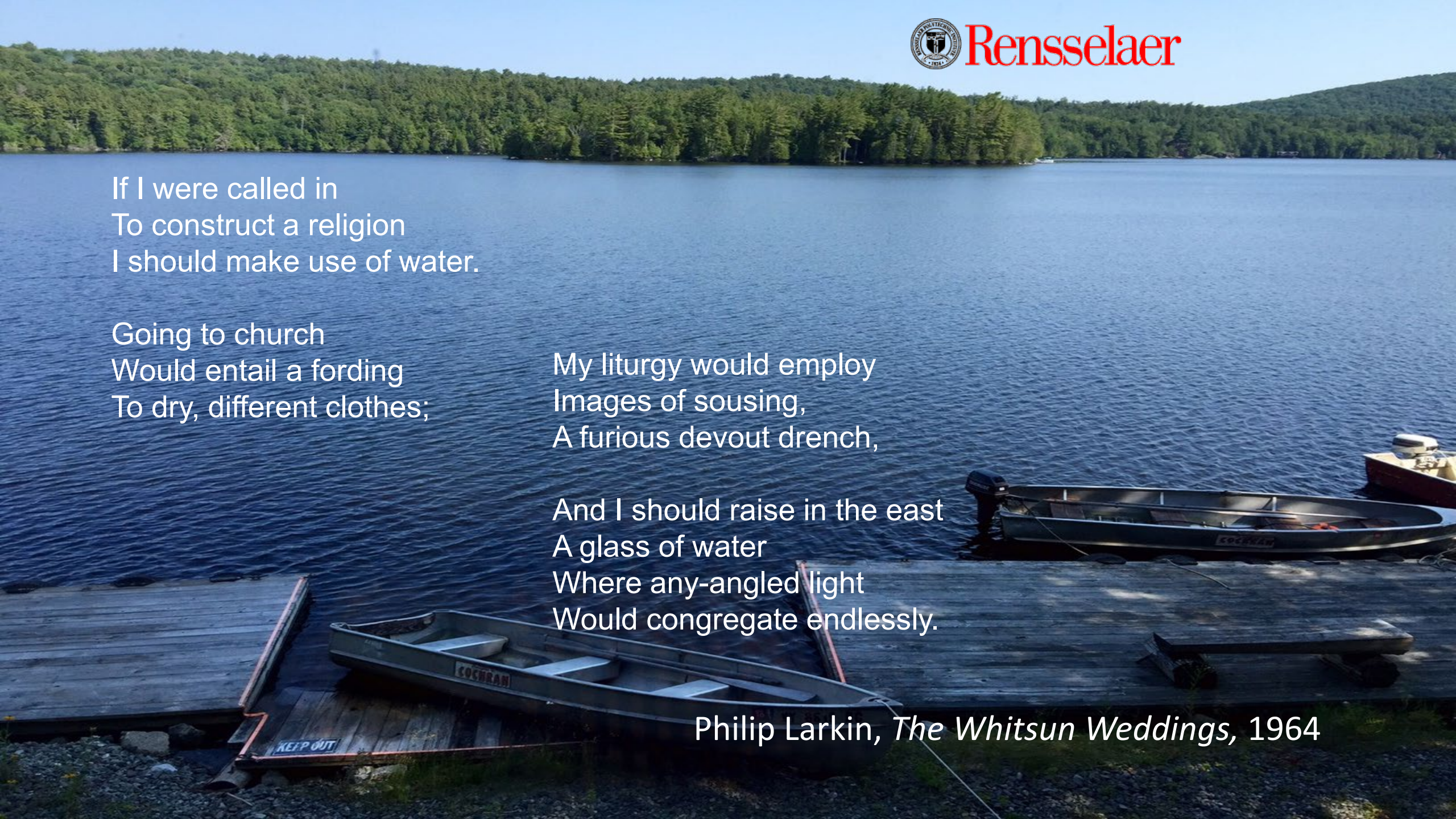
Water: A Matrix of Life
A new Molecular Perspective

Shekhar Garde

Department of Chemical & Biological Engineering

Rensselaer Polytechnic Institute, Troy, NY.

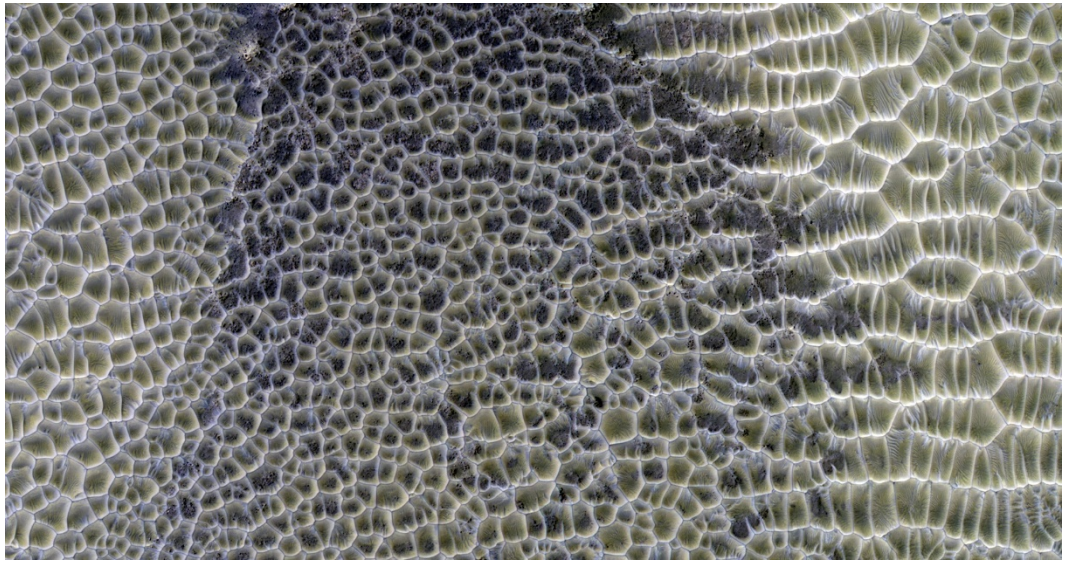
Rensselaer


Rensselaer
If I were called in
To construct a religion
I should make use of water.
Going to church
Would entail a fording
To dry, different clothes;
My liturgy would employ
Images of sousing,
A furious devout drench,
And I should raise in the east
A glass of water
Where any-angled light
Would congregate endlessly.
COCHRAN
KEEP OUT
Philip Larkin, *The Whitsun Weddings,* 1964

Honeycomb Martian Dunes Could Be a Clear Sign of... Water

Home > News > Space Junk

18 Jun 2022, 02:20 UTC · by **Daniel Patrascu**

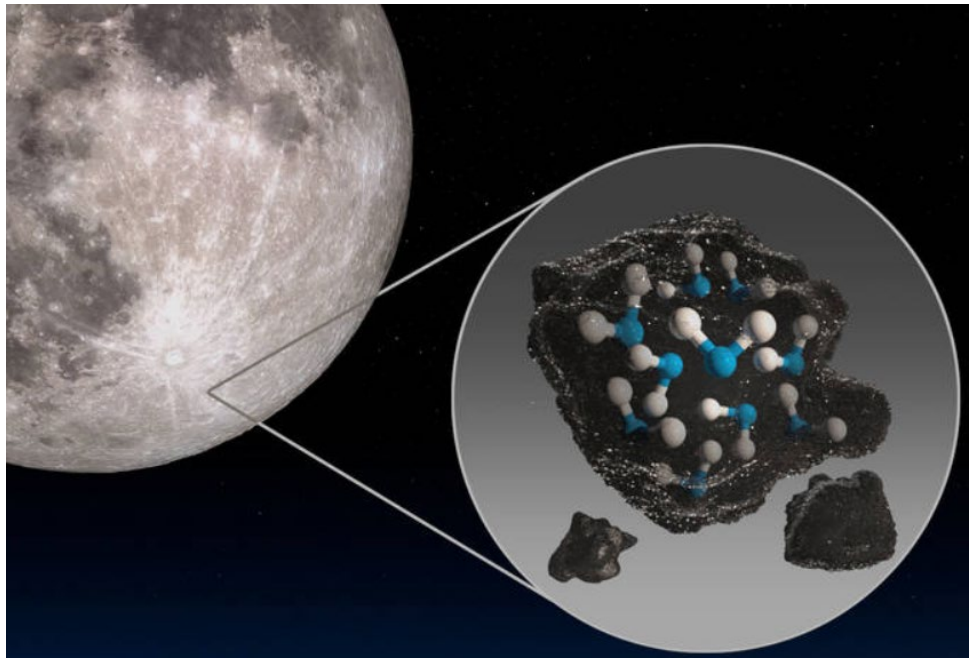


Water ⇨ Life

Oct 26, 2020

RELEASE 20-105

NASA's SOFIA Discovers Water on Sunlit Surface of Moon



NATION

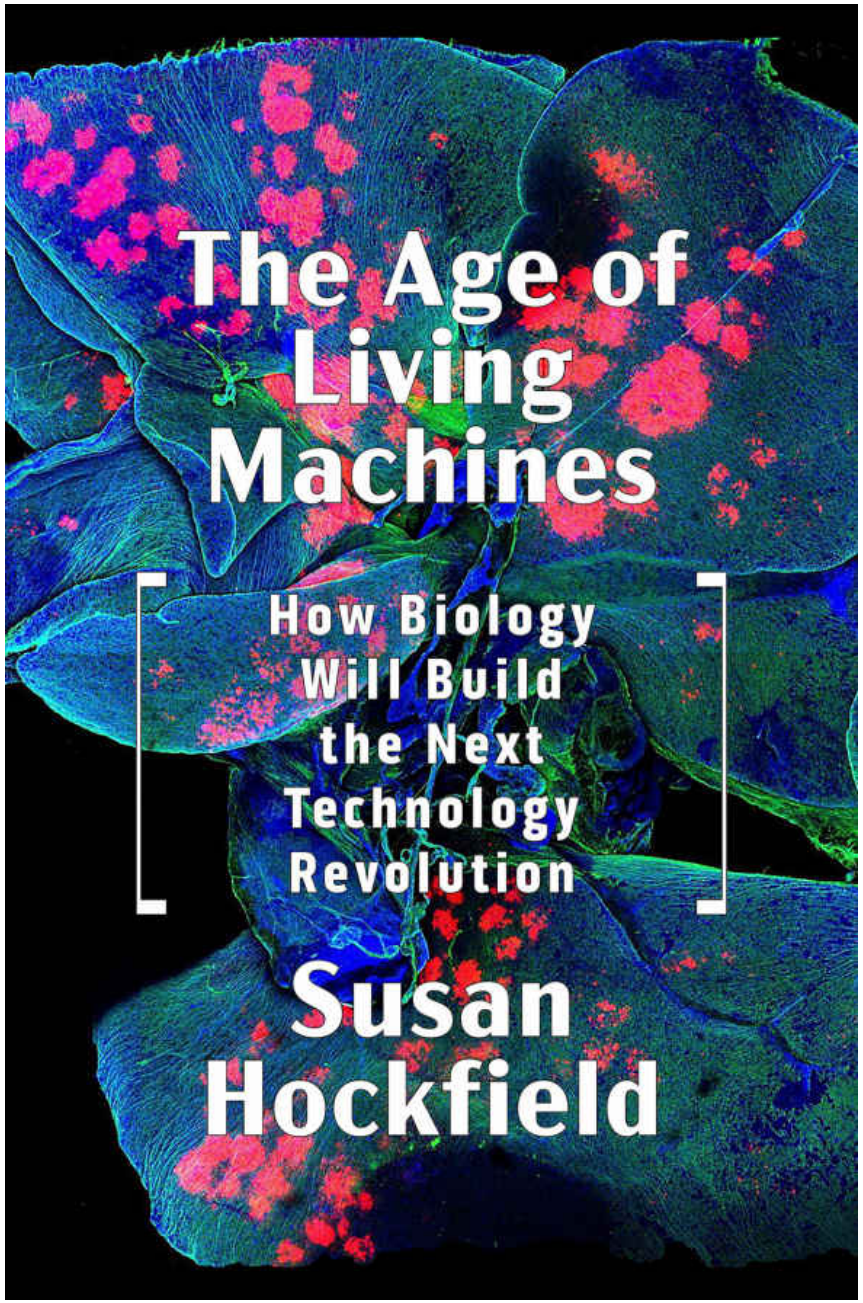
A place for life on Mars? New discovery is 'best evidence yet' it's possible.

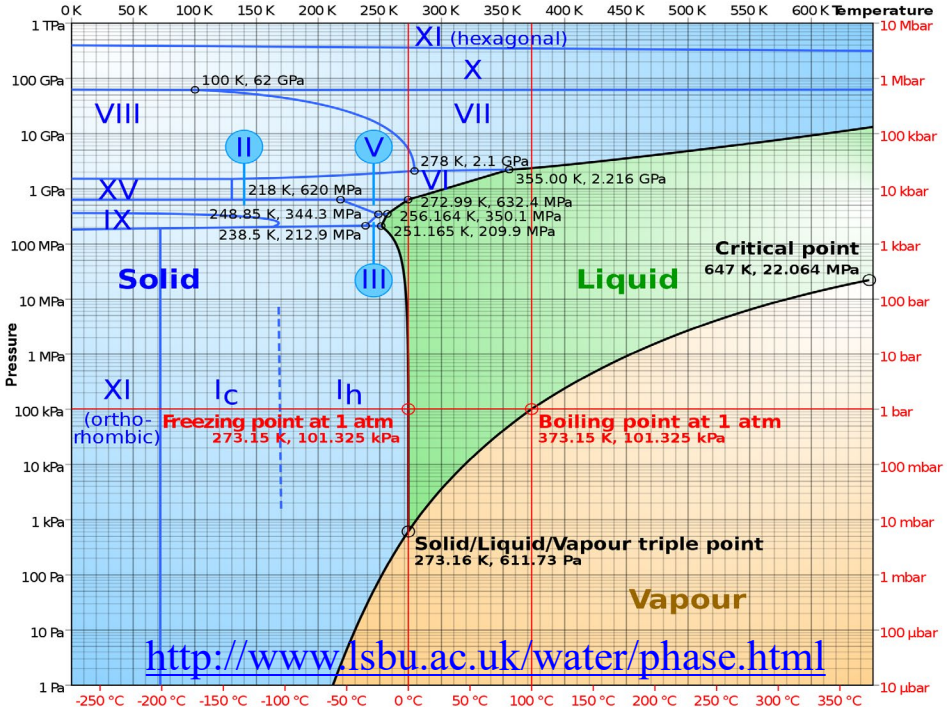
Scientists Monday announced they've found evidence of liquid water on Mars -- which they say is buried deep underground in cracks several miles under the planet's surface.

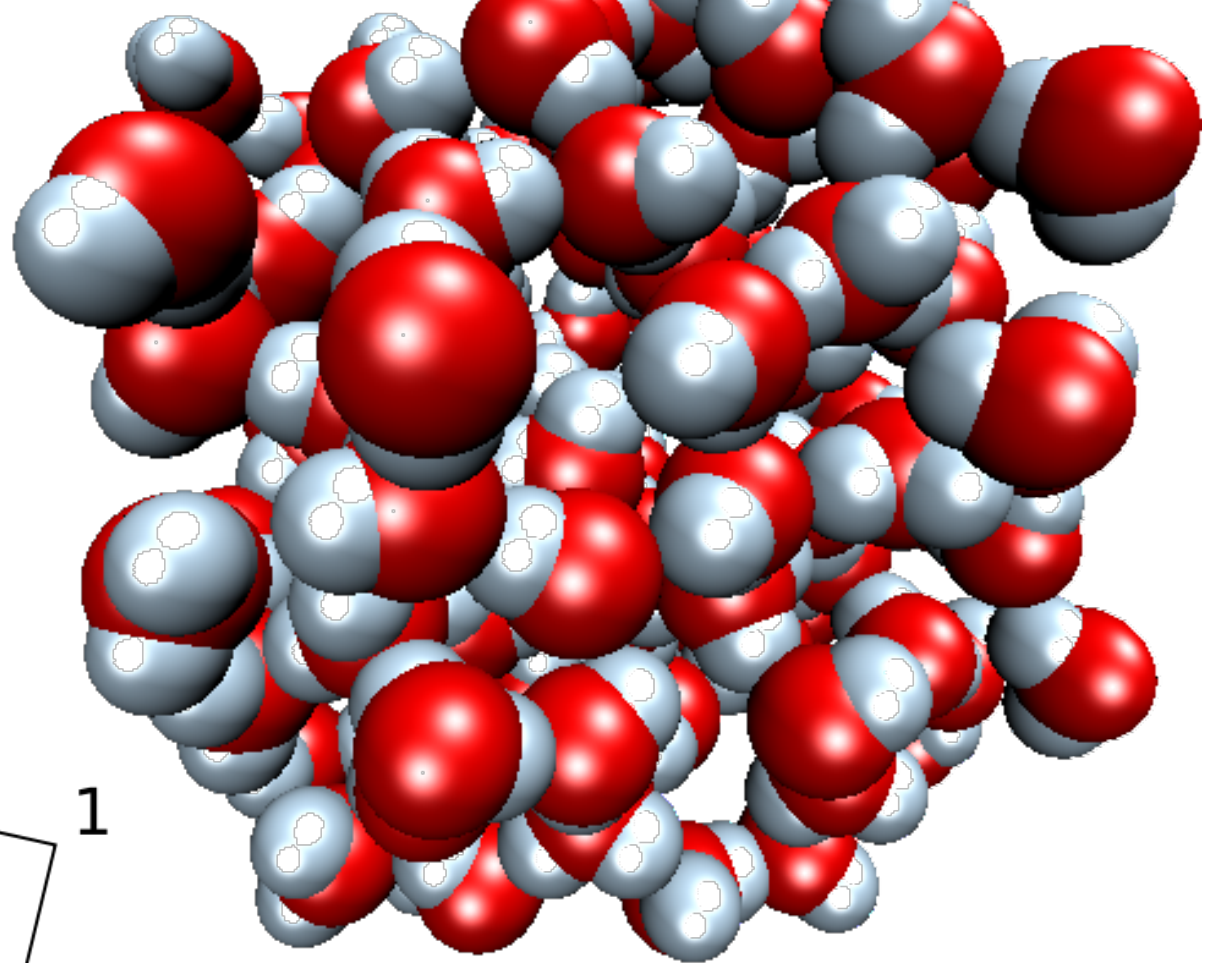
Doyle Rice
USA TODAY

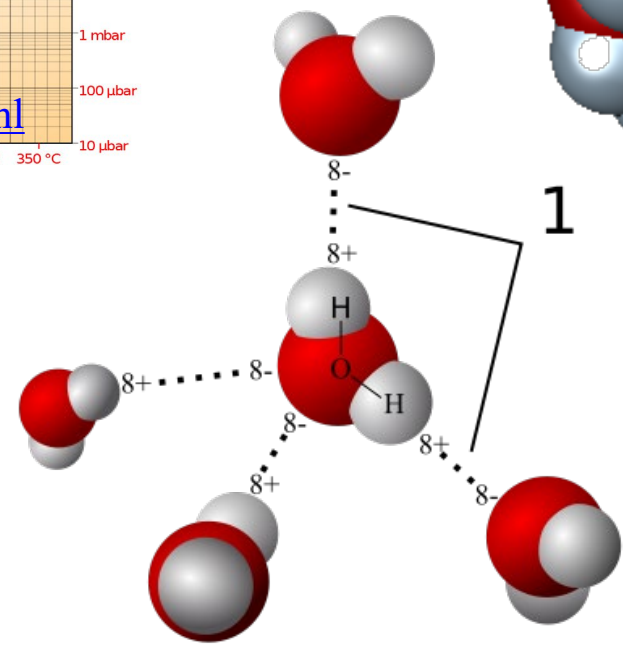
Published 3:00 p.m. ET Aug. 12, 2024 | **Updated 12:28 p.m. ET Aug. 14, 2024**

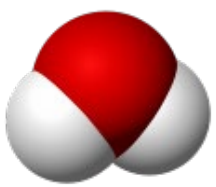
Water ⇨ Life

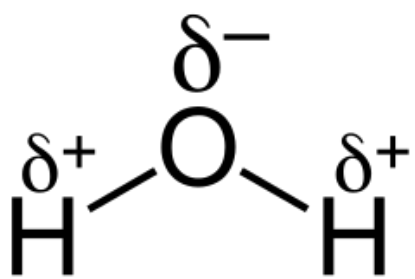


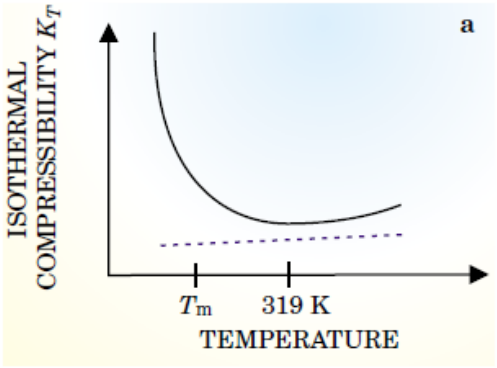

0 K
50 K
100 K
150 K
200 K
250 K
300 K
350 K
400 K
450 K
500 K
550 K
600 K
Temperature
1 TPa
100 GPa
10 GPa
1 GPa
100 MPa
10 MPa
1 MPa
100 kPa
10 kPa
1 kPa
100 Pa
10 Pa
1 Pa
Pressure
10 Mbar
1 Mbar
100 kbar
10 kbar
1 kbar
100 bar
10 bar
1 bar
100 mbar
10 mbar
1 mbar
100 µbar
10 µbar
-250 °C
-200 °C
-150 °C
-100 °C
-50 °C
0 °C
50 °C
100 °C
150 °C
200 °C
250 °C
300 °C
350 °C
XI (hexagonal)
X
VII
VIII
II
V
VI
XV
IX
III
100 K, 62 GPa
278 K, 2.1 GPa
355.00 K, 2.216 GPa
218 K, 620 MPa
272.99 K, 632.4 MPa
248.85 K, 344.3 MPa
256.164 K, 350.1 MPa
238.5 K, 212.9 MPa
251.165 K, 209.9 MPa
Critical point
647 K, 22.064 MPa
Solid
Liquid
XI
(ortho-
rhombic)
Ic
Ih
Freezing point at 1 atm
273.15 K, 101.325 kPa
Boiling point at 1 atm
373.15 K, 101.325 kPa
Solid/Liquid/Vapour triple point
273.16 K, 611.73 Pa
Vapour
http://www.lsbu.ac.uk/water/phase.html

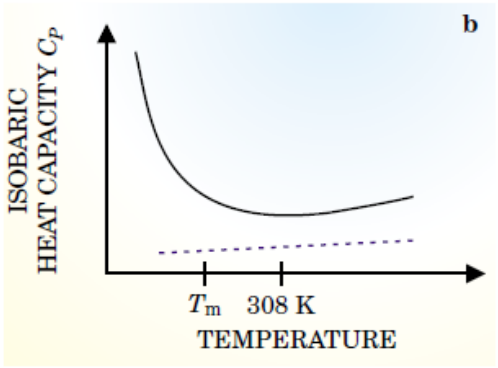


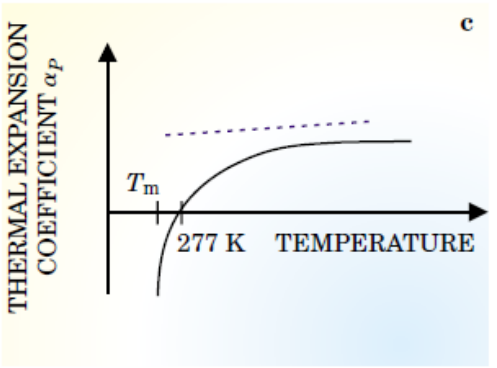

8-
8+
1
H
O
H
8+
8-
8-
8+
8+
8-




δ−
δ+
O
δ+
H
H







Supercooled and Glassy Water

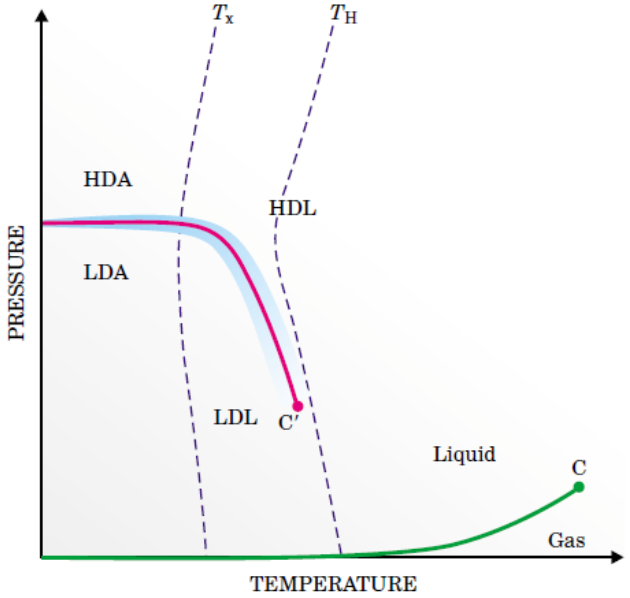
Cold, noncrystalline states play an important role in understanding the physics of liquid water. From recent experimental and theoretical investigations, a coherent interpretation of water's properties is beginning to emerge.

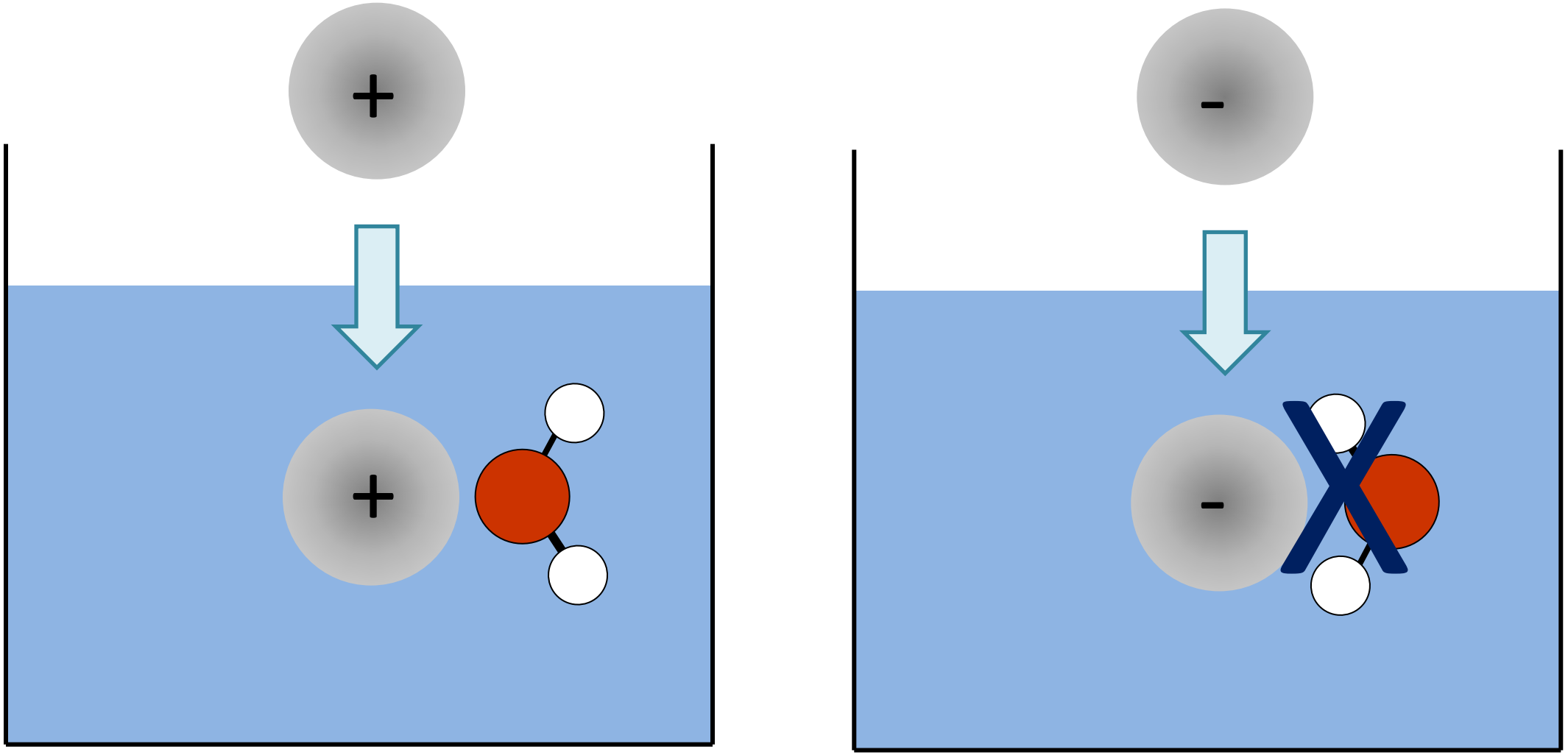
Pablo G. Debenedetti and H. Eugene Stanley

Physics Today, June 2003.

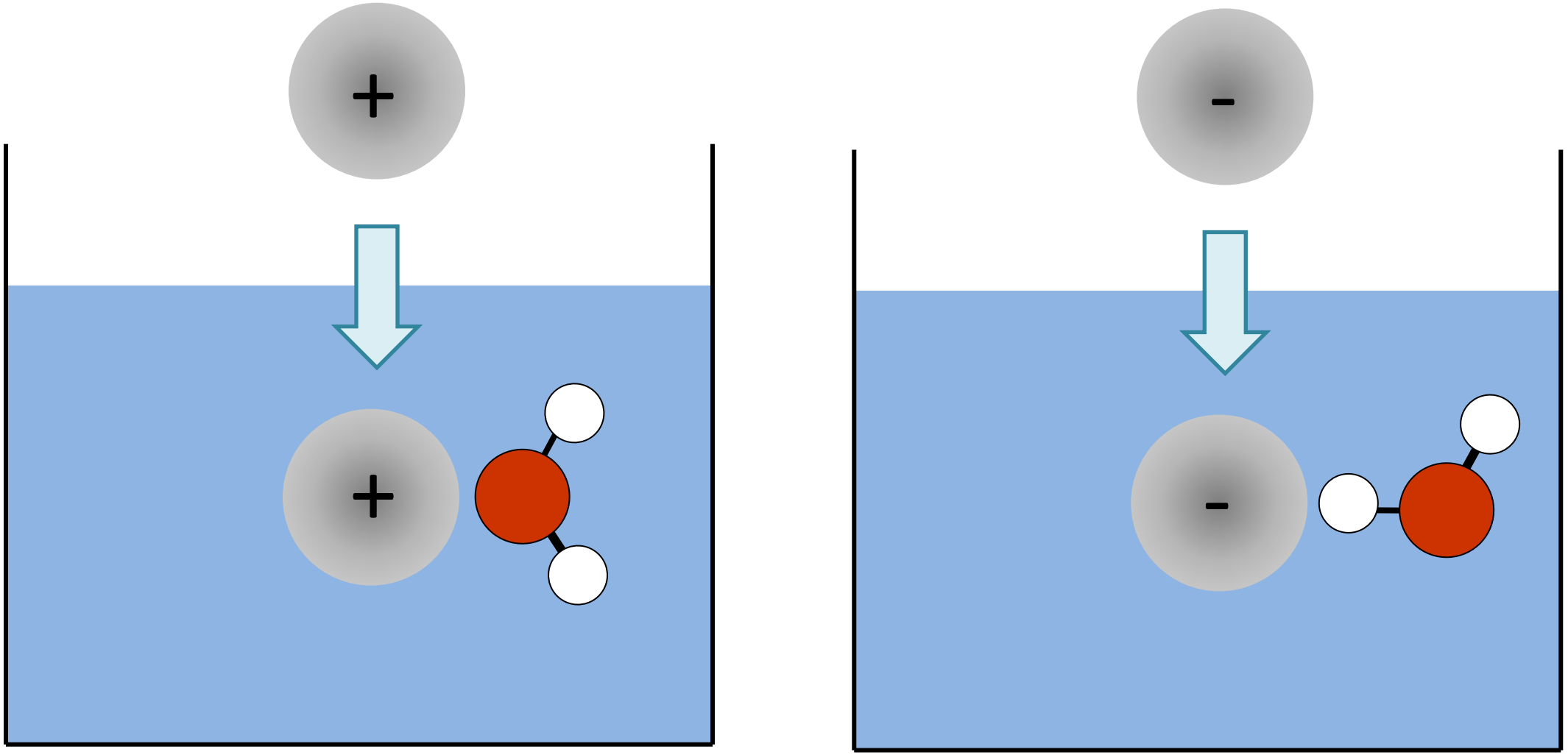
War Over Supercooled Water

Physics Today, Aug 18, 2018.

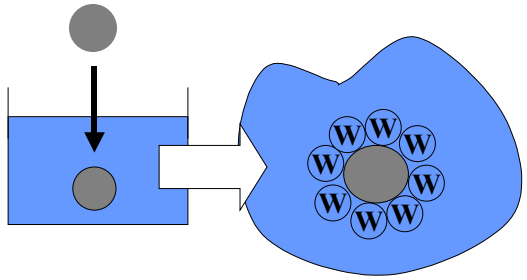


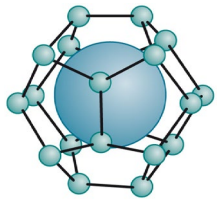


Adding salt to water…



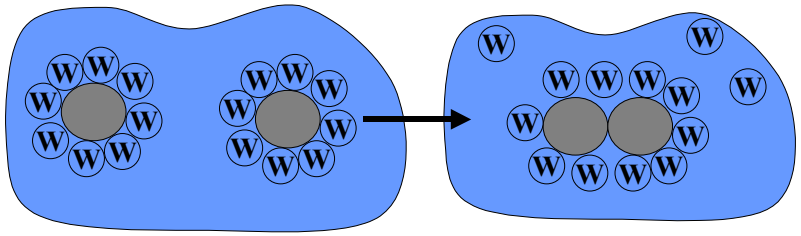
Water is not just a dipole!





$\Delta S < 0$
$\Delta Cp > 0$
$\Delta G > 0$

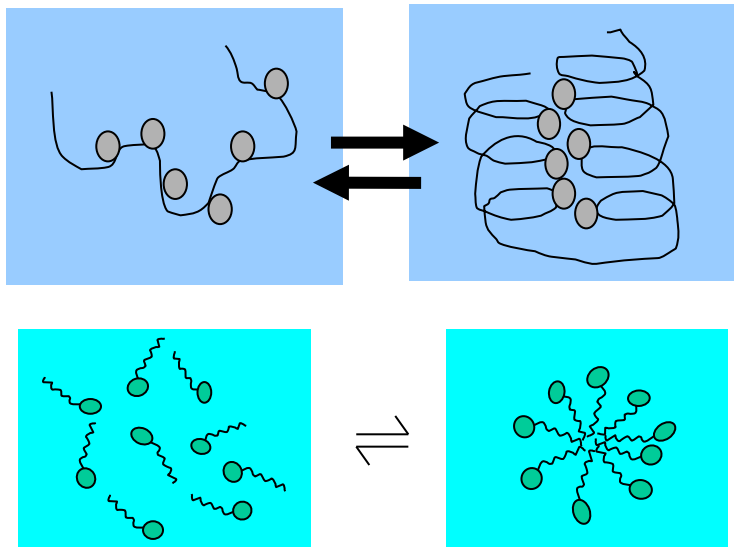
Dissolving methane/oily stuff in water is thermodynamically **unfavorable.**



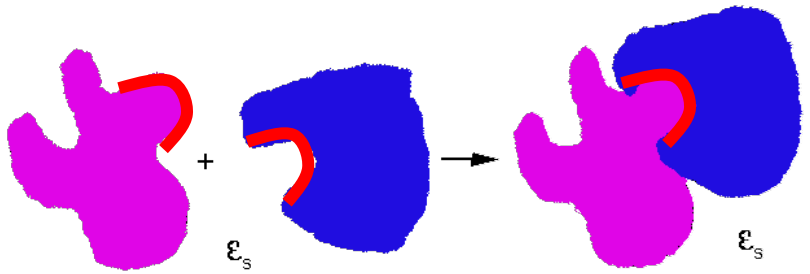
$\Delta S > 0$
$\Delta G < 0$

Water entropy drives **hydrophobic association!**

Water structure ⇒ Water-mediated interactions

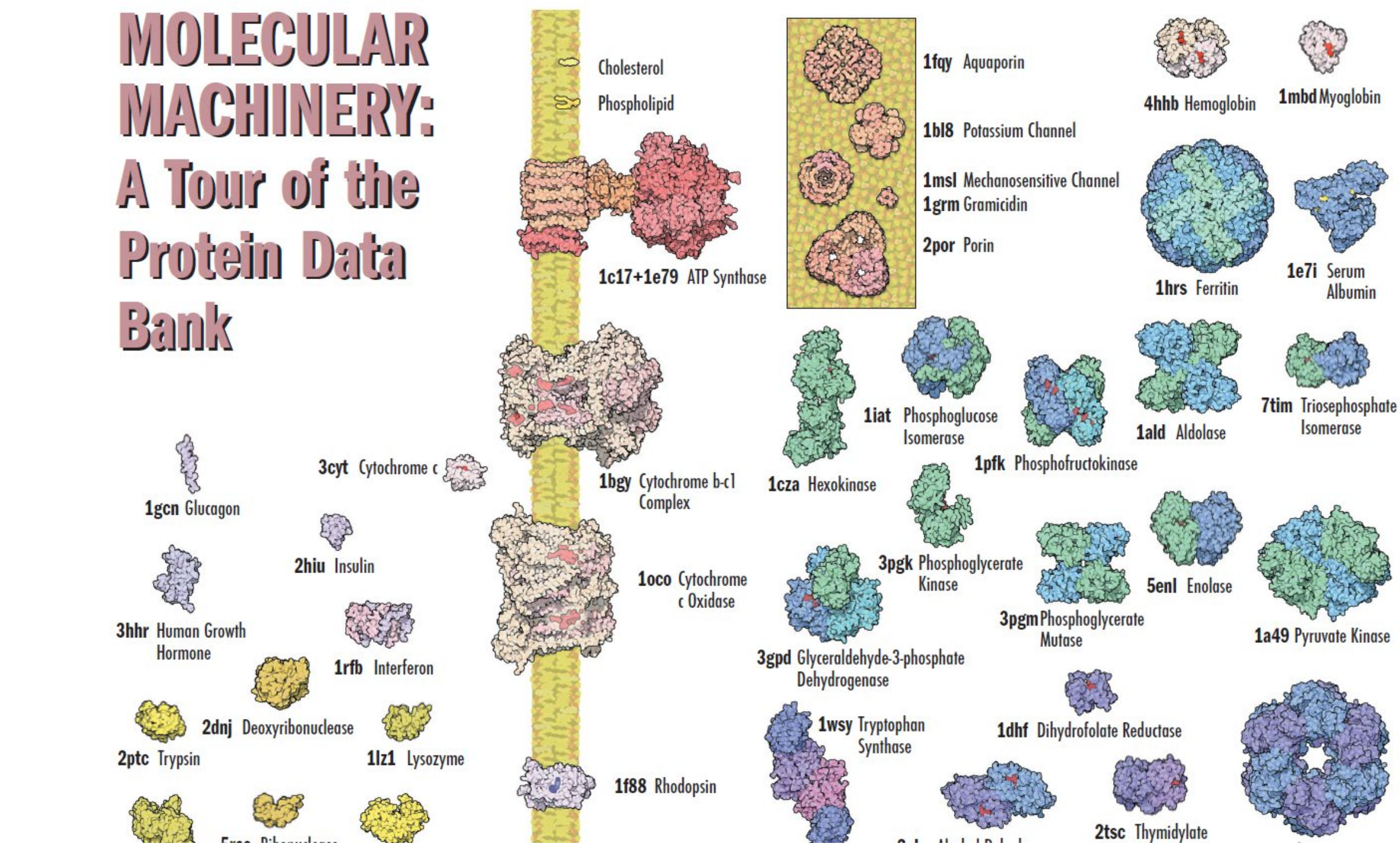


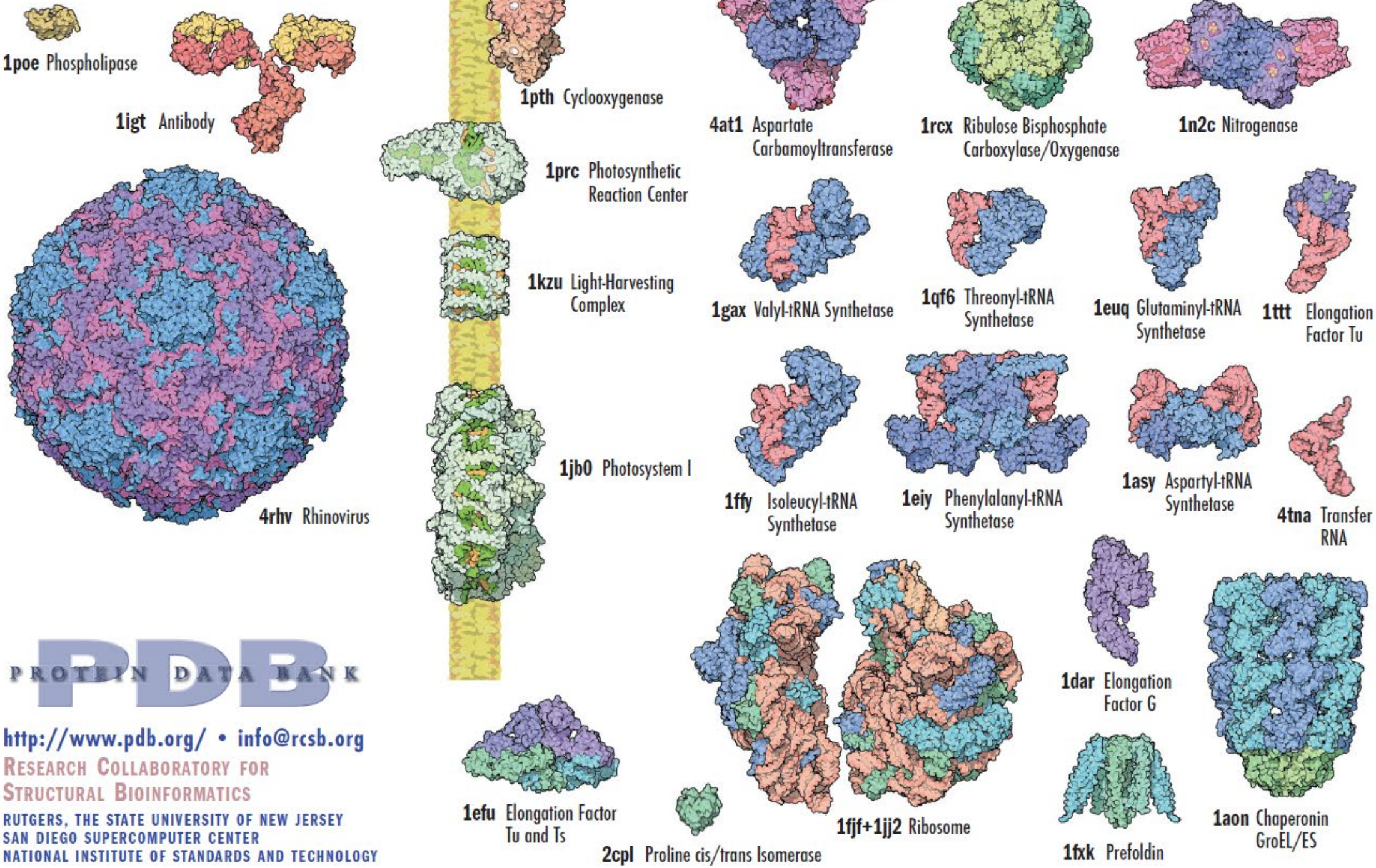
Hydrophobic residue



Binding / Recognition

MOLECULAR MACHINERY: A Tour of the Protein Data Bank



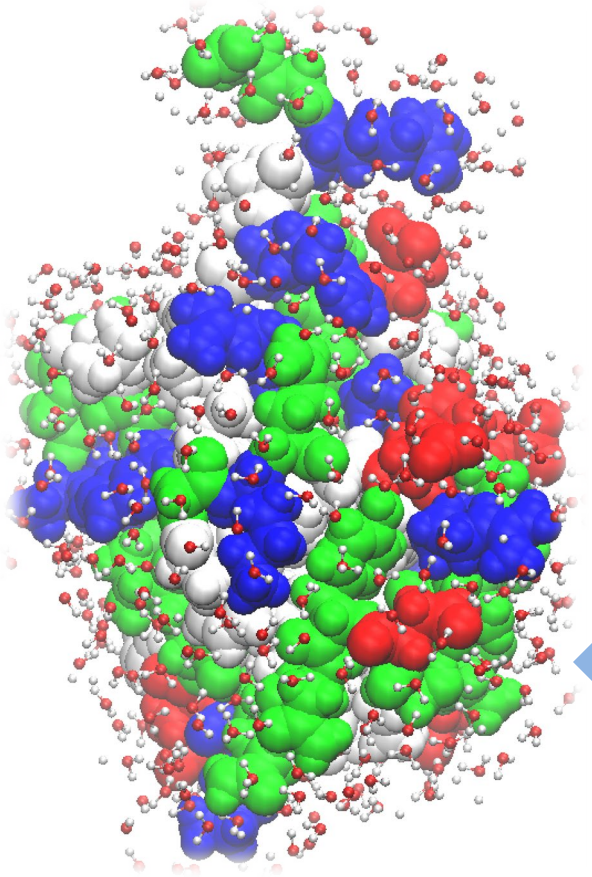


PROTEIN DATA BANK

http://www.pdb.org/ • info@rcsb.org

RESEARCH COLLABORATORY FOR STRUCTURAL BIOINFORMATICS

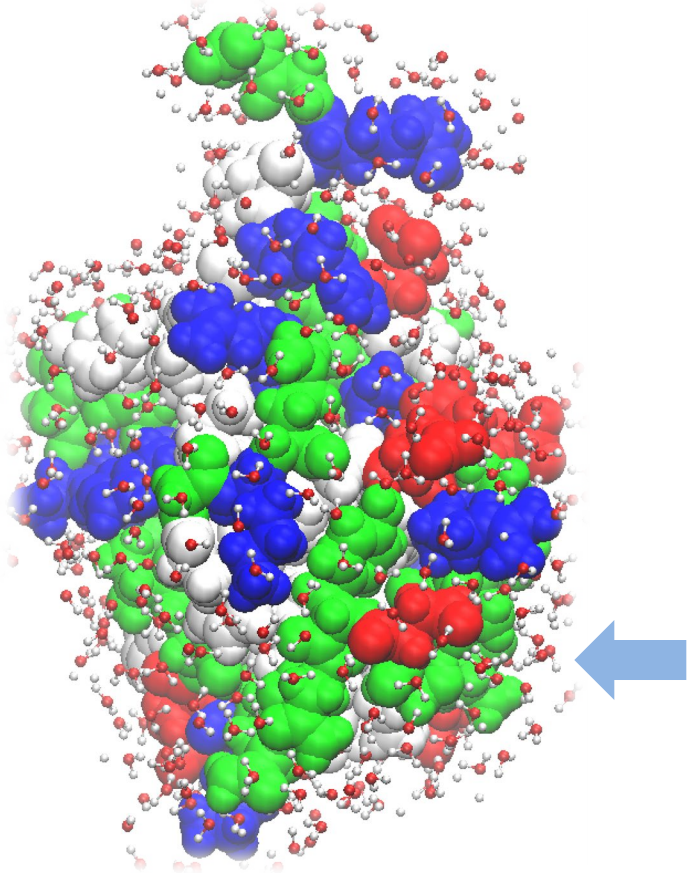
RUTGERS, THE STATE UNIVERSITY OF NEW JERSEY
SAN DIEGO SUPERCOMPUTER CENTER
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY



Focus on water?

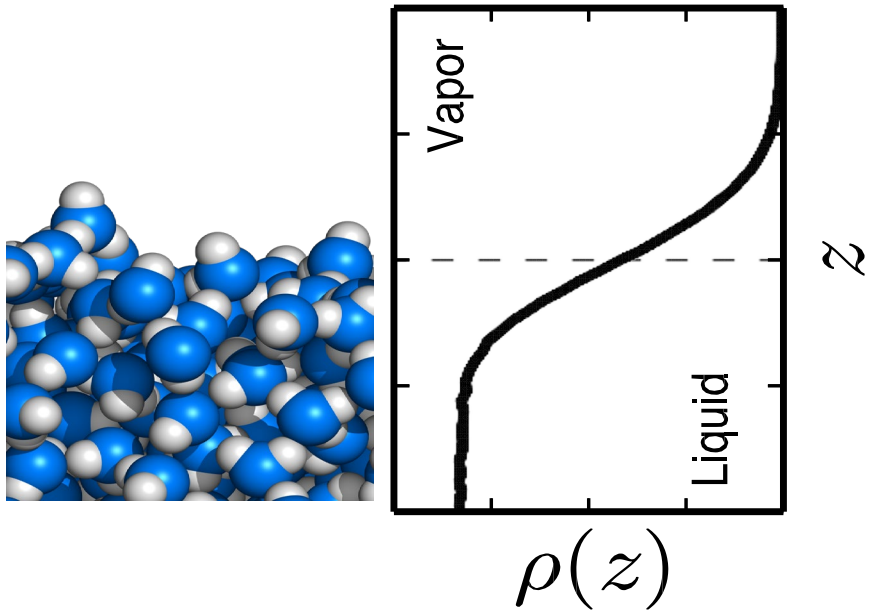
How do we characterize hydrophobicity of proteins from a molecular perspective?

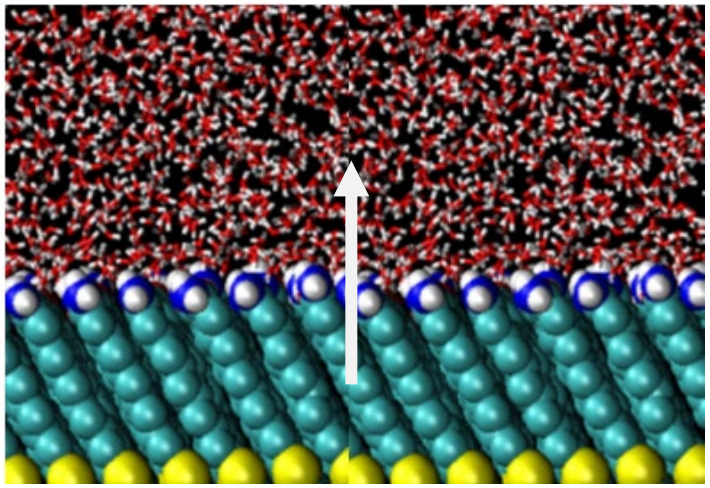
A new perspective on characterizing **hydrophobicity** of proteins and nanoscale surfaces



Focus on water density near the protein surface

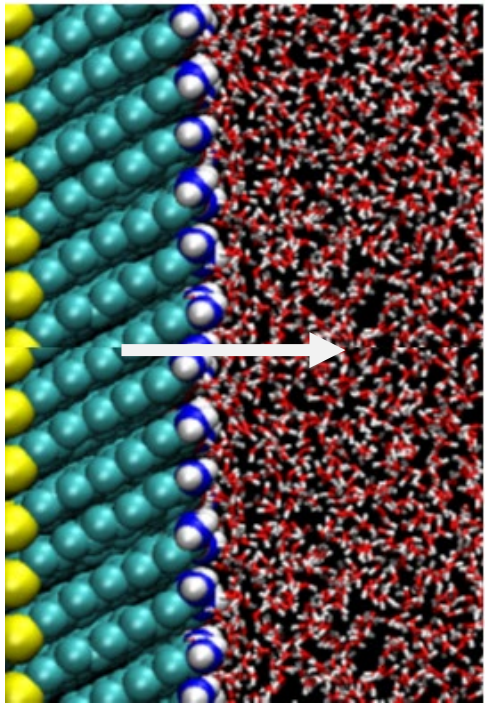
Expectation of density profile at a hydrophobic interface



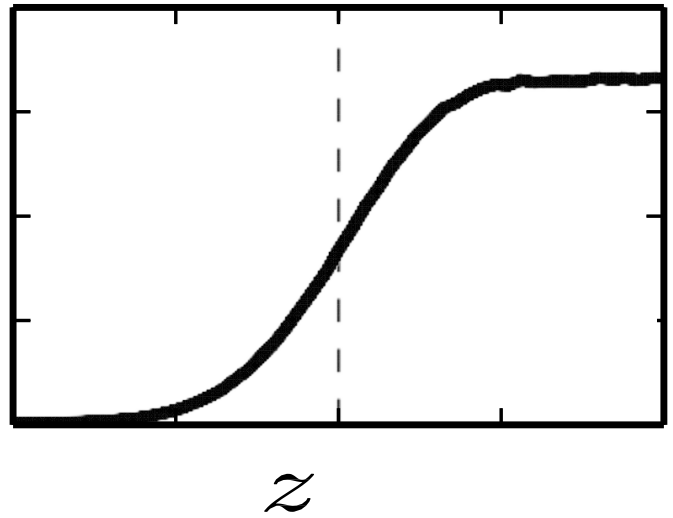


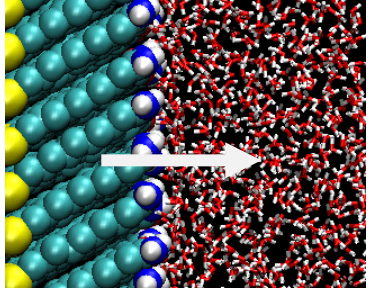
Does **the local water density** provide useful signature of hydrophobicity?

$-CF_3$, $-CH_3$, $-OCH_3$, $-CONHCH_3$, $-CN$, $-OH$, and $-CONH_2$



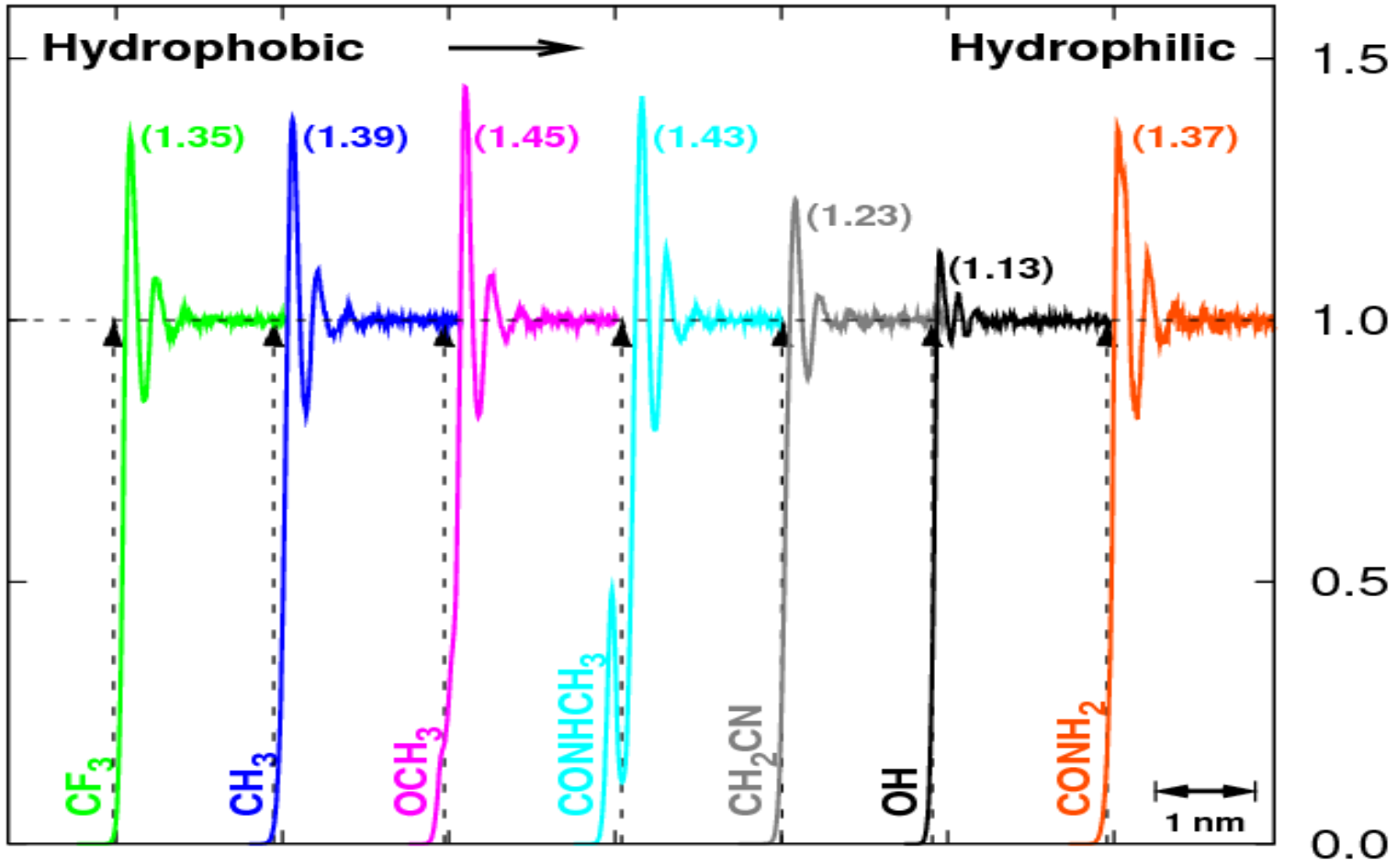
sigmoidal density profile near a hydrophobic (-CF3, -CH3) surface?





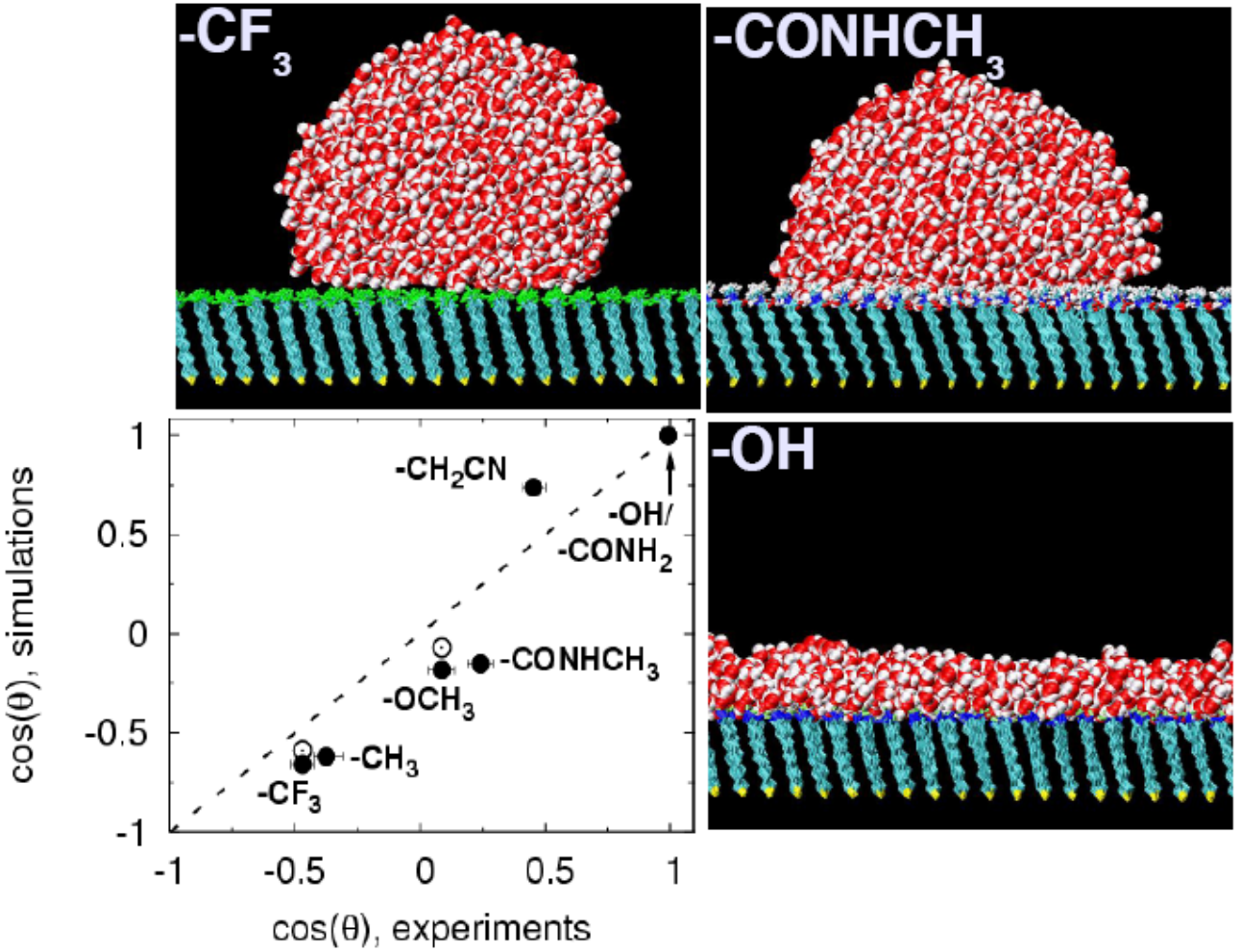
Water density profiles near different surfaces

Local density of water/bulk density

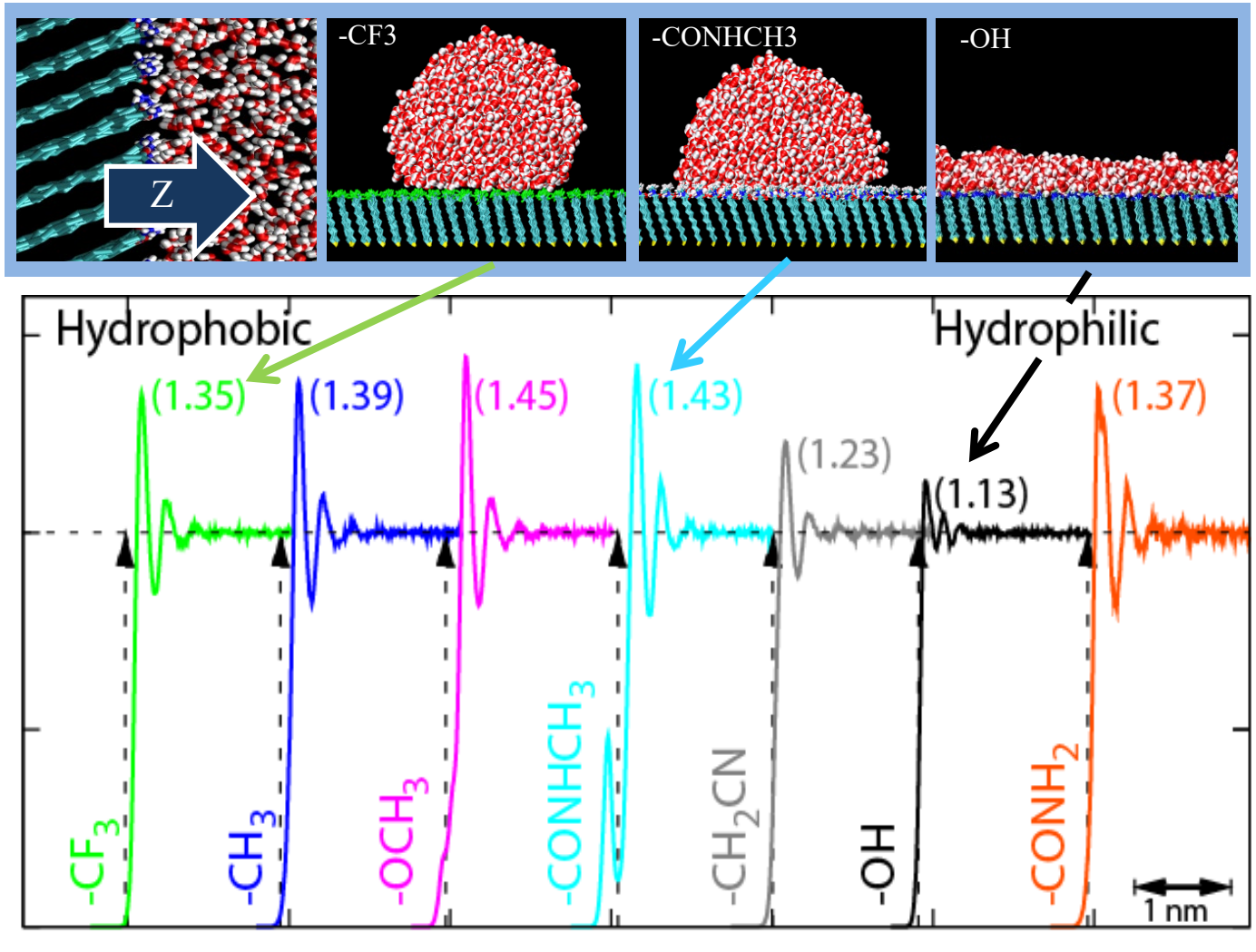


Strange result! Something wrong?

Are contact angle measurements consistent with chemistry?



Local water density serves as a poor signature of hydrophobicity

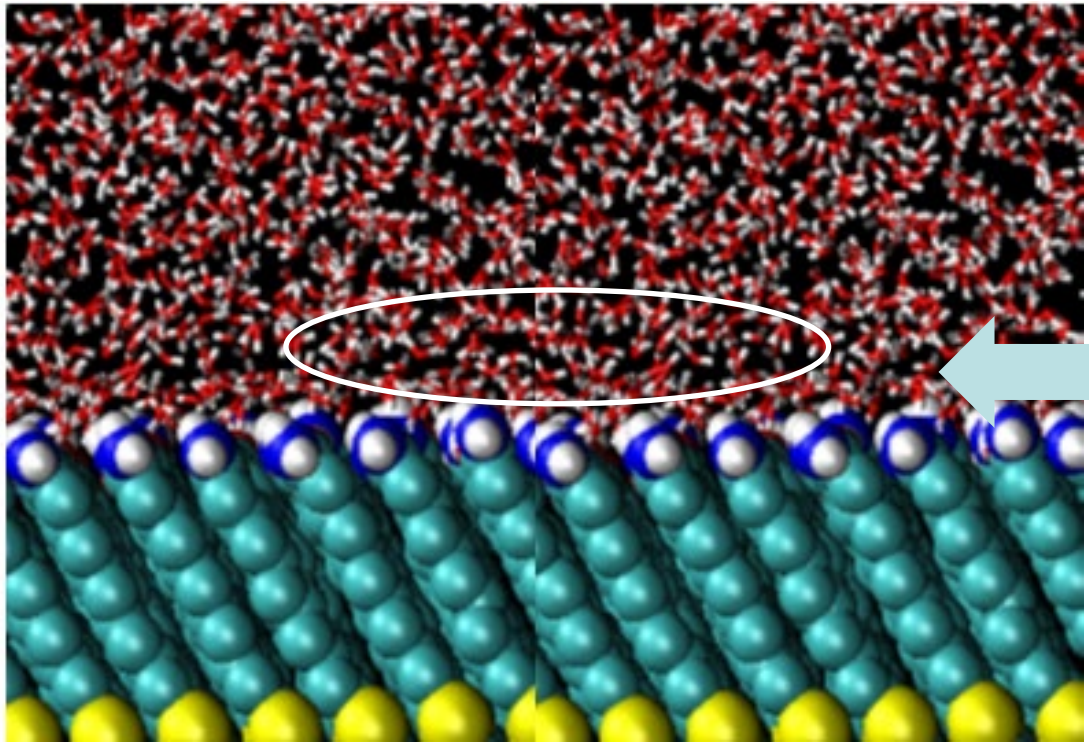


Water density normalized by bulk density

Godawat, Jamadagni, and Garde PNAS, 2009

(If not the average density or the width), what are the microscopic signatures that inform on the hydrophobicity/philicity of the underlying surface?

The Big Idea!



Quantify
water density fluctuations
near the interface!

Godawat, Jamadagni, and Garde PNAS, 2009

THE NEW YORKER

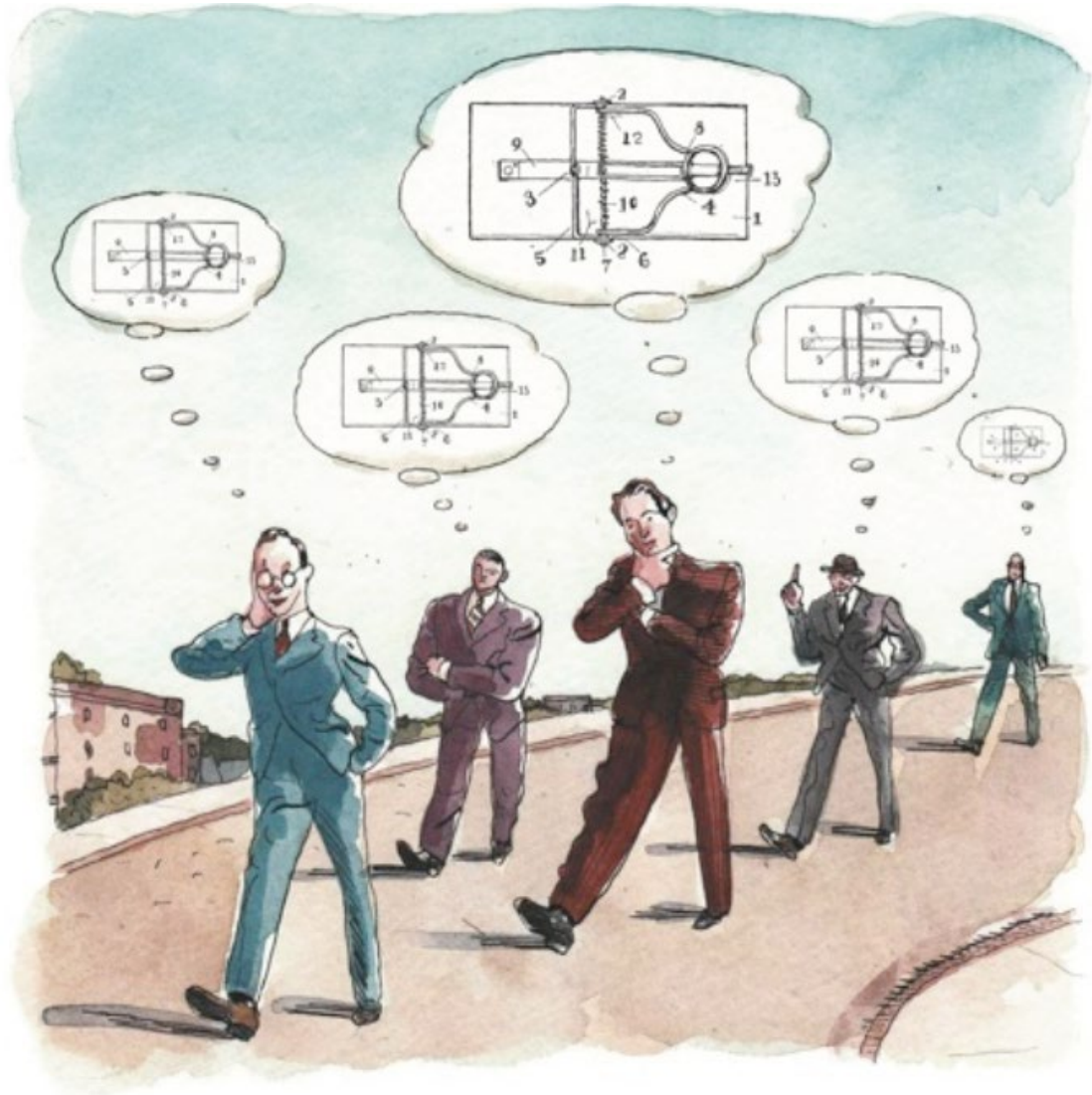
ANNALS OF INNOVATION

IN THE AIR

Who says big ideas are rare?

by Malcolm Gladwell

MAY 12, 2008



The history of science is full of ideas that several people had at the same time.

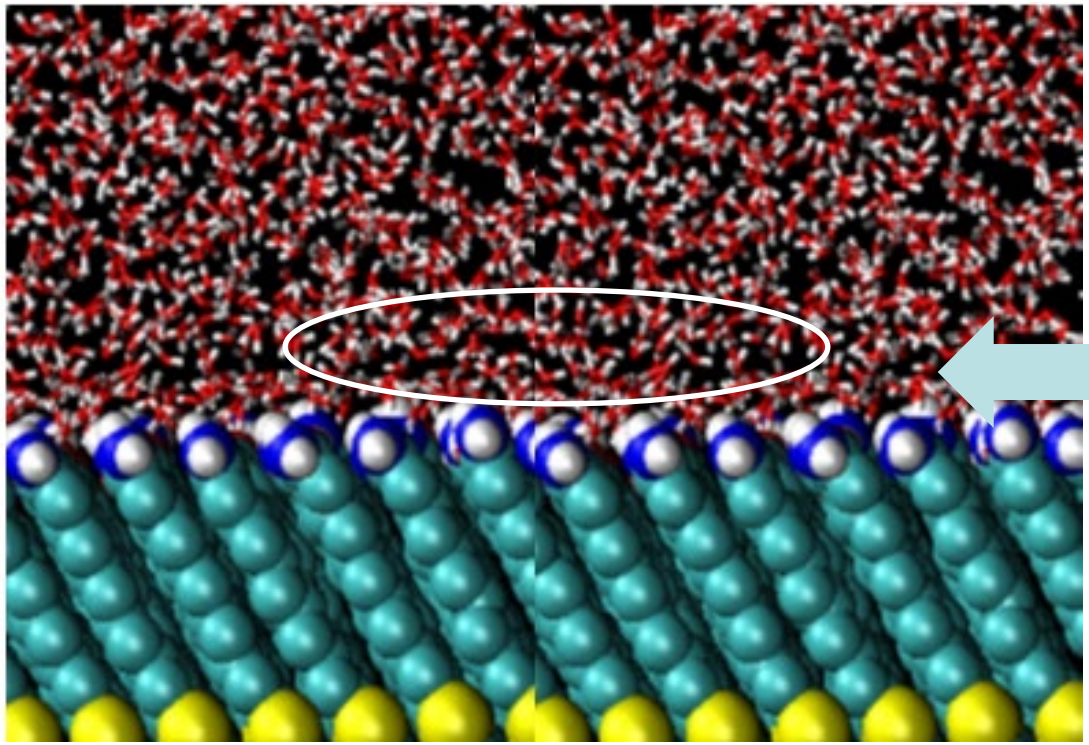
Stigler's law and Pinning tails on donkeys?

The statistician Stephen Stigler once wrote an elegant essay about the futility of the practice of eponymy in science—that is, the practice of naming a scientific discovery after its inventor. As Stigler pointed out, "It can be found that Laplace employed Fourier Transforms in print before Fourier published on the topic, that Lagrange presented Laplace Transforms before Laplace began his scientific career, that Poisson published the Cauchy distribution in 1824, twenty-nine years before Cauchy touched on it in an incidental manner, and that Bienaymé stated and proved the Chebychev Inequality a decade before and in greater generality than Chebychev's first work on the topic." For that matter, the Pythagorean theorem was known before Pythagoras; Gaussian distributions were not discovered by Gauss.

The examples were so legion that Stigler declared the existence of Stigler's Law: "No scientific discovery is named after its original discoverer." There are just too many people with an equal shot at those ideas floating out there in the ether. We think we're pinning medals on heroes. In fact, we're pinning tails on donkeys.

Stigler's Law was true, Stigler gleefully pointed out, even of Stigler's Law itself. The idea that credit does not align with discovery, he reveals at the very end of his essay, was in fact first put forth by Merton. "We may expect," Stigler concluded, "that in years to come, Robert K. Merton, and his colleagues and students, will provide us with answers to these and other questions regarding eponymy, completing what, but for the Law, would be called the Merton Theory of the reward system of science."

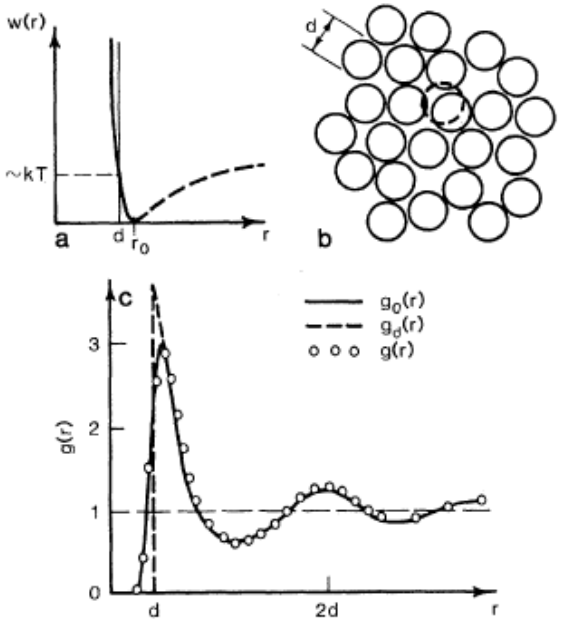
The Big Idea!



Quantify
water density fluctuations
near the interface!

1. David Chandler
2. Calculations by my student Sarupria (PRL, 2009)
3. A clearer picture → John Weeks

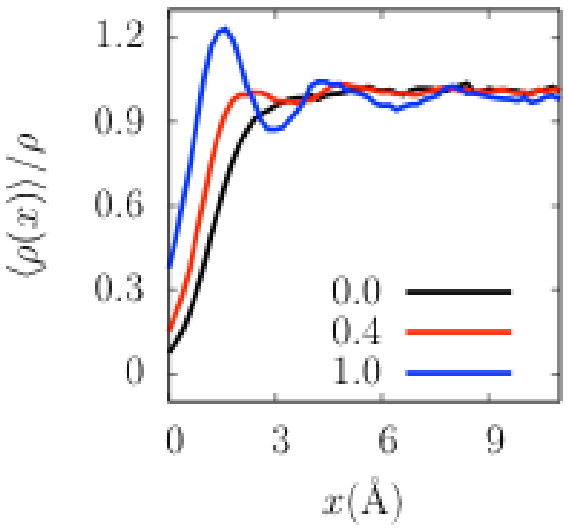
Homogeneous (bulk) fluid → **hard-sphere reference** describes structure well.



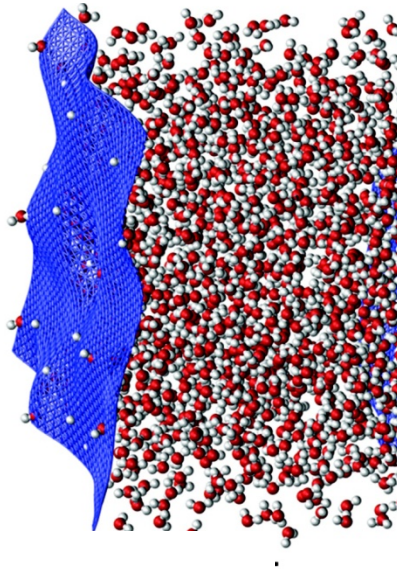
Attractions serve as a mean field, and do not affect structure dramatically.

Not so for a fluid near a hard-wall!

Why?



REPULSIVE



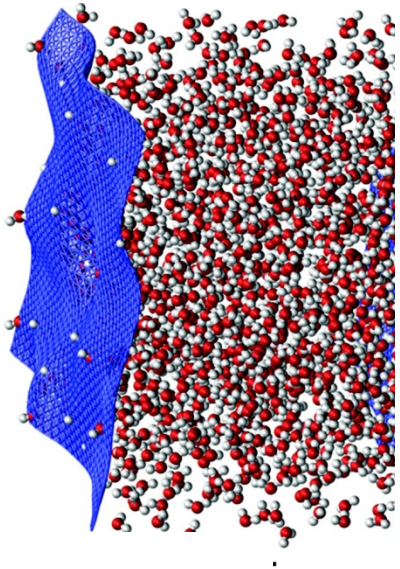
A. J. Patel, P. Varilly and D. Chandler, *J. Phys Chem. B*, **114**, 1632 (2010).

Science, 1983

Van der Waals Picture of Liquids, Solids, and Phase Transformations

David Chandler, John D. Weeks, Hans C. Andersen

REPULSIVE



Not so for a fluid near a hard-wall!

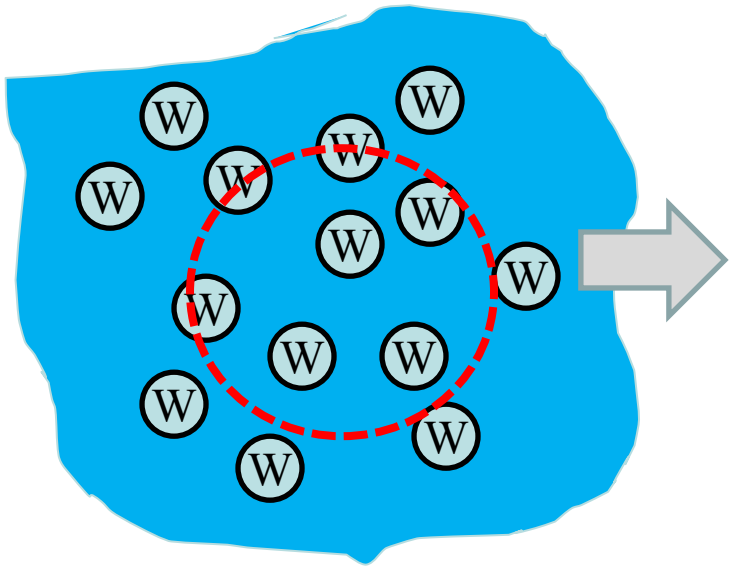
Why? →

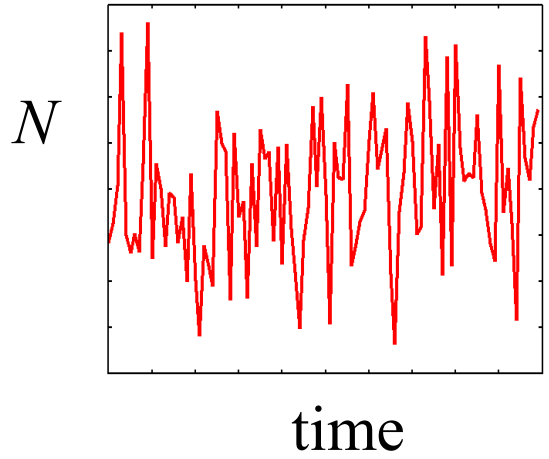
Exceptions and Qualifications

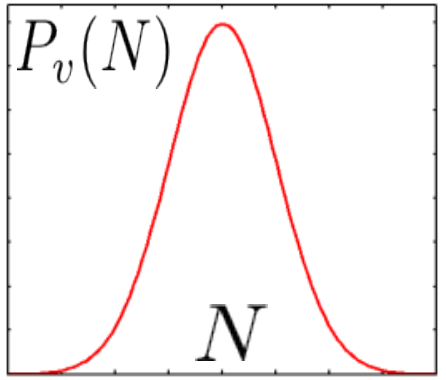
Of course, even for these cases where there are no strong associative forces, the picture will break down at low densities where the compressibility is sufficiently high to allow for relatively long wavelength fluctuations [that is, at lower densities, the repulsive cores are not nearly as effective in screening (*16*) the interparticle correlations caused by the attractions]. For example, Eq. 12 predicts incorrect (classical) behavior at the critical point.

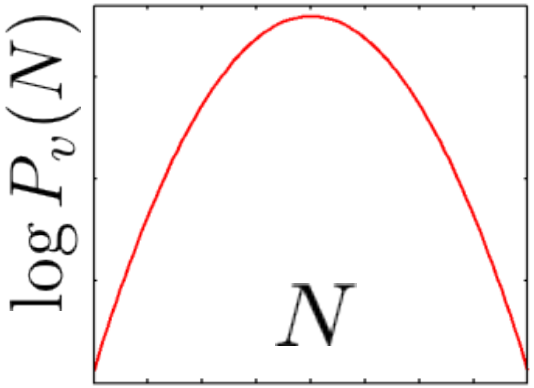
vdW attractions mask dewetting, yet, (some) features of vapor-liquid like nature of the interface must survive.

Quantifying density fluctuations









$$\Delta G = \quad \mu^{\mathrm{ex}} = -k_{\mathrm{B}}T \log P_v(0)$$

Proc. Natl. Acad. Sci. USA
Vol. 93, pp. 8951–8955, August 1996
Biophysics

An information theory model of hydrophobic interactions

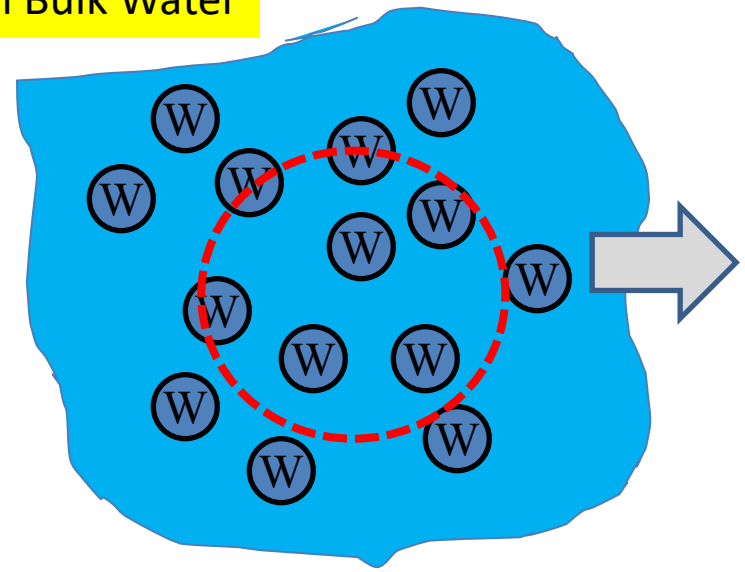
(solvation/hydrophobic effects/biomolecule solution structure)

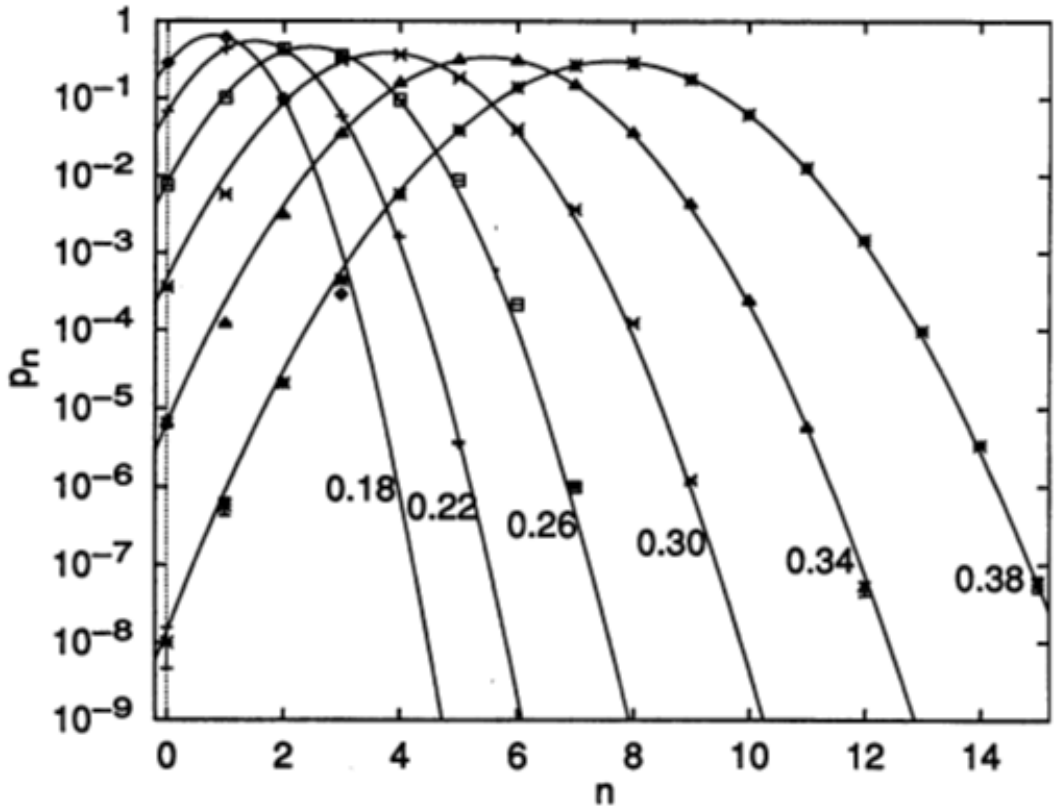
GERHARD HUMMER*, SHEKHAR GARDE*†, ANGEL E. GARCÍA*, ANDREW POHORILLE‡§, AND LAWRENCE R. PRATT*¶

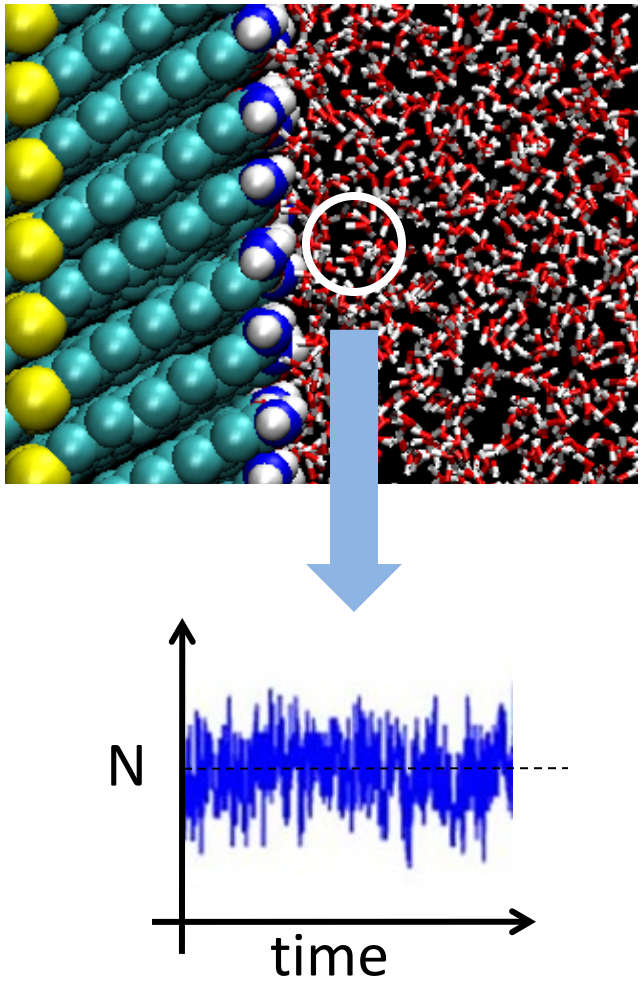
*Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545; ‡Department of Pharmaceutical Chemistry, University of California, San Francisco, CA 94143; and §National Aeronautics and Space Administration, Ames Research Center, MS-239-4, Moffett Field, CA 94035-1000

Communicated by David Chandler, University of California, Berkeley, CA, February 27, 1996 (received for review December 13, 1995)

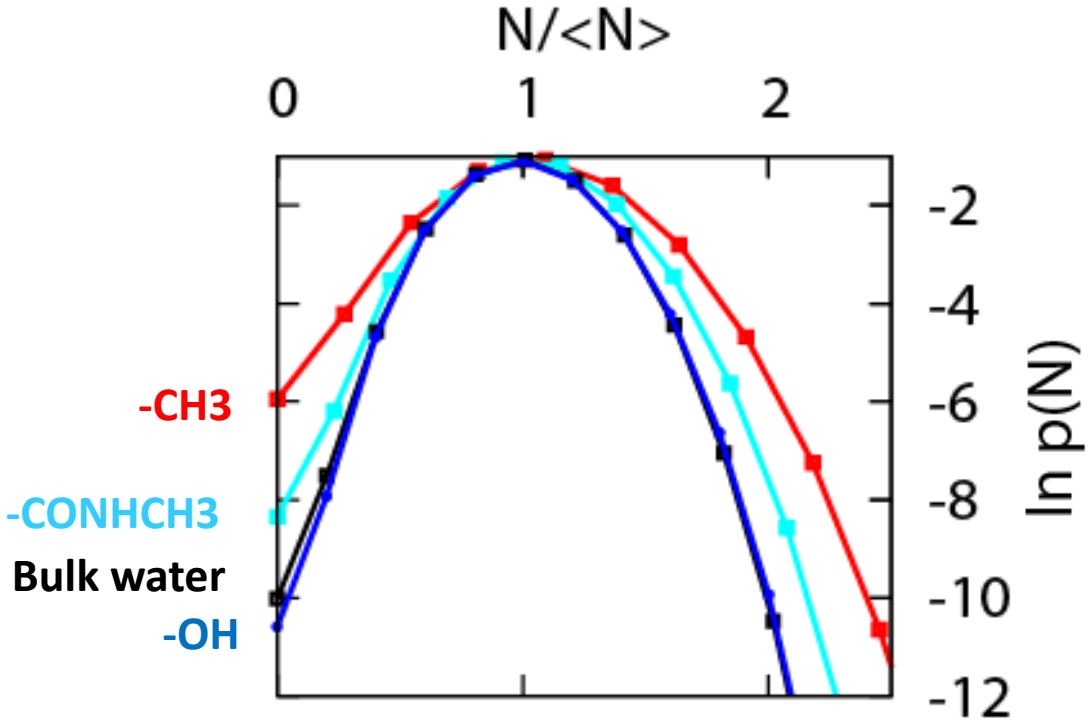
In Bulk Water





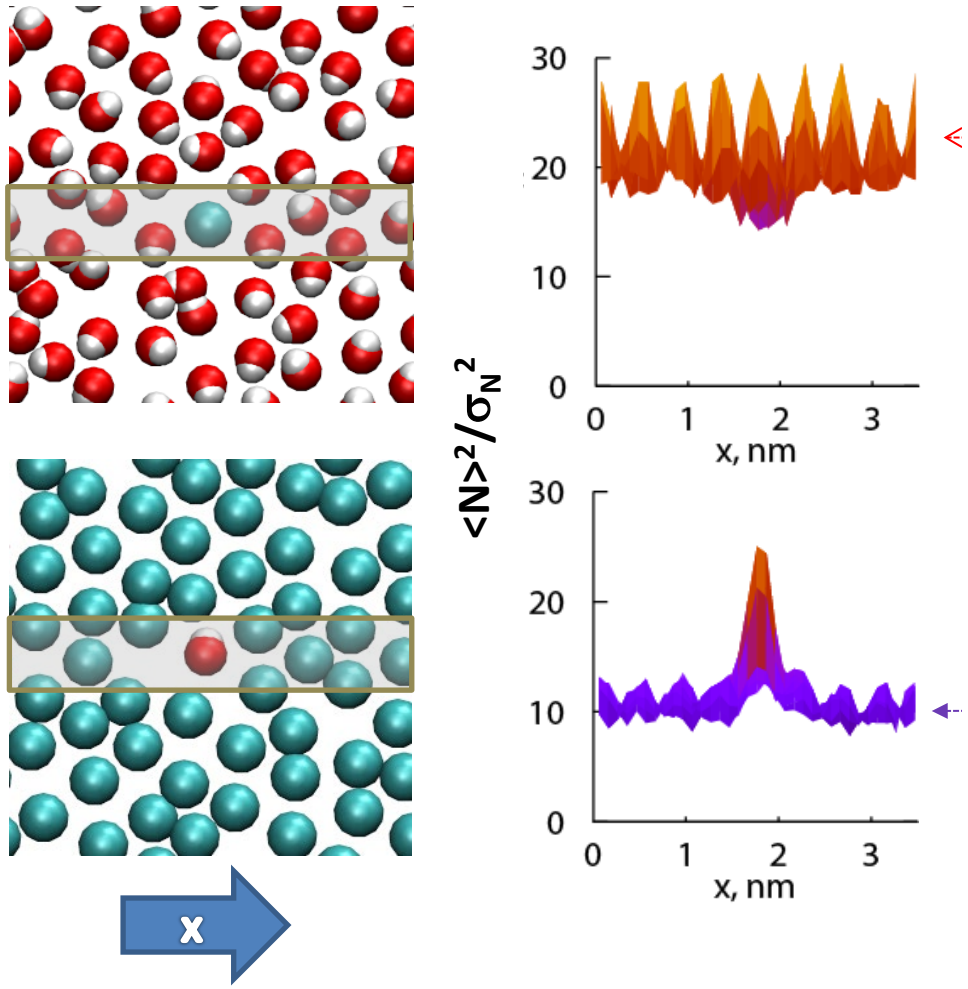


Fluctuations are enhanced near hydrophobic surfaces and are bulk-like near hydrophilic surfaces



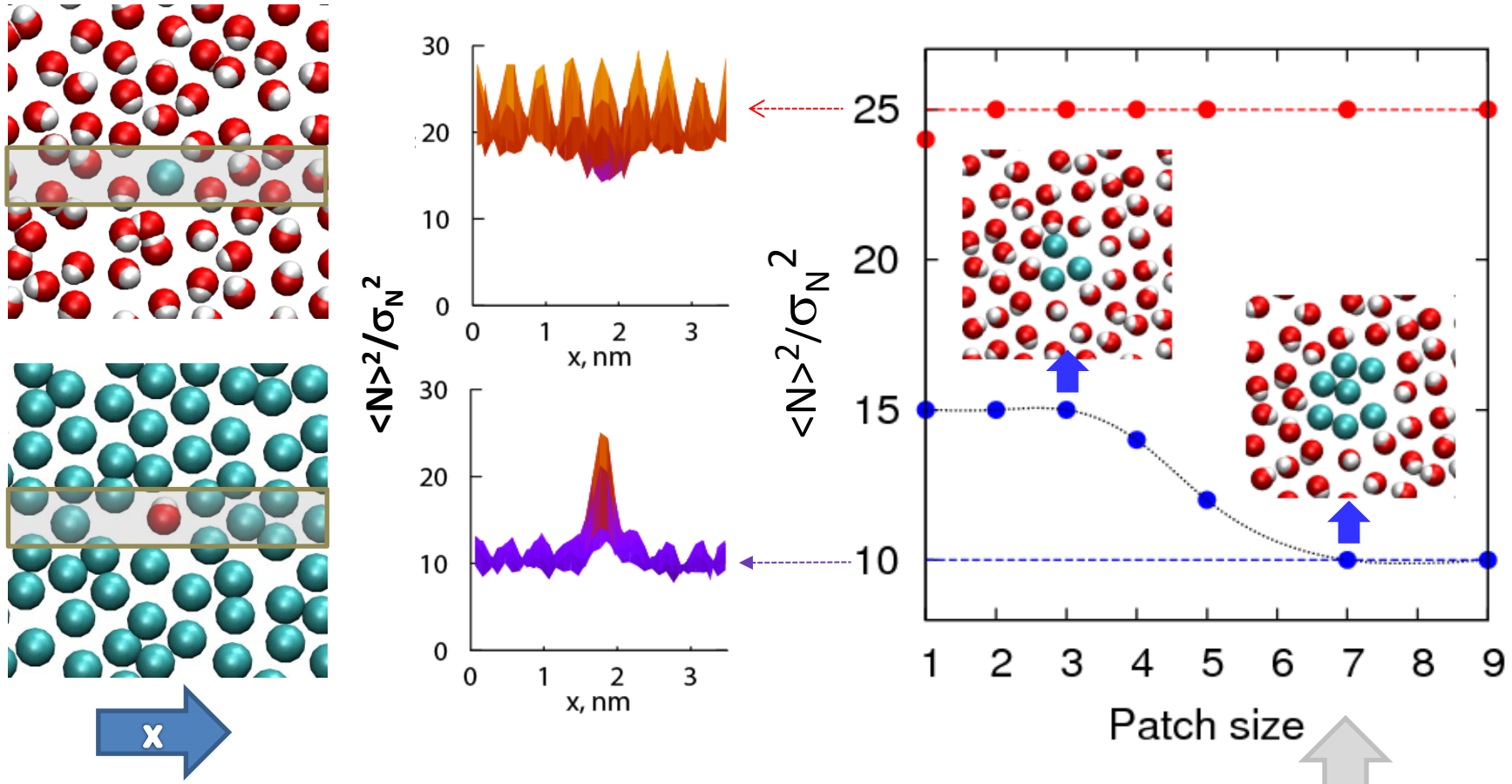
Godawat, Jamadagni, and Garde PNAS, 2009

Hydrophobicity of a group depends on the context



Acharya et al. Faraday Discussions, 2010

Hydrophobicity of a group depends on the context



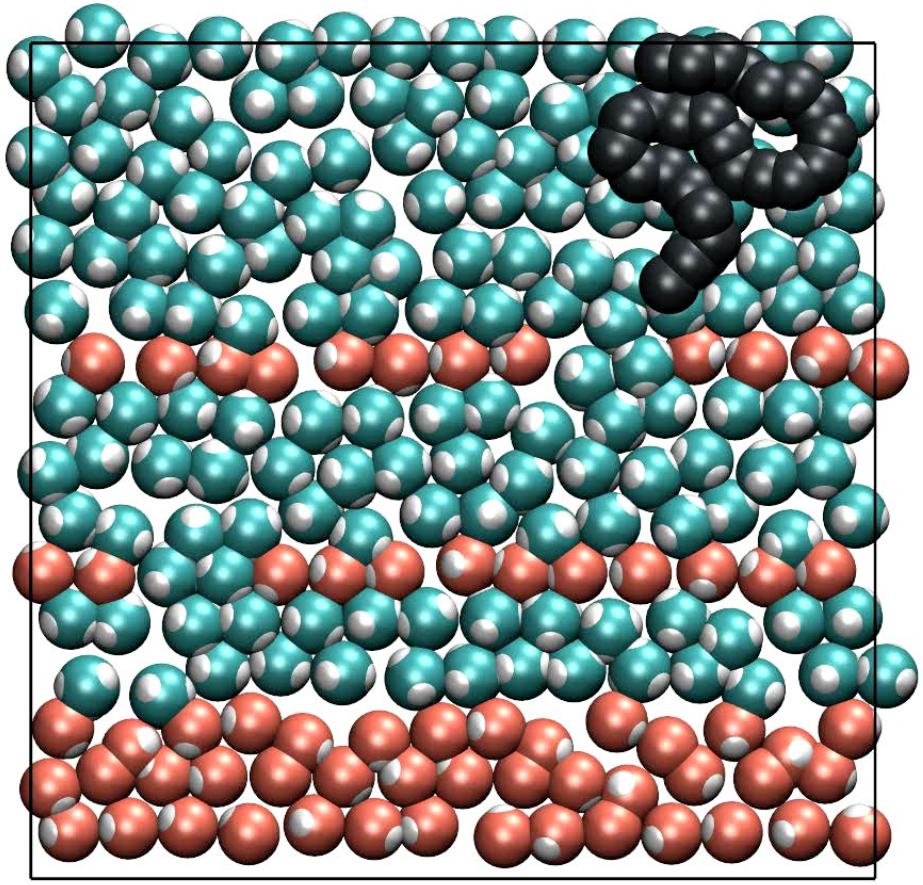
How big does the hydrophobic patch have to be before it is "hydrophobic"?

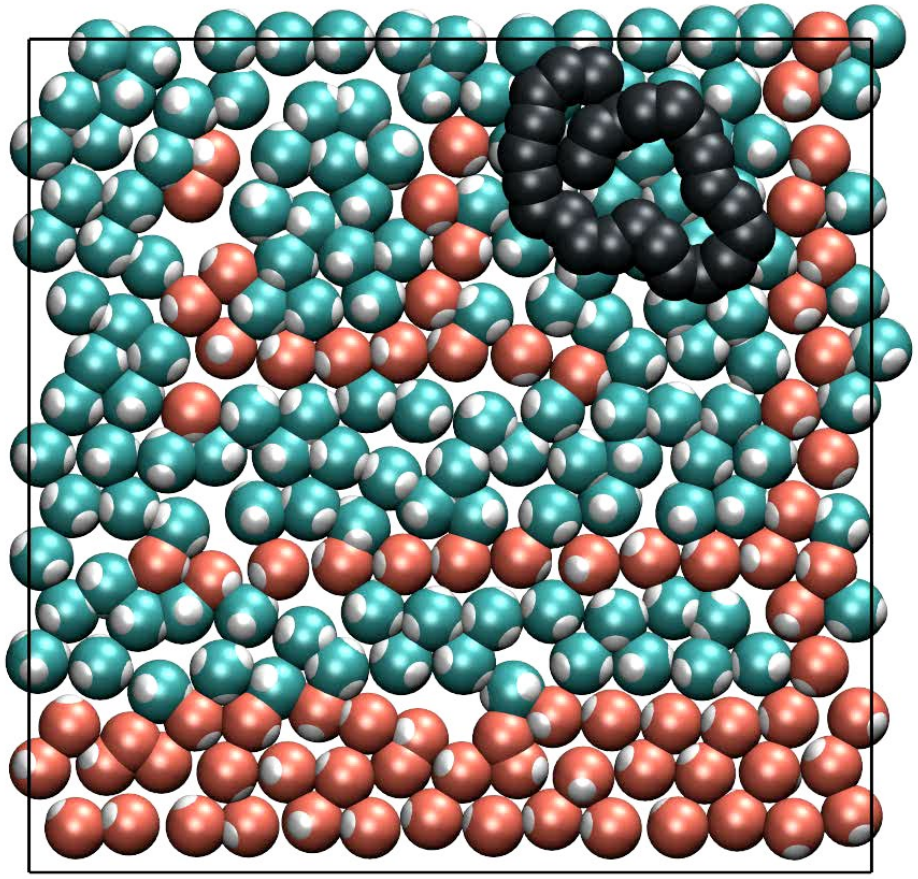
7+ & contiguous

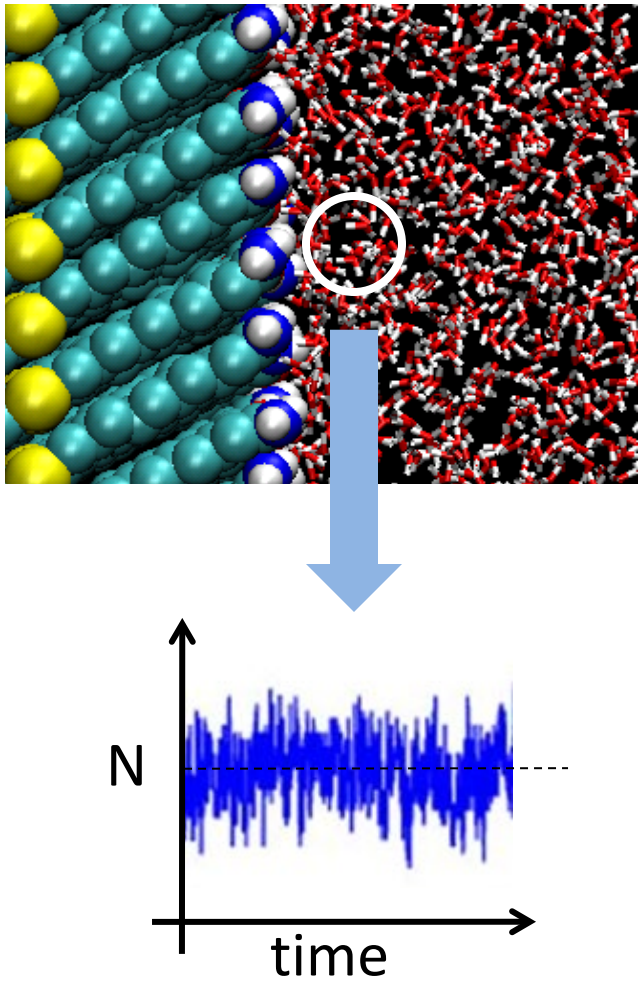
Acharya et al. Faraday Discussions, 2010

Detour

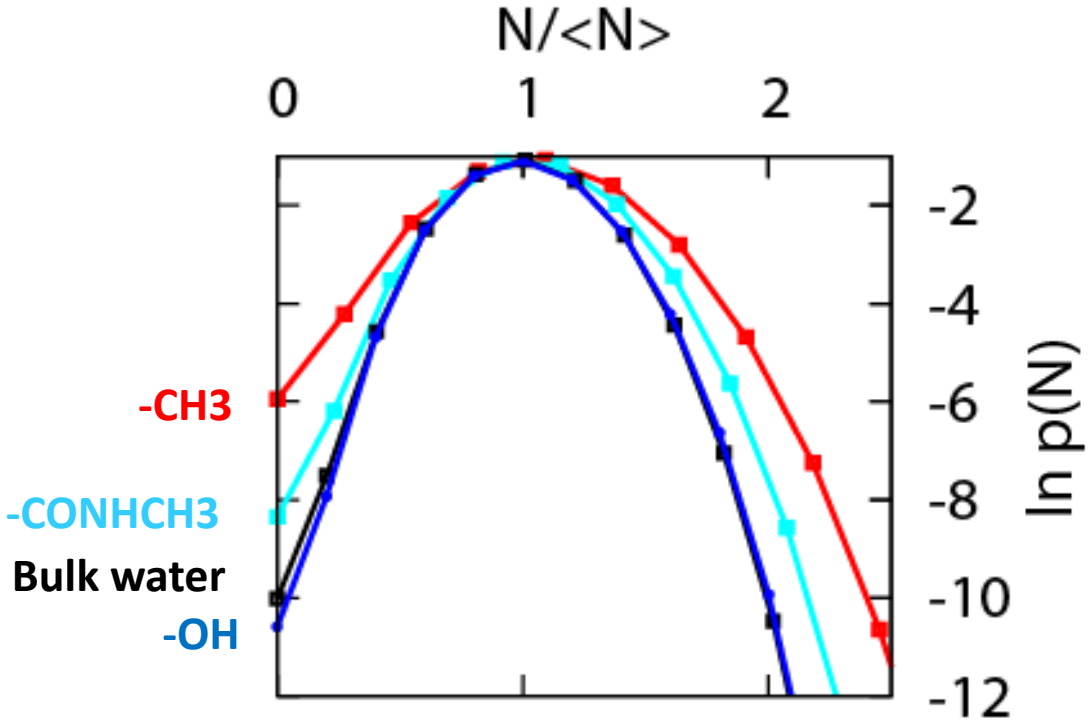
Solving mazes



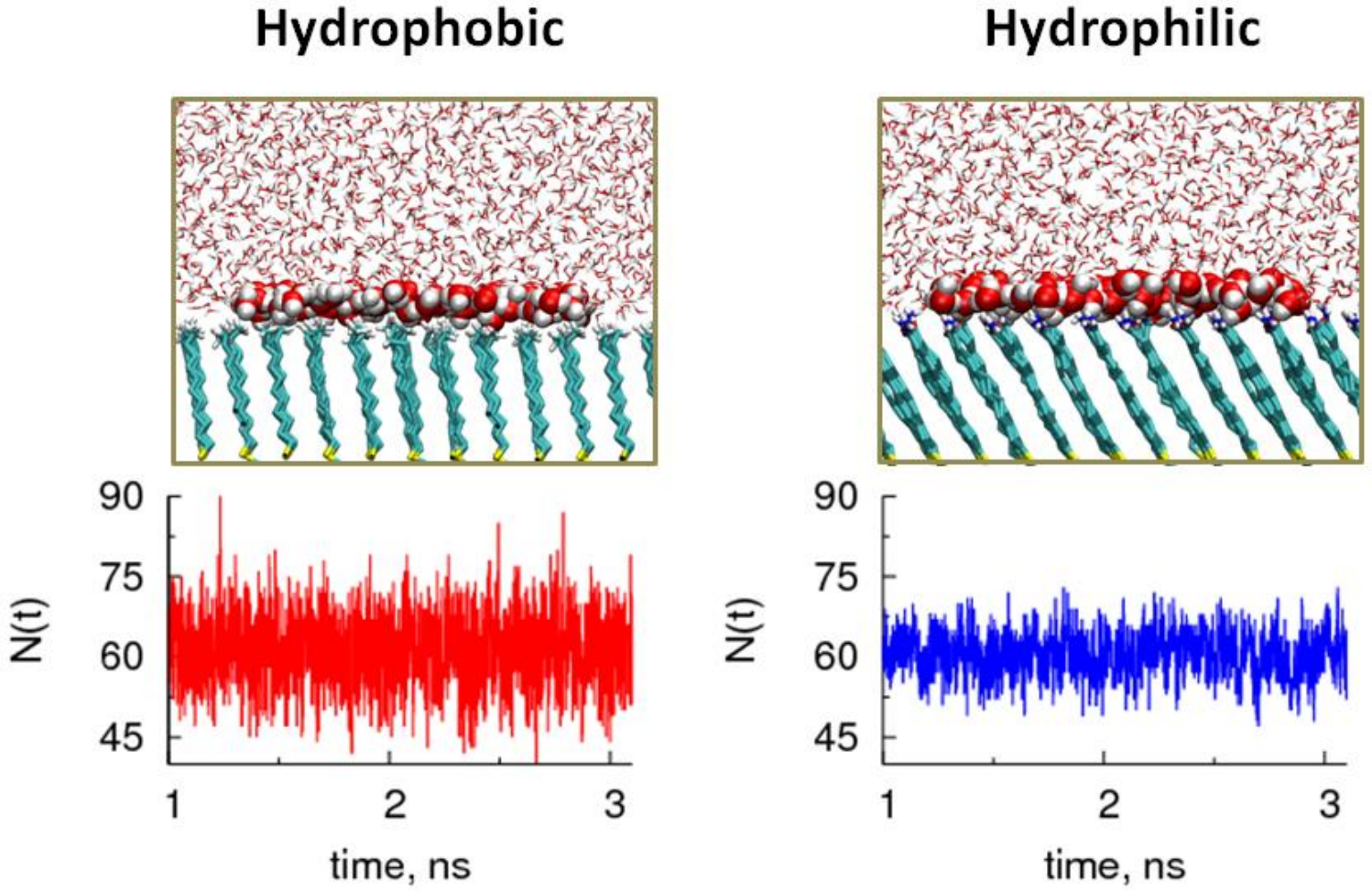




Fluctuations are enhanced near hydrophobic surfaces and are bulk-like near hydrophilic surfaces



Godawat, Jamadagni, and Garde PNAS, 2009



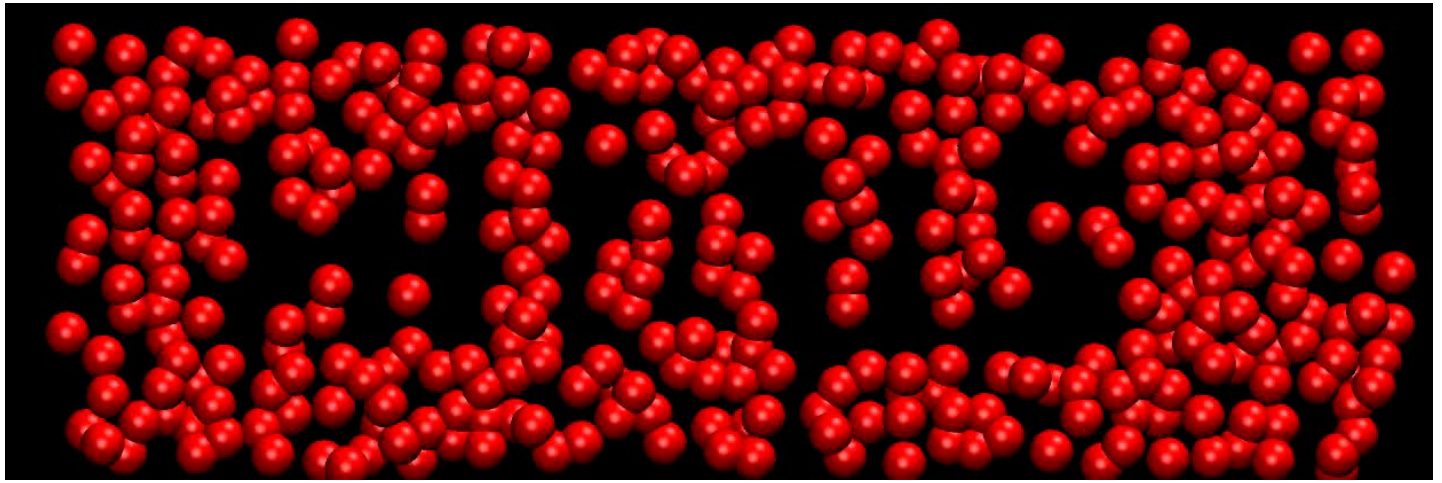
Fluctuations are enhanced near hydrophobic surfaces
and are bulk-like near hydrophilic surfaces

Godawat, Jamadagni, and Garde PNAS, 2009

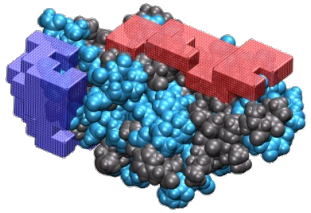
Amish Patel

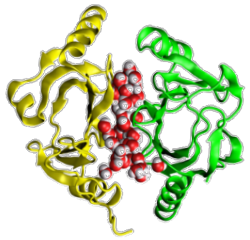
Measuring rare density fluctuations (in the tails): a special umbrella sampling technique

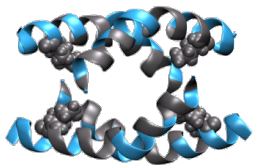
INDirect Umbrella Sampling



$P_v(N)$ in arbitrary shaped volumes (INDUS)

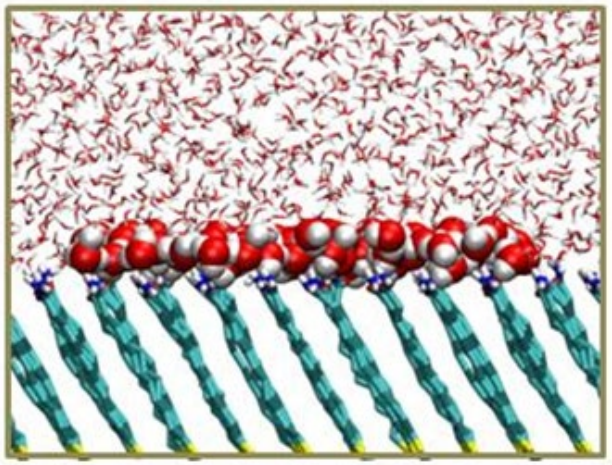






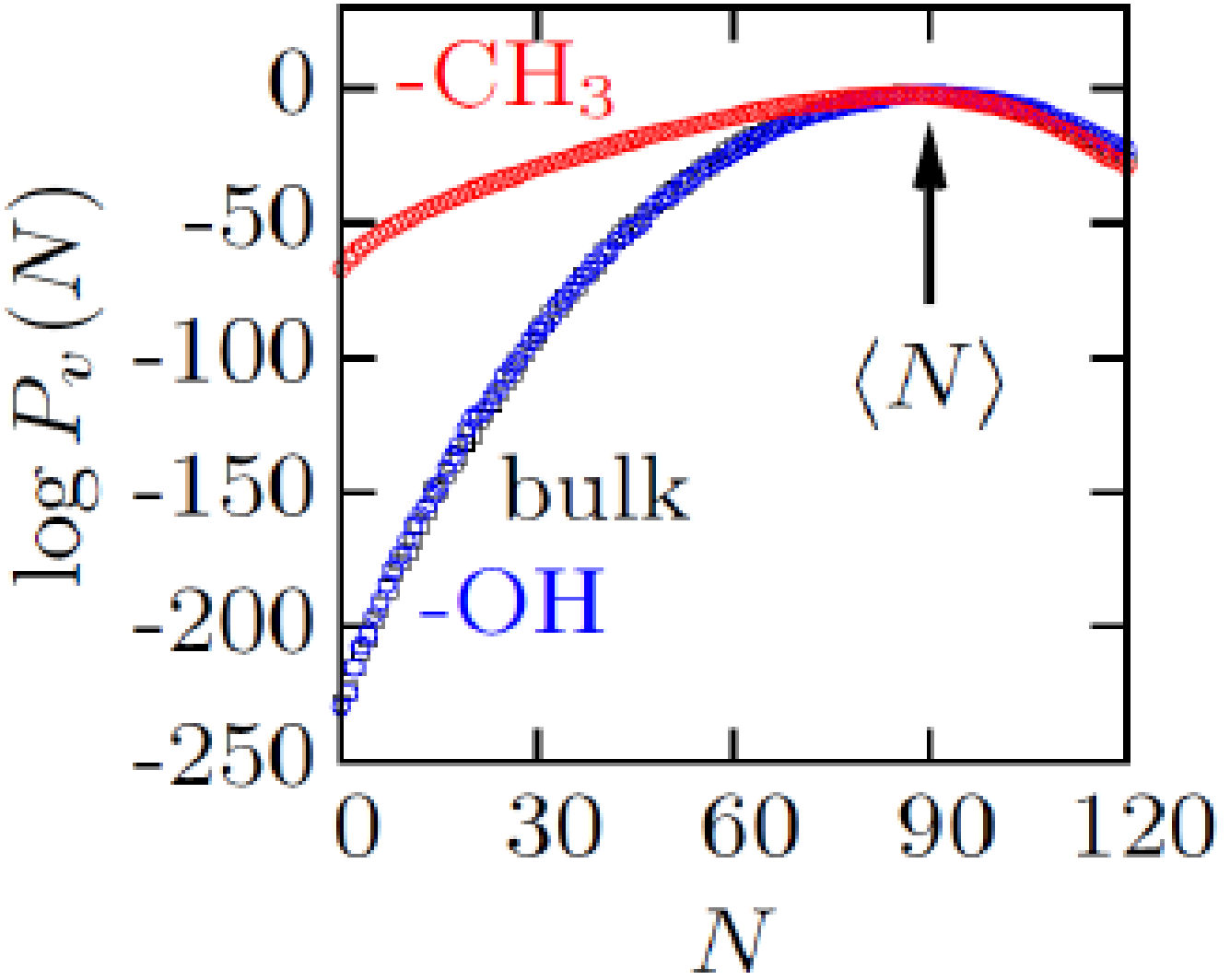
Patel, Varilly, Chandler, and Garde, Journal of Statistical Physics, 2012.

Water density fluctuations – a signature of hydrophobicity

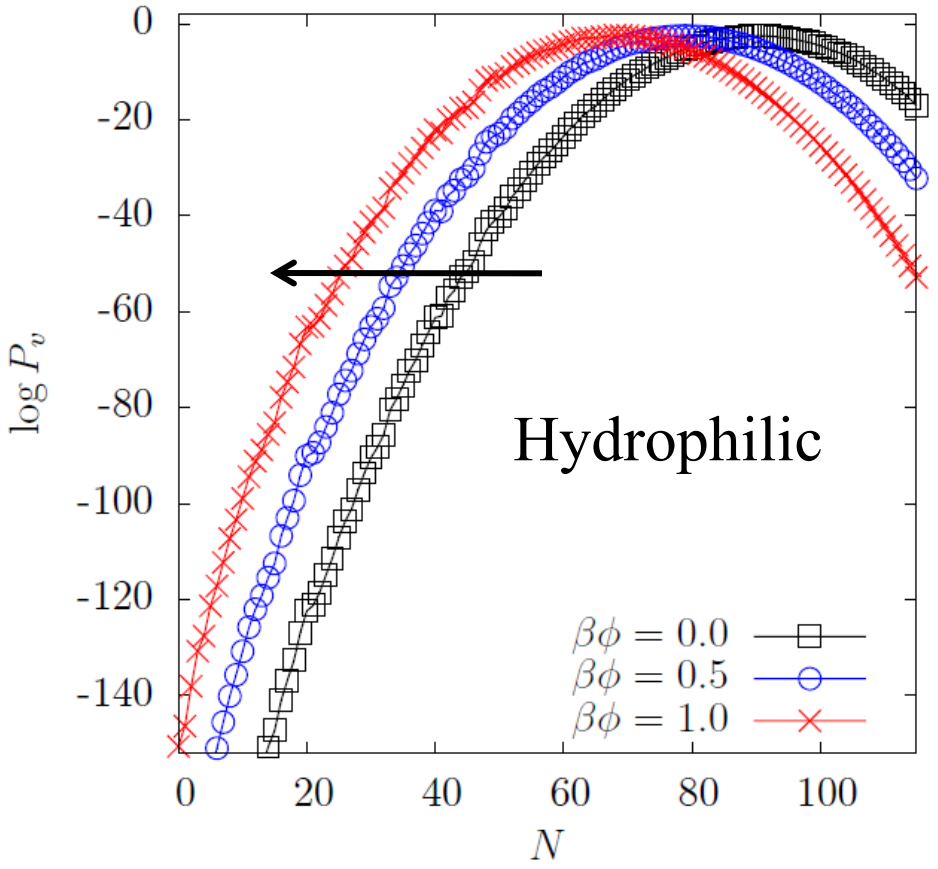


- <N> about the same near –OH and –CH3 surfaces.
- Fat tail → enhanced fluctuations
- P(0) is higher near the hydrophobic surface

$$\mu^{\mathrm{ex}} = -k_{\mathrm{B}}T \log P_v(0)$$

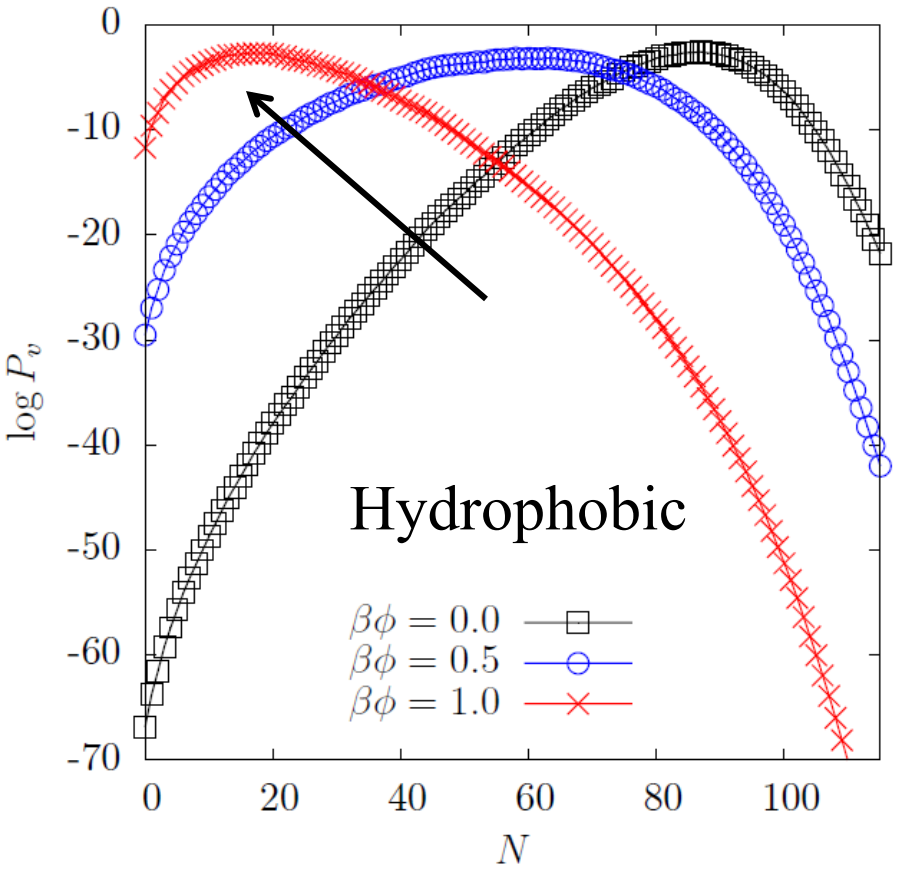


Detour



Why are fat tails in the density fluctuations important?

Fat tails make the water density very sensitive to perturbations.



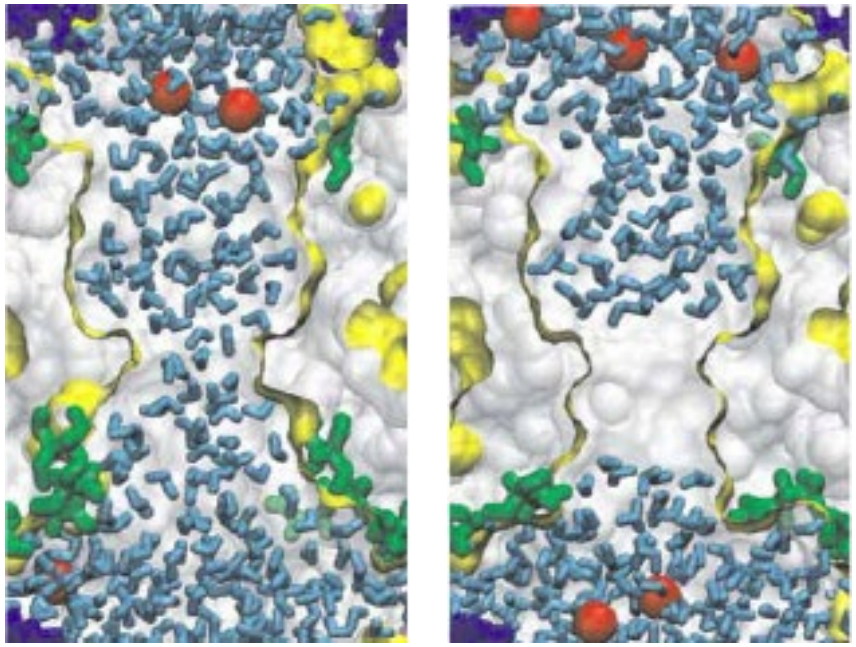
A. J. Patel, P. Varilly, S. N. Jamadagni, M. F. Hagan, D. Chandler, and S. Garde
"Sitting at the edge: How biomolecules use hydrophobicity to tune their interactions and function",
J. Phys. Chem. B , 116, 2498-2503 (2012)

Biophysical Journal Volume 86 May 2004 2883–2895

Water Dynamics and Dewetting Transitions in the Small Mechanosensitive Channel MscS

Andriy Anishkin and Sergei Sukharev
Biology Department, University of Maryland, College Park, Maryland

Are fat tails important in biological function?



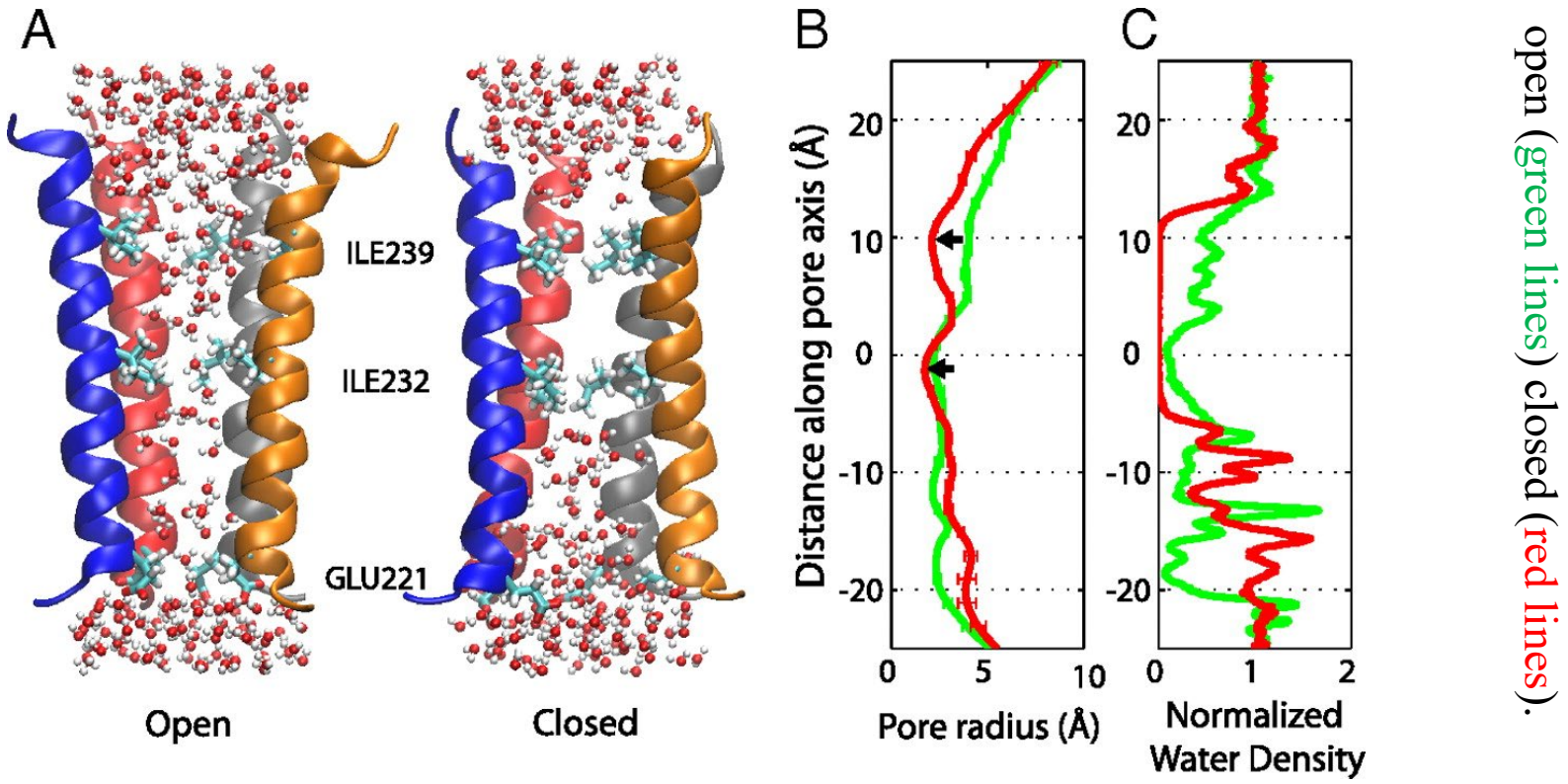
The heptameric structure of the mechano sensitive channel of E-coli, MscS**, has a relatively wide yet highly hydrophobic trans-membrane pore (region).**

We infer that MscS **gate** involves **a vapor-lock mechanism** where limited changes of geometry or surface polarity can locally switch the regime between water-filled (conducting) and empty (non conducting) states.

Pore opening and closing of a pentameric ligand-gated ion channel

Fangqiang Zhu and Gerhard Hummer[1] PNAS, 2010

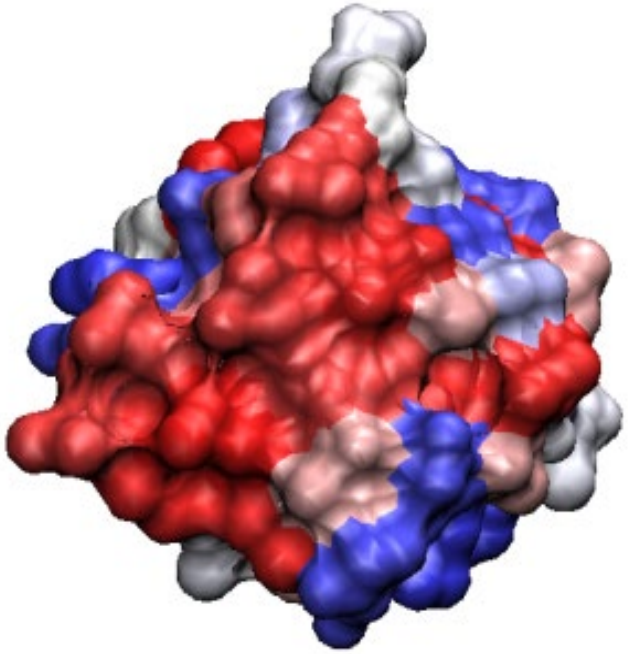
Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD 20892-0520



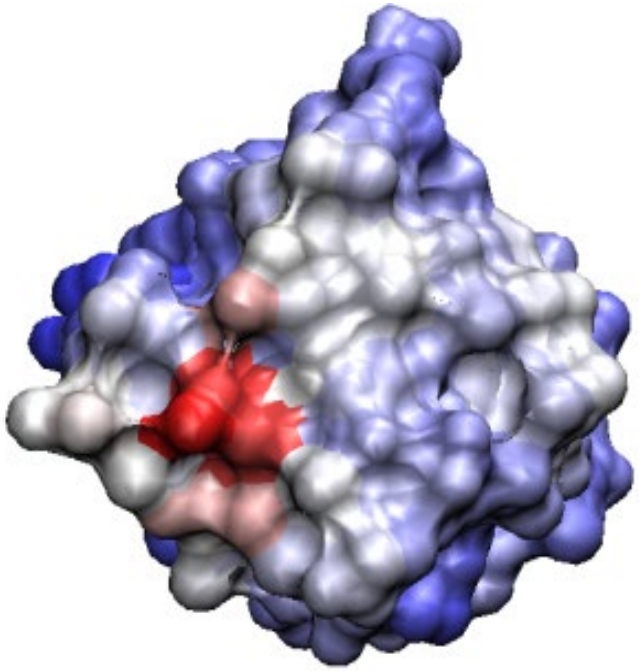
open (green lines) closed (red lines).

* In the **open state**, the region between the isoleucine rings **is fully hydrated**; upon channel **closure**, a ~15-Å long segment of the **central pore becomes completely dry**.
* **Drying of the pore is induced by remarkably subtle changes** in the pore width near the hydrophobic constriction.

hydrophobin II



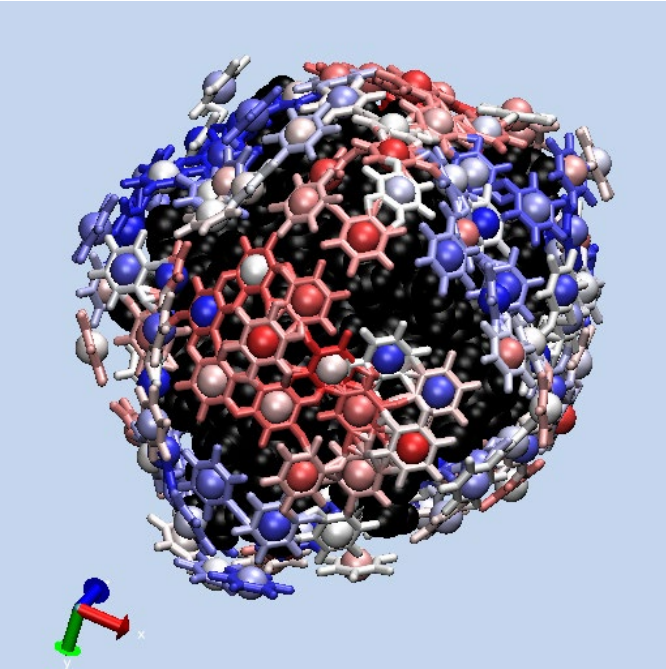
Hydropathy scale mapping

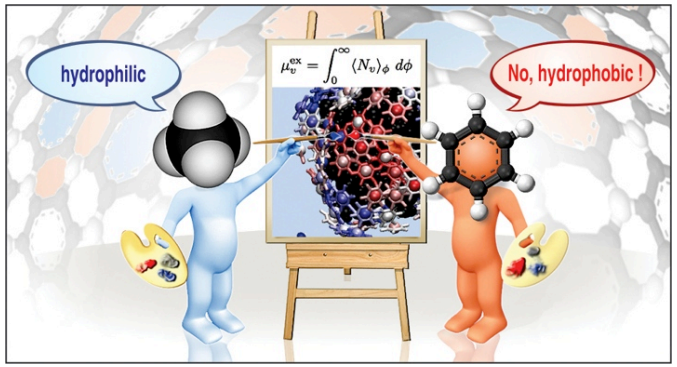


Fluctuation based mapping

The "observer context"

(hydrophobicity of a protein surface depends on who is looking!)





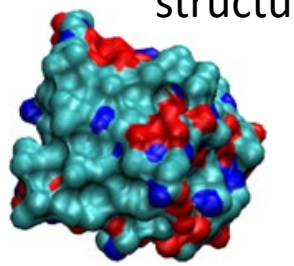
Patel and Garde, J. Phys. Chem. B, 2014.

Future: A Hydration Data Bank

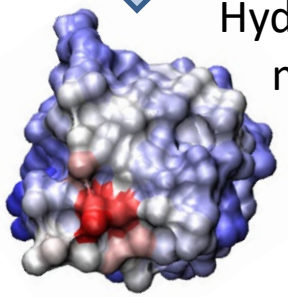
Protein data bank

Hydration data bank

X-ray/NMR structure



Hydration map



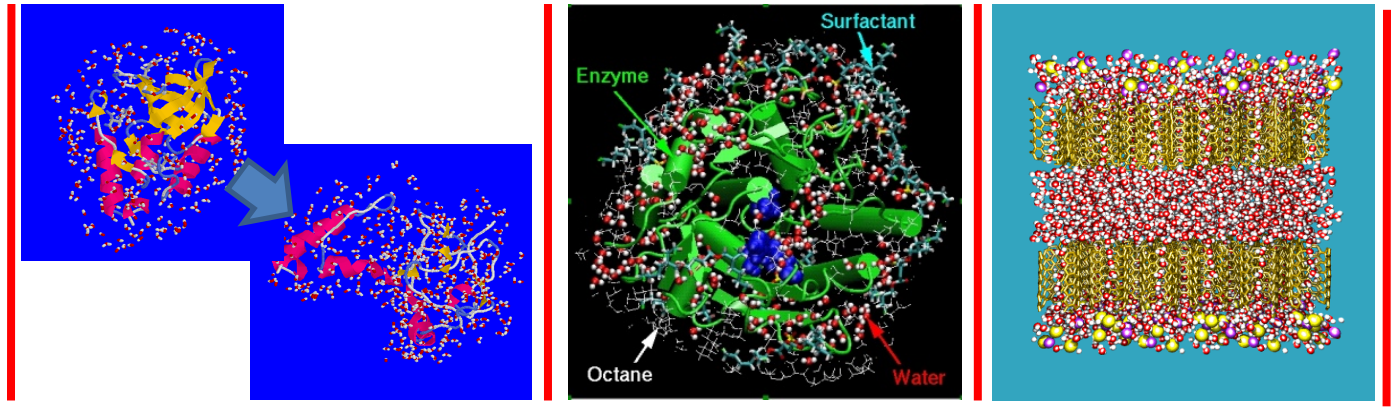
Fundamental understanding

Protein interactions

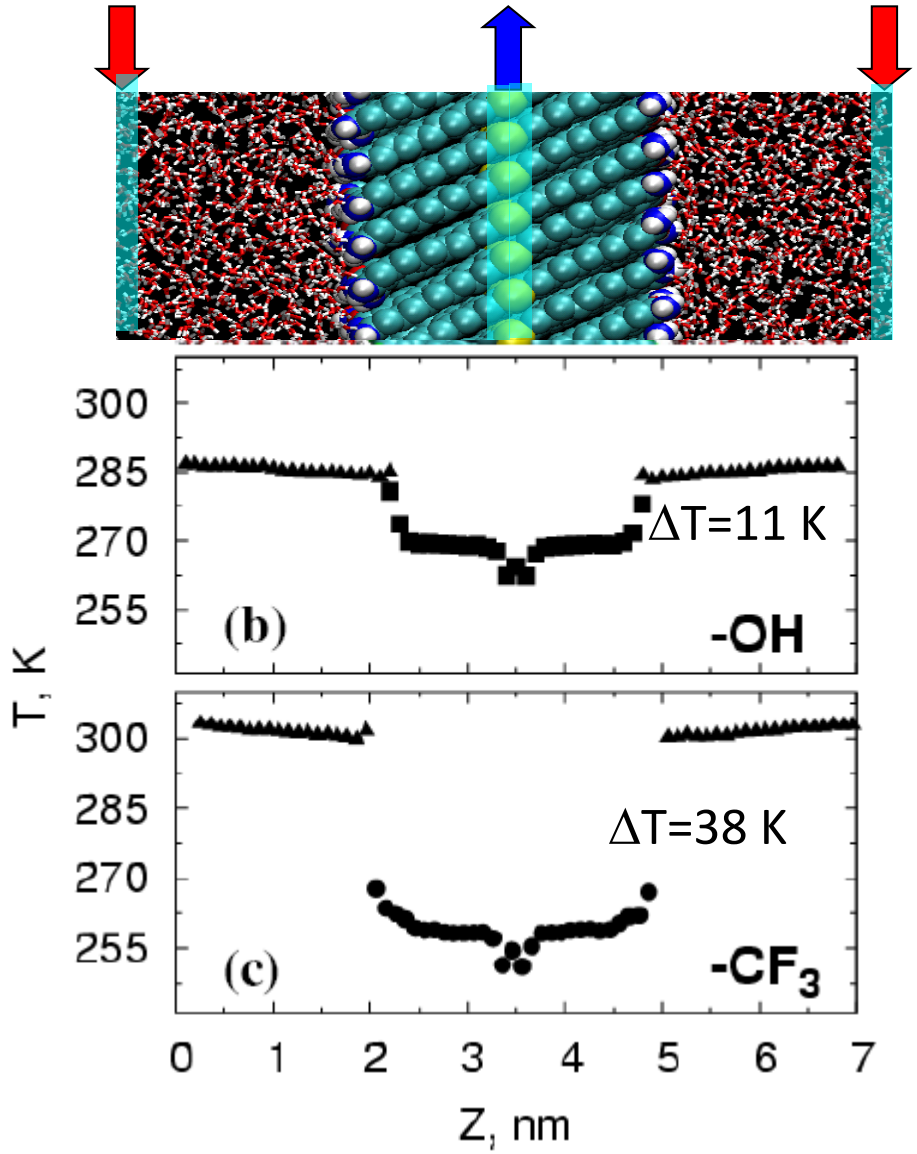
Drug design discovery

Water density fluctuations of water near an interface provide an excellent measure of hydrophobicity of a given interface and can be used to map hydrophobicity of protein surfaces and predict their interactions.

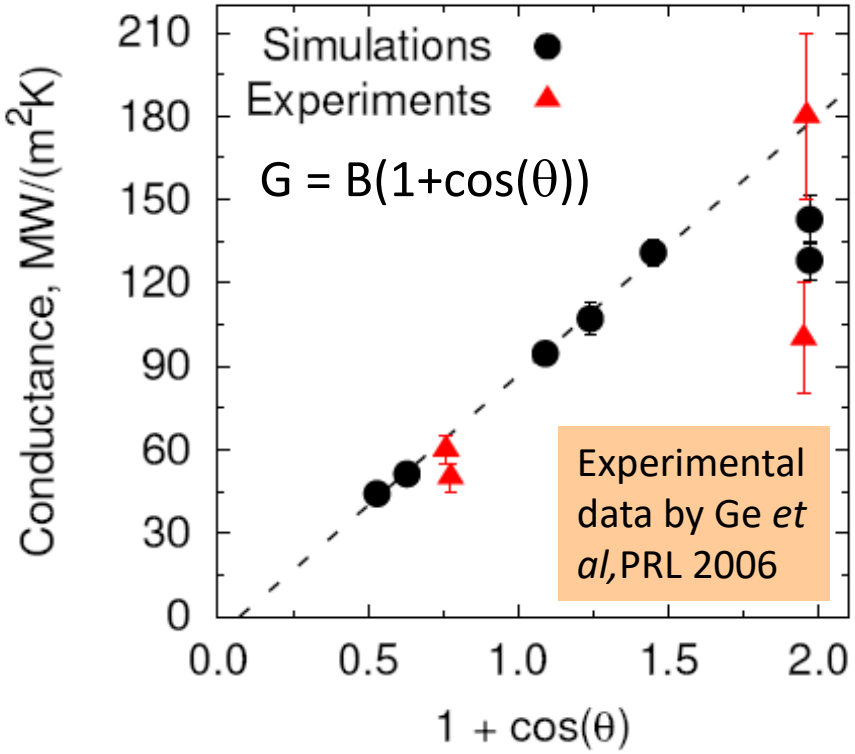
Biomolecules use the special positioning of water (**near the edge**) near hydrophobic surfaces to regulate their interactions and function.



Interfacial thermal conductance and water structure/wetting



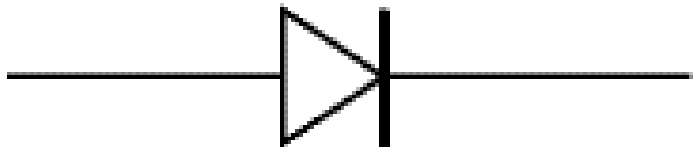
Interfacial Conductance, G = Flux/ΔT

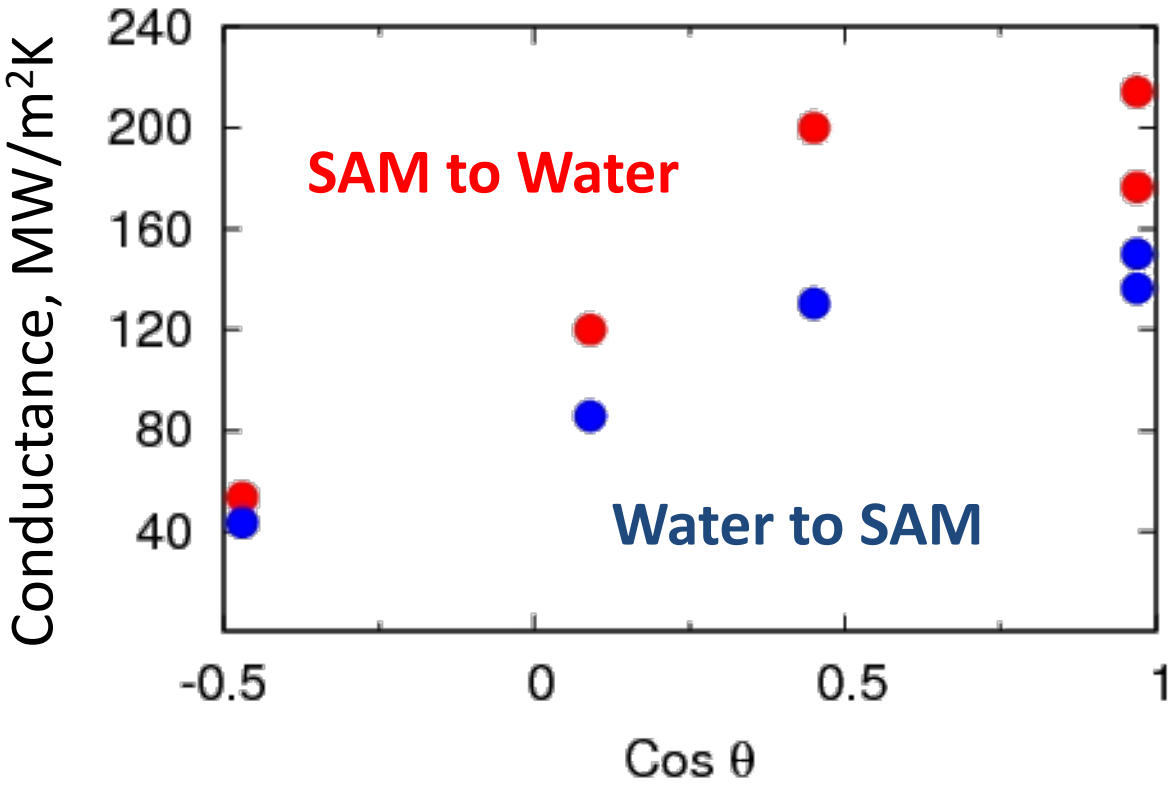


Shenogina, Godawat, Keblinski, Garde, *Physical Review Letters*, 2009

Rectification of heat transfer?

Electrical diode?





Heat transfer from monolayer to water is more efficient!

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$$$$$

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