Anomalies of water and simple liquids

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1. **Z. Yan**, S. V. Buldyrev, N. Giovambattista, and H. E. Stanley, "Structural Order for One-Scale and Two-Scale Potentials," *Phys. Rev. Lett.* 95, 130604 (2005).(37 citations)
2. **Z. Yan**, S. V. Buldyrev, N. Giovambattista, P. G. Debenedetti, and H. E. Stanley, "A Family of Tunable Spherically-Symmetric Potentials that Span the Range from Hard Spheres to Water-like Behavior," *Phys. Rev. E* 73, 051204 (2006). (27 citations)
3. P. Kumar, **Z. Yan**, L. Xu, M. G. Mazza, S. V. Buldyrev, S.-H. Chen, S. Sastry, and H. E. Stanley, "Glass Transition in Biomolecules and the Liquid-Liquid Critical Point of Water," *Phys. Rev. Lett*. 97, 177802 (2006). (22 citations)
4. **Z. Yan**, S. V. Buldyrev, P. Kumar, N. Giovambattista, P. G. Debenedetti, H. E. Stanley, "Structure of the First- and Second-Neighbor Shells of Simulated Water: Quantitative Relation to Translational and Orientational Order," *Phys Rev E*, 76, 051201 (2007).
5. **Z. Yan**, S. V. Buldyrev, P. Kumar, N. Giovambattista, H. E. Stanley, "Correspondence between Phase Diagrams of the TIP5P Water Model and a Spherically Symmetric Repulsive Ramp Potential," *Phys. Rev. E* 77, 042201 (2008)
6. **Z. Yan,** S. V. Buldyrev, , H. E. Stanley, "Relation of Excess-entropy to anomalies of water", (accepted to *Phys. Rev. E*).
7. L. Xu, F. Mallamace, **Z. Yan**, F. W. Starr, S. V. Buldyrev, H. Eugene Stanley, "Interpretation of the Breakdown of Stokes-Einstein Relation in Water", (submitted to Nature Physics).

Motivation and questions ?

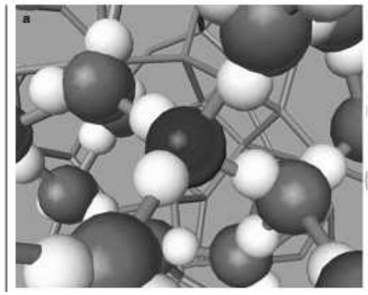
Motivation:

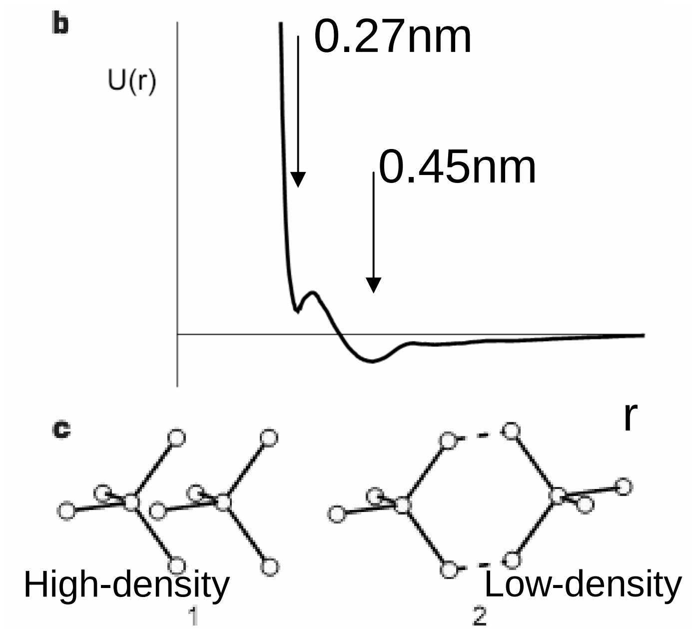
We try to understand water' s anomalies using a simple model

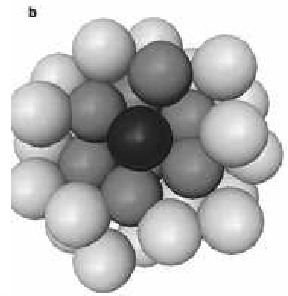
1. Are the strong orientational tetrahedral interactions in water necessary for water-like anomalies ?
2. Can we find water-like anomalies in simple liquid (monatomic model with simple spherically symmetric potential without orientational interaction) ? If YES
   (1) Why can spherically symmetric potential generate water-like anomalies ?
   (2) How do the anomalies of simple potential compare with water ?
3. How to predict the anomalous regions of water and simple liquids ?

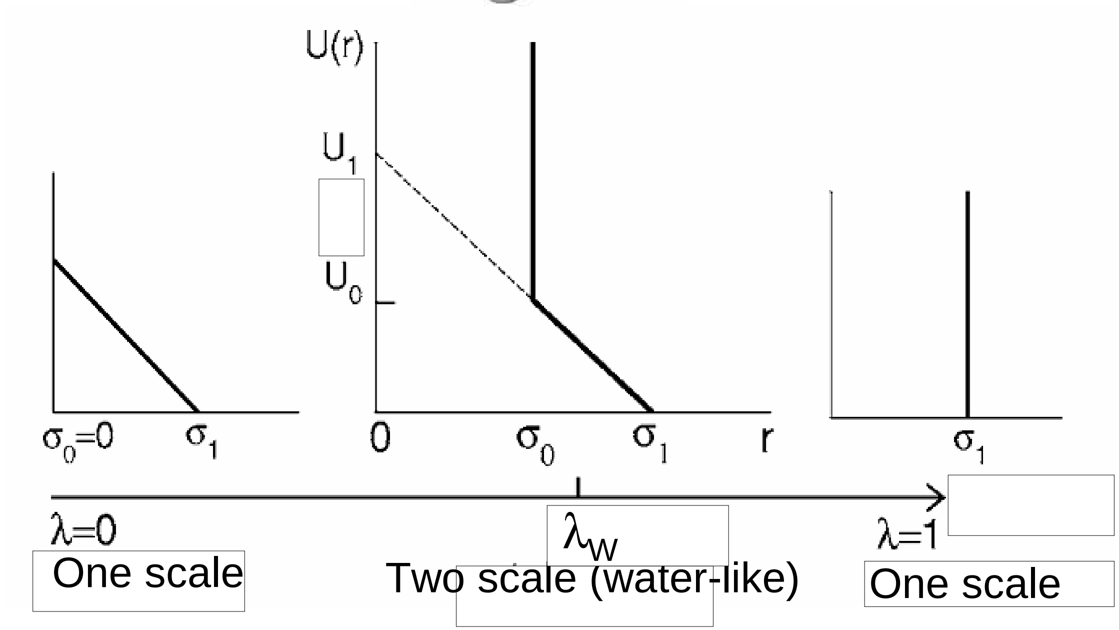
Does ramp potential leads to water-like anomalies ?

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









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

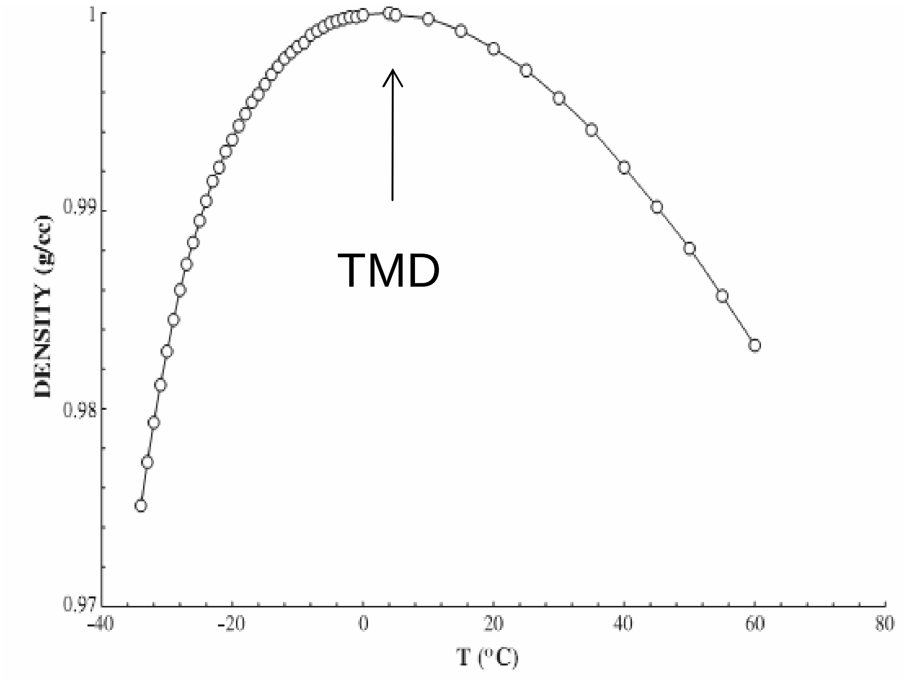
$$\lambda_w \approx 0.27\text{nm} / 0.45\text{ nm} \approx 0.6$$

Pictures:O. Mishima and H. E. Stanley, Nature 396, 26 (1998).
S. Sastry, Nature 409, 18 (2001). Z. Yan et.al, Phys. Rev. E 73, 051204 (2006).

Water anomalies

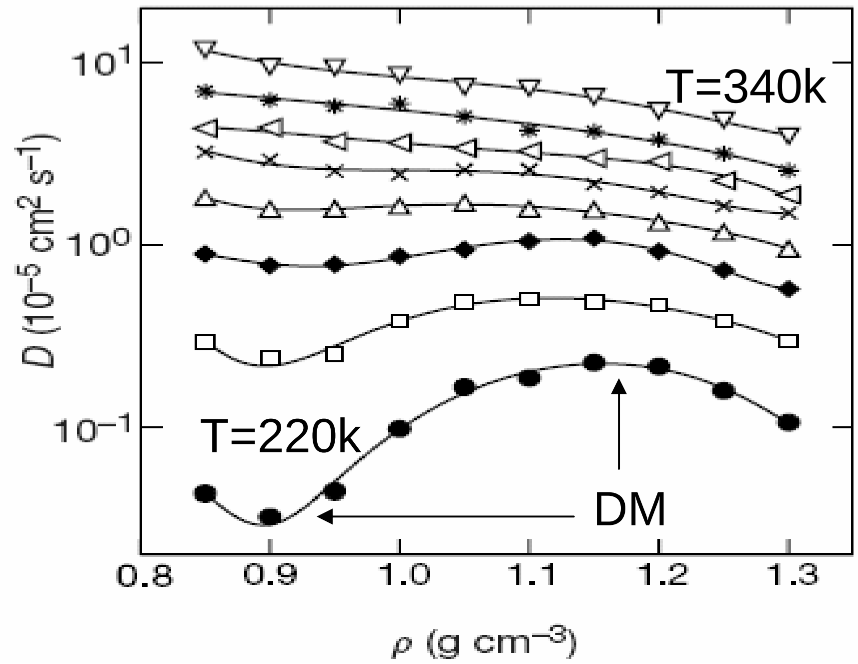
(a) Density anomaly

TMD: Temperature of Maximum Density



(b) Diffusion anomaly

DM: Diffusion Maximum/Minimum



J. R. Errington and P. G. Debenedetti, Nature 409, 318 (2001).
J. Bailar et. al, University Chemistry 1965, p. 41

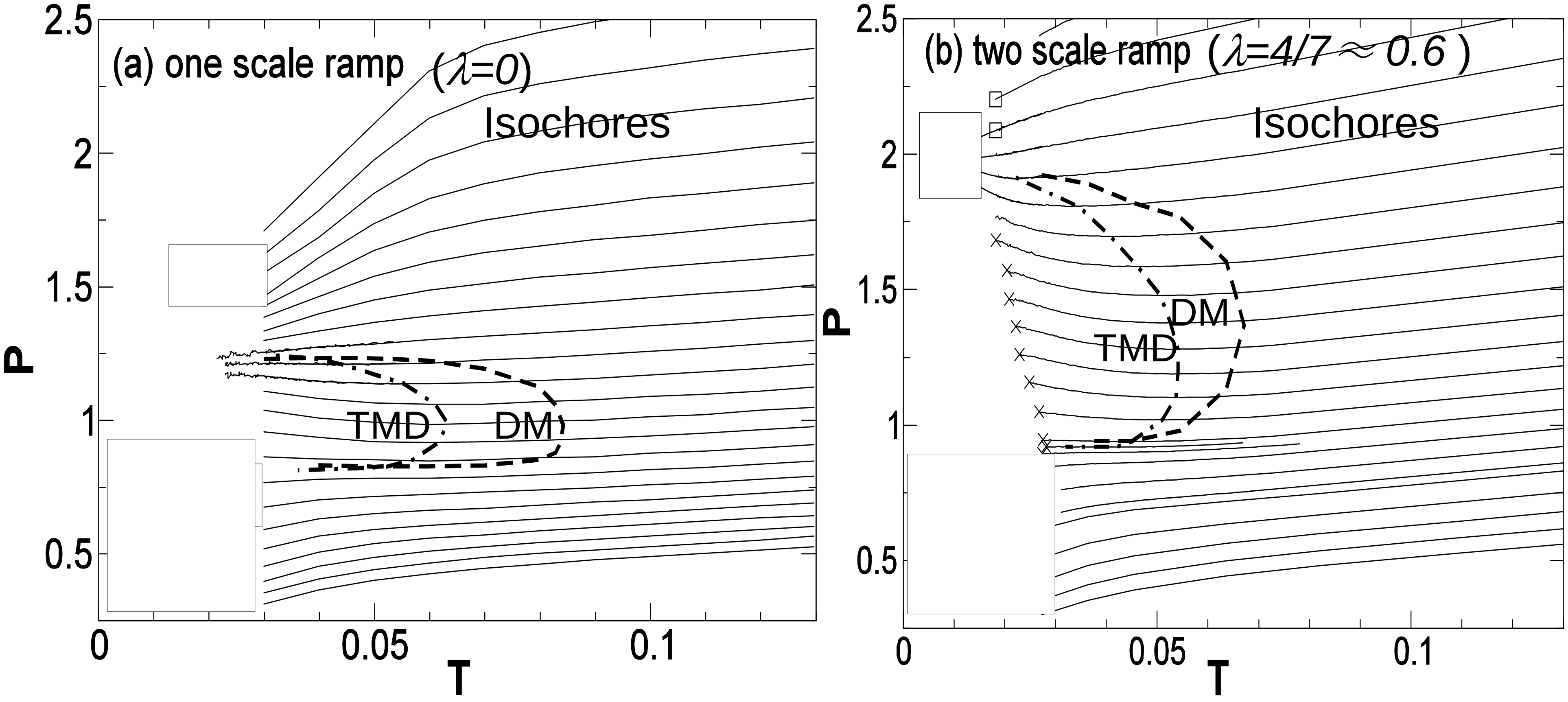
Result #1: Both one-scale and two-scale spherically symmetric potential show density and diffusion anomalies

$$\alpha_P = 1/V\,(\partial V/\partial T)_P = -1/V\,(\partial V/\partial P)_P\,(\partial P/\partial T)_V$$

Is there structural anomaly related to density and diffusion anomaly?

TMD: Temperature of Maximum Density

DM: Diffusion Maximum/Minimum

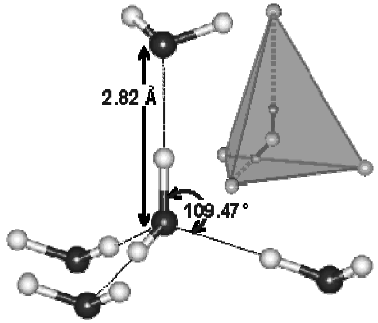


How to quantify structural order

Two basic types of order:

- . Orientational order *q* (or Q): quantifies specific local structure (space angle)

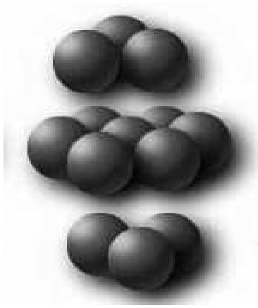
Water: tetrahedral local order,



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

q=1, tetrahedral local structure
q=0, random local structure

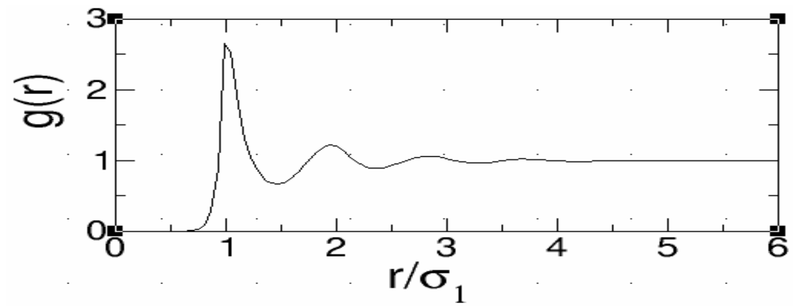
Ramp potential:
HCP, or FCC
structure



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

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

- Translational order t: quantifies degree to adopt preferential separations



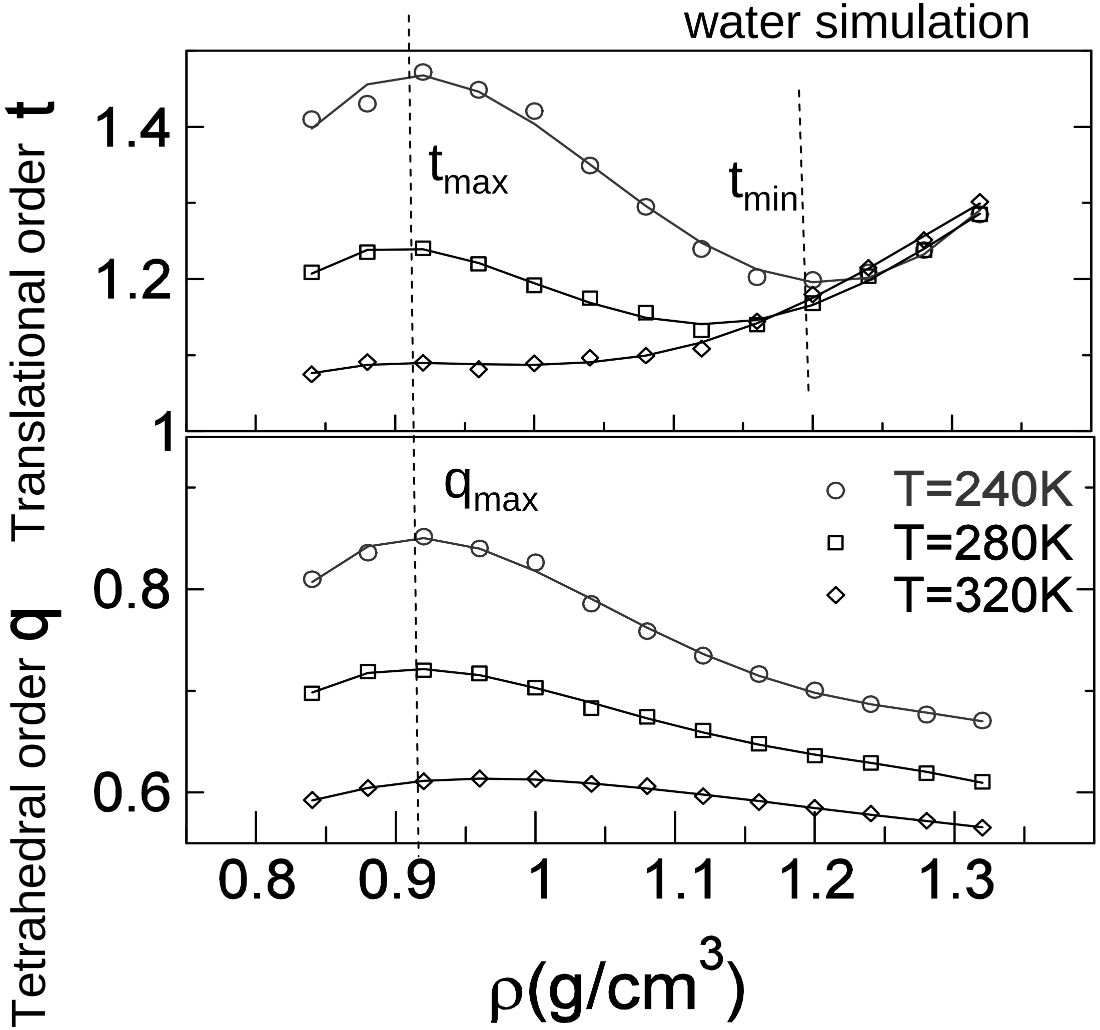
$$t \equiv \int_0^{r_c} \left|g(r) - 1\right| dr$$

t=0, random
t become larger if more particles adopt preferential separations

The order parameters increases with the increasing order of system

Picture:http://www.lsbu.ac.uk/water/hbond.html

Result #2: Structural anomaly of water: both *t* and *q* decrease with density



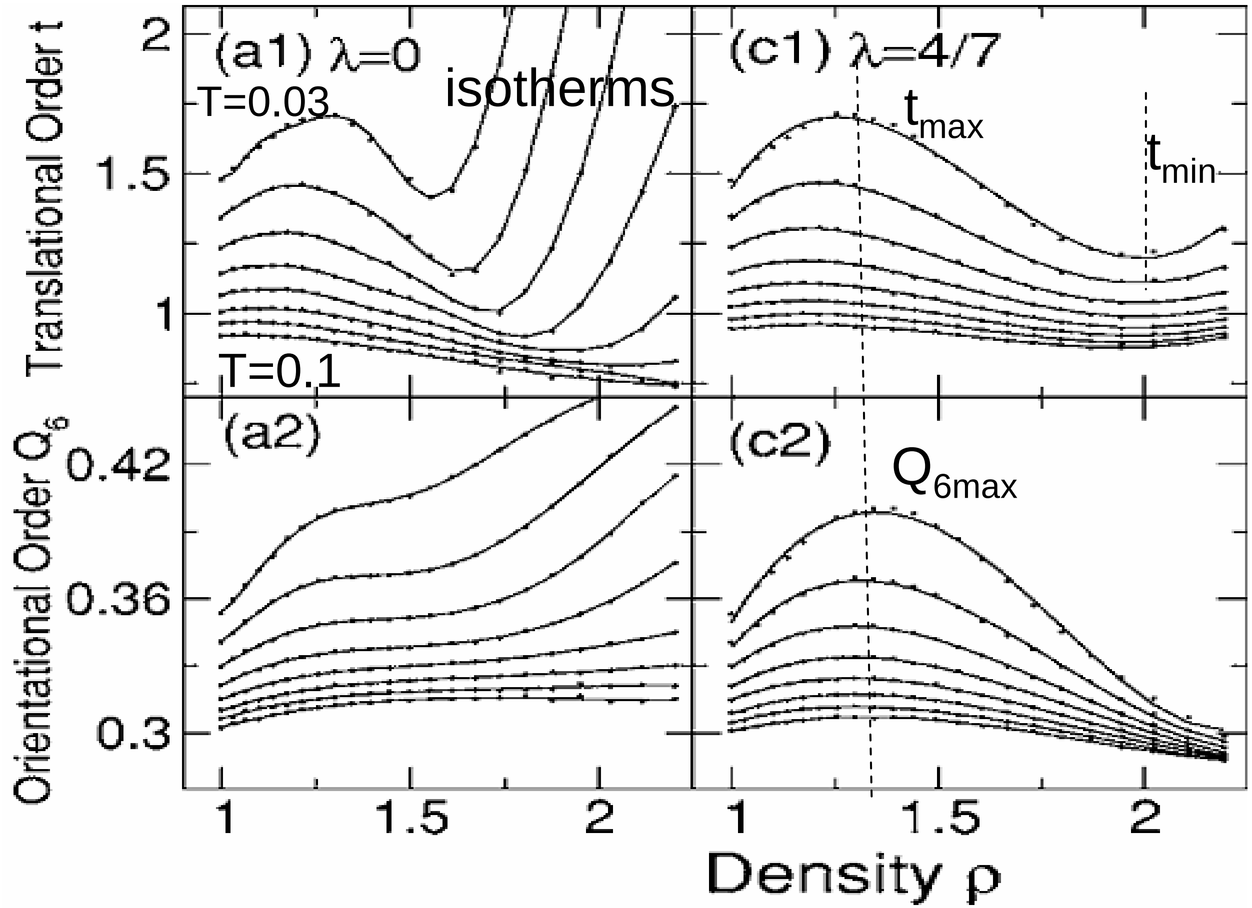
anomaly region:
0.9<ρ<1.2

anomaly region:
0.9< ρ

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

Result #3: Structural order for ramp potentials

One scale ramp (λ=0)   Two scale ramp ($\lambda \approx$0.6)



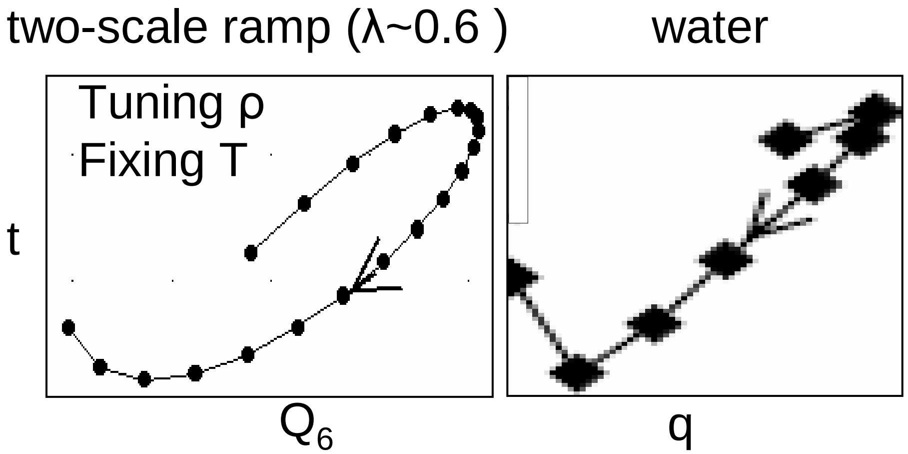
anomaly region:
1.3< ρ <2

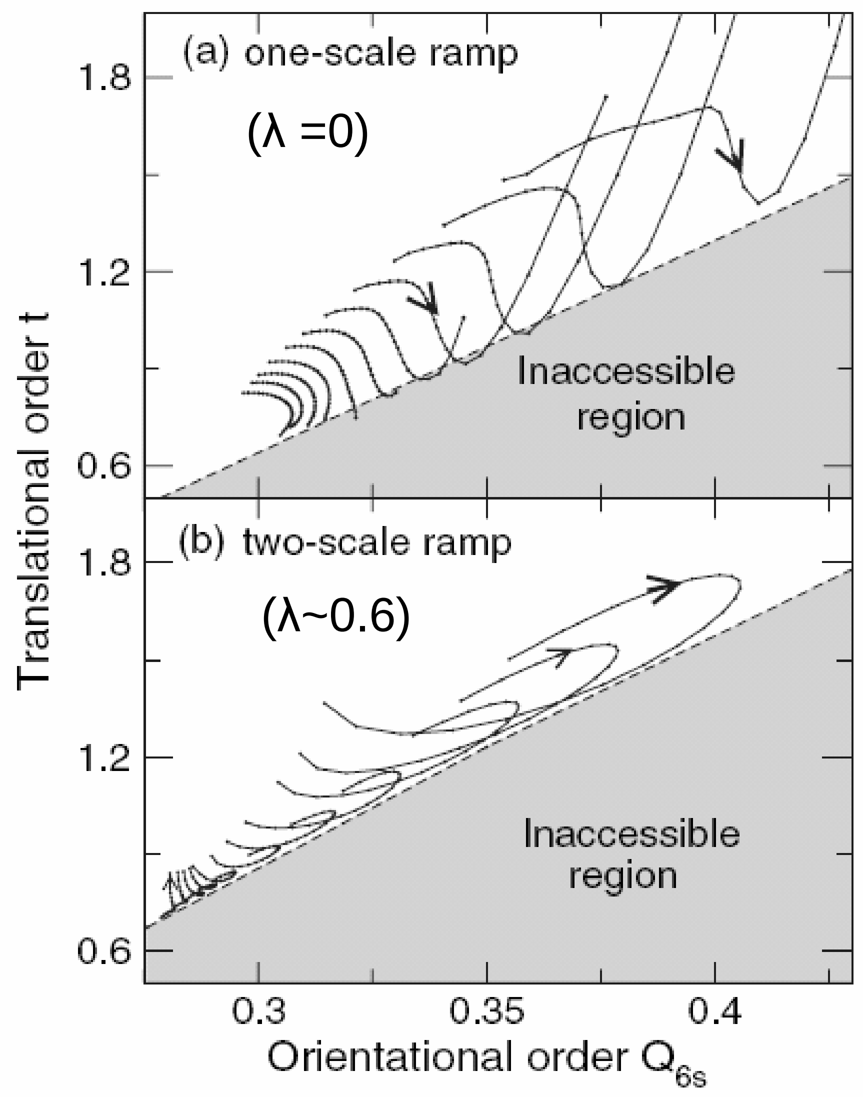
anomaly region:
1.3< ρ

Only around λ~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).
Z. Yan, et. al, *Phys. Rev. E* 73, 051204 (2006).

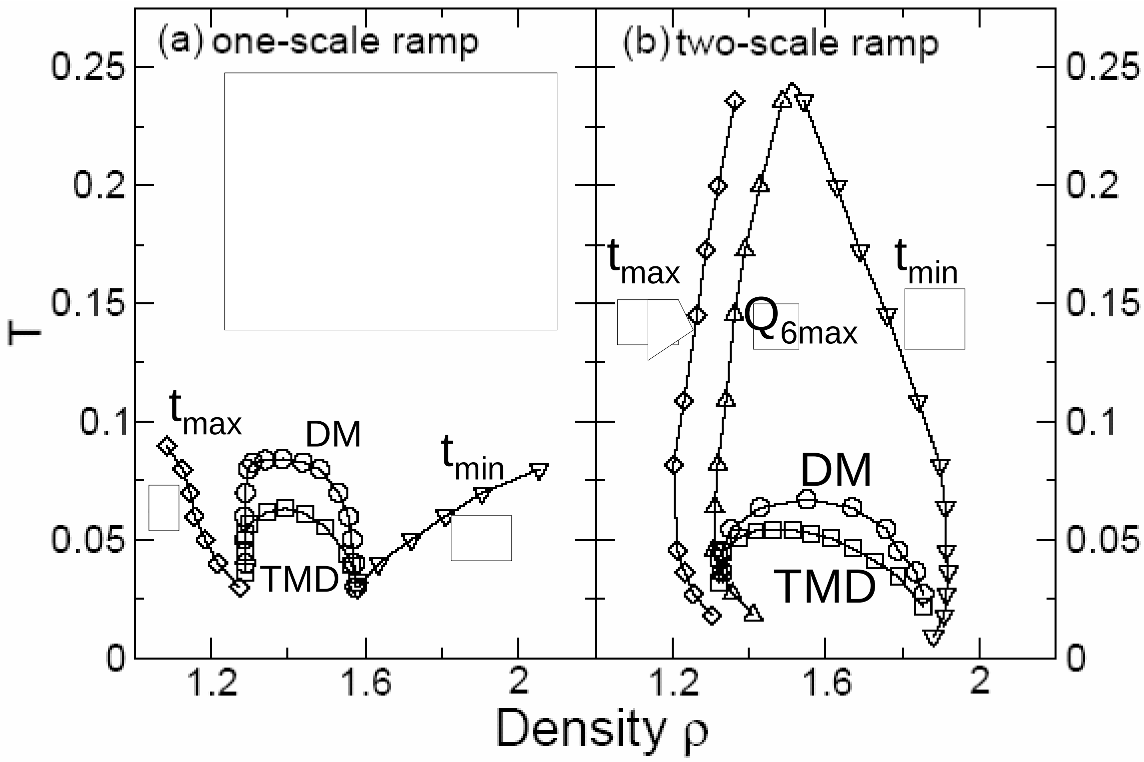
Result #4: Two-scale spherically symmetric ramp potential order map is similar to water

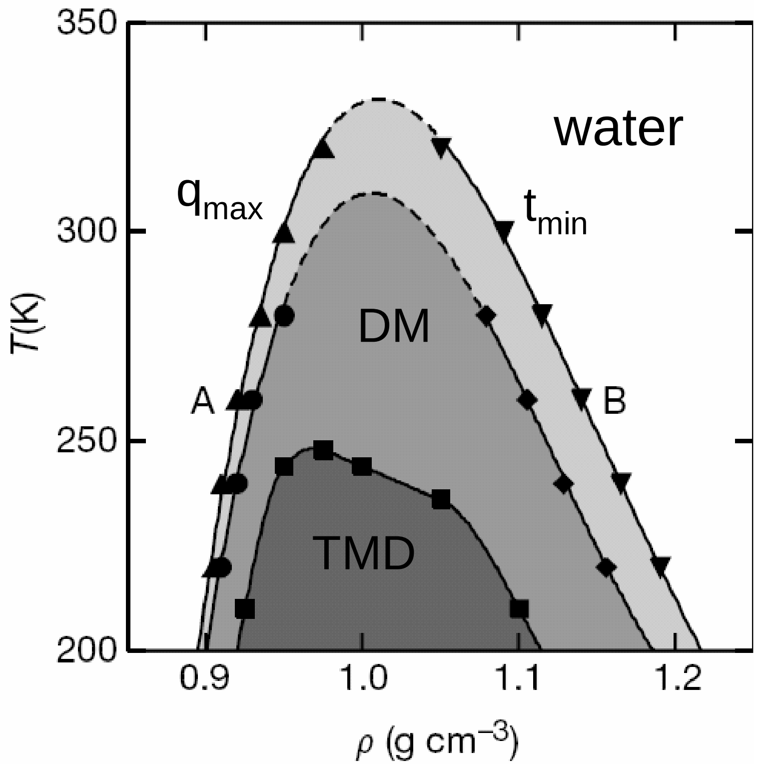




Result #5 :Anomalous regions of density, diffusion and structure

Is two-scale ramp similar to water ?

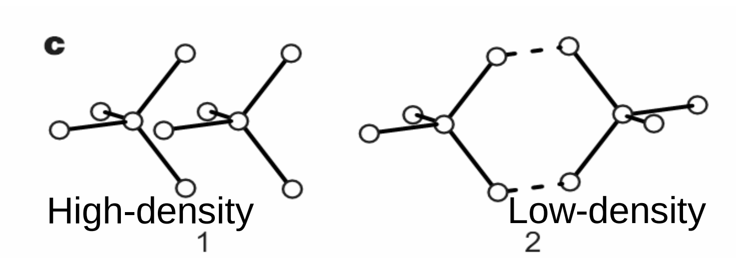


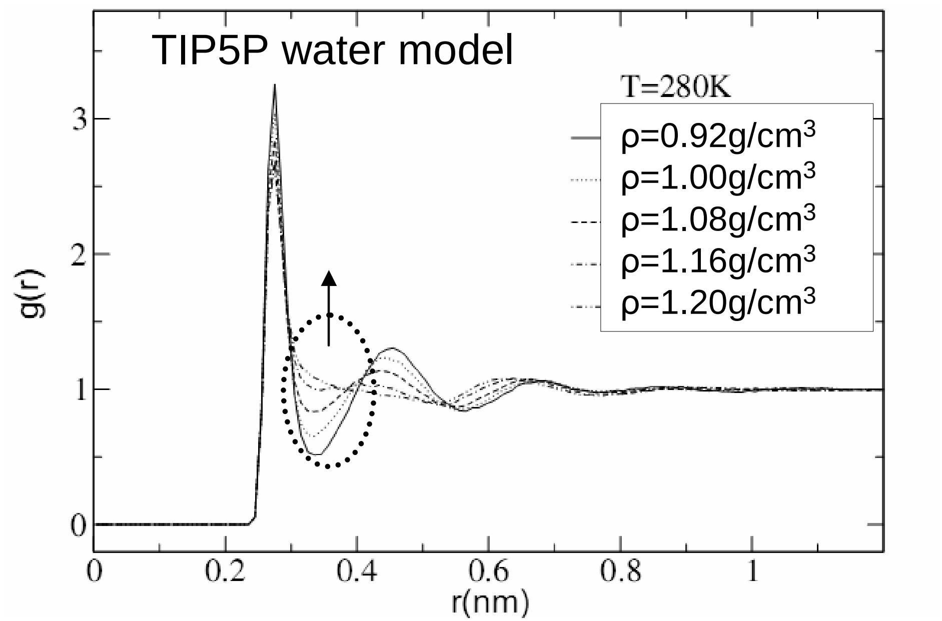


Result #6: Water-like Low density / High density structural change

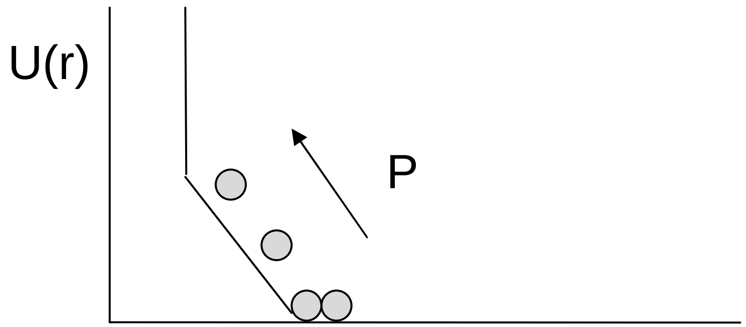
Ramp potential has water-like LDL/HDL structural change.
Ramp system mimics the flexibility of the second shell of water

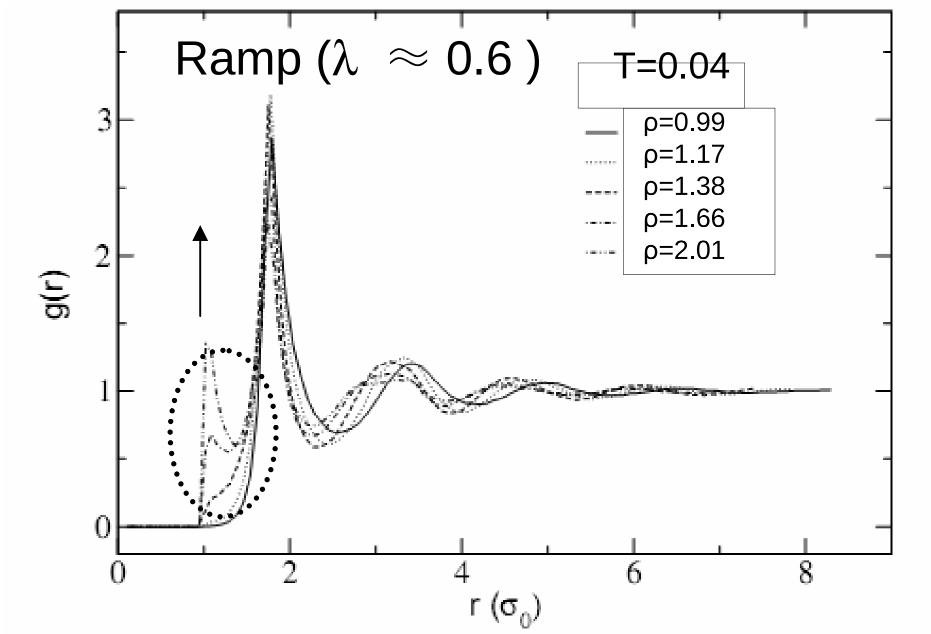
Water





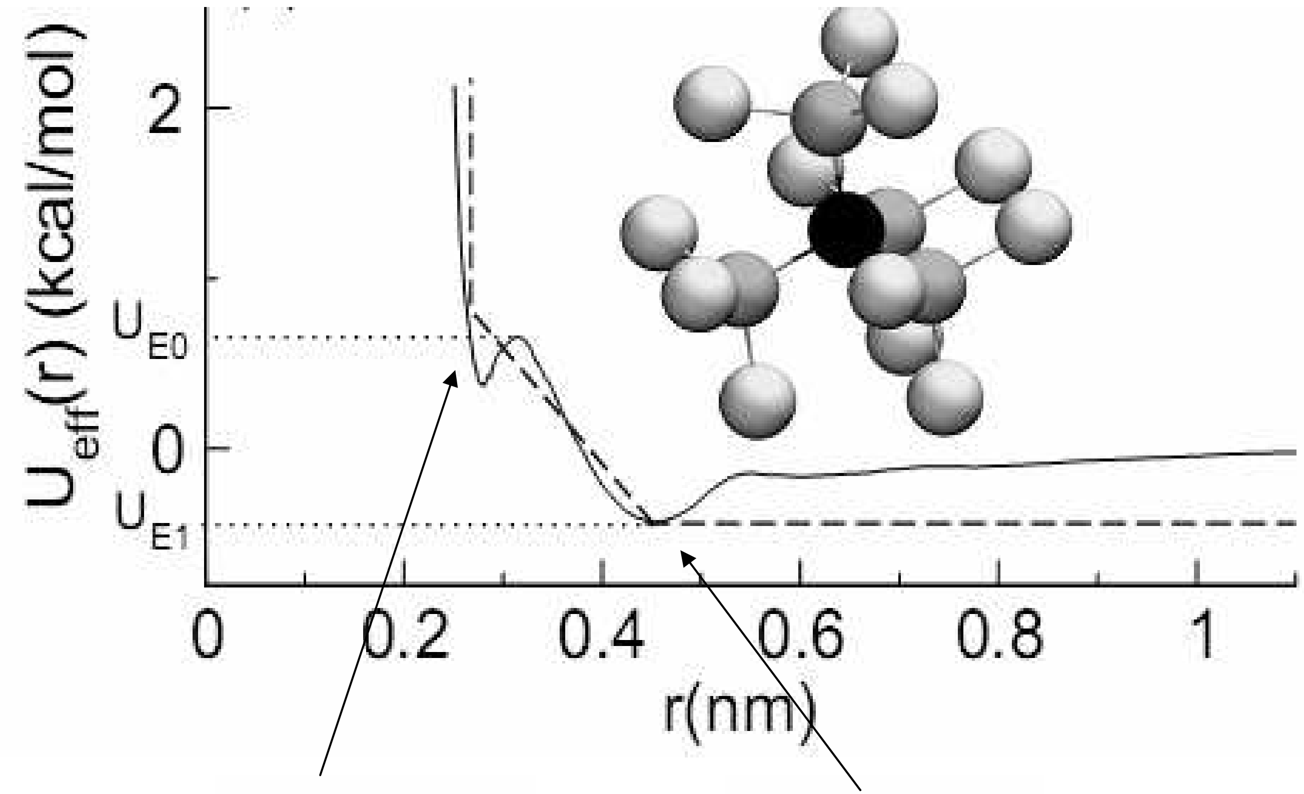
Two scale Ramp ($\lambda \approx 0.6$)





Compare anomalous regions: physical parameter of two scale ramp potential ($\lambda \approx 0.6$)

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



$\sigma_0 = 0.267\ \mathrm{nm},$ $\sigma_1 = 0.45\ \mathrm{nm}$

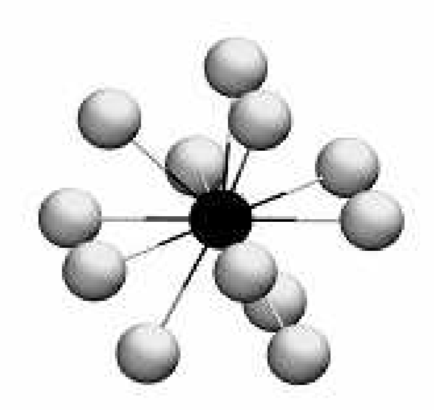
$$U_0 = U_{\mathrm{eff}}(\sigma_0) - U_{\mathrm{eff}}(\sigma_1) = 1.31\ \mathrm{kcal/mol}.$$

Assign real physical parameter to ramp potential

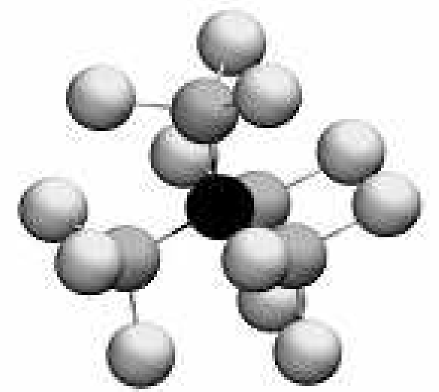
Z. Yan, et.al, *Phys. Rev. E* 77, 042201 (2008).

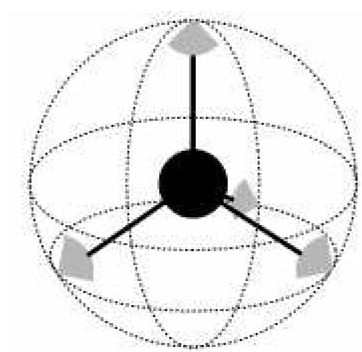
Result #7: Effective number density of water is ***twice*** of ramp particles.

Ramp



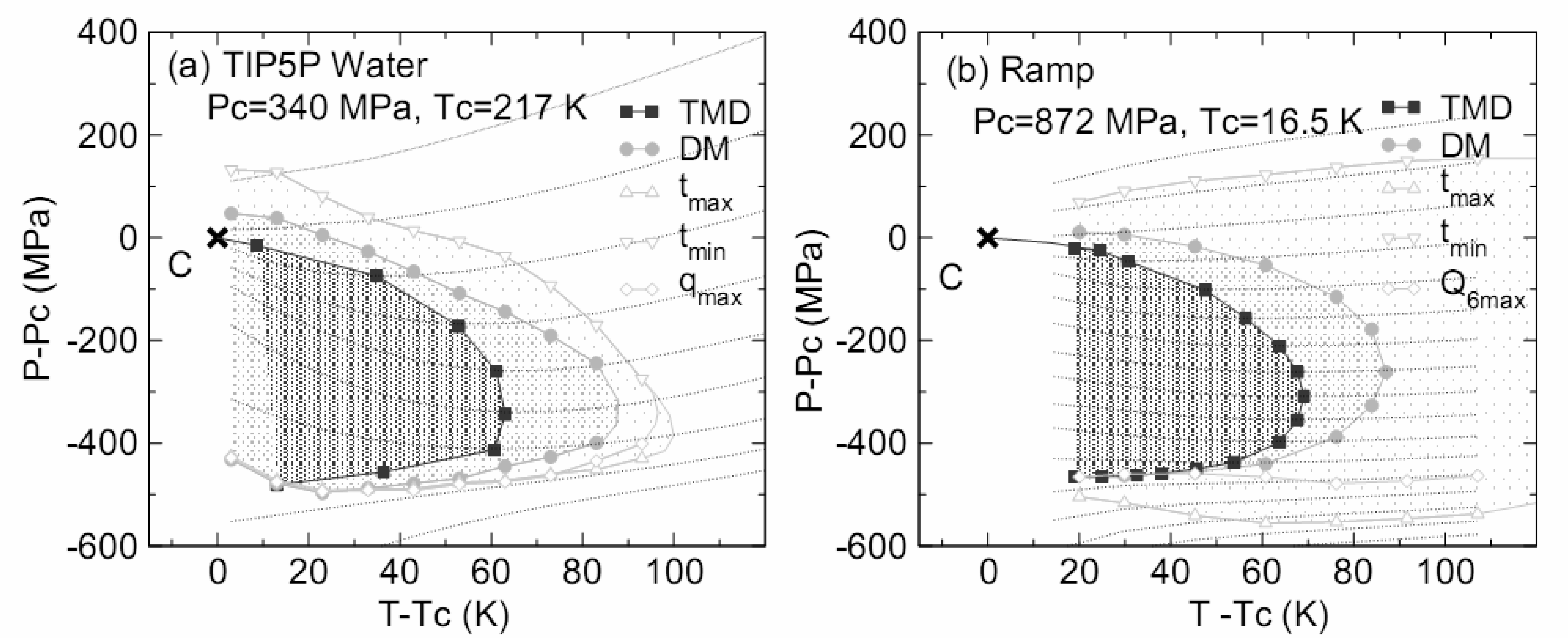
Water





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

Result #8: 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*

Z. Yan, et.al, *Phys. Rev. E* 77, 042201 (2008).

How to estimate the anomalous regions

Excess entropy: $$S_{ex} \equiv S - S_{ig} \equiv S + k_B \ln \rho - c(T).$$

Density anomaly: $\left(\frac{\partial \rho}{\partial T}\right)_P > 0 \xrightarrow{\left(\frac{\partial \rho}{\partial T}\right)_P = \rho^2 \left(\frac{\partial \rho}{\partial P}\right)_T \left(\frac{\partial S}{\partial \rho}\right)_T} \left(\frac{\partial S}{\partial \rho}\right)_T > 0$

$\downarrow S_{ex}$

$\left(\frac{\partial S_{ex}}{\partial \ln \rho}\right)_T > c\ k_B$ with $c = 1$

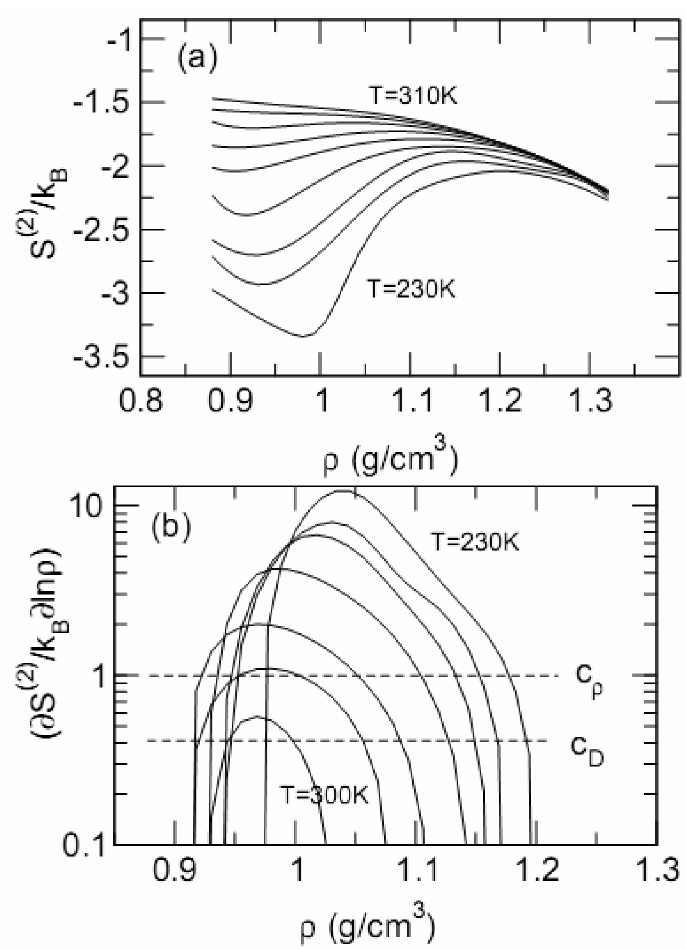
Diffusion anomaly: $\left(\frac{\partial D}{\partial \rho}\right)_T > 0 \xrightarrow{D\frac{\rho^{1/3}}{T^{1/2}} = 0.6\ \exp(0.8 S_{ex}/k_B)} \left(\frac{\partial S_{ex}}{\partial \ln \rho}\right)_T > c\ k_B$ with $c = 0.42$

For different T, finding the range of density between which the value of $(\partial S_{ex}/k_B \partial \ln \rho)_T > 1$ or 0.42

Y. Rosenfeld, J. Phys.: Condens. Matter 11, 5415 (1999).
J. R. Errington, T. M. Truskett, and J. Mittal, J. Chem. Phys. 125, 244502 (2006)

Result #9: Excess entropy of TIP5P water

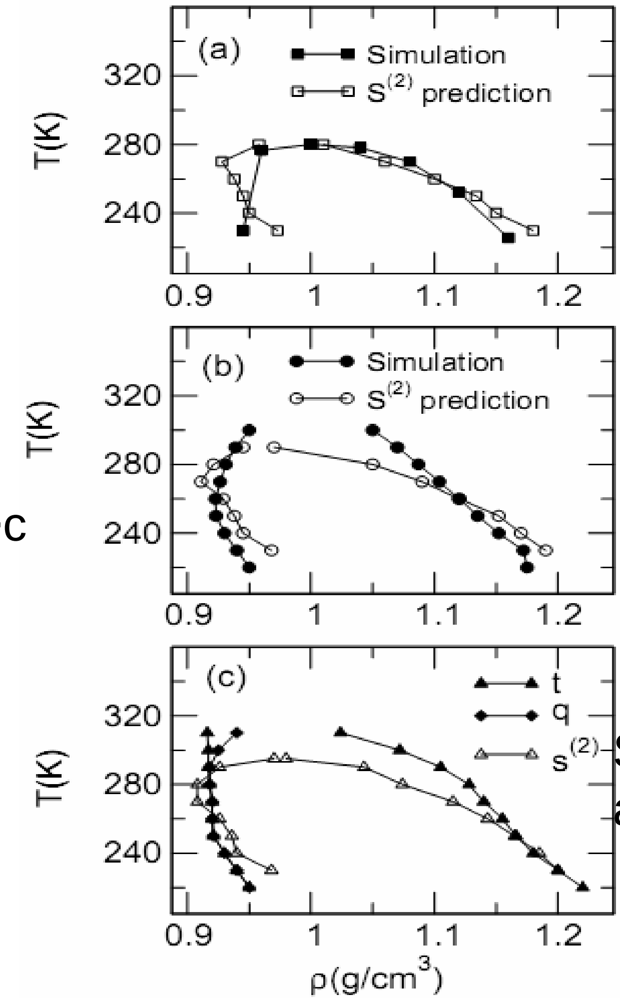
Compute S_{ex} : $S_{ex} \approx S^{(2)} = -2\pi\rho k_B \int \{g(r)\ln[g(r)] - [g(r)-1]\} r^2 dr$



$(\partial S_{ex}/k_B\partial \ln \rho)_T > c$

$C_\rho = 1$

$C_D = 0.42$



Density anomaly

Diffusion anomaly

Structural anomaly

Excess entropy has similar anomaly as structural anomaly, and it can be used to estimate anomaly regions. Similar results for water-like ramp liquids.

R. E. Nettleton and M. S. Green, J. Chem. Phys. 29, 1365 (1958). Z. Yan et.al, PRE, accepted.

Conclusion: Answers 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 $\lambda \approx$ ***0.6*** *seem necessary.*

   (1) Why can spherically symmetric potential generate water-like anomalies ?
   Water-like HDL/LDL structural change, mimicking change in the second shell of water

   (2) How close the anomalies of simple potential compare with water ?
   Anomalous regions can be closely compared in phase diagram in real units

3. How to predict the anomaly regions of water and simple liquids from structure?
   We can use excess entropy to predict anomaly regions.

Publications

1. **Z. Yan**, S. V. Buldyrev, N. Giovambattista, and H. E. Stanley, “Structural Order for One-Scale and Two-Scale Potentials,” ***Phys. Rev. Lett****.* 95, 130604 (2005).(34 citations)

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Thank you all !

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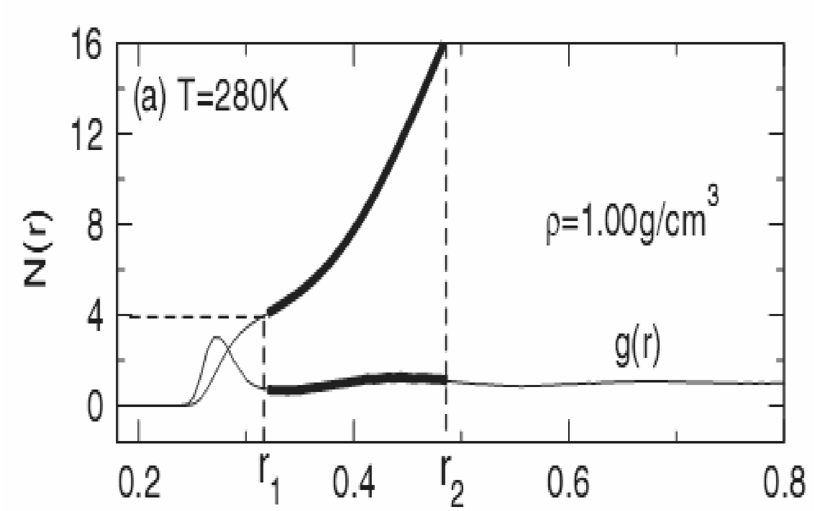
Committee member:
Professor H. Eugene Stanley, Professor William Skocpol, Professor William Klein, Professor Karl Ludwig, Professor Ed Kearns, and Professor Emanuel Katz

Family and friends

Structural order in the first and second shells of water

Define the first and second shell:
1. The first shell is relatively stable, has 4 nearest neighbors
2. The second shell are defined as next 12 nearest neighbors,

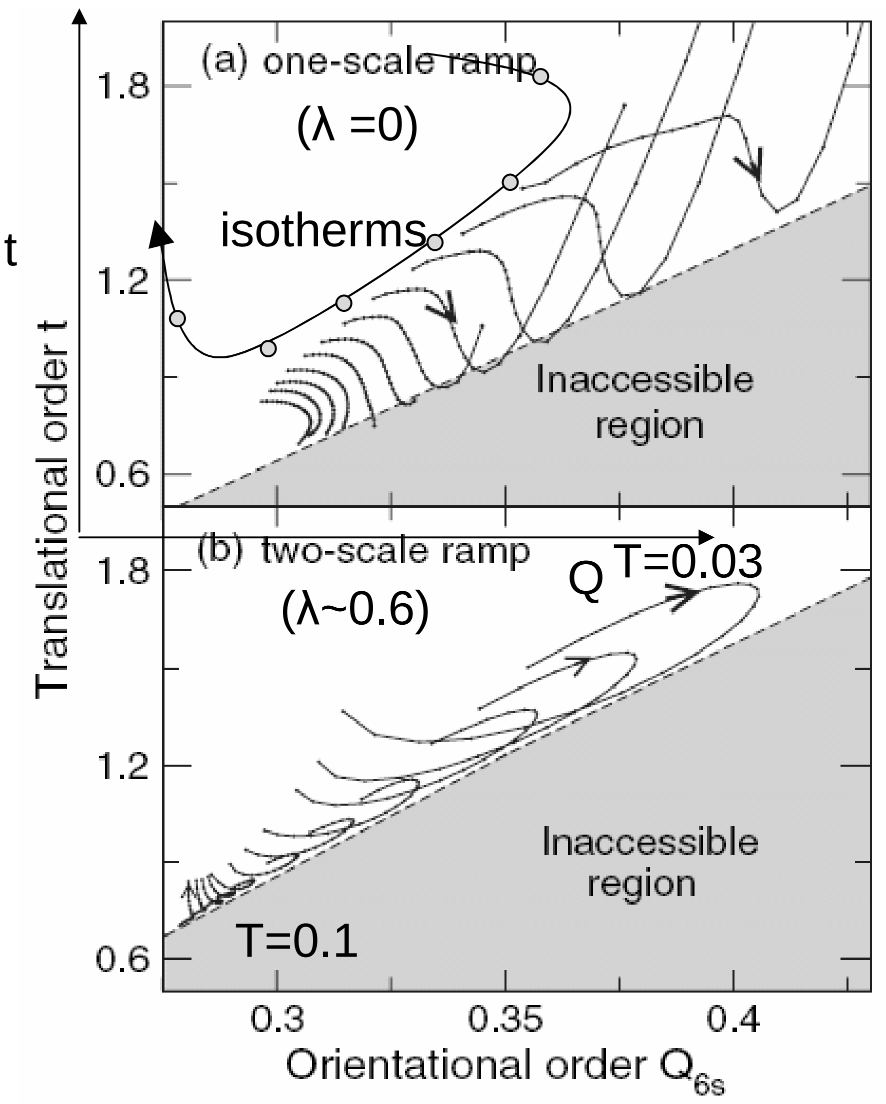


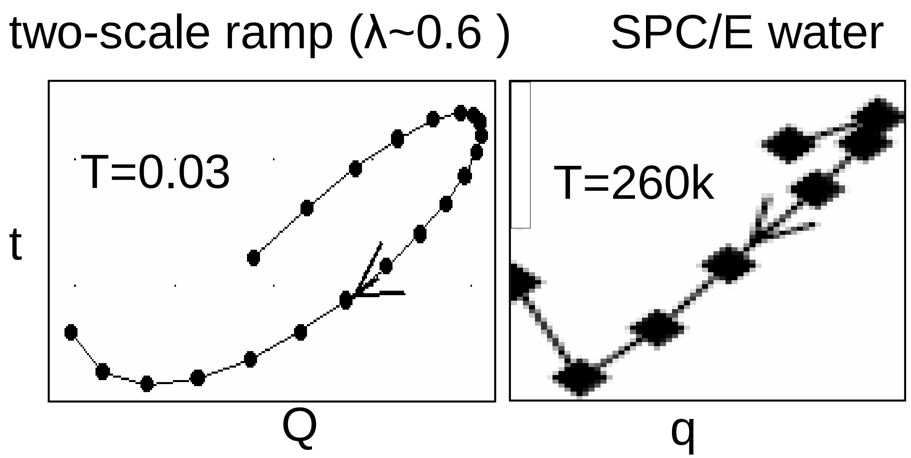
$$t = t_1 + t_2 + t_3$$

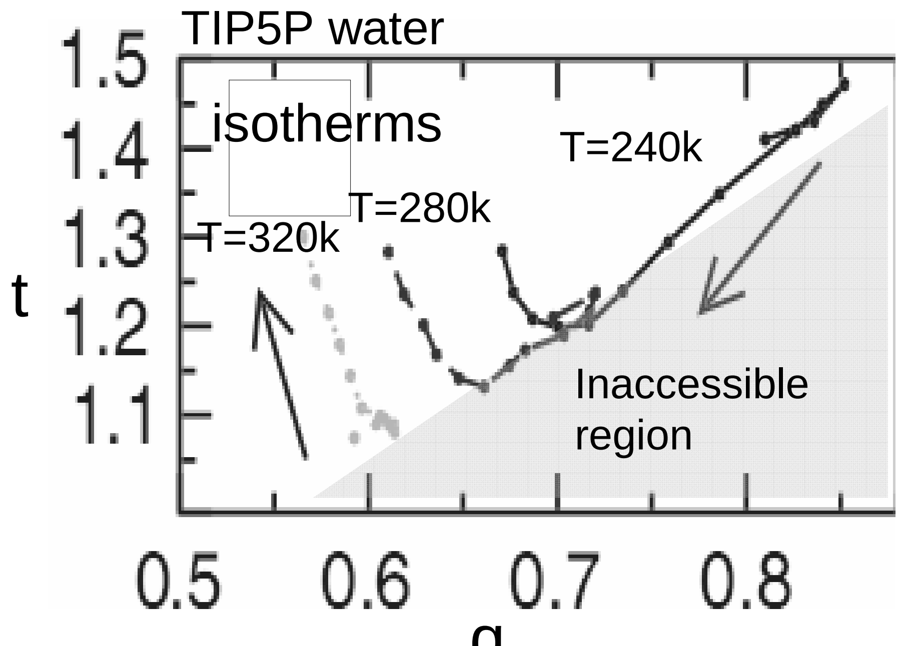
t_1 ← q, t_2 ← Q_6

We can investigate the structural order for the first and second shell separately

Result #4: Order maps







Two-scale spherically symmetric ramp potential order map: similar to water