Liquid-Liquid Phase Transitions and Water-Like Anomalies in Liquids

Erik Lascaris

Final oral examination
9 July 2014
Outline

• Anomalies in water and simple models

• Liquid-liquid phase transition in water

• Liquid-liquid phase transition in silica

• Conclusions
Outline

• Anomalies in water and simple models

• Liquid-liquid phase transition in water

• Liquid-liquid phase transition in silica

• Conclusions
Water has many anomalies (compared to other liquids)

• Famous website by Martin Chaplin
  http://www1.lsbu.ac.uk/water/anomalies.html
  now lists 70 anomalies!
  (on 9 July 2014)

• Today we focus on 3 of them
1. Density anomaly

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

At 1 atm, *Temperature of Maximum Density* (TMD) is 4 °C
In water, self-diffusion increases as density and pressure increase (at low T)
3. Melting line with negative slope

Most liquids:

- Solid
- Liquid
- Gas

Water:

- Triplet point
- Critical point

Applying pressure can melt ice!
Water has many anomalies
(compared to other liquids)

• Where do these come from?

• What is their origin?

Let’s try a simple model!
Hard core + linear ramp potential

- Monatomic particles (spheres)
- Pairwise interaction: $F = -\frac{dU}{dr}$
- Particles can partially overlap
PT diagram

Melting line with negative slope
PT diagram

**Density anomaly**

increase T $\rightarrow$ increase density
PT diagram

**Diffusion anomaly**

increase P $\rightarrow$ increase diffusivity
How can we explain these anomalies?
Two length scales

- Particles have (1) no overlap or (2) partial overlap.
Two length scales

- Particles have (1) no overlap or (2) partial overlap
- Increase $T \rightarrow$ more overlap $\rightarrow$ density increase

Potential energy $U(r)$ vs. distance between particles $r$.
Two length scales

- Particles have (1) no overlap or (2) partial overlap
- Increase $T \rightarrow$ more overlap $\rightarrow$ density increase
- Increase $P \rightarrow$ more overlap $\rightarrow$ diffusion increase

Low pressure  
High pressure
Two length scales

- Particles have (1) no overlap or (2) partial overlap
- Increase $T \rightarrow$ more overlap $\rightarrow$ density increase
- Increase $P \rightarrow$ more overlap $\rightarrow$ diffusion increase

![Potential energy graph](image)
Two length scales

- Particles have (1) no overlap or (2) partial overlap
- Increase $T \rightarrow$ more overlap $\rightarrow$ density increase
- Increase $P \rightarrow$ more overlap $\rightarrow$ diffusion increase

![Potential energy plot](Image)

Low pressure

High pressure
Two length scales

- Particles have (1) no overlap or (2) partial overlap
- Increase $T \rightarrow$ more overlap $\rightarrow$ density increase
- Increase $P \rightarrow$ more overlap $\rightarrow$ diffusion increase

When $T$ or $P$ too high:
Normal liquid again!
Melting line

• Clapeyron relation for slope melting line $dP/dT$:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_{\text{liquid}} - S_{\text{crystal}}}{V_{\text{liquid}} - V_{\text{crystal}}}$$

• Change in entropy always positive: $\Delta S > 0$
• Usually crystal more dense than liquid: $\Delta V > 0$
• However, two length scales leads to $\Delta V < 0$
Changing the model

To obtain a better understanding: try different potentials

Hard Core + Linear Ramp

Linear Ramp
PT diagram

Hard Core + Linear Ramp

Linear Ramp
Changing the model

To obtain a better understanding: try different models
PT diagrams of Cut Ramp potential

Several anomalies:

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

All within same pressure range!
PT diagrams of Cut Ramp potential

How can we explain this?

Look at Radial Distribution Function!
Radial Distribution Function (RDF)

RDF = probability for atom to find a neighbor a distance $r$ away (normalized to ideal gas)
RDF of Linear Ramp (0% cut)

Low pressure
(no anomalies)
RDF of Linear Ramp (0% cut)

Low pressure (no anomalies)
RDF of Linear Ramp (0% cut)

Low pressure (no anomalies)
RDF of Linear Ramp (0% cut)

Medium pressure
(inside anomaly region)
RDF of Linear Ramp (0% cut)

High pressure
(no anomalies)
RDF of 50% Cut Ramp

Low pressure (no anomalies)
RDF of 50% Cut Ramp

Medium pressure (no anomalies)
RDF of 50% Cut Ramp

High pressure
(no anomalies)
Two “competing” length scales

0% cut: anomalies

50% cut: no anomalies

Within anomaly region, some particles are on the ramp

Particles are either near \( r=0 \) or \( r=1 \) but rarely on the ramp!
Anomalies: conclusions

For anomalies to occur, we require:

• Need **two length scales** in potential
  – Liquid has two preferred liquid states

• Length scales need to be **“competing”**
  – Anomalies occur when liquid is in between states

Water has anomalies → does it have two length scales?
Two length scales in water!

When cooled super fast, it’s possible to create two types of “glassy” water!

Low-Density Amorphous ice (LDA)

High-Density Amorphous ice (HDA)

Katrin Amann-Winkel (2013)
Loerting Group, Universität Innsbruck
Liquid-liquid phase transition in water

**Hypothesis**
(Poole/Sciortino/Essmann/Stanley, Nat. 1992)

- Two liquids below nucleation temperature:
  - Low density liquid (LDL)
  - High density liquid (HDL)

- Separated by liquid-liquid phase transition (LLPT) line

- Line ends in a liquid-liquid critical point (LLCP)
Outline

• Anomalies in water and simple models

• Liquid-liquid phase transition in water (using ST2 model)

• Liquid-liquid phase transition in silica

• Conclusions
ST2 water model

Isochores in NVT ensemble

**NVT**: Simulations with constant *Number of molecules*, constant *Volume*, and constant *Temperature*

Isochores are found by connecting data points of the same density

Adapted from: Poole *et al.*, JPCM **17**, L431 (2005)
Isochores in NVT ensemble

**NVT**: Simulations with constant *Number of molecules*, constant *Volume*, and constant *Temperature*

Isochores are found by connecting data points of the same density

Adapted from: Poole *et al.*, JPCM **17**, L431 (2005)
Isochores in NVT ensemble

$NVT$: Simulations with constant $\text{Number of molecules}$, constant $\text{Volume}$, and constant $\text{Temperature}$

Isochores are found by connecting data points of the same density

Adapted from: Poole et al., JPCM 17, L431 (2005)
Isochores in NVT ensemble

NVT: Simulations with constant Number of molecules, constant Volume, and constant Temperature

Isochores are found by connecting data points of the same density

Isochores cross at the Liquid-Liquid Critical Point (LLCP)

Adapted from: Poole et al., JPCM 17, L431 (2005)
Measuring location (T, P) of the LLCP

• It’s hard to locate LLCP accurately using only crossing isochores...

• Alternative method:  
  Fitting order parameter to 3D Ising model!

• Requires NPT (constant *Pressure*) simulations
“Phase flipping” in NPT ensemble

Density as a function of time:
Density distribution

Phase flipping $\rightarrow$ histogram of density

LDL

HDL
Energy distribution

Phase flipping $\rightarrow$ histogram of energy
Order parameter distribution

2D histogram of energy & density
Order parameter distribution

2D histogram of energy & density

Order parameter: \( M = \rho + 27.6 \ E \)
Order parameter distribution

Order parameter $M$ can be fit to 3D Ising model

Order parameter: $M = \rho + 27.6 \, E$
Outline

• Anomalies in water and simple models

• Liquid-liquid phase transition in water

• **Liquid-liquid phase transition in silica** (using WAC model and BKS model)

• Conclusions
Two models of silica (SiO$_2$)

- Simple 1:2 mixture of Si and O ions
- Each ion has a charge + electrostatics
- Repulsive potential between ions to prevent Si-O fusion

**WAC model**
- Woodcock, Angell, and Cheeseman
- Introduced 1976
- Ions: $\text{Si}^{+4}$ and $\text{O}^{-2}$

**BKS model**
- van Beest, Kramer, and van Santen
- Introduced 1990
- Ions: $\text{Si}^{+2.4}$ and $\text{O}^{-1.2}$
PT diagram of BKS

LLCP? Crossing isochores?

No LLCP at low $T$

---

Saika-Voivod, Sciortino, and Poole

Lascaris, Hematti, Buldyrev, Stanley, and Angell
PT diagram of WAC

LLCP? Crossing isochores?

Maybe LLCP at low T!

Saika-Voivod, Sciortino, and Poole

Lascaris, Hematti, Buldyrev, Stanley, and Angell
Response functions WAC

At critical point: all response functions should diverge!

Maxima are at different (T,P) → no LLCP!
Why is WAC closer to LLCP than BKS?

Studies by Molinero *et al.* suggest that “tetrahedrality” of the liquid plays a role.

Liquids like water and SiO$_2$ form tetrahedral bonds.

Rigid bonds lead to fast crystallization into hexagonal crystal.
Why is WAC closer to LLCP than BKS?

Studies by Molinero *et al.* suggest that “tetrahedrality” of the liquid plays a role

Rigid bonds lead to fast crystallization into hexagonal crystal

High-Density Liquid
- Compact
- Liquid with high diffusivity

Floppy bonds lead to high-density liquid
Why is WAC closer to LLCP than BKS?

Studies by Molinero et al. suggest that “tetrahedrality” of the liquid plays a role.

Rigid bonds lead to fast crystallization into hexagonal crystal.

Liquid-liquid phase transition requires existence of two liquids: LDL and HDL.

Low-Density Liquid
- Expanded
- Local structure closer to crystal

High-Density Liquid
- Compact
- Liquid with high diffusivity
Why is WAC closer to LLCP than BKS?

Studies by Molinero *et al.* suggest that “tetrahedrality” of the liquid plays a role.

Conclusion:

**bond stiffness needs to be *just right***

- Too stiff → crystallization
- Too flexible → only HDL
- Just right → LDL + HDL
Si-O-Si bond angle distribution

Distribution WAC is sharper: stiff

Distribution BKS more broad: floppy

Hard to compare: bond angle depends on temperature!
Bond angle as spring system

Pretend Si-O-Si bond angle is controlled by a spring:
Bond angle as spring system

Pretend Si-O-Si bond angle is controlled by a spring:

Imaginary spring (spring constant $k_2$)

WAC more stiff $\rightarrow$ closer to LLCP
Outline

• Anomalies in water and simple models

• Liquid-liquid phase transition in water

• Liquid-liquid phase transition in silica

• Conclusions
Conclusions (1)

• Simple models explain origin of anomalies:
  – Two length scales
    • Low density structure (expanded)
    • High density structure (collapsed)
  – Region with anomalies is where these structures energetically compete
Conclusions (2)

• Best way to locate liquid-liquid critical point (LLCP) is by fitting order parameter to 3D Ising

• We did not find LLCP in silica models WAC, BKS

• Liquid-liquid phase transitions might be related to bond angle stiffness
  – Modeling liquid as network of springs might help predicting if liquid has a LLCP
Also a big THANKS to my collaborators:

- Gene Stanley (advisor)
- Sergey Buldyrev
- Austen Angell
- Mahin Hemmati
- Giancarlo Franzese
- Tobias Kesselring
- Hans Herrmann
- Gianpietro Malescio

Liquid-Liquid Phase Transitions and Water-Like Anomalies in Liquids

THANK YOU!