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November 2, 2022

Real-Time Dynamics of Hydrogen and Its Isotopic Molecules Revealed by the Non-Empirical Quantum Molecular Dynamics Method

Kim Hyeon-Deuk (Kyoto University)

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1. Nuclear Quantumness Plays a Role.

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 -Nuclear quantumness (Zero Point Energy and Nuclear Delocalization)
 -No empirical parameter
 -No external model
 -Real-time dynamics
- Many-body system

3. Examples
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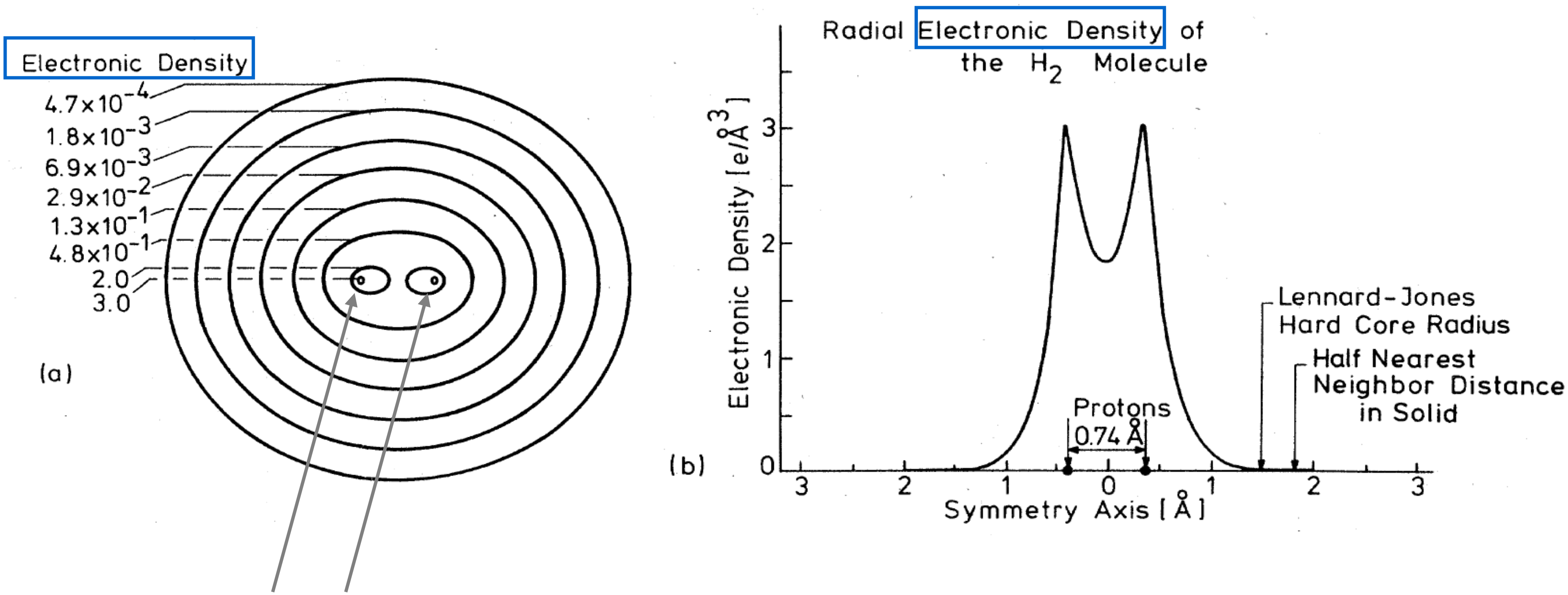
  -Solid
  -Supercooled Liquid
  -Supercritical Fluid
  -Gas
  -Non-Equilibrium Heat Flux
  -Non-Equilibrium Flow

4. The Nuclear and Electron Wave Packet Molecular Dynamics method with the Quantum Rotation

Electron Distribution in H_2



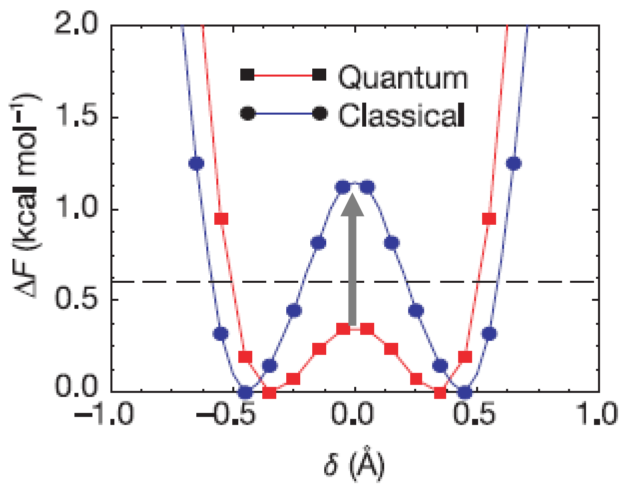
Hydrogen nuclei are treated as classical mass points

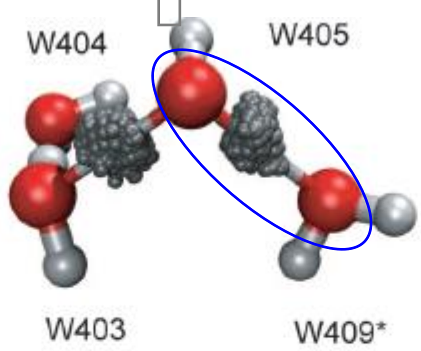
Silvera, Rev. Mod. Phys. **52** (1980) 393

Nuclear Quantumness ①

Zero Point Energy
Nuclear Delocalization

O-H···O





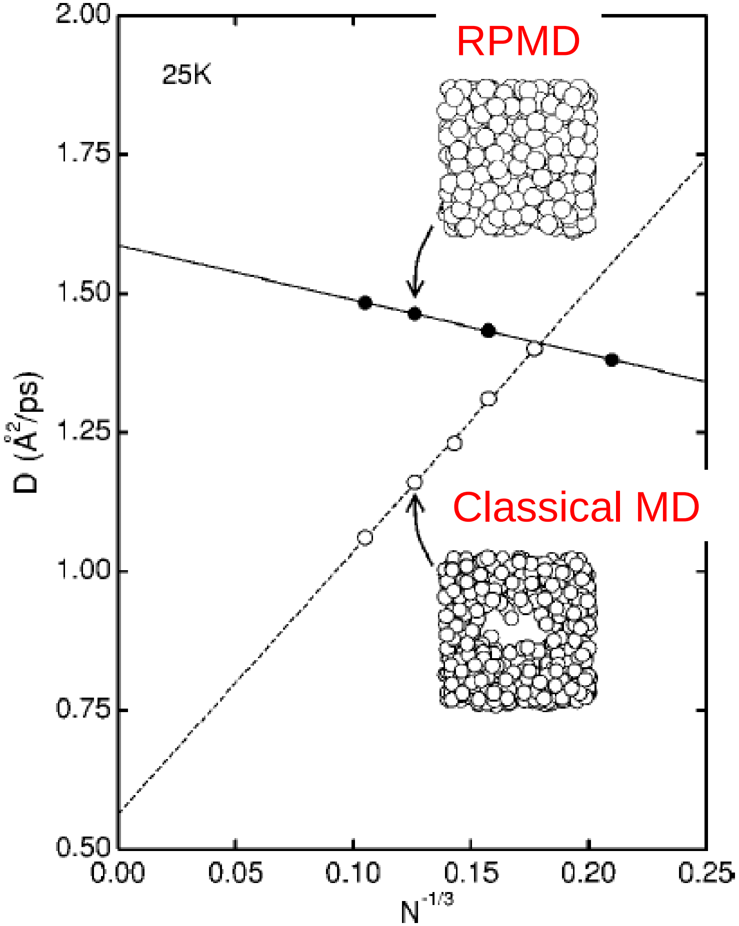
proton displacement $\delta = R_{O_aH} - R_{O_bH}$

Tuckerman et al., Nature **417**(2002) 925

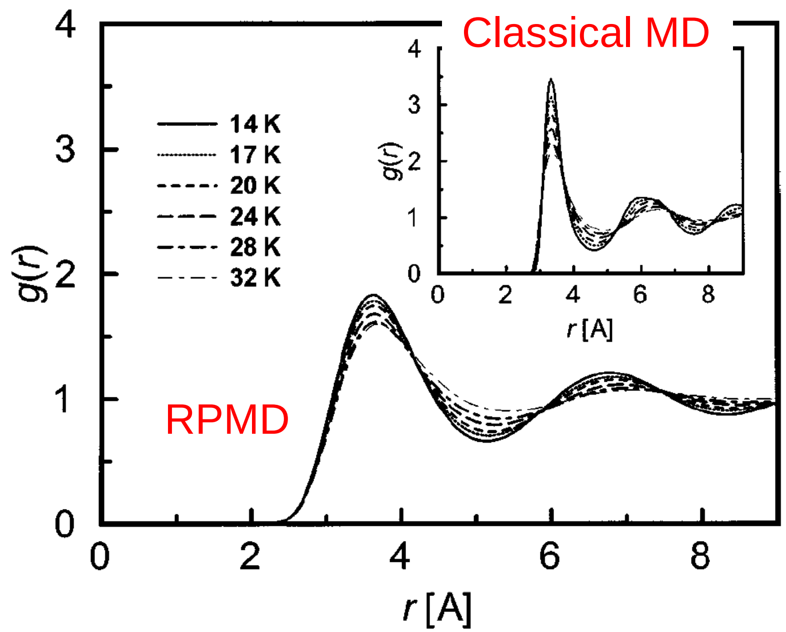
Nuclear Quantumness ②

RPMD=Ring Polymer Molecular Dynamics Method
with the Nuclear Quantumness

Diffusion



Radial Distribution Function



Miller and Manolopoulos, J. Chem. Phys. **122** (2005) 184503

Yonetani and Kinugawa, J. Chem. Phys. **120** (2004) 10624

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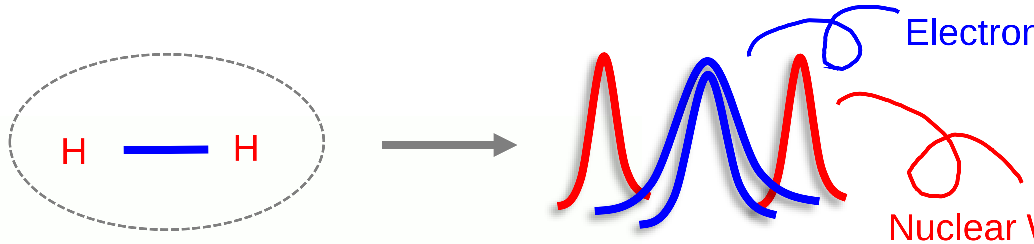
Nuclear and Electron Wave Packet Molecular Dynamics (NEWPMD)



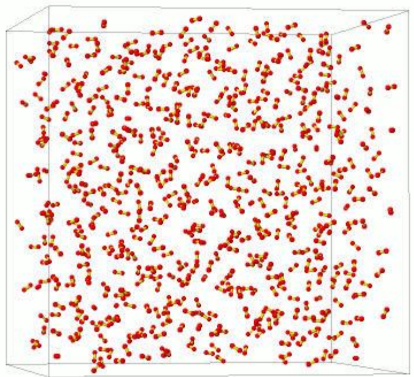
✔ Radial Distribution Function

✔ Diffusion Coefficient

✔ Viscosity

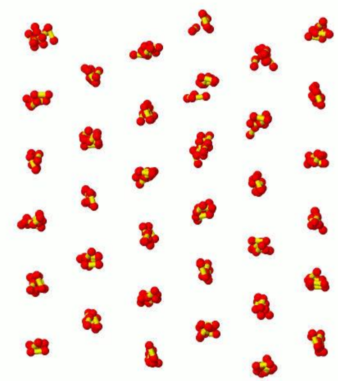
✔ Vibrational Frequency Shift

✔ Isotope Effects (D_2 and T_2)



J. Chem. Phys. (Commun.) **140** (2014) 171101
Phys. Rev. B **90** (2014) 165132
J. Phys. Chem. B, **122** (2018) 8233
Phys. Chem. Chem. Phys. **23** (2021) 22110

25 K | Liquid | Solid | 2.5 K



✔ Freezing Temperature

✔ Vibrational Displacement

✔ Solid Phonon Mode~40cm^{-1}

✔ Discrete H-H frequency ~ a few cm^{-1} in 4000cm^{-1}

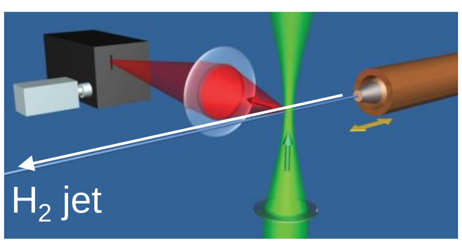
J. Chem. Phys. (Commun.) **143** (2015) 171102

Supercooled | Nonequilibrium

✔ Boson Peak ~30~40cm^{-1}

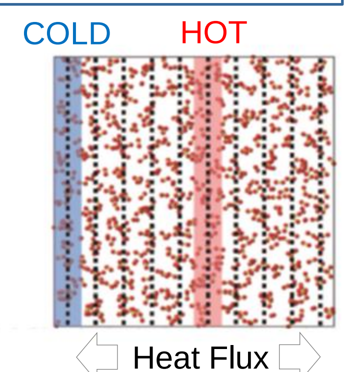
Liquid
V
✔ Vibrational Frequency
V
Solid

✔ Optimal Mixing Rate for Cooling



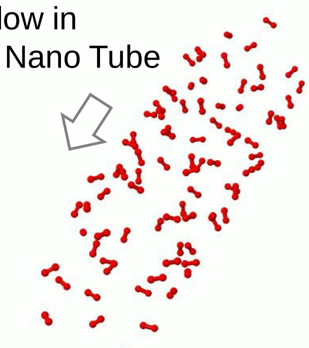
Supercooling Exp.

Phys. Chem. Chem. Phys. (Commun.) **18** (2016) 2314
J. Phys. Chem. Lett. **11** (2020) 4186



✔ Thermal Conductivity

Nano Flow in Carbon Nano Tube



J. Phys. Chem. Lett. **8** (2017) 3595
J. Phys. Chem. Lett. **13** (2022) 3579

CPU time: 6 minutes for 1 ps dynamics of 1200 molecules with 16 cores

Time-Dependent Nuclear and Electron Wave Function

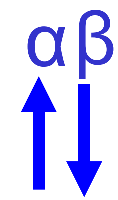
J. Chem. Phys. (Communication) **140** (2014) 171101
Chem. Phys. Lett. **532** (2012) 124

a,b $H_A - H_B$ *c,d* $H_C - H_D$

Time-Dependent Nuclear and Electron Wave Function

$$\psi(t) = \mathcal{A}[\underbrace{\phi_a(\mathbf{q}_1)\phi_b(\mathbf{q}_2)}_{(a,b)}\underbrace{\phi_c(\mathbf{q}_3)\phi_d(\mathbf{q}_4)}_{(c,d)}\Theta(1,2,3,4)]\underbrace{\Phi_A(\mathbf{Q}_1)\Phi_B(\mathbf{Q}_2)}_{H_A - H_B}\underbrace{\Phi_C(\mathbf{Q}_3)\Phi_D(\mathbf{Q}_4)}_{H_C - H_D}$$

$\mathcal{A}$: Antisymmetrizer

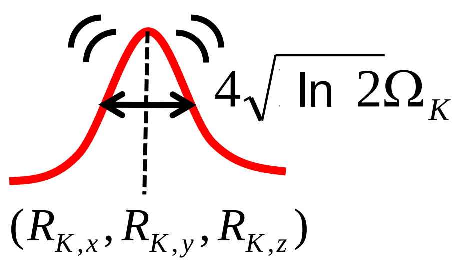


Perfect-Pairing Valence Bond Theory : (*a*,*b*) (*c*,*d*) in Singlet

$$\Theta(1,2,3,4) = \frac{(\alpha(1)\beta(2) - \beta(1)\alpha(2))}{\sqrt{2}}\frac{(\alpha(3)\beta(4) - \beta(3)\alpha(4))}{\sqrt{2}}$$

Gaussian Nuclear Wave Packet (NWP)

$$\Phi_K(\mathbf{Q}_i) \equiv \left(\frac{1}{2\pi\Omega_K^2(t)}\right)^{\frac{3}{4}} \exp\left[-\frac{(\mathbf{Q}_i - \mathbf{R}_K(t))^2}{4\Omega_K(t)^2} + \frac{i\Pi_K(t)}{2\Omega_K(t)}(\mathbf{Q}_i - \mathbf{R}_K(t))^2 + i\mathbf{P}_K(t)\cdot(\mathbf{Q}_i - \mathbf{R}_K(t))\right]$$



⇨ Nuclear Quantumness
Zero Point Energy
Nuclear Delocalization

ħ=1
electron charge =1
electron-mass scaled

Time-Dependent Wave Function

$$\psi(t) = \mathcal{A}[\underbrace{\boxed{\phi_{\rm a}(\mathbf{q}_1)}\phi_{\rm b}(\mathbf{q}_2)}_{(a,b)}\underbrace{\phi_{\rm c}(\mathbf{q}_3)\phi_{\rm d}(\mathbf{q}_4)}_{(c,d)}\Theta(1,2,3,4)]\underbrace{\Phi_{\rm A}(\mathbf{Q}_1)\Phi_{\rm B}(\mathbf{Q}_2)}_{H_A-H_B}\underbrace{\Phi_{\rm C}(\mathbf{Q}_3)\Phi_{\rm D}(\mathbf{Q}_4)}_{H_C-H_D}$$

Gaussian Electron Wave Packet (EWP)

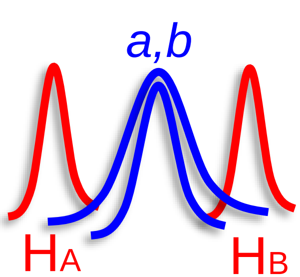
$$\boxed{\phi_k(\mathbf{q}_i)} \equiv \left(\frac{1}{2\pi\rho_k^2}\right)^{\frac{3}{4}} \exp\left[-\frac{(\mathbf{q}_i - \mathbf{r}_k(t))^2}{4\rho_k^2}\right]$$

Isolated $H_A - H_B$

- ➢ Thawed EWP $0.398 + 0.360\, R_{HH}(t)$ Å and $0.176 + 0.244\, R_{HH}(t)$ Å

- ➢ Born-Oppenheimer Approximation

$$\mathbf{r}_{\rm a}(t) = \mathbf{r}_{\rm b}(t) = \frac{\mathbf{R}_{\rm A}(t) + \mathbf{R}_{\rm B}(t)}{2} \quad \text{and} \quad \mathbf{r}_{\rm c}(t) = \mathbf{r}_{\rm d}(t) = \frac{\mathbf{R}_{\rm C}(t) + \mathbf{R}_{\rm D}(t)}{2}$$



Time-Dependent Variational Principle

Action Integral

$$\Gamma \equiv \int L dt = \int dt \langle \psi, t | i \frac{\partial}{\partial t} - \hat{H} | \psi, t \rangle$$

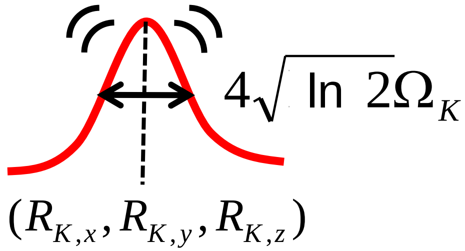
Kinetic energy of elec.
Coulomb energies
electron-electron
nucleus-nucleus
nucleus-electron

Hamiltonian

$$\hat{H} = \sum_{i=1}^{4} - \frac{1}{2M_{\text{nuc}}} \frac{\partial^2}{\partial \mathbf{Q}_i^2} + V(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4; \mathbf{Q}_1, \mathbf{Q}_2, \mathbf{Q}_3, \mathbf{Q}_4)$$

$$\delta\Gamma / \delta \mathbf{R}_K = 0, \text{ etc.}$$

NWP



Equations of Motion

$$\dot{\mathbf{R}}_K = \frac{\partial H_{\text{ext}}}{\partial \mathbf{P}_K}, \qquad \dot{\mathbf{P}}_K = - \frac{\partial H_{\text{ext}}}{\partial \mathbf{R}_K},$$

$$\dot{\Omega}_K = \frac{1}{3} \frac{\partial H_{\text{ext}}}{\partial \Pi_K}, \qquad \dot{\Pi}_K = - \frac{1}{3} \frac{\partial H_{\text{ext}}}{\partial \Omega_K}$$

$$H_{\text{ext}} \equiv \sum_{K}^{\text{A,B,C,D}} \left[\frac{\mathbf{P}_K^2}{2M_{\text{nuc}}} + \frac{3\Pi_K^2}{2M_{\text{nuc}}} + \frac{3\hbar^2}{8M_{\text{nuc}}\Omega_K^2} \right] + \langle V_{\text{ke,elec}} \rangle + \langle V_{\text{ee}} \rangle + \langle V_{\text{nn}} \rangle + \langle V_{\text{ne}} \rangle$$

Kinetic Energy of Electrons

Electrostatic Energies
electron-electron
nucleus-nucleus
nucleus-electron

Many-Body H_2 Hamiltonian

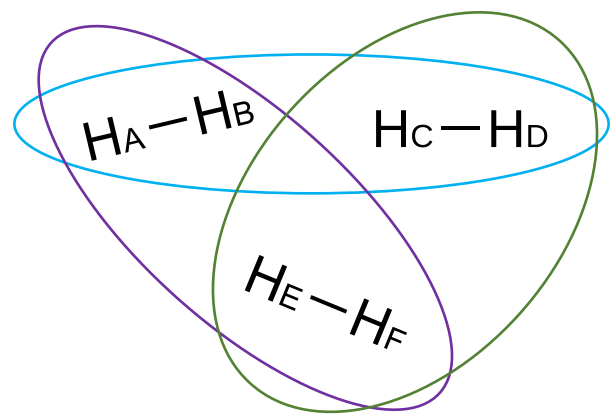
N_{mol}-Body Hamiltonian

$$H_{\rm ext}(N_{\rm mol}) \equiv \sum_{K}^{N_{\rm nuc}} \left[\frac{\mathbf{P}_K^2}{2M_{\rm nuc}} + \frac{3\Pi_K^2}{2M_{\rm nuc}} + \frac{3\hbar^2}{8M_{\rm nuc}\Omega_K^2}\right] + \sum_{I>J}^{N_{\rm nuc}} \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|}\,{\rm erf}\left(\frac{|\mathbf{R}_I - \mathbf{R}_J|}{2^{\frac{1}{2}}\left(\Omega_I^2 + \Omega_J^2\right)^{\frac{1}{2}}}\right)$$
$$+ \sum_{ab>cd}^{N_{\rm mol}} V^{ab,cd} - \sum_{ab}^{N_{\rm mol}} (N_{\rm mol} - 2)\, v^{ab}$$

Subtracting Multiple Counting

$N_{\rm nuc}$: Number of Nuclei

$N_{\rm mol}(= N_{\rm nuc}/2)$: Number of Molecules

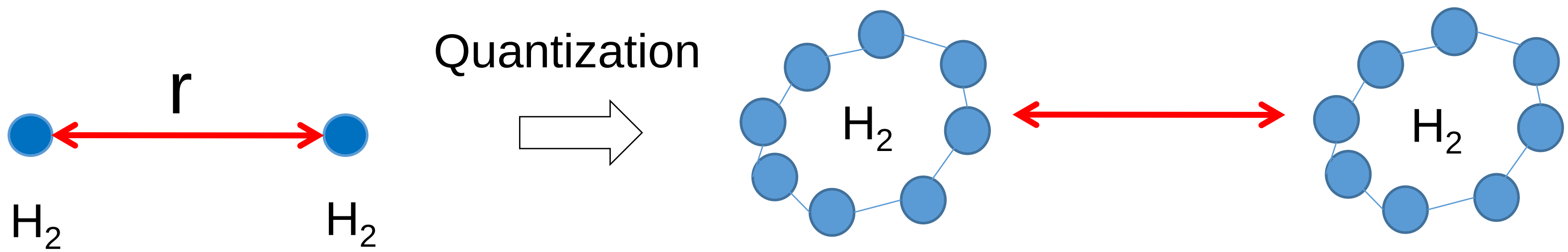


$$V^{ab,cd} = \frac{1}{\Delta}(J_0 + \bar{J}_2 + \bar{J}_3)$$

$v^{ab} \equiv \langle v^{ab}_{\rm ke,elec}\rangle + \langle v^{ab}_{\rm ee}\rangle + \langle v^{ab}_{\rm ne}\rangle$: Single Hydrogen Molecule Energy

Semiquantum Path Integral Method

Centroid Molecular Dynamics
Ring Polymer Molecular Dynamics



Silvera–Goldman Model

$$V(r) = e^{\alpha - \beta r - \gamma r^2} - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} - \frac{C_9}{r^9} + \frac{C_{10}}{r^{10}} \right) f_c(r)$$

$$f_c(r) = \begin{cases} e^{-(r_c/r - 1)^2}, & \text{if } r \leqslant r_c \\ 1, & \text{otherwise} \end{cases}$$

Ring Polymer

$$Z_n = \frac{1}{(2\pi\hbar)^{9Nn}} \int \int \prod_{j=1}^{3N} \prod_{k=1}^{n} d\mathbf{p}_j^{(k)} d\mathbf{r}_j^{(k)} e^{-\beta_n H_n(\{\mathbf{p}_j^{(k)}\},\{\mathbf{r}_j^{(k)}\})}$$

$$H_n(\{\mathbf{p}_j^{(k)}\},\{\mathbf{r}_j^{(k)}\}) = \sum_{j=1}^{3N} \sum_{k=1}^{n} \left[\frac{(\mathbf{p}_j^{(k)})^2}{2m_j} + \frac{1}{2} m_j \omega_n^2 (\mathbf{r}_j^{(k)} - \mathbf{r}_j^{(k-1)})^2 \right] + \sum_{k=1}^{n} V(\mathbf{r}_1^{(k)}, \ldots, \mathbf{r}_{3N}^{(k)})$$

Silvera-Goldman Model

8 Empirical Parameters
No Intramolecular Degree of Freedom
Limited Thermodynamic States

+

Path Integral

Equilibrium Thermal State
No Real-Time Trajectory
Unstable for Long Time
High Computational Cost
Not Applicable for $T \to 0$

Silvera, Rev. Mod. Phys. **52** (1980) 393
Miller and Manolopoulos, J. Chem. Phys. **122** (2005) 184503

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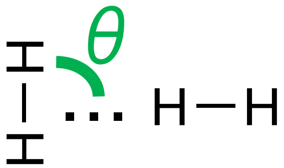
2D Radial Distribution Function

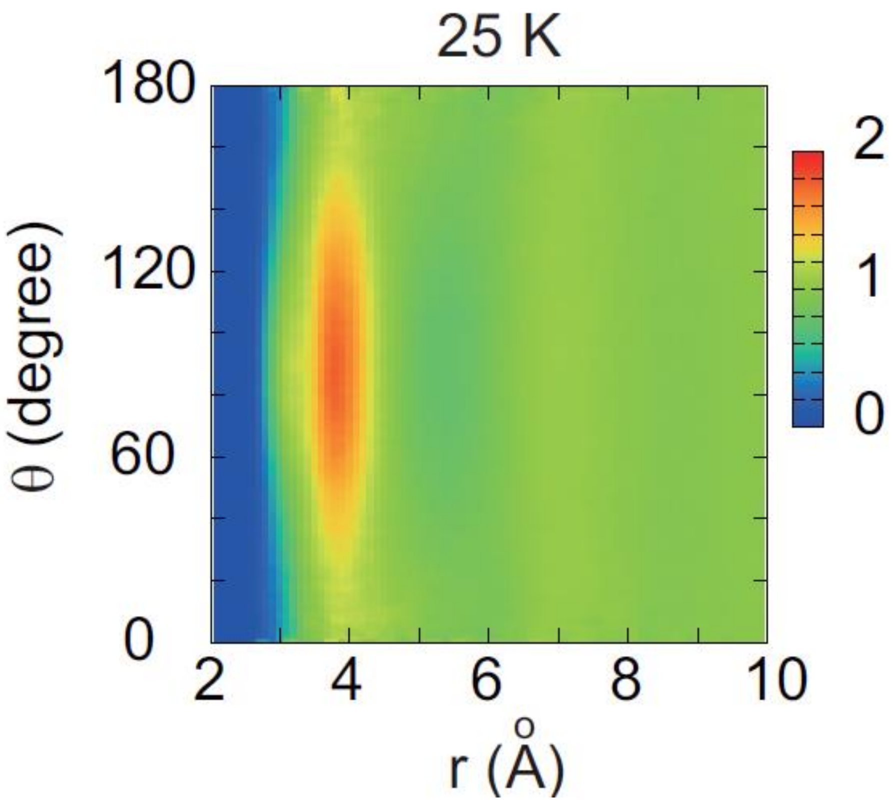
number of NWPs within a small region of radii r~r +dr and angle θ~ θ+d θ

T-Shape



$$g(r,\theta) = \frac{\langle n(r,\theta)\rangle}{2\pi n_0 r^2 dr \sin\theta d\theta}$$

total number density



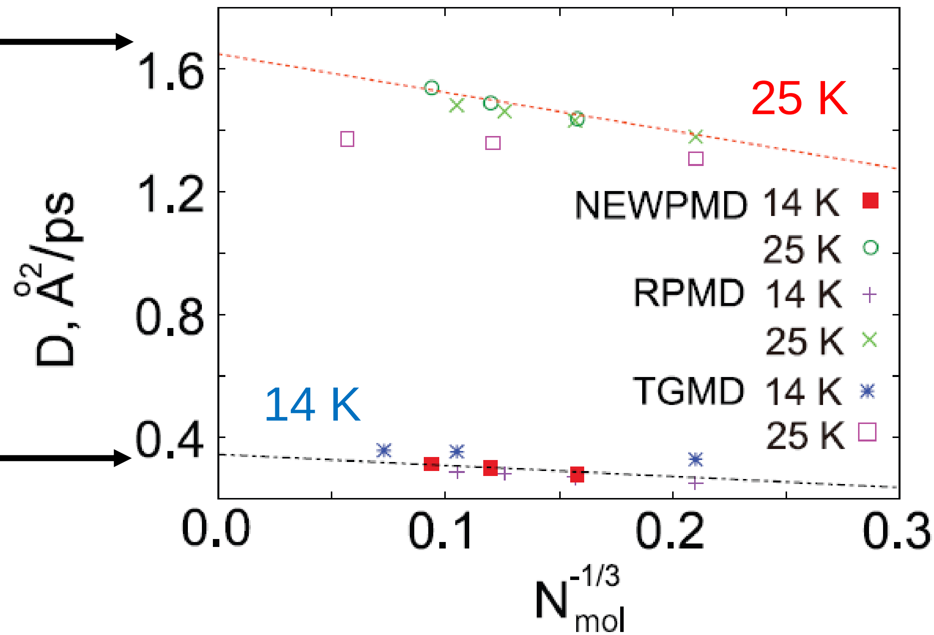
Transport Coefficient

$$D(N_{\mathrm{mol}}) = \lim_{t\to\infty} \frac{\langle |\boldsymbol{R}(t) - \boldsymbol{R}(0)|^2 \rangle_{N\mathrm{mol}}}{6t}$$

R(*t*) : Position Vector of H_2 Center

1.65 →
(exp. ~1.6)

0.345 →
(exp. ~0.35)

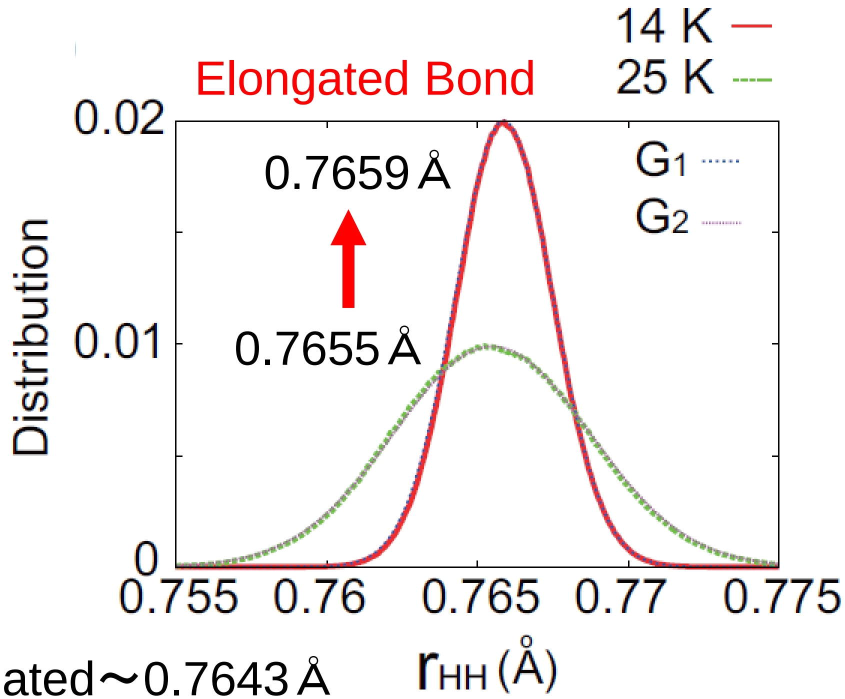


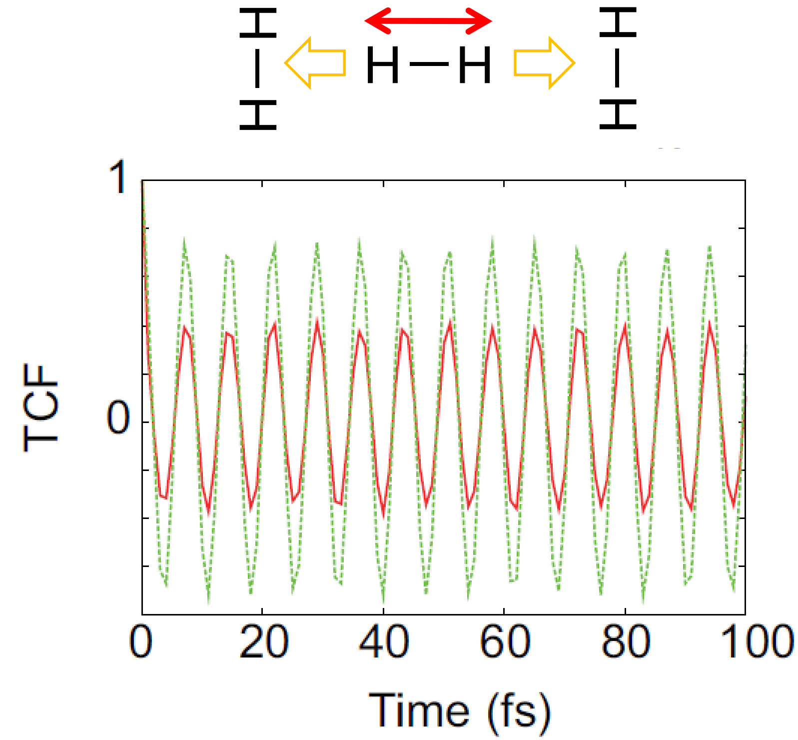
System Size Scaling : $D(N_{\mathrm{mol}}) = D(\infty) - \frac{2.837 k_B T}{6\pi\eta l} N_{\mathrm{mol}}^{-1/3}$

Molar Length : $l = 3.55$ Å and 3.76 Å

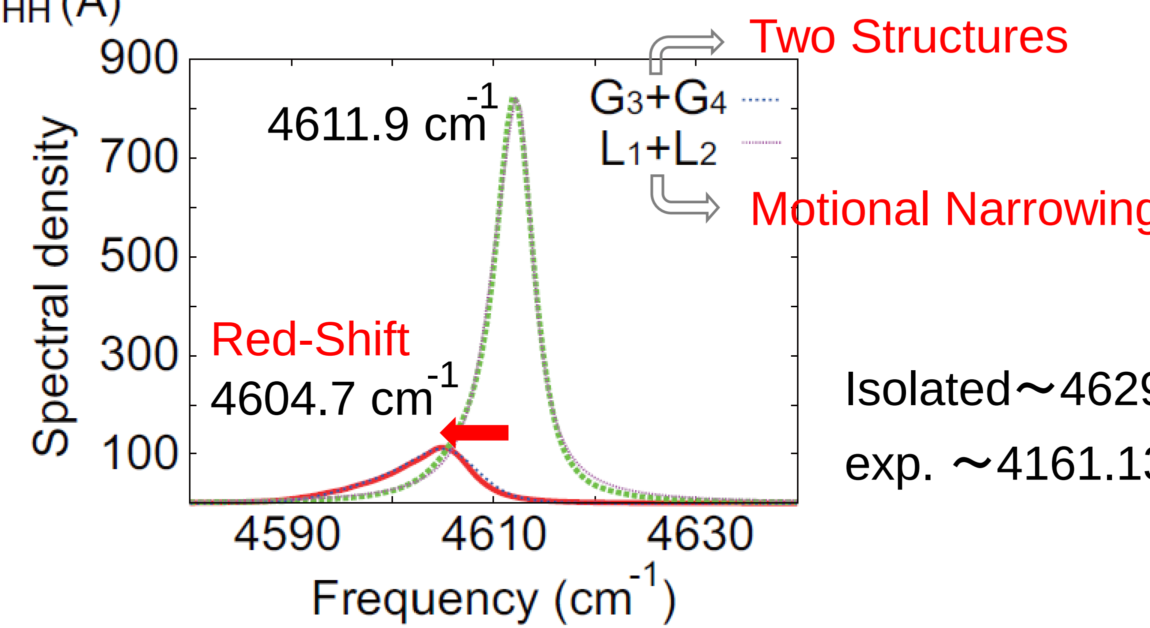
Viscosity : $\eta = 2.3\mathrm{X}10^{-5}\ {}^{-5}\mathrm{N}\cdot\mathrm{s\ m}^{-2}$ and $1.10\mathrm{X}10^{-5}\ \mathrm{N}\cdot\mathrm{s\ m}^{-2}$
(exp. ~$2.5\mathrm{X}10^{-5}$) (exp. ~$0.94\mathrm{X}10^{-5}$)

H-H Bond in H_2 Liquid



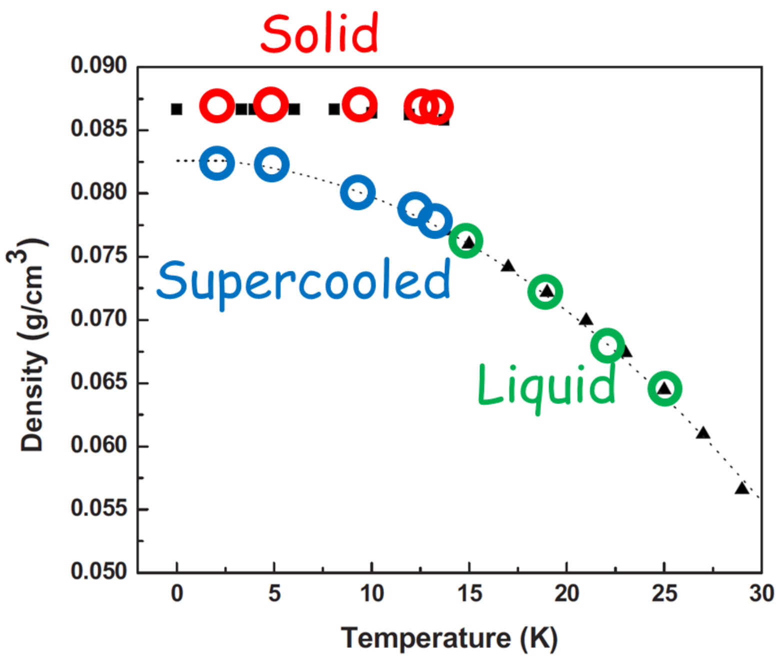


Isolated～0.7643 Å
Exp. ～0.755 Å

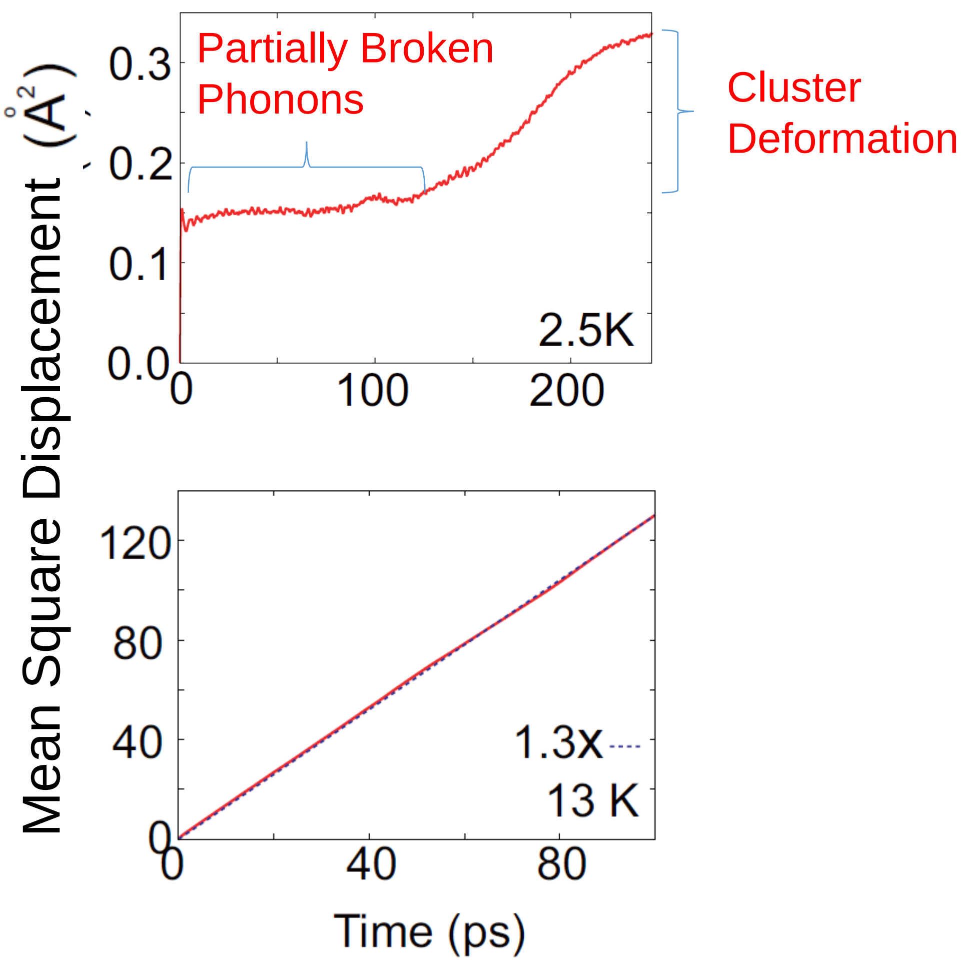


Isolated～4629.2 cm $^{-1}$
exp. ～4161.13 cm $^{-1}$

Mean Square Displacement in Supercooled Liquid



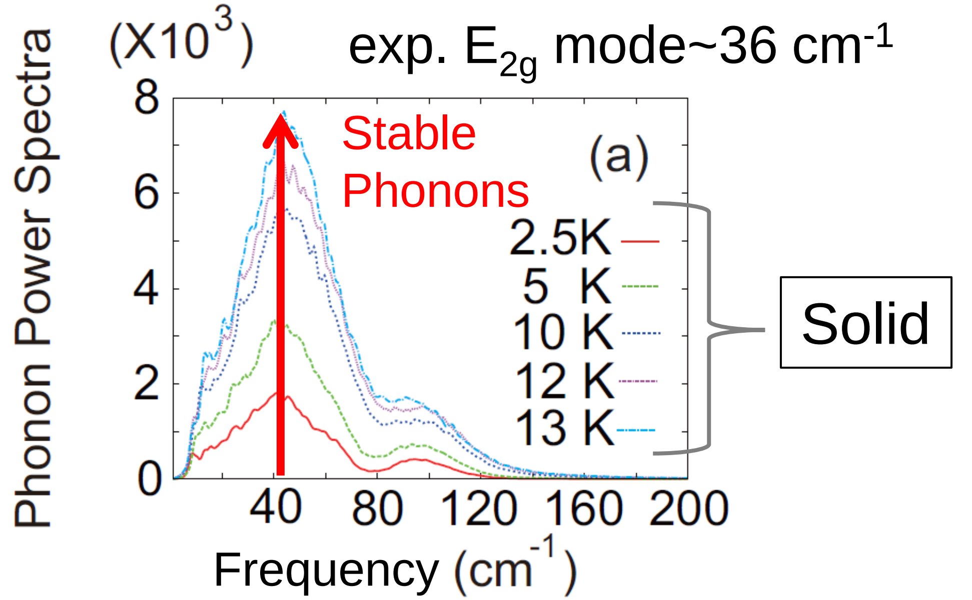
Plateau & Relaxation

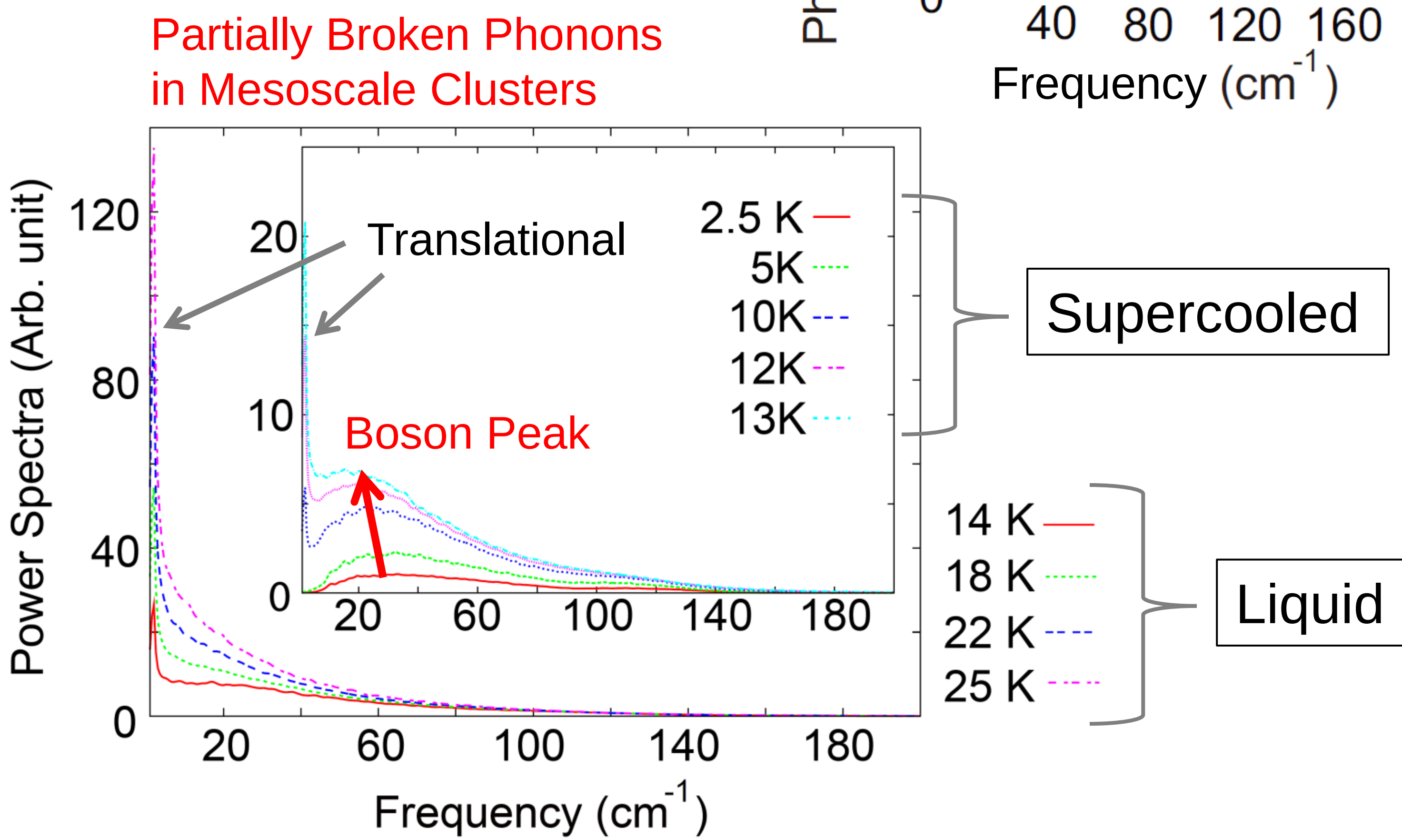


Boson Peak

$$\langle | \int dt \sqrt{R_K^2(t)} \; \exp(-i\omega t) |^2 \rangle$$

$\boldsymbol{R}_K(t)$: Position Vector of K-th H_2 Center



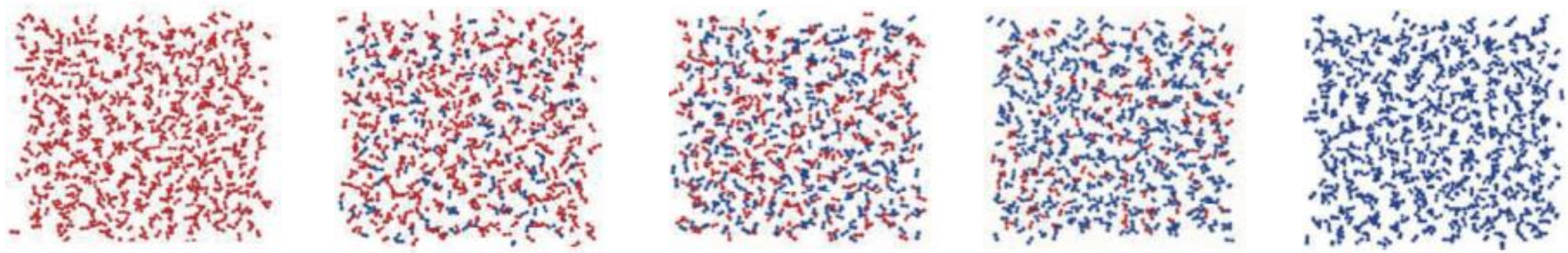


Radial Distribution Function (RDF)

@ D_2 Vapor-Pressure Density

H_2:D_2 Mixtures

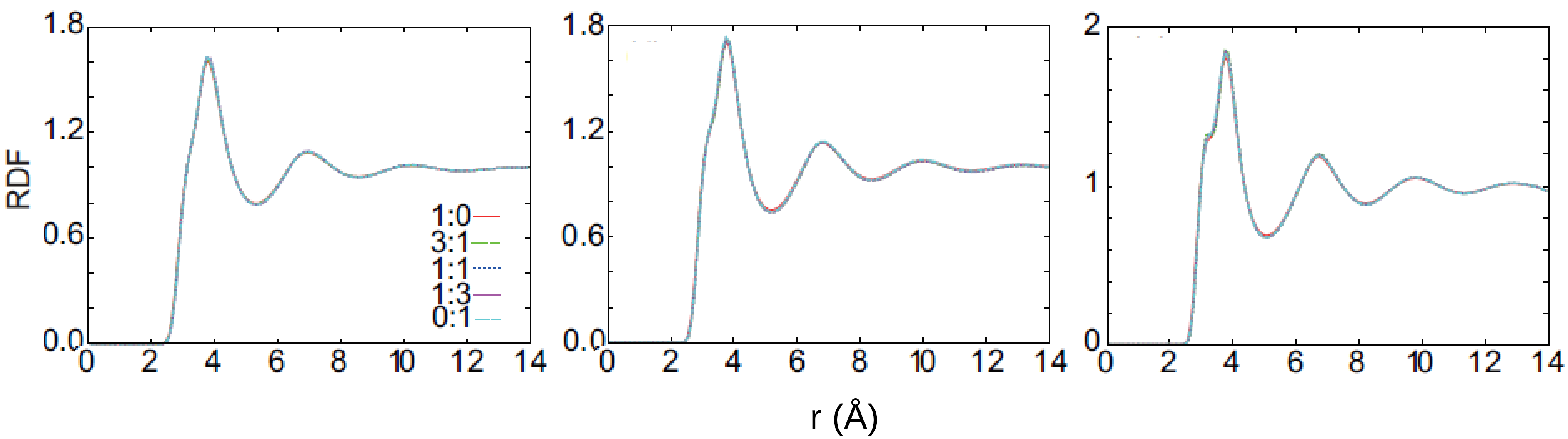
1:0 3:1 1:1 1:3 0:1



$$\text{RDF} \quad \frac{\langle n(r) \rangle}{4\pi r^2 dr n_0}$$

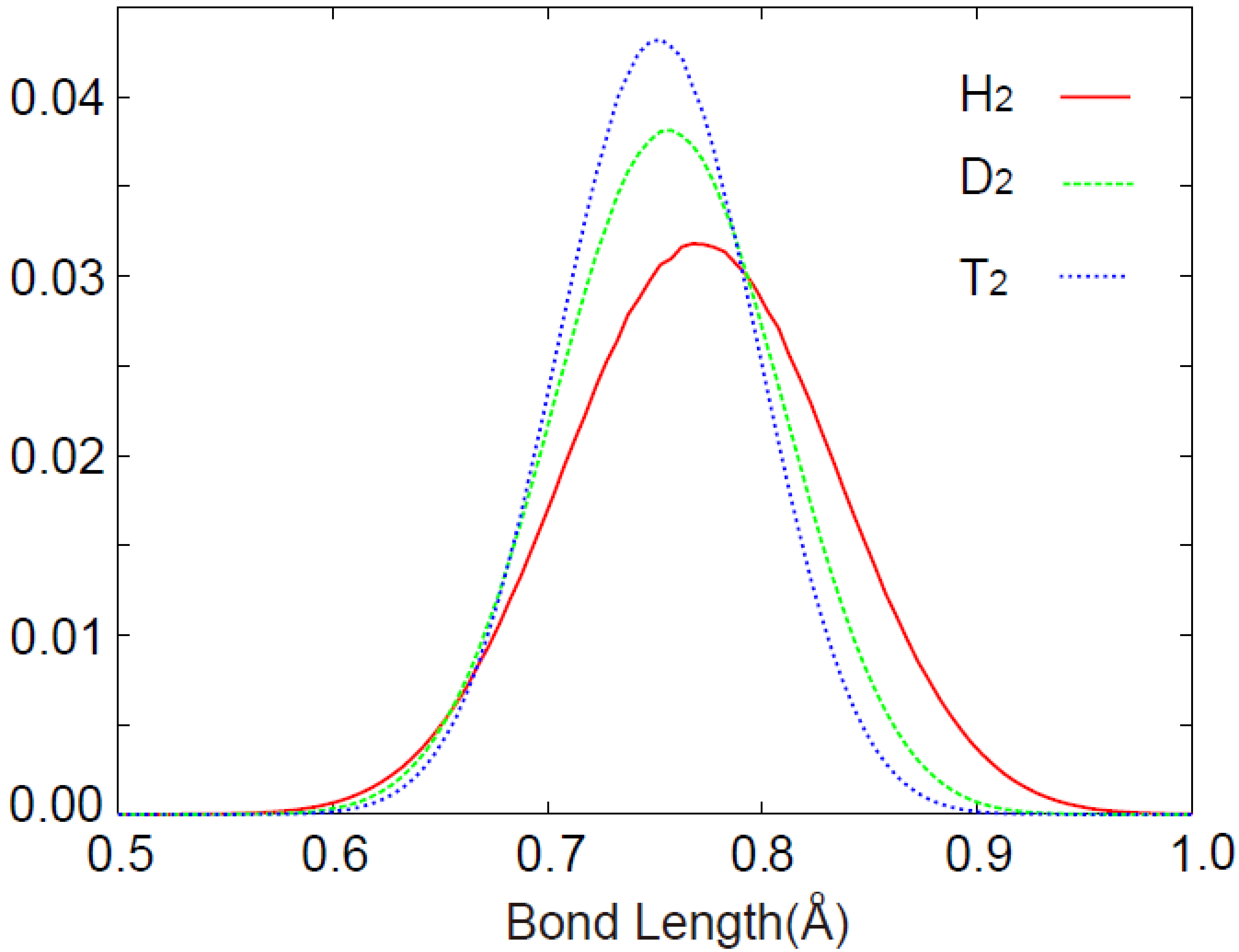
- $\langle n(r) \rangle$: number of NWPs within radius r~r +dr
- n_0: total number density

30 K 25 K 18 K



Isotope Effects –Bond Length-

25 K @ D_2 Vapor-Pressure Density

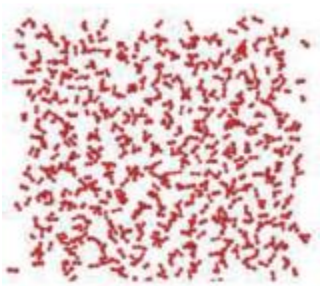


Diffusion of Isotope Mixtures

@ D_2 Vapor-Pressure Density

H_2:D_2 Mixtures

1:0



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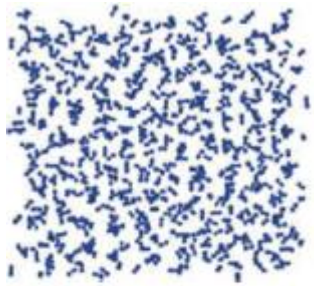
0:1



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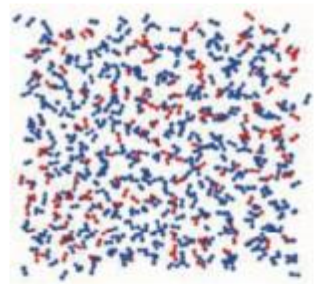
1:3



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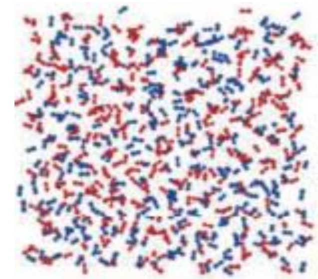
1:1



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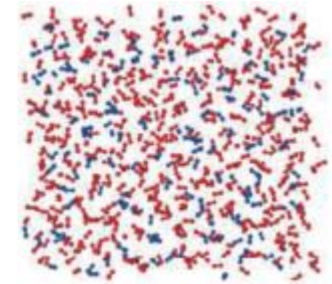
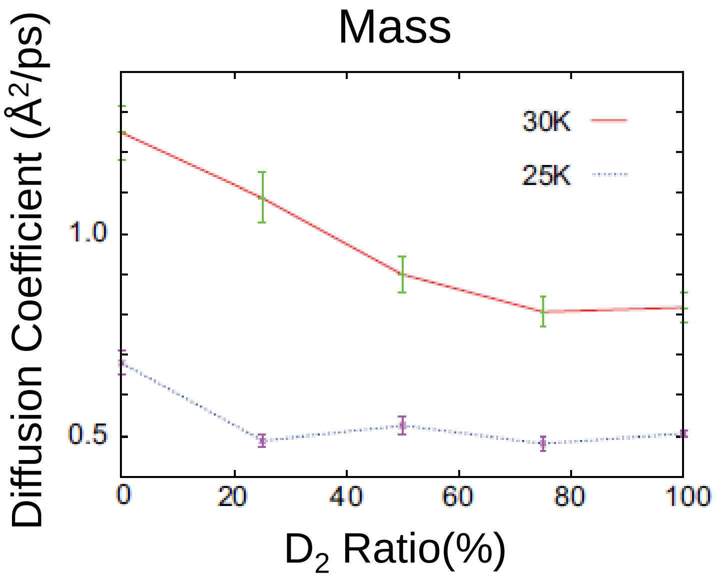
3:1



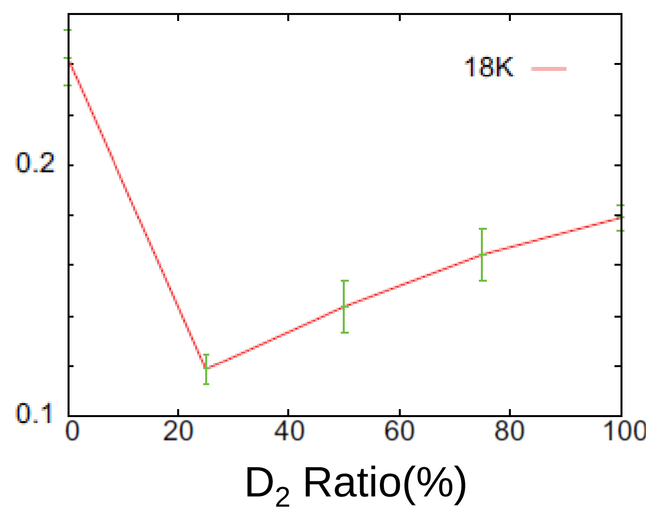
$$D(N_{\mathrm{mol}}) = \lim_{t\to\infty} \frac{\langle |\boldsymbol{R}(t) - \boldsymbol{R}(0)|^2 \rangle_{N\mathrm{mol}}}{6t}$$

R(*t*) : Position Vector of H_2 Center

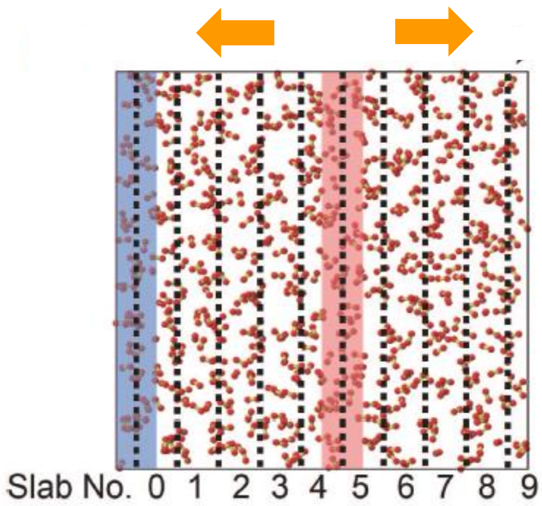
Mass

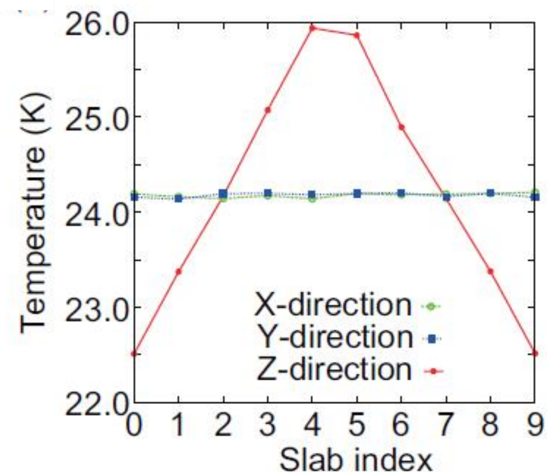


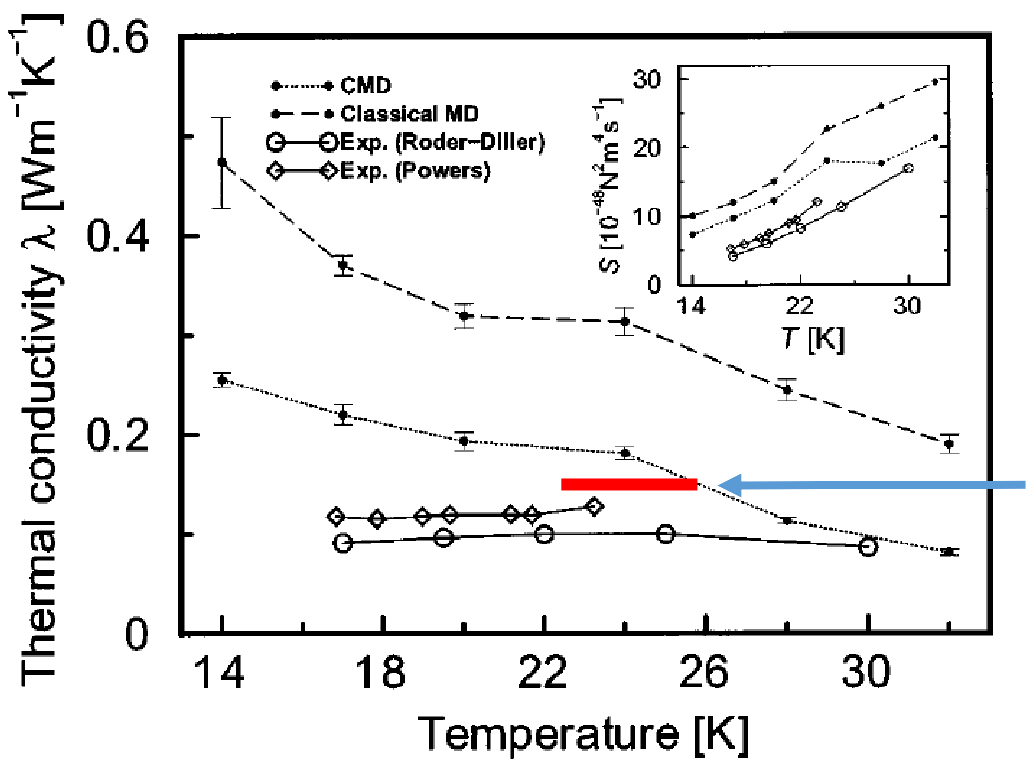
Supercooling v.s. Mass



Non-Equilibrium Heat Conduction







Heat Flux

$$J = -\lambda \nabla T$$

Current Result

~0.16 $Wm^{-1}K^{-1}$

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