Second critical point in supercooled water: fact or fiction?

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Beam layout
Total scattering from disordered materials

$$Q = \frac{4\pi \sin \theta}{\lambda}$$
SANDALS (liquids diffractometer)

Scattering detectors

Sample position

Incident neutron beam
ISIS XRD
Out of the instrument comes some data:

(Total scattering data from amorphous silica)

What does it tell us?
The liquid structure factor:

\[ F_d(Q) = \sum_{\alpha, \beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_\alpha c_\beta b_\alpha b_\beta \left\{ 4\pi \rho \int r^2 \left( g_{\alpha\beta}(r) - 1 \right) \frac{\sin Qr}{Qr} dr \right\} \]

The partial structure factors, \( H_{\alpha\beta}(Q) \)

The site-site radial distribution functions, \( g_{\alpha\beta}(r) \)

Atomic fraction of component “\( \alpha \)”

The atom scattering factor or “form factor”
Introduce Empirical Potential Structure Refinement, EPSR

- Use harmonic constraints to define molecules.
- Use an existing “reference” potential for the material in question taken from the literature (or generate your own if one does not exist).
- Use the diffraction data to perturb this reference potential, so that the simulated structure factor looks like the measured data.
Water data after structure refinement.
Water partial \( g(r) \)'s

![Graph showing partial radial distribution functions for different types of bonds in water, including H-H, O-H, and O-O bonds.][1]

[1]: Replace with actual image link or description for better understanding.
Beyond $g(r)$: the spatial density function
9%
25%
Water under pressure
Water at 268K, 0.26kbar
Water at 268K, 2.09kbar
Water at 268K, 4.00kbar
Motivation for this talk.

2015:

DOI: 10.1021/acs.jpcclett.5b00827

Liquid–Liquid Phase Transition and Its Phase Diagram in Deeply-Cooled Heavy Water Confined in a Nanoporous Silica Matrix

Zhe Wang,† Kanae Ito,† Juscelino B. Leão,‡ Leland Harriger,‡ Yun Liu,‡,§ and Sow-Hsin Chen*,†
Motivation for this talk.

Which followed on from several recent papers:-

**Evidence of the existence of the high-density and low-density phases in deeply-cooled confined heavy water under high pressures**

Zhe Wang, Kao-Hsiang Liu, Leland Harriger, Juscelino B. Leão, and Sow-Hsin Chen

**Density and anomalous thermal expansion of deeply cooled water confined in mesoporous silica investigated by synchrotron X-ray diffraction**

Kao-Hsiang Liu, Yang Zhang, Jey-Jau Lee, Chia-Cheng Chen, Yi-Qi Yeh, Sow-Hsin Chen, and Chung-Yuan Mou

**Density hysteresis of heavy water confined in a nanoporous silica matrix**

Motivation for this talk.

Which in turn followed on from earlier papers in this series:

Observation of the density minimum in deeply supercooled confined water

Dazhi Liu*, Yang Zhang*, Chia-Cheng Chen†, Chung-Yuan Mou†, Peter H. Poole‡, and Sow-Hsin Chen*§

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Edited by H. Eugene Stanley, Boston University, Boston, MA, and approved April 16, 2007 (received for review February 13, 2007)
Motivation for this talk.
So the key question arises:

- Do the data shown by Chen and coworkers support the idea of a liquid-liquid transition in confined water?

Many people have questioned several aspects of this work, including myself!
FRONTIERS ARTICLE

Radical re-appraisal of water structure in hydrophilic confinement

Alan K. Soper

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So what is all the fuss about?

\[ \chi \sim \left( \frac{T}{T_s} - 1 \right)^\gamma \]

with

\[ T_s = 228 \, K \]

(Speedy and Angell, 1976)
So what is all the fuss about?

\[ C_p \sim \left( \frac{T}{T_S} - 1 \right)^\gamma \]

with

\[ T_S = 228 \text{ K} \]
Second critical point scenario

(Poole et al., Nature, 1992)
(ST2 water model)

$T_C \sim 235\, K$

$P_C \sim 220\, MPa$

Hotly contested by some, particularly Limmer and Chandler
So what is all the fuss about?

(Kanno et al. Science 1975)

2nd Critical Point scenario

Hotly contested by some, particularly Limmer and Chandler
Second critical point scenario

(Holten and Anisimov, 2012)

(“athermal” mixture of “LDL” and “HDL”)

\[ T_C \sim 227 \text{ K} \]

\[ P_C \sim 13 \text{ MPa} \]

Unresolved question:-
- What exactly are HDL and LDL?
Chen's experiment:

- Circumvent $T_H$ by confining water in MCM41
Something odd here:

- Nothing in DSC trace, but Bragg peaks in diffraction pattern!
\[ I(Q) \sim \langle |C(Q)|^2 \rangle_{\Omega_Q} \]

\[
C(Q) = \int dx dy dz (\rho(x, y, z) - \rho_0) \exp[i(Q \cdot r)]
\]
Approximation: \[ \rho(x, y, z) \approx \bar{\rho}(r) M(z) \]

\[ \int_{-L}^{+L} dz \, M(z) \exp(iQ_z z) \approx 2 \bar{M} L \frac{\sin Q_z L}{Q_z L} \]

This only exists when \( Q_z \lesssim 1/L \).

\( Q_{\text{Bragg}} = 0.2\text{Å}^{-1}, \ L \sim 10000\text{Å} \)

\( \therefore \) Bragg intensities are DOMINATED by radial component.

\[ \bar{C}(Q) = 2\pi \int_0^R \left( \bar{\rho}(r) - \rho_0 \right) J_0(Qr) r dr \]
Diffraction pattern from dry MCM41

Porod (interfacial) scattering

Bragg peaks from hexagonal lattice of pores

Atomic structure of substrate
Chen experiment concentrates on (100) peak
From these data, speculate on LL transition.
Many problems with existing analysis!
They don't know the pore size.

Literature states amount of water absorbed is \( \sim 0.5 \text{g/g of substrate} \)

Literature also states \( r_p = 7.5 \text{Å} \)

\[
M(r_p) = \frac{\rho_w \pi r_p^2}{\rho_s \left( \frac{\sqrt{3}}{2} d^2 - \pi r_p^2 \right)}
\]
It is claimed MCM41 is not microporous. Not proven.

- One piece of evidence cited is this study:

  *Langmuir* 2009, 25, 939–943

  Is There Any Microporosity in Ordered Mesoporous Silicas?

  A. Silvestre-Albero,† E. O. Jardim,† E. Bruijn,‡ V. Meynen,‡ P. Cool,‡
  A. Sepúlveda-Escribano,† J. Silvestre-Albero,†,* and F. Rodríguez-Reinoso†

- Claim based on unchanged absorption isotherms when \( n \)-nonane is introduced

  - \( N \)-nonane unlikely to penetrate into the small micropores in silica.
EPSR simulations - MCM41 plus $N_2$
It is claimed water cannot freeze in MCM41 pore if small enough. Not proven.
Observing hysteresis does not prove liquid-liquid transition.

- Hysteresis is likely to be observed in any first order transition.
- Difficult to ensure sample is uniformly heated, even if performed slowly.
- Latent heat of transition has to be supplied or removed.
- In present case, size of hysteresis depended on the heating/cooling protocol.
Fails to take account of the behaviour of the whole diffraction profile

Soper, 2013
Most vexing of all: where are the density fluctuations?
Anyone who has ever done a scattering experiment near a critical point knows there will be a large rise in scattering at low Q.

Mancinelli et al., JPCL, 2010.

Low Q intensity declines monotonically with lowering temperature!

No sign of crossing a “Widom” line!
Is this pathological science?

- On the subject of observing critical point fluctuations, Zhang, PNAS, 2011:
  - “… If such a critical point does exist as illustrated in Fig. 1, at low pressures along the extension of the coexistence line in the one phase region, a critical divergence of the response functions along with the correlation length should be observed (48). However, in confinement such as the quasi-1D pores of MCM-41-S, the correlation length is geometrically constrained by the walls of silica; hence it can grow only along the pore axis direction, making it even more challenging to identify whether there is a critical point. ...”

- Yet the pores are ∼1 μm long. Surely there is plenty of room for observable critical fluctuations?

- If there are no critical point fluctuations, how do we know it is a critical point??
My own EPSR simulations of water in MCM41 (Soper, CPL 2013)

These changes occur at constant no. of water molecules in pore.
Pure water excess entropy calculations

- Baranyai & Evans (1989) Lennard-Jones:

\[ s_2 = \frac{\rho}{2} k \int \left( g^{(2)}(r) - 1 - g^{(2)}(r) \ln g^{(2)}(r) \right) \, dr \]

\[ s^{(2)}(r) = \frac{\rho}{2} k \int_0^r \left( g^{(2)}(r') - 1 - g^{(2)}(r') \ln g^{(2)}(r') \right) \, dr' \]

- Lazaridis & Karplus (1996) – water:

\[ s_{tot}^{(2)}(r) = \frac{\rho}{2} k \int_0^r \left\langle g^{(2)}(r', \omega_L, \omega_M) \rightangle - 1 \]

\[ -g^{(2)}(r', \omega_L, \omega_M) \ln g^{(2)}(r', \omega_L, \omega_M) \rangle \omega_L, \omega_M \, dr' \]
The orientational pair correlation function
Pure water excess entropy calculations

- Integral over 6 coordinates:

\[ r, \omega_L = (\theta_L, \phi_L), \omega_M = (\phi_M, \theta_M, \chi_M) \]

• Form spherical harmonic expansion:

\[
g(r, \omega_L, \omega_M) = 1 + \sum_{l_1 l_2 l} \sum_{m_2 m} \sum_{n_1 n_2} h(l_1, l_2, l; n_1, n_2; r) \times C(l_1, l_2, l; n_1, m_2, m) \times D_{m_2 n_2}^{l_2}(\omega_M)^* D_{m_0}^l(\omega_L)
\]
**Pure water excess pair entropy calculations**

- Allows two subsidiary quantities to be defined:
  - *Radial* excess entropy:
    \[ g_c(r) = \langle g(r, \omega_L, \omega_M) \rangle \omega_L \omega_M \]
    \[ = 1 + h(000; 00; r) \]
  - *Spatial* excess entropy:
    \[ g_{sd}(r, \omega_L) = \langle g(r, \omega_L, \omega_M) \rangle \omega_M \]
    \[ = 1 + \sum_{l_1} \sum_{n_1} h(l_1, 0, l_1; n_1, 0; r) \]
    \[ \times C(l_1, 0, l_1; n_1, 0, n_1) D_{n_10}^{l_1}(\omega_L) \]
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Try to summarise

- Claims that confined water shows a liquid-liquid transition are not supported by the available evidence
  - Lack of observable critical point fluctuations;
  - Inattention to “small” details, such as
    - the pore size conundrum;
    - the fact that small Bragg peaks appear even in MCM41-S-15, but nothing appears in DSC trace;
    - the fact that the apparent 10% (?) drop in density of the water when it enters MCM41 is ignored;
    - raw data are rarely shown.
  - Unwillingness to accept or take seriously alternative explanations of the data.
  - A case of pathological science?
- Most likely scenario: this is (if it is anything at all) actually a liquid-solid transition.
What we CAN say...

• In real confinement (MCM41), and when supercooled, water shows a steady increase in tetrahedrality with lowering the temperature;

• Low density water shows an initial *increase* in entropy when the density is increased at low temperature;

• The initial increase is followed by subsequent *decrease* in entropy on further densification;

• Entropy changes do not relate simply to tetrahedrality;

• So far no hint of a sharp L-L transition, but continuous transitions remain highly likely.
Thank you for your attention!