Liquid-liquid phase transitions and water-like anomalies

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Departmental seminar

with

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Cui Zhang, Giulia Galli, Giancarlo Franzese, Gene Stanley

Content

- Introduction to liquid-liquid phase transition (LLPT) and anomalies
- Spherical water model
- ST2 model
- Locating the liquid-liquid critical point (LLCP)
- Conclusions

Content

- **Introduction to liquid-liquid phase transition (LLPT) and anomalies**
- Spherical water model
- ST2 model
- Locating the liquid-liquid critical point (LLCP)
- Conclusions

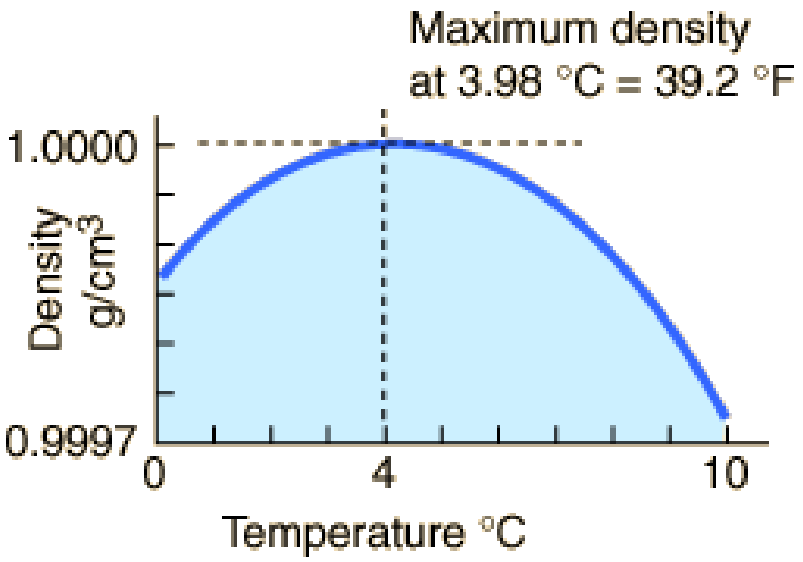
Water!

- Water is most common liquid on Earth
- Many experiments done on water
- Water has many unusual properties (69 anomalies)

www.lsbu.ac.uk/water/anmlies.html

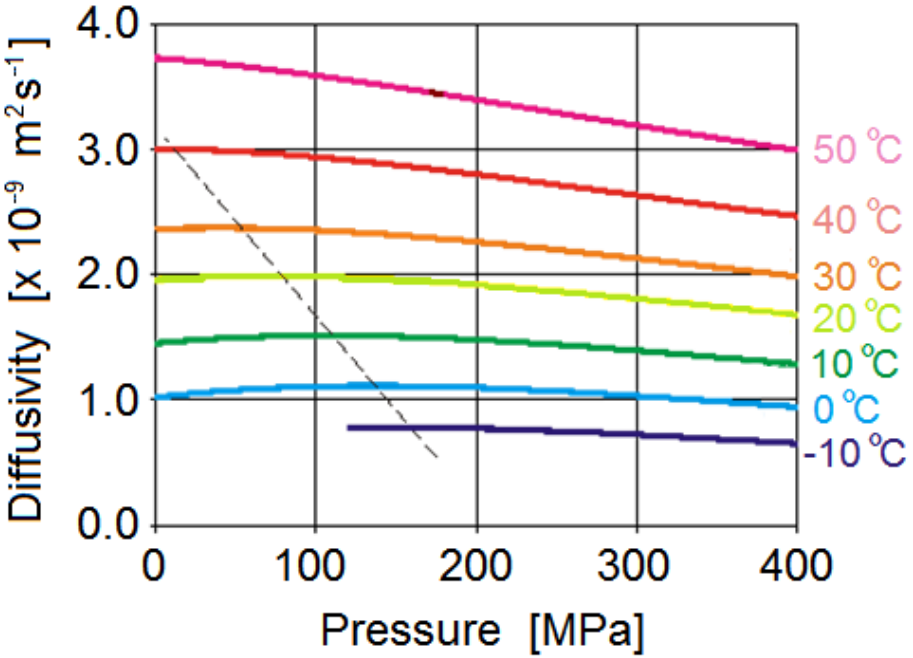
Water anomalies

Density anomaly



Density **increases** as T increases

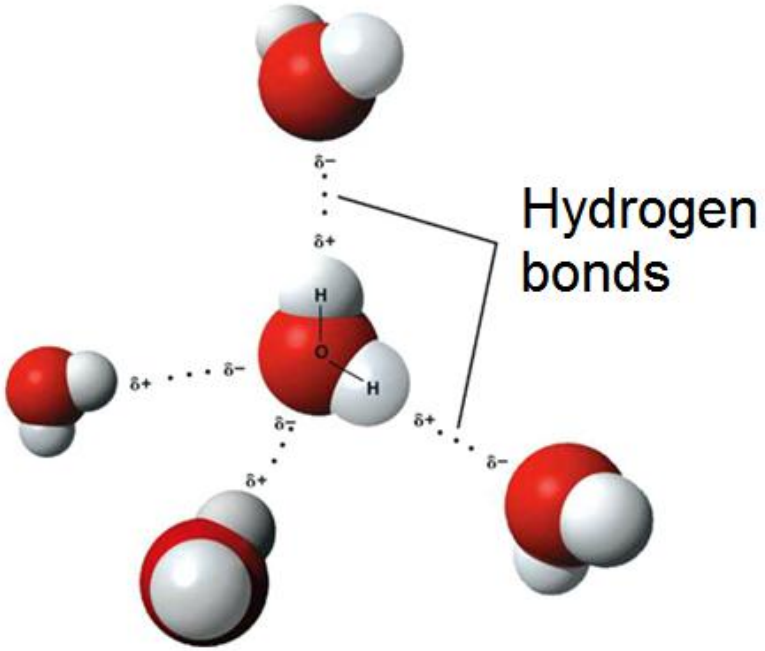
Diffusion anomaly



Self-diffusion **increases** as P increases

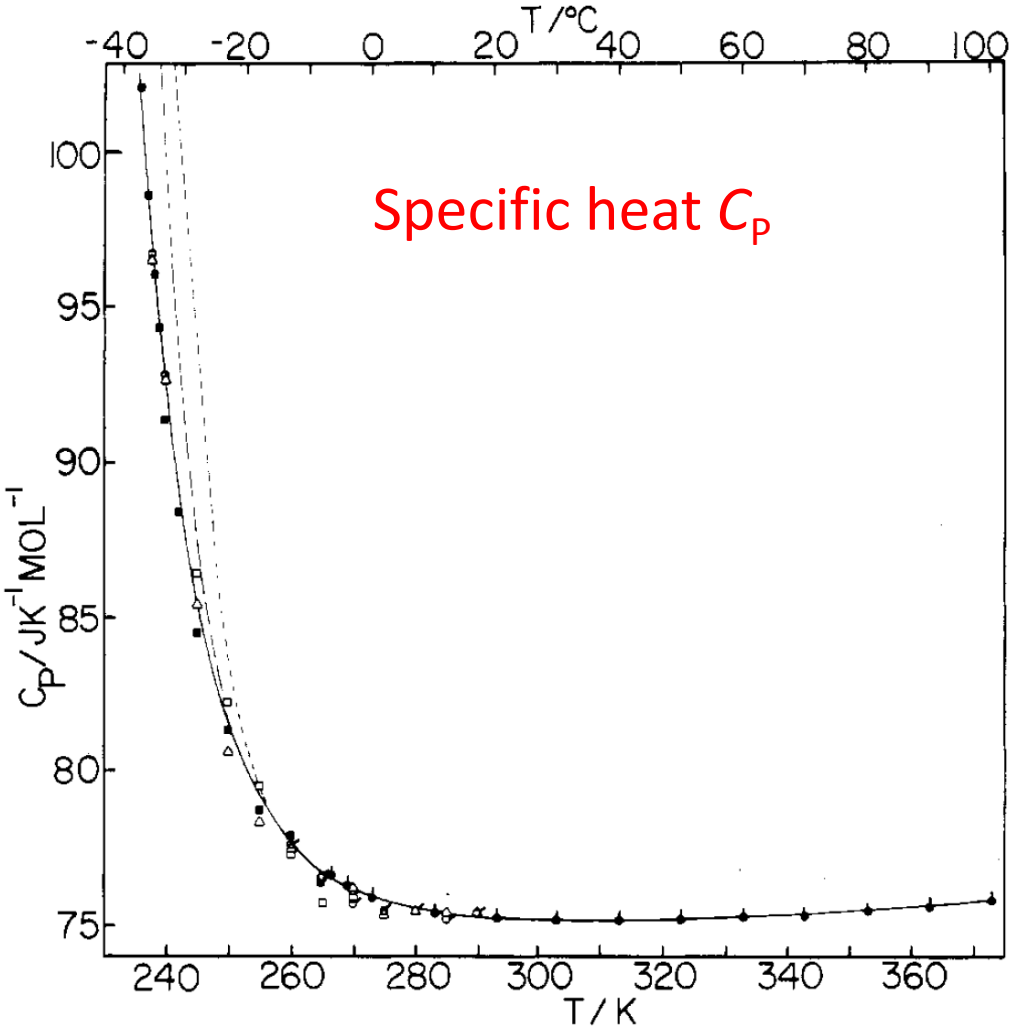
Water anomalies explained?

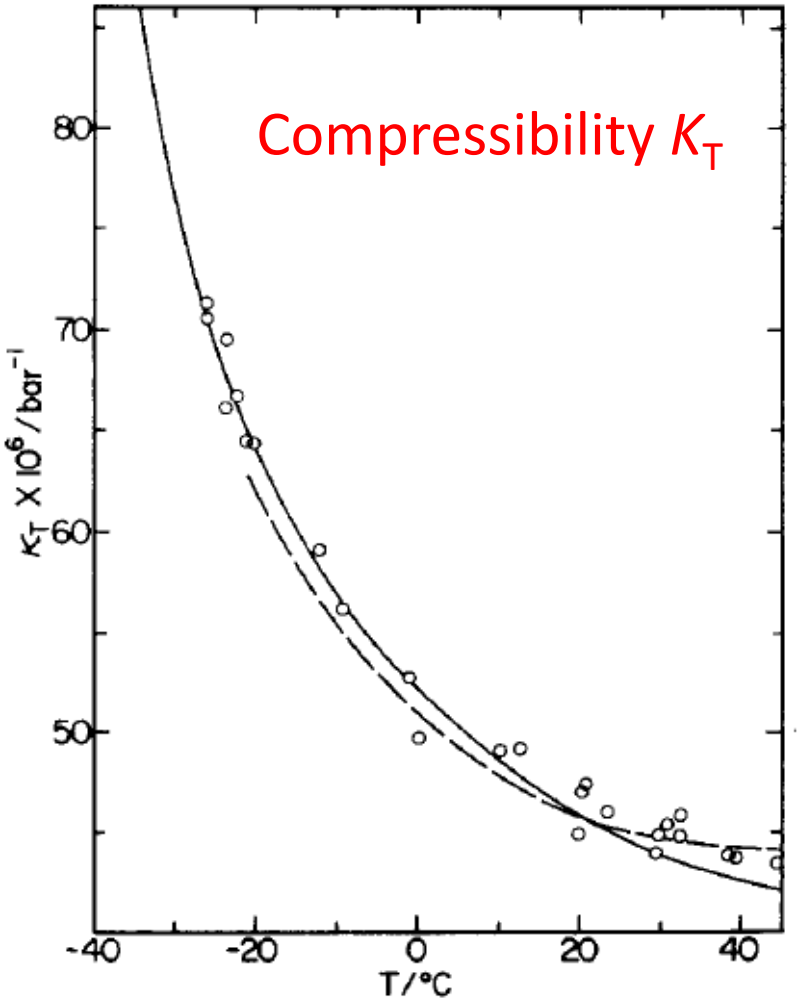
- Are anomalies caused solely by H-bonds?



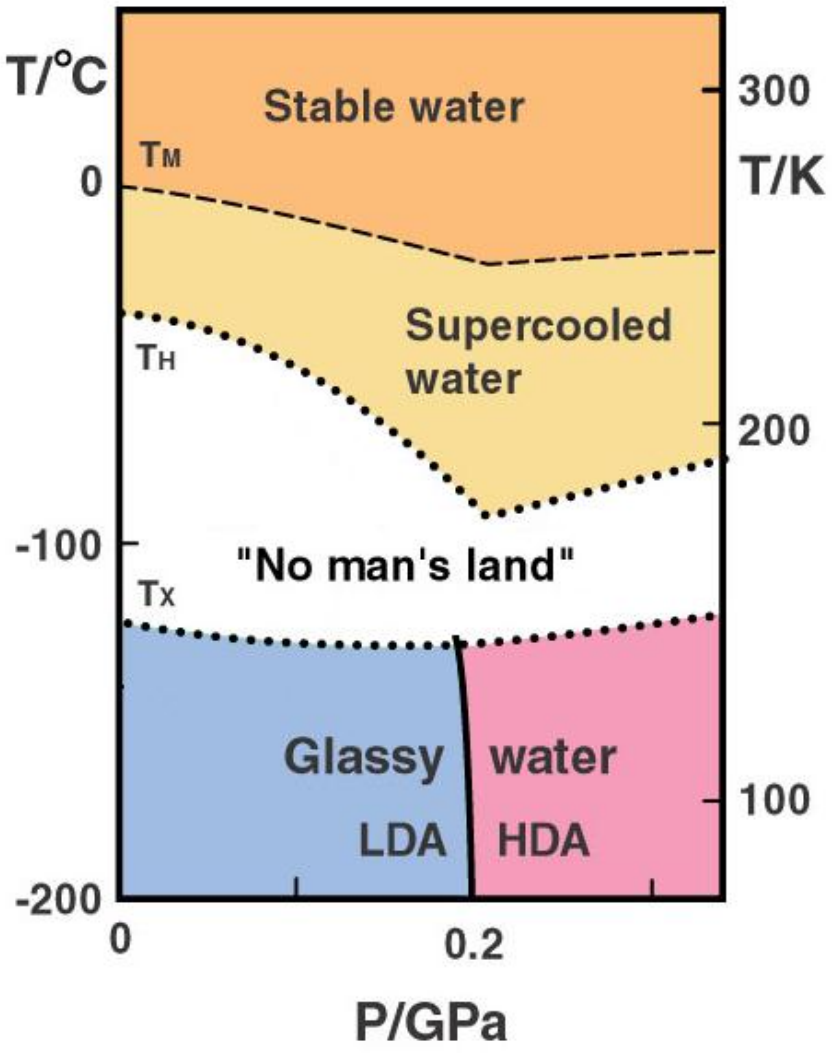
- **No!**
  Other liquids without H-bonds also show same anomalies!

Supercooled water: C_P & K_T diverge





Amorphous ice: HDA & LDA

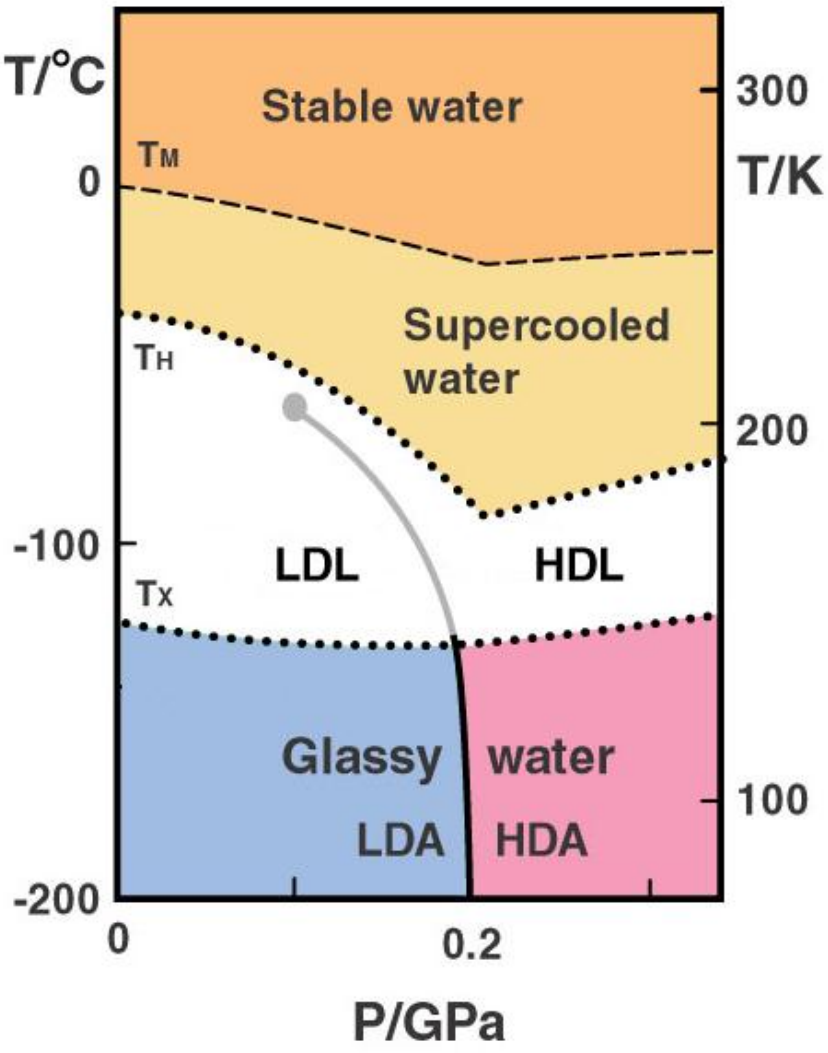


Experiments by Katrin Winkel, *et al.*

LLPT hypothesis for water

(Poole/Sciortino/Essmann/Stanley, 1992)

- Two liquids below nucleation temperature:
  - Low density liquid (LDL)
  - High density liquid (HDL)
- Separated by liquid-liquid phase transition
- Ending in liquid-liquid critical point



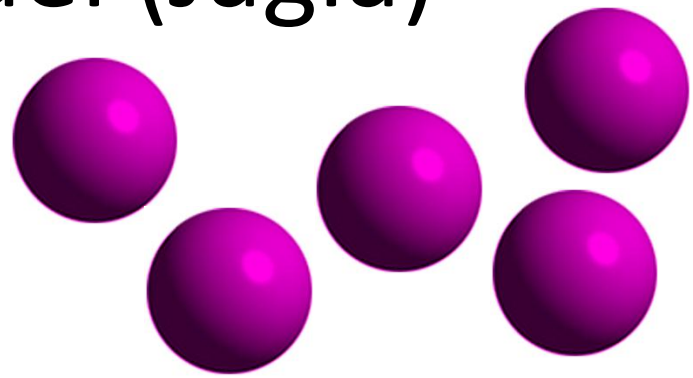
Main question

- **Main question:** where do anomalies come from and how are they related to LLPT / LLCP?

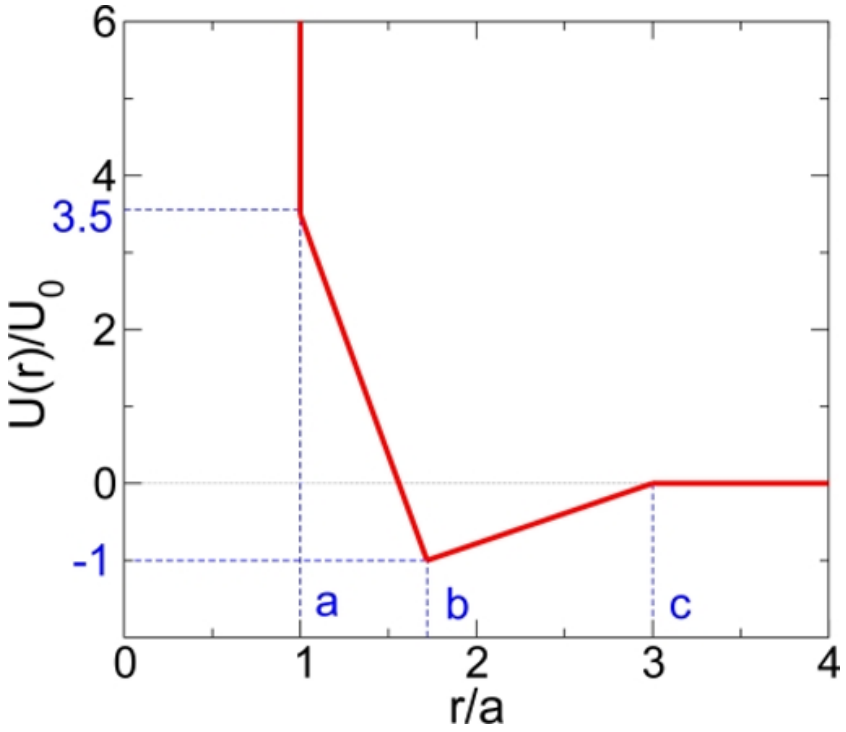
- Start with a simple model!

- Introduction to LLPT & anomalies
- **Spherical water model**
- ST2 model
- Locating the critical point (LLCP)
- Conclusions

Spherical water model (Jagla)

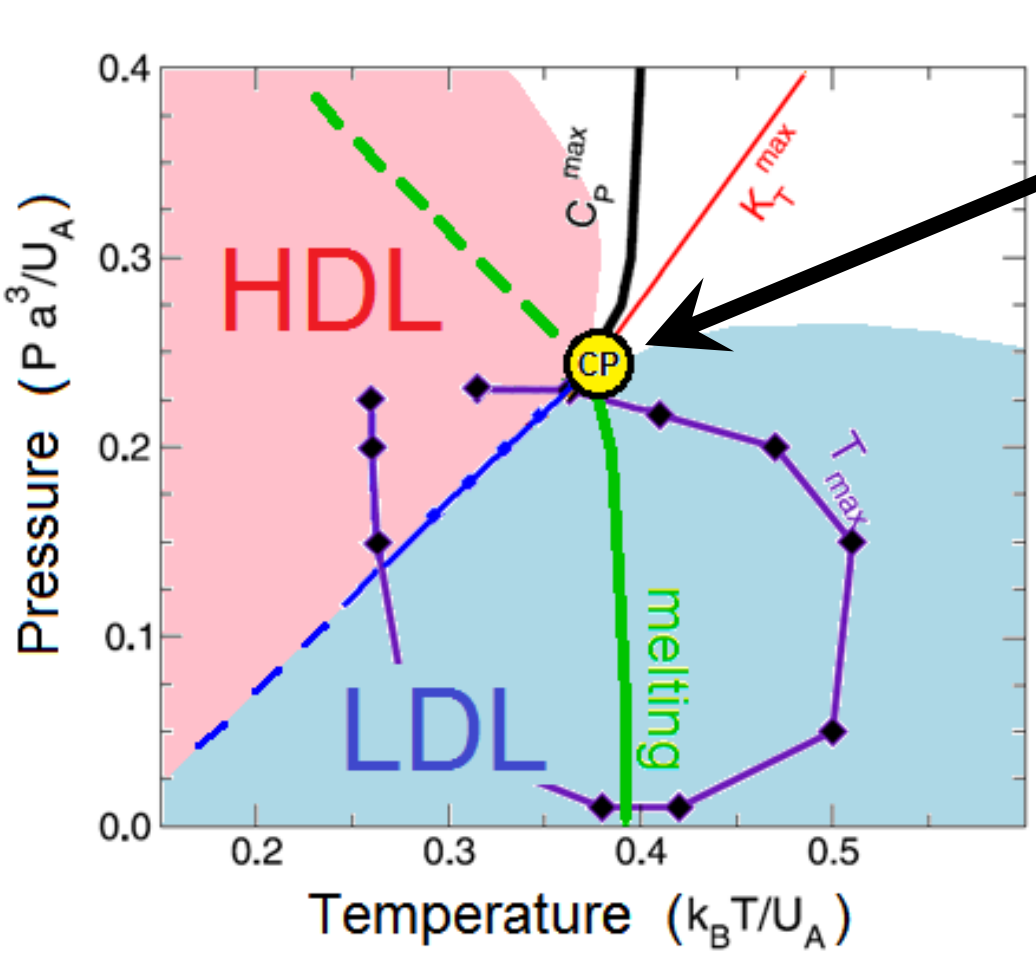


- Monatomic particles
- Pairwise interaction
- Hard core
  + soft core
  + potential well



E. A. Jagla, J. Chem. Phys. **111**, 8980 (1999)

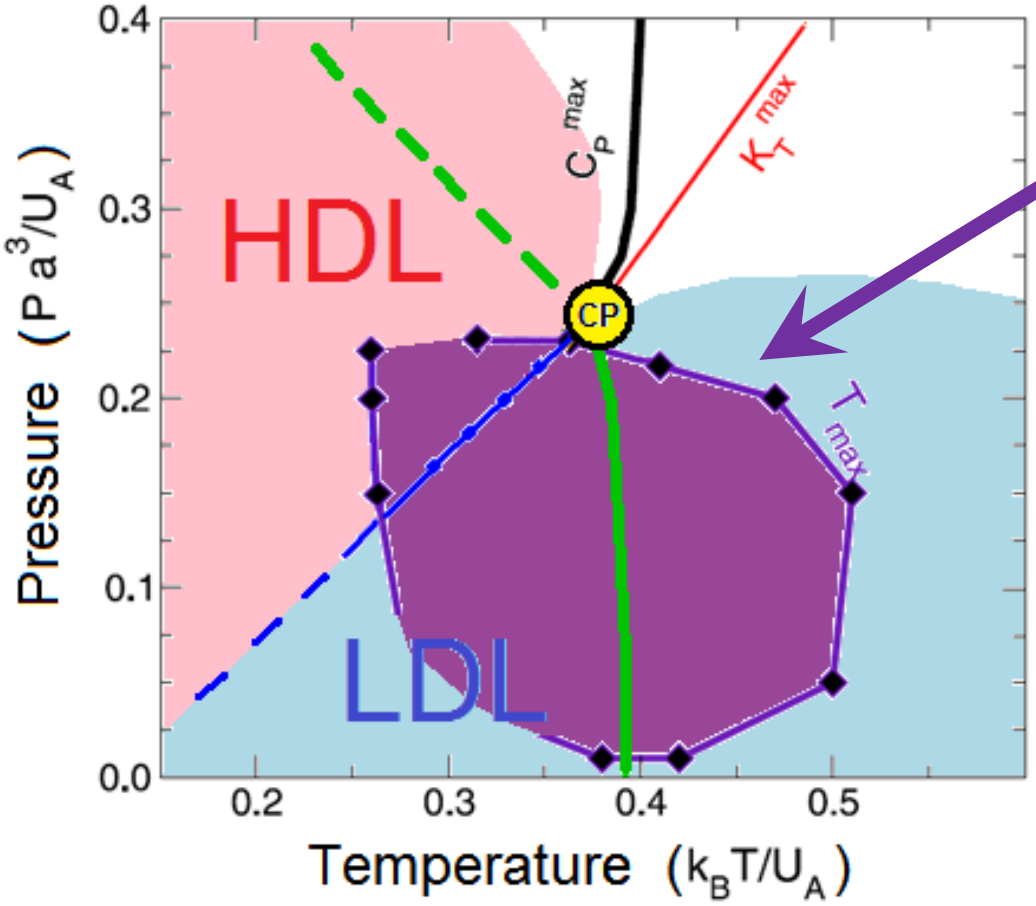
Phase diagram: LLPT & anomalies



Liquid-liquid critical point

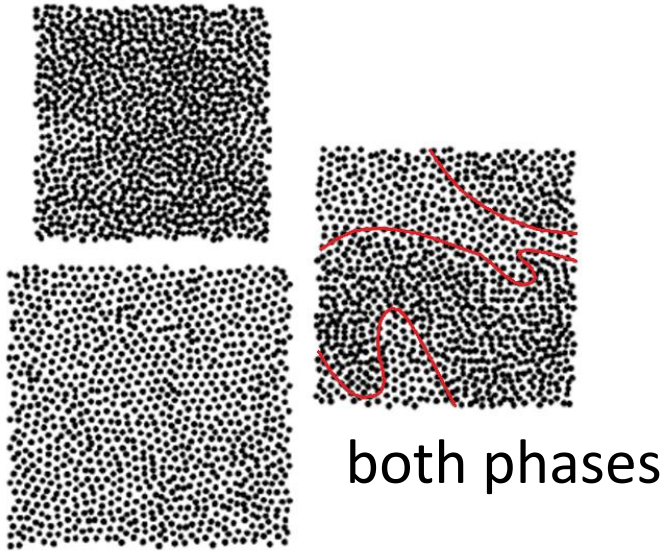
L. Xu, S. Buldyrev, C. A. Angell, H. E. Stanley, Phys. Rev. E **74**, 031108 (2006)

Phase diagram: LLPT & anomalies



Density anomaly

HDL phase



both phases

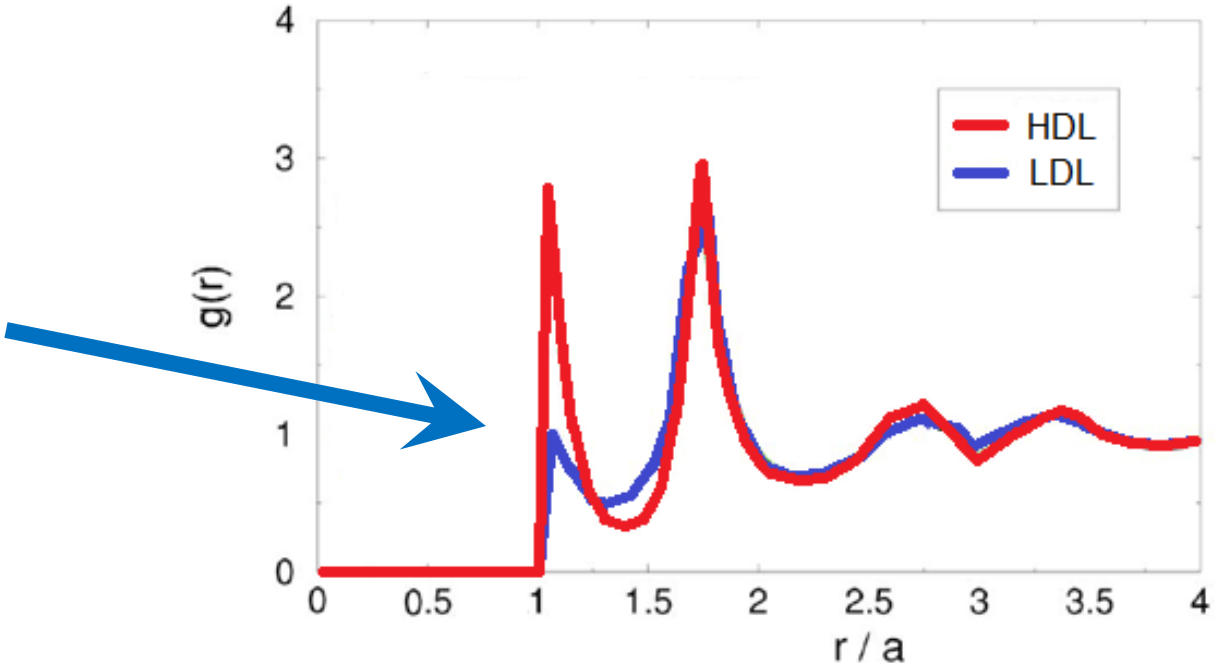
LDL phase

L. Xu, S. Buldyrev, C. A. Angell, H. E. Stanley, Phys. Rev. E **74**, 031108 (2006)

Radial distribution function

- $g(r)$ = probability for atom to find another atom a distance r away

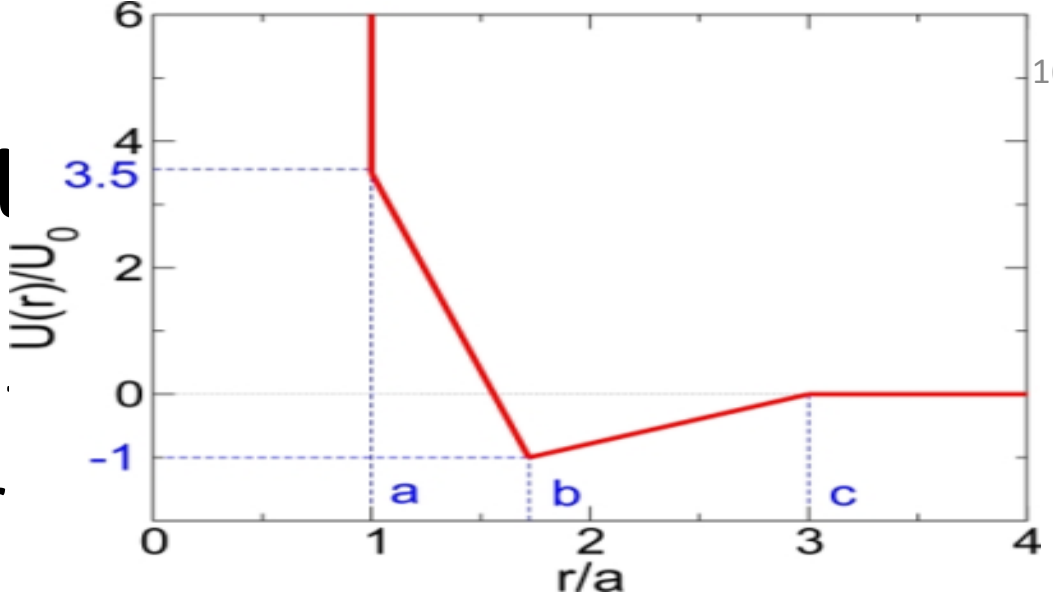
- LDL has tiny first peak!



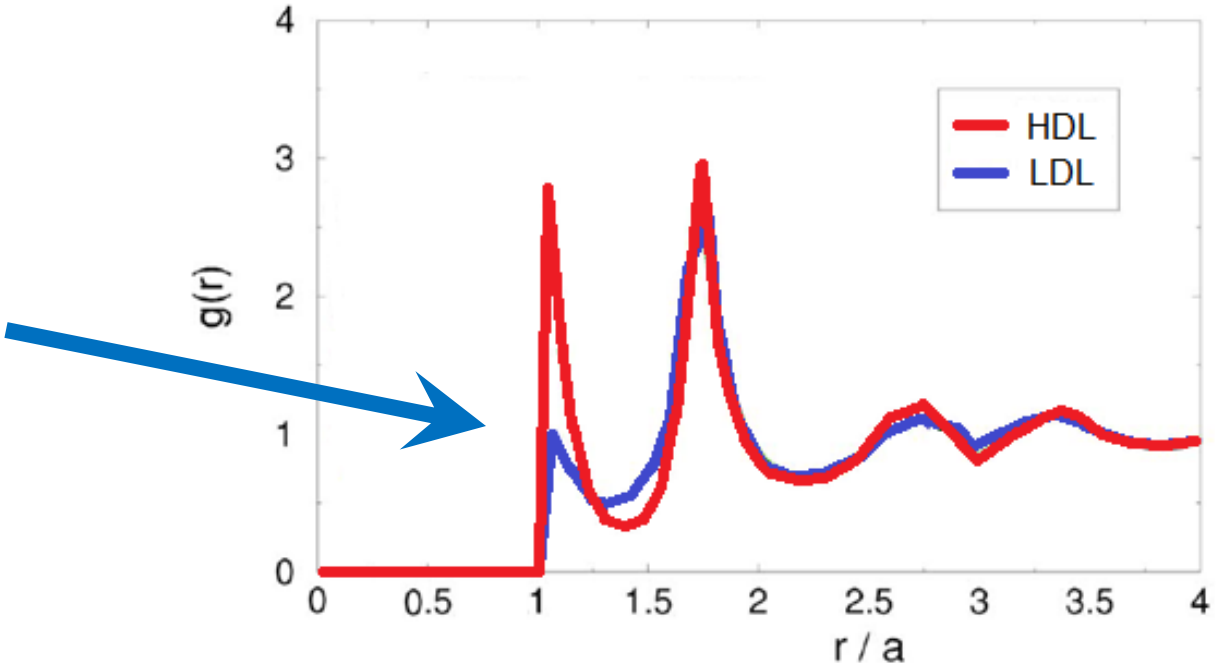
L. Xu, S. Buldyrev, C. A. Angell, H. E. Stanley, Phys. Rev. E **74**, 031108 (2006)

Radial dist

- $g(r)$ = probability atom a distance r



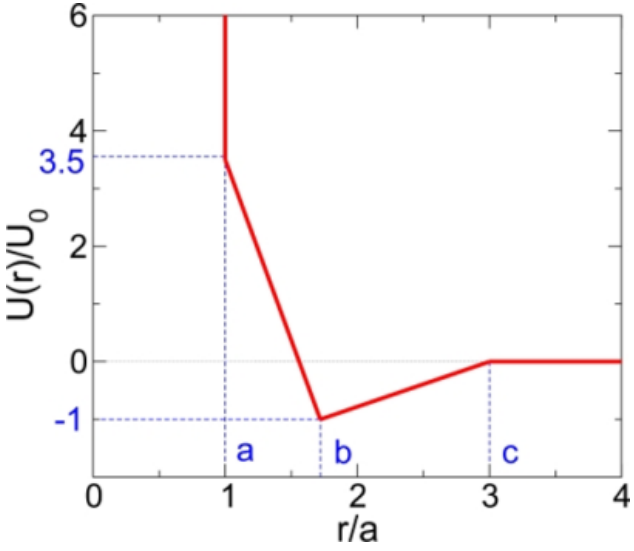
- LDL has tiny first peak!

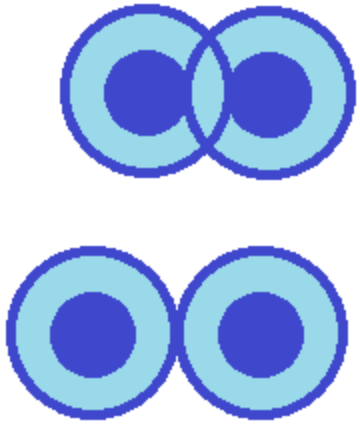


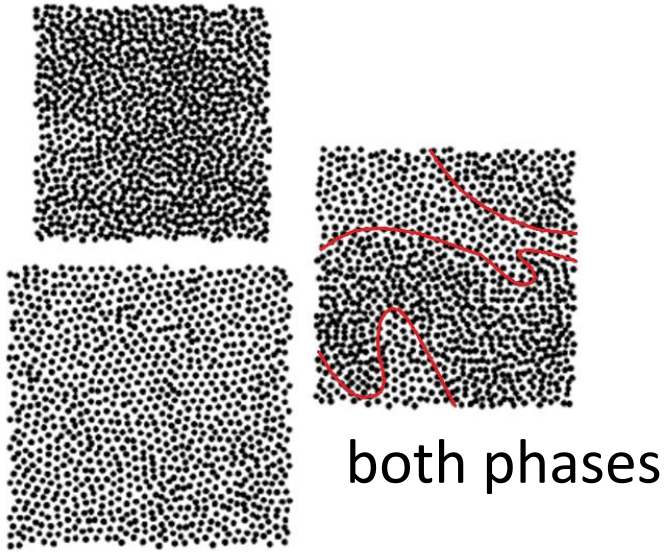
L. Xu, S. Buldyrev, C. A. Angell, H. E. Stanley, Phys. Rev. E **74**, 031108 (2006)

Two competing length scales

- **Two liquids (LDL and HDL)**

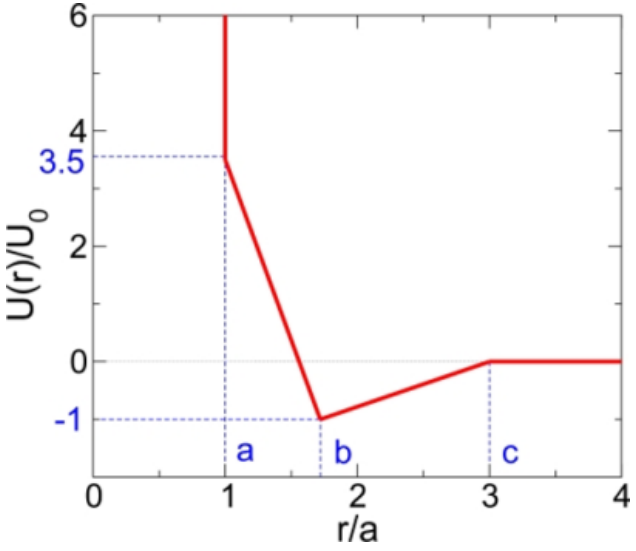


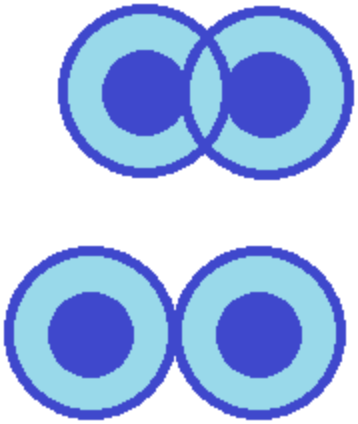




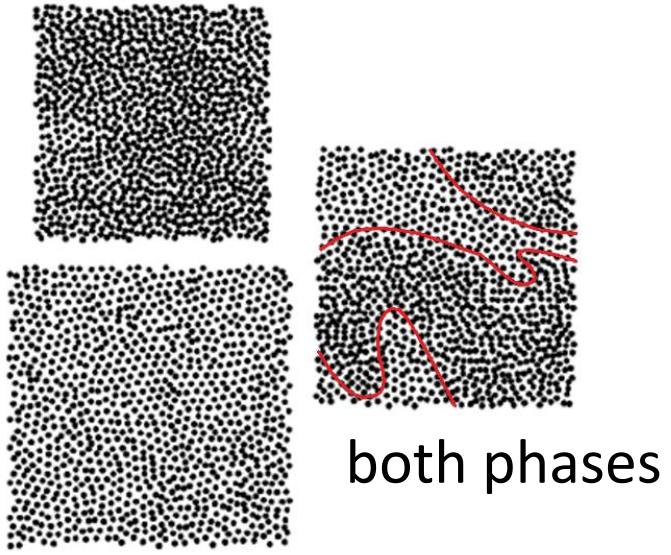
Two competing length scales

- Two liquids (LDL and HDL)
- **Higher T leads to overlap → density anomaly**





HDL phase

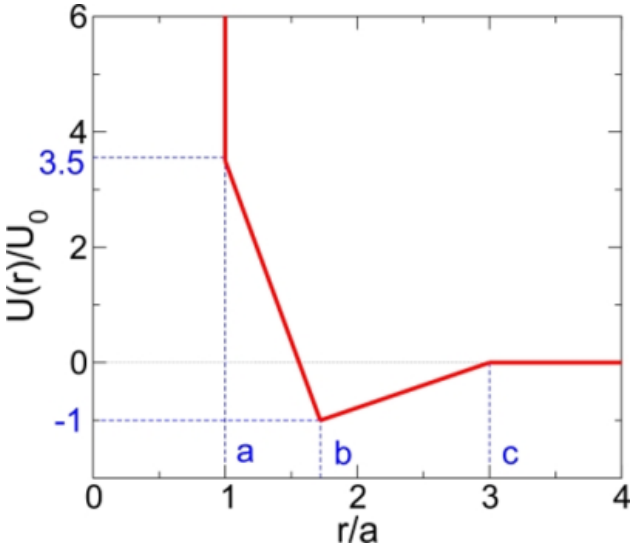


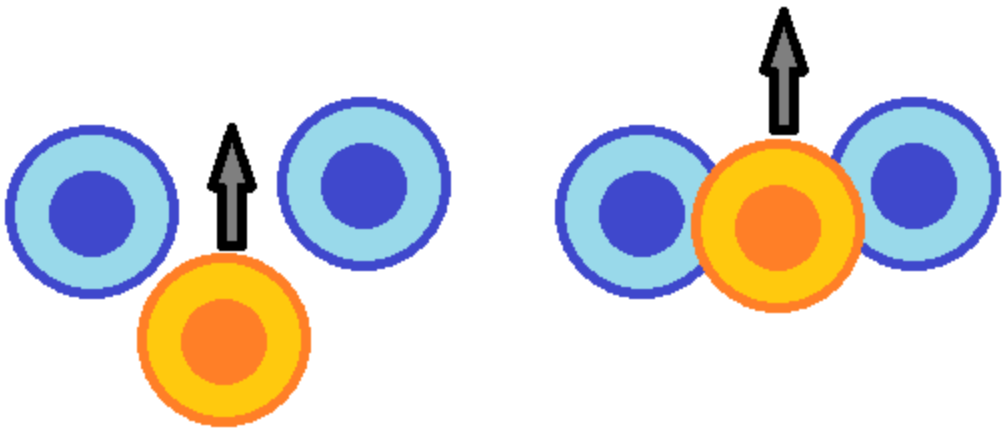
both phases

LDL phase

Two competing length scales

- Two liquids (LDL and HDL)
- Higher T leads to overlap → density anomaly
- **Higher P leads to overlap → diffusion anomaly**





Conclusion spherical water model

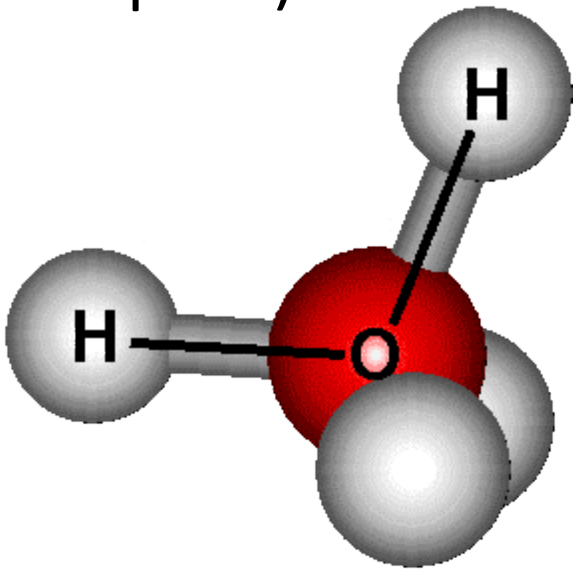
- Origin of anomalies and LLPT
  are clear in this model:
  two competing length scales

- Now consider more realistic models!

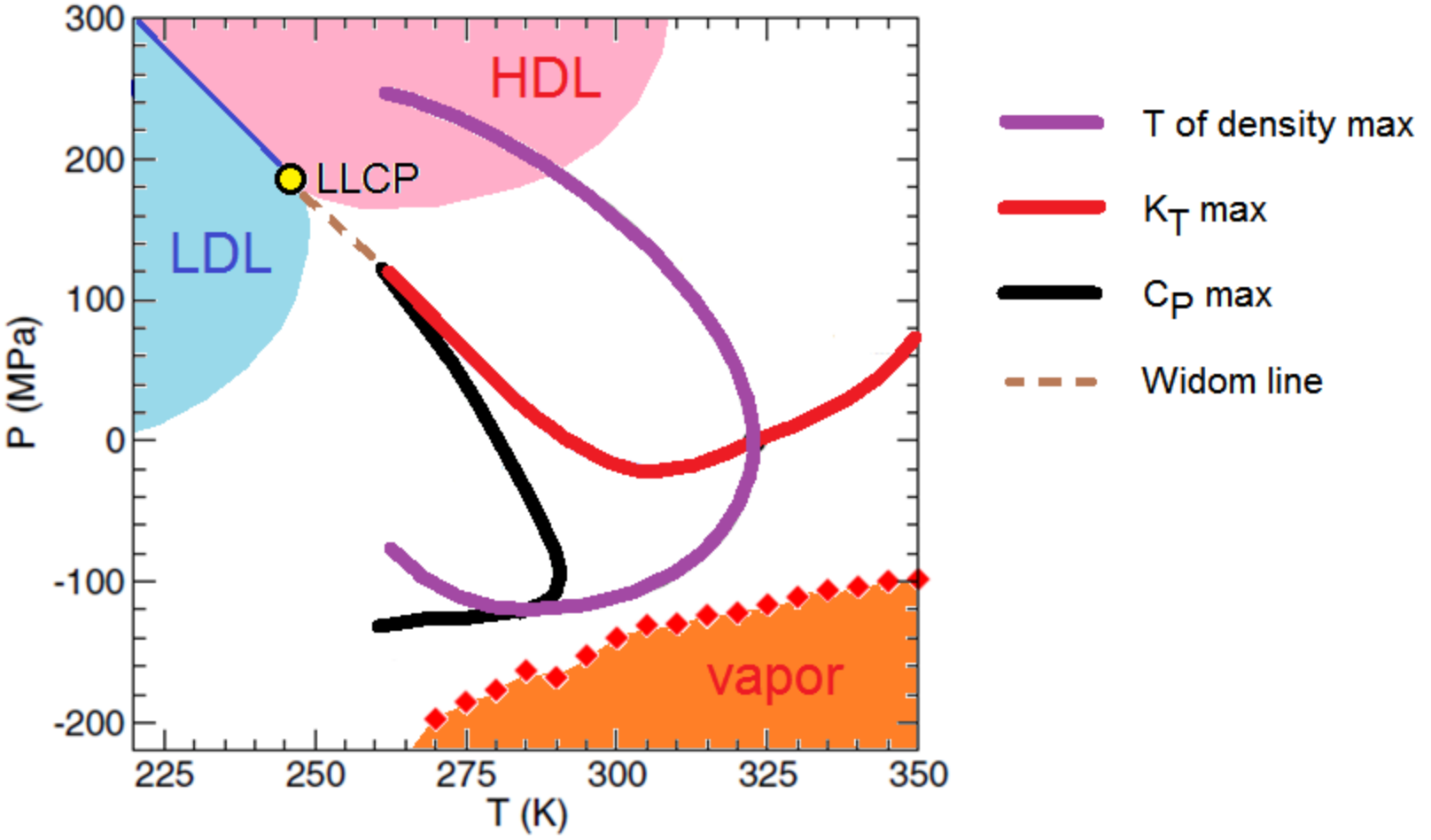
- Introduction to LLPT & anomalies
- Spherical water model
- **ST2 model**
- Locating the critical point (LLCP)
- Conclusions

ST2 water model

- Each water molecule has 5 “atoms”
- 4 charges (2 hydrogen atoms & 2 lone pairs) with electrostatic interaction
- 1 oxygen atom with Lennard-Jones interaction

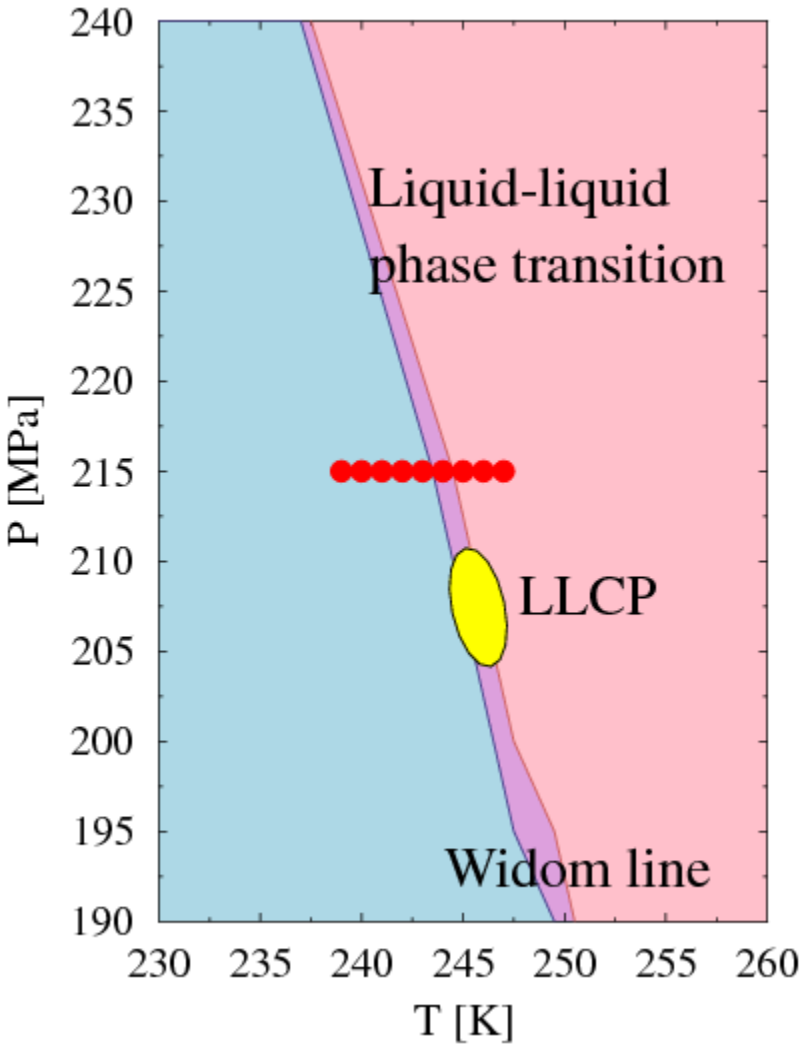


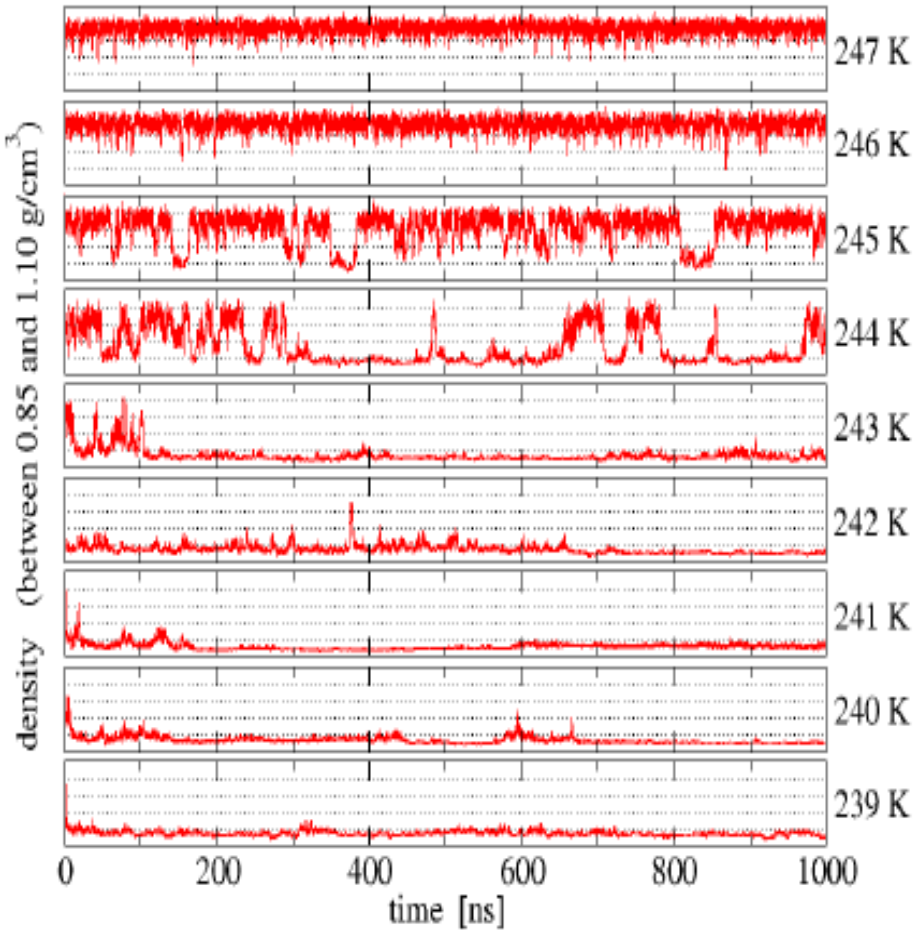
ST2 phase diagram



Poole, *et al.*, JPCM **17**, L431 (2005)

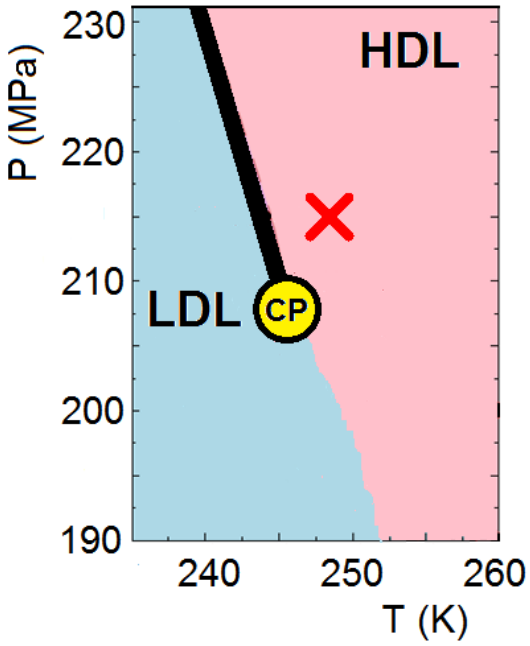
“Phase flipping” in NPT ensemble

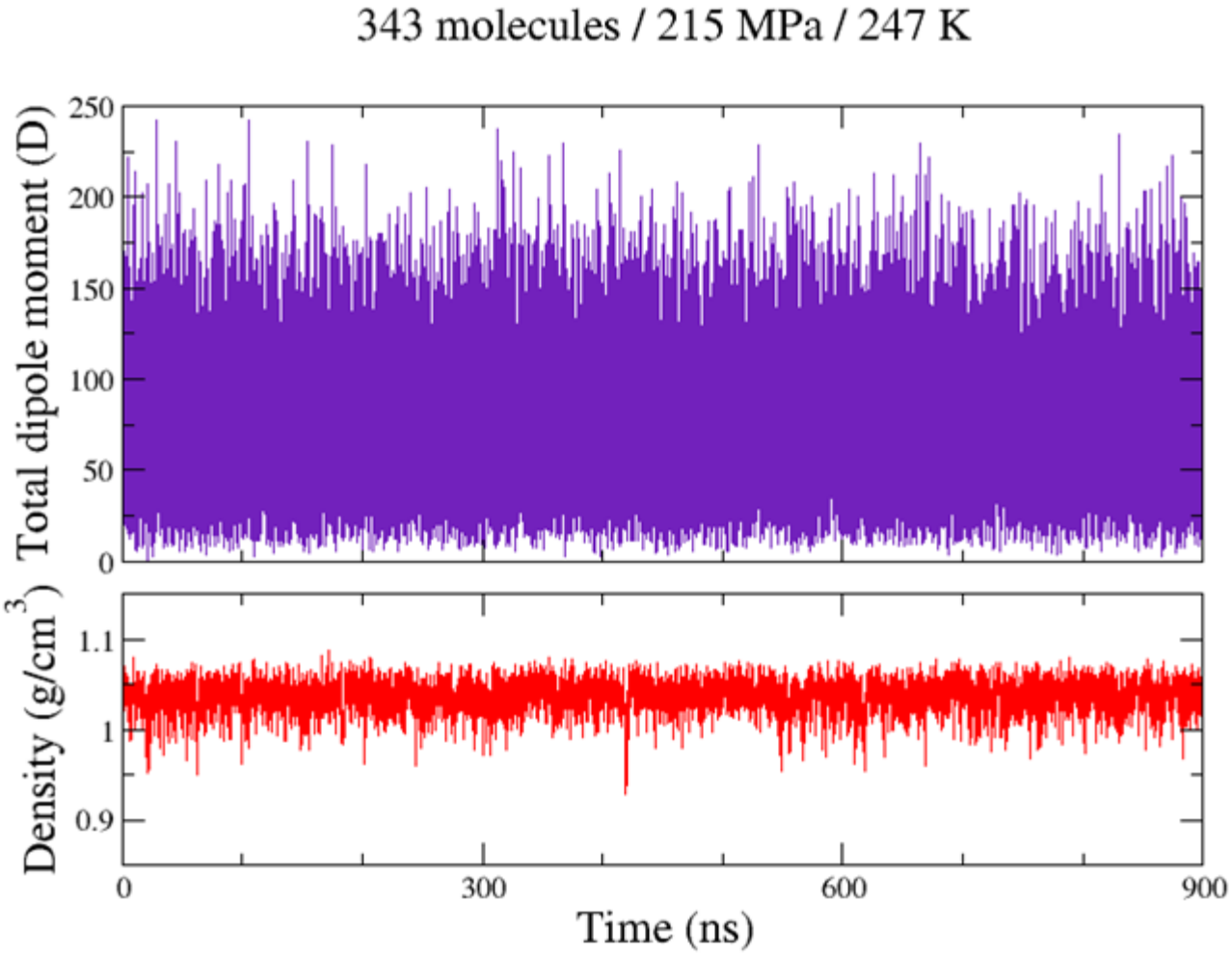




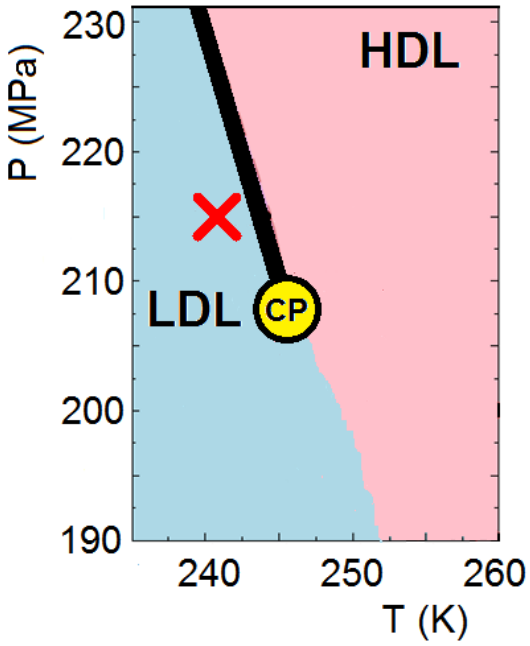
T. A. Kesselring, *et al.*, Sci. Rep. **2**, 474 (2012)

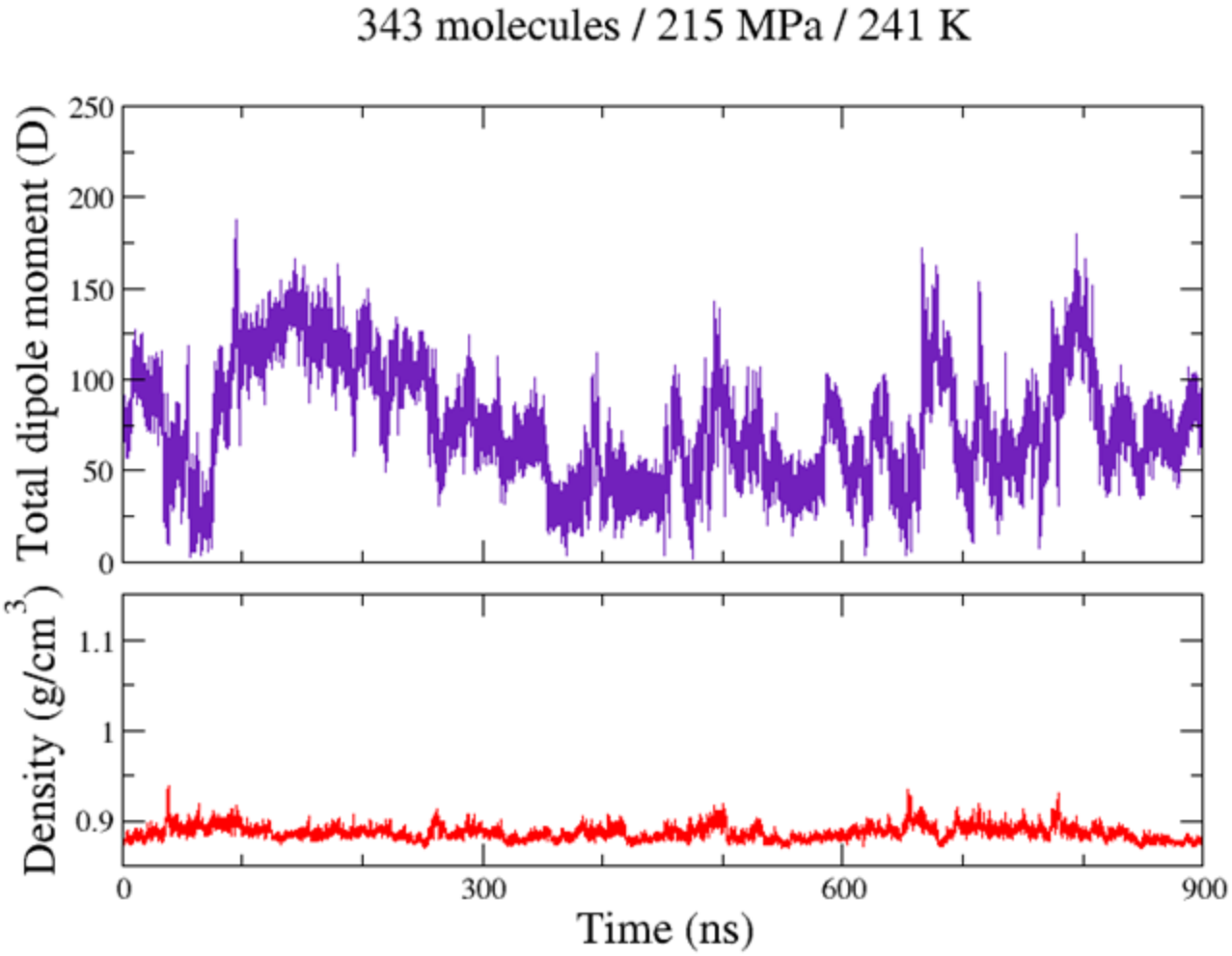
Total dipole moment in HDL



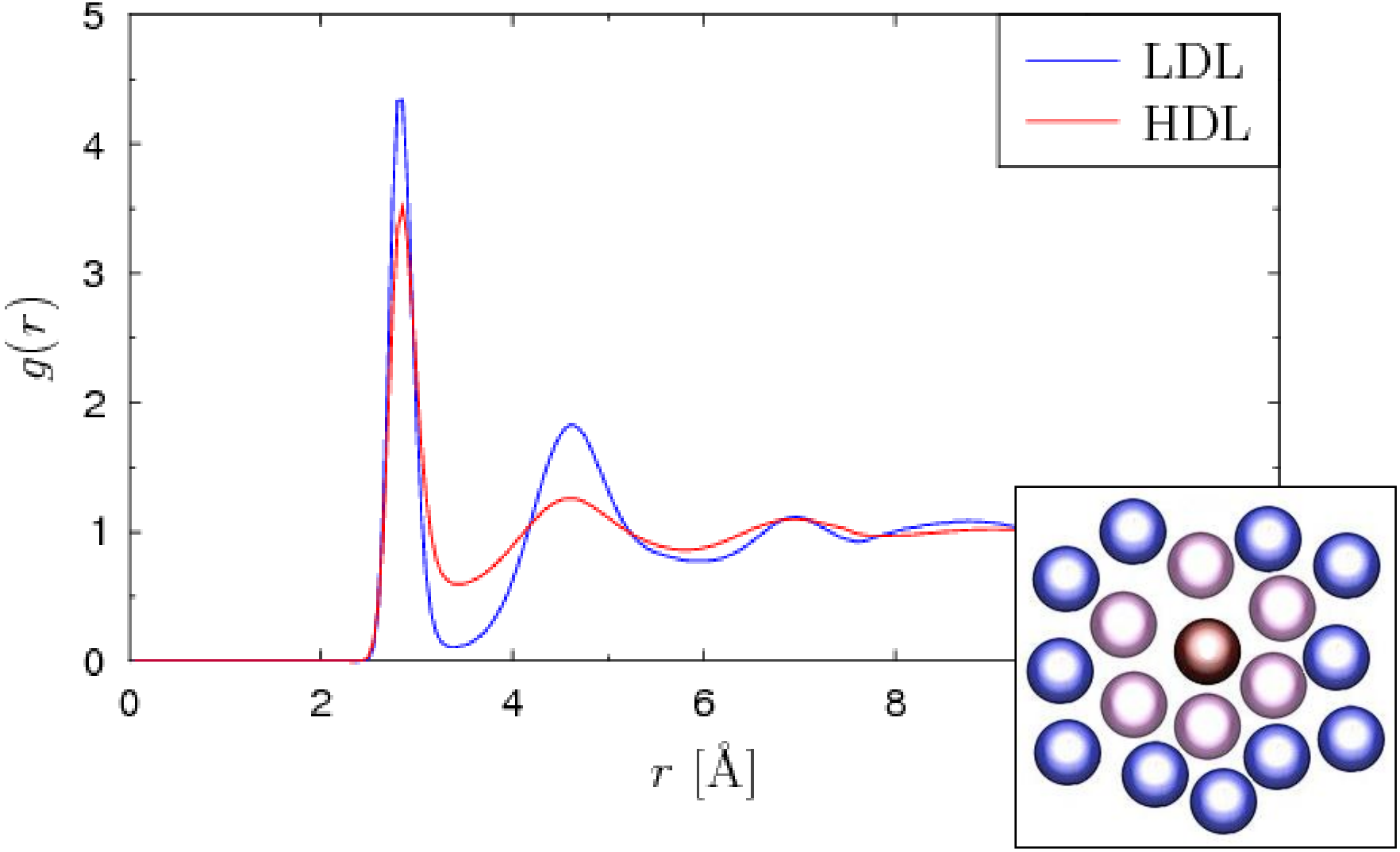


Total dipole moment in LDL





ST2 radial distribution function



Structural parameter q_3

$$q_\ell(i) \equiv \sum_m \frac{1}{N} \sum_{j \in n(i)} Y_\ell^m(\varphi_{ij}, \vartheta_{ij}) \qquad -\ell \le m \le \ell$$

1. Calculate spherical harmonics Y_ℓ^m for each pair (i,j)
2. Average over all neighbors $n(i)$ of molecule i
3. Sum over all m

- Each molecule has its own number
- For perfect diamond: $q_3 \approx 0.73$
- For completely random: $q_3 = 0$

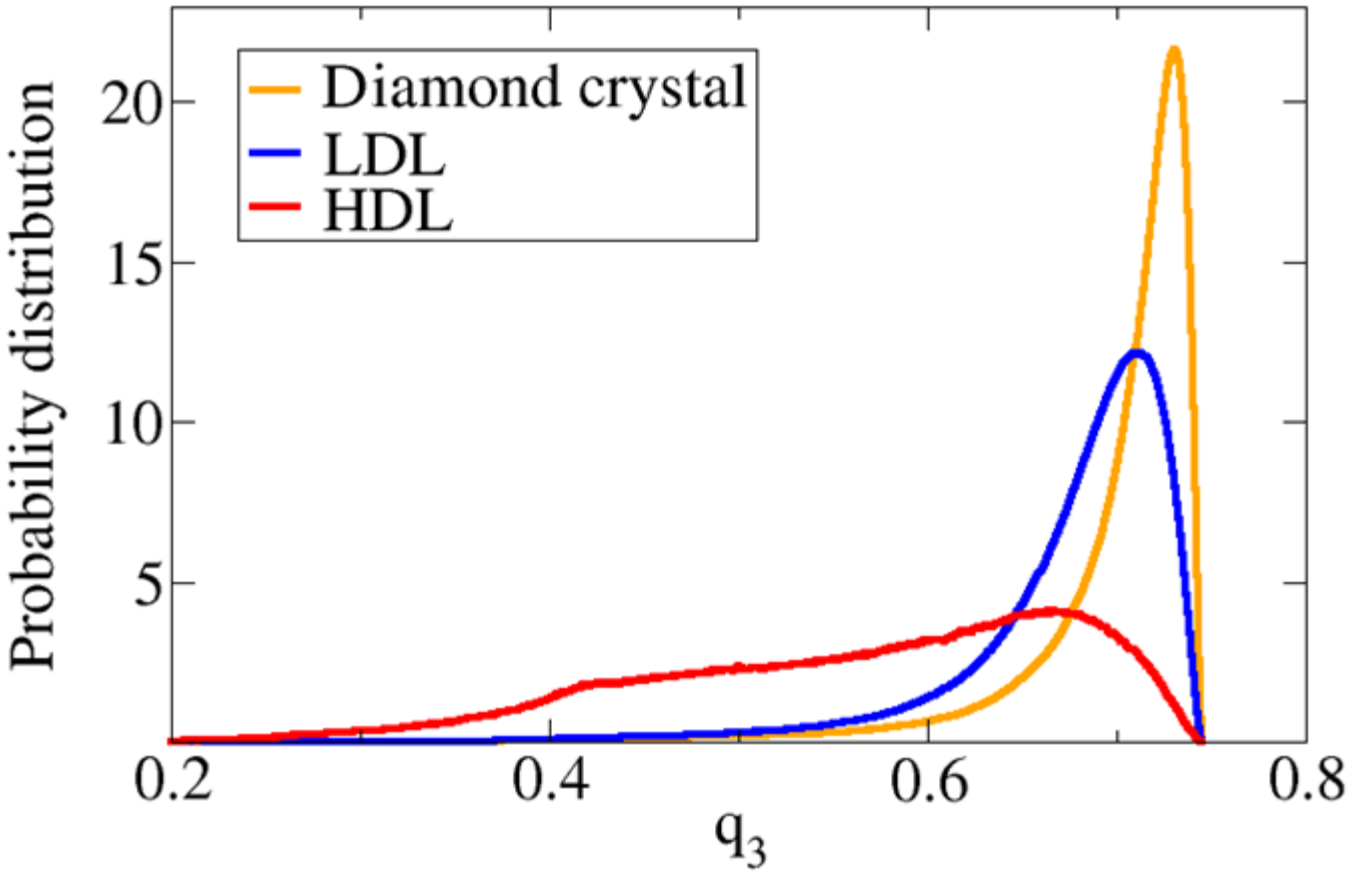
$$Y_0^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$$

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\sin\theta\, e^{-i\varphi}$$

$$Y_1^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\,\cos\theta$$

$$Y_1^1(\theta,\varphi) = \frac{-1}{2}\sqrt{\frac{3}{2\pi}}\,\sin\theta\, e^{i\varphi}$$

q_3 histogram

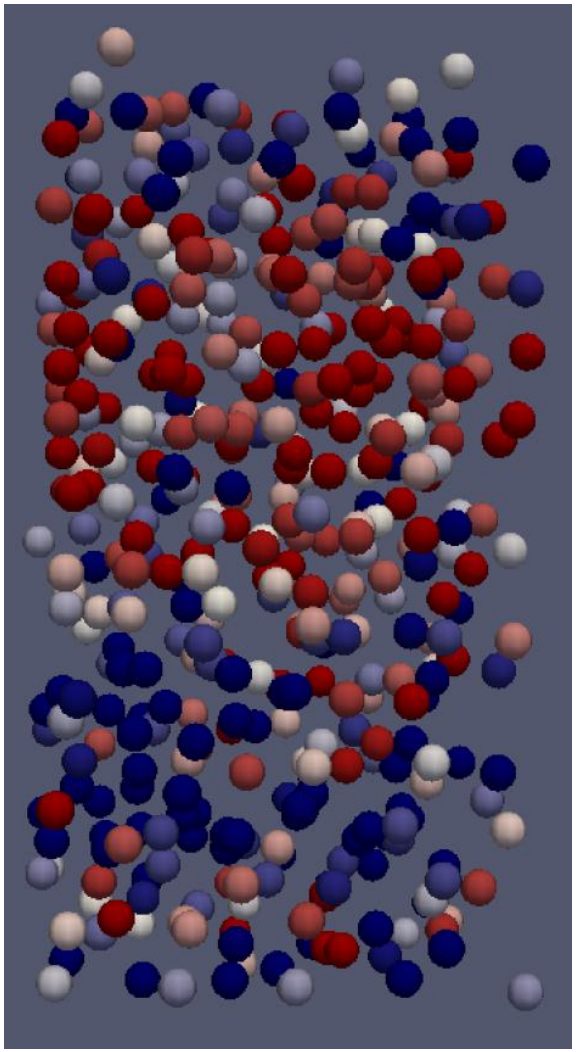


Again: LDL and HDL have clearly different structures

Phase segregation

- Structural parameters such as q_3 allow for real-time determination of local structure!

- Phase segregation can be witnessed in simulations



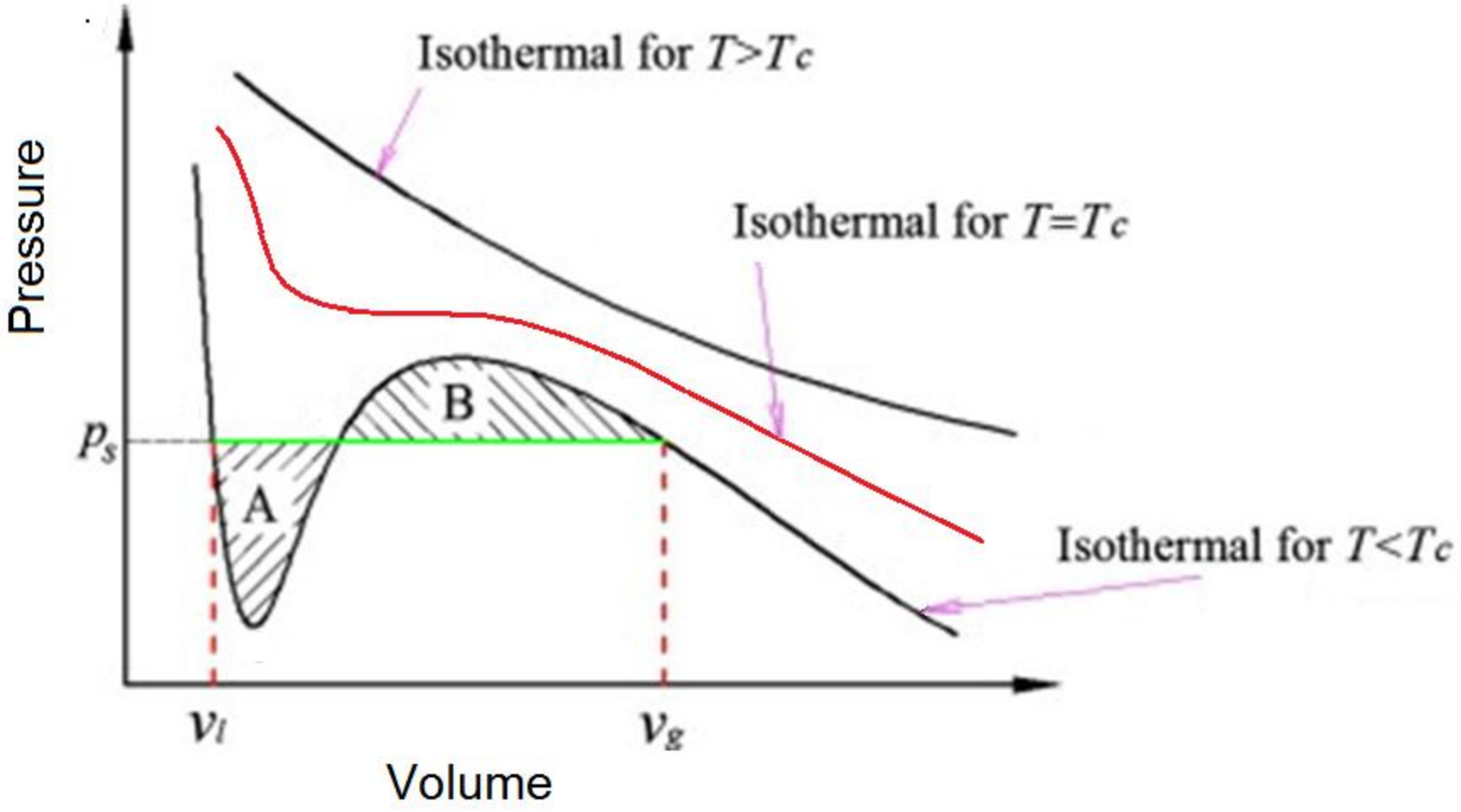
Conclusion ST2

- ST2 allows for two liquid structures to exist simultaneously (at same P, T)

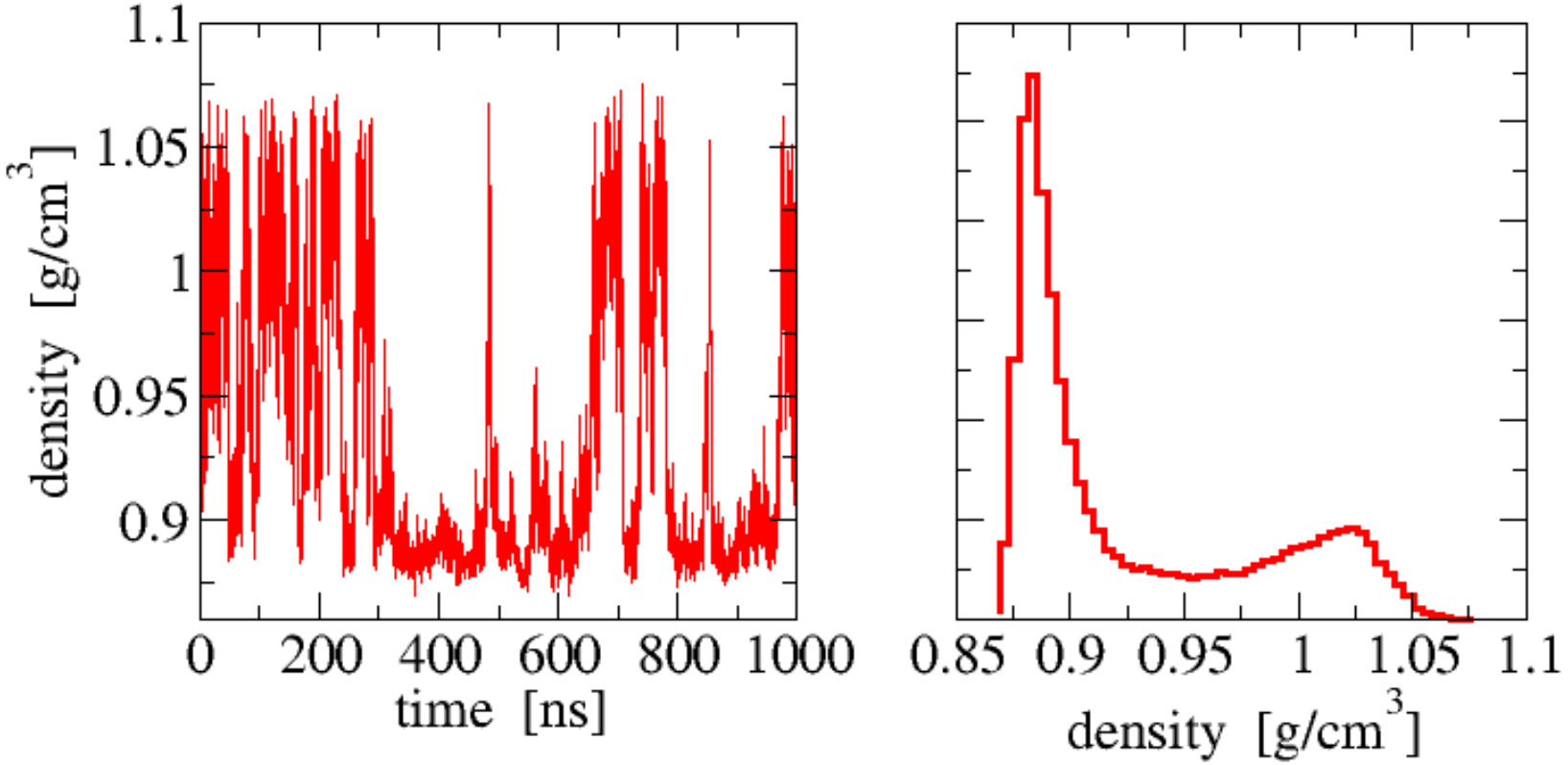
- This leads to LLPT and anomalies

- Introduction to LLPT & anomalies
- Spherical water model
- ST2 model
- **Locating the critical point (LLCP)**
- Conclusions

Via PV diagram

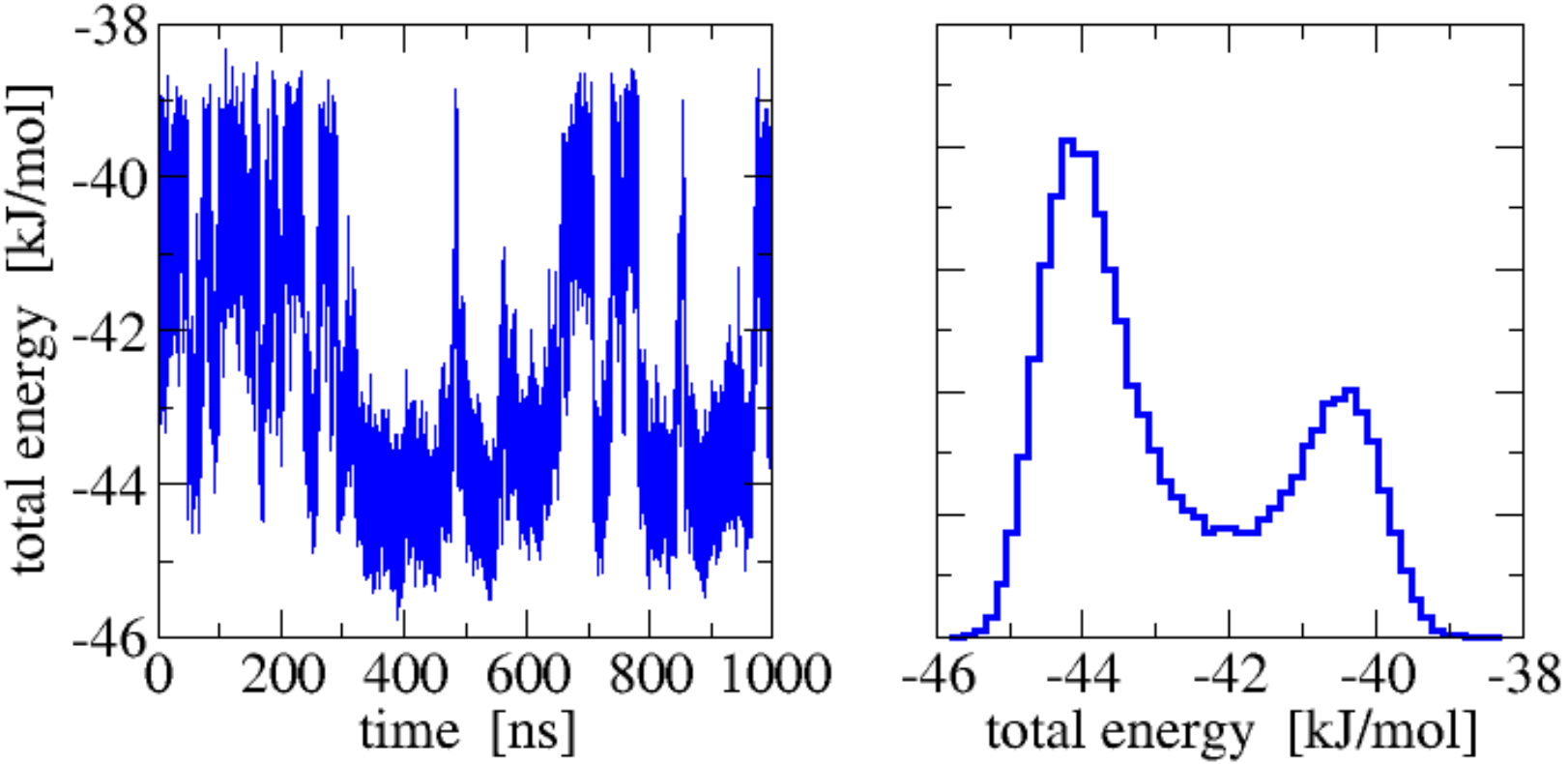


Via order parameter distribution (NPT)



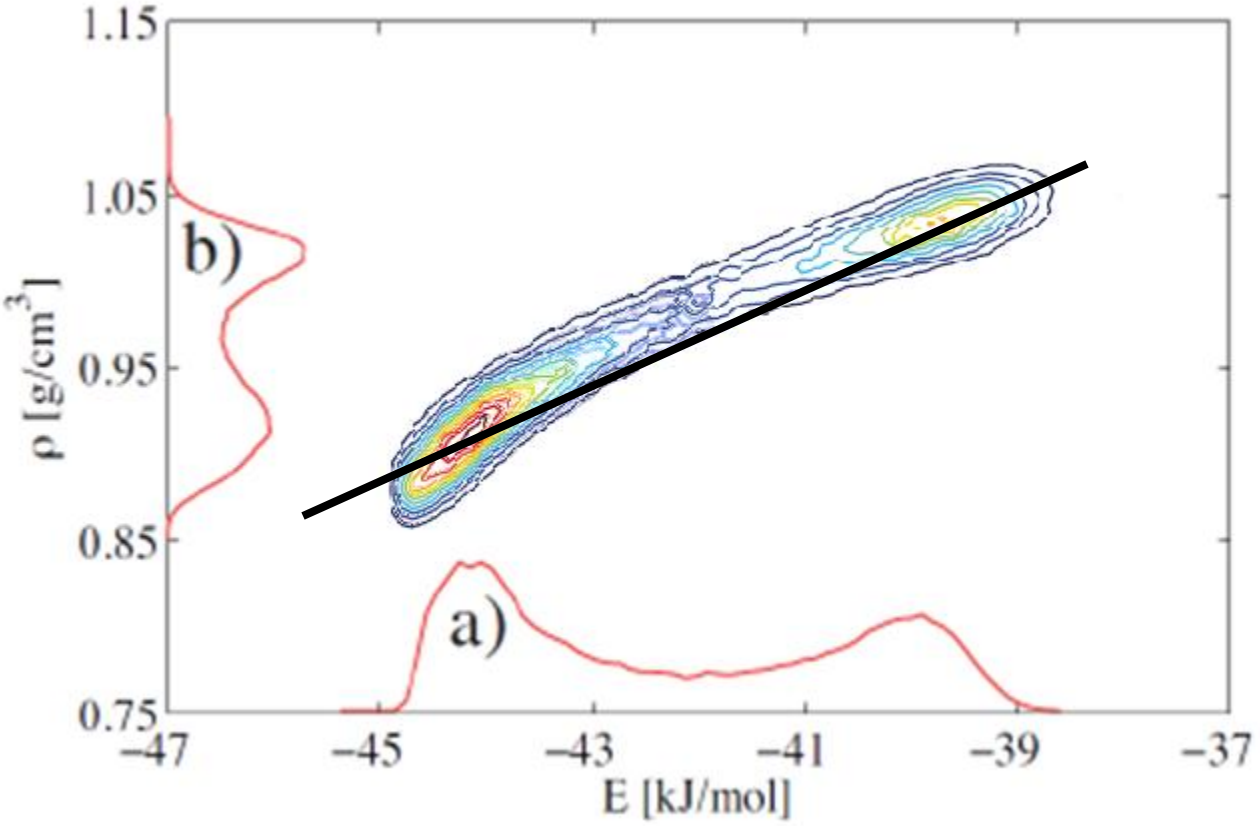
Phase flipping → histogram of density

Via order parameter distribution (NPT)



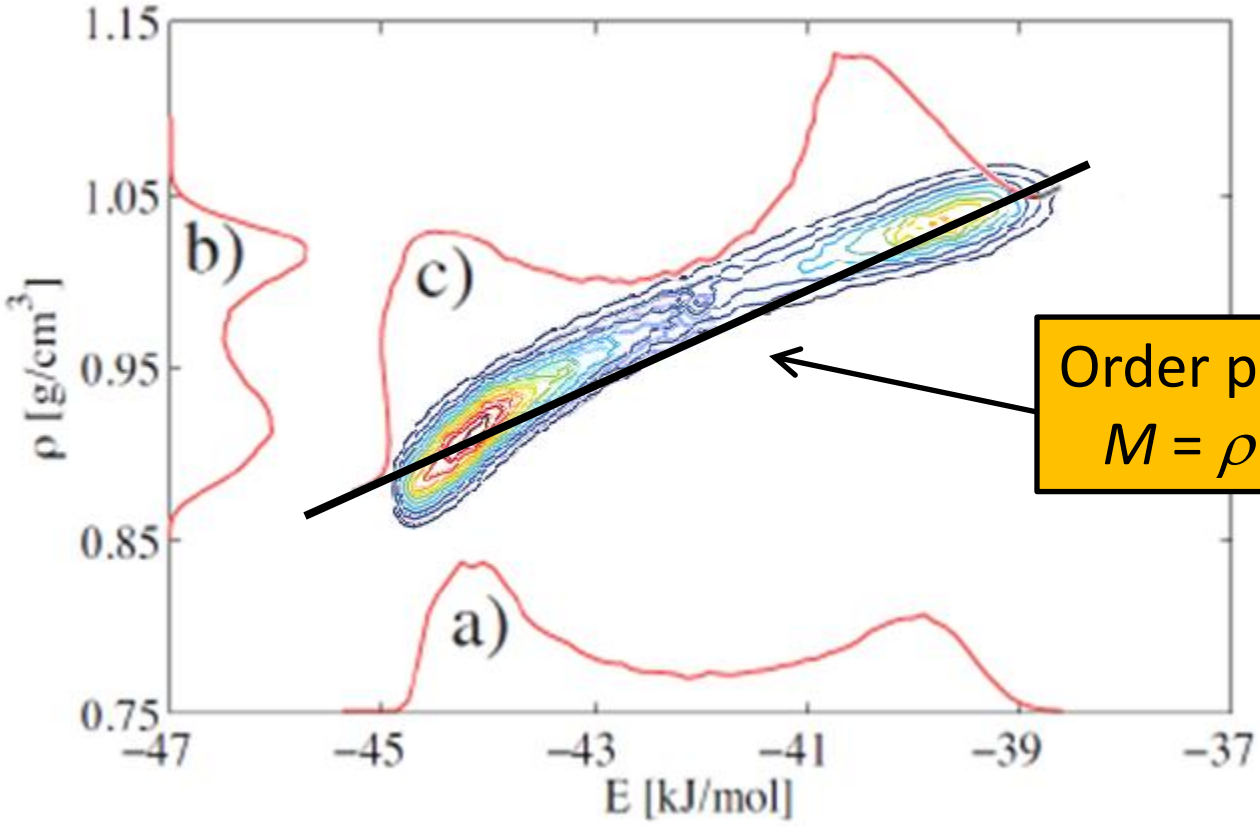
Phase flipping → histogram of energy

Via order parameter distribution (NPT)



2D histogram of energy & density

Via order parameter distribution (NPT)



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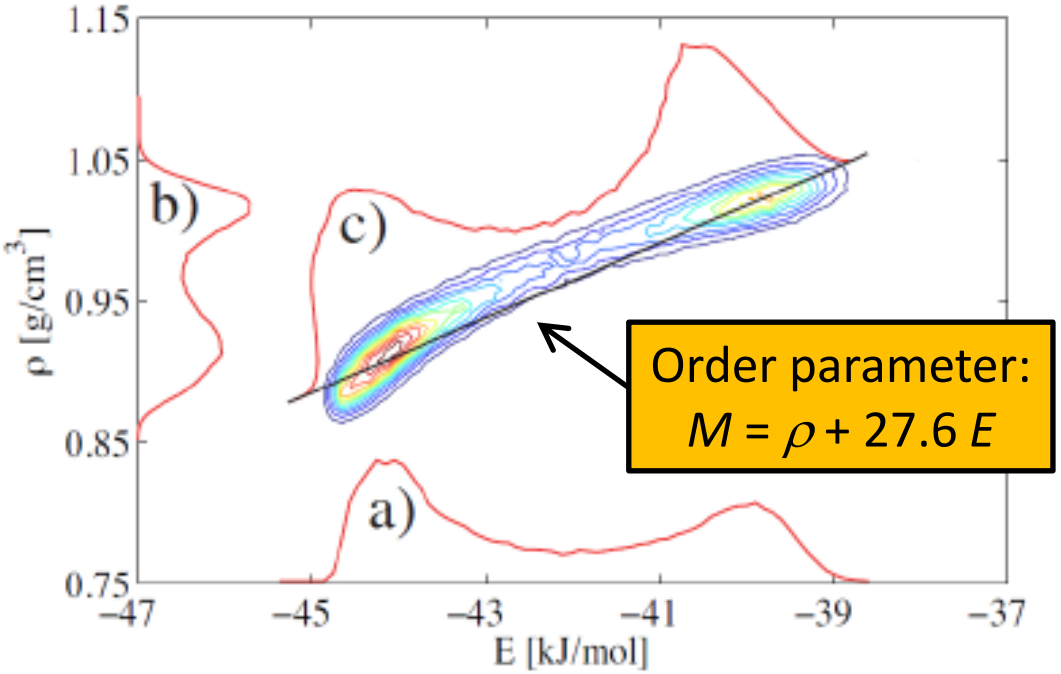

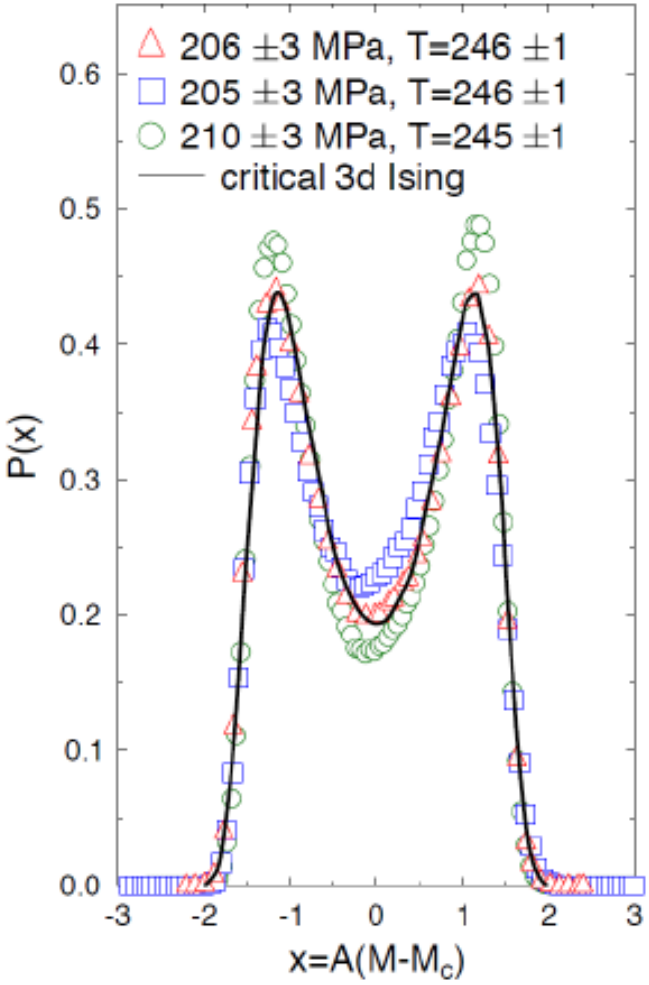

Order parameter *M* can be fitted to 3D Ising model

- Introduction to LLPT & anomalies
- Spherical water model
- ST2 model
- Locating the critical point (LLCP)
- **Conclusions**

Conclusions

- Simple models can have LLPT + anomalies because of two length scales and therefore two liquid structures
- Atomic models can have LLPT + anomalies because of two liquid structures
- LLCP falls in 3D Ising universality class which can be used to locate LLCP accurately

The End