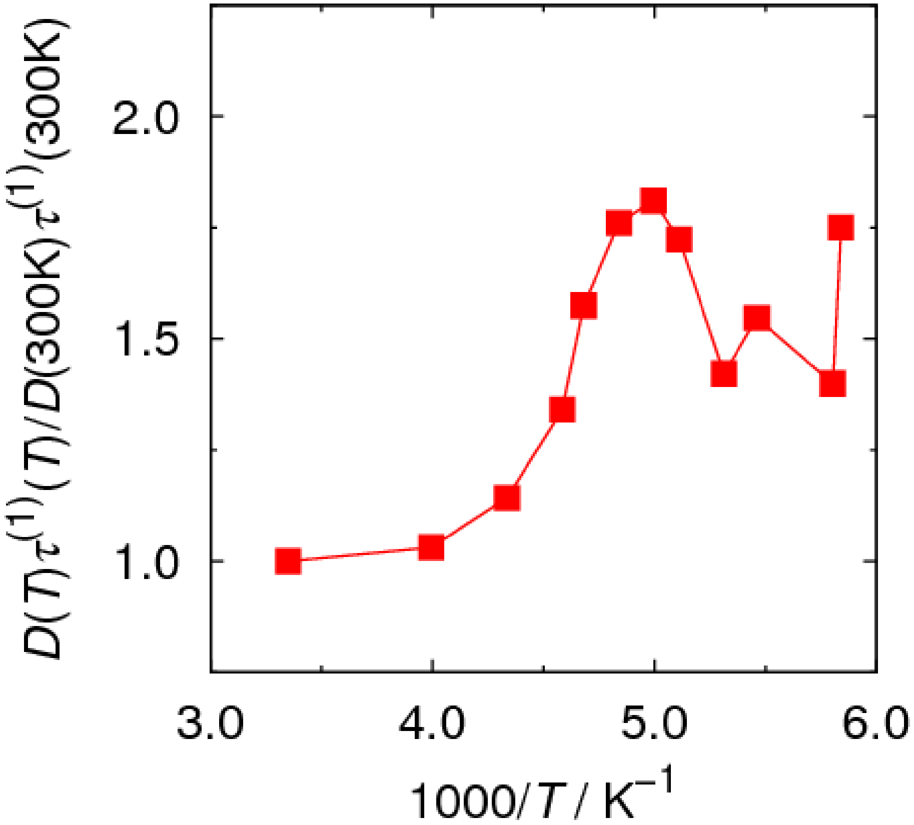
Temperature vs. density

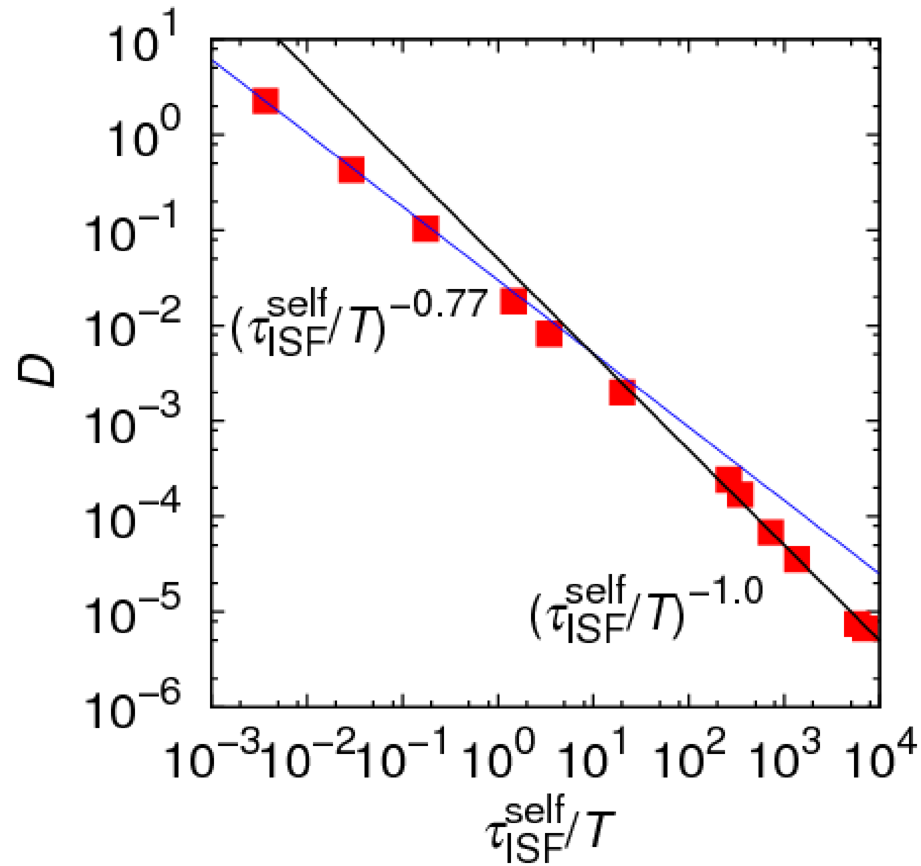


✓**Maximum at 277K**

✓**Minimum at 190k**

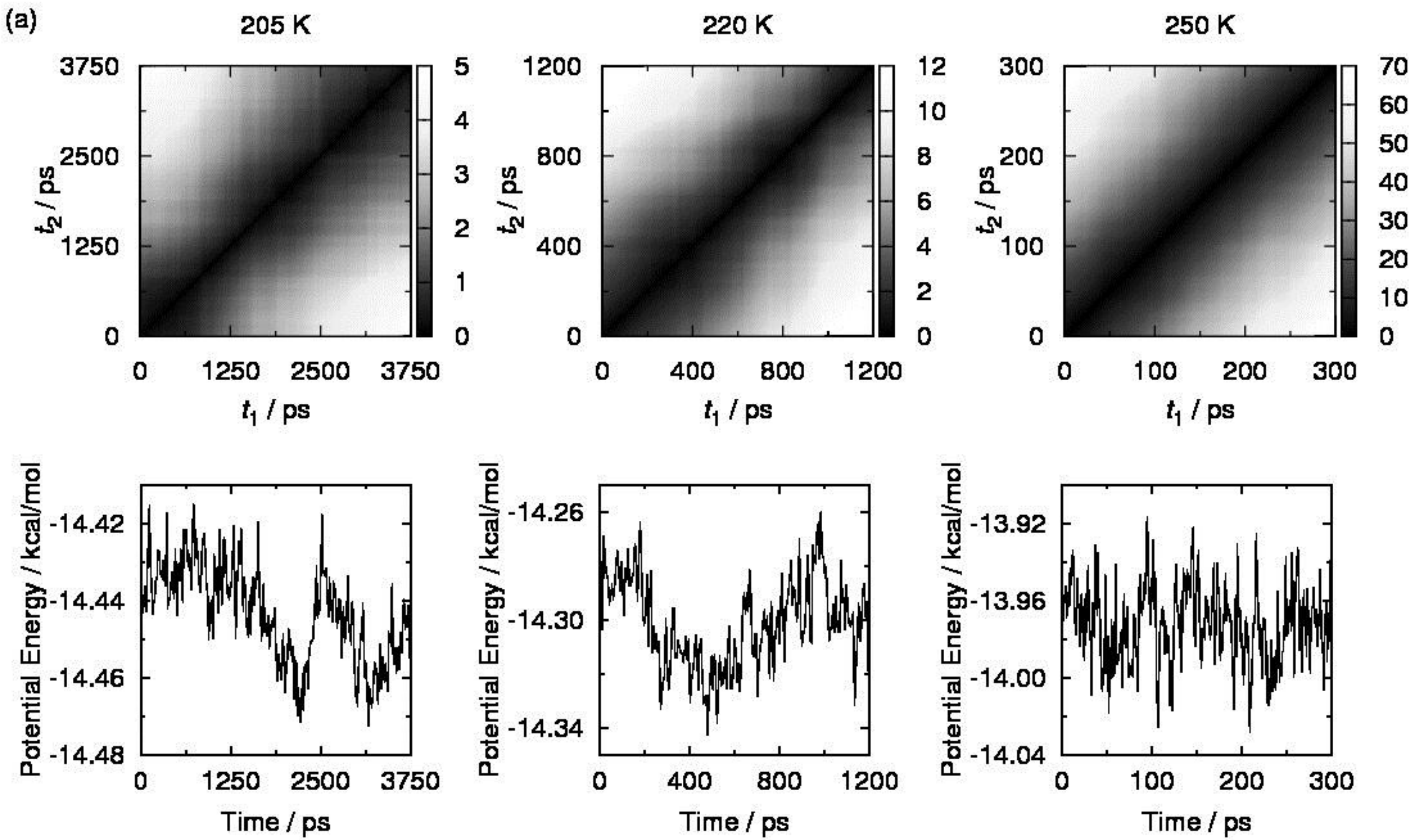
Temperature vs. coupling of rotational and translation motion



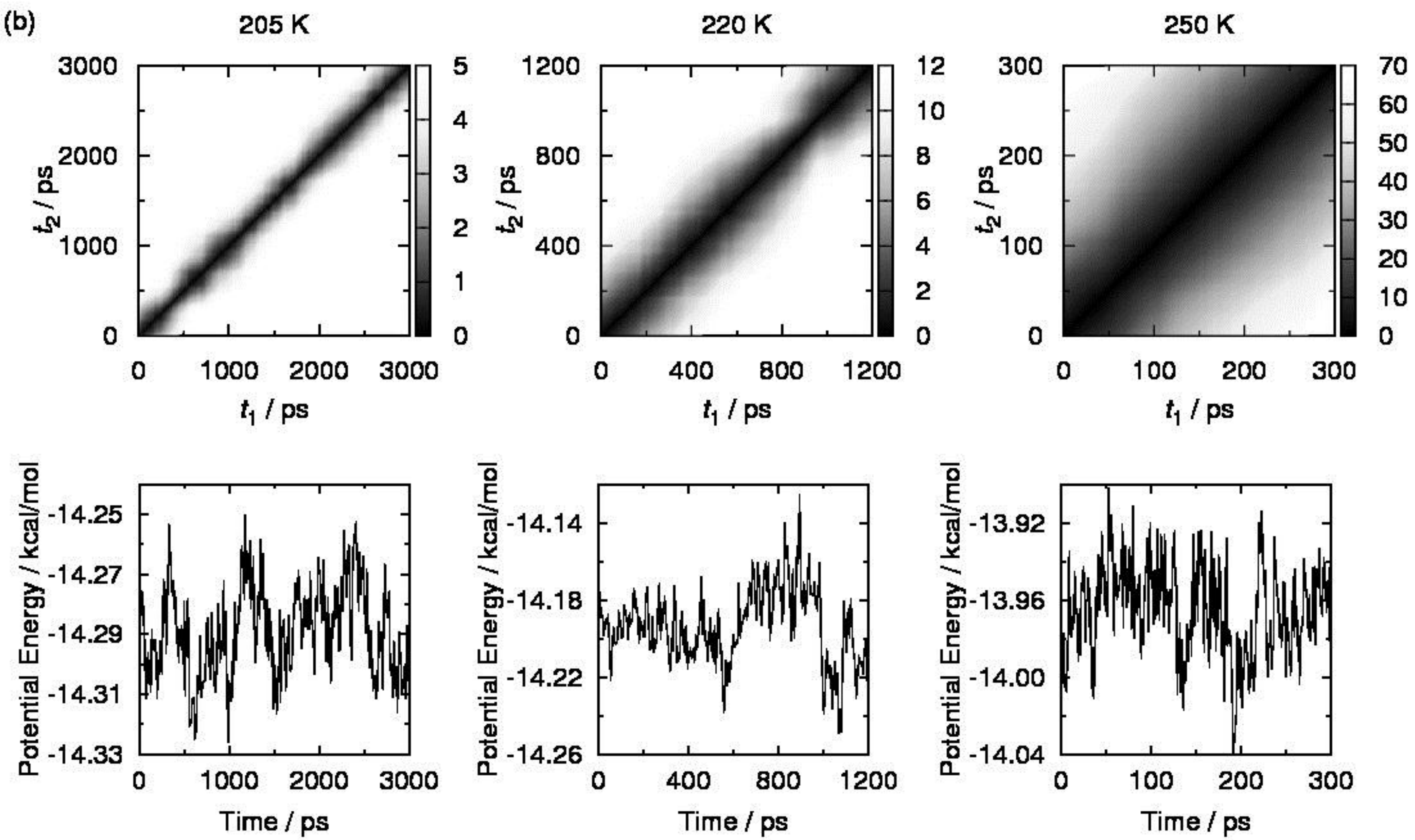


- Fractional Stokes-Einstein behavior above 220K
- Stokes-Einstein behavior recovered below 190K

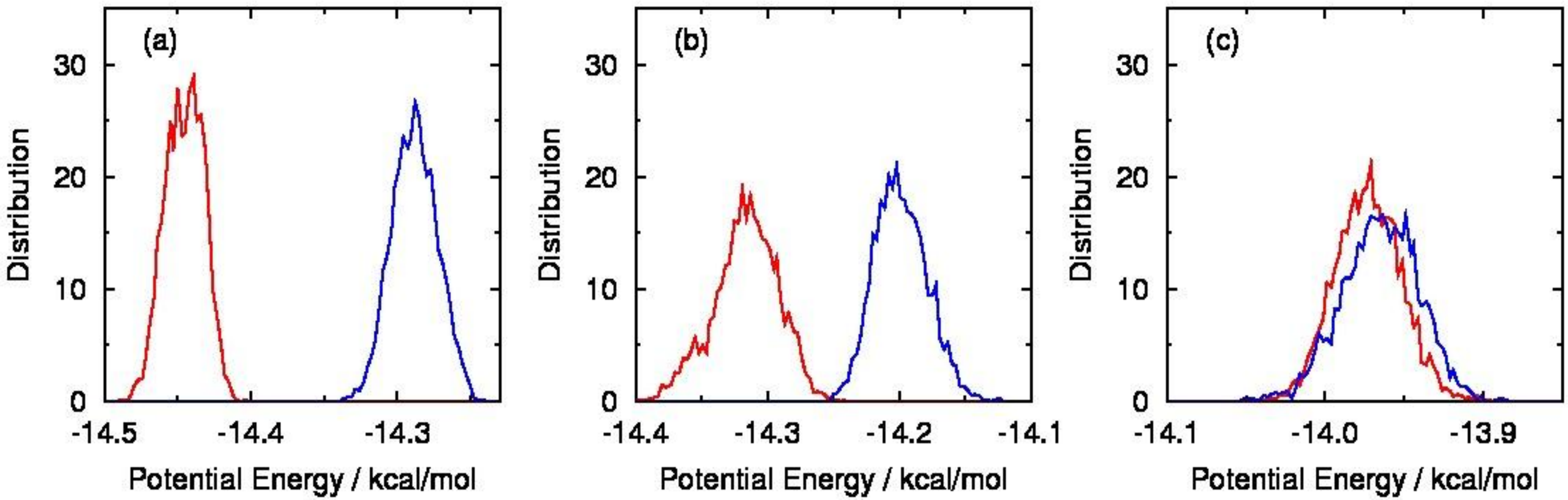
Inherent structure energies and the corresponding distance matrices, at constant pressure



Inherent structure energies and the corresponding distance matrices, at constant volume



Distribution of IS energy



205 K

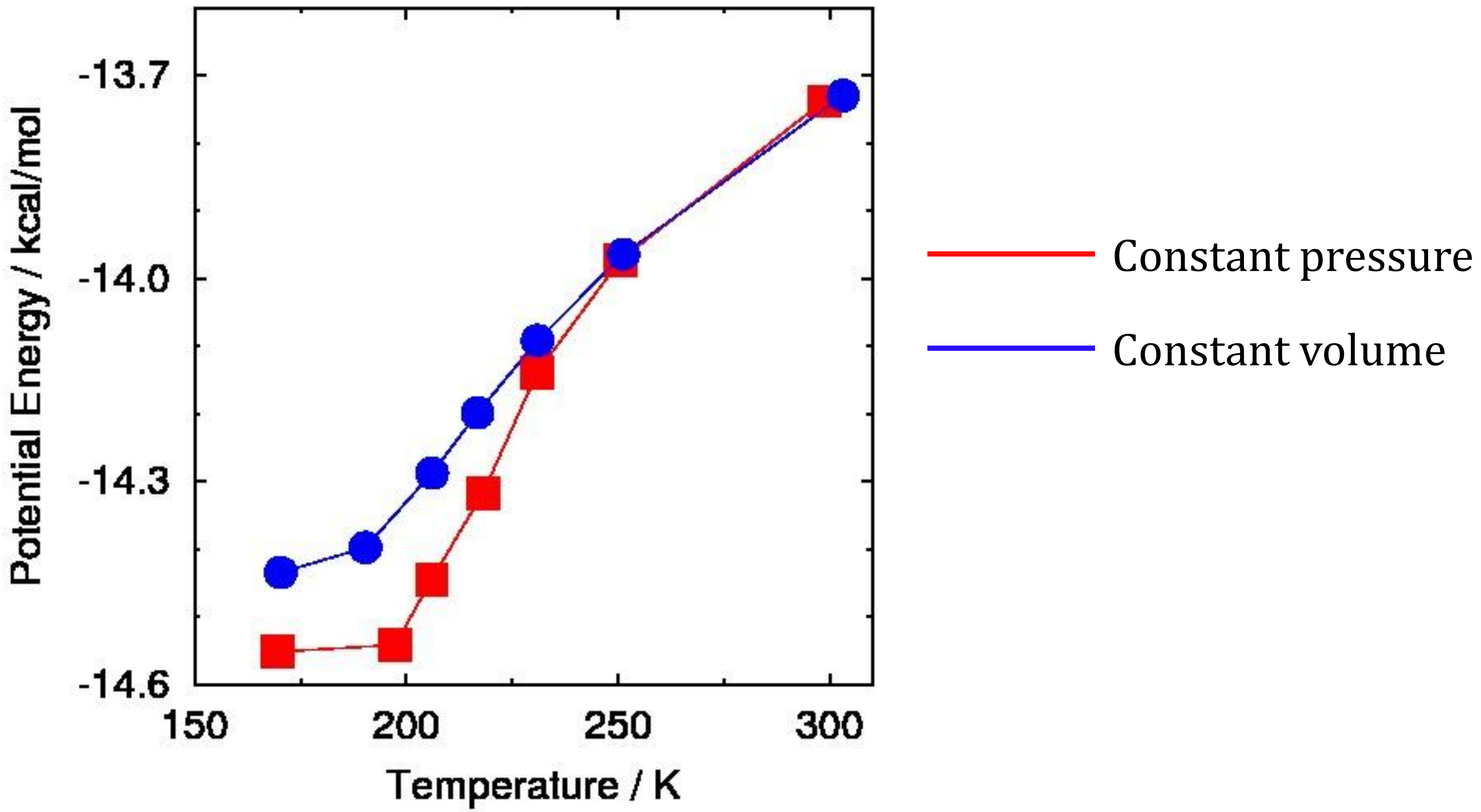
220 K

250 K

Constant pressure

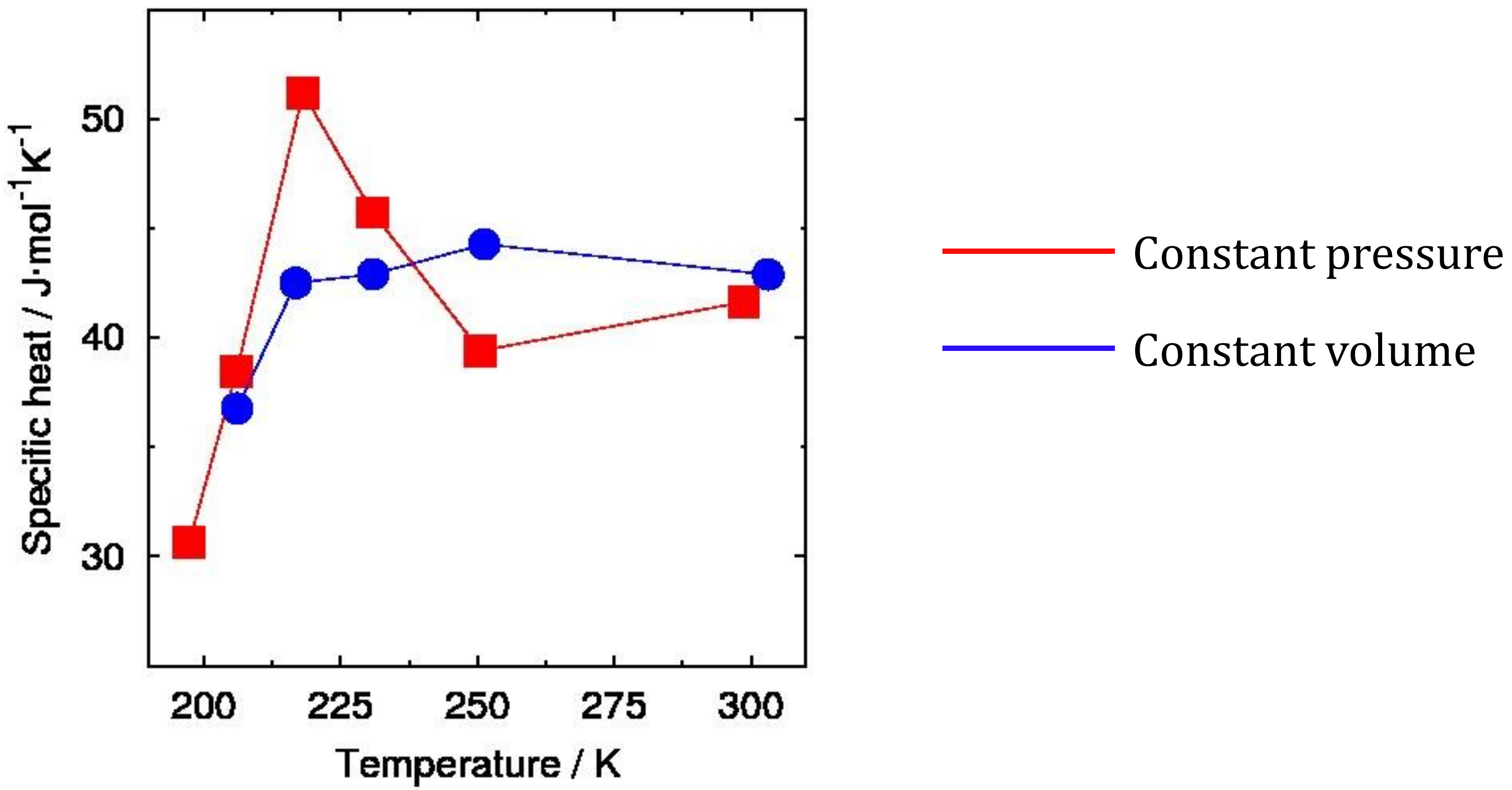
Constant volume

Temperature vs. average IS energy



Sharper fall for the constant pressure conditions

Specific heat obtained from IS

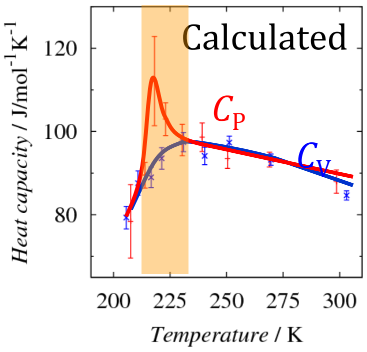


Sharper rise below 250K under constant pressure conditions

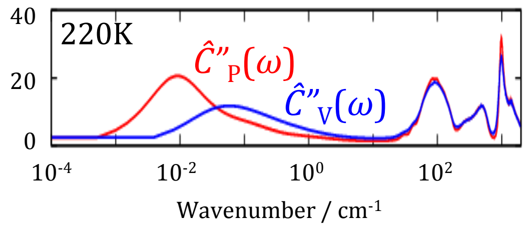
Summary

Anomalous temperature dependence of C_P of water

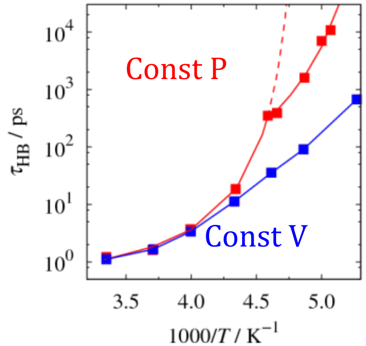
- **Slowing-down of HB network dynamics in C_P**
  - **Time scale of HB network dynamics is several hundred ps ~ several ns at 220 K**



- **Emergence of correlated dynamics with decreasing temperature**
  - **~6th hydration shell consisting of ~340 water molecules**



- **Transition from fragile liquid to weakly fragile (or strong) liquid at ~ 220 K**
  - **T_{VFT} in the low-Temp branch ~ T_{glass} proposed by Angell et al**
  - **Analysis of 'fragile-strong' transition based on three-time correlation function***



- **Preliminary theory of ice nucleation**
- **Glass transition around 170 K.**

Acknowledgements

- ✓ S. Saito, I. Ohmine, and B. Bagchi, *J. Chem. Phys.* **138**, 094503 (2013).
- ✓ S. Saito and B. Bagchi, PCCP (ENERGY LANDSCAPE SPL ISSUE)

Prof. Shinji Saito

Prof. Iwao Ohmine

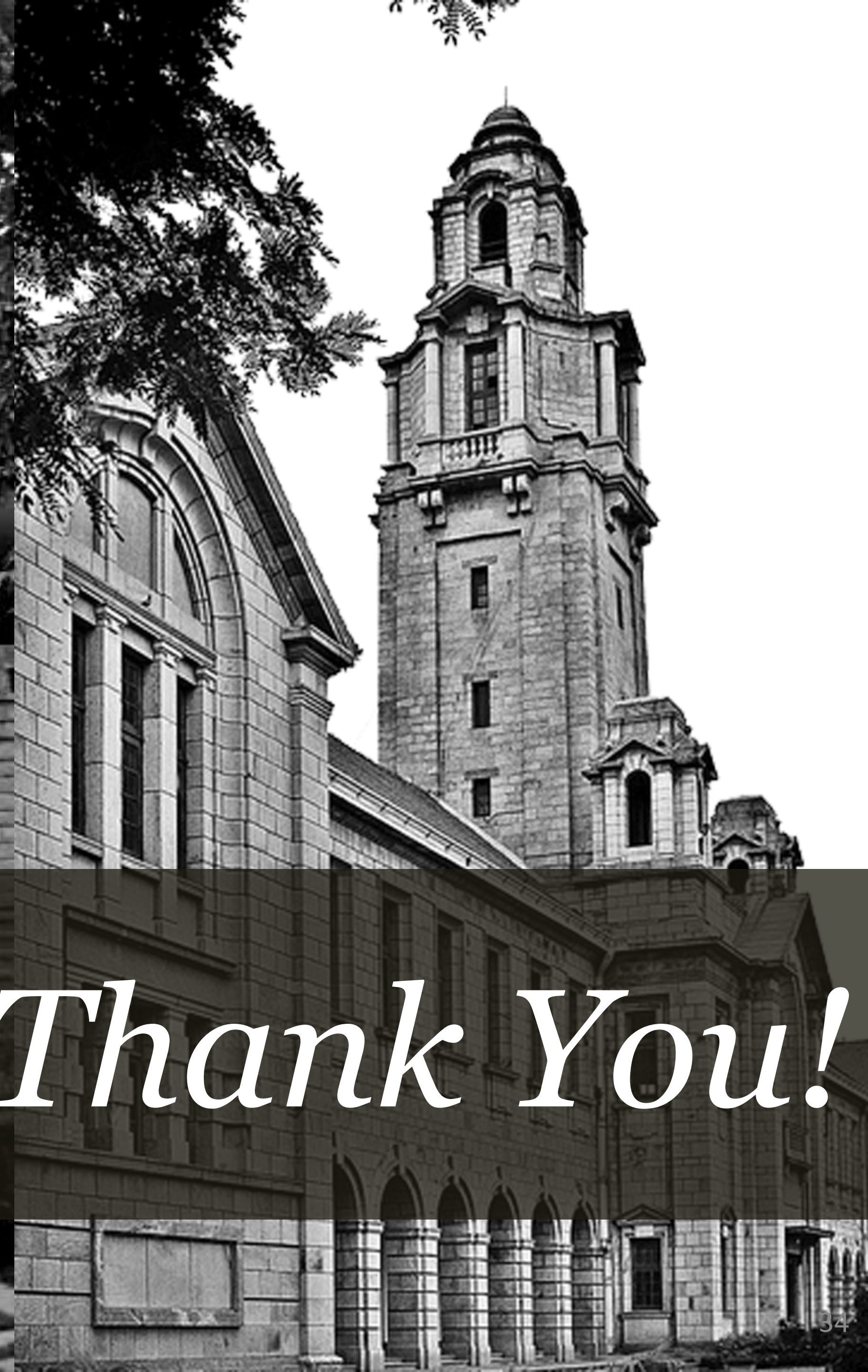
Dr. Mantu Santra

Dr. Rakesh Sharan Singh

Indo-Japan research grant

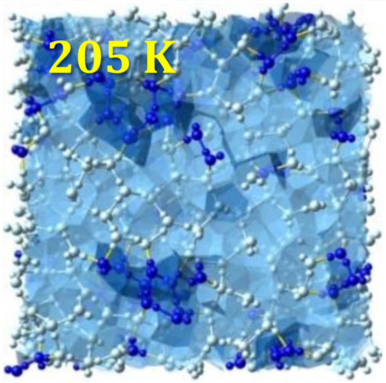
CSIR INDIA

Department of Science & Technology
Ministry of Science & Technology

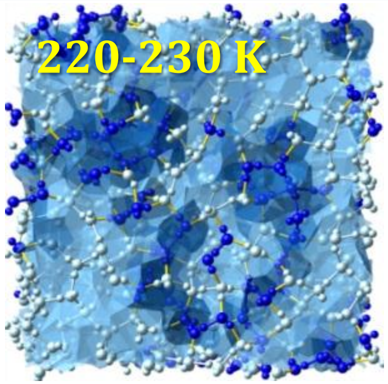


Thank You!

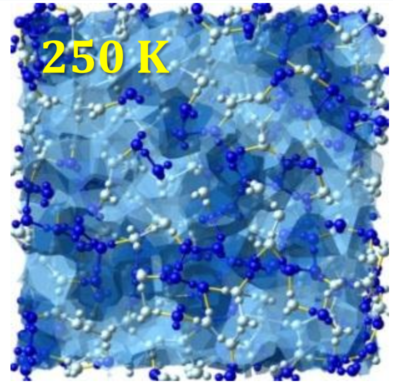
Temperature dependence of local density fluctuation



Percolation of ice-like molecules



Large local density fluctuation

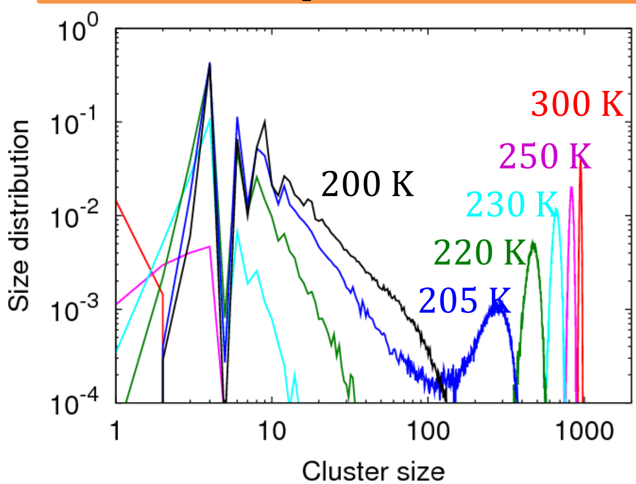


Percolation of liquid-like molecules

Ice-like molecule:
a 4-coordinated molecule which is coordinated to four 4-coordinated molecules

Liquid-like molecule:
otherwise

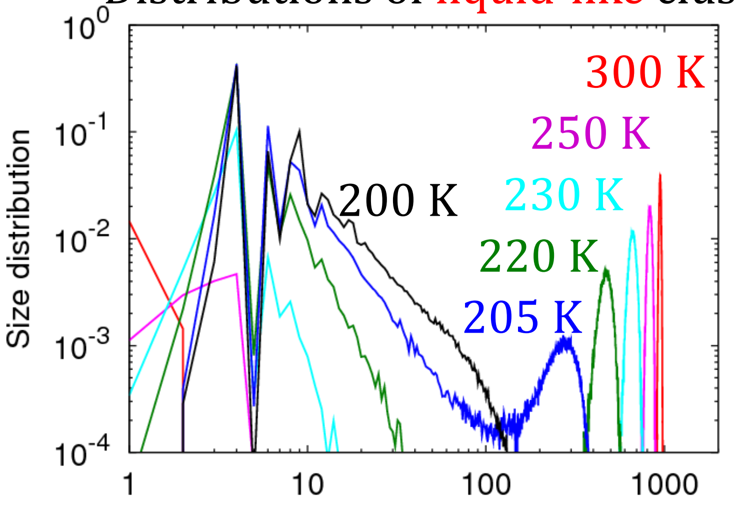
Temp. dep. of size-distribution of clusters of liquid-like molecules



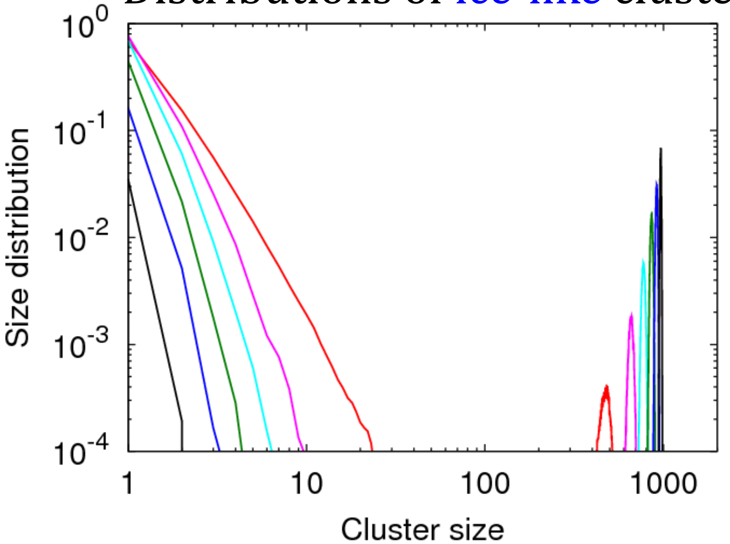
- **Large clusters of liquid-like molecules at T > 250 K**
- **Percolation transition of clusters of liquid-like molecules at ~ 220 K**
- **Emergence of large clusters of ice-like molecules at T < 220 K**

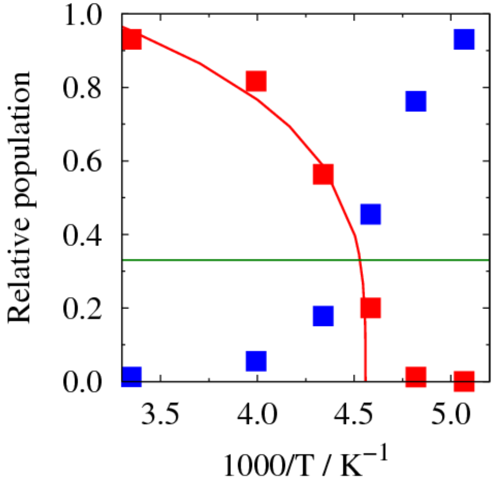
Percolation-like transition of liquid-like cluster

Distributions of liquid-like clusters

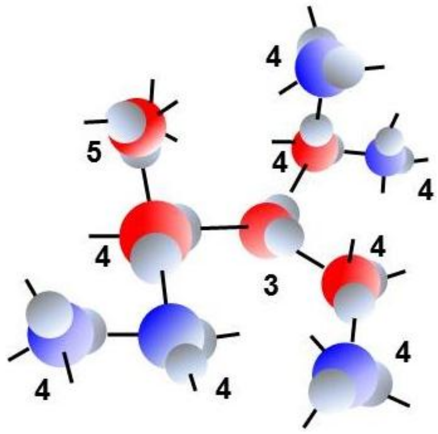


Distributions of ice-like clusters

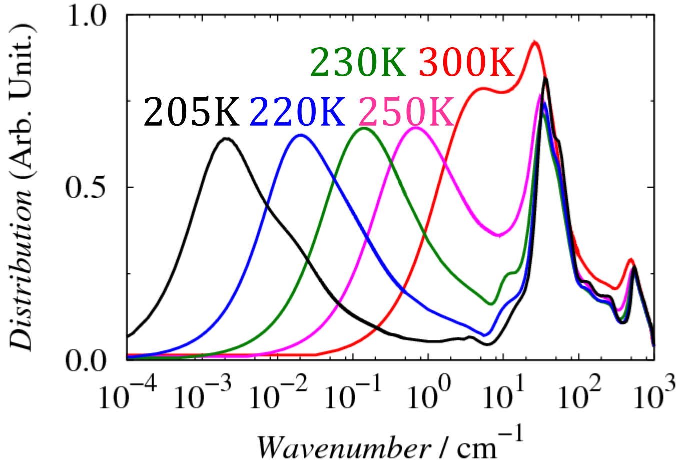




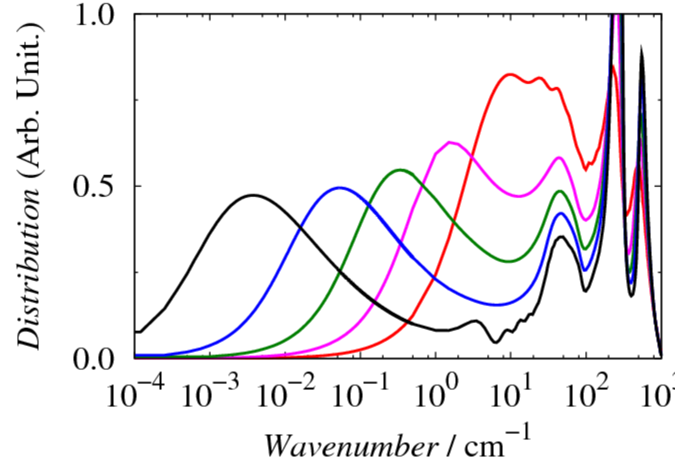
Liquid-like molecule:
A molecule which has at least one 3- or 5-coord. Molecule within its 1st hydration shell



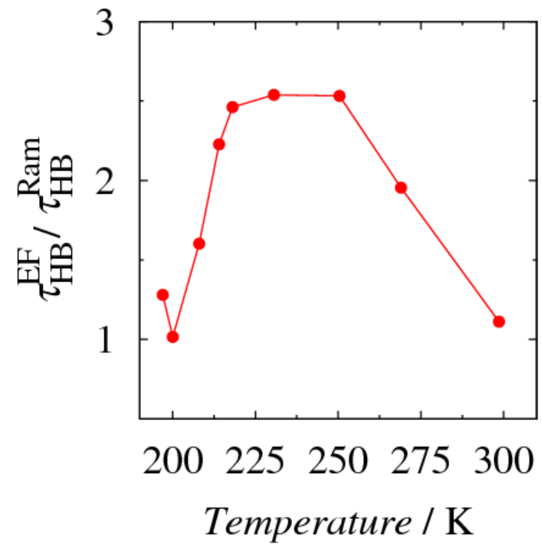
Temperature dependence of 2D IR and Raman spectra



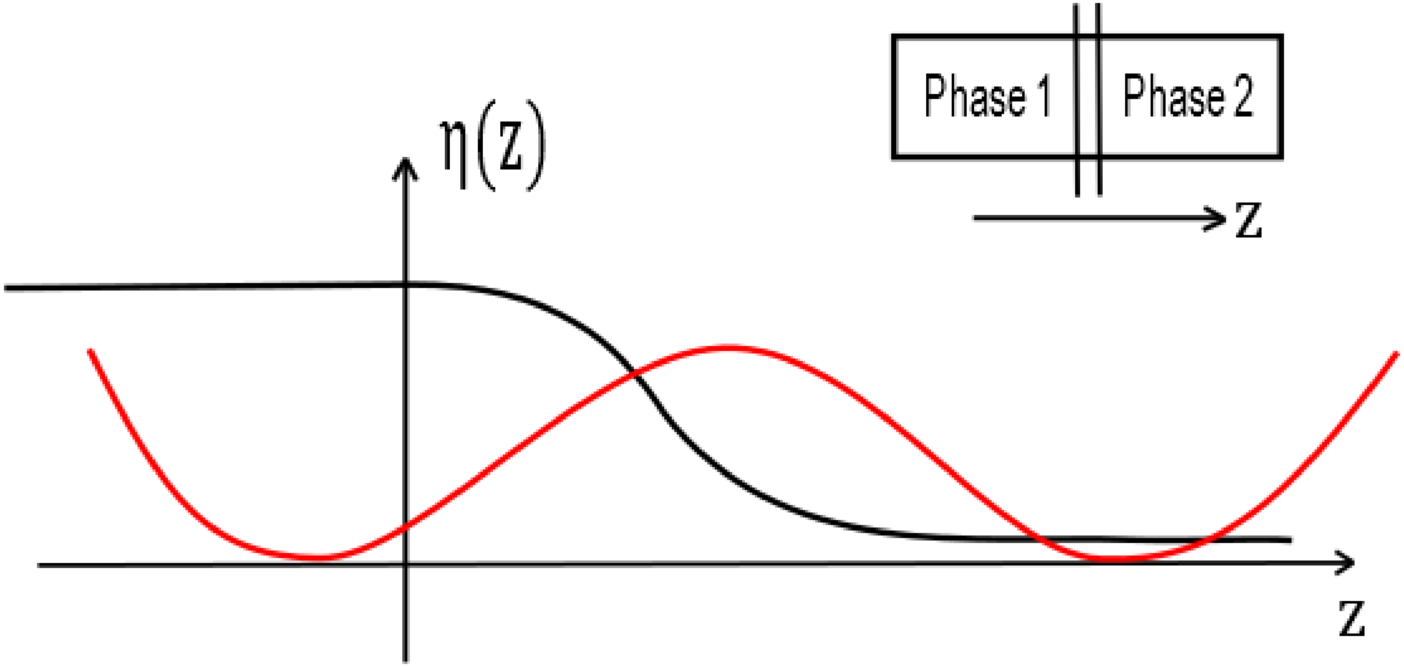
Spectra of **electric field parallel to OH stretch** (related to 3-pulse IR PE of OH stretch)



Spectra of **Raman spectrum**



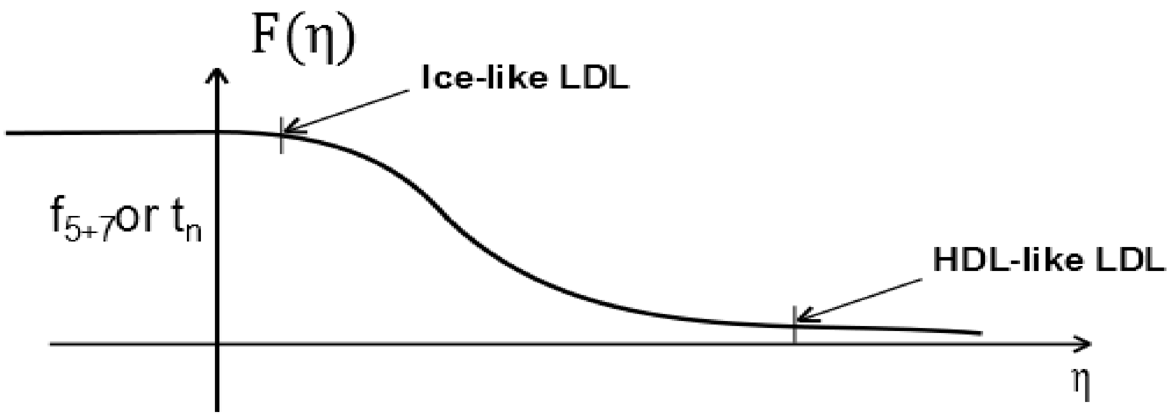
Emergence of correlated dynamics
by examining different spectroscopic method because of the difference in their correlation lengths

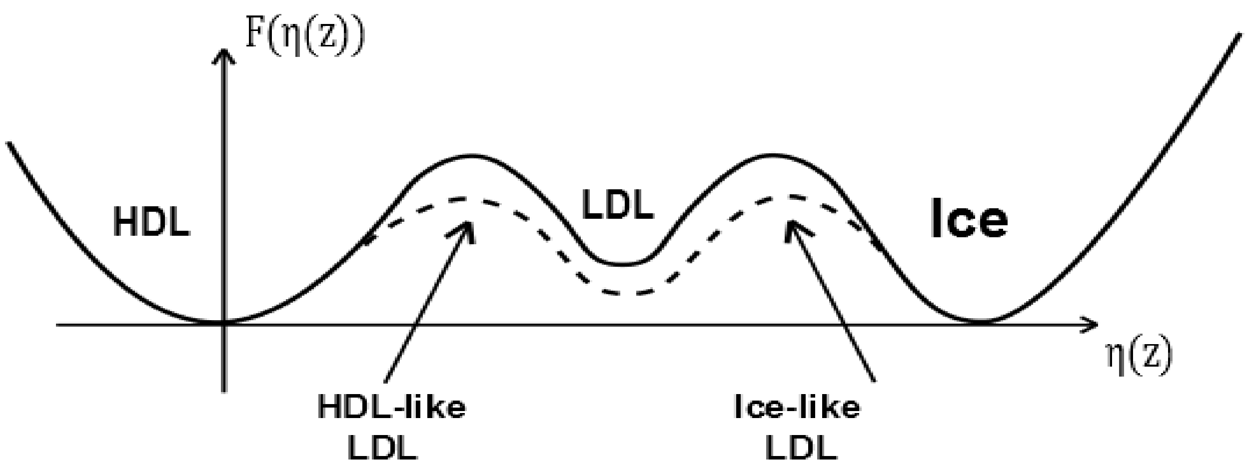


At Equilibrium :

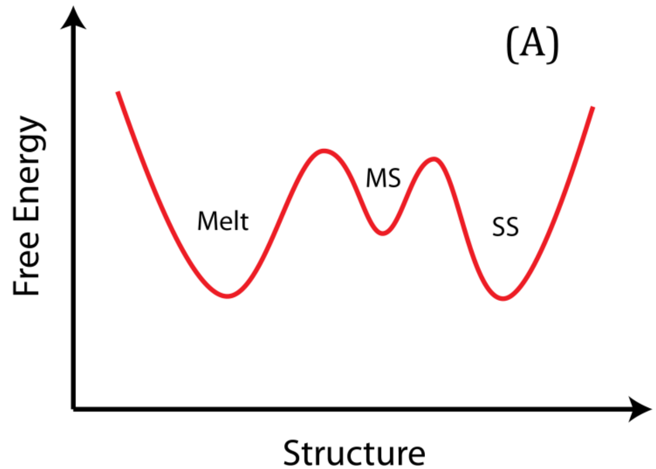
$$\delta F = \int dz\,\eta(z)\,F(\eta(z)) + \frac{1}{2}K\int dz\left(\frac{\partial \eta(z)}{\partial z}\right)^2$$

▪

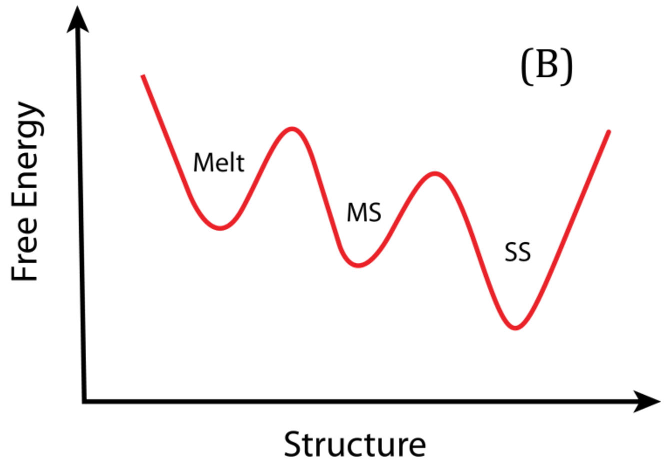

F(η)
Ice-like LDL
f5+7or tn
HDL-like LDL
η


F(η(z))
HDL
LDL
Ice
η(z)
HDL-like
LDL
Ice-like
LDL

Case of one metastable intermediate phase



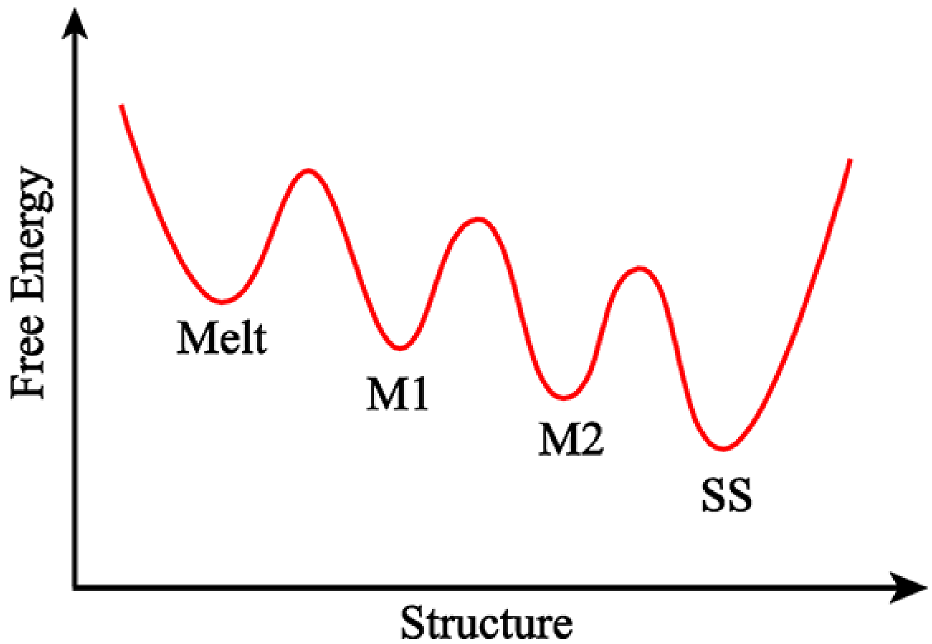
At coexistence of melt and stable solid phase

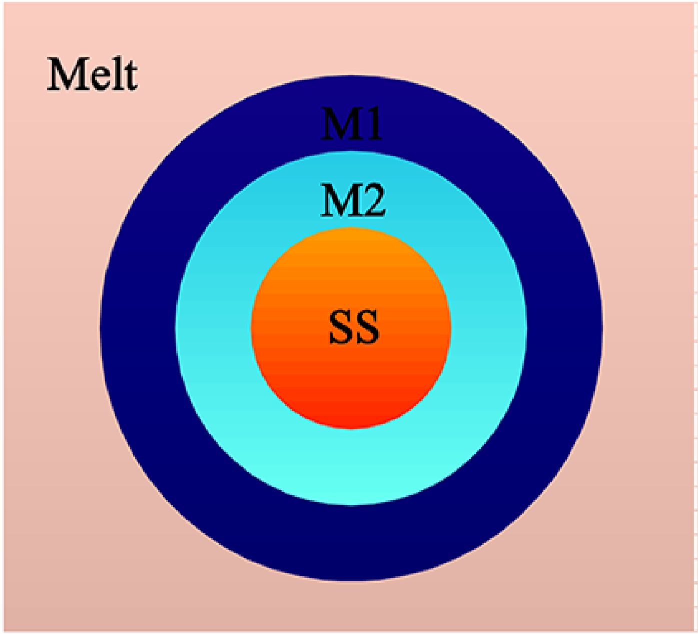


Under supersaturated state

Nucleation of ice – wetting of Ice by LDL within HDL

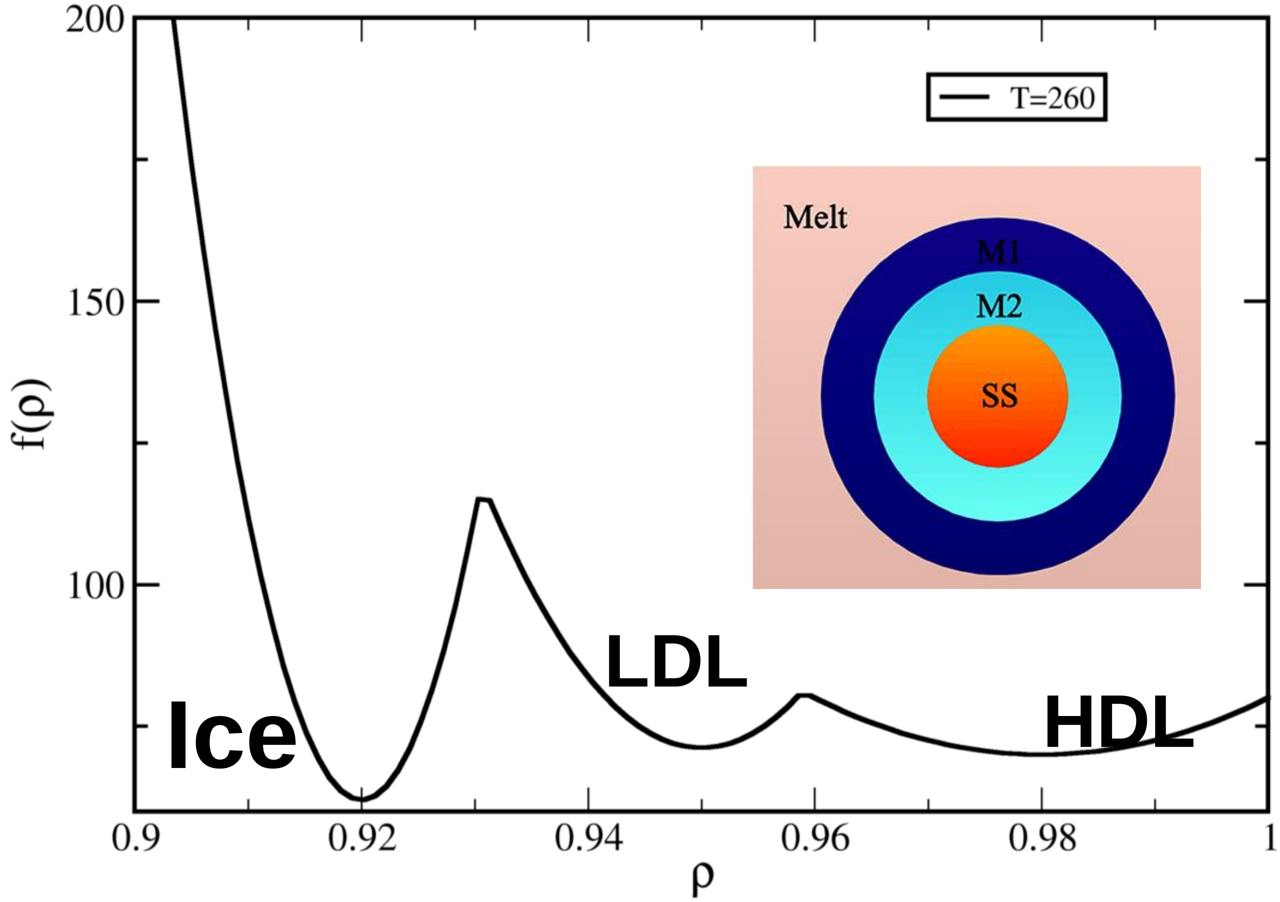
Density functional theory



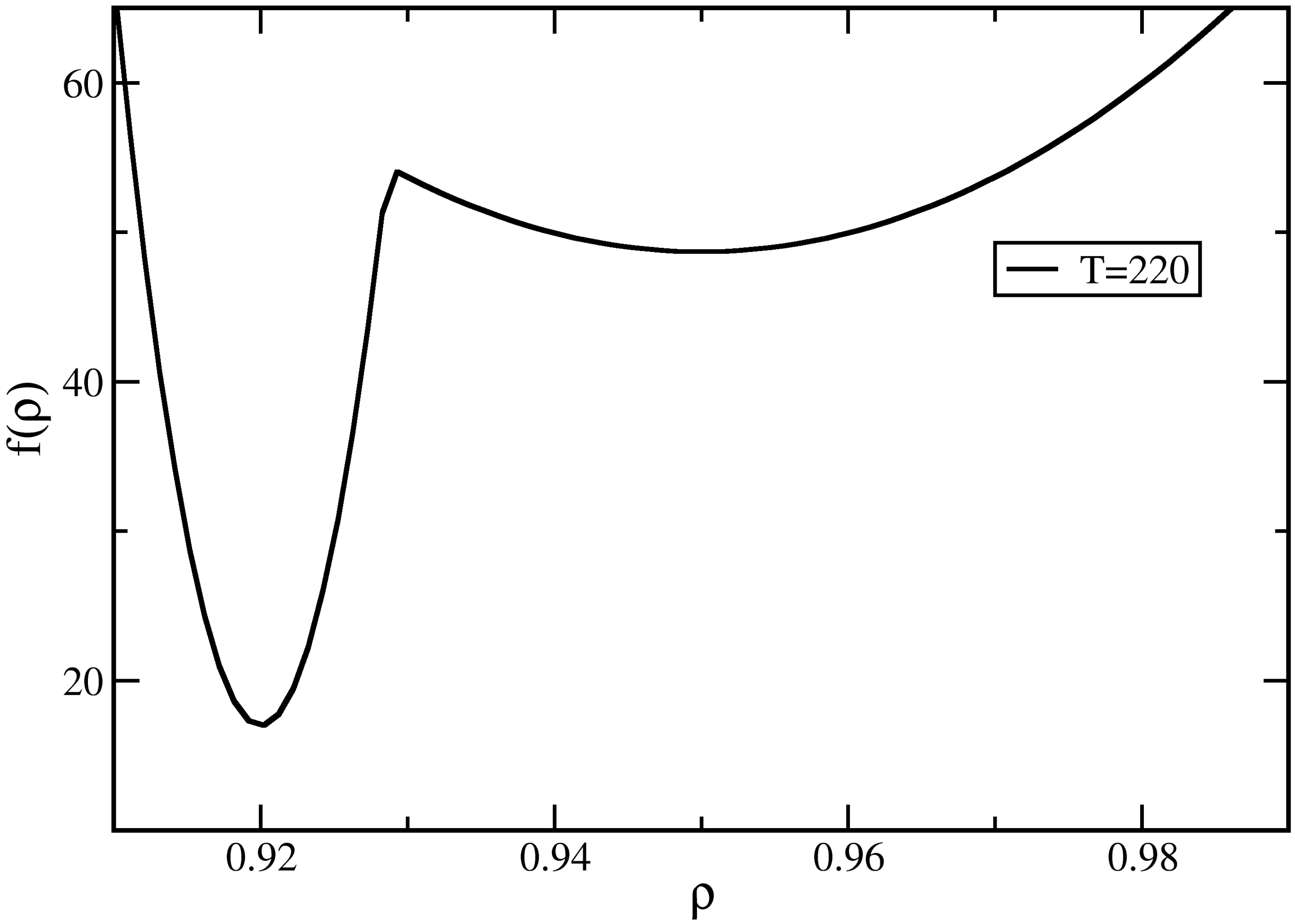


Santra, Singh and Bagchi, JPC (Wolynes Festchrift, 2013)

Free energy surface



Free energy surface



Nucleation barrier