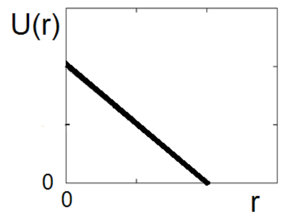

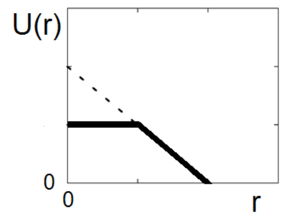

The Cut Ramp Potential

A simple model with water-like behavior

E. Lascaris, G. Malescio, S.V. Buldyrev, and H.E. Stanley,
"Cluster formation, water-like anomalies, and re-entrant melting for a new family of bounded repulsive interaction potentials",
Phys. Rev. E **81**, 031201 (2010)

Outline

- Water and its anomalies
- What is the cause of these anomalies?
  (conclusion: more research needed)
- The Cut Ramp Potential
- Conclusions

Outline

- **Water and its anomalies**
- What is the cause of these anomalies?
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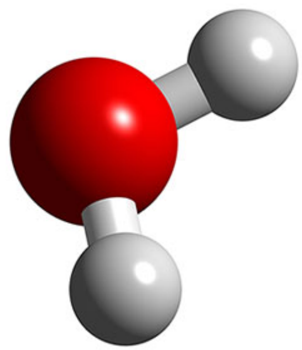
Water is very anomalous…



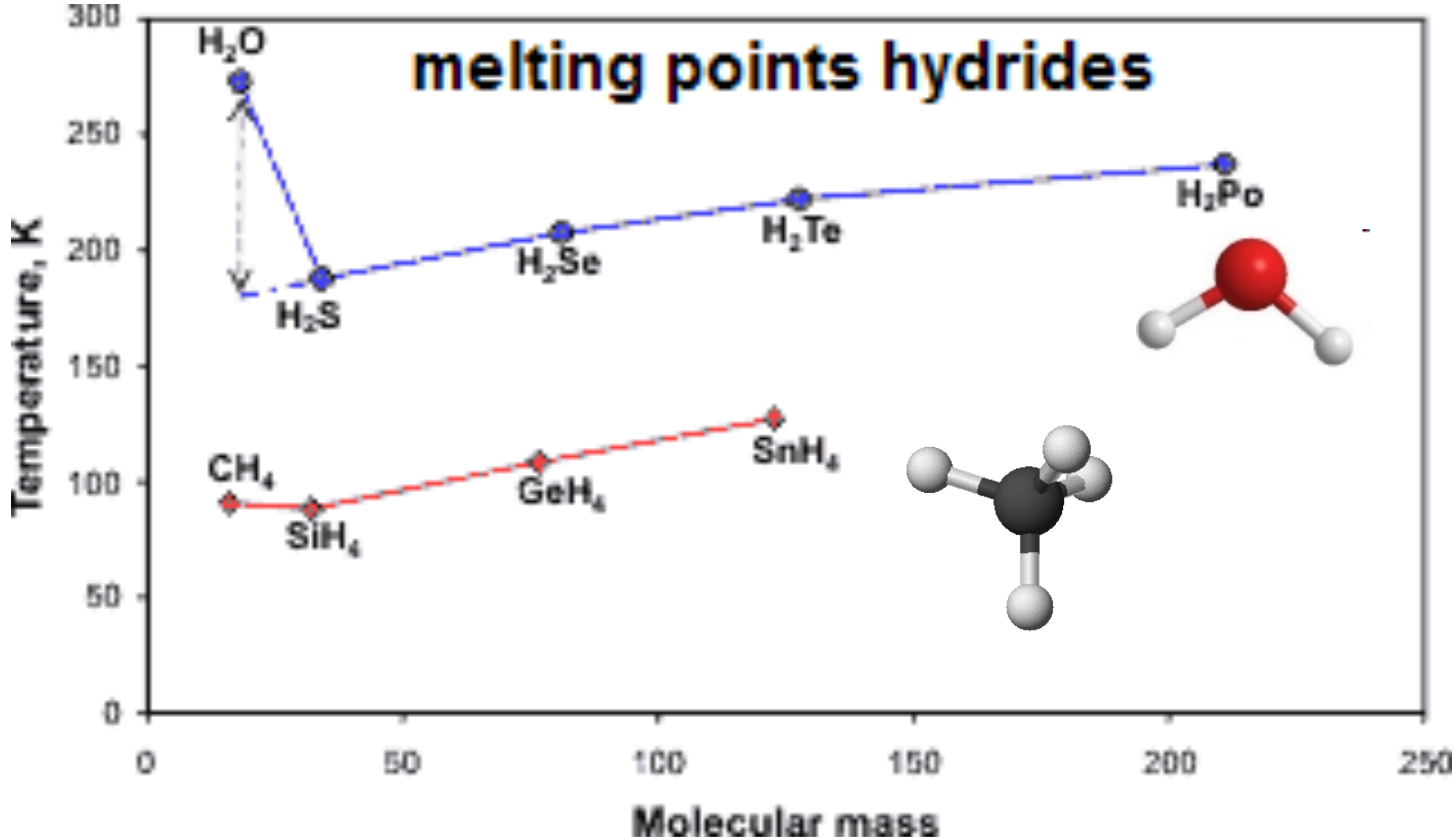
A simple molecule…

…but compared to most other liquids, water has many strange properties…

and is therefore very interesting!

Melting temperature

Hydride = element + H atoms



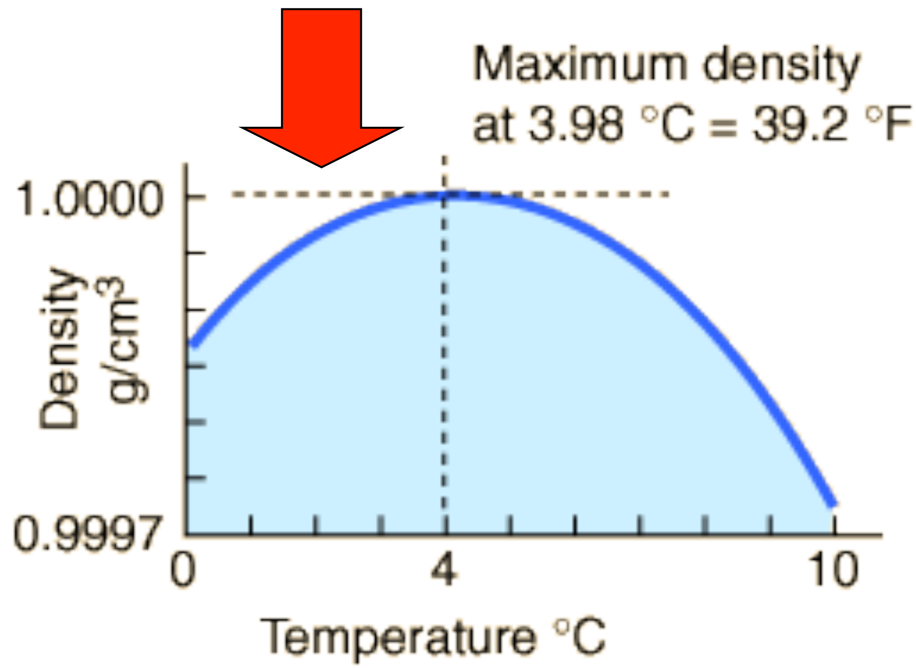
Ice floats on water

Usually, the density of the solid is higher than of the liquid

Density of ice is lower than density of water

Density anomaly

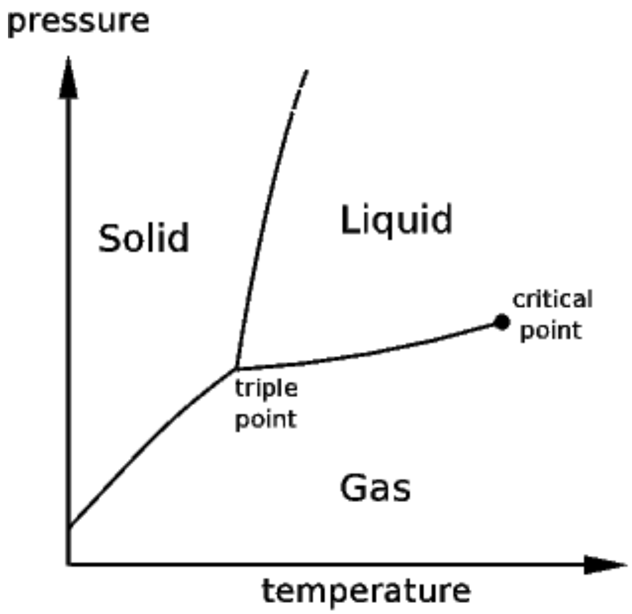
As we increase T, density ***increases***!



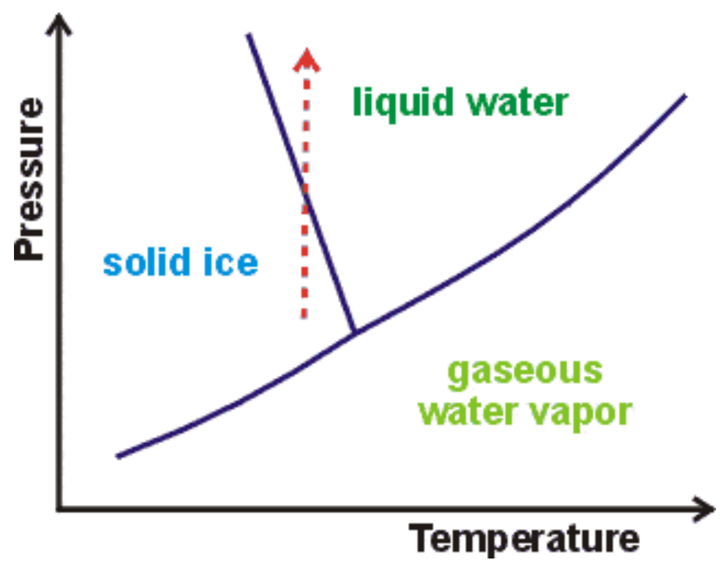
At 1 atm *Temperature of Maximum Density* (TMD) is 4 °C

Melting line with negative slope

Most liquids:



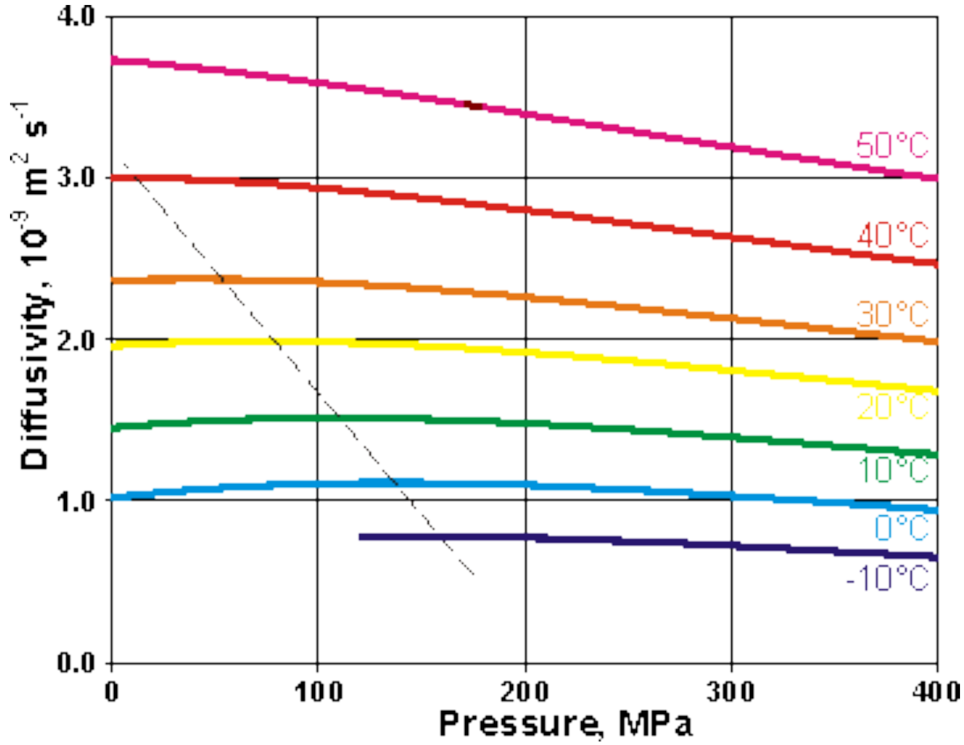
Water:



Applying pressure can **melt** ice!

Diffusion anomaly

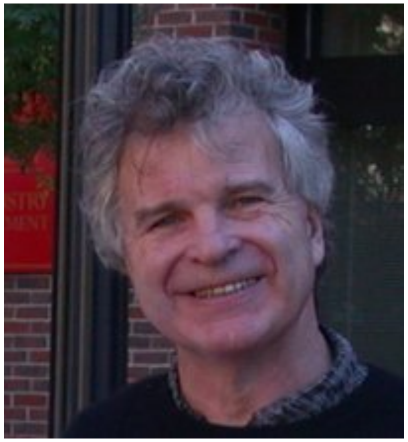
Usually, self-diffusion goes down as P increases…



In water, self-diffusion **increases** as density and pressure increase (at low T)

Water group anomaly

Gene Stanley’s water group at BU has an anomalously large size



Water attracts unusual large amount of grad students (at low pressure)

And many, many more anomalies

Water has

- unusually high specific heat capacity
- unusually high viscosity
- unusually high surface tension
- unusually low compressibility
- wide variety of crystal structures (15 known)

All 67 (as of Aug 2010) anomalies are listed on

http://www1.lsbu.ac.uk/water/anmlies.html

Why study these anomalies?

- Because we are scientists and we like to study stuff!

- To improve our understanding of water (and other liquids)

  Example: knowing "what matters" allows for faster simulations (e.g. when to use QM and when not to use it)

- Understanding these anomalies allows us to engineer liquids with certain properties

  Example: a polymer with an unusually high viscosity

Outline

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- **What is the cause of these anomalies?**
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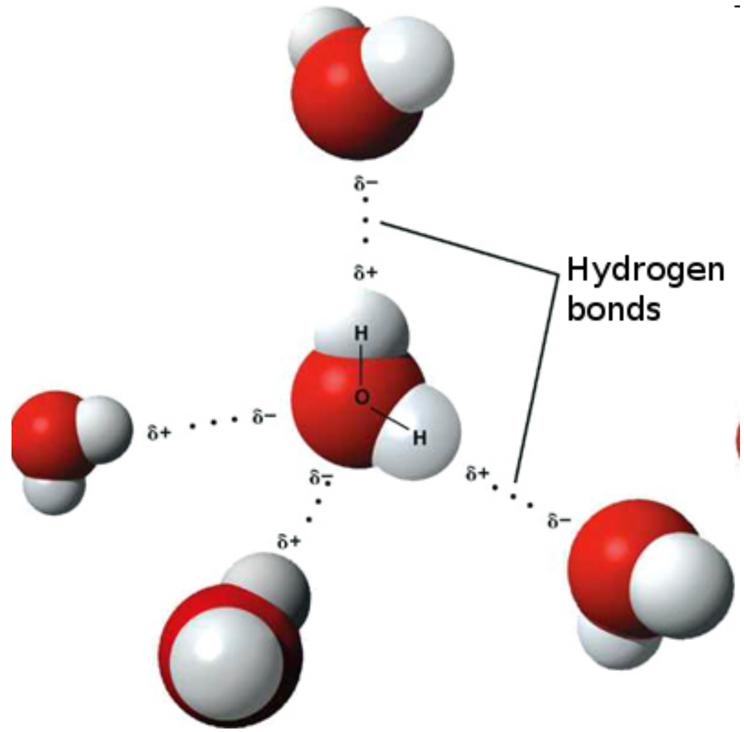
Cause of anomalies in water

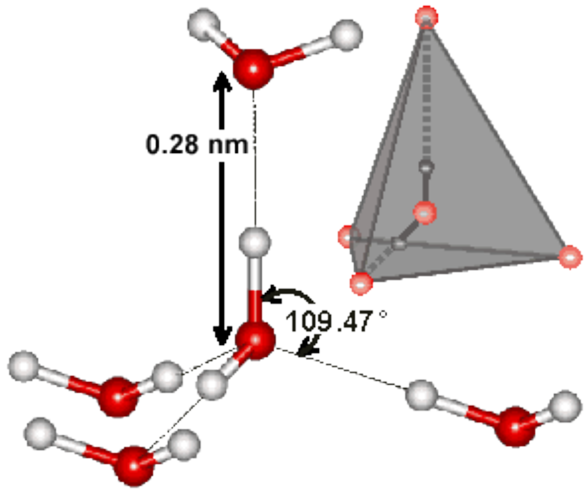
What feature makes water so unique?

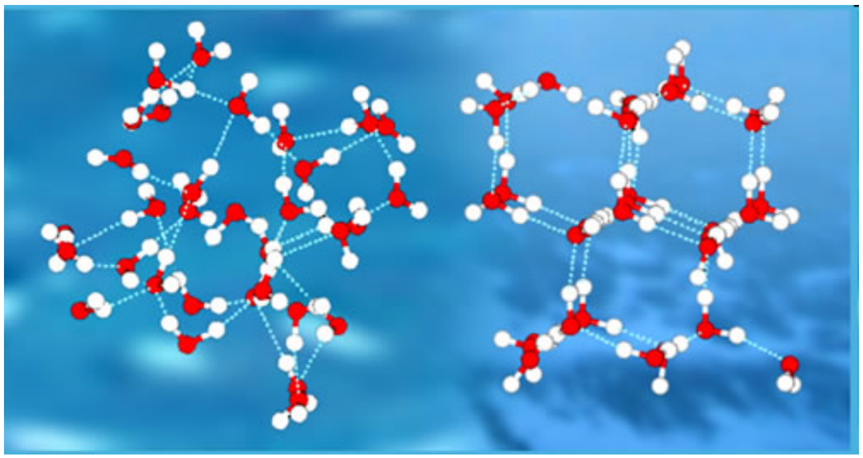
Hydrogen bonds!



A simple explanation for
high melting temperature

Tetrahedral bonds





H-bonds are long compared to size of molecule

Explains

- why ice floats on water
- why applying pressure can melt ice
- why C, Si, Ge also shown certain anomalies

Key question!

But are directional bonds really necessary?

Can we have anomalies without these?

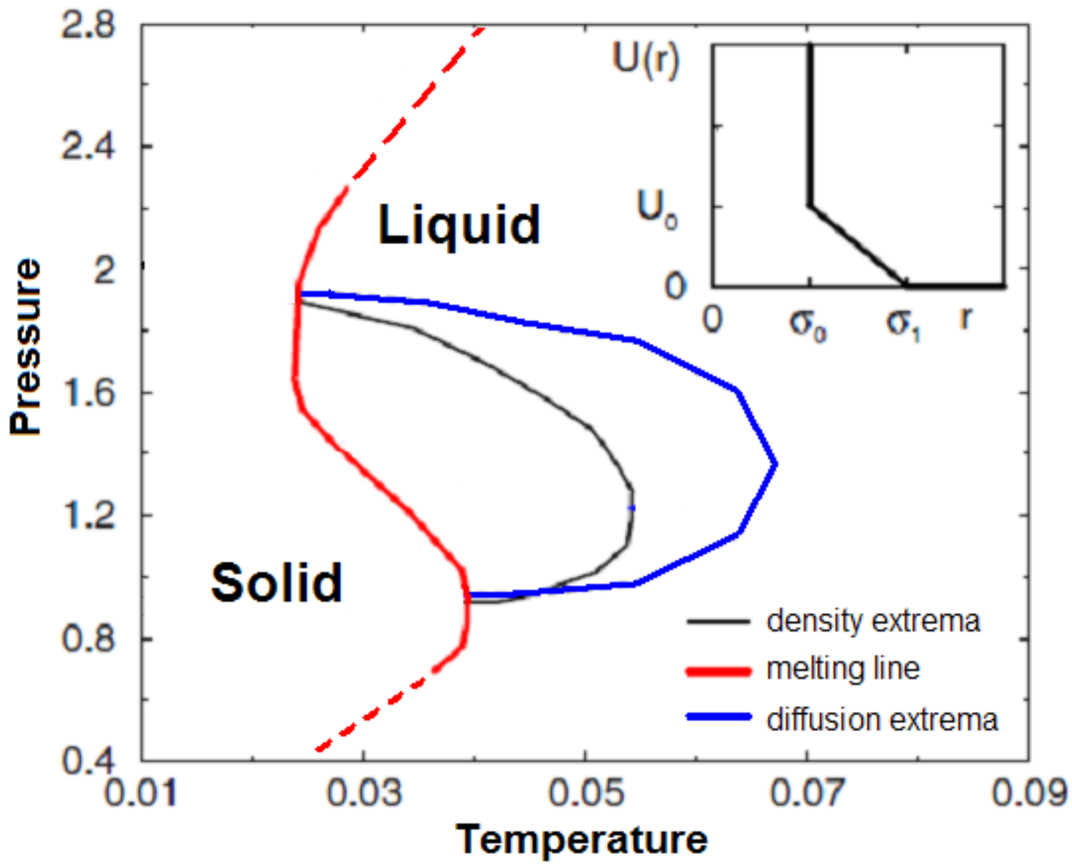
Yes!

Simulations with certain spherically symmetric interactions display anomalies

An example...

Hard Core + Linear Ramp model

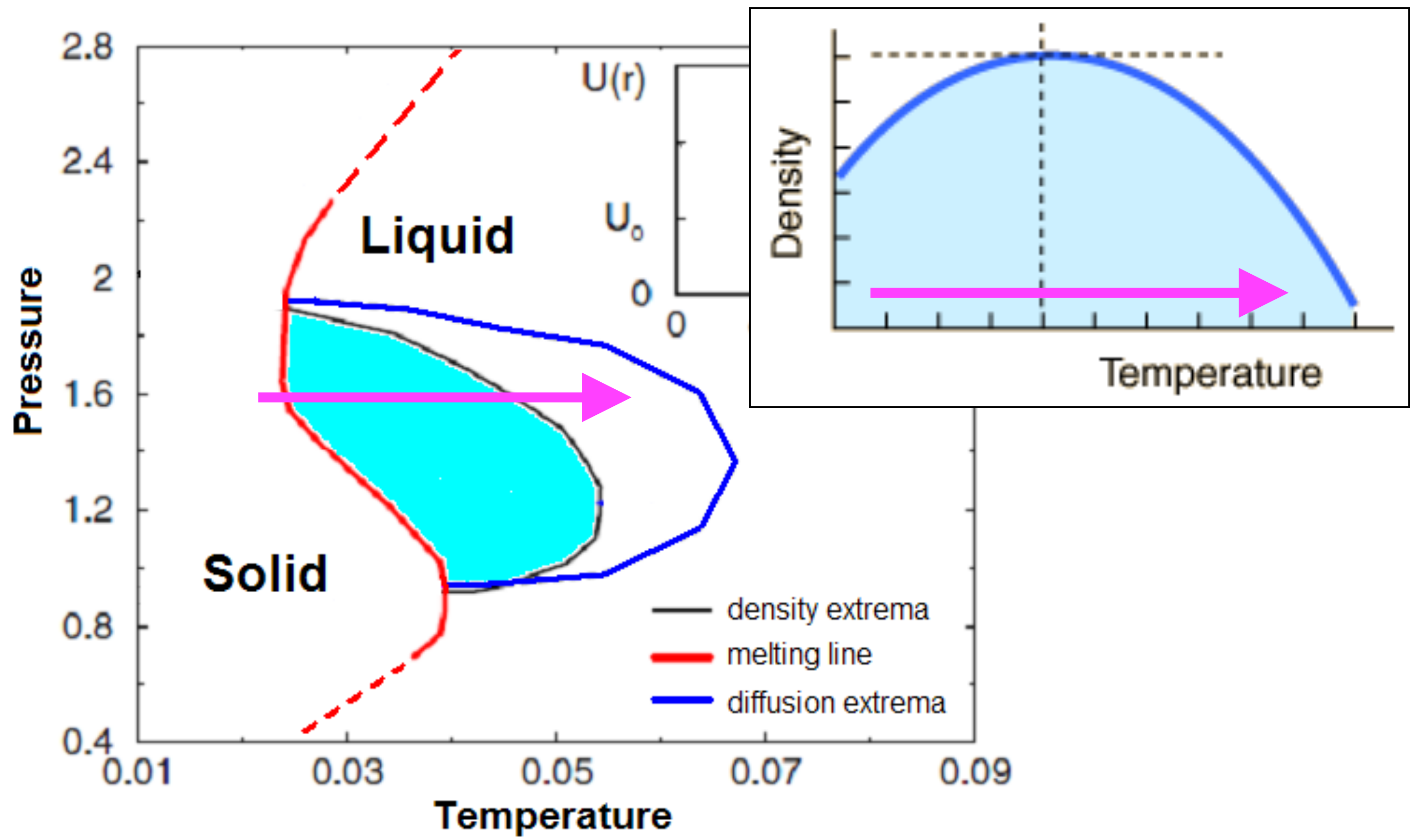
A spherically symmetric pair interaction in 3D



Phase diagram

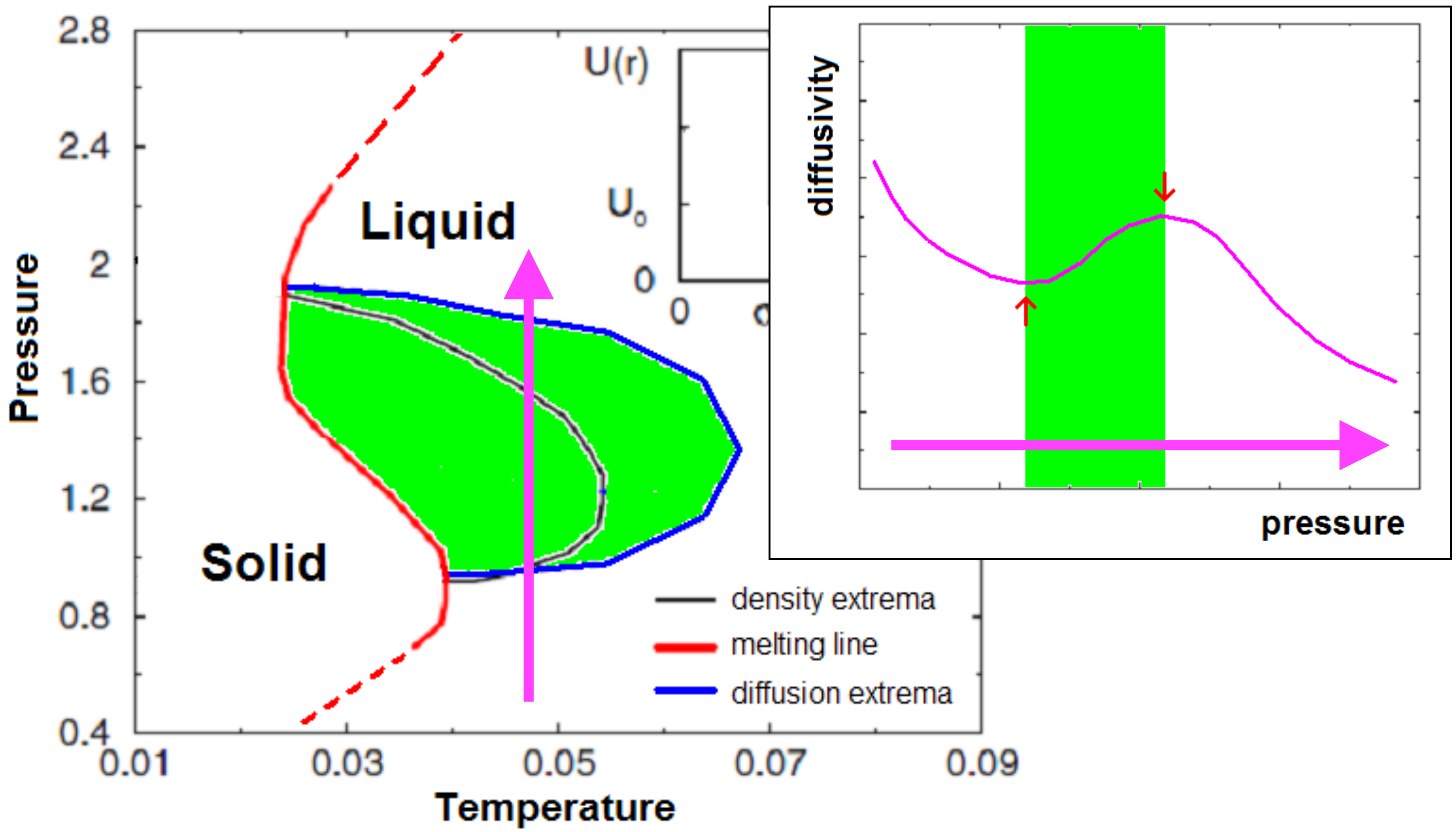
Hard Core + Linear Ramp model

A spherically symmetric pair interaction in 3D



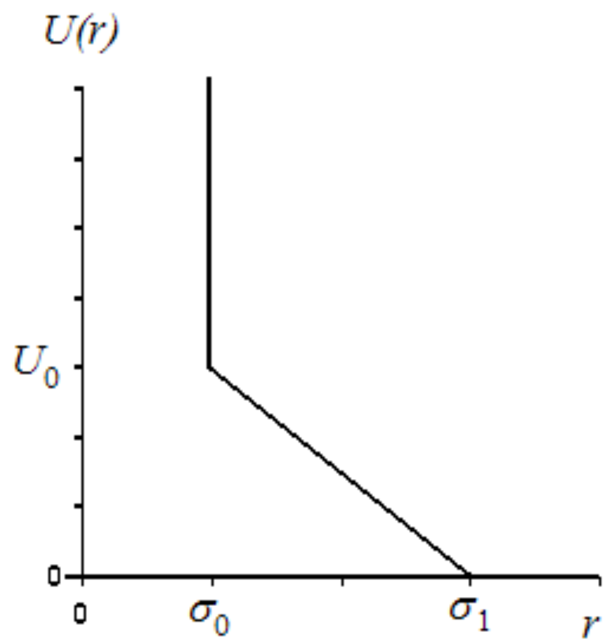
Hard Core + Linear Ramp model

A spherically symmetric pair interaction in 3D



Anomalies explained!

Potential has two length scales that compete

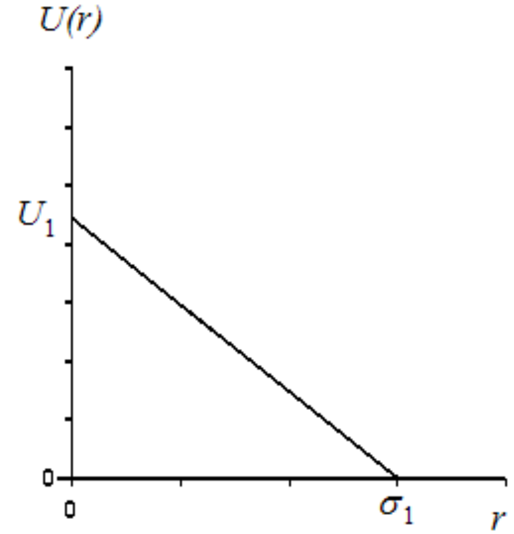


- At low P (and low T), σ_1 is more important
- At high P (and high T), σ_0 is more important

For water:
H-bond vs. no H-bond

Surprise!

Potentials like the ***Linear Ramp Model*** also show anomalies!



…and it only has 1 length scale

? ? ?

Conclusion:
more research needed

Outline

- Water and its anomalies
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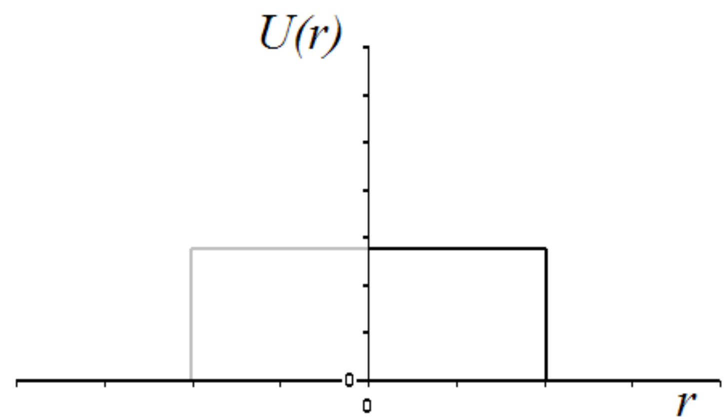
Two similar potentials

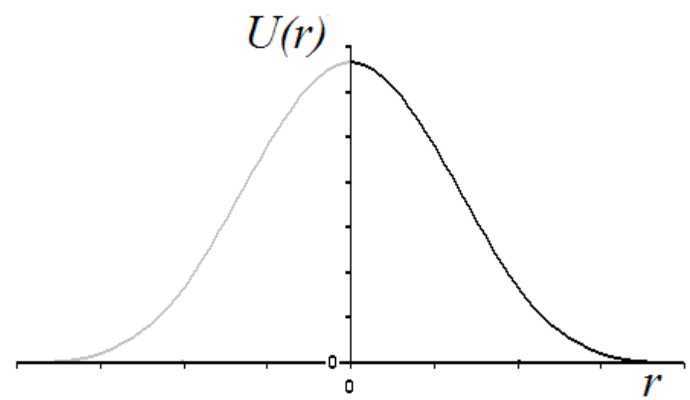
Penetrable Sphere Model

No anomalies



Gaussian Core Model

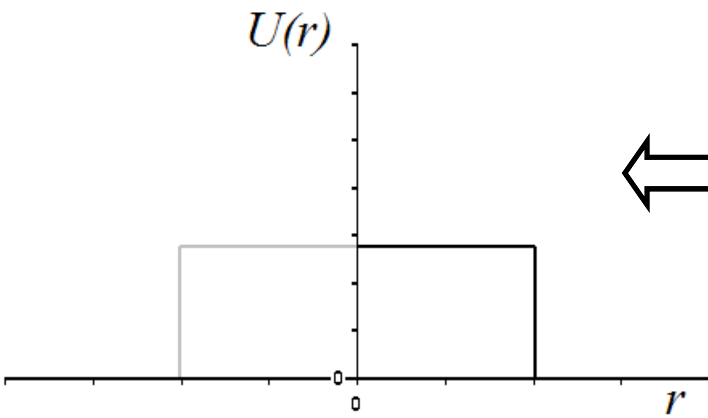
Several water-like anomalies

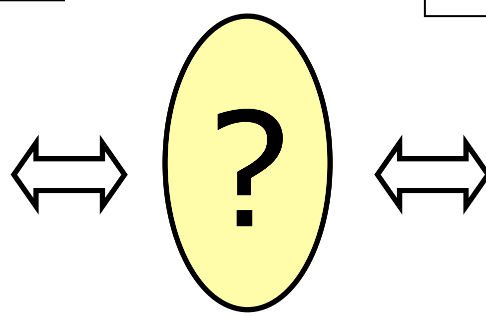


A *new* idea!

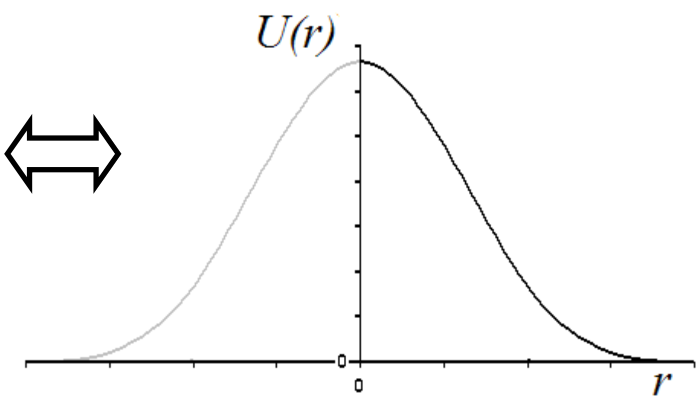
To find cause of anomalies
for potentials like these,
we invent a new potential
"in between" Penetrable Sphere Model
and Gaussian Core Model

Penetrable Sphere Model





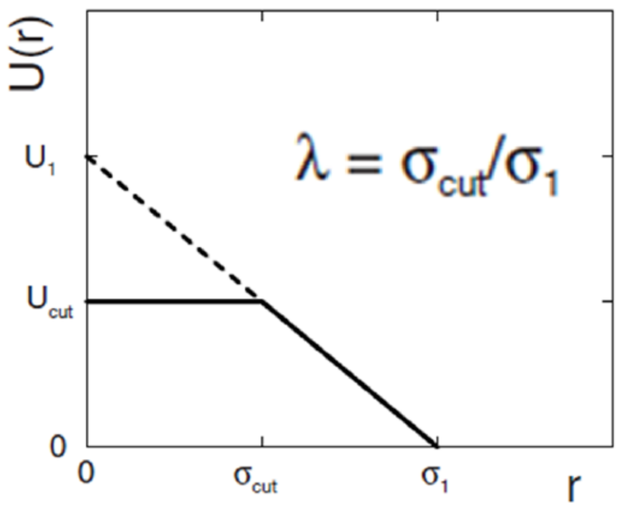
Gaussian Core Model



No anomalies

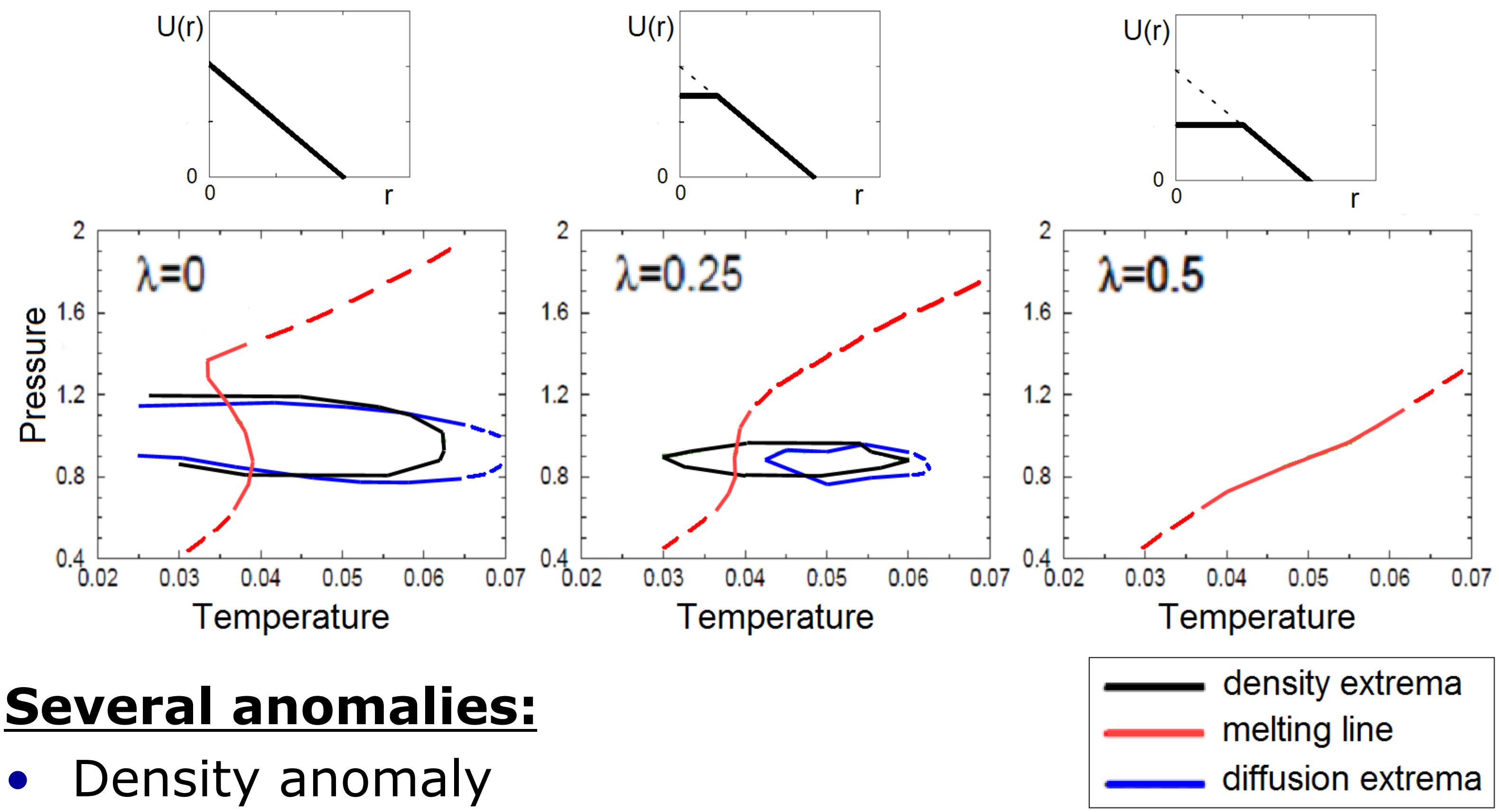
Anomalies

Introducing: the Cut Ramp Potential



- For $\lambda=0$ equivalent to "Linear Ramp Model" (has water-like anomalies)
- Similar to "Gaussian Core Model" (has water-like anomalies)
- For $\lambda \rightarrow 1$ equivalent to "Penetrable Sphere Model" (**no** water-like anomalies)

Phase diagram of Cut Ramp Potential

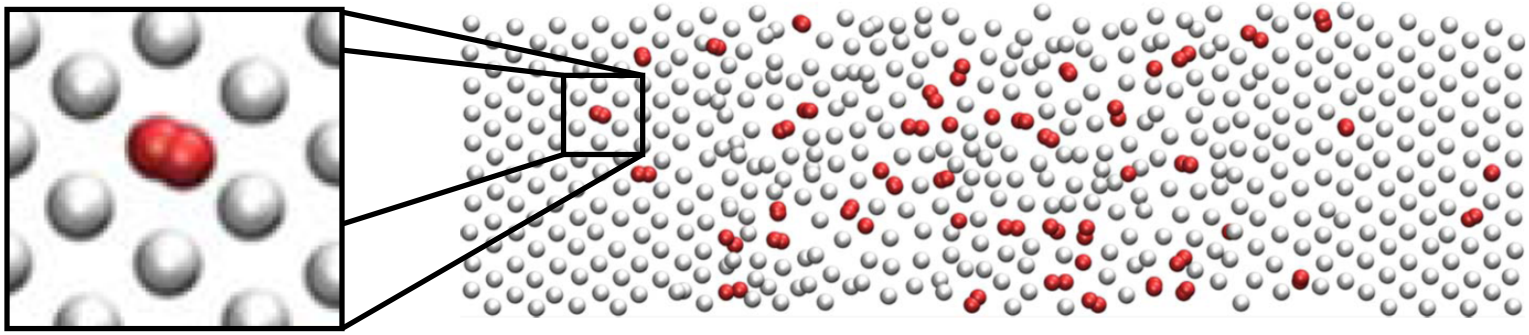


Several anomalies:

- Density anomaly
- Melting line with negative slope
- Diffusion anomaly

All within same pressure range!

Particle overlap ("clustering")



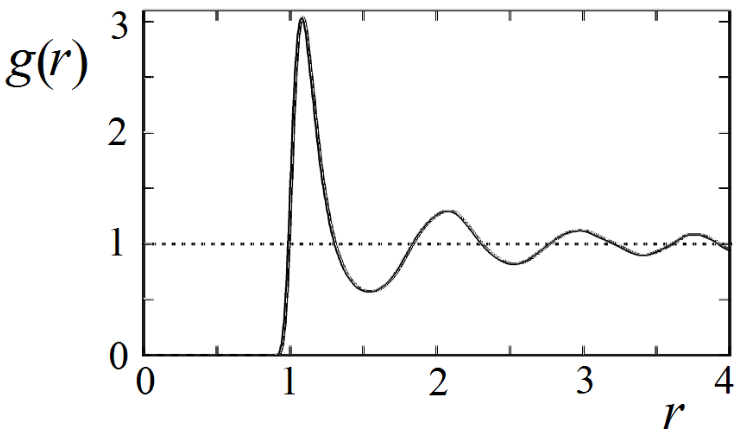
- No hard core means particles can (fully) overlap.
- How do we "count" the number of particles overlapping?

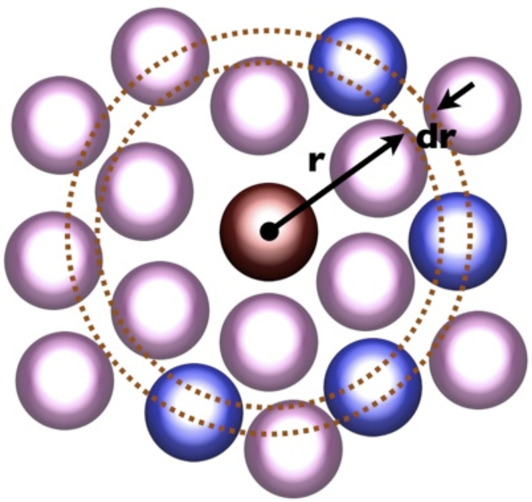
Answer: use the Radial Distribution Function, g(r)

Radial Distribution Function, g(r)

g(r) = histogram of particle distances

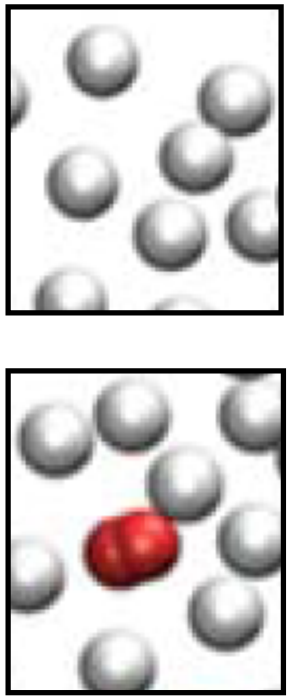
1. Divide space around particle into shells size dr
2. Count the number of particles in each shell
3. Do this for each particle
4. Normalize such that g(r)=1 for r= ∞

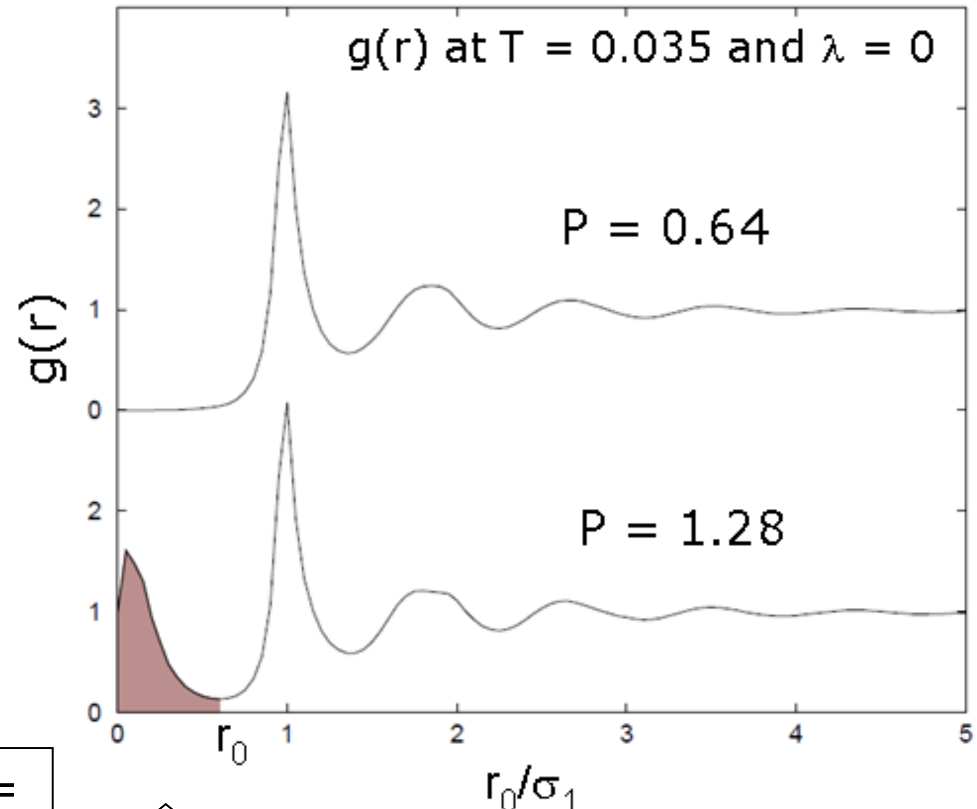




Can be measured via e.g. X-ray diffraction

Definition of "amount of overlap"



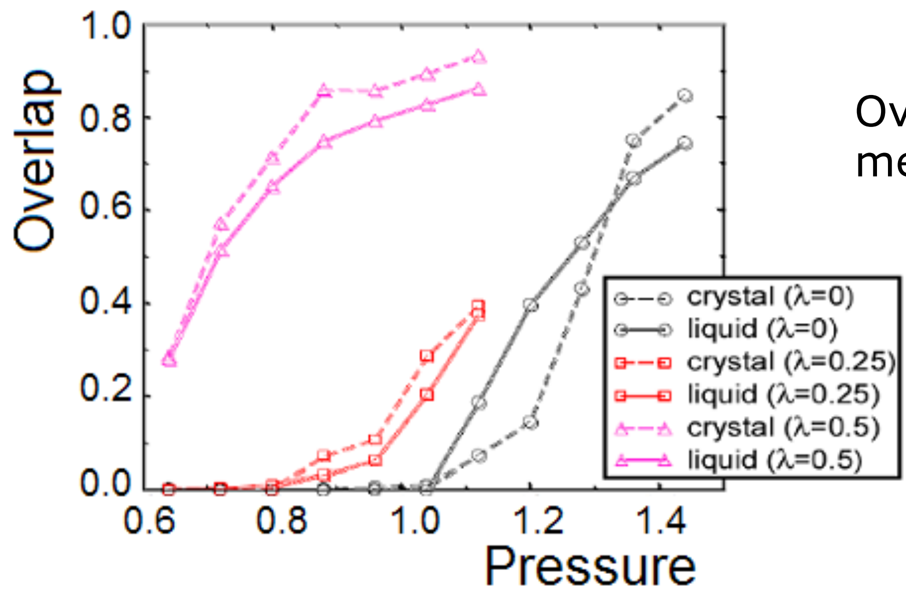


Amount of overlap = average number of neighbors N_C within distance $r < r_0$

Overlap anomaly

Also anomaly in overlap:

- (overlap in crystal) > (overlap in liquid)
- ***Except*** within the anomalous region!



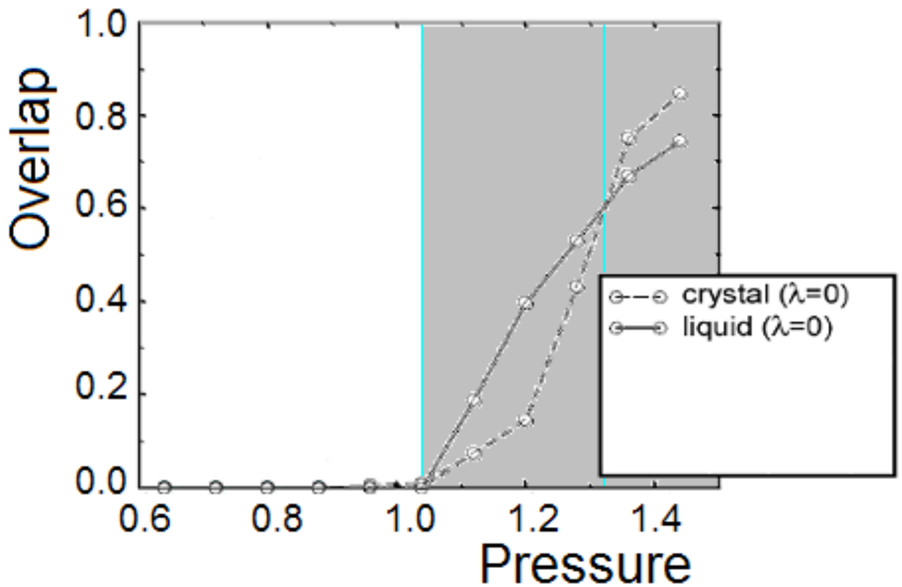
Overlap on melting line

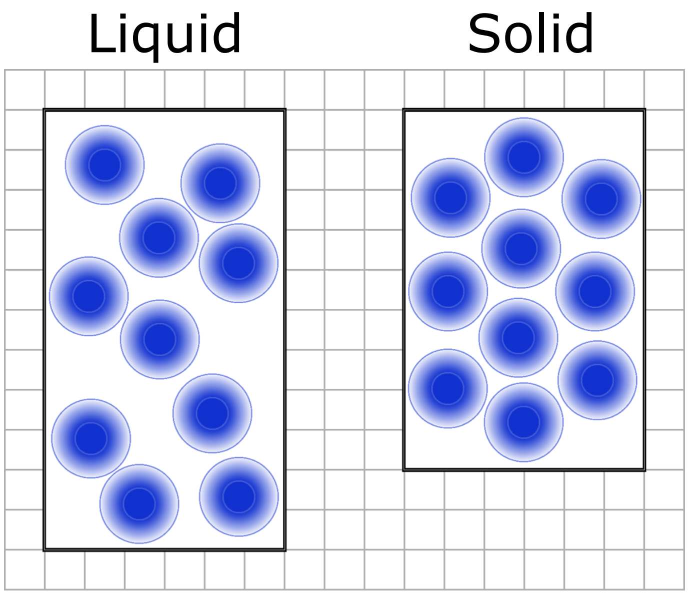
Hypothesis:
All anomalies are related to the "overlap anomaly".

Imagine a little experiment…

- Let’s take a look at liquid & crystal
- Starting at low pressure
- Slowly increasing pressure

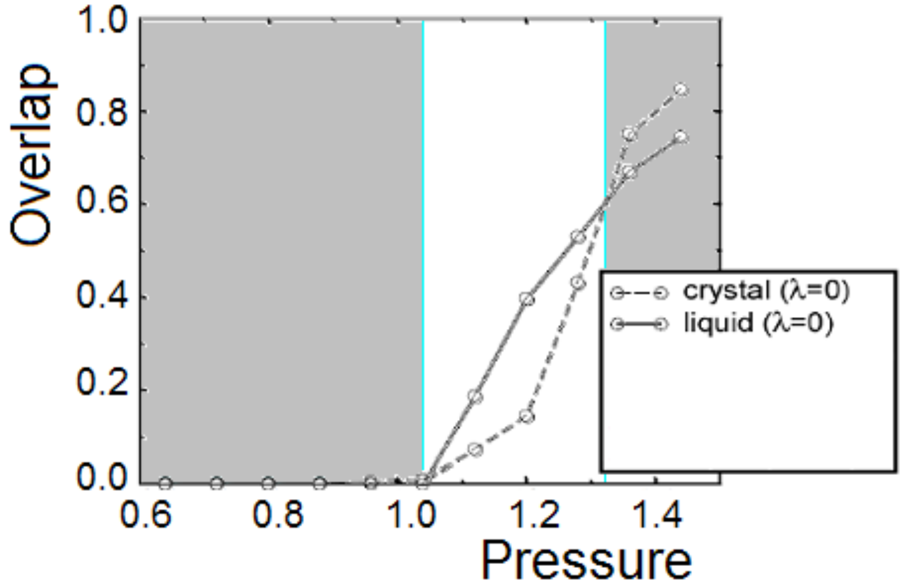
Low pressure regime

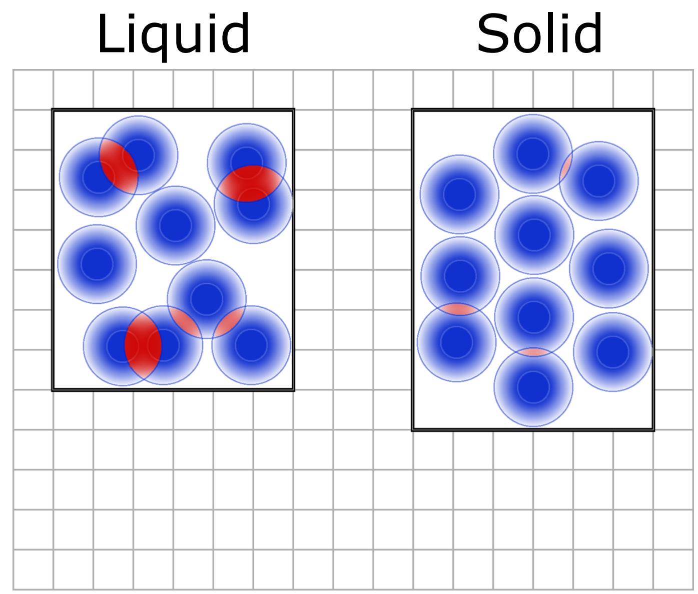




- No overlap
- System behaves like normal liquid / crystal

Pressure within anomalous region (1)



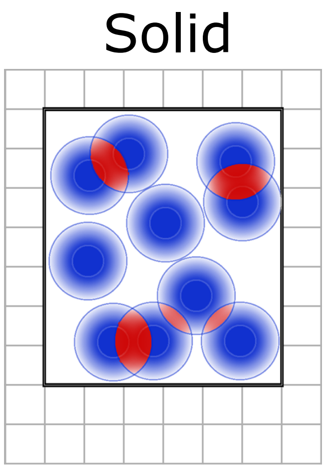


Partial overlap in liquid, but almost no overlap in solid!

Why?

Pressure within anomalous region (2)

Partial overlap in liquid, but almost no clustering in solid



Because:

Partial overlap would break crystal structure

If a particle would overlap with another…

(1) A hole appears, and the particle hops back

⇨ Little overlap in crystal

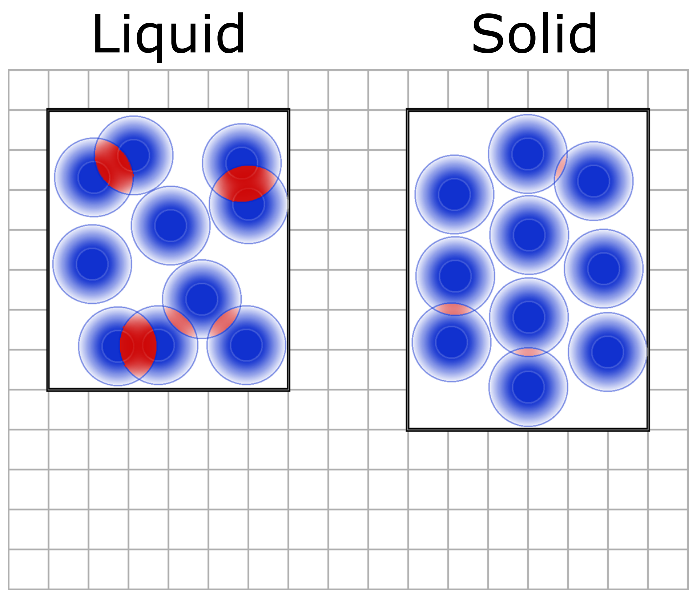
(2) A hole appears, and the crystal collapses into a liquid

⇨ Melting temperature is lowered!
(i.e. melting line has negative slope)

Pressure within anomalous region (3)

Partial overlap also leads to:

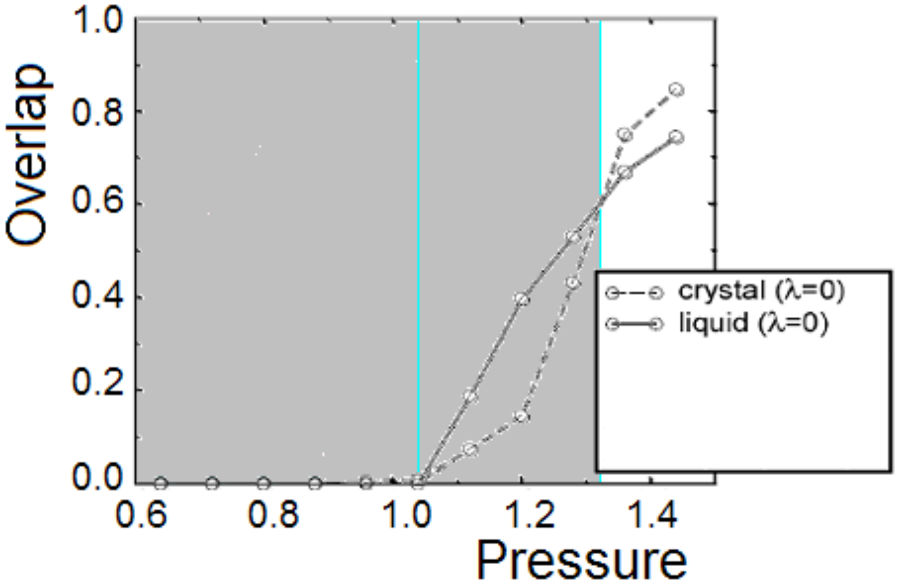
- Higher diffusion (i.e. diffusion anomaly) because particles can temporary “climb” up potential ramp
- More space available, so smaller volume needed, thus higher density than usual (i.e. density anomaly)

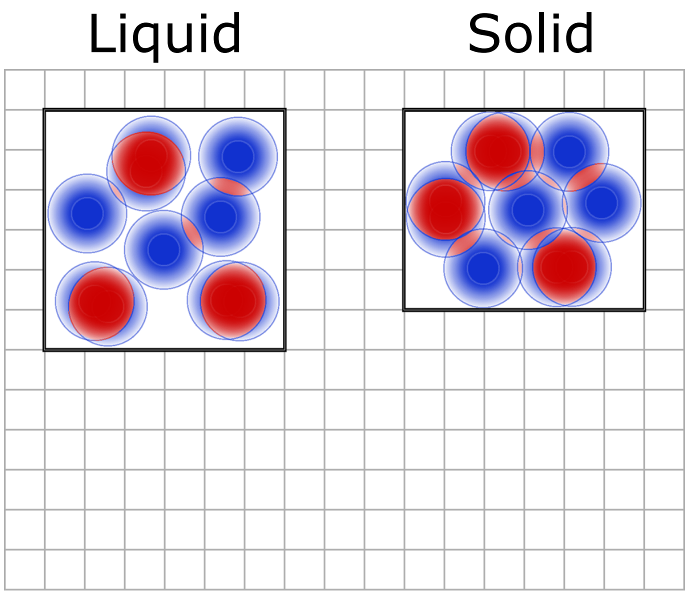


Conclusion:

Partial overlap causes anomalies!

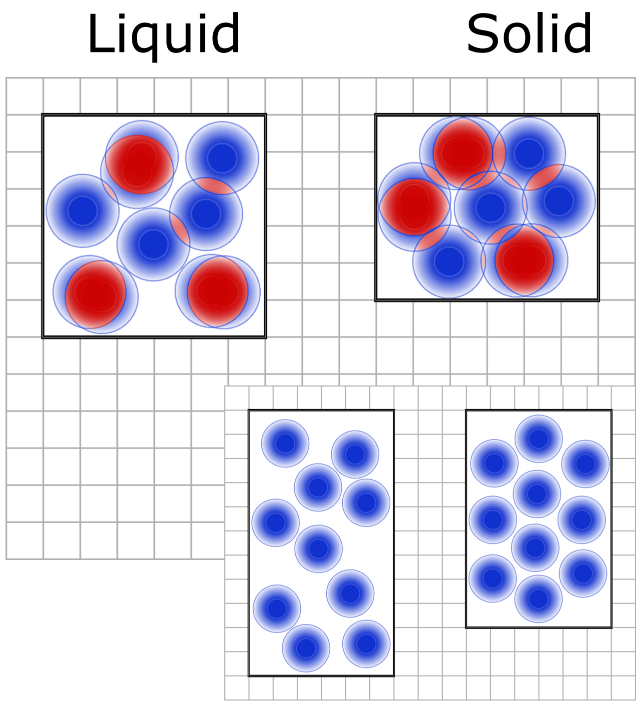
High pressure regime





High pressure regime

- At high P, particles can reach top of potential
- Full overlap
- Same situation as at low P, but with **clusters** replacing (some of) the particles!
- No anomalies at low P, so none at high P



Conclusion:
Full overlap kills anomalies!

(similar to Penetrable Sphere Model)

Outline

- Water and its anomalies
- What is the cause of these anomalies?
  (conclusion: more research needed)
- The Cut Ramp Potential
- **Conclusions**

Conclusions – cut ramp potential

- Cut ramp potential displays water-like anomalies, depending on cut height λ
- Cut height λ and pressure determine amount of overlap ("clustering")
- Partial overlap causes anomalies
  - Density anomaly
  - Negative slope melting line
  - Diffusion anomaly
- Full overlap restores liquid to "normal" structure, preventing anomalies

Conclusions – anomalies

TAKE HOME MESSAGE:

- General cause for anomalies is: "existence of two competing length scales"
- It's not always clear what those scales are
  - For Linear Ramp Model those scales are the *ramp size* σ_1 and *zero* (i.e. full overlap)
- Sometimes there is no competition
  - For Penetrable Sphere Model full overlap too easy

END OF TALK

Thank you!

Application to Macromolecules