

E = H₂O: The Secret Life of Water

Presented in the International Embryo Physics Course
<http://www.embryophysics.org>

July 7, 2010

By

Gerald H. Pollack

Department of Bioengineering, University of Washington
ghp@u.washington.edu



E = H₂O

The Secret Life of Water

Gerald H. Pollack, PhD
University of Washington
Seattle, Washington

the edge



A scenic coastal landscape featuring a large, rugged cliff made of layered rock. The ocean in the foreground has white-capped waves crashing against the rocks. In the upper left, there are small buildings perched on the cliff edge. The sky is clear and blue. A red, semi-transparent rectangular box is overlaid on the image, containing the text "the rest".

the rest

to begin....

Things we *ought to know*
about water
but don't...



Why does water vapor coalesce
into discrete units?



The background of the image is a dark, cloudy night sky. Several bright, branching lightning bolts are visible, striking from the clouds towards the ground. In the lower right foreground, the dark silhouettes of evergreen trees are visible against the lighter sky. The overall atmosphere is one of a powerful natural event.

How can water sustain
huge charge separation?

A close-up photograph of several bright red, translucent gelatin dessert cubes stacked together. They have a slightly textured surface and appear to be melting or softening, with some liquid visible at the bottom.

gelatin dessert (95% water)...

Why doesn't the water dribble out?



M Nydén, N Lorén, M Rudemo and M Kvarnström, Chalmers, Sweden

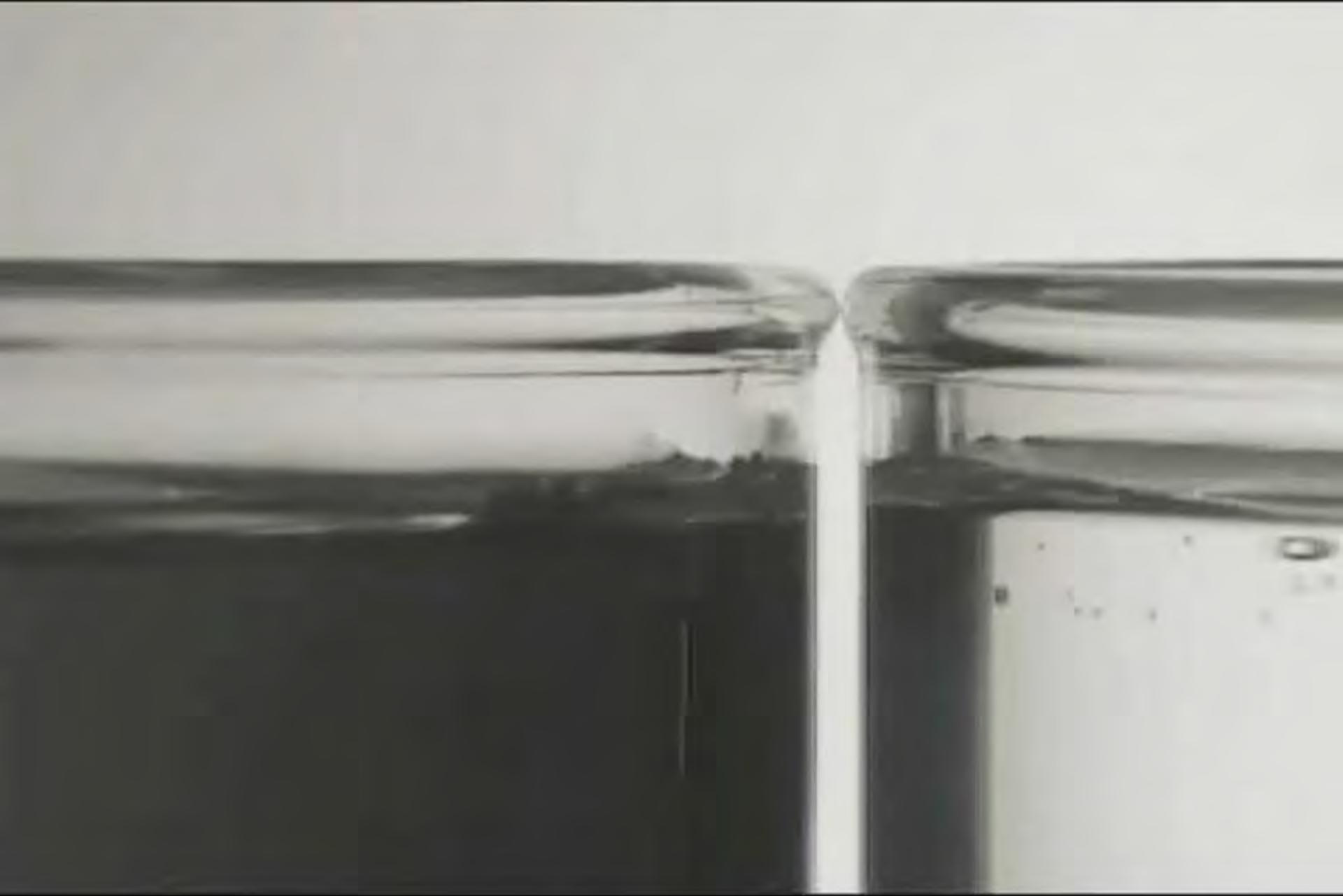
another unknown...







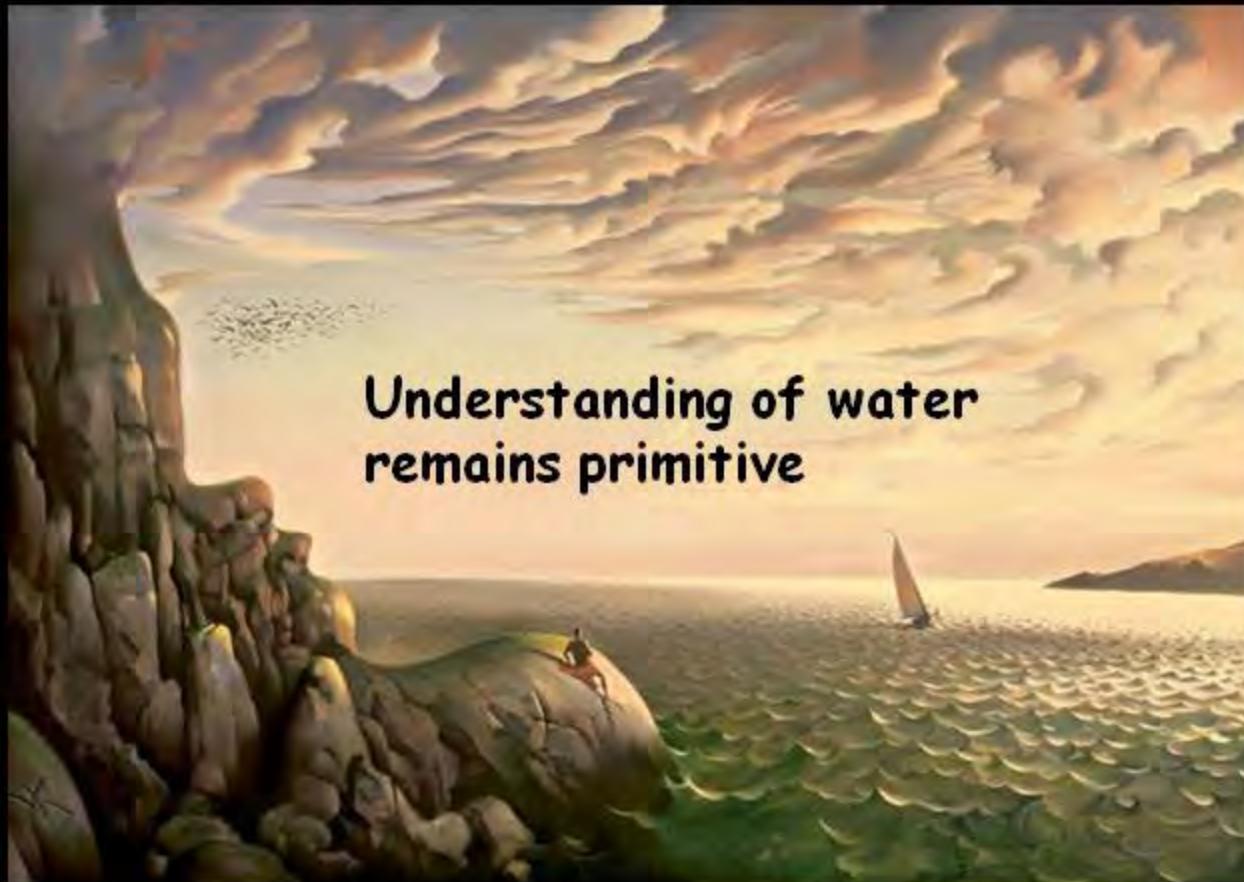
How can a few molecular layers create tension so high?



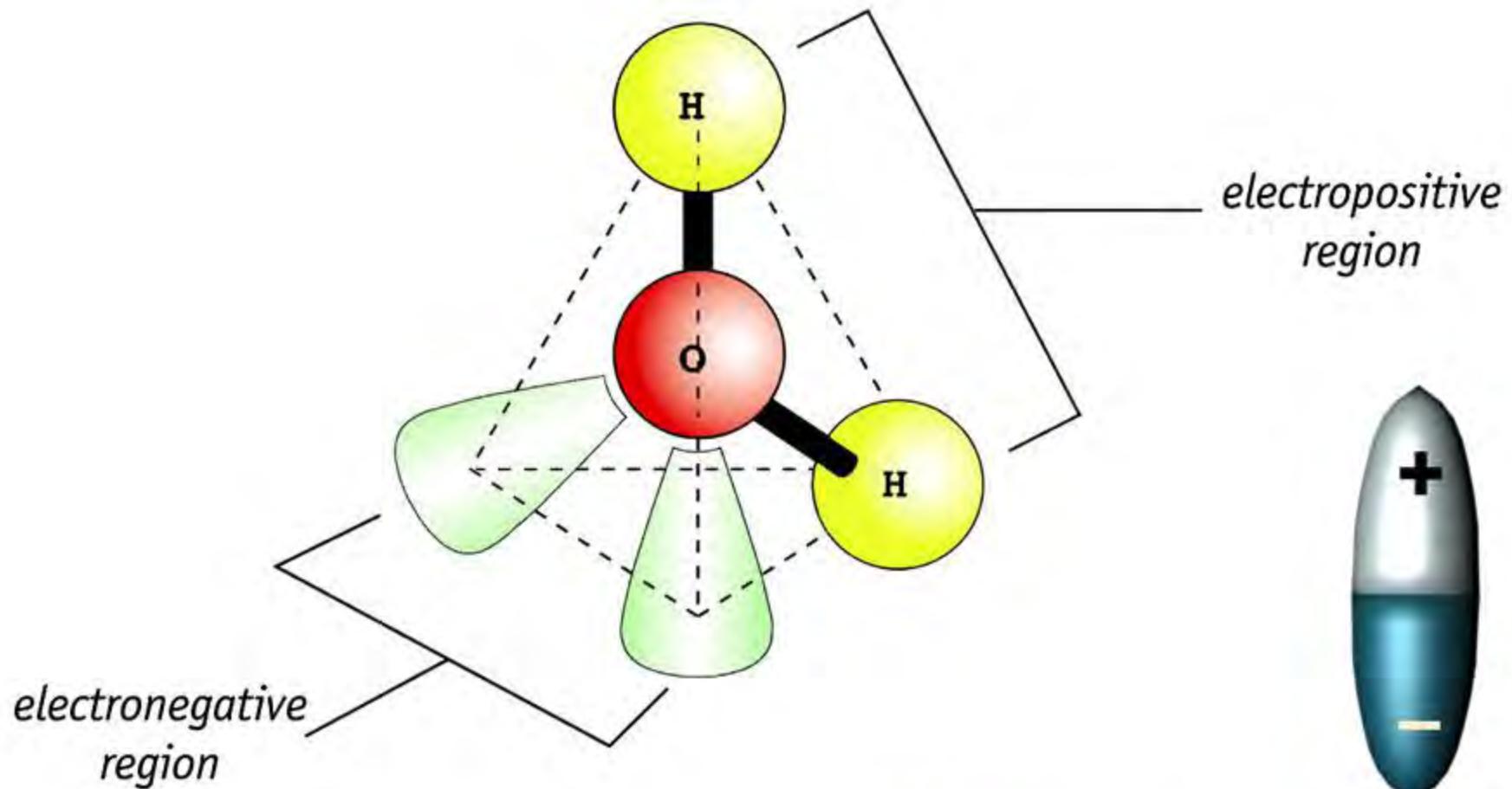
Elmar Fuchs, Wetsus



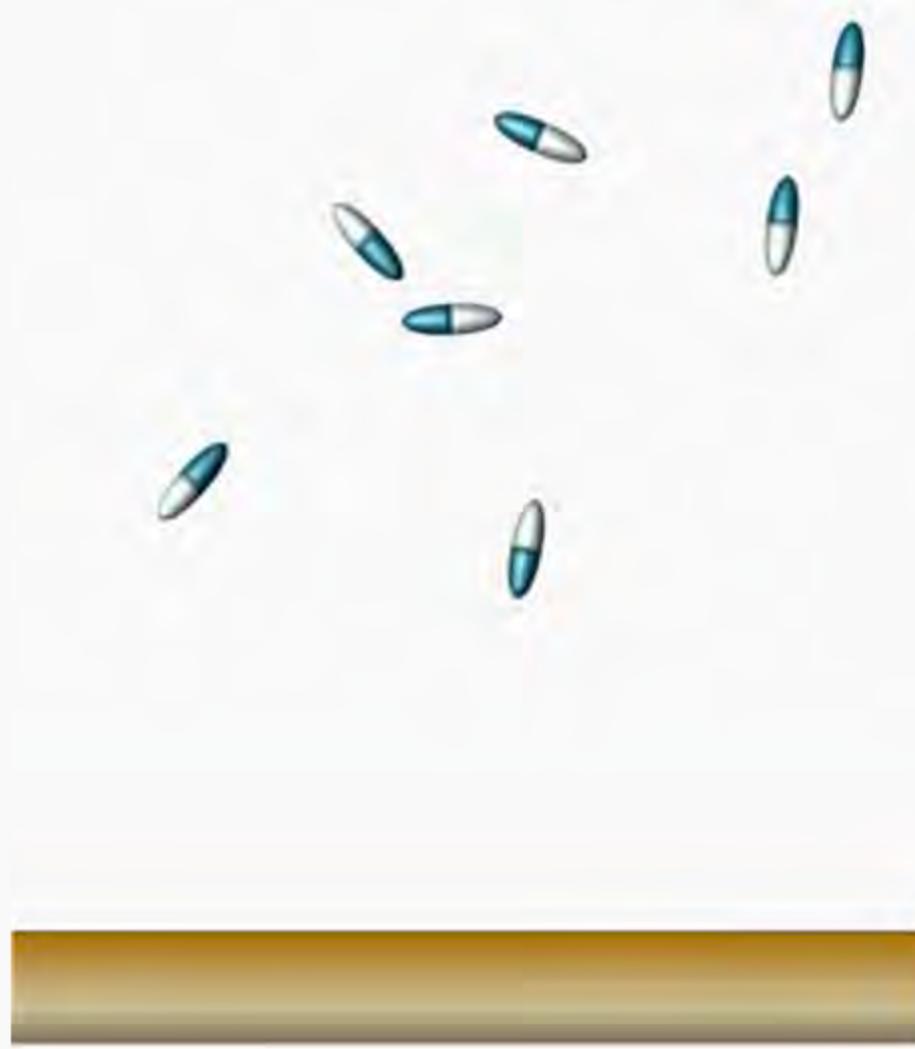
Many counterintuitive observations
Many unresolved mysteries...



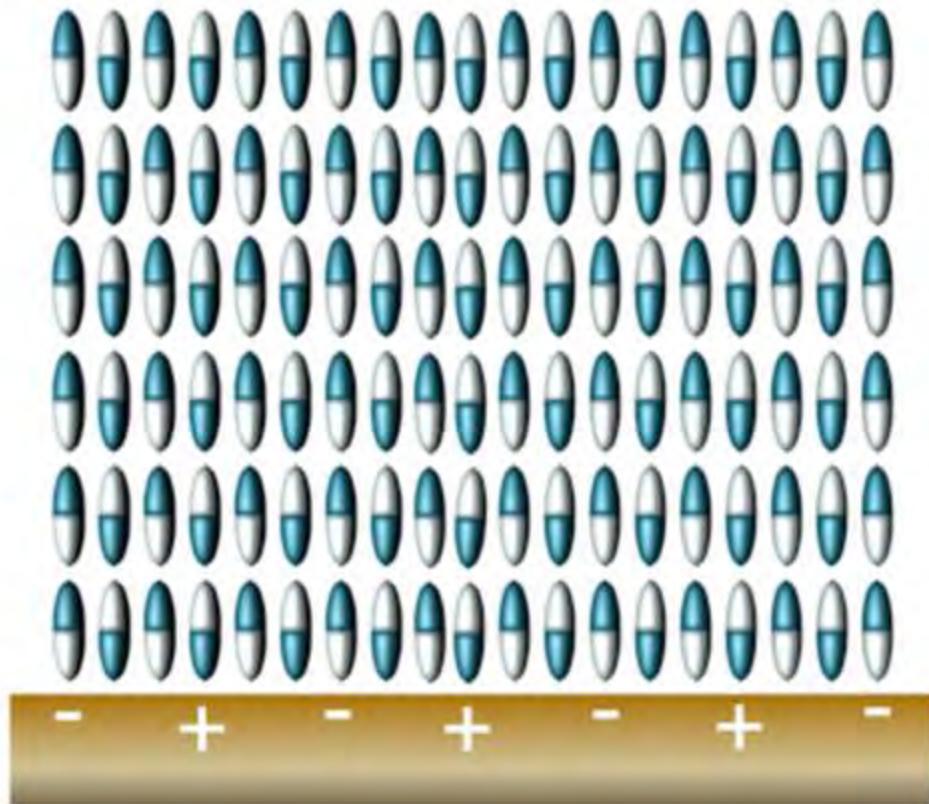
Understanding of water
remains primitive



Water is a *dipole*

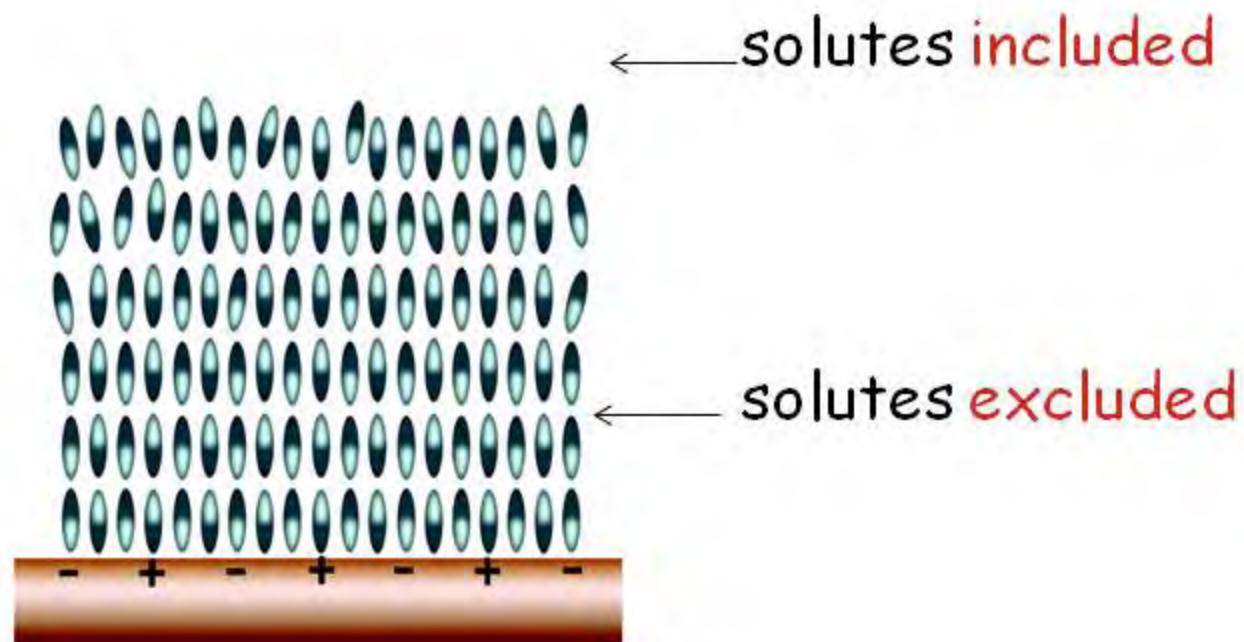


i. klyuzhin



Initial experimental approach:

Test for solute distribution



PVA
gel

10 μm

PAA gel

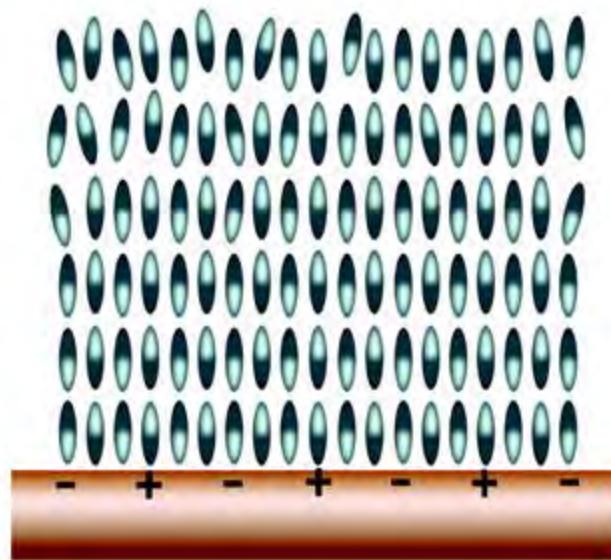
Exclusion zone
(EZ)

200 μm

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)

Seems to imply very long range ordering



May provide fresh basis for understanding of water

Getting to the basis...

Questions to Answer

- Is the exclusion phenomenon general?
- Does it really arise from water ordering?
- Can water ordering explain anomalies?
- What energy creates this order?
- Might these findings apply more broadly?

Question #1: Generality

- Surfaces
- Solutes

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

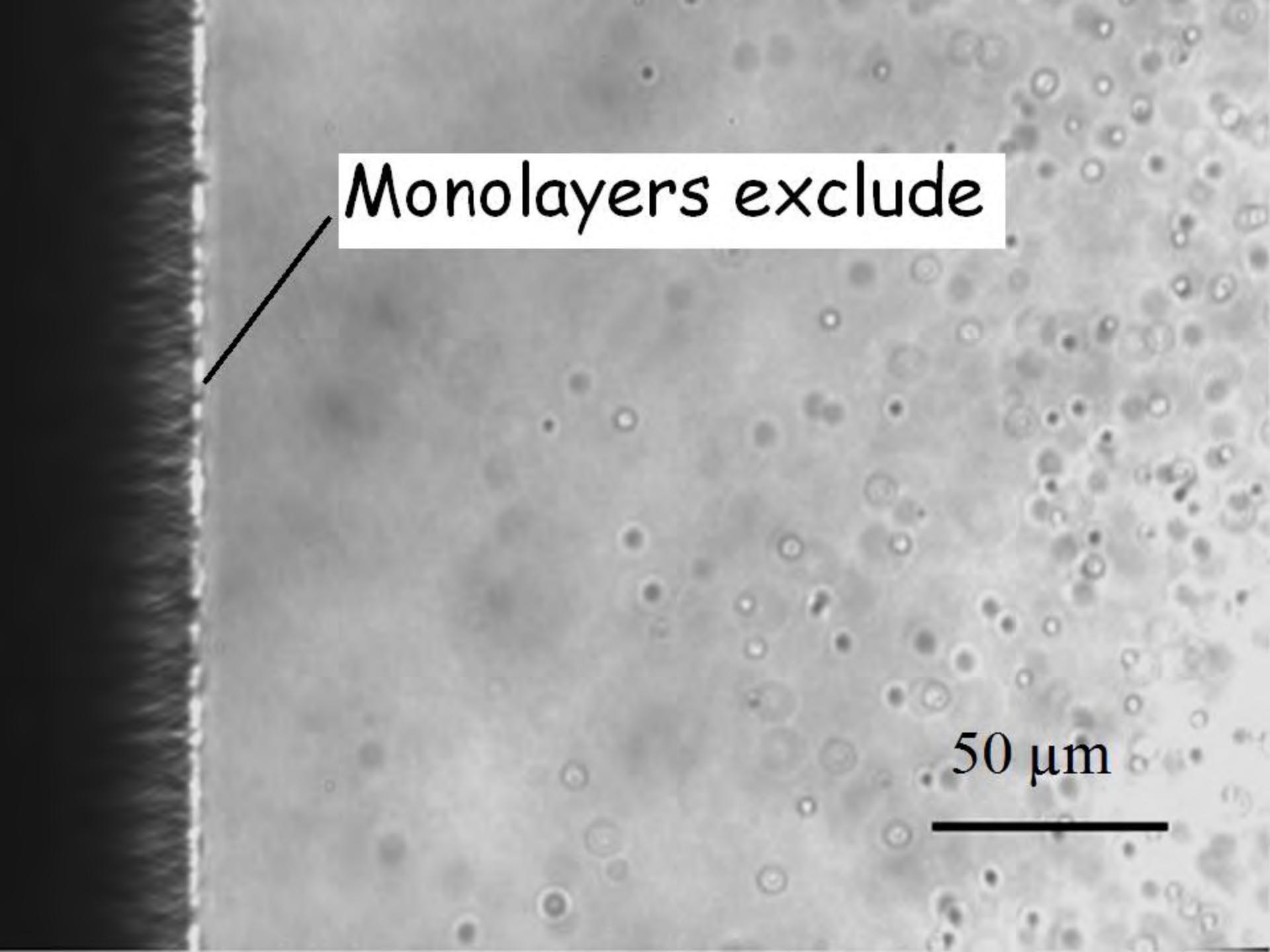
Biological specimens exclude

microsphe res

muscle



200 μm

A grayscale micrograph showing a dense layer of small, circular particles on the right side. On the far left, there is a vertical strip with a distinct, wavy or ribbed texture, likely representing a substrate or a different material. A white rectangular box is overlaid on the image, containing the text "Monolayers exclude". A black line points from the bottom-left corner of this box towards the vertical textured strip.

Monolayers exclude

50 μm

A horizontal black line representing a scale bar, positioned below the text "50 μm".

Polymers exclude

200 μm

Nafion

Microspheres

Generality?

- Surfaces: Numerous **hydrophilic** surfaces show exclusion
- Solutes

Generality?

- Surfaces: Numerous hydrophilic surfaces show exclusion
- Solutes

Excluded particles

- Polystyrene microspheres
- Silica microspheres
- Erythrocytes
- Bacteria
- Colloidal gold (4 - 7 nm)
- Quantum dots
- Ash, dirt

Excluded solutes...

fluorophore-
labeled
albumin

0 s

Nafion

50 μ m

10 s

50 μ m

360 s

50 μ m

1000 s

50 μ m

Smaller solutes excluded...

pH-sensitive dye(s)

H^+

H^+

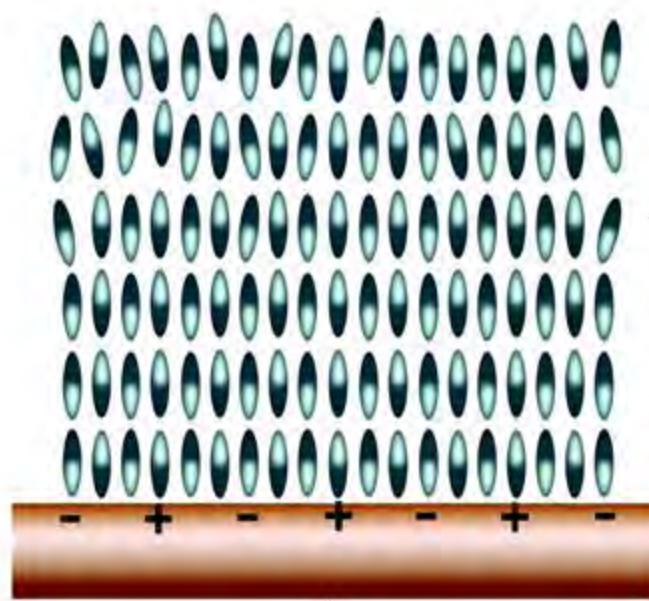
H^+

Nafion

dye excluded

1 mm

Answer to Q1: Generality

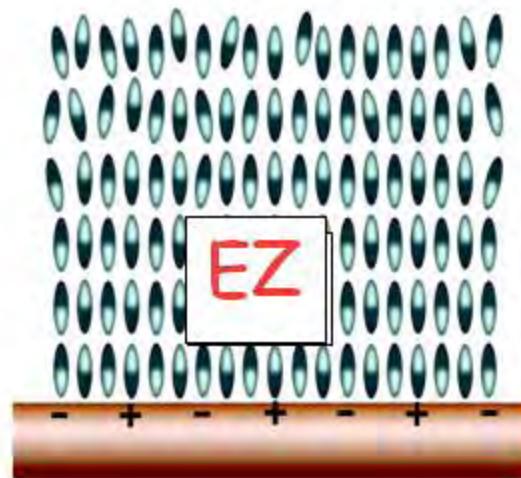


← many solutes excluded

many hydrophilic surfaces
generate exclusion zones

Question #2

Is this zone
physically different
from bulk water?



Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR -- tests molecular freedom

gel
gel
*

F 5.0 kg

W 710
L 581

Date: 6 Jun 2003

Time: 2:08

PVA gel

60 μm



water

mm

0

t2,d,t1: 1

Dark means
molecules
can't easily
rotate

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR -- EZ water molecules constrained

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation -- temperature x emissivity

Infrared radiation image



E. Khijniak

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation -- EZ structure more stable

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci.*, 127: 19-27, 2006

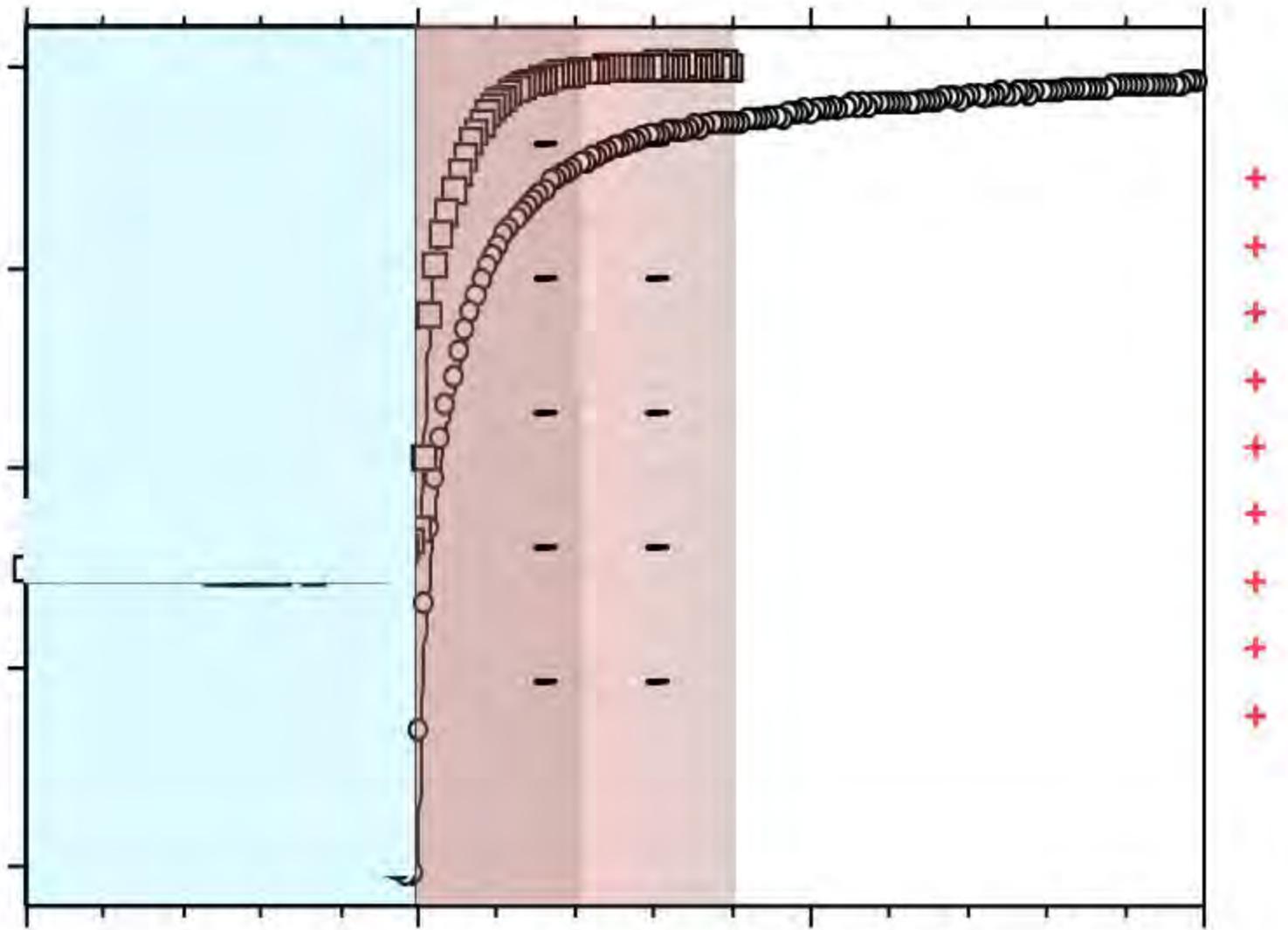
Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

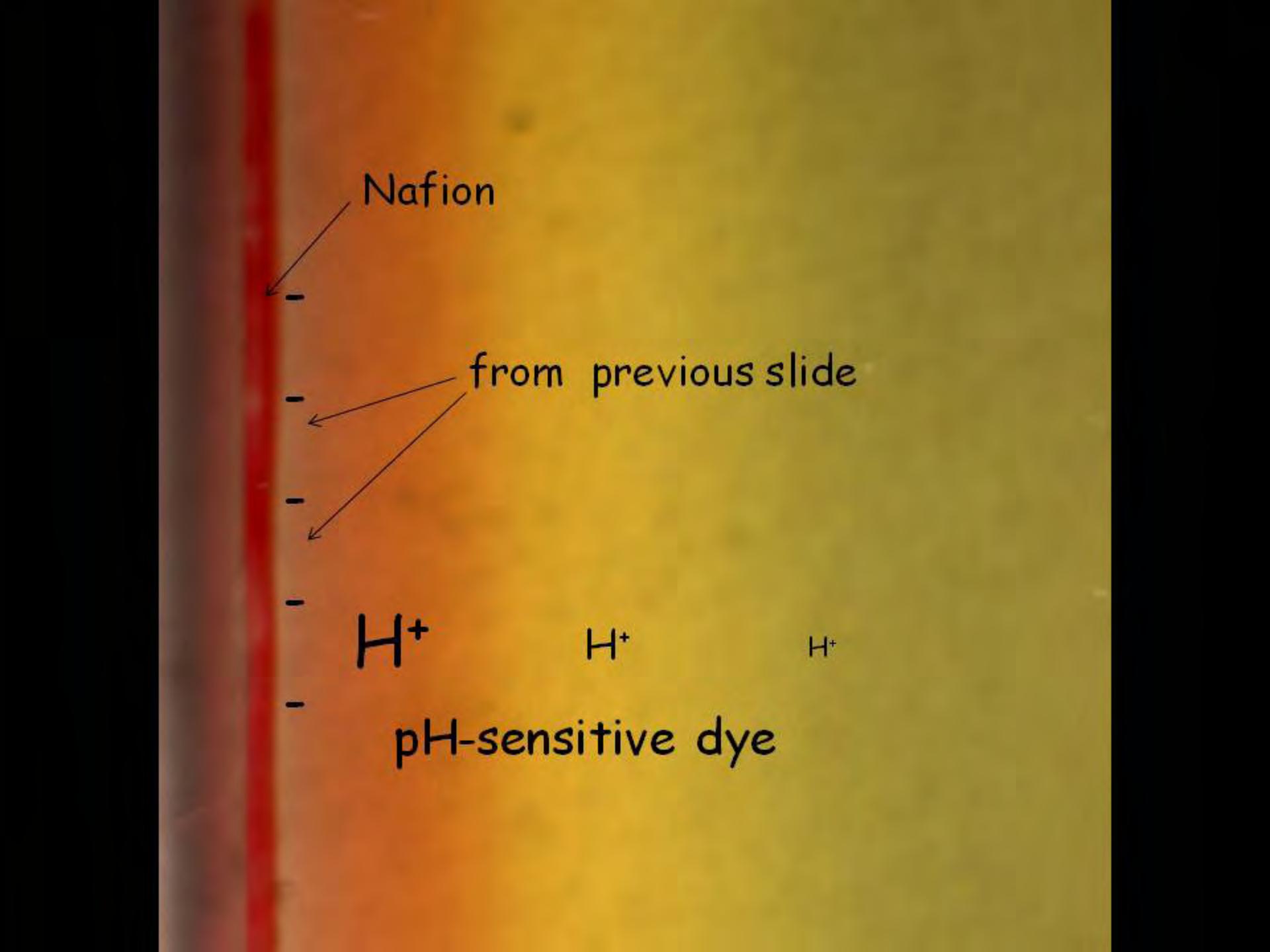
Zheng et al., *J. Coll. Interface Sci.*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential -- gradients imply charge separation





Nafion

from previous slide

H^+

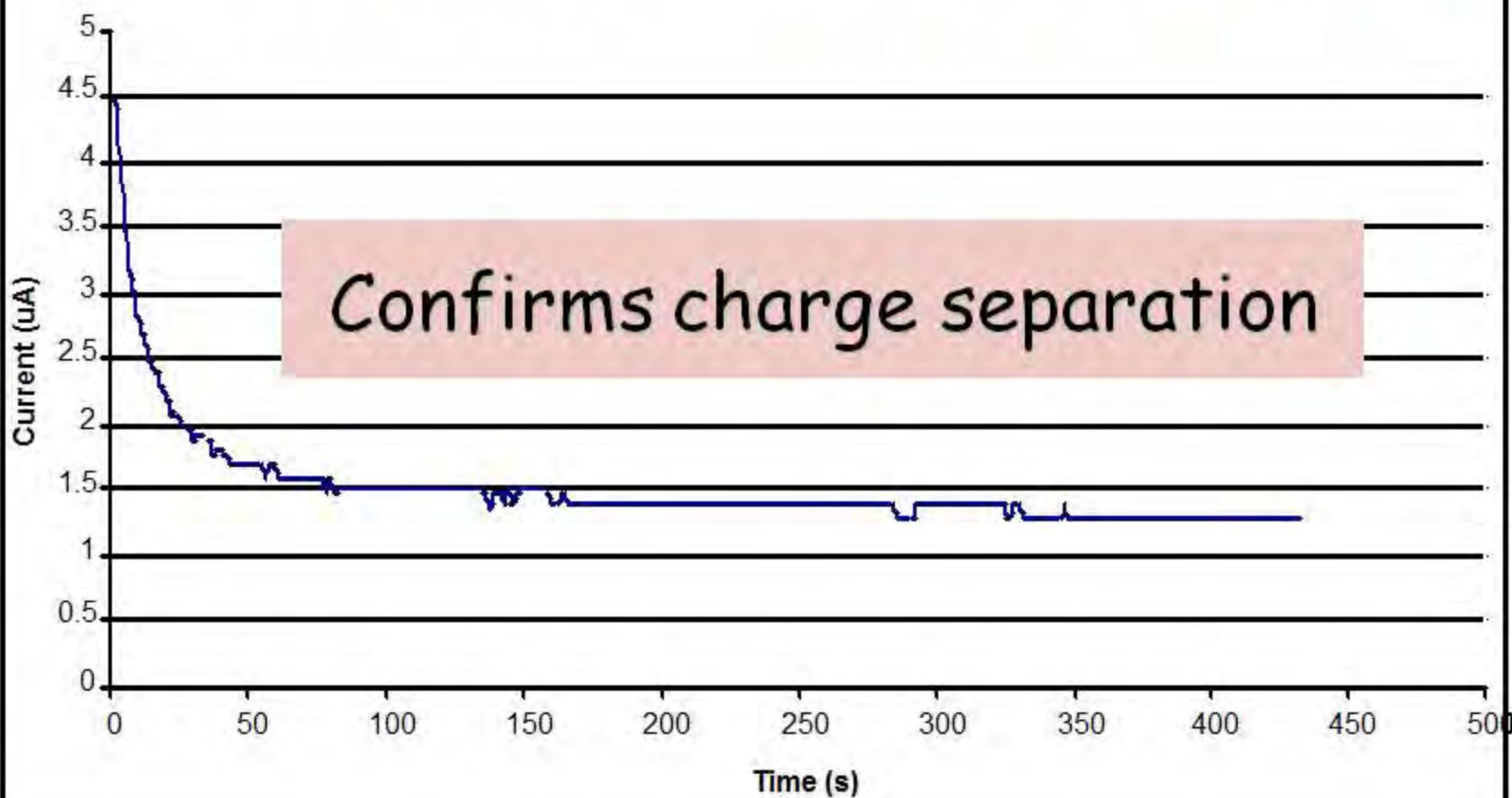
H^+

H^+

pH-sensitive dye

Time

Current flow between exclusion zone and water beyond



exclusion

beyond

surface area

exclusion

beyond

A charged battery in water



Another charged battery in water...



Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential -- EZ has negative charge

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

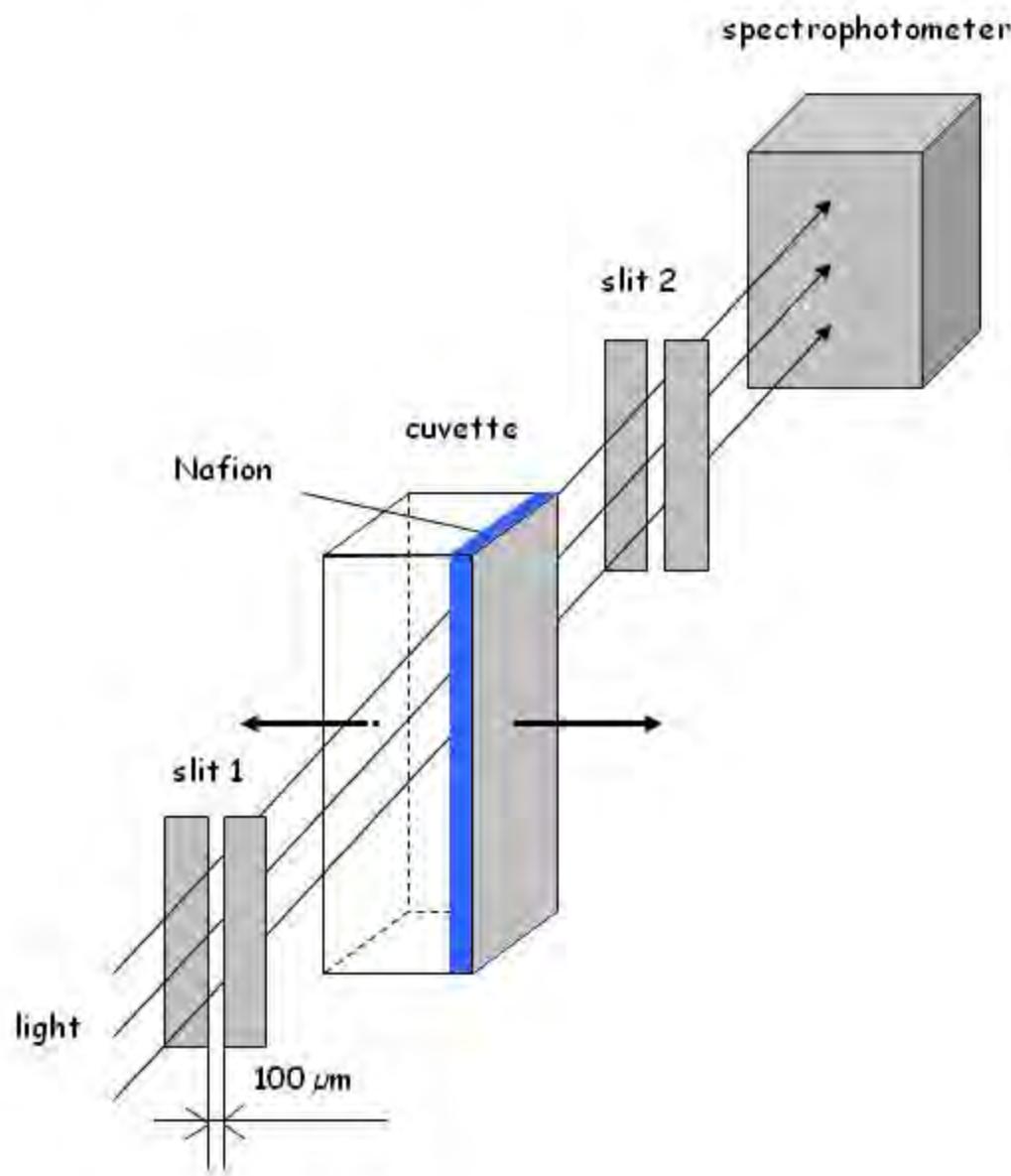
NMR

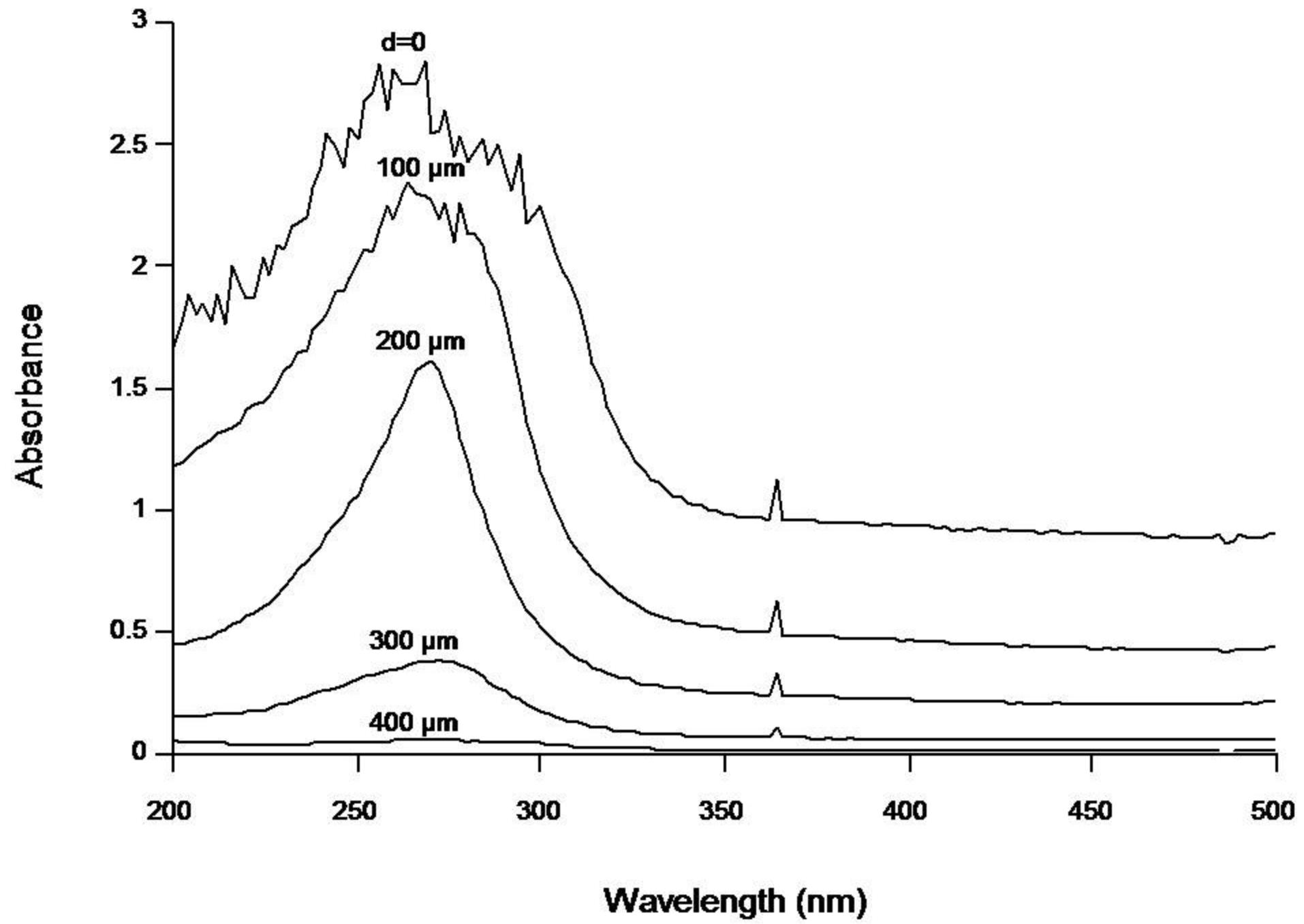
Infrared radiation

Electrical potential

Light-absorption spectrum - distinguishes electron excit. states

UV-VIS absorption spectrum





Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential

Light-absorption spectrum- EZ absorbs at 270 nm

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

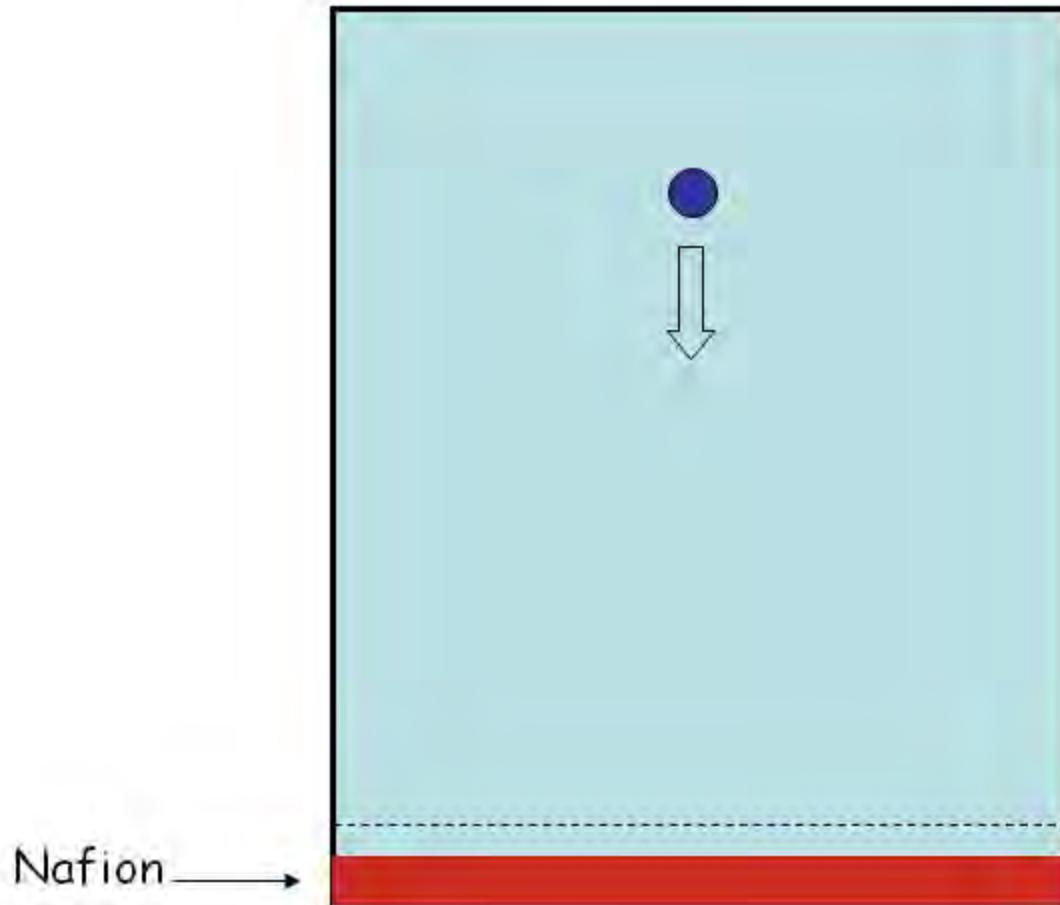
Infrared radiation

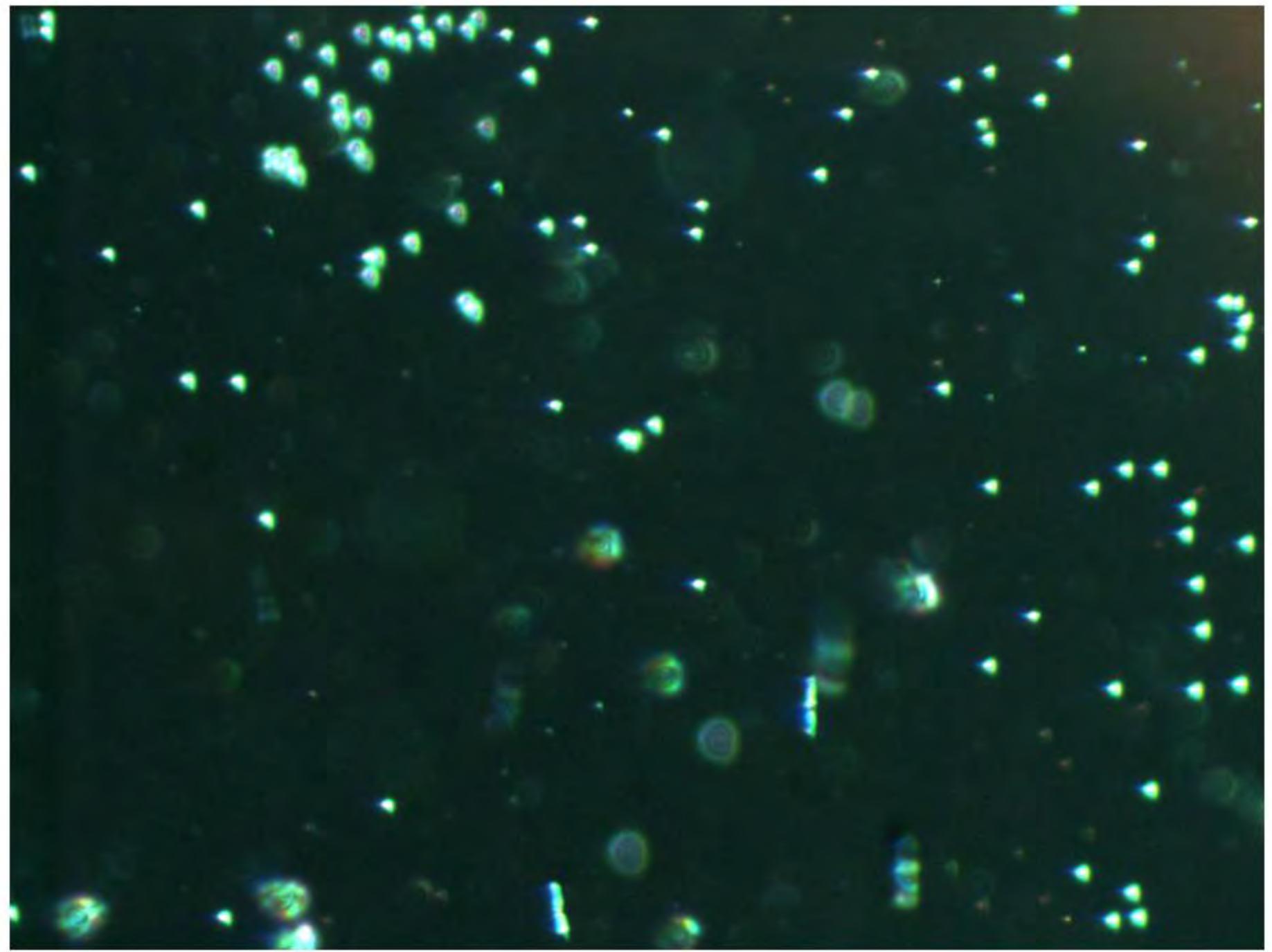
Electrical potential

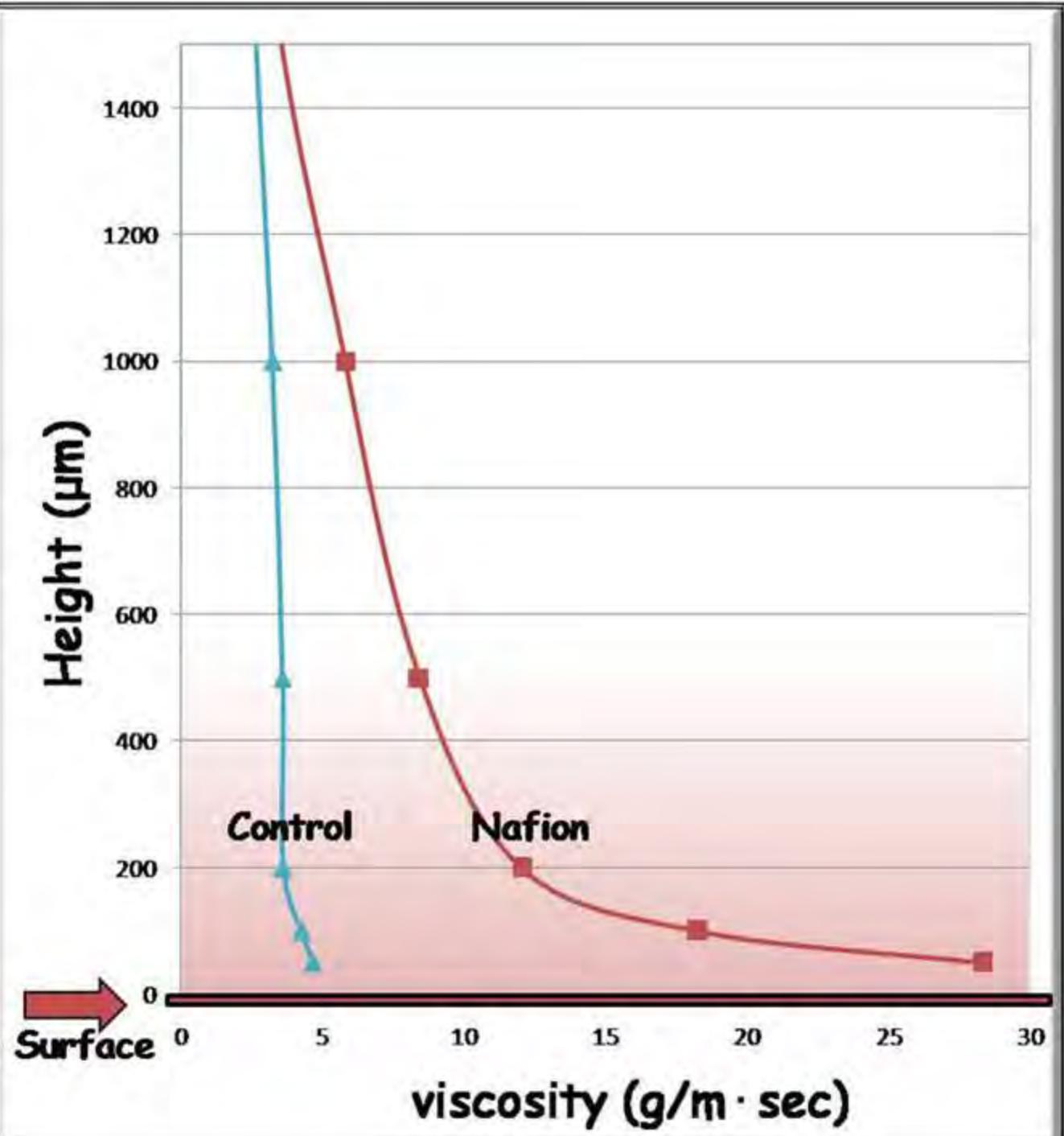
Light-absorption spectrum

Viscosity (falling ball viscometer) - higher viscosity?

Falling ball viscometry







Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential

Light-absorption spectrum

Viscosity (falling ball viscometer) - EZ is more viscous

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential

Light-absorption spectrum

Viscosity (falling ball viscometer)

Polarizing microscopy -- are molecules oriented?

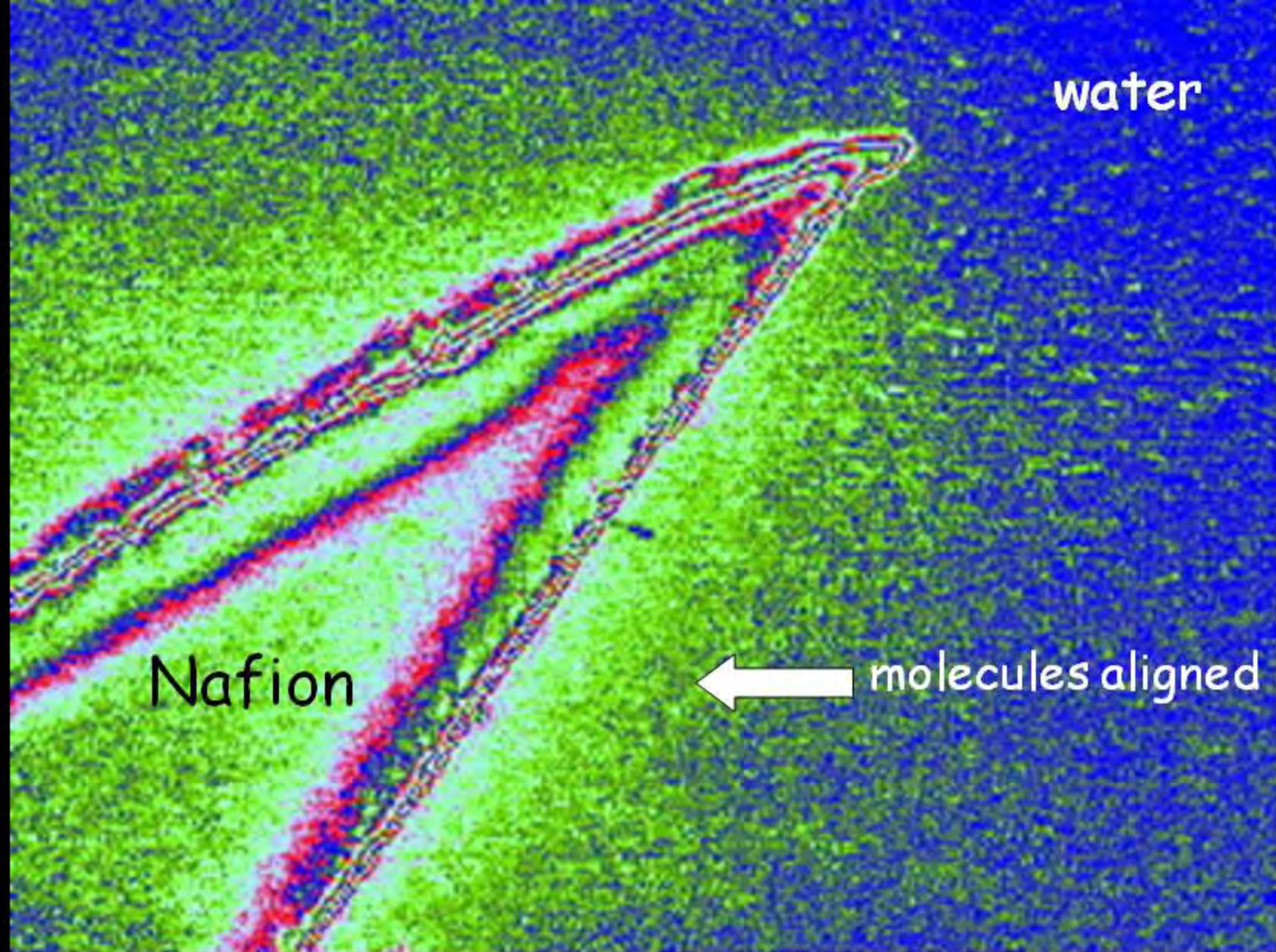
Polarization micrograph

Agarose gel

water

← molecules aligned

50 µm



Collaboration with Werner Kaminsky, UW Dept. Chemistry

200μ

A scanning electron micrograph showing a textured, layered surface. Several diagonal lines point from numerical labels to specific features on the surface. The labels are: 0.4 / 141, 0.9 / 141, 1.5 / 137, 0.7 / 142, 0.3 / 135, and 0.9 / 135. The word "Nafion" is written in red text at the bottom right.

0.4 / 141
0.9 / 141
1.5 / 137
0.7 / 142
0.3 / 135
0.9 / 135

M. Shribak (Woods Hole)

Nafion

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential

Light-absorption spectrum

Viscosity (falling ball viscometer)

Polarizing microscopy -- EZ molecules aligned

Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential

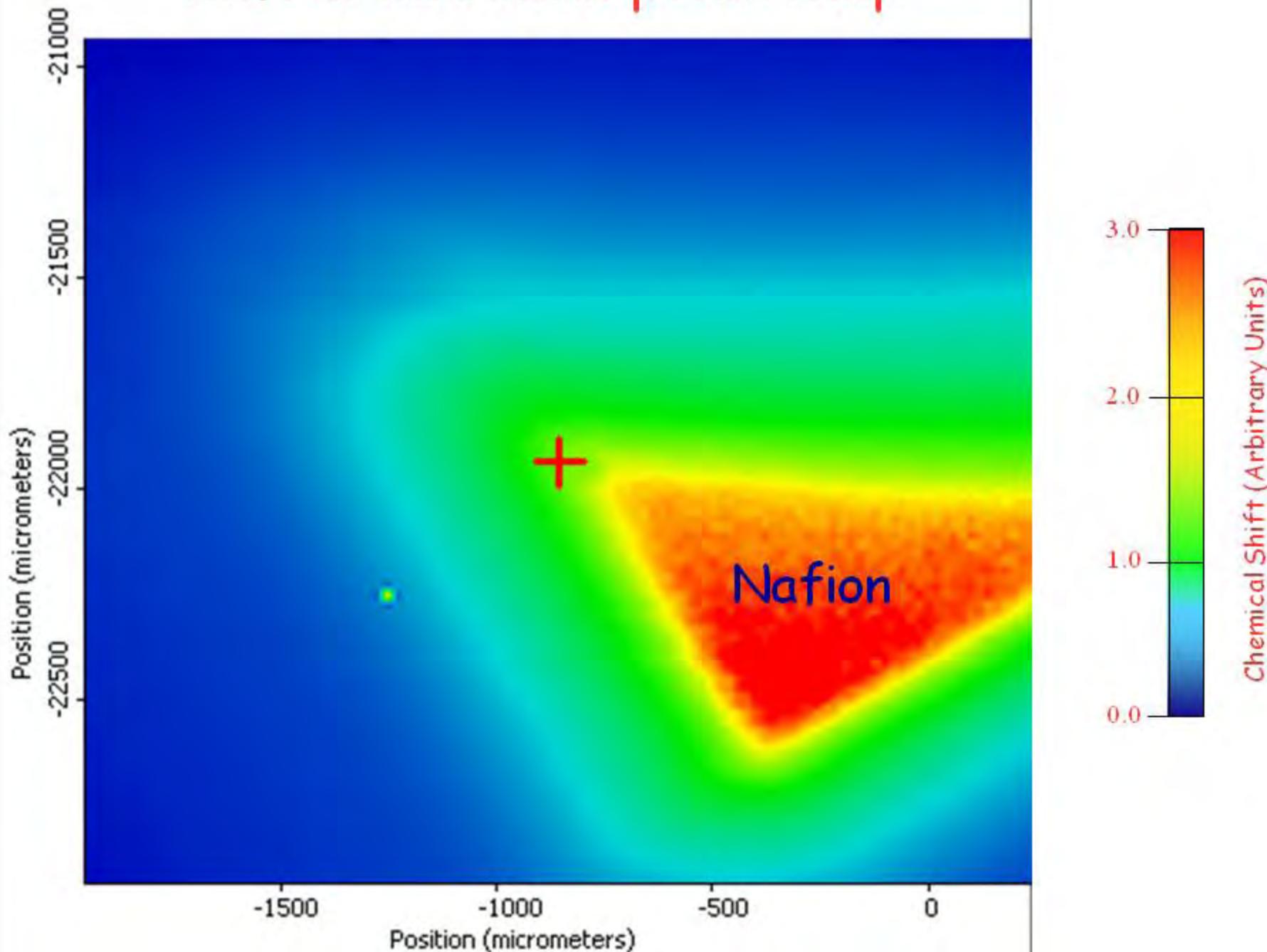
Light-absorption spectrum

Viscosity (falling ball viscometer)

Polarizing microscopy

Infrared absorption - molecular structure different?

Infrared Absorption Map



Evidence that EZ is physically different

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009.

NMR

Infrared radiation

Electrical potential

Light-absorption spectrum

Viscosity (falling ball viscometer)

Polarizing microscopy

Infrared absorption - molecular structure different

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)

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009

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)
- 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)

Zheng et al., *Adv. Colloid and Interface Sci*, 127: 19-27, 2006

Chai et al., *J Phys Chem*, 112: 2242 - 2247, 2008

Zheng et al., *J. Coll. Interface Sci*, 332: 511-514, 2009

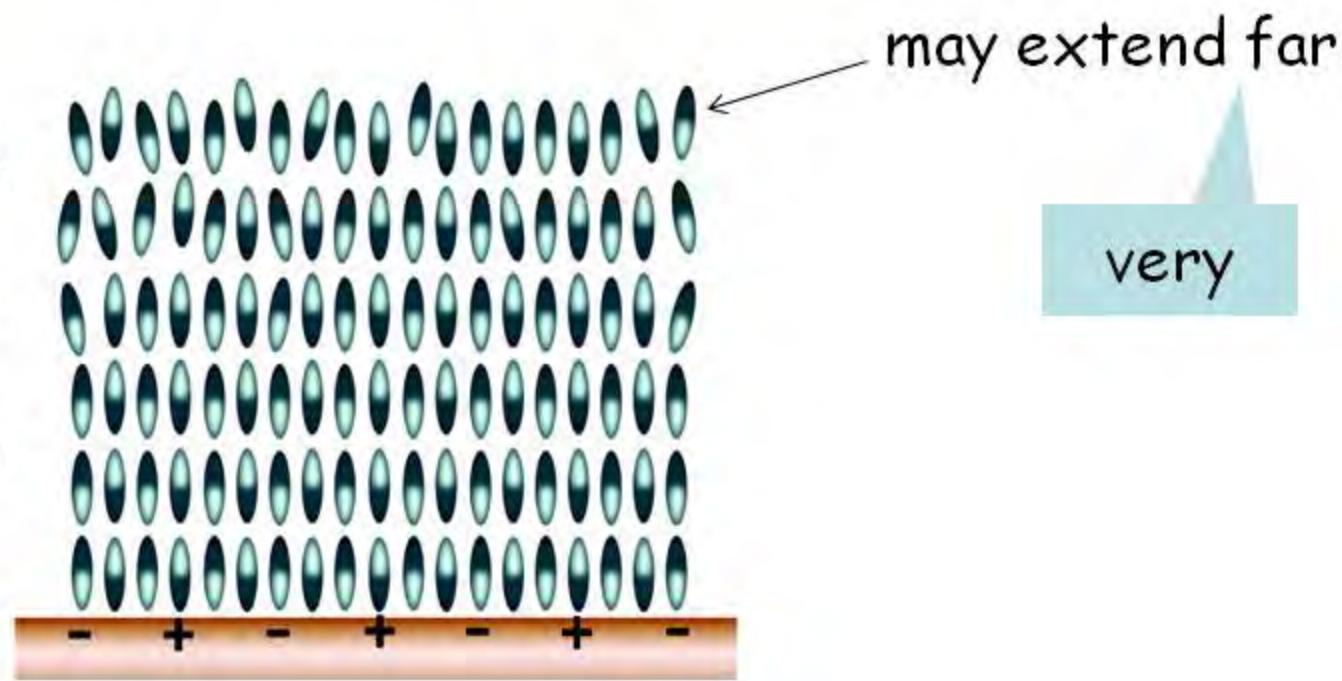
Summary, so far

Liquid crystalline

Negative charge

Excludes solutes

(Non-dipolar?)



Fourth phase of water?

(Sir Wm. Hardy, 1912)

The Depth of the Surface Zone of a Liquid*

J. C. HENNIKER

Stanford Research Institute, Stanford, California

TABLE OF CONTENTS

	Page
I. Introduction	321
II. Direct Evidence of Deep Surface Orientation...	324
A. Refractive Index.....	325
B. Multimolecular Adsorption.....	325
C. X-Ray Diffraction.....	324
D. Electron Diffraction.....	325
E. Surface Viscosity.....	325
F. Adhesion.....	326
G. Extent of Orientation.....	326
H. Cohesive Strength.....	326
III. Indirect Evidence of Deep Surface Orientation..	327
A. Electrical Conductance of Oils	327
B. Dielectric Constant	327
C. Multimolecular Adsorption.....	327
D. X-Ray Diffraction.....	328
E. Schiller Layers.....	328
F. Soap Films.....	329
G. Mechanical Strength of Liquid Films.....	329
H. Flow in Narrow Tunnels.....	330
I. Adhesion.....	330
IV. Circumstantial Evidence of Deep Surface Orientation.....	332
A. Rigidity.....	325
B. Elasticity.....	326
C. Viscosity.....	327
D. Vapour Pressure.....	324

sions of a monolayer of oriented molecules. The recognition of this truth came at the same time as the rejection of the assumption of classical physics that direct intermolecular forces are of long range, of the order of one micron. The long range forces were abandoned in favor of electrical forces directly effective for only a few angstrom units. Subsequently attention has been so focused on the dominant role of the outermost layer of molecules that the inevitable polarizing effect of this oriented layer upon the molecules immediately adjacent to it has been overlooked.

The fact that liquid molecules are already close-packed and that they are therefore readily oriented

"... hundreds of microns in depth"

was described by von Smekal in 1926. Quite another kind of orientation is possible in chain-like structures such as fluids and solids, namely, a strain transmitted from molecule to molecule. It is this kind of orien-

tation which may be influenced by a small value,

either of the molecule

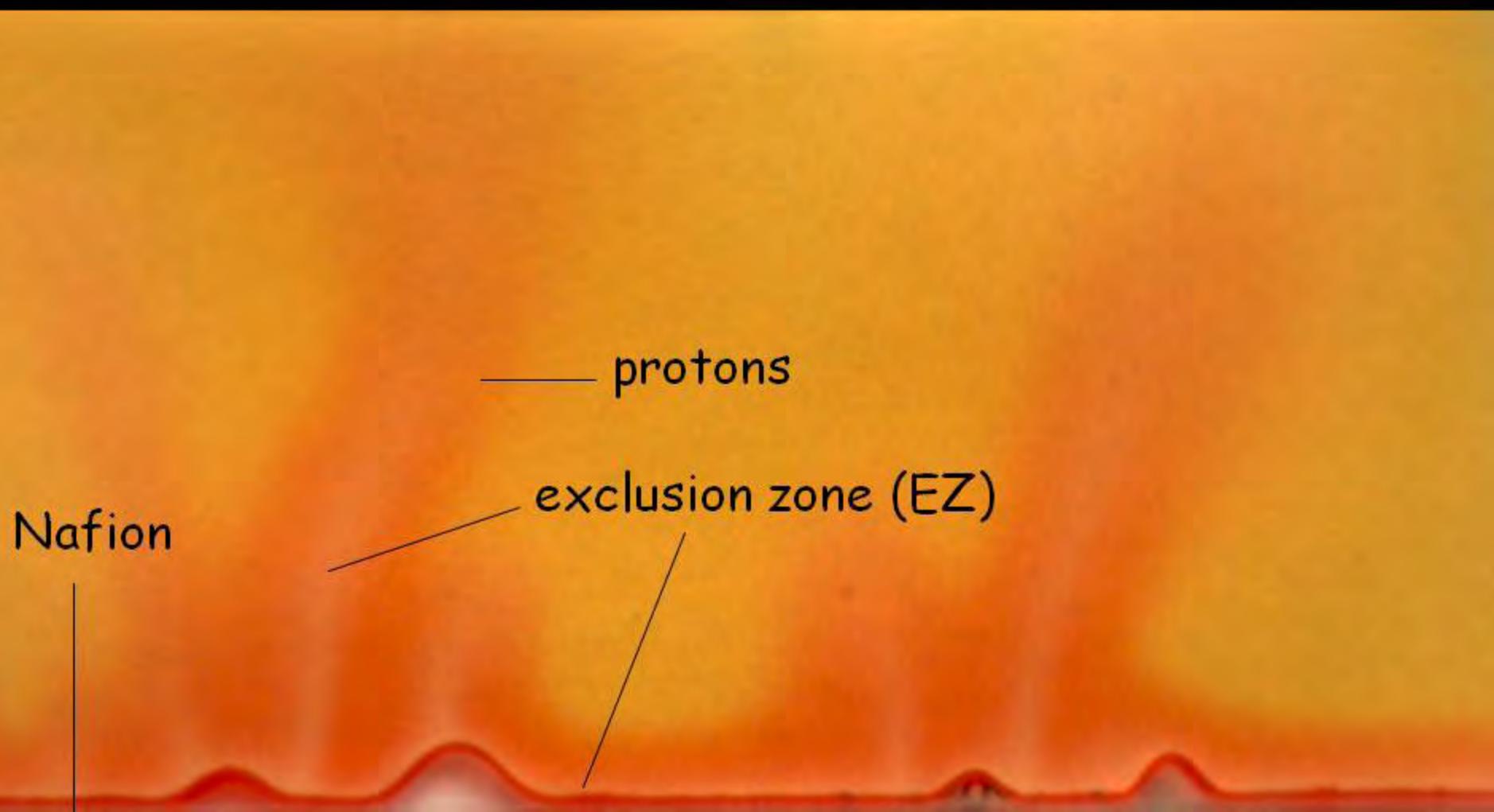
Answer to Question #2
Is EZ physically distinct from bulk?

Yes
Liquid crystalline

Question #3: Can crystalline water explain counter-intuitive anomalies?

What behavior do we expect from a crystal?

Crystals can grow



Crystalline elements
stick together

Crevices are filled with liquid crystal

Crystalline water is gel-like

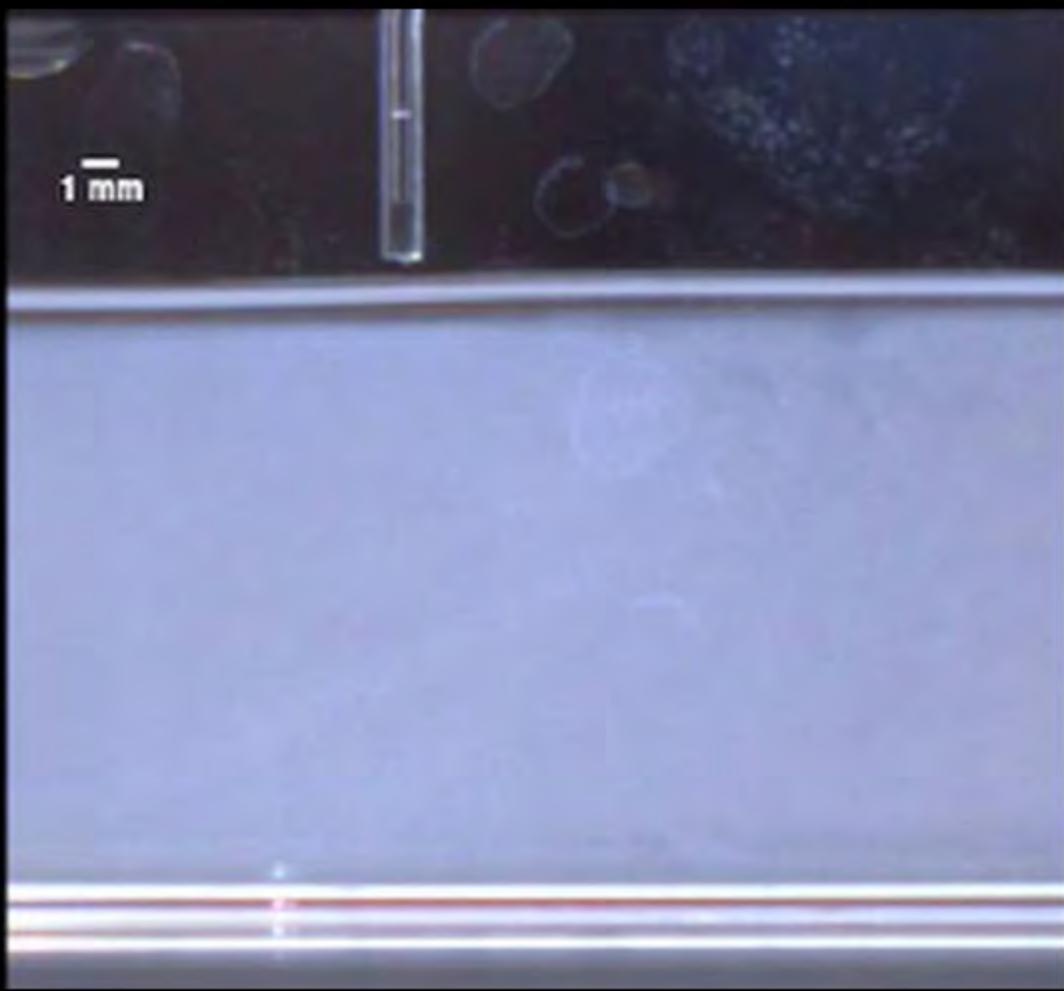
Gel-like water fills your cells

Crystalline water grows
at air-water interface

air meniscus clear zone water + microspheres



Clear zone similar to EZ
Negative potential
Thick gel-like band





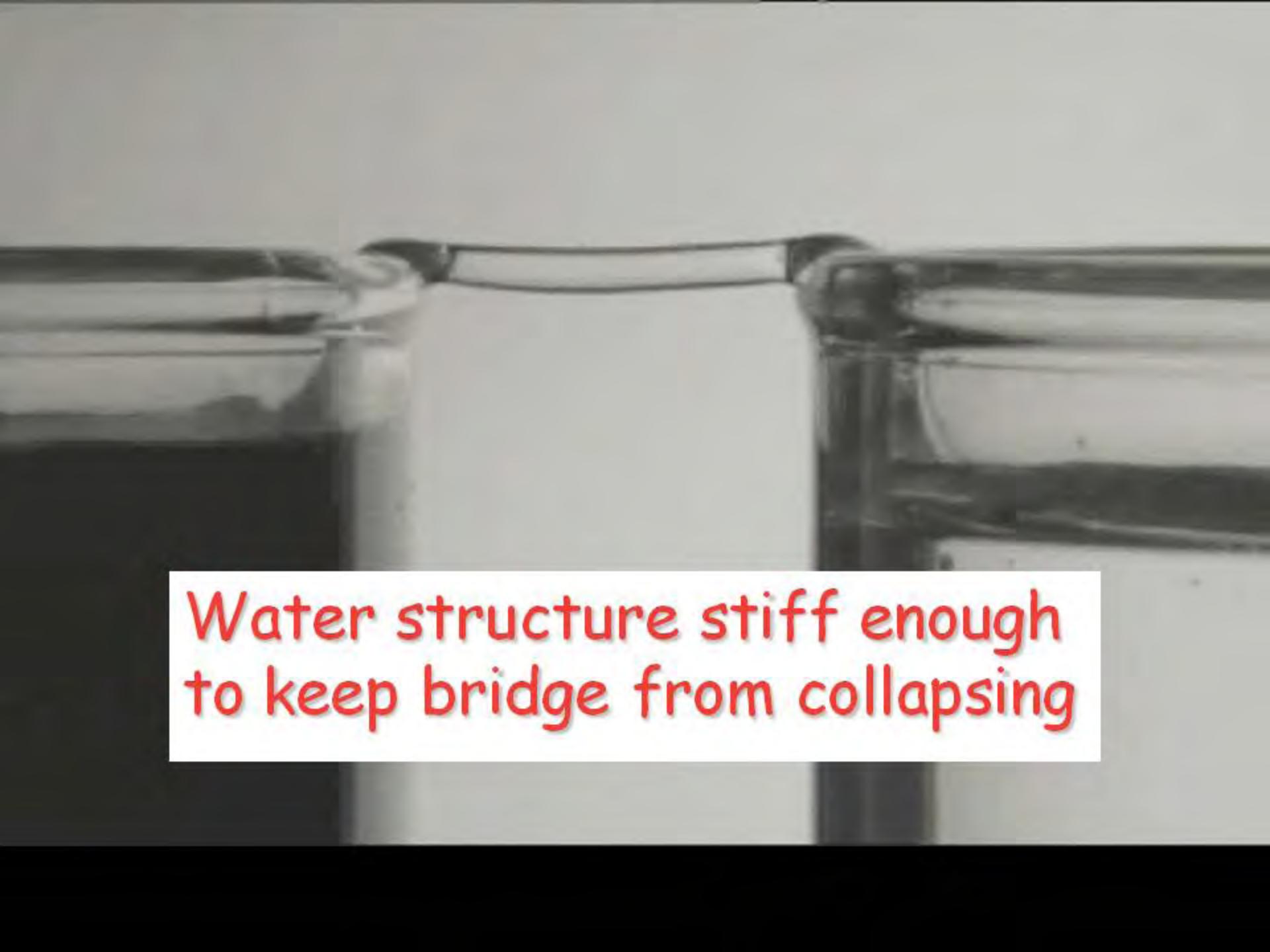
Many structured layers
create high surface tension





Water surface

Crystals can be pretty stiff



Water structure stiff enough
to keep bridge from collapsing

Crystalline zone keeps protons (hydronium ions) out



Answer to Question #3

Yes

Liquid crystalline water
explains many anomalies

It explains why water battery charges remain separated

Question #4

What charges the water battery?



(Incident radiant energy)

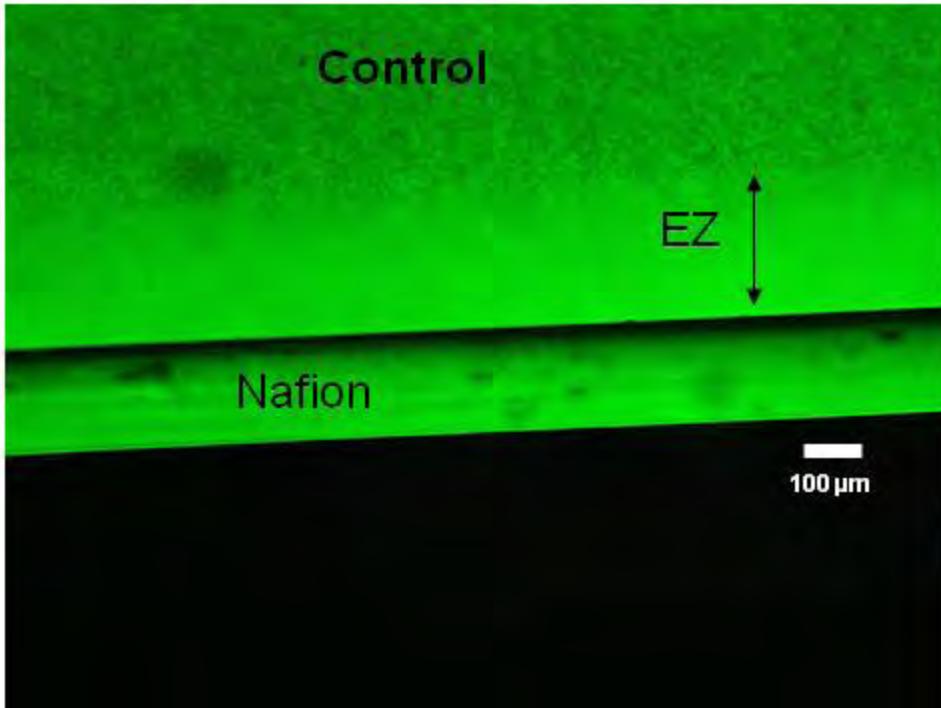
Light point source here

Exclusion zone

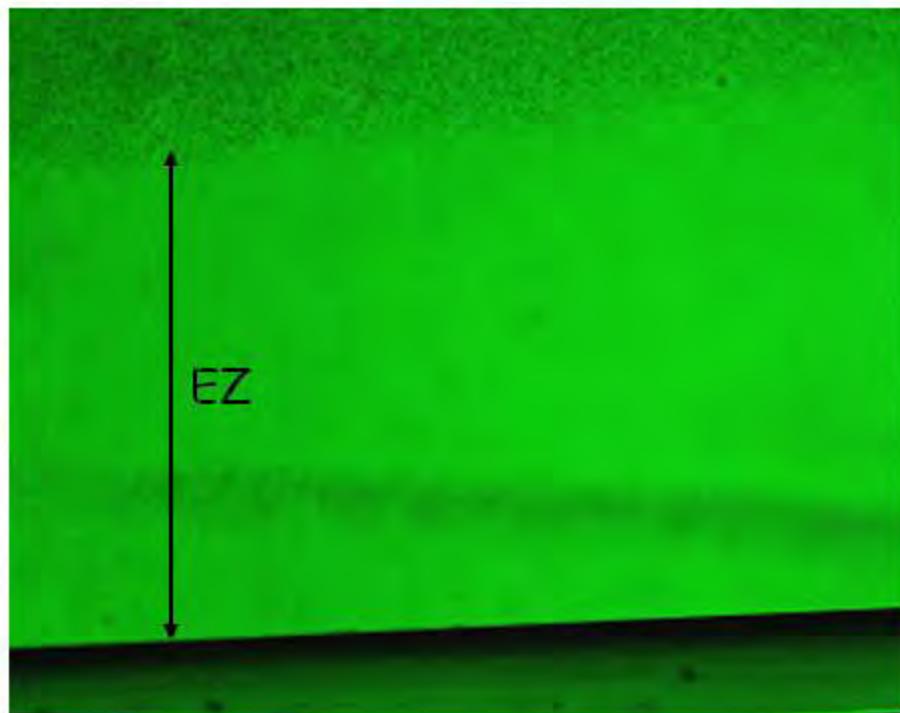
Nafion

100 μm

Near infrared illumination



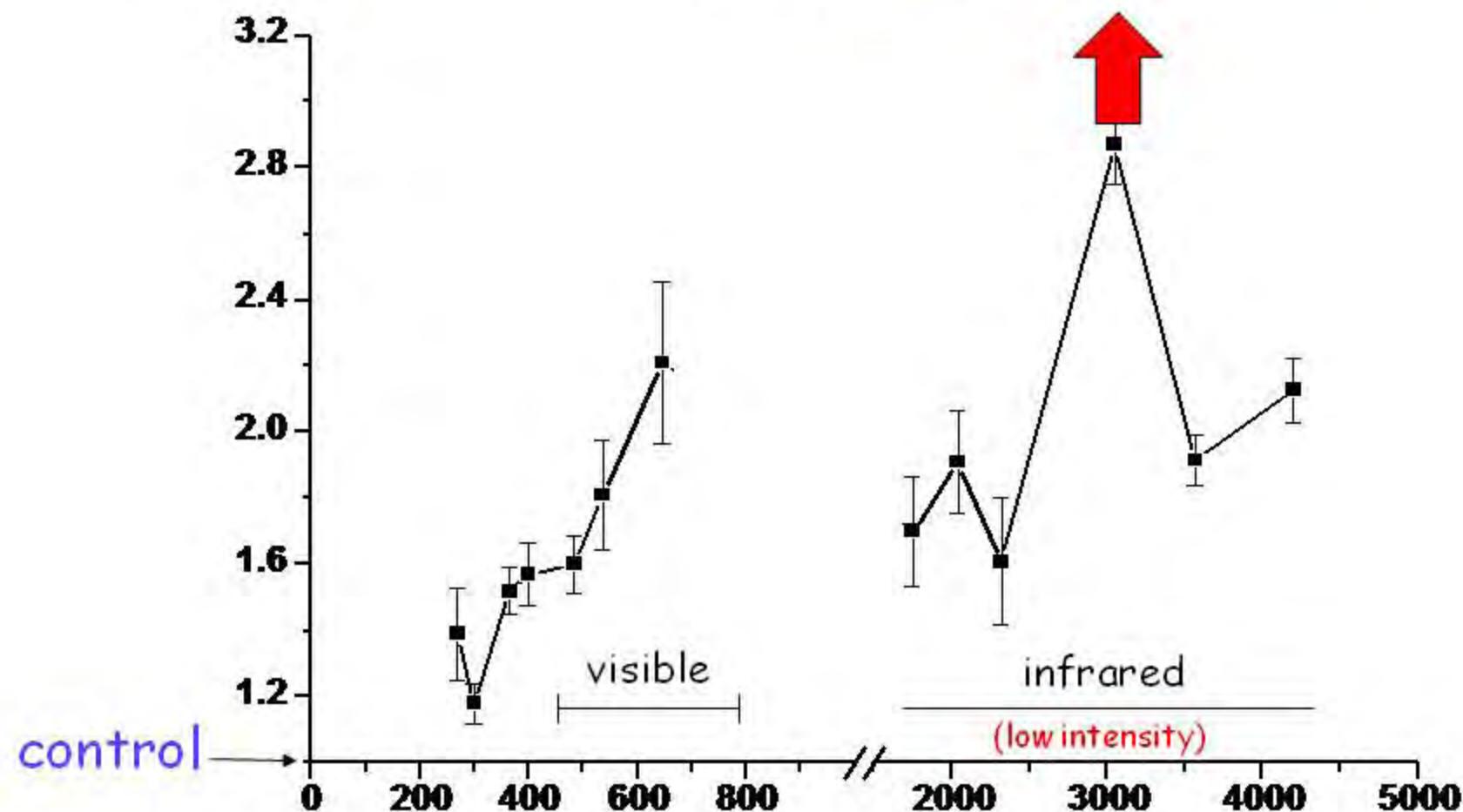
With illumination – 5 min



temperature rise $< 1^\circ$

Effect of Wavelength on EZ Size

(5 min exposure)



exclusion

beyond

surface area

Incident radiant energy
builds exclusion zone
and separates charge

exclusion

beyond

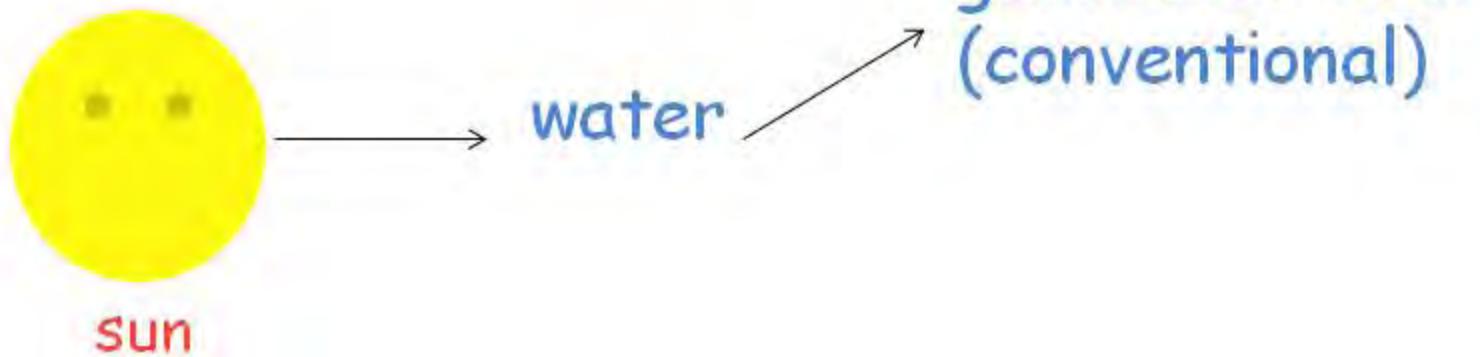
Answer to Question #4 Energy?

EZ buildup powered by photonic energy...

Orders water

Charges the water battery

Possible Energy Flow in Universe



Possible Energy Flow in Universe



water

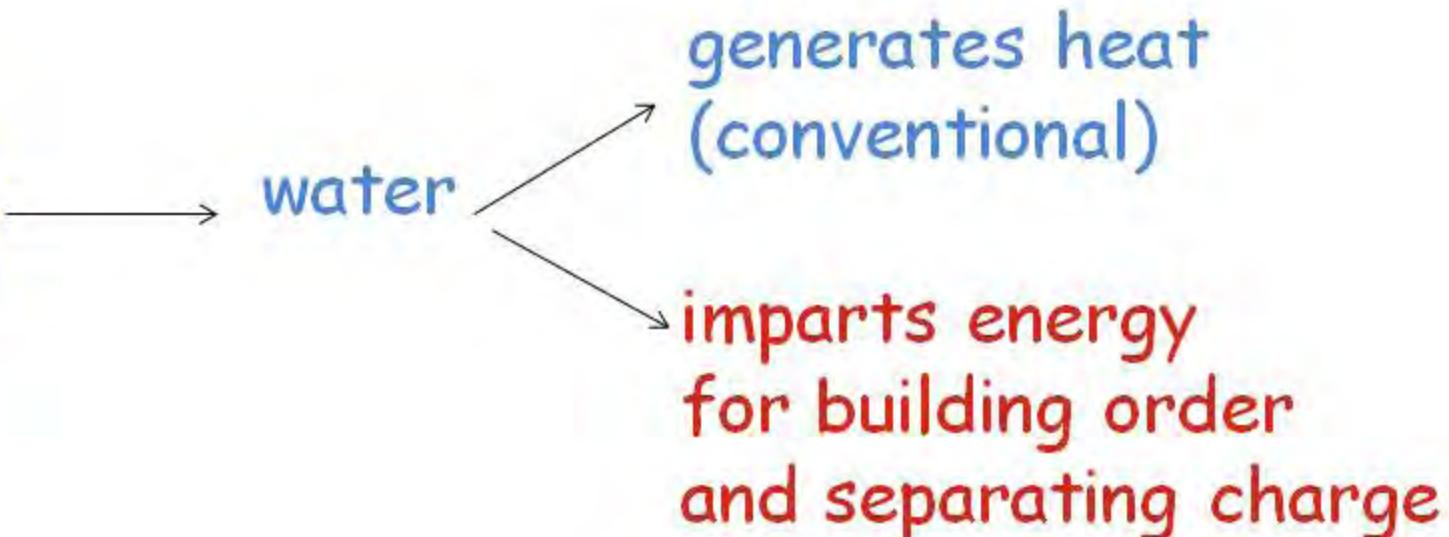
generates heat
(conventional)

imparts energy
for building order
and separating charge

Possible Energy Flow in Universe

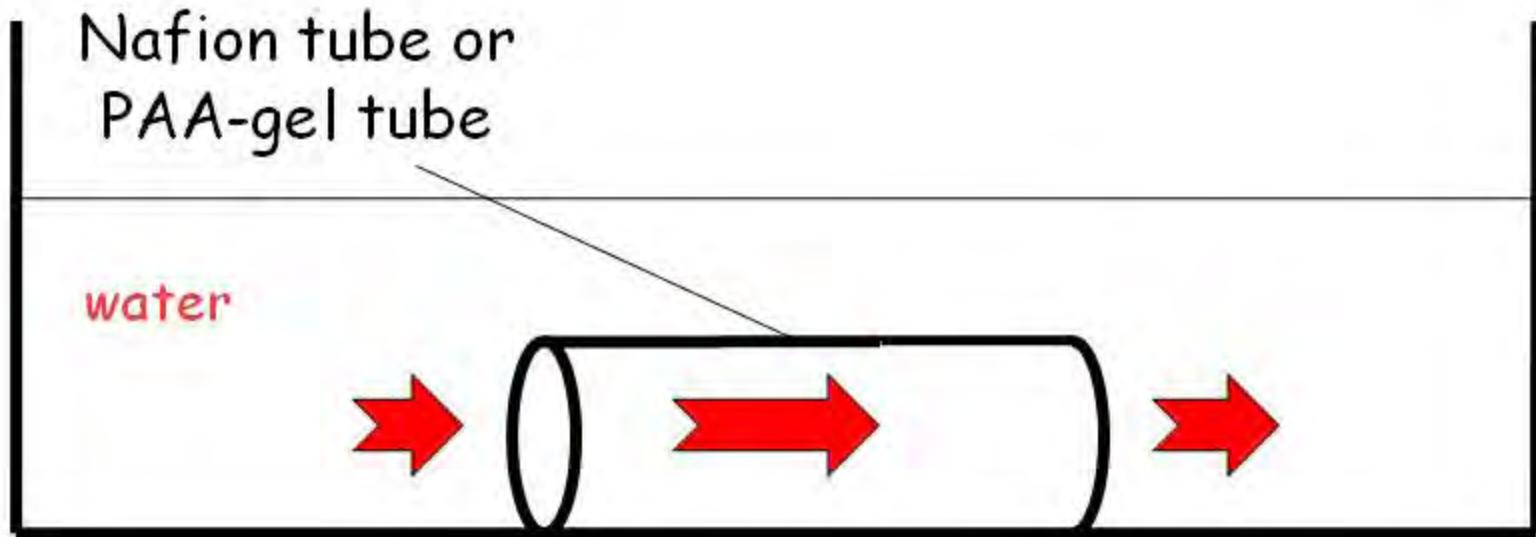


sun



imparts energy to our cells

Incident radiant energy can be harvested...

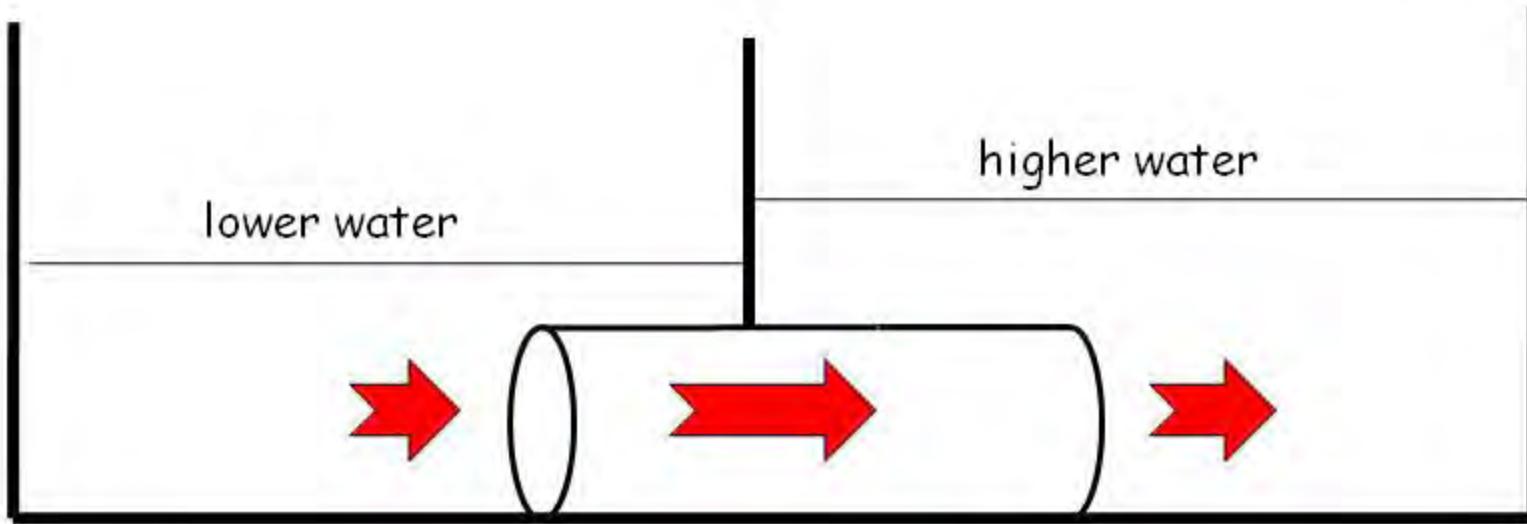


nafion

exclusion zone

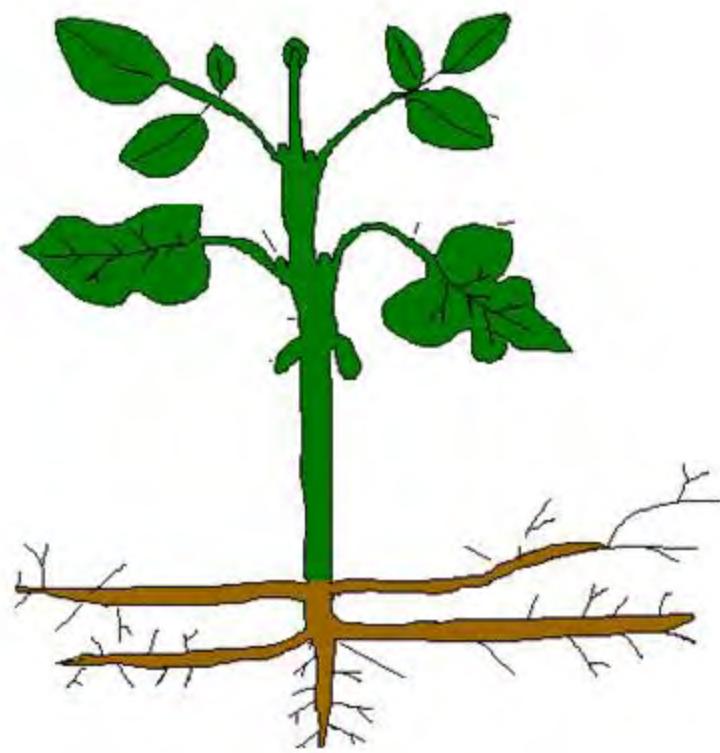
Polyacrylic acid gel

EZ



Incident radiant energy harvested **to do work**

Evidence that incident energy **MUST** be absorbed



Incident energy might drive Brownian excursions

Light energy **in**



Motion energy **out**

Question #5

Why is all of this important?

- Foundational for any/all science involving water and light
 - physics
 - chemistry
 - biology
- Foundational for engineering of **genuinely** new practical devices

Question #5

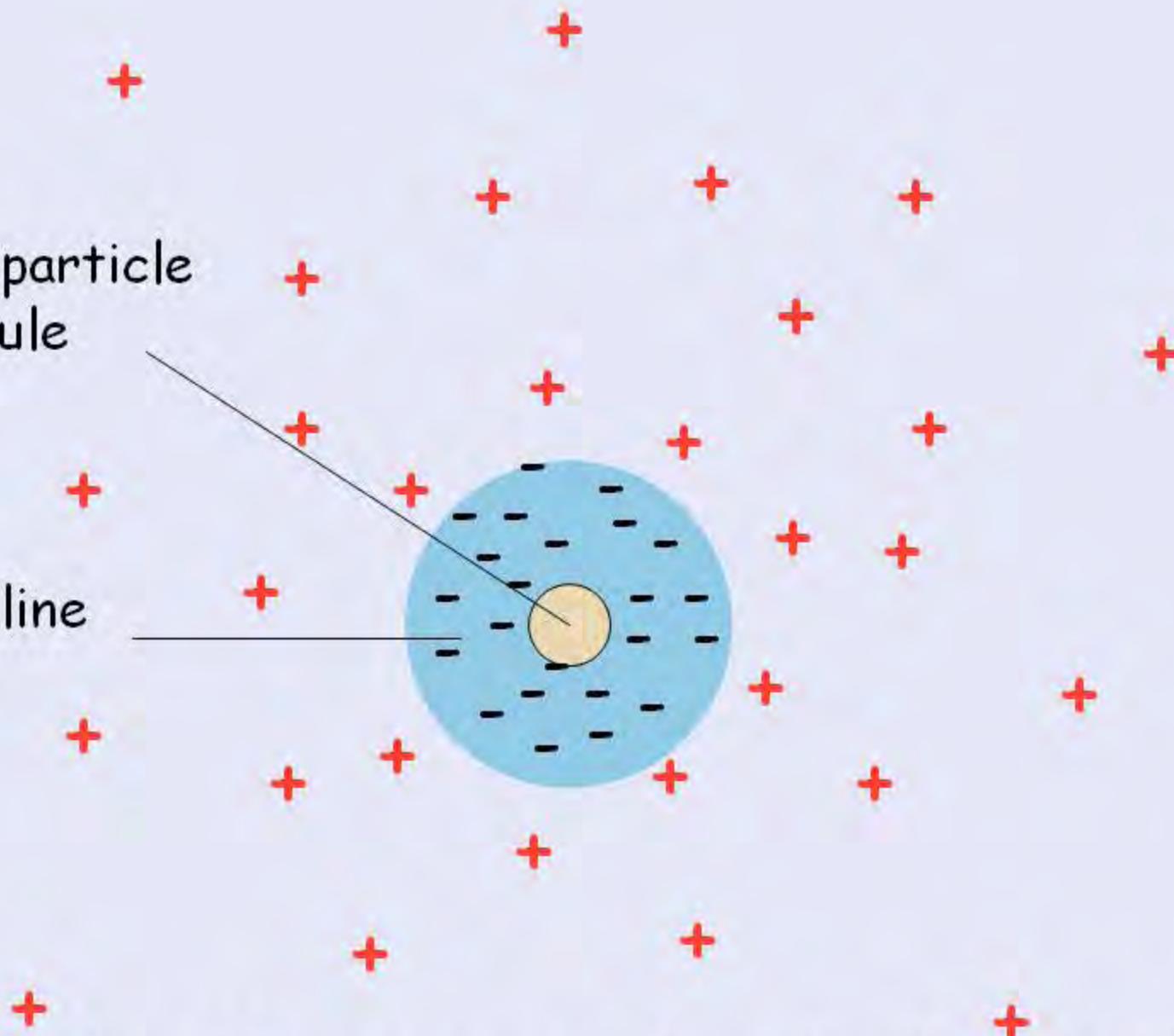
Why is all of this important?

- Foundational for any/all science involving water and light
 - physics
 - chemistry
 - biology
- Foundational for engineering of **genuinely** new practical devices

Example:
water,
light,
particles

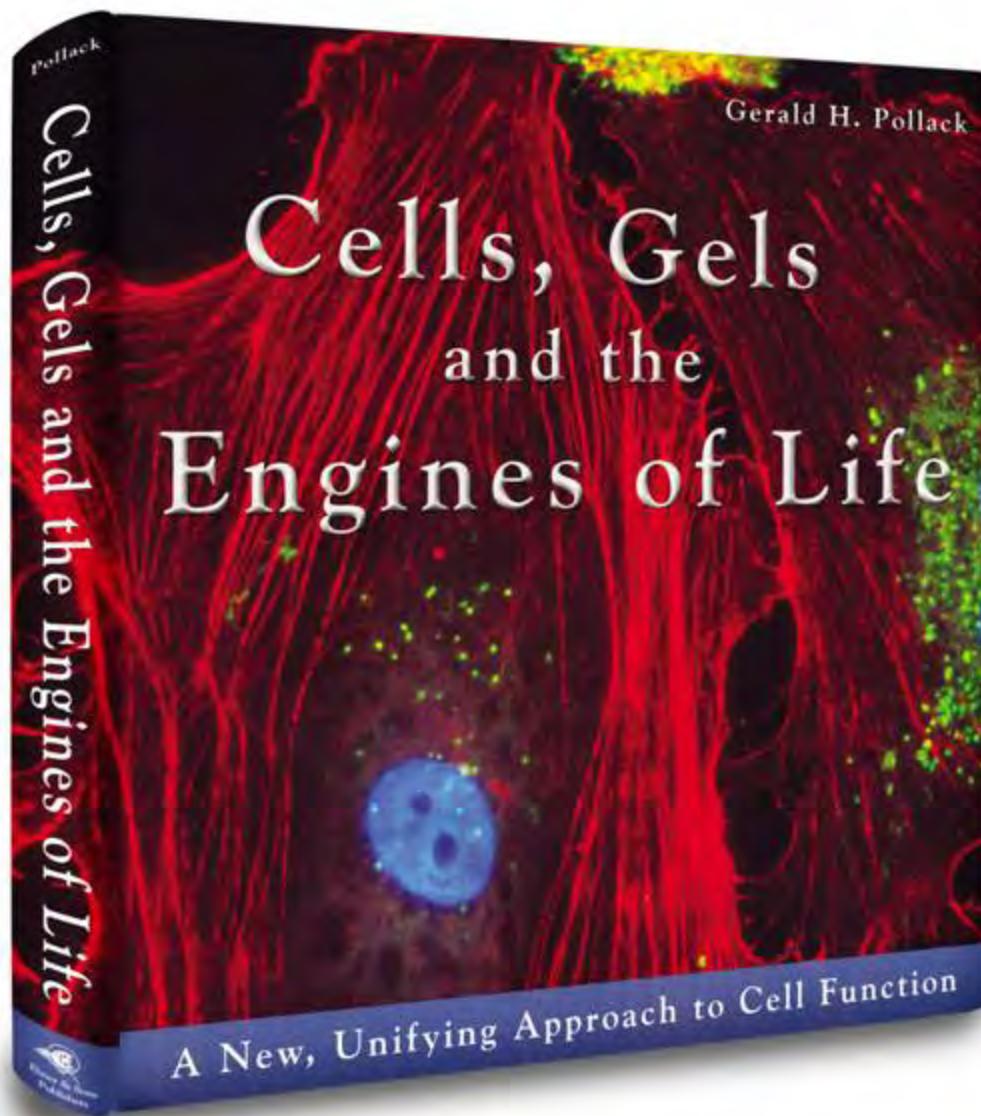
charged particle
or molecule

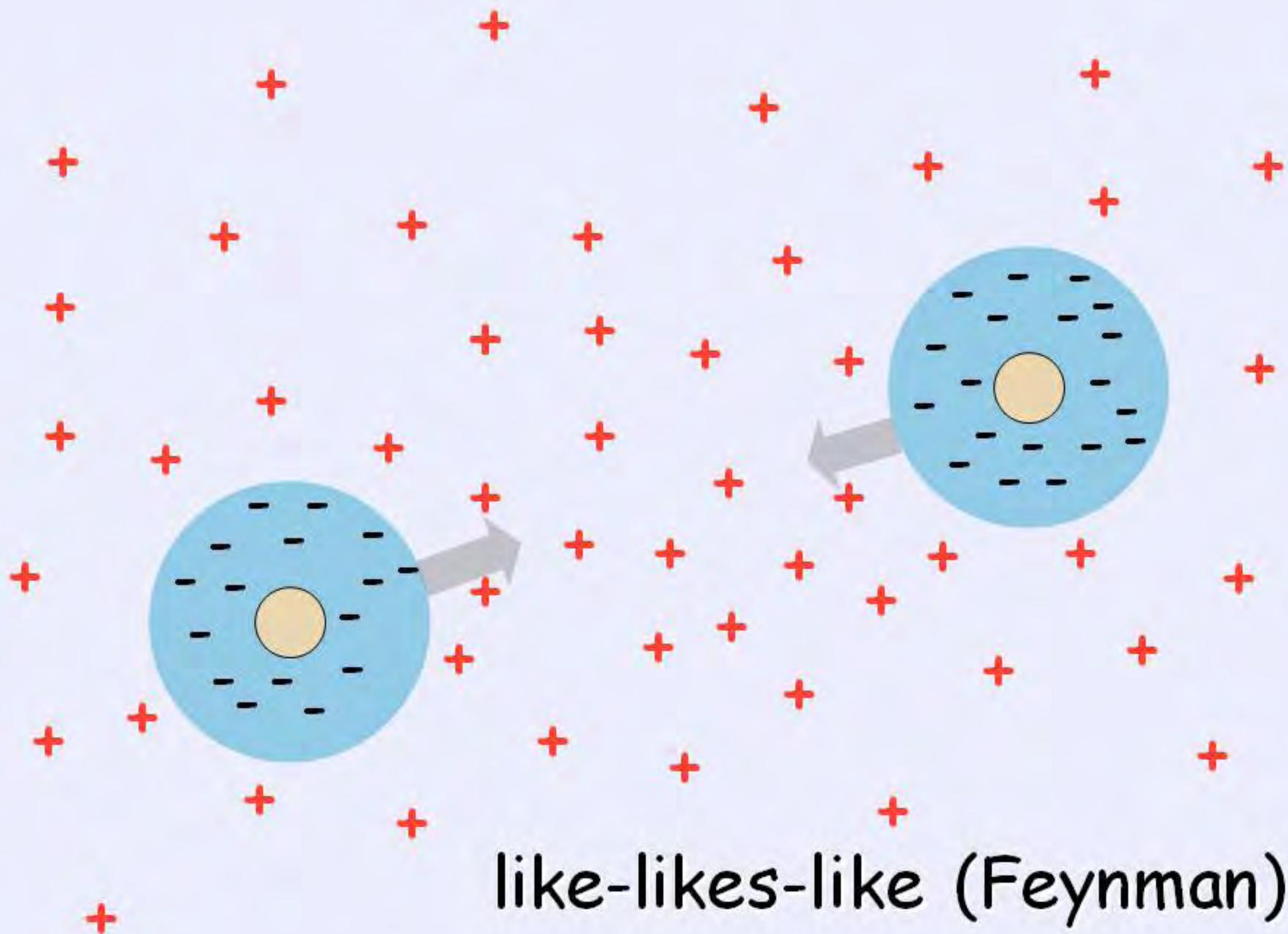
liquid
crystalline
water

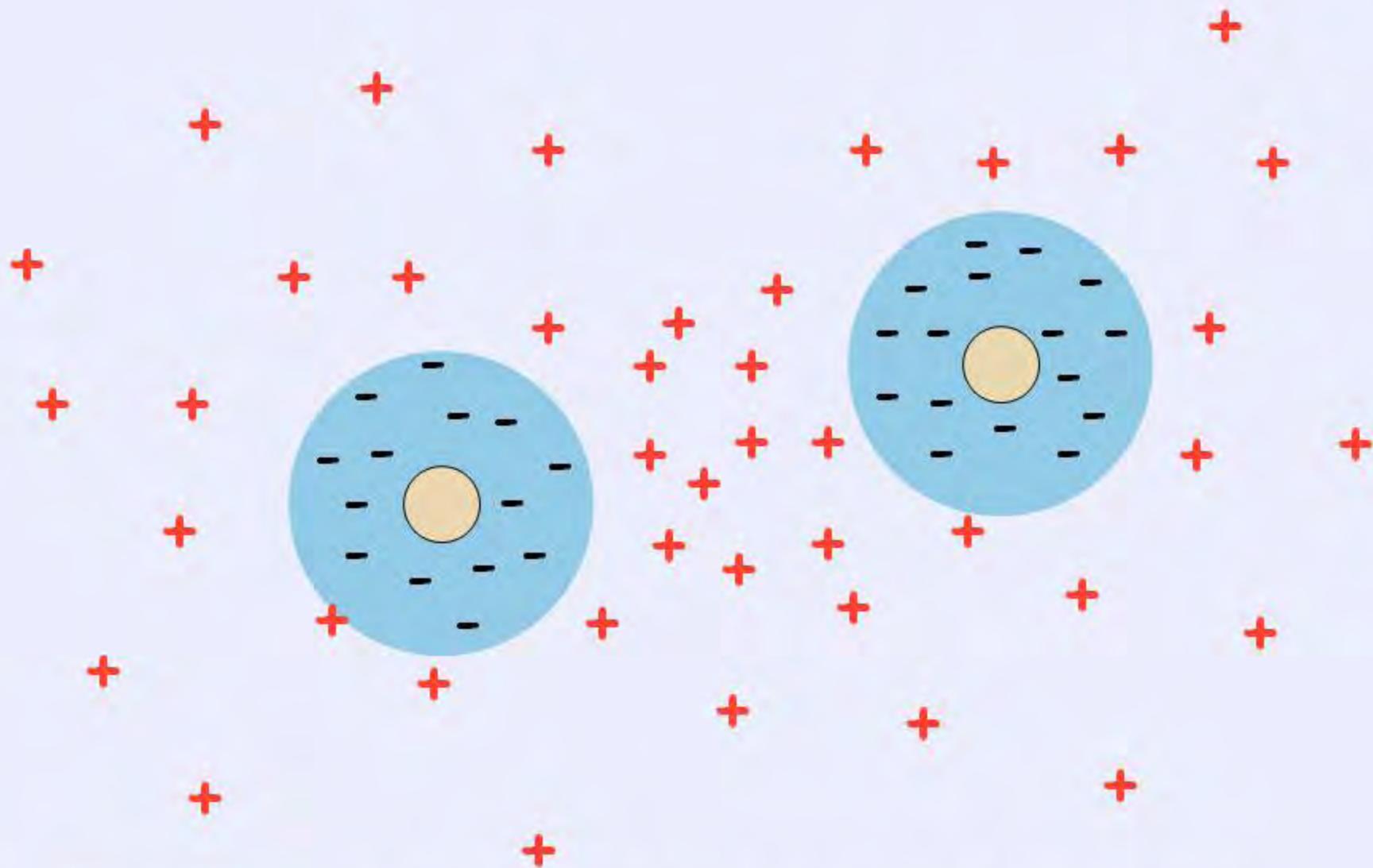


in all aqueous chemical reactions

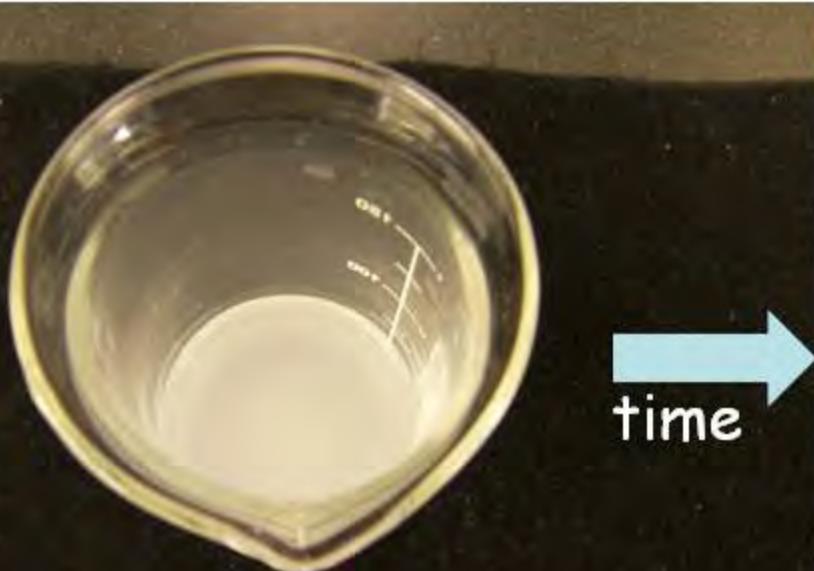
including chemical reactions **in cells...**







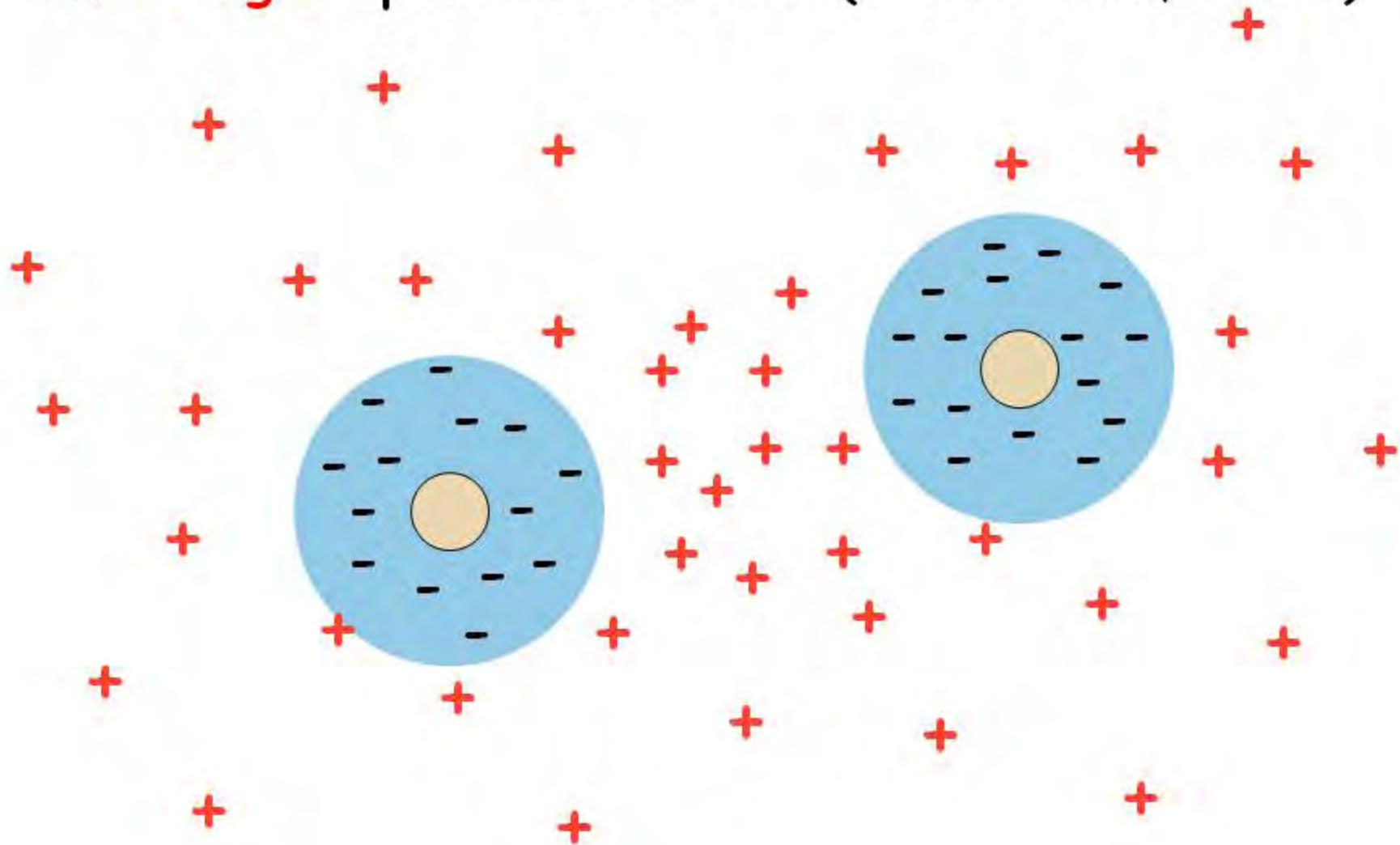
Stability: attractive force = repulsive force



charged microspheres
suspended in water

courtesy Norio Ise
Kyoto University

More light: particles closer (Zhao et al., 2008)



A photograph of a bright, fluffy white cumulus cloud against a clear, pale blue sky. The cloud is positioned in the upper half of the frame, with its base slightly lower. In the foreground, the dark green, pointed tops of several evergreen trees are visible at the bottom edge.

aerosol clusters attract
because like-likes-like

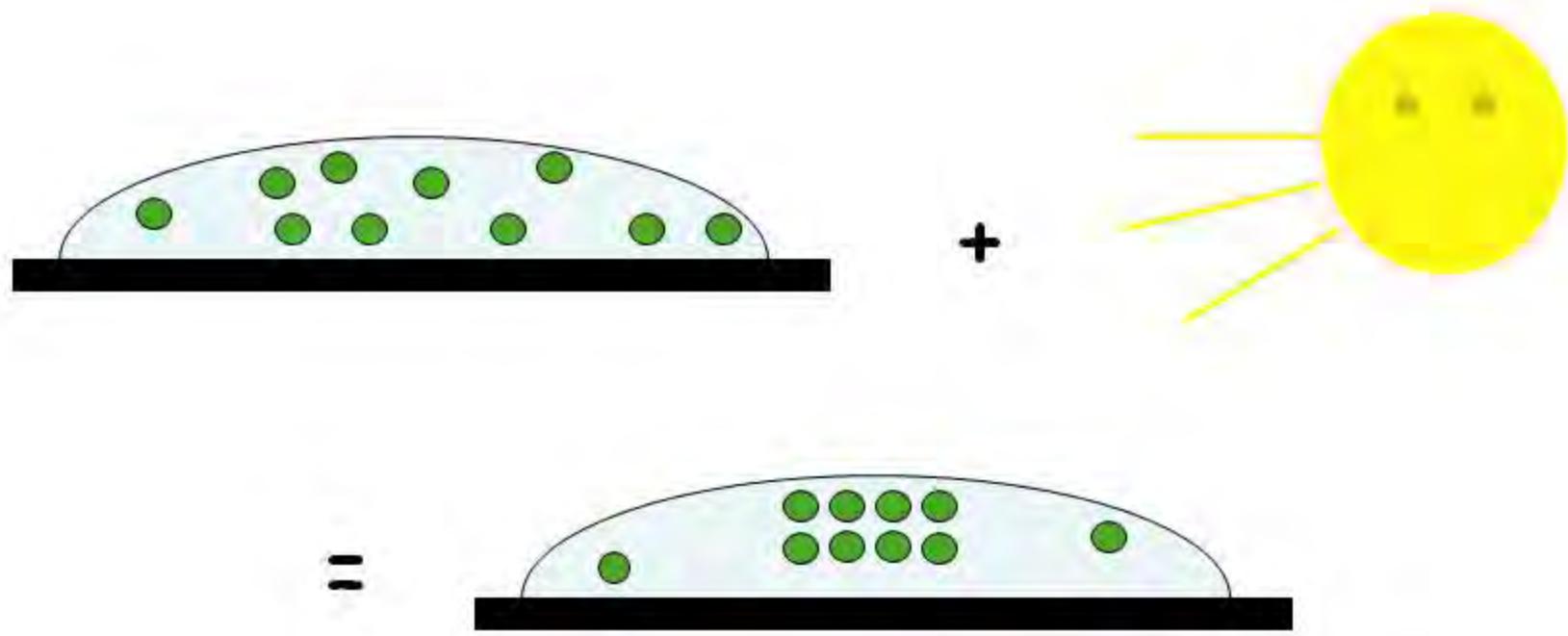
(powered by light)

A special example of
like-likes-like...

Origin of Life

Step 1?

dispersed molecules coalesce



Aggregate keeps growing (like cell) **self assembly**

Has negative charge (like cell)

Has potential energy (like cell)

Has capacity to divide (like cell)

Step 1 in origin of life may be
light-induced aggregation

All that's needed:

the sun's energy
molecules
water

Is life being created continually?

Question #5: Why is all of this important?

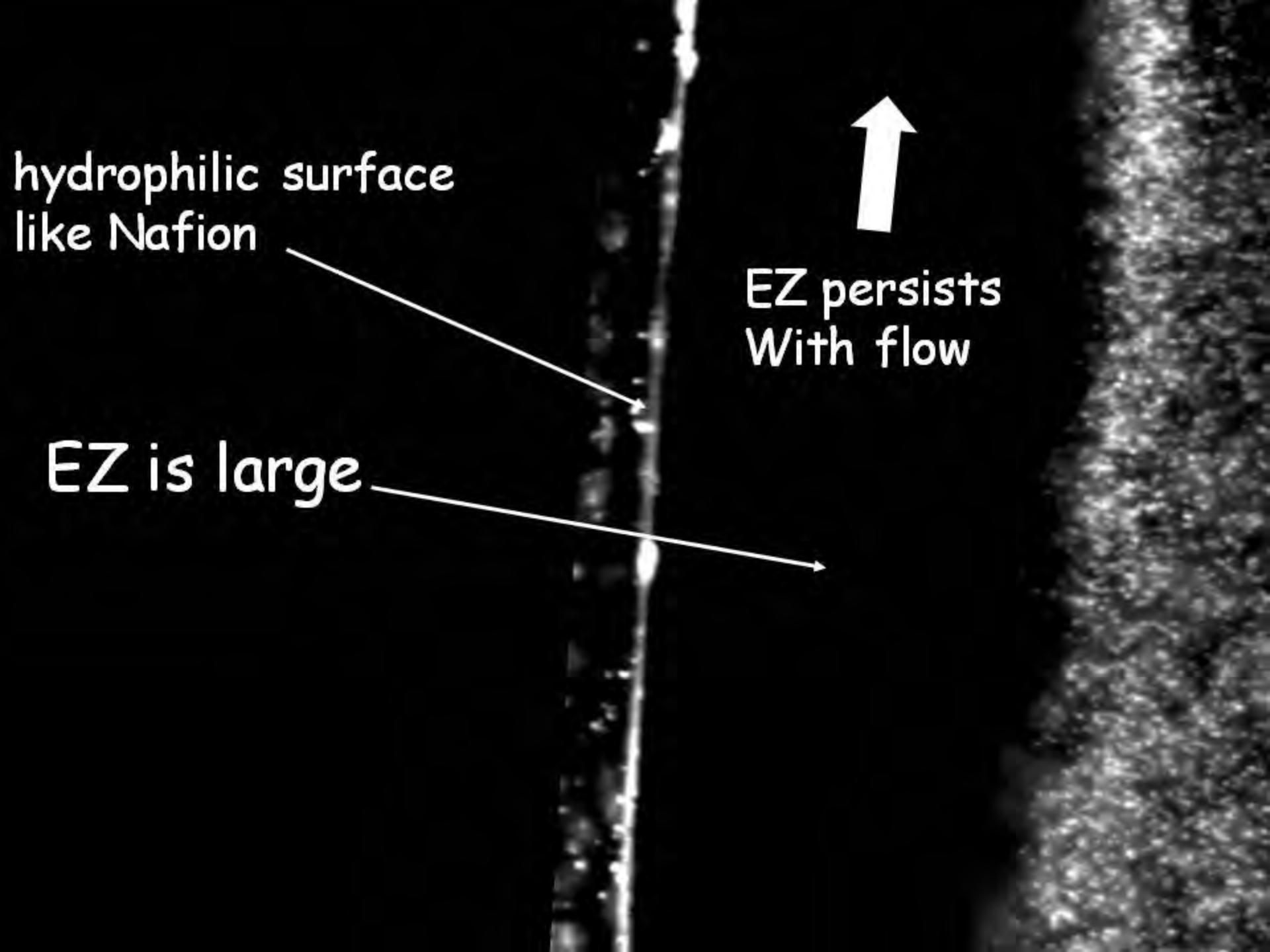
- Foundational for any/all science involving water and light
 - physics
 - chemistry
 - biology
- Foundational for engineering of **genuinely** new practical devices

unifying

Question #5: Why is all of this important?

- Foundational for any/all science involving water and light
 - physics
 - chemistry
 - biology
- Foundational for engineering of **genuinely** new practical devices

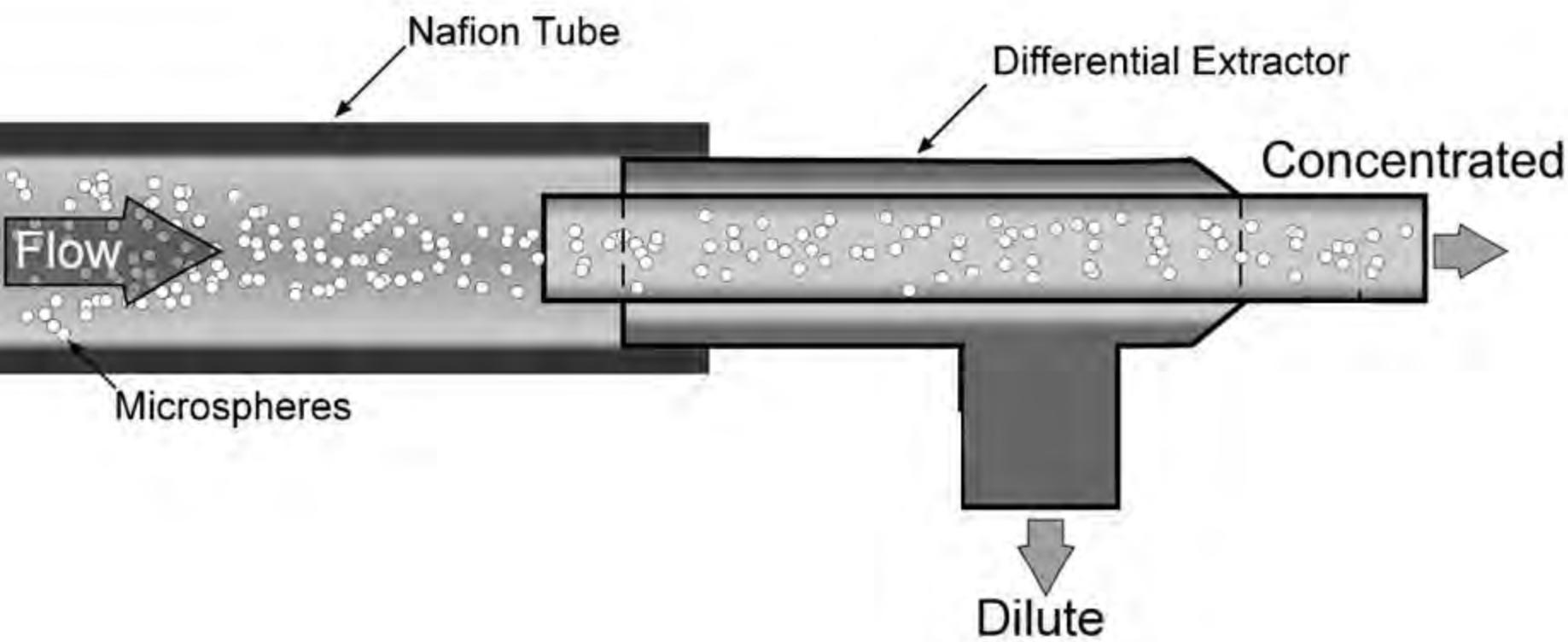
Purifying Contaminated Water

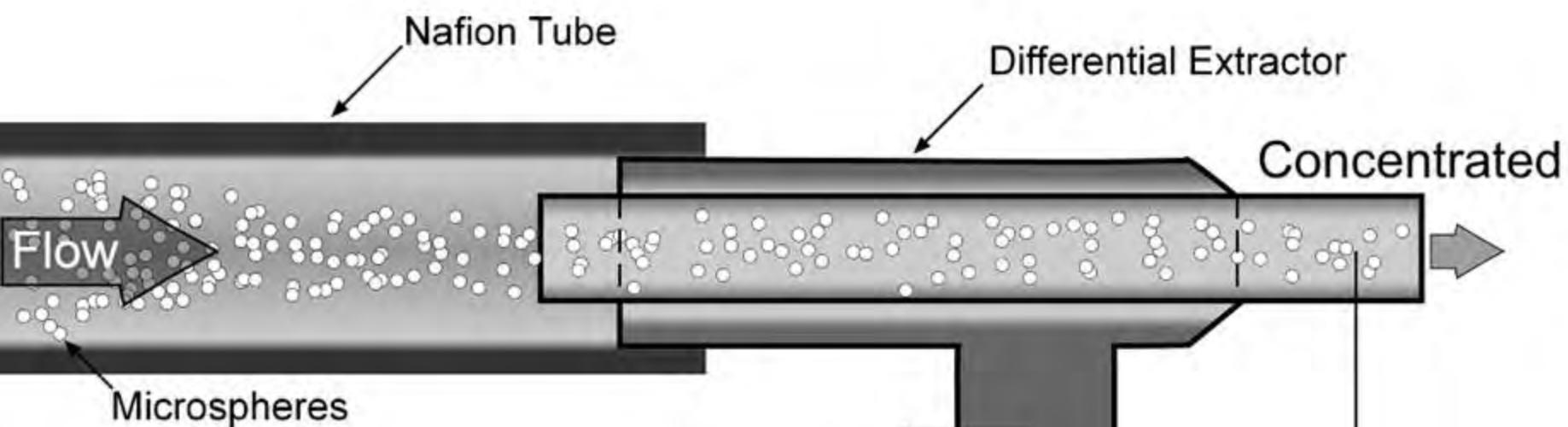


hydrophilic surface
like Nafion

EZ is large

EZ persists
With flow





Dilute

1:200 separation achieved

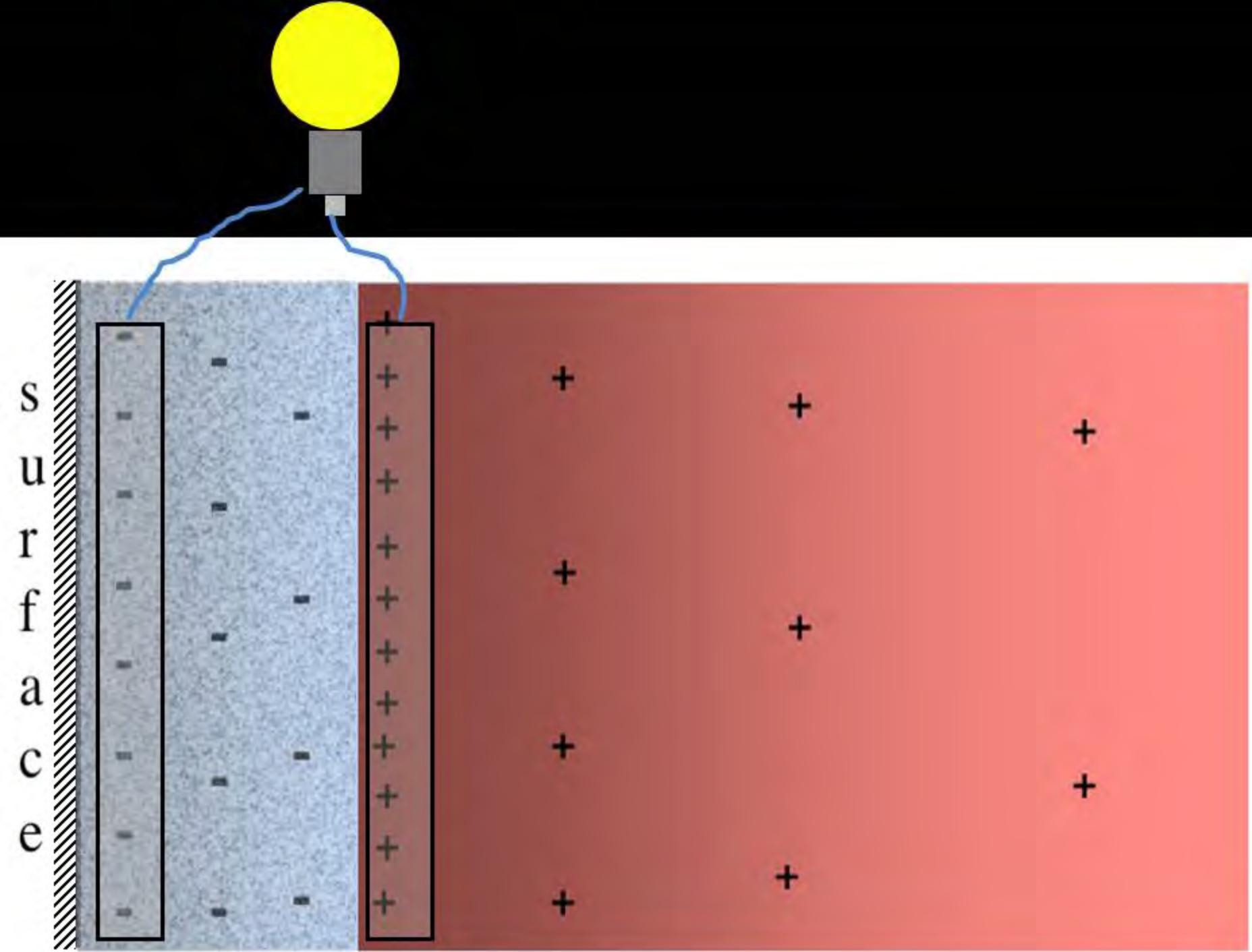
Bacteria separable

Scaling up for practicality

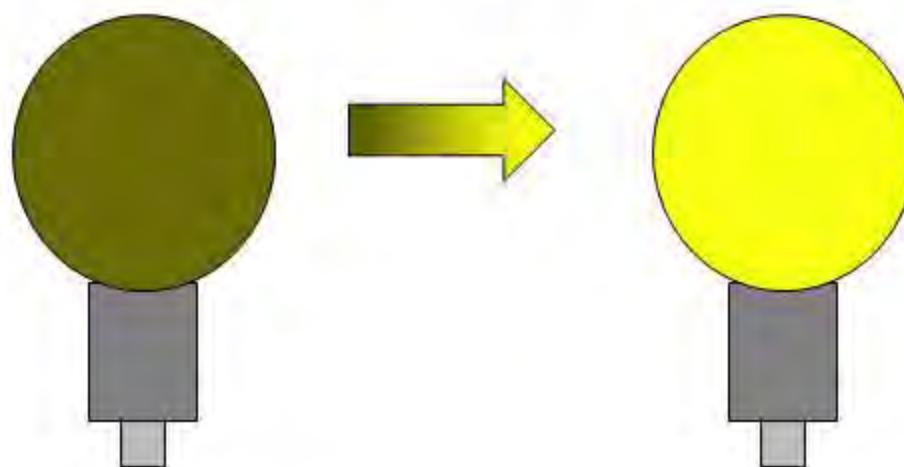
Exploring separation of salt

2

Electrical Energy from Light and Water...



light
↓
charge separation
in water
↓
energy harvest



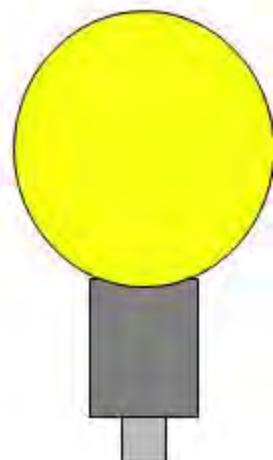
light



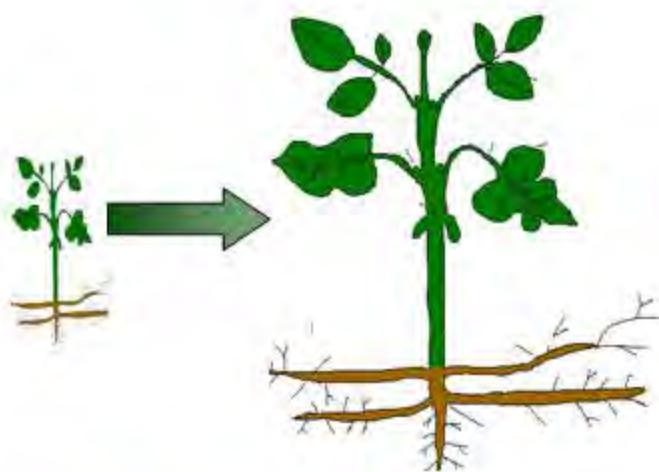
charge separation
in water



energy

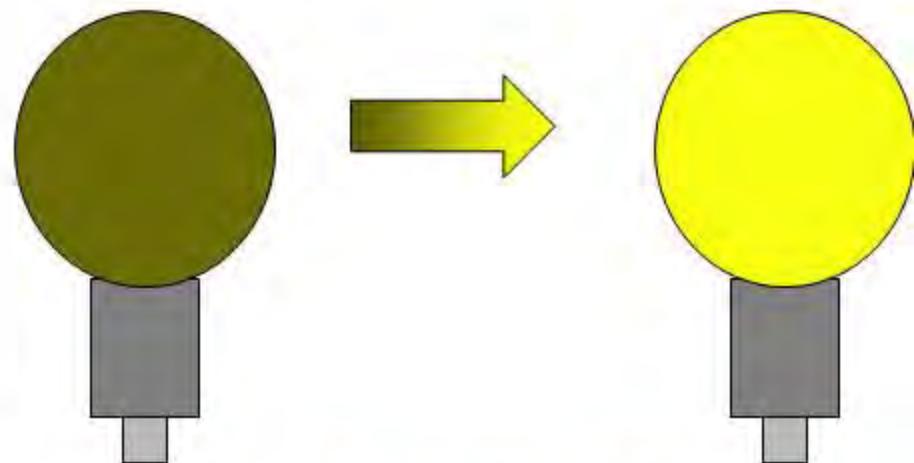


light
↓
charge separation
in water
↓
energy



photosynthesis

light
↓
charge separation
in water
↓
energy



generic photosynthesis?

Electrical power from
generic photosynthesis

Can this replace oil?

Question #5: Why is all of this important?

- Foundational for any/all science involving water and light | ✓✓
 - physics
 - chemistry
 - biology
- Foundational for engineering of genuinely new practical devices | ✓✓

also good to drink...



and inspirational to watch

and fascinating to study

Many thanks!

The interface is interesting