The Fourth Phase of Water: Beyond Solid, Liquid and Vapor

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Vermont 2012
Role of water in cell biology...
gel

Bulk water plus particles

Exclusion Zone EZ

10 µm
Another example

200 µm

Nafion

Microspheres
Basic finding confirmed

- Felix Blyakhman (Ural State Univ)
- Wei-Chun Chin (U. Cal. Merced)
- Toshio Hirai (Shinshu University)
- Mark Banaszak Holl (Univ. of Michigan)
- Tom Lowell (Vermont Photonics)
- Diedrich Schmidt (Tsukuba)
- Gerhard Artmann (Aachen)
- David Maughan (U. Vermont)
- Miklos Kellermayer (Budapest)
- Fettah Kosar (Harvard)
- Jacques Huyghe (Eindhoven)
- Nikolay Bunkin (Moscow)
Questions to Answer

- Is the exclusion phenomenon general?
- Does it really arise from water ordering?
- What energy creates this order?
- Can the ordered zone explain everyday phenomena?
Question #1: Generality

- **Surfaces:** gels, polymers, biological surfaces, monolayers

- **Solute excluded:** down to mw 100 and lower
Small solutes excluded...

pH-sensitive dye(s)

Nafion

dye excluded
many solutes excluded

many hydrophilic surfaces generate exclusion zones
Question #2

Is this zone physically different from bulk water?
Evidence that exclusion-zone (EZ) water is physically different from bulk water

• EZ water molecules more constrained (NMR)
• EZ molecules more stable (infrared radiation)
• EZ has negative charge (electrical potential)
• EZ absorbs at 270 nm (light-absorption spectrum)
• EZ is more viscous (falling ball viscometry)
• EZ molecules aligned (polarizing microscopy)
• EZ molecular structure different (IR absorption)
• EZ optical properties different (refractive index)

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Nafion

from previous slide

\[ H^+ \quad H^+ \quad H^+ \]

pH-sensitive dye
Current flow between exclusion zone and water beyond

Confirms charge separation
A charged battery in water

Separated charges should attract
(a) time = 0

(b) ribbon deflects as EZ grows
Charges genuinely separated
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Summary, so far

- Liquid crystalline
- Negative charge
- Excludes solutes
- (Non-dipolar?)

Fourth phase of water?
(Sir Wm. Hardy, 1912)
Summary, so far

Liquid crystalline
Negative charge
Excludes solutes
(Non-dipolar?)

Fourth phase of water?
(Sir Wm. Hardy, 1912)
Non-dipolar EZ Structure?

• Negative charge (dipoles neutral)
• 270-nm absorption (ring-like structures)

• Structure should have precedent
Precedent: ICE

remove protons = negative charge; non solid
right shift
Advantages of sheet-like EZ

- Precedent ✔
- Negative charge ✔
- Ring-like structures (270-nm absorption) ✔
- Able to accommodate helical structures ✔
- Large sheets eliminate Brownian instability ✔
unstable?

stable
Advantages of sheet-like EZ

• Precedent
• Negative charge
• Ring-like structures (270-nm absorption)
• Able to accommodate helical structures
• Large sheets eliminate Brownian instability
• Tight lattice keeps hydronium ions out
Crystalline zone keeps protons (hydronium ions) out

Battery charge remains separated
Advantages of sheet-like EZ

- Precedent
- Negative charge
- Ring-like structures (270-nm absorption)
- Able to accommodate helical structures
- Large sheets eliminate Brownian instability
- Tight lattice keeps hydronium ions out
Is the sheet-like honeycomb actually seen?
ATP synthase-subunit c

ordered hexagonal sheets of water

McGeoch and McGeoch
Interface 2008
Answer to Question #2

Is EZ physically distinct from bulk?

Yes

Layered honeycomb structure
Question #3

What charges the water battery?

(Incident radiant energy)
Exclusion Zone expands

infrared most powerful
Reduce incident radiant energy
Answer to Question #4
Energy?

EZ buildup powered by photonic energy...

Orders water
Charges the water battery
Possible Energy Flow in Universe

sun → water

generates heat (conventional)
Possible Energy Flow in Universe

- Sun
- Water
  - Generates heat (conventional)
  - Imparts energy for building order and separating charge
Possible Energy Flow in Universe

sun → water

- generates heat (conventional)
- imparts energy for building order and separating charge

Can this energy be harvested?
Energy can be harvested...
Polyacrylic acid gel

PAA gel

EZ

EZ
work done

system **MUST** absorb energy

water *transduces* light energy
E = H₂O
Question #4

Can EZ existence help explain everyday phenomena?

five examples
Charged aerosol droplets come together because of like-likes-like mechanism.
charged particle or molecule

liquid crystalline water
like-likes-like (Feynman)
Stability: attractive force = repulsive force
Particles stick together because of like-lies-like
2. Sandcastles
3. Ice
Ice Formation Paradox

Creating order commonly requires energy input

Creating order in ice requires energy withdrawal

Does ice violate general rule? No
ICE

Why?

intimately tied to EZ

remove protons $\rightarrow$ exclusion zone

protons + exclusion zone $\rightarrow$ ice

ice precursor
add protons
Is EZ really necessary for ice formation?
Freeze initiates in EZ
ice \((EZ + \text{protons})\)
Testing the proton rush...

replace microspheres with pH-sensitive dye
red color = many protons
cooling plate

room temperature

pH = 7

beginning to freeze

pH = 3

drop

freezing
Ice formation involves protons

$$EZ + \text{protons} = \text{ice}$$
Energy paradox resolved

*liquid crystal (EZ)*

ordered

energy from charge separation

energy from charge separation

*solid crystal (ice)*

more ordered

Increased order **DOES** require energy
Reverse: Melting

Melting should produce EZ water

Absorption spectra

melted water samples

270 nm = signature of EZ
4. Low friction
hydronium ions

hydrophilic material
Liquid layer known since Michael Faraday

$EZ + \text{protons?}$
Pressure should produce EZ + protons

ice

EZ
Pressing harder should give lower friction!
5. Biological applications
Low friction: why your joints don’t squeak

Should be filled with protons
Injury-induced swelling
sprain
No restraint to swelling
Ouch!
Swelling arises from buildup of large EZ layers
Obtaining energy: Can we get energy from the environment (like plants)
Might radiant energy help drive blood flow?

Laboratory studies: radiant energy drives the flow

Might radiant energy help drive blood flow?
Might absorbed external energy assist blood flow?
Radiant energy may help power cells

Cells are full of EZ water

Separated charges drive reactions
EZs Central for Biological Function

Anesthetics (impair function): diminish EZ size

Aspirin (enhance function): builds EZ

EZ water central to function
Practical Use of Radiant Energy?
Getting energy from sunlight and water

EZ water  bulk water
Obtaining drinking water

hydrophilic material

contaminated water

Excluded stuff
Excluded salt?

EZ
Main Conclusions
WATER’S PHASES

- ice
- EZ
- water
- vapor
Where we’ve come...

chemical

health

biological

filtration

electricity

salination

food

radiant energy

weather
Fun to study...
Why only one cloud when the vapor rises all over?
Water forming a bridge?
Water is a dipole.
Initial experimental approach:

Test for solute distribution
Question #1: Generality

- Surfaces
- Solutes
Question #1: Generality

- Surfaces: hydrophobic vs. hydrophilic
- Solutes
Hydrophilic gel surfaces do exclude

- Polyvinyl alcohol
- Polyacrylic acid
- Polyacrylamide
- PolyHEMA
- Collagen
- Agarose
Monolayers exclude
Generality?

• Surfaces: Numerous hydrophilic surfaces show exclusion
• Solutes
Generality?

• Surfaces: Numerous hydrophilic surfaces show exclusion
• Solute
Excluded particles

- Polystyrene microspheres
- Silica microspheres
- Erythrocytes
- Bacteria
- Colloidal gold (4 - 7 nm)
- Quantum dots
- Ash, dirt
solutes...
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Takehome message:
the shaky edifice of science
UV-VIS absorption spectrum
Another charged battery in water...
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Question #3: Can crystalline water explain counter-intuitive anomalies?

What behavior do we expect from a crystal?
Crystalline elements stick together
gelatin dessert (95% water)...

Why doesn't the water dribble out?
Crevices are filled with liquid crystal

Crystalline water is gel-like
Crystalline water grows at air-water interface
Clear zone similar to EZ
Negative potential
Thick gel-like band
Many structured layers create high surface tension
water
water
water
Crystals can be pretty stiff
Water structure stiff enough to keep bridge from collapsing
Answer to Question #3

Yes

Liquid crystalline water explains many anomalies
It explains why water battery charges remain separated
Near infrared illumination

With illumination – 5 min

temperature rise < 1°
Evidence that incident energy **MUST** be absorbed

*Converted to work*
A charged battery in water
Evidence that exclusion-zone (EZ) water is physically different from bulk water

- EZ water molecules more constrained (NMR)
- EZ molecules more stable (infrared radiation)
- EZ has negative charge (potential measurement)
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including chemical reactions in cells...
Possible things to include
Evaporation – see older talks
   Anesthetics + aspirin
   Freezing
   Lubrication/friction – see Vancouver extra session
Practical Use of Radiant Energy?
Getting energy from sunlight and water
hydrophilic material

contaminated water

Excluded stuff
Excluded salt?

EZ
Water’s Fourth Phase

Understanding the gentle beauty of nature
Effect of Wavelength on EZ Size

(5 min exposure)

- **Control**
- **Visible** (low incident intensity)
- **Infrared**
Charged aerosol droplets come together because of like-likes-like
Injury-induced swelling

• EZ water builds up next to protein surfaces
• Tendency to swell tissue
• Cross-links btw. proteins restrain swelling
• Injury tears cross-links
• EZ water builds unrestrained; tissue swells
EZ Size Modulates Function

Impairment - anesthetics: diminish EZ

Enhancement - aspirin: builds EZ

EZ water central to function