# Anomalies of water and simple liquids

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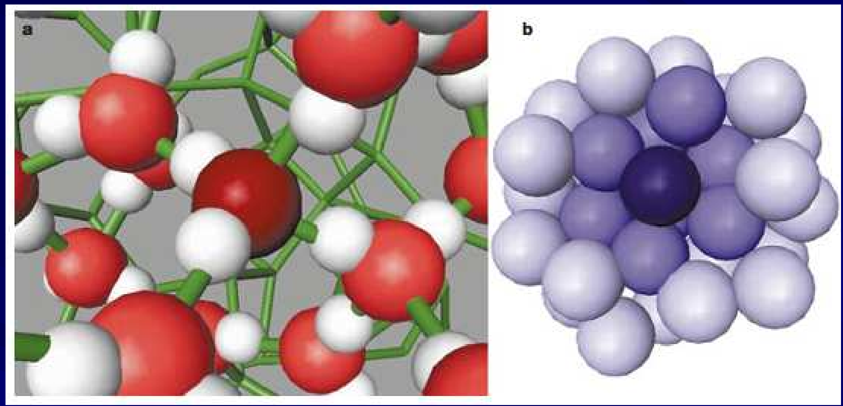
1. **Z. Yan**, S. V. Buldyrev, N. Giovambattista, and H. E. Stanley, ***Phys. Rev. Lett***. 95, 130604 (2005).
2. **Z. Yan**, S. V. Buldyrev, N. Giovambattista, P. G. Debenedetti, and H. E. Stanley, ***Phys. Rev. E*** 73, 051204 (2006).
3. **Z. Yan**, S. V. Buldyrev, P. Kumar, N. Giovambattista, P. G. Debenedetti, H. E. Stanley, ***Phys Rev E***, 76, 051201 (2007).
4. **Z. Yan**, S. V. Buldyrev, P. Kumar, N. Giovambattista, H. E. Stanley, PRE in press (2008).
5. P. Kumar, **Z. Yan**, L. Xu, M. G. Mazza, S. V. Buldyrev, S.-H. Chen, S. Sastry, and H. E. Stanley, ***Phys. Rev. Lett***. 97, 177802 (2006).

# Purpose and questions ?




Purpose:
We try to understand water' s anomalies using a simple model

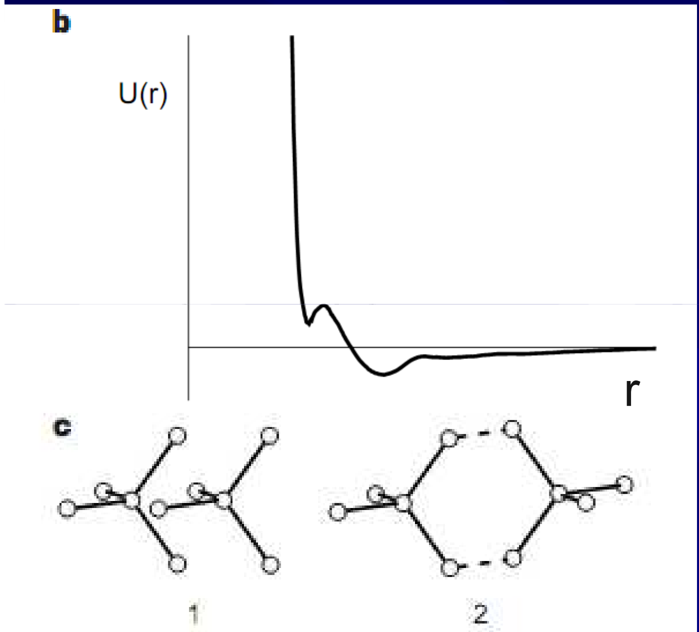
1. Are the strong orientational tetrahedral interactions in water necessary for water-like anomalies ?
2. Can we find water-like anomalies in simple liquid (monatomic model with simple spherically symmetric potential without orientational interaction) ?

   If YES
3. How do the anomalies of simple potential compare with water ?

S. Sastry, Nature 409, 18 (2001)

# The simple model: two-scale ramp potential

Effective potential of water ⟶ Two-scale spherically symmetric ramp potential

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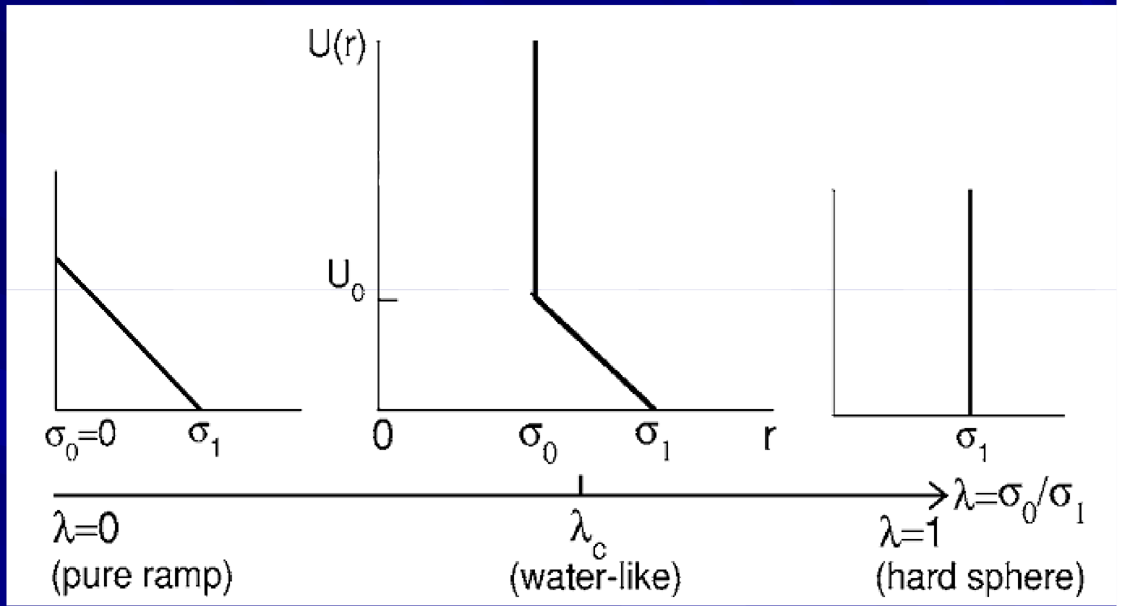



$\lambda_w \approx 0.27\text{nm} / 0.45\text{ nm} \approx 0.6$

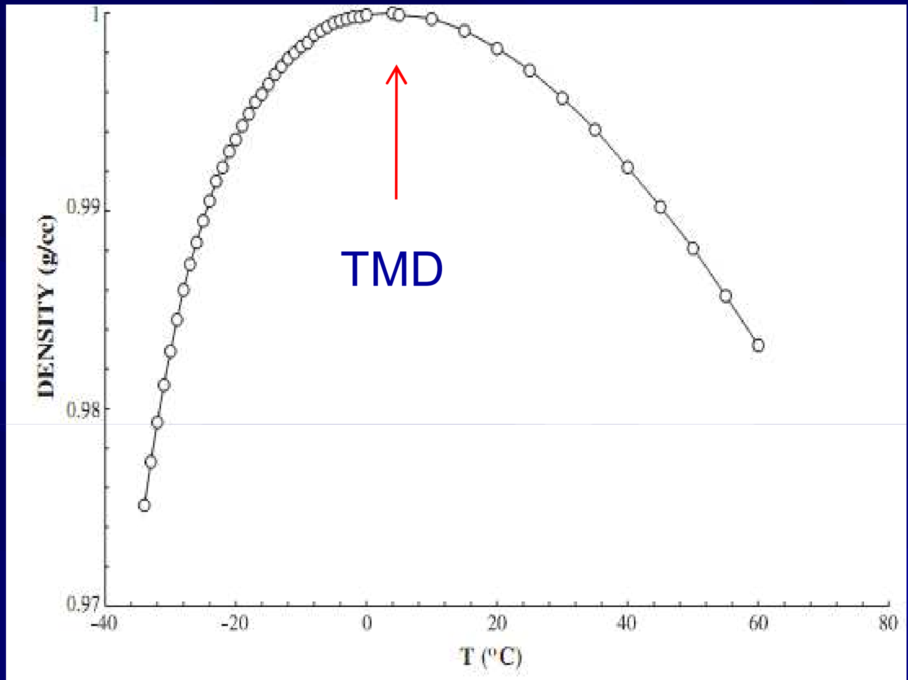
$$\lambda = \sigma_0 / \sigma_1 \in [0, 1]$$

Does ramp potential lead to water-like anomalies ?


O. Mishima and H. E. Stanley, Nature 396, 26 (1998) .
Z. Yan et.al, Phys. Rev. E 73, 051204 (2006).

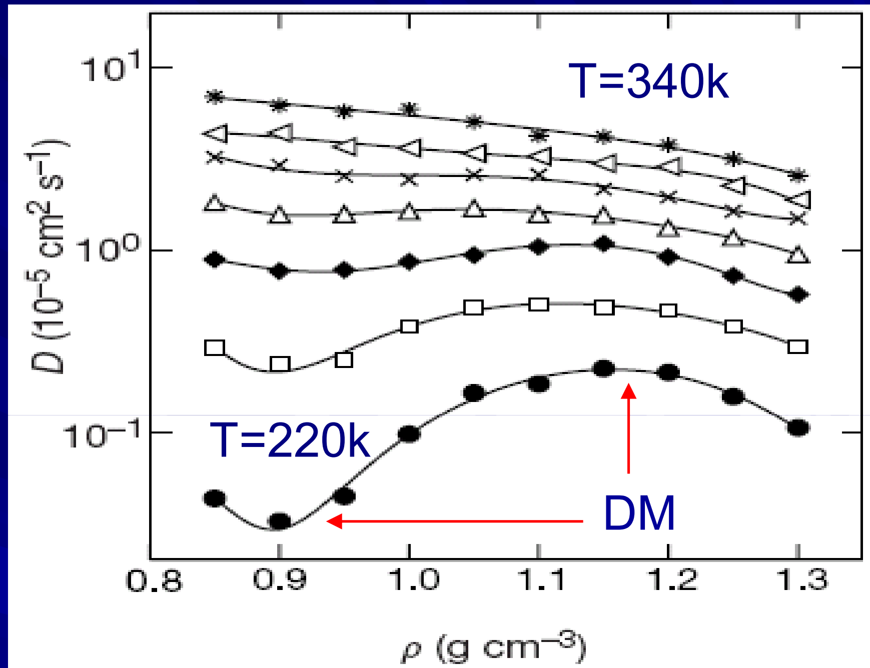
# Anomalies of water

Density anomaly of water




TMD: Temperature of Maximum Density

Diffusion anomaly of water



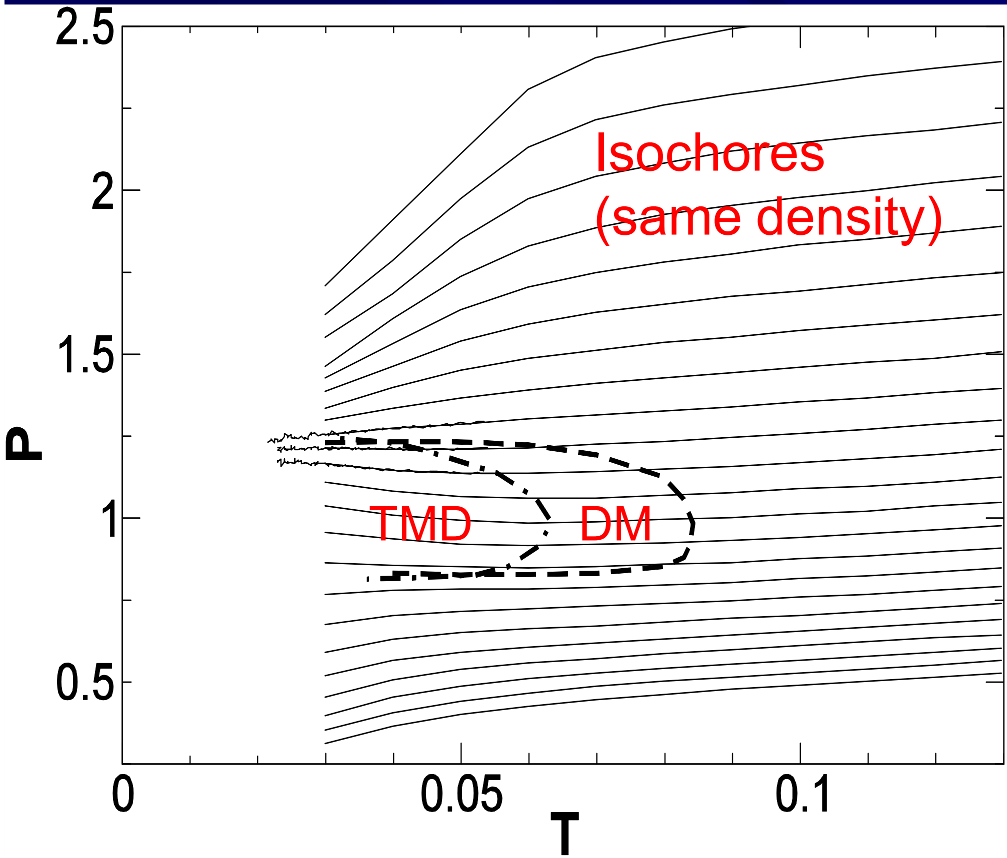

DM: Diffusion Maximum/Minimum

Water also has structural anomaly: structural order decrease with increasing density at constant *T*. Structural anomaly is coupled with density and diffusion anomaly.

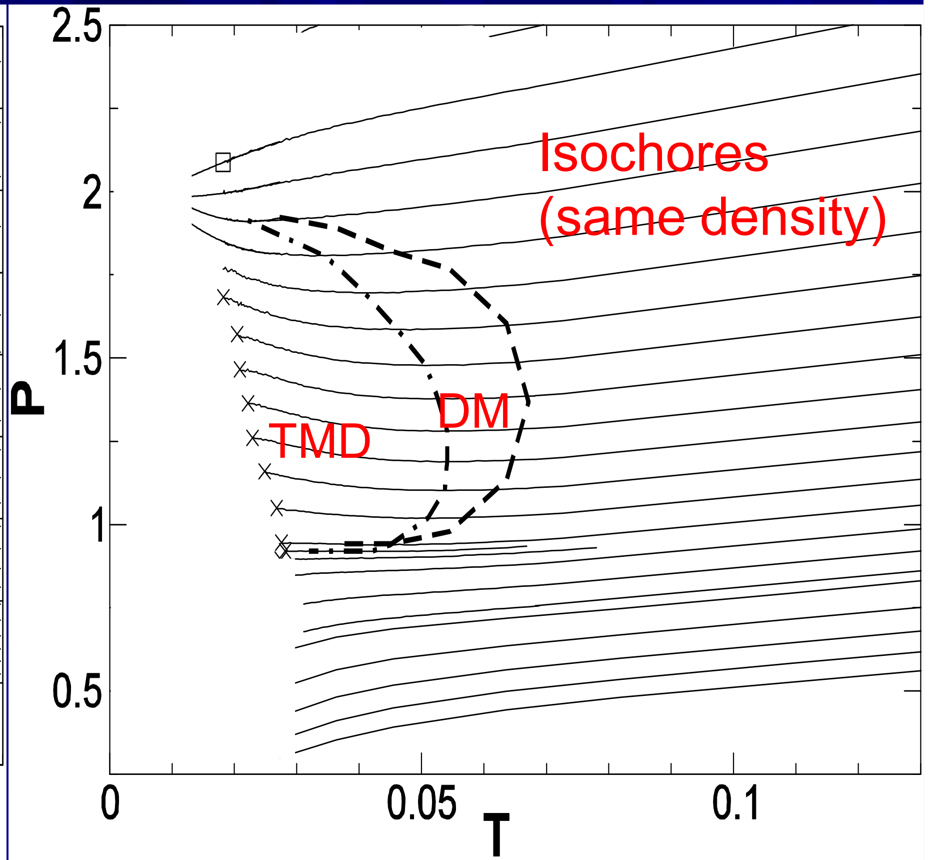
J. R. Errington and P. G. Debenedetti, Nature 409, 318 (2001).

# Result: phase diagrams of ramp

pure ramp ($\lambda$=0 )




water-like ($\lambda$=4/7≈ 0.6 )




TMD: Temperature of Maximum Density

DM: Diffusion Maximum/Minimum

$$(\partial V / \partial T)_P = -(\partial V / \partial P)_P \, (\partial P / \partial T)_V$$

Region of DM encloses the region of TMD

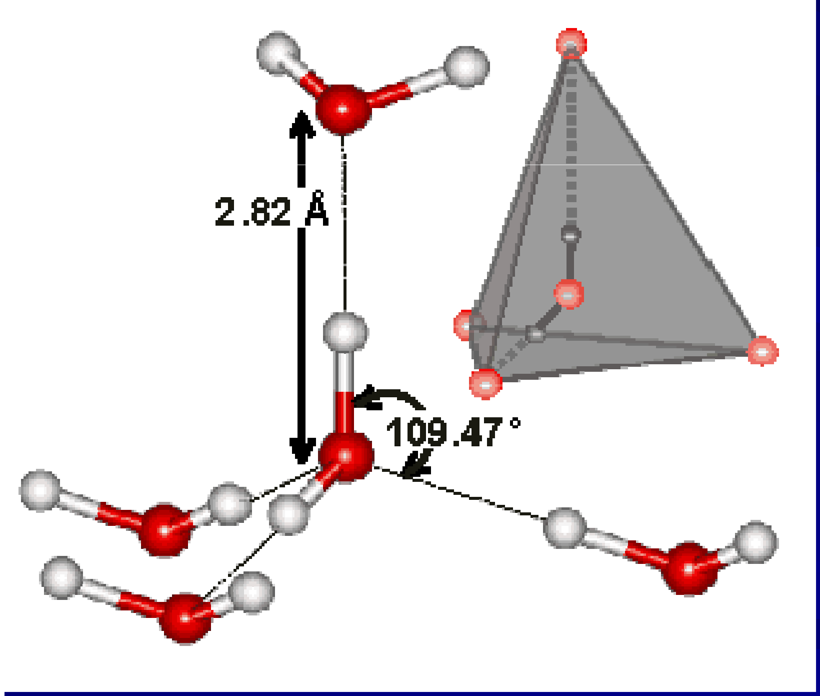
*But what about structural anomaly ?*

# How to quantify structural order

Two basic types of order parameters: orientational and translational

- . Orientational order: degree to adopt specific local structure (space angle)

  (1) Water: tetrahedral

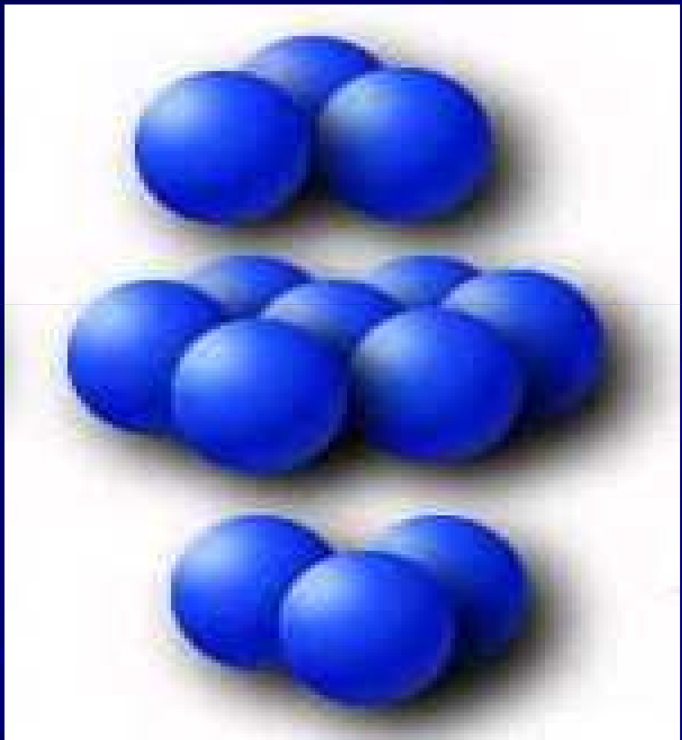



$$q = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\psi_{jk} + \frac{1}{3}\right)^2$$

q=1, tetrahedral
q=0, random

The order parameters increases with the increasing order of system

(2) Orientational order of Ramp potential:
degree to adopt HCP, or FCC



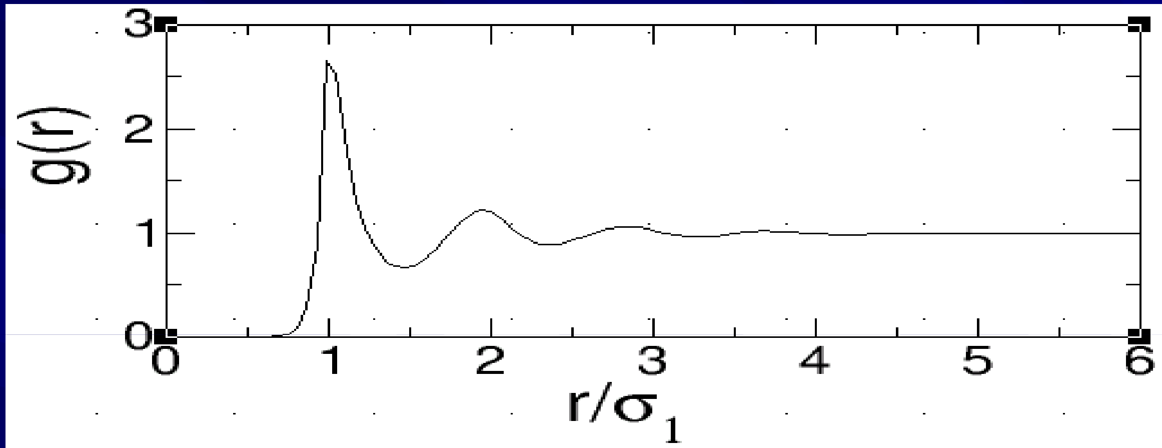
$$Q_{\ell i} \equiv \left[ \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{m=\ell} |\overline{Y}_{\ell m}|^2 \right]^{\frac{1}{2}}$$

$Q_6$ = 0.574, fcc;  0.485, hcp
$Q_6$ = 0.28, random

The order parameters increases with the increasing order of system

- Translational order *t* :

  degree to adopt preferential separations (distance)

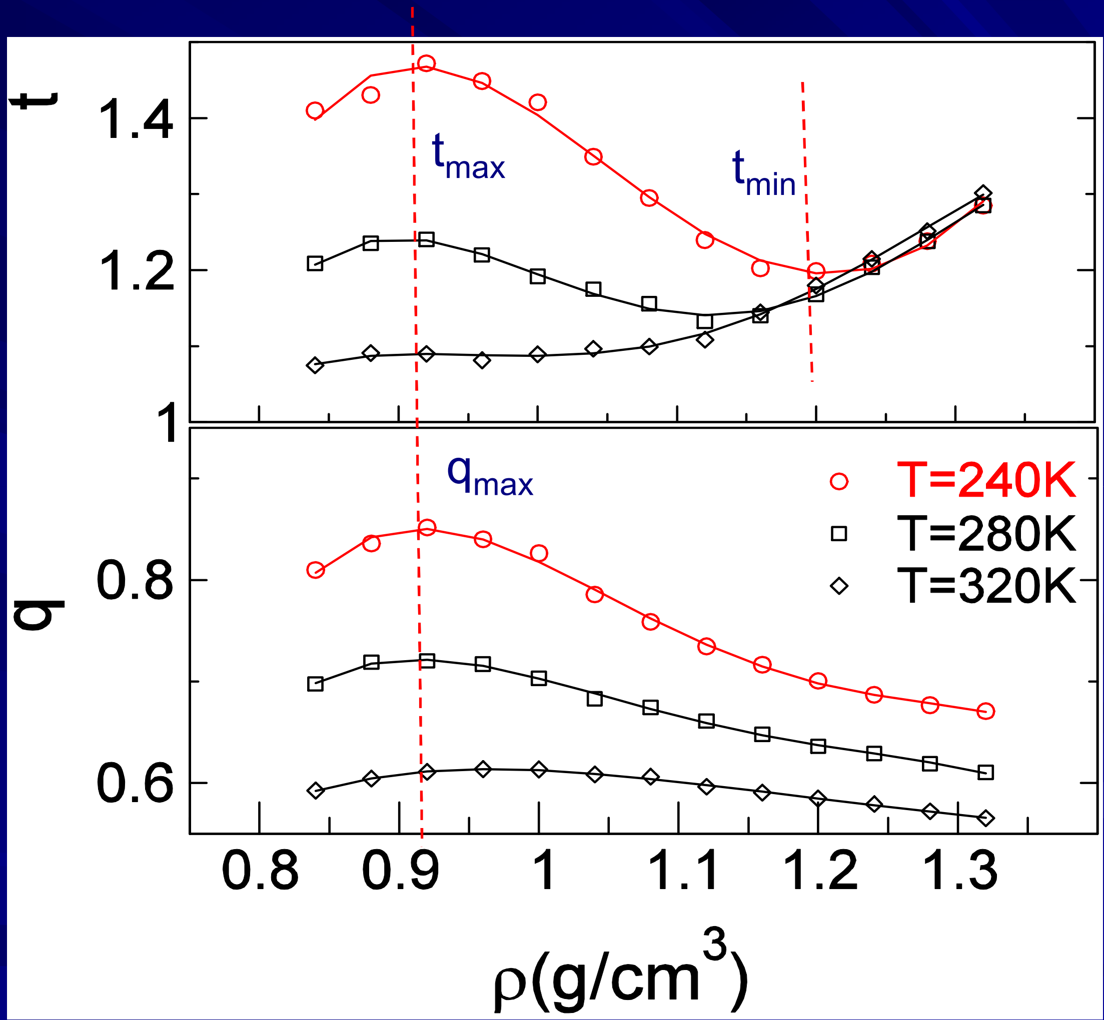



$$t \equiv \int_0^{r_c} \left| g(r) - 1 \right| dr$$

*t* = 0, random,

*t* become larger if more particles adopt preferential separations

# Result: Structural order of water

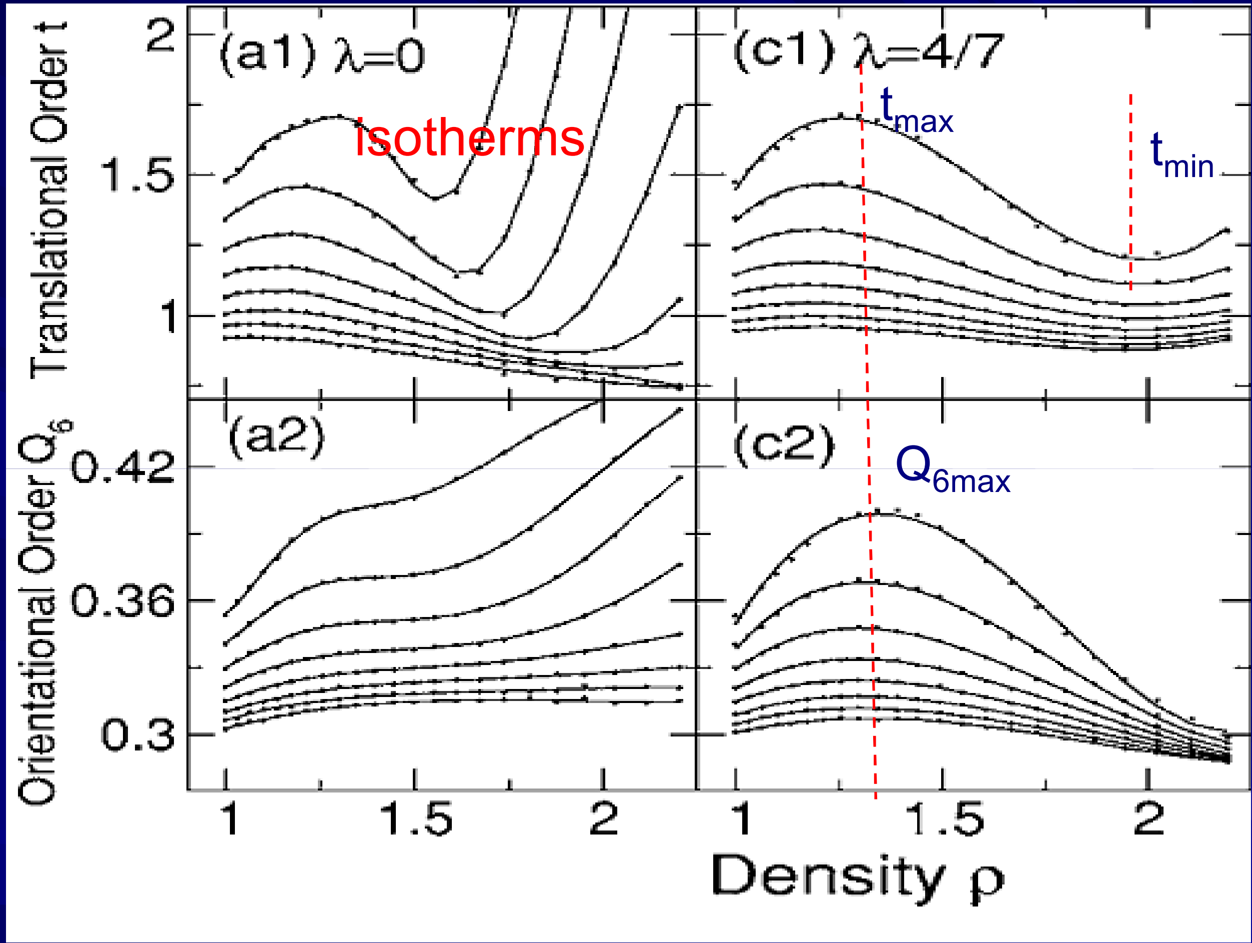



Structural anomaly of water: both *t* and *q* decrease with density

. **Z. Yan** et. al, ***Phys Rev E***, 76, 051201 (2007).

# Result: structural order for ramp potentials

Pure ramp ($\lambda$=0) Water-like ($\lambda$~0.6 )

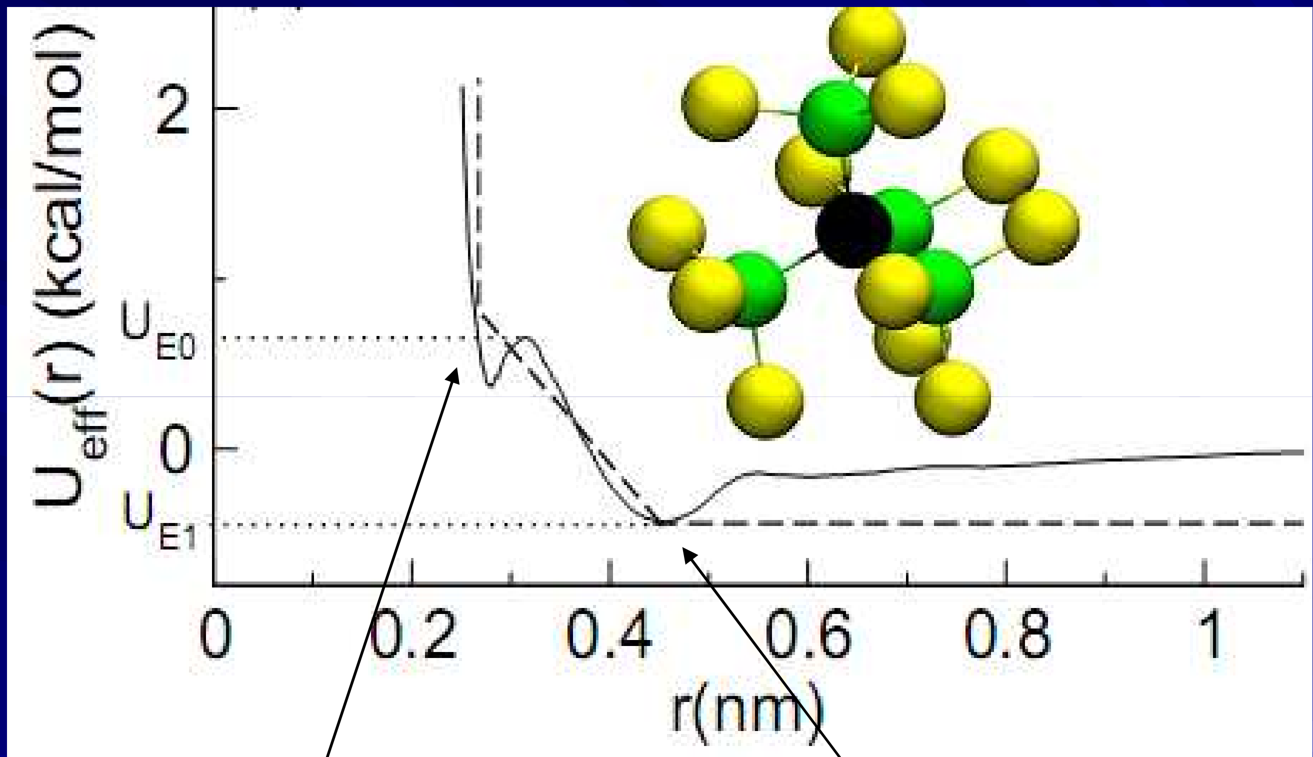



Only around $\lambda$~0.6, both *t* and $Q_6$ decrease with density, exhibit water-like structural anomaly

Z. Yan et. al, *Phys. Rev. Lett.* 95, 130604 (2005).

# Compare anomalous regions: physical parameter of water-like ramp potential (λ~0.6 )

Map ramp to water effective potential $U_{eff}(r)$




$\sigma_0 = 0.267$ nm, $\sigma_1 = 0.45$ nm

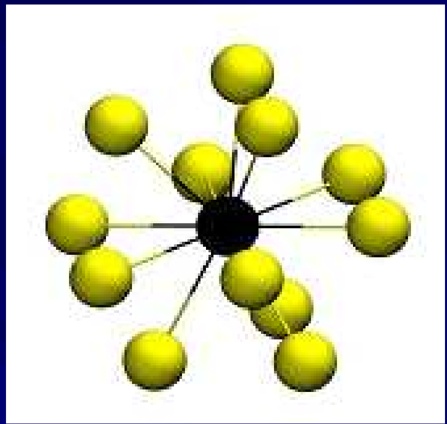
$$U_0 = U_{\text{eff}}(\sigma_0) - U_{\text{eff}}(\sigma_1) = 1.31 \text{ kcal/mol.}$$

Assign real physical parameter to ramp potential

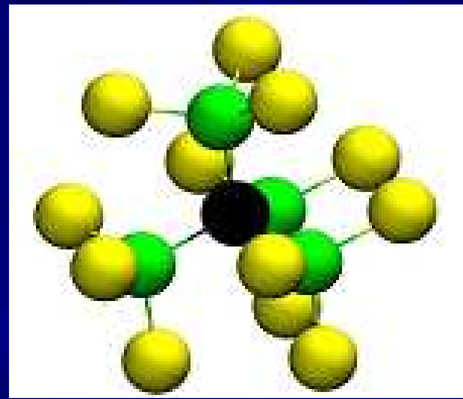
**Z. Yan**, et.al, PRE in press (2008).

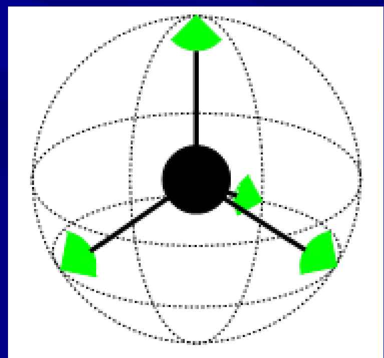
# Effective mass of ramp particle

Ramp



Water

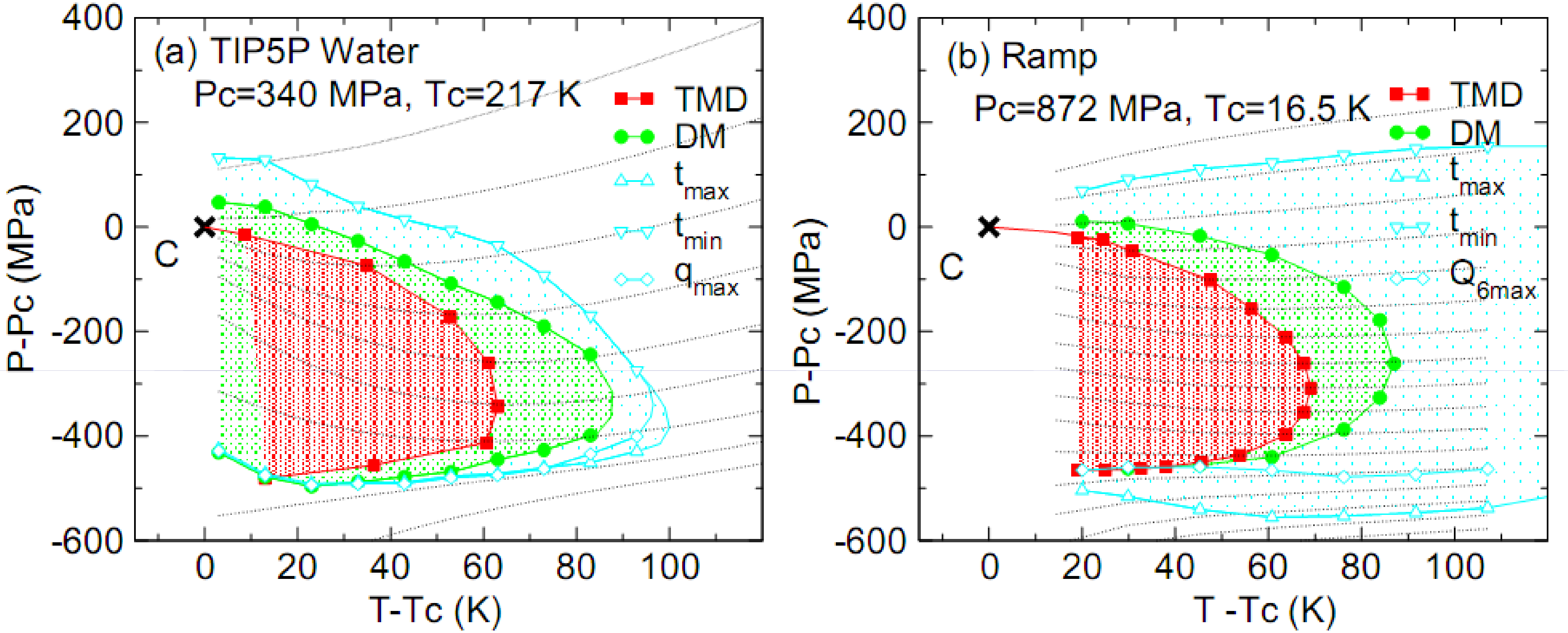




Effectively
1+4*1/4 =2 water molecules

Effective number density of water is twice of ramp.

# Anomalous regions in the phase diagram of ramp potential are similar to water




1. Use real units for ramp
2. Density and pressure of ramp are doubled
3. Shift *P, T* by LL critical point

**Z. Yan**, et.al, PRE in press (2008).

# Conclusion: Answer to all questions

1. Are the strong orientational tetrahedral interactions necessary for water-like density, diffusion and structural anomalies ?

   No

2. Can we find water-like anomalies in simple liquids (monatomic model with simple Spherically Symmetric potential) ?

   YES, two characteristic length scales with ratio $\lambda$ ~ ***0.6*** seems necessary,

3. How close the anomalies of simple potential compare with water ?

   Can be closely compared in real units

Thank you !