# Anomalies of H<sub>2</sub>O



# Challenge Most abundant, least known 125 big Qs of Science 2006 Ice floating? Surface tension? **Slippery of ice surface?** Ice like H<sub>2</sub>O molecules? Mono or mixed structures? **Bond length & structure order? Bio-interaction & climate change?**



# Outline

- I. Principles
- **II. Recent progress** 
  - 1. H<sub>2</sub>O under compression
  - **2.**  $H_2O$  at cool
  - 3.  $H_2O$  with < 4 neighbours
  - 4. H<sub>2</sub>O size, separation, order, density
- **III. Prospects**
- **IV. Summary**

#### **Principles:**

Segmented H bond



# Master-slave-segmented, flexible, fluctuating, and polarizable H-bond



	d <sub>x</sub> (nm)	E <sub>x</sub> (eV)		Θ <sub>D</sub> (K)	T <sub>m</sub> (K)	Interaction
H-O	0.10	4.0	>3000	>3000	>5000	Exchange
H:O	0.17	0.10	<300	198	273	Van der Waals
00	-	-	-	-		Repulsion
C-C	0.154	1.84	1331	2230	3800	Exchange



#### Forces driving relaxation $\Delta d_{\rm L} > // \Delta d_{\rm H}$



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# Length, stiffness, core level shift, T<sub>c</sub>

$$\frac{1}{2}\mu(\Delta\omega)^{2}(r-d_{x})^{2} = \frac{1}{2}k_{x}(r-d_{x})^{2} \cong \frac{1}{2}\frac{\partial u(r)}{\partial r^{2}}\Big|_{r=d_{x}}x^{2}$$

$$\propto \frac{1}{2} \frac{E_x}{\mu d_x^2} (r - d_x)^2$$

$$\Delta \omega_x \propto \frac{\sqrt{E_x / \mu_x}}{d_x} \cong \sqrt{Y_x d_x / \mu_x}$$
$$E_x \propto d_x^{-m}$$
$$T_C \propto \Delta E_v \propto E_H$$



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#### **EDGE ARTICLE**

Dynamic Article Links

#### The hidden force opposing ice compression<sup>†</sup>

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# **1.** H<sub>2</sub>O under compression

- Low-compressibility
- Proton symmetrization
- Asymmetric phonon relaxation
- T<sub>c</sub> depression

#### **Fact: corporative Raman shifts**



Yoshimura, et al., J. Chem. Phys. 124, 024502 (2006).

#### **Lagrangian-Laplace mechanics**







$(d_{_{H}} / 0.9754)$		(1	+9.510	+2.893	$\left(P^{0}\left(GPa\right)\right)$
<i>d</i> <sub><i>L</i></sub> / 1.7683	=	1	-3.477	-10.280	$10^{-4} P^{1}$
(V/1.0600)		(1	-238.0	+47.00 )	$\left( 10^{-5}P^2 \right)$





Chem Sci, 2012. 3: 1455.

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# 2. H<sub>2</sub>O at cool





Cross, JACS, 1937. **59**: 1134. Gilberg, et al., JCP 1982, 76, 5039. Mallamace, et al, PNAS, 2007, 104, 18387. Erko, PCCP, 2012. **14**: 3852.

#### **Principle: thermodynamic disparity**



#### **Raman shift: stiffness relaxation**





MD-NPT power spectra of  $H_2O$  showing three zones with the freezing stiffening of the high-frequency phonons and freezing softening of the low-frequency phonons.



H<sub>2</sub>O upon cooling.



<u>V-shaped H<sub>2</sub>O motifs are intact albeit fluctuations at high T.</u>



#### Density, Elasticity, and Stability Anomalies of Water Molecules with Fewer than Four Neighbors

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# **3.** H<sub>2</sub>**O with < 4 neighbors**

- Ice-like and hydrophobic
- Volume expansion & polarization
- Charge densification & entrapment
- O 1s binding energy shift
- Stiffer phonon stiffening



# **Principle: BOLS + NEP**



#### **DFT optimization**









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N=12

#### **O:H-O segmental length relaxation**



Algorithm independent: size trends and corporative relaxation

#### **O:H-O segmental stiffness relaxation**





Experimental data: Hirabayashi, *J. Mol. Struct.* **795**, 78 (2006). Ceponkus, *JPCA* **116**, 4842 (2012).

$$T_{mN}/T_{mBulk} = \Delta E_{1sN}/\Delta E_{1sBulk} = \left(d_{HN}/d_{Hbulk}\right)^{-m} = C_H^{-4}$$



Wilson, JCP **117**, 7738(2002). Ceponkus, JPCA **116**, 4842 (2012). Hirabayashi J. Mol. Struct. **795**, 78(2006). Abu-Samha, J. Phys. B **42**, 055201 (2009). Bjorneholm, JCP **111**, 546 (1999). Winter, JCP **126**, 124504 (2007). 28

#### Water droplet dances:

Antonini et al, PRL 2013. **111**: 014501. Wang et al, Proc Roy Soc A 2012. 468: 2485.





## Delayed freezing of water droplet on hydrophobic:

Singh et al, APL 2013. 102: 243112.



# Viscositization by confining SiO<sub>2</sub> plates sputtering:



# 4. Size, separation, structural order, and mass density





$$\rho = \frac{M(10m_p + 8m_n)}{V(\text{Order} + D\text{istance})} = \frac{M}{a^3} = 1(gcm^{-3})$$

$$\begin{cases} d_{oo} = d_L + d_H = 2.6948\rho^{-1/3} & (1) \\ d_L = 2.5621 \times \left[1 - 0.0055 \times \exp(d_H/0.2428)\right] & (2) \end{cases}$$



#### III Prospects

- **1. Skin supersolidity**
- 2. Salt dissolution
- **3. Machano-freezing of 25 °C water**
- 4. Cancer cells
- 5. Isotopic effect
- 6. Organic (N, F) OH molecules
- 7. General rule of NTE
- 8. Coulomb repulsion modulation
- 9. Food and drug

#### 1. Skin supersolidity of ice and water



#### 2. Mechano-freezing of 25 °C water Pressure loss from 1.35-0.85 GPa at freezing





#### 3. Salt-induced phonon relaxation (opposite to P effect)



#### 4. Cancer cells: Abramczyk, J Bio Chem 02, 158 (2011)







# 5. Isotope effect: Marechal, J. Mol. Struct. 1004, 146 (2011) 6. Organic molecules (NOH): Zou, J Phys Chem B 116, 9796 (2012)



#### 7. Negative thermal expansion (NTE)

Graphite and Cu: X.L. Liu, Q.H. Tang and T.C. Wang, Sci China, 2011,500.





G. Ernst, C. Broholm, G. R. Kowach and A. P. Ramirez, Phonon density of states and negative thermal expansion in ZrW2O8, *Nature*, 1998, **396**(6707), 147–9.



# IV Summary

- Mono-phase of fluctuated-tetrahedron
- Ultra-short-range interactions
- Coulomb repulsion
- Asymmetric relaxation
- Skin supersolidity slippery and tension
- Thermodynamic disparity NTE
- Size, separation, order, and mass

# Thank you!

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$$\begin{cases} f_{dH} > \left(f_{dL} + f_{rL} + f_{rH}\right) \\ f_{dL} > \left(f_{dH} + f_{rL} + f_{rH}\right) \\ f_{dH} = f_{dL} \end{cases} \Rightarrow \Delta d_{O-O} \begin{cases} > 0 \\ < 0 \\ = 0 \end{cases}$$

Segmented, flexible, polarizable, fluctuating O:H-O bond:

Segmental disparity

- 3 short-range interactions
  - 3 forces; ∆d<sub>H:0</sub> >// ∆d<sub>H-0</sub>



**Summary:** 

#### ZPS: CN-resolved bond-length & bond-energy USA patent, 2010



\* Diamond is an interlock of two fcc cells.