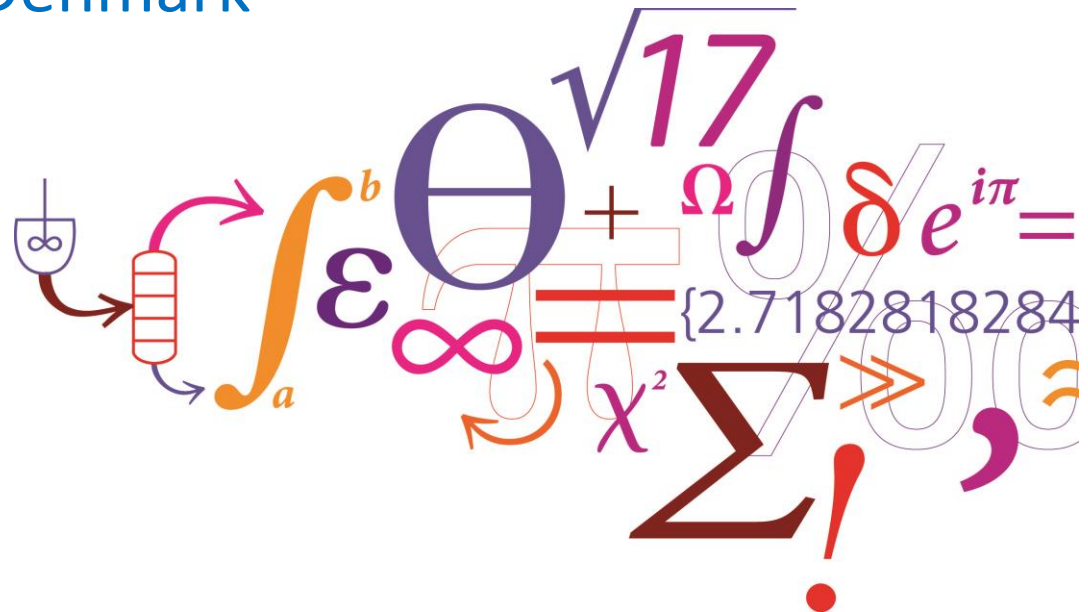


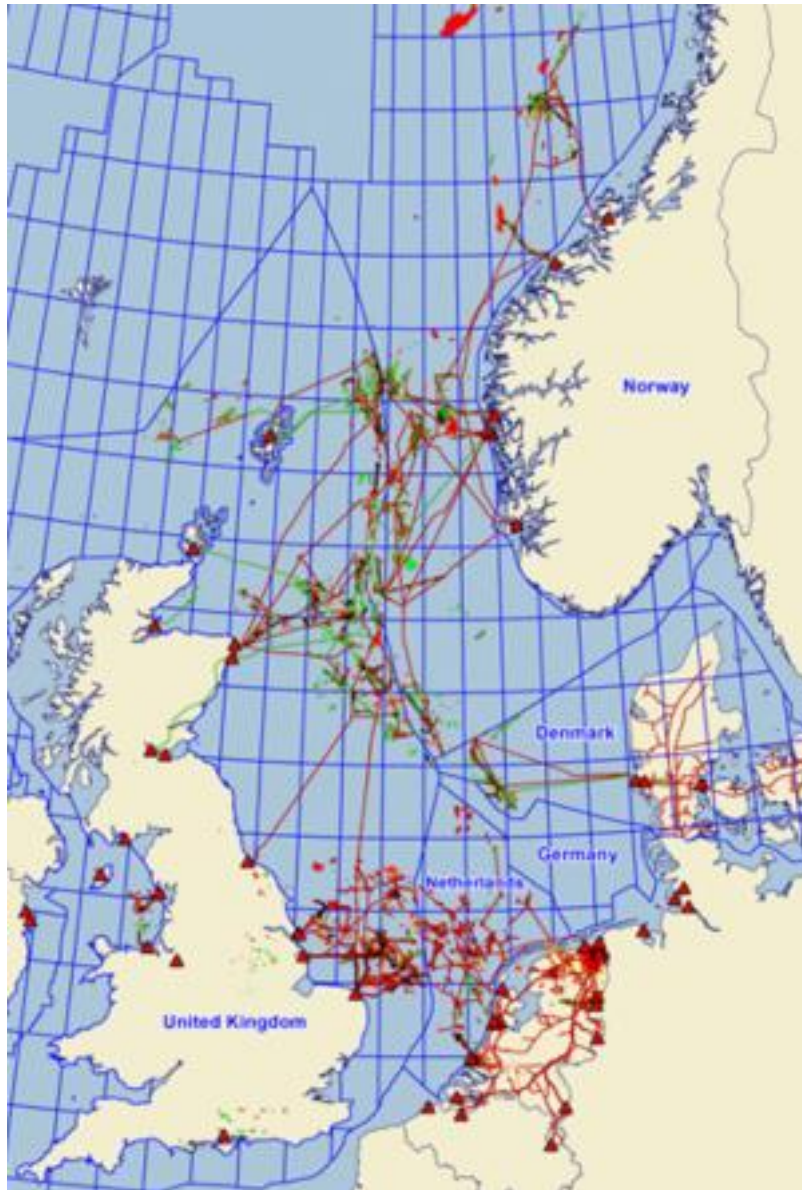
Thermodynamics of Water and Water Solutions – Questions, Myths and some Answers

Georgios M. Kontogeorgis, Xiaodong Liang,
Bjørn Maribo-Mogensen, Ioannis Tsivintzelis

Center for Energy Resources Engineering (CERE)
Department of Chemical and Biochemical Engineering
Technical University of Denmark



Oil platforms in the North Sea



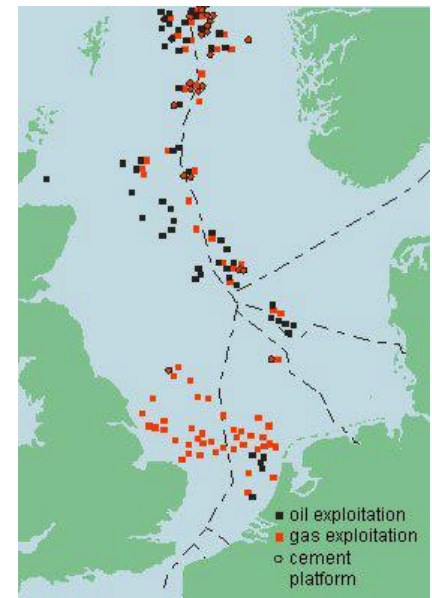
(2007)

982 oil and gas platforms in the North Sea. (drilling, service, etc)
Great Britain and Norway own the majority of the oil and gas platforms, namely 590 and 193 respectively.

The Netherlands: 143 platforms

Denmark: 53

Germany: 3.



Environmental challenges in oil & gas

- Decrease/optimize the amount of chemicals e.g. methanol and glycols (CPA, SAFT)
- Use more environmentally friendly chemicals e.g. antifreeze proteins
- CO₂ – CCS

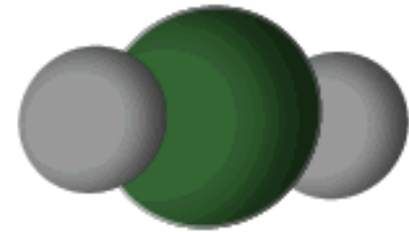


Photo: Petrobras

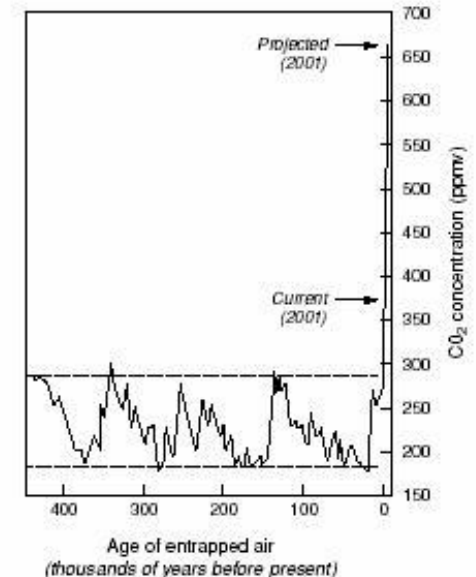


FIGURE 2 Atmospheric carbon dioxide concentration over the past 400,000 years. Past data from Vostok ice-core record; future projections from IPCC Third Assessment "business as usual" scenario. Sources: Hibbard et al. (2001), Vostok ice core data from Petit et al. (1999); projection from Prentice et al. (2001).

SmartWater project

How injection of water of different salinity or other chemical modifications can improve oil recovery

- Experimental: wettability alteration of the rock – effect of reservoir type
- Experimental: displacement experiments →
- Experimental: oil-water interactions, emulsions
- Modeling: Flows in porous media with chemical transformations

Alexander Shapiro

Kaj Thomsen

Philip Fosbøl

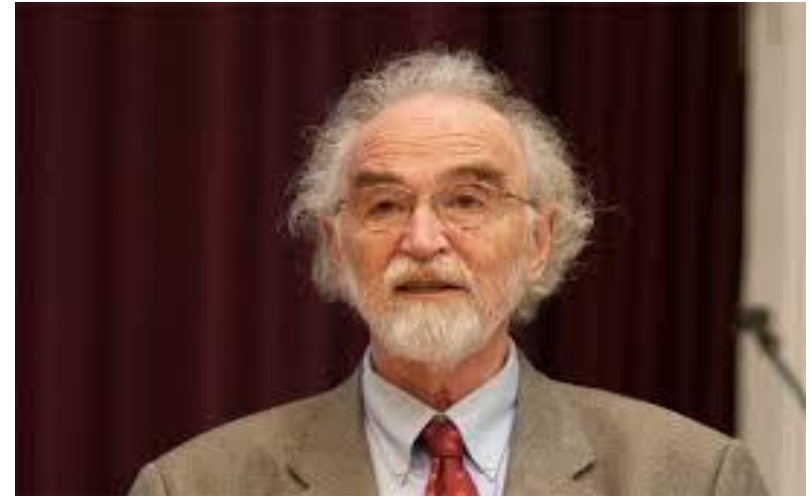
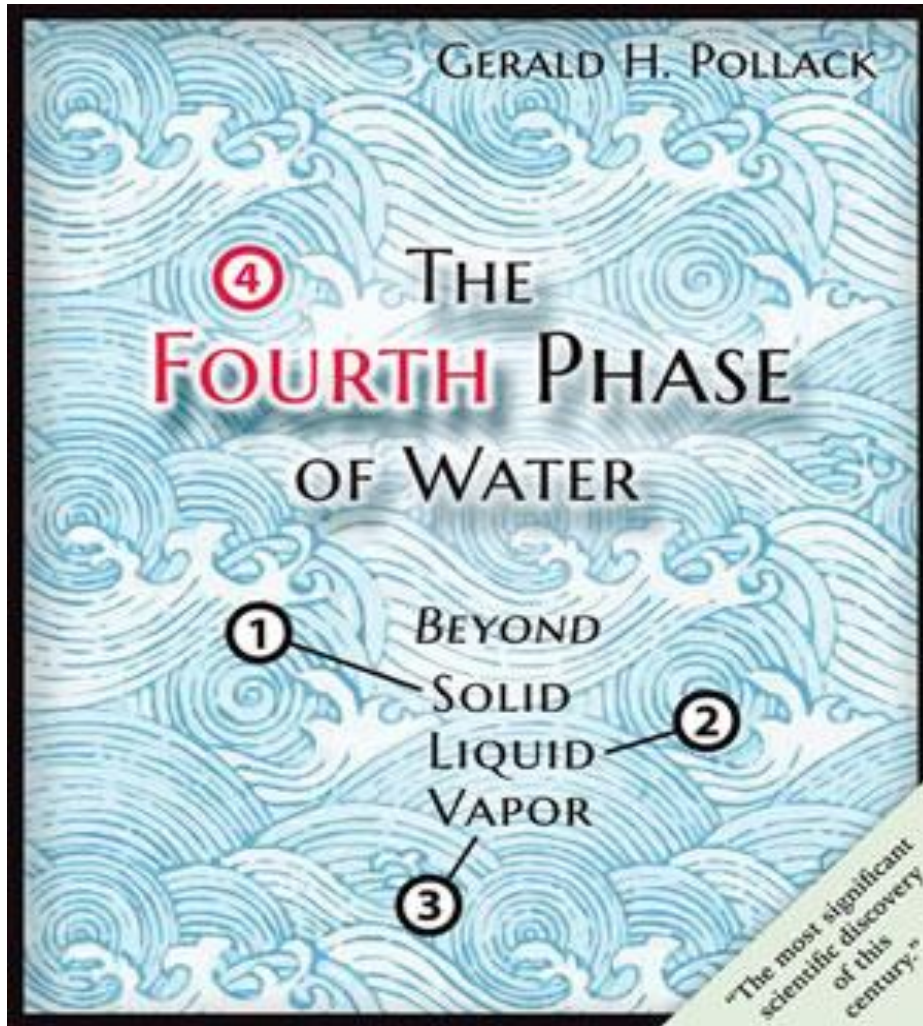
Mærsk

DONG

Collaboration with DTU-Byg and DTU-Kemi



The book I read during Summer 2013 vacations



"The most significant scientific discovery of this century"
"The most interesting science book I've ever read"
"As good as a Dan Brown novel"

Outline

- Water (thermo) physical properties
- Water structure and hydrophobic effect
- 1. Monomer fraction data (Experimental)
- 2. Association thermodynamic theories
- Monomer fraction calculations from theories
- 3. A new theory and a new insight
- Conclusions

Lecture messages:

The mystery of water's structure and water's monomer fraction

- Water is one VERY strange molecule
- Water's "experimental" monomer fraction data
- Thermodynamic theories against "experimental" monomer fraction data (X_A)
- New theory links dielectric constant with X_A resulting to alternative "exper." X_A -data
- How do thermodynamic theories compare to new theory's "exp" X_A -data ?
- Do all these give us insight into water's structure ?

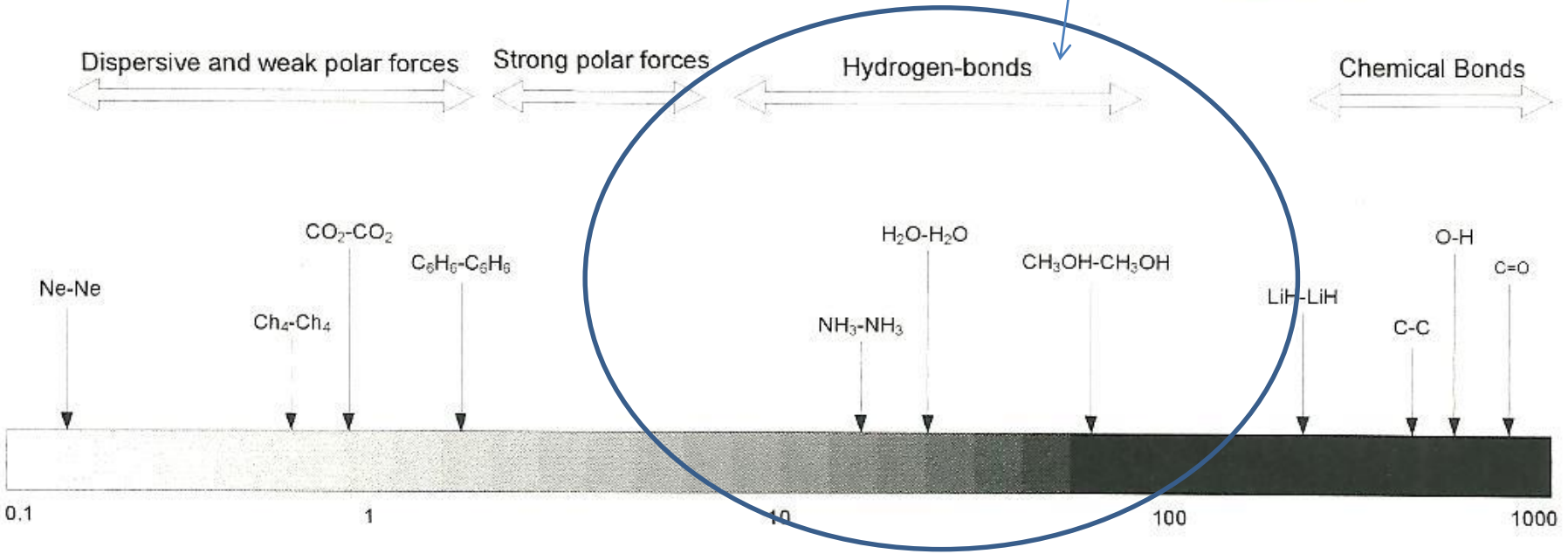
What really matters is the hydrogen bonding!



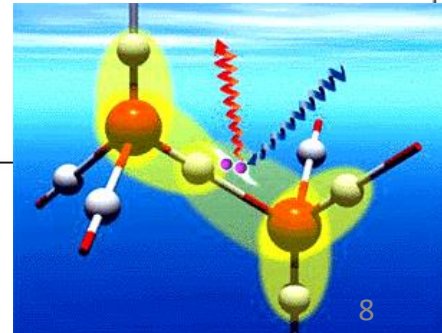
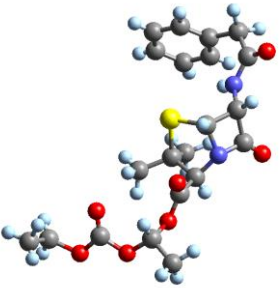
Figure 2.30 Secondary structure of biopolymers, due to hydrogen bonding: (a) α -helix formed by proteins, (b) β -sheet formed by proteins or double helix of DNA. (Reproduced with permission from T. E. Ever and J. G. York, *Biotechnology and Education*, Wiley, New York, 1976)

potential energy r^{-6}

(charge-dipole) r^{-2}



Bond Energy [kJ / mol]

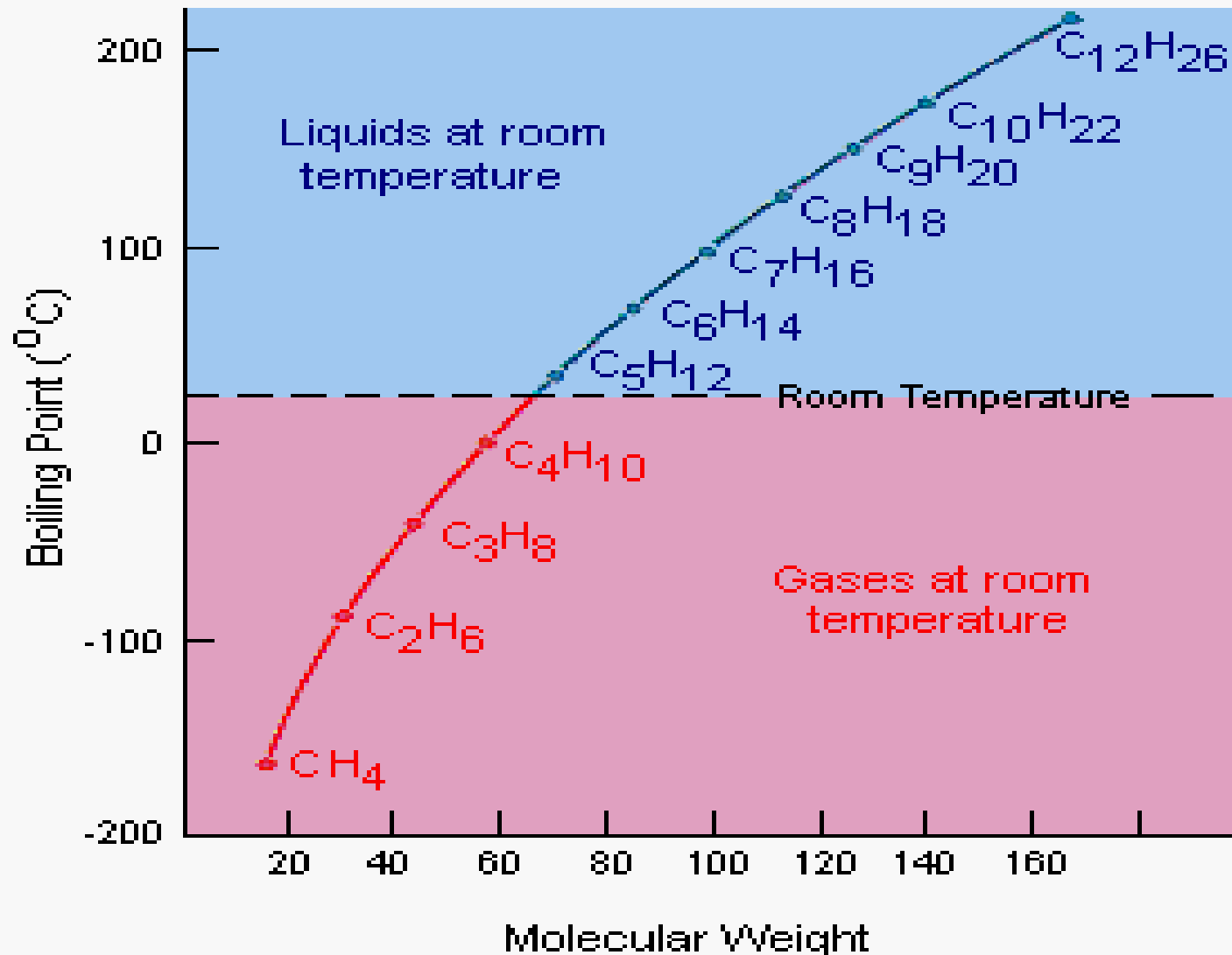


Hydrogen Bonds Dominate Properties

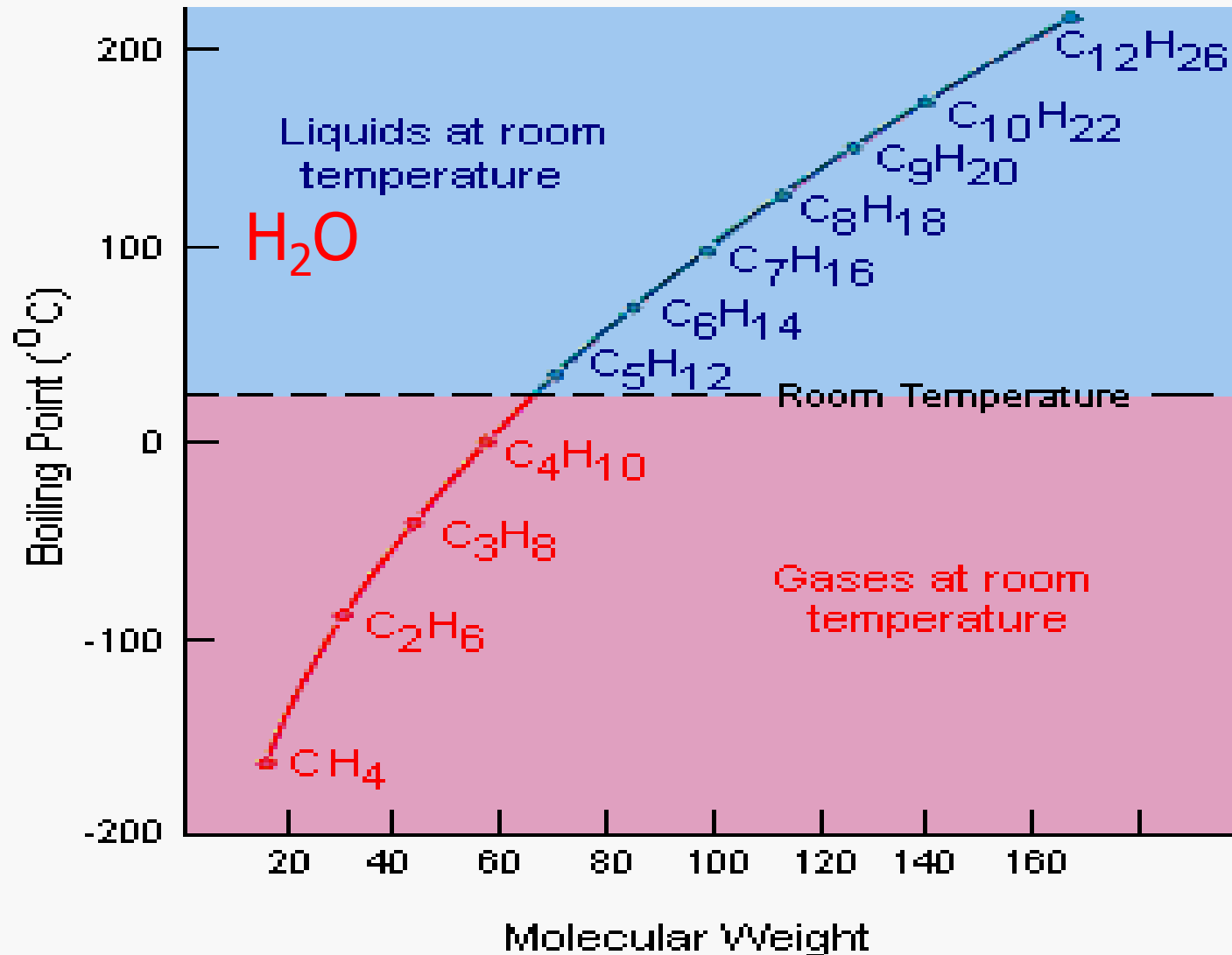
Israelachvili, 1985. *Academic Press*

Molecule	MW	Dipole Moment (D)	T _b (°C)
Ethane	30	0	-89
Formaldehyde	30	2.3	-21
Methanol	32	1.7	64
n-butane	58	0	-0.5
Acetone	58	3.0	56.5
Acetic Acid	60	1.5	118
n-Hexane	86	0	69
Ethyl propyl ether	88	1.2	64
1-pentanol	88	1.7	137

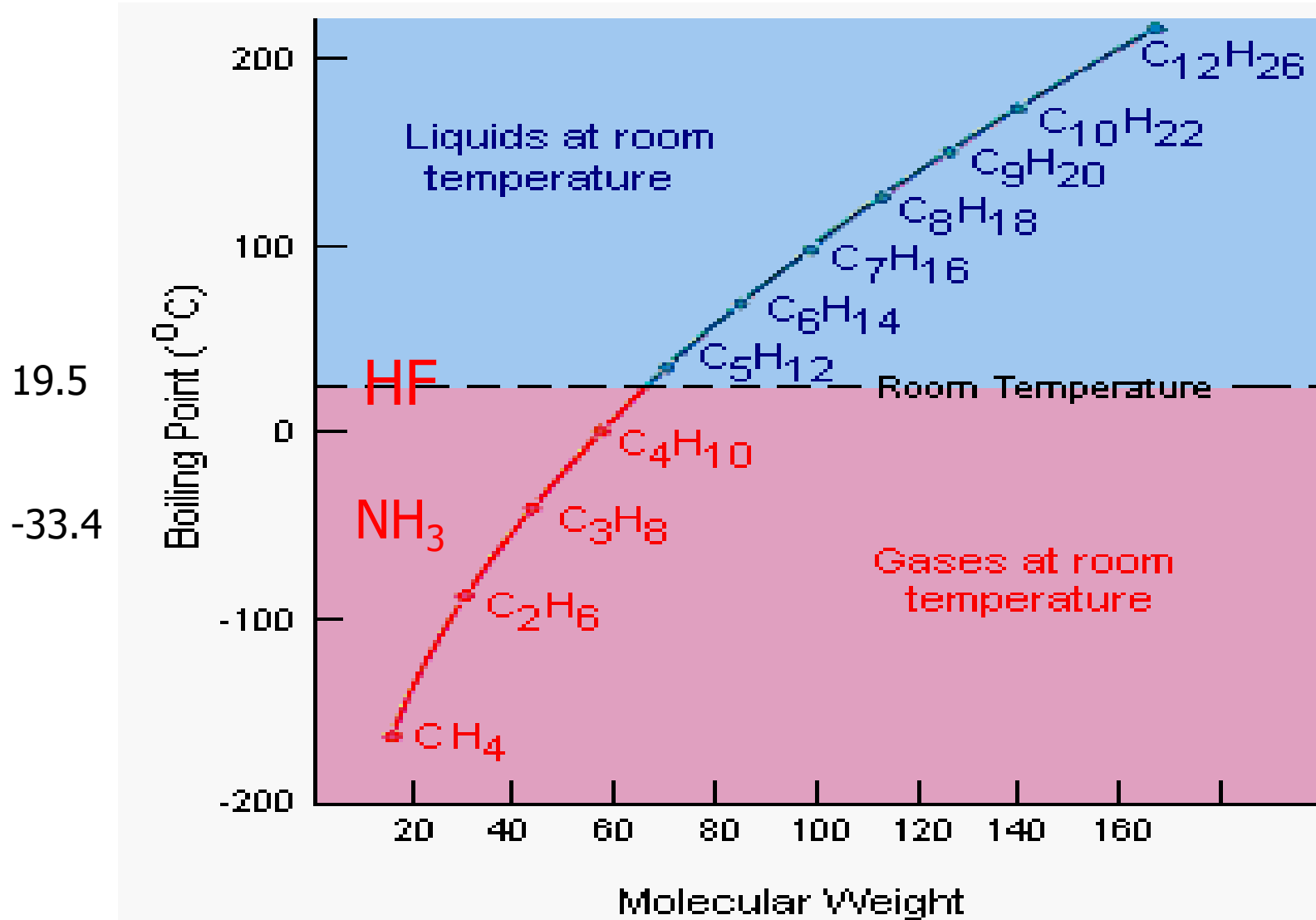
Water is a Liquid !!



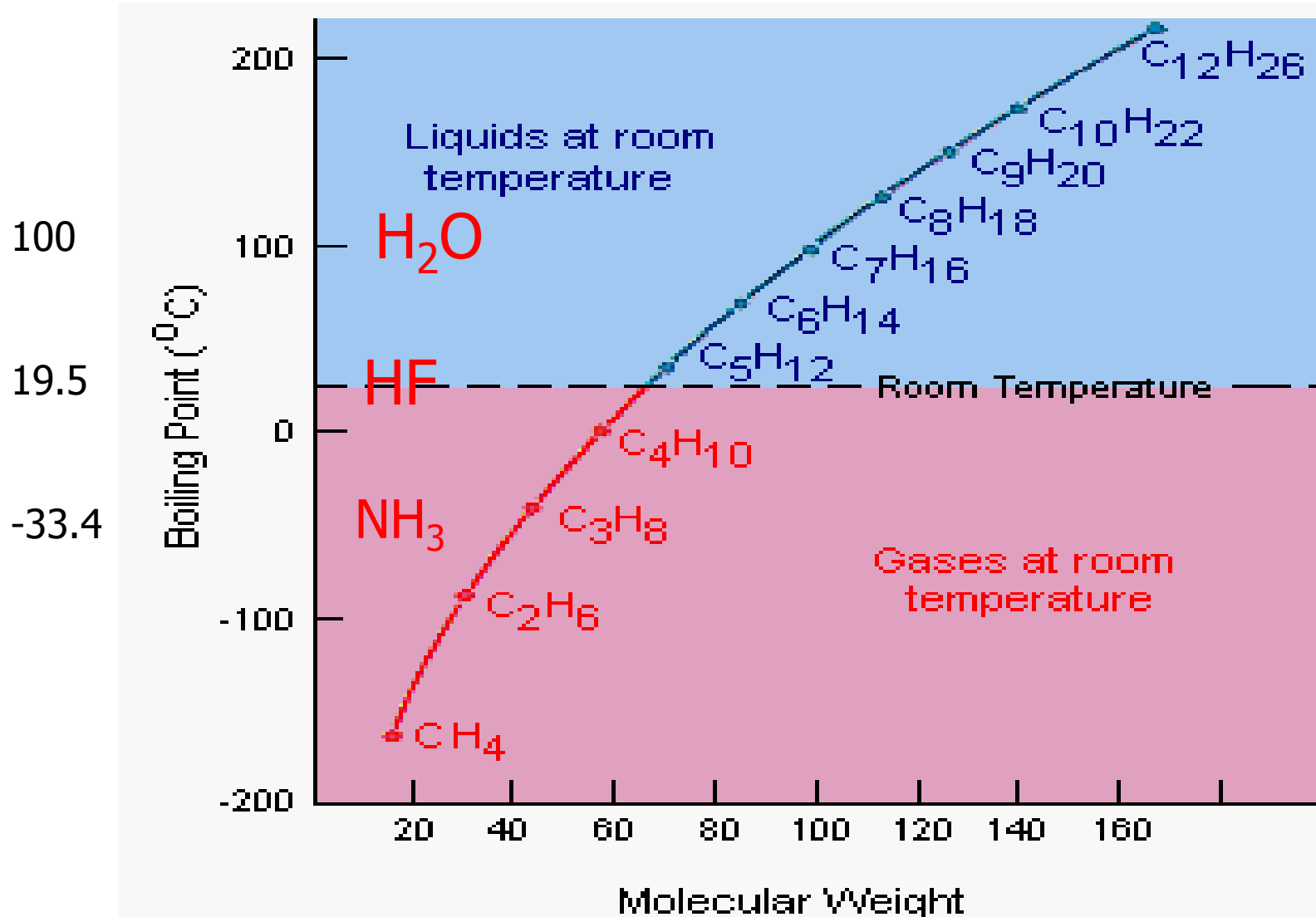
Water is a Liquid !!



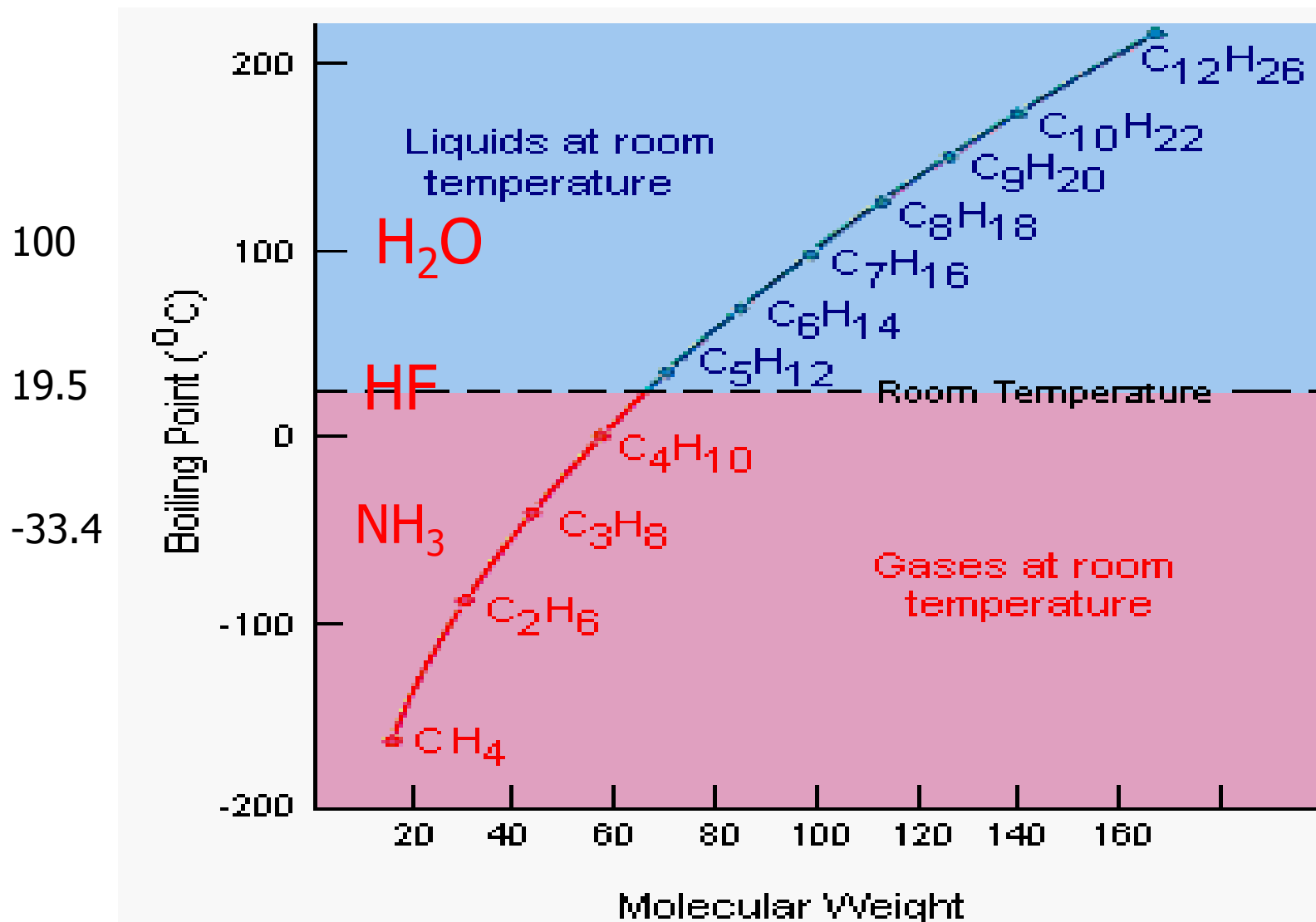
Water is a Liquid !!



Water is a Liquid !!

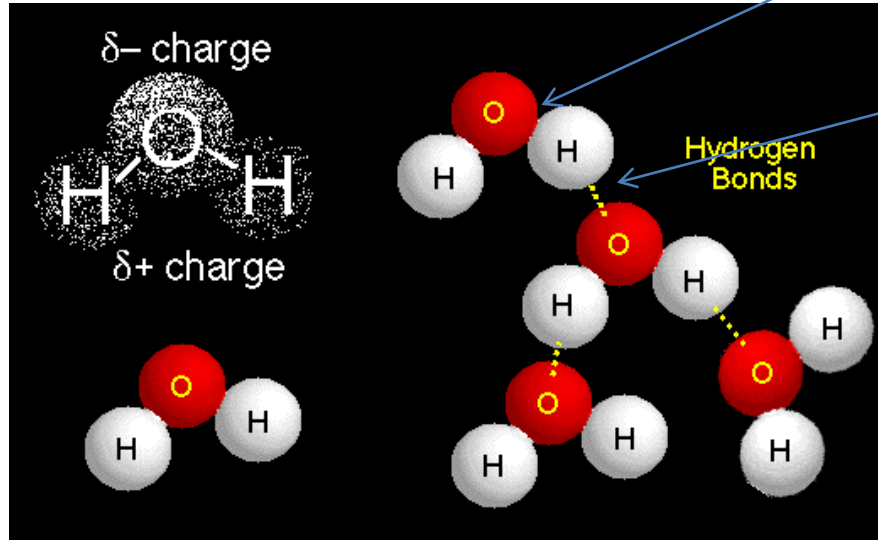


Water is a VERY strange molecule!



<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch14/liquids.php>

The Physical Picture of Water HB Structure



0.1 nm

0.176 nm \ll 0.26 nm (vdW radii)

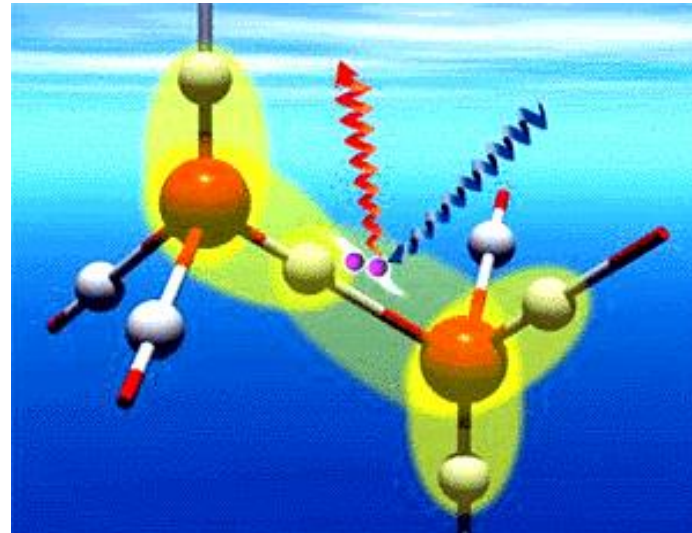
Water – 3D structure

H_2O – liquid

H_2S – gas

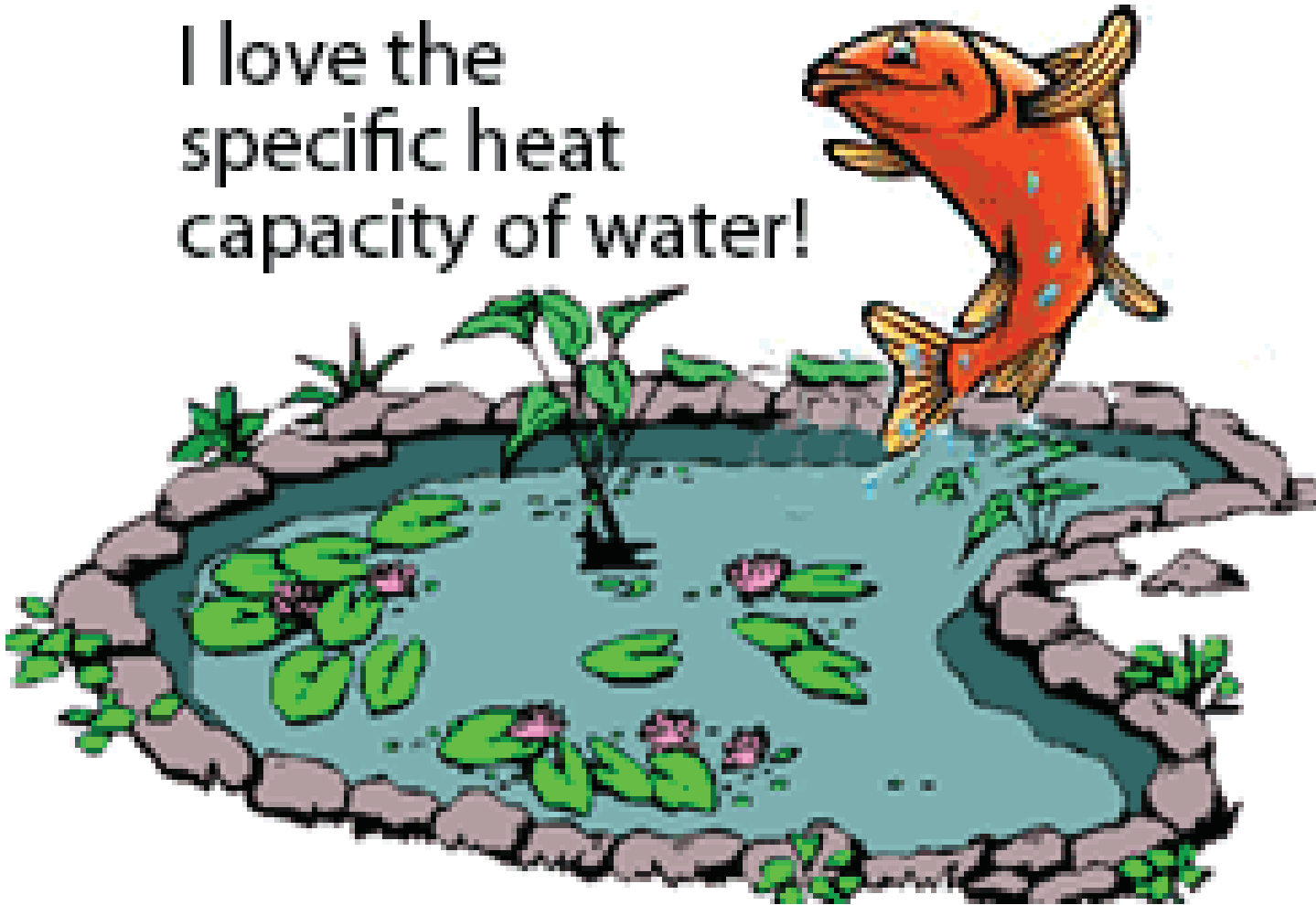
CH_4 – gas

Why ?



Water has a high heat capacity

I love the
specific heat
capacity of water!



Why is Europe
warmer
Than
Northern
Canada ?

Gulf stream +
Water salt content +
Water heat capacity

$C_p = 4.184 \text{ J}/(\text{g}\cdot\text{K})$ [room T] – it takes a lot of time to warm up and cool down !

Water has a High Surface Tension value

$\gamma \times 10^3 / (\text{J m}^{-2})$ ambient conditions

3/4 = hydrogen bonding, polar
1/4 = dispersion

liquids		solids		
n-Hexane	18	Teflon	20	<i>low energy interfaces</i>
Toluene	28	Polystyrene	40	
Water	72	NaCl	110	<i>high energy interfaces</i>
Mercury	480	Tungsten	>1000	

not so well defined



Water ! High surface tension or what ?

Photos from G. Pollack Book !

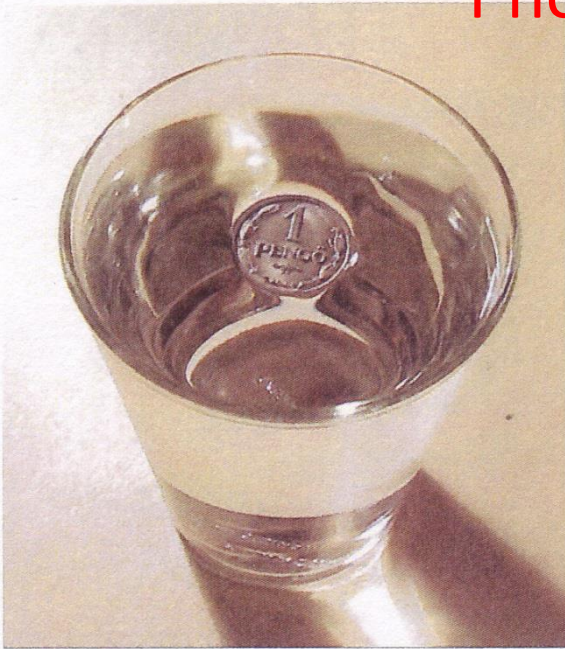


Fig. 16.1 *Evidence of water's high surface tension.*



"Jesus Christ" lizards in Costa Rica

Surface layers are less than 1 nm thick

Something more significant than a few extra bonds in thin film seems necessary to account for water's unusual surface properties ? (G.Pollack, Ch.16)

Super hydrophobic surfaces – simply absence of hydrophilicity ? (Pollack)



Science News - On Line, March 1, 2003



Scientific American, Sept. 2003

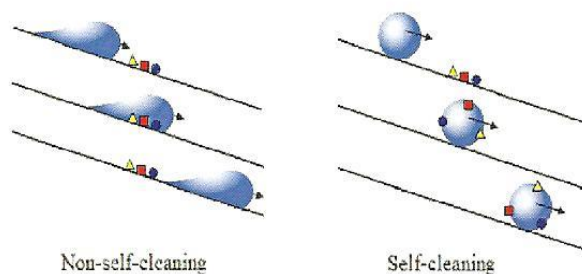
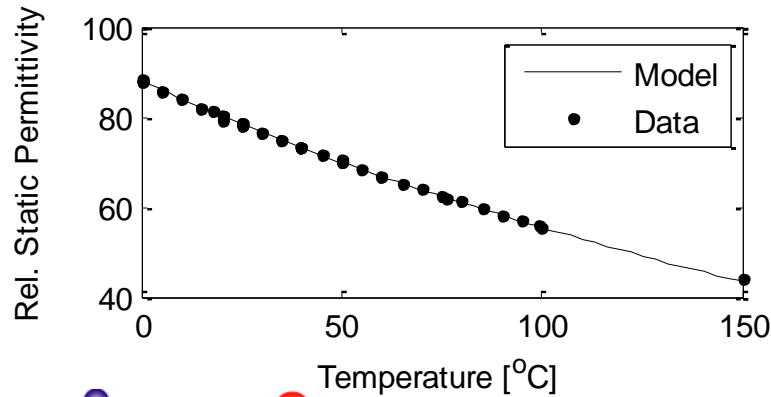
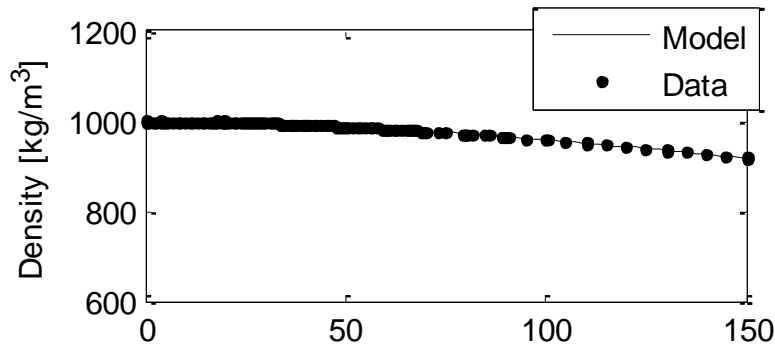


Figure 2.7: Schematic images of a non-self-cleaning surface (left) and a self-cleaning surface (right). Adapted from [21].

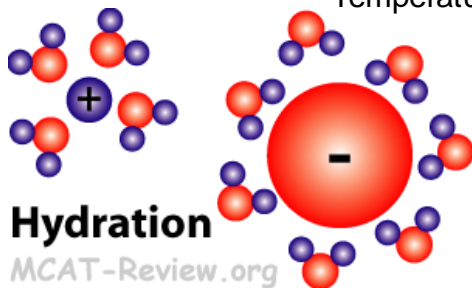
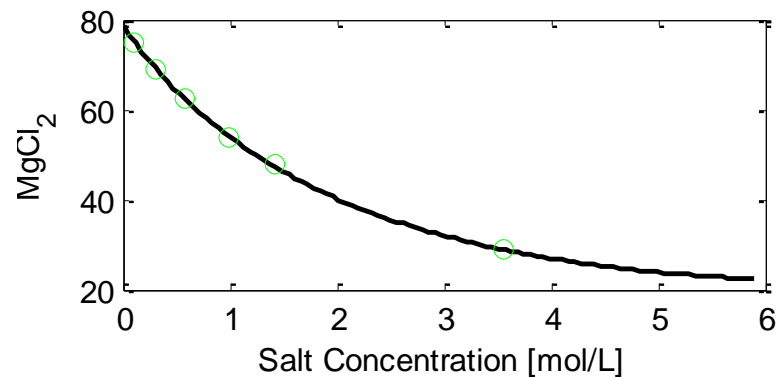
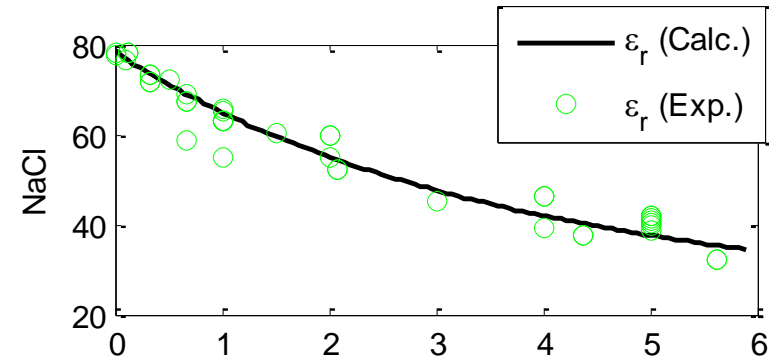
Johannes M. Holmgren & Johan M. Persson
M.Sc. Thesis (Lund, 2008)

Water is *not* just the medium

Pure Water



Water with Salts



Presence of ions decreases the static permittivity

Ion hydration shells are formed by e.g. water surrounding the molecules

Primitive models: solvent is a dielectric continuum – not explicitly treated, only via its dielectric constant and density

Anomalous dielectric constant of water

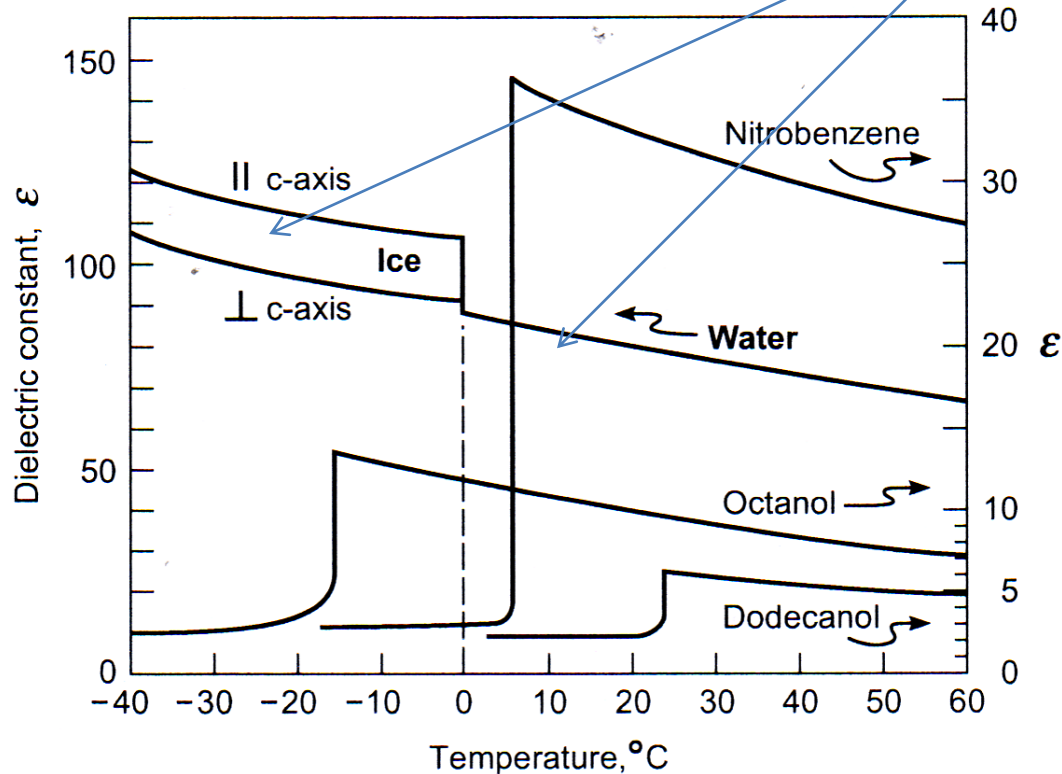


FIGURE 8.1 Static dielectric constants as a function of temperature of some “normal” polar liquids and water. For all the normal liquids ϵ falls abruptly on freezing to a value that is close to the square of the refractive index, indicating that the thermal rotations of the dipolar molecules have stopped. However, for water, ϵ rises on freezing and continues to rise to -70°C , after which it falls. The high polarizability may be due to proton hopping along the H-bond network (see Figure 8.2a) rather than molecular rotations. [Data compiled from Landolt-Börnstein (1982), Hasted (1973), and Hobbs (1974). Two classic papers that discuss the dielectric constants of water and ice are Pauling (1935) and Hollins (1964).]



Water has very high solubility parameter

But still universal solvent ! (salts,...)

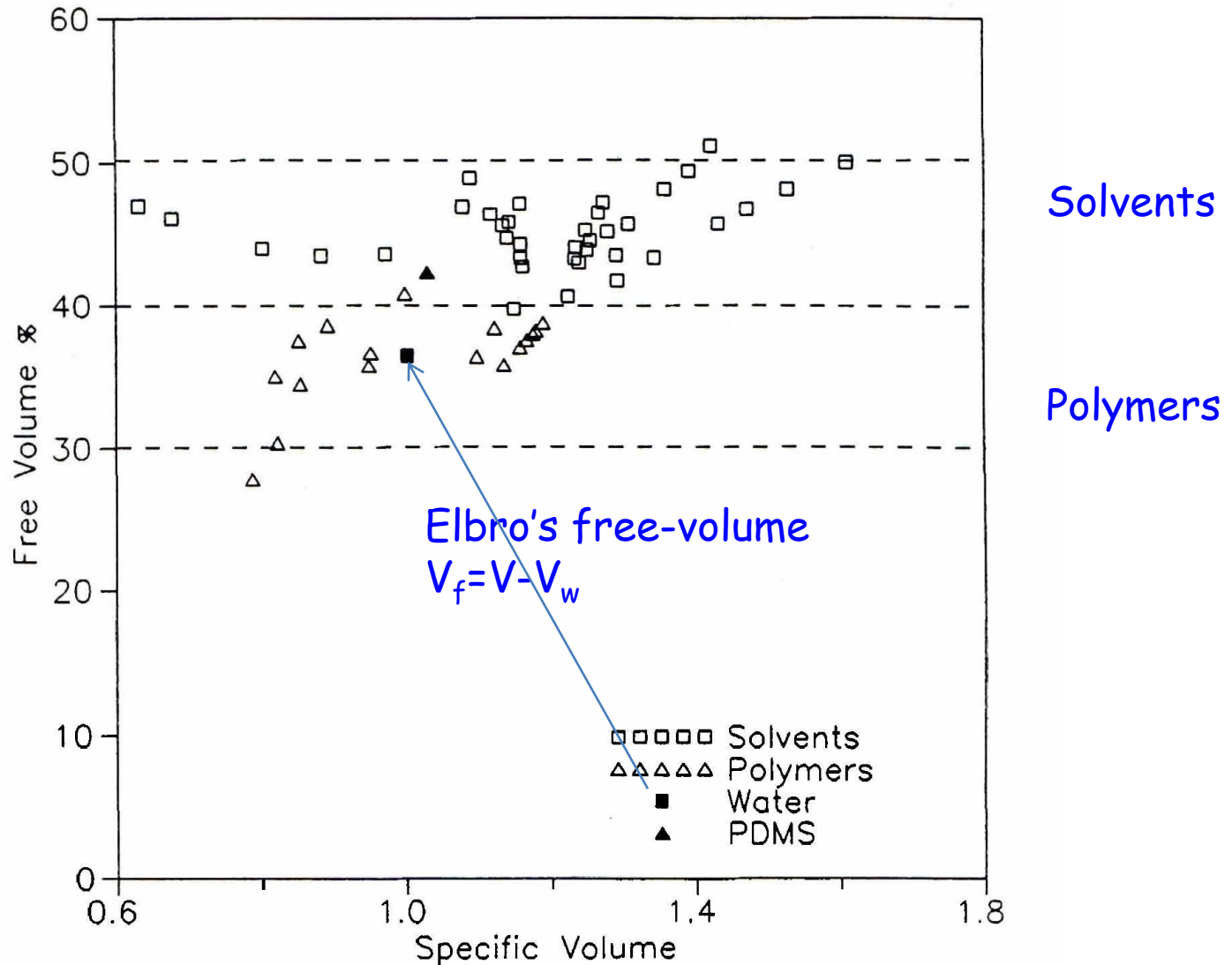
"Like" dissolves "Like"

$$\delta = \sqrt{c} = \sqrt{\frac{\Delta H^{vap} - RT}{V}}$$

Solvent	Sol.Parameter	Polymer	Sol.Parameter
MEK	18.5	Teflon	12.7
Hexane	14.9	PDMS	14.9
Styrene	19.0	PE	16.2
Cyclohexanone	19.0	PS	17.6
Acetone	19.9	PMMA	18.6
CCl ₄	17.6	PVC	19.4
Water	47.9	PET	21.9
Toluene	18.2	PAN	31.5

$$|\delta_1 - \delta_2| \leq 1.8 \left(\frac{\text{cal}}{\text{cm}^3} \right)^{1/2} \quad \text{Solubility Parameter Values in } (\text{J}/\text{cm}^3)^{1/2}$$

Water has a low free-volume – in the polymer range

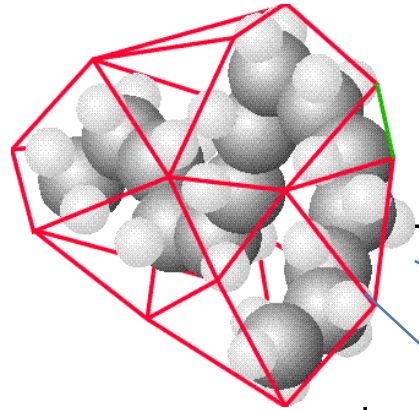


Water – an uncomparable molecule

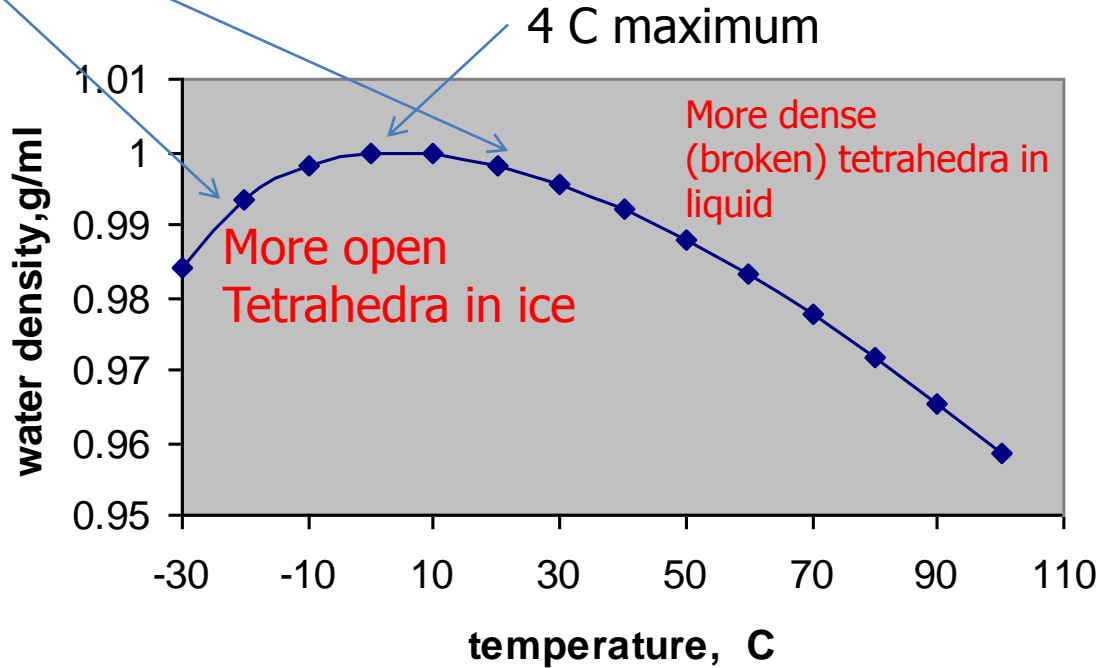


Figure 2.23 Secondary structure of hemoglobin, due to hydrogen bonding. (a) α -helix formed by protein, (b) β -sheet formed by protein, (c) double helix of DNA. Reproduced with permission from C. S. Hammett, J. G. Voet, Biochemistry, 2nd Edition, Wiley, New York (1990).

Tetrahedral structure (4 neighbors/molecule)
Coulombic-type hydrogen bonds – not quasi-covalent



water density versus temperature



High T_b , C_p

High Polarity (?)

Very high Dielectric Constant

And Surface tension



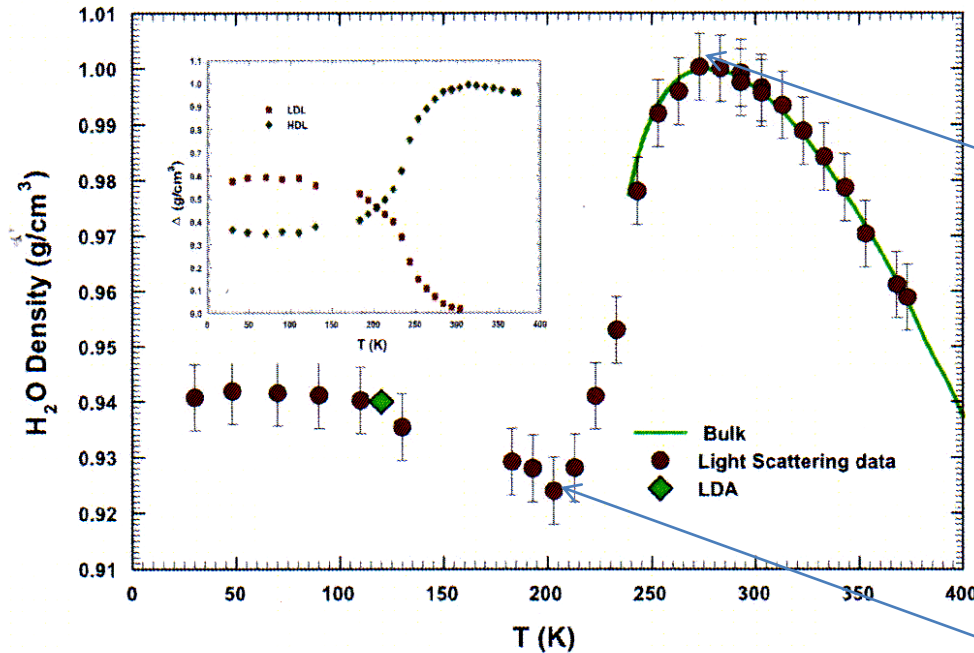
Full of hydrogen bonds and much more ...



Water density anomalies

Use of
Monomer
Fraction
Data
At all T
(see later)

Scattering
Raman
FTIR
measurements

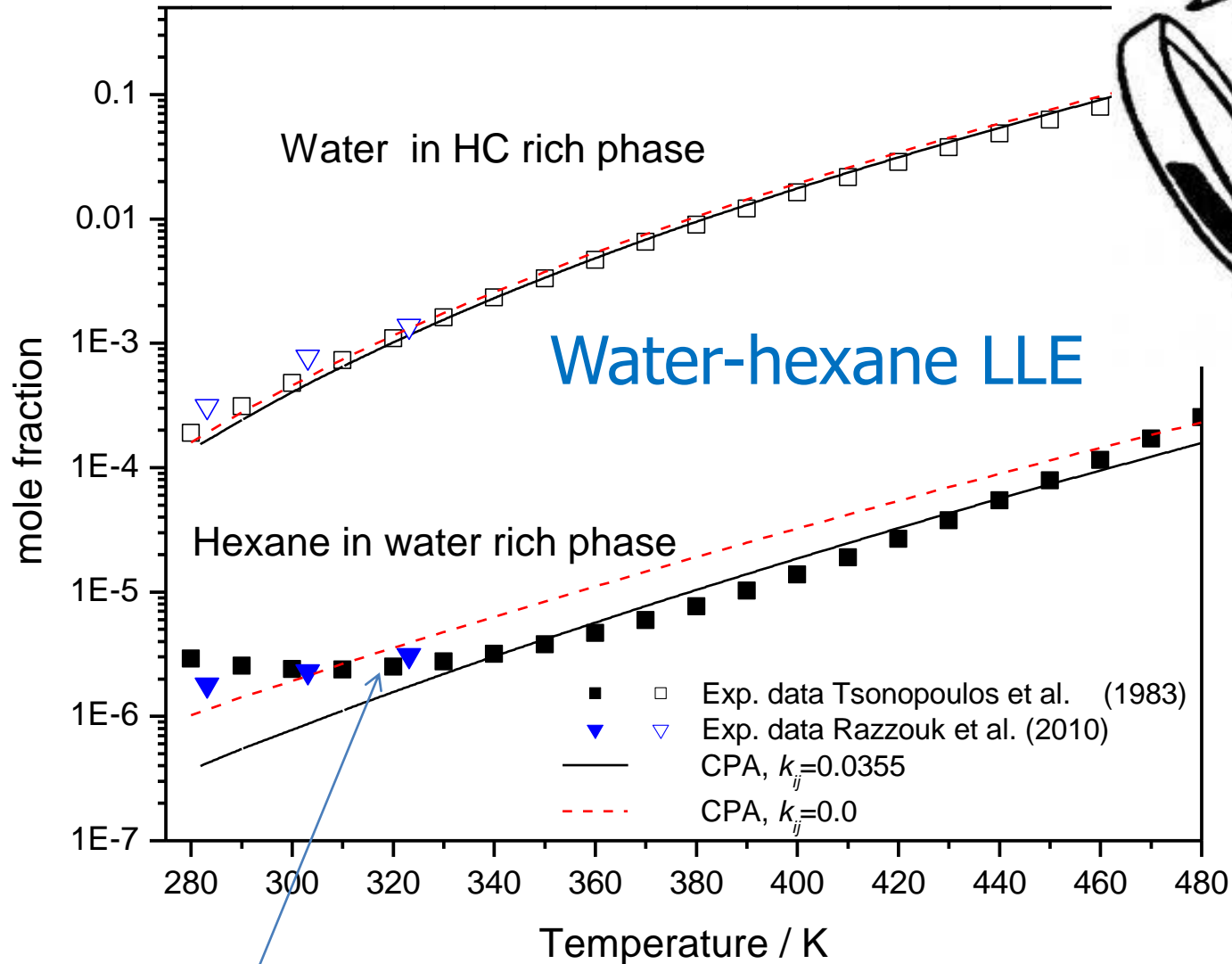


Maximum
(277 K)

Minimum
(203 K) – also
From MD simulations

Fig. 2. The temperature dependence of calculated ρ_{H_2O} . The density values measured in pure bulk water in the range $239 < T < 423$ K (32–34) are reported as a solid line. As one can see, a minimum is evident at $T_M = 203 \pm 5$ K. For $T < T_M$ density smoothly rounds off to the constant value $\rho = 0.940 \pm 0.003$ g/cm^3 in the LDA phase. Inside this latter phase, by means of the method of decompression and warming, the density has been measured at 120 K, obtaining a value $\rho_{LDA} \approx 0.94$ g/cm^3 , plotted as a green diamond (31). (*Inset*) The contribution Δ of the HDL (green diamonds) phase and LDL (red squares) phase to H_2O density as a function of temperature. The two Δ cross at ≈ 203 K. LDL and HDL are defined according to the LLPT hypothesis (6).

Oil and Water don't mix !



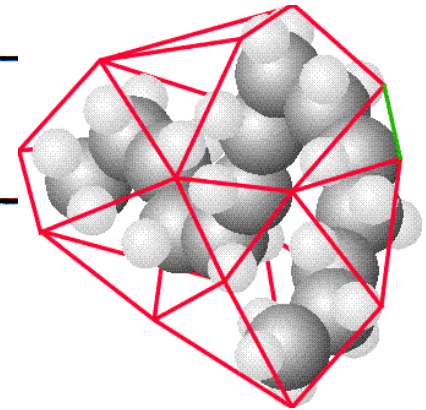
The minimum of the HC solubility in water

Razzouk et al., 2010
J.Chem.Eng.Data, 55: 1468

Why don't they mix ?

Table 4-12 Change in standard molar Gibbs energy (Δg^0), enthalpy (Δh^0), and entropy ($T\Delta s^0$), all in kJ mol^{-1} , for the transfer of hydrocarbons from their pure liquids into water at 25°C (Tanford, 1980).

Hydrocarbon	Δg^0 (kJ mol^{-1})	$= \Delta h^0$ (kJ mol^{-1})	$- T\Delta s^0$ (kJ mol^{-1})
Ethane	16.3	-10.5	-26.8
Propane	20.5	-7.1	-27.6
<i>n</i> -Butane	24.7	-3.3	-28.0
<i>n</i> -Hexane	32.4	0	-32.4
Benzene	19.2	+2.1	-17.1
Toluene	22.6	+1.7	-20.9



An entropic effect

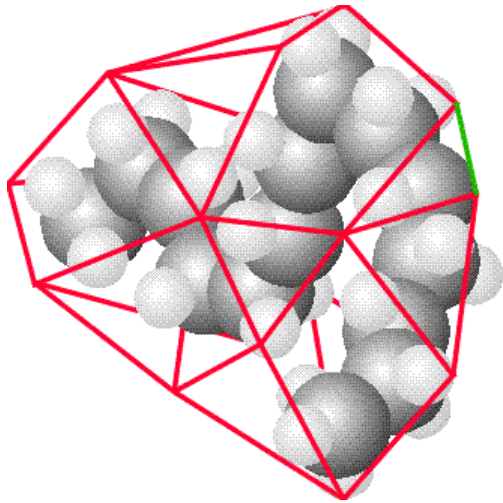
Prausnitz et al., 1999
Gill and Wadso, 1976

Almost equal to the water-HC interfacial energy

More structured water in mixture!

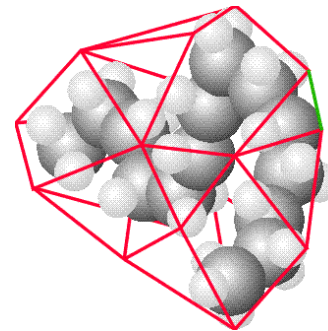
Source: Israelachvili, Dixit et al., 2002 (Nature)

Alkane-alkane interaction
Also very strong \gg vdW forces in free space
(hydrophobic interaction, "bond"!)



Water alone
5 nearest neighbors

3.0-3.5 H.Bonds/molecule



Water + alkanes

Water MORE structured !

4 H.Bonds/molecule

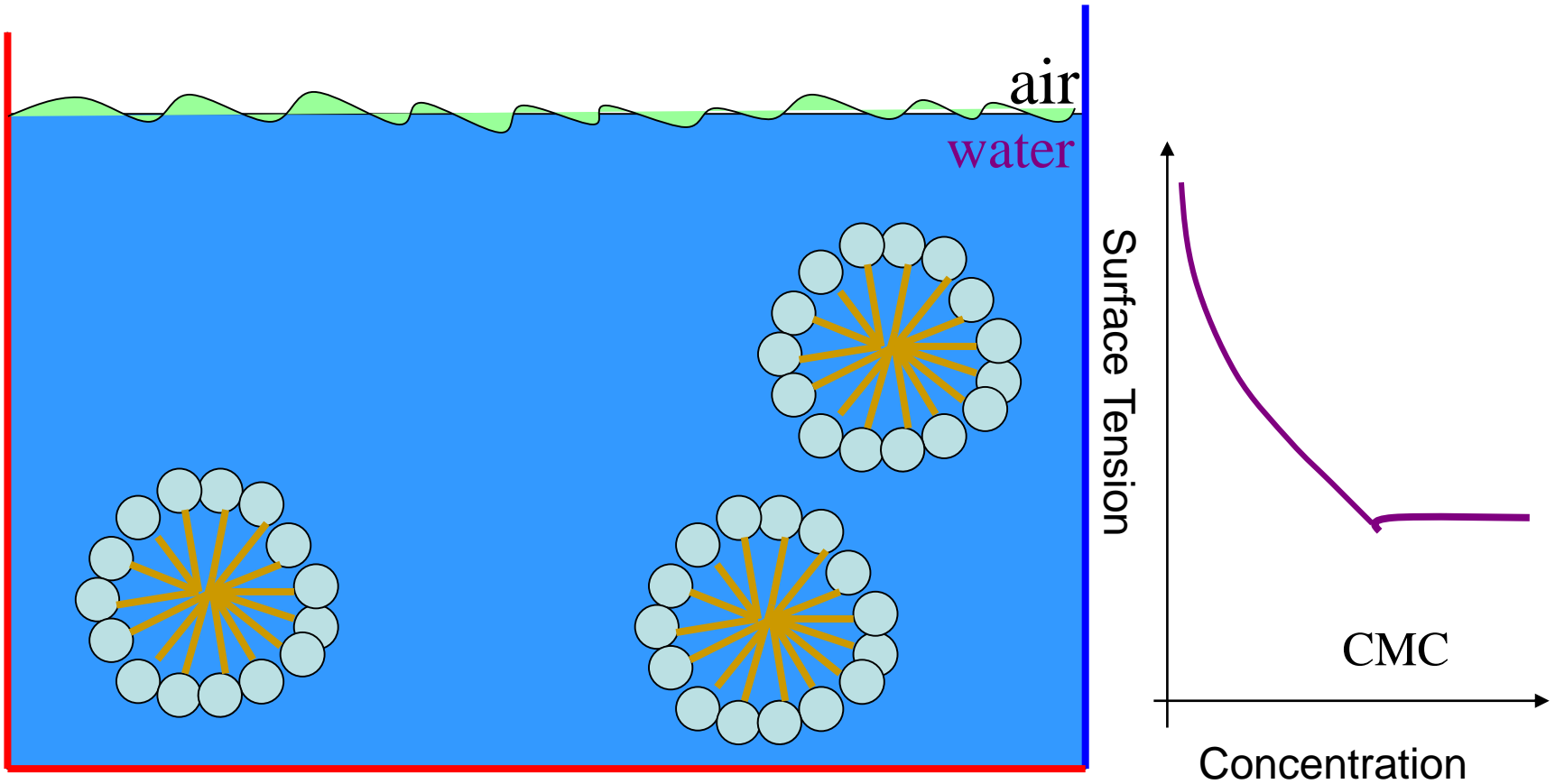
3 H.Bonds/molecule in water-methanol

Water molecules stick together when the enemies appear !

Water molecules simply love themselves too much !

Water structure more important than the HBs !

Micelle Formation in Surfactant Solutions



non-ionic surfactant

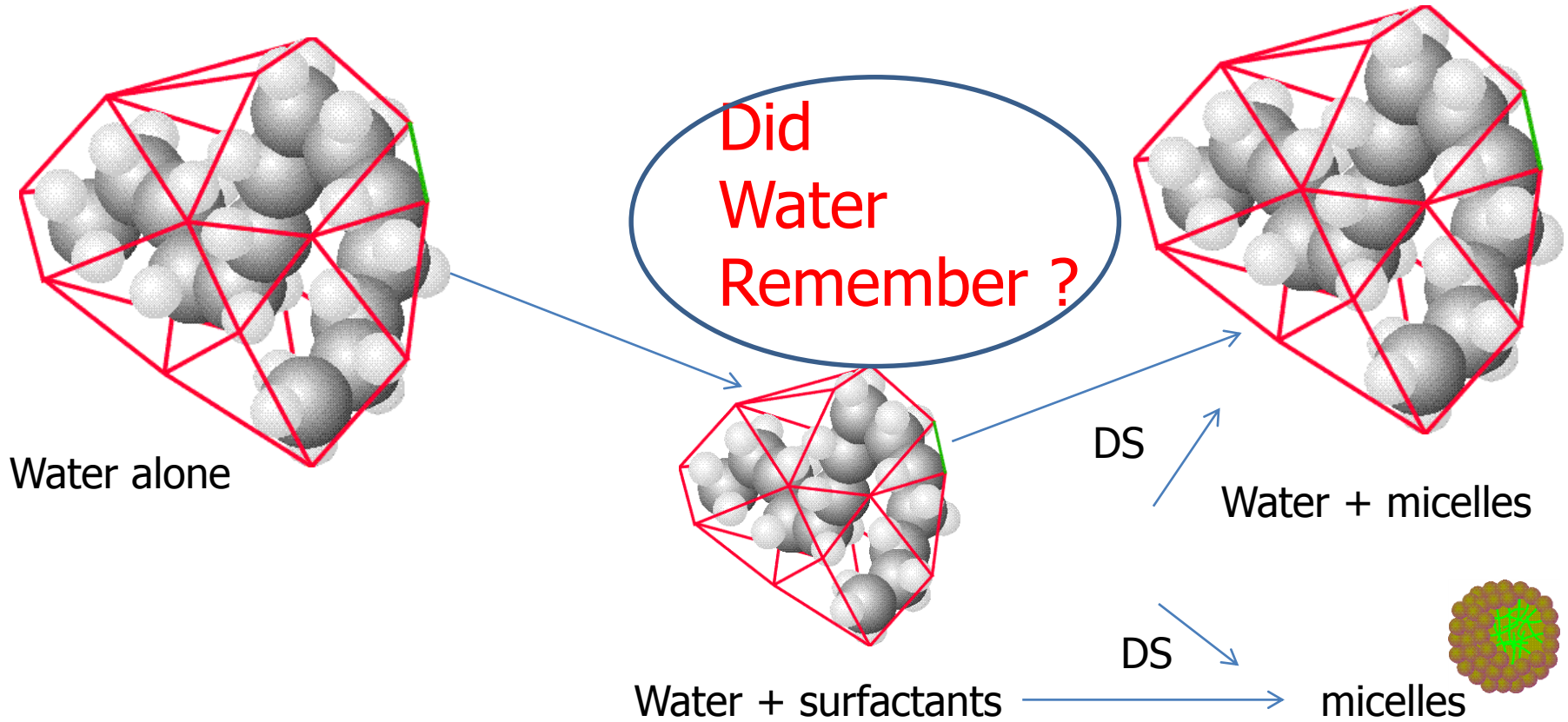
The micellization process – an entropic phenomenon
(understood via the hydrophobic effect)

$$\Delta G = \Delta H - T\Delta S$$

Surfactant	Gibbs energy change of micellization (KJ/mol)	Enthalpy change of micellization (KJ/mol)	Entropy change of micellization (J/K mol)
SDS	-21.9	+2.51	+81.9
C ₁₂ E ₆	-33.0	+16.3	+49.3
Dodecyl pyridinium bromide	-21.0	-4.06	+56.9
N,N dimethyl dodecyl amine oxide	-25.4	+7.11	+109.0
N-dodecyl-N,N-dimethyl glycine	-25.6	-5.86	+64.9

Disorder Eventhough We Create Micelles ?

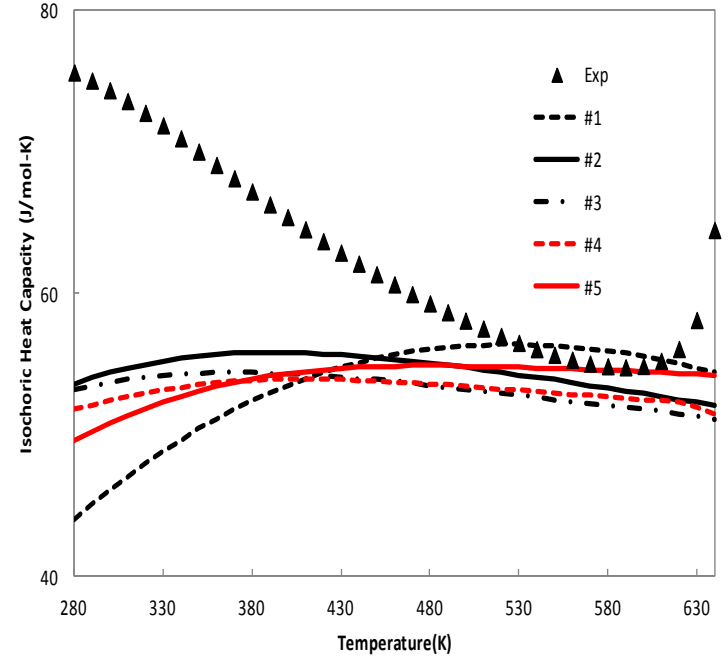
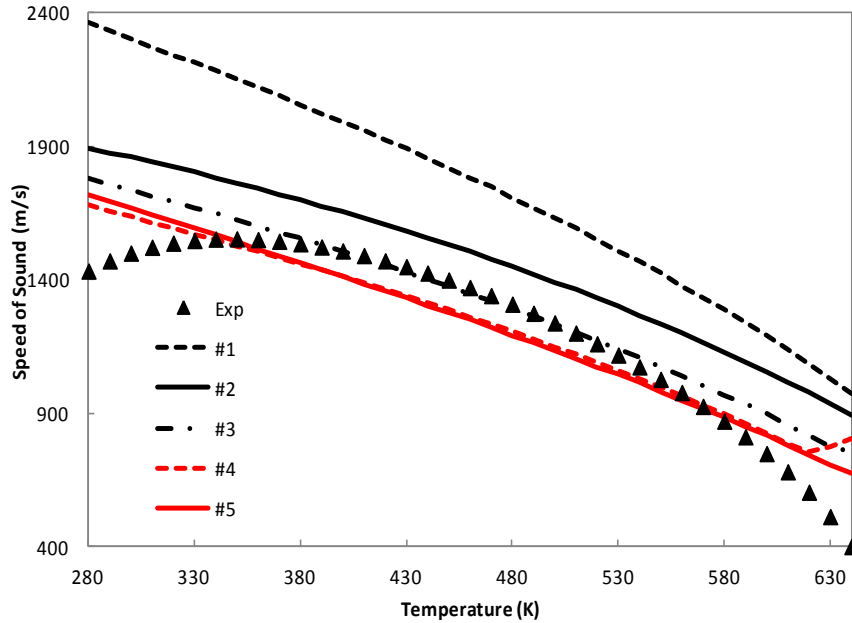
Micellization is (almost always) an entropic effect, i.e. the driving force behind aggregation of surfactant molecules is a large positive value of entropy of micellization! Why ?



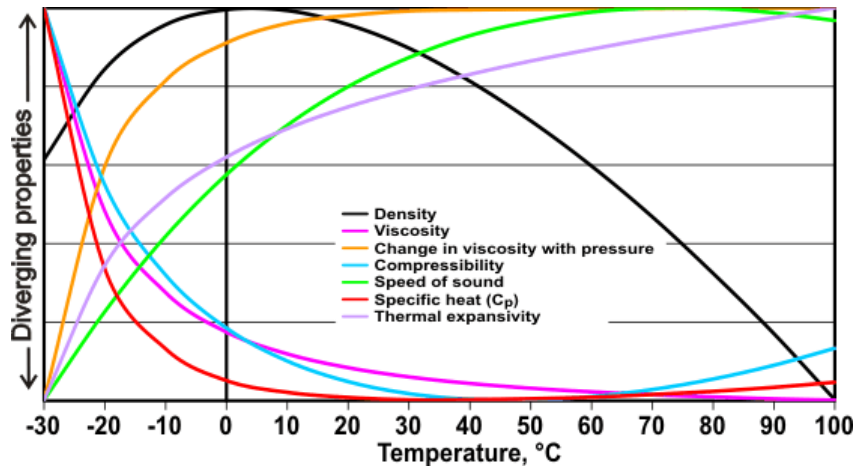
The protagonist Is WATER !!

More maxima and minima in water properties

Curves are PC-SAFT results with different parameter sets

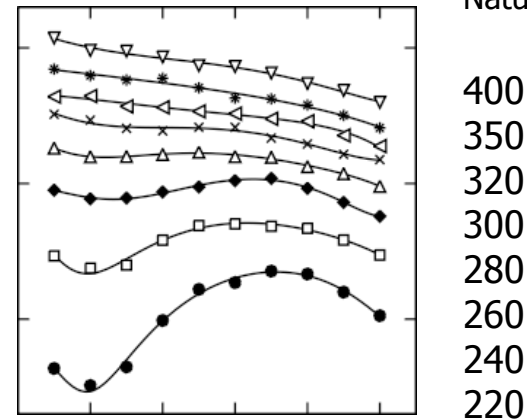


<http://www.lsbu.ac.uk/water/anmlies.html>



Diffusion vs. density

Errington, 2001
Nature, 409, 318



Is all water the same ?



www.shutterstock.com - 36454



Any good for "Frappe" ?

Natural water from Venezuela 40 000 more active than ordinary water – analyzed by Russians biophysicists

Water structure – water from country of origin – water not the same in all places in Earth

"Dead water" vs. Natural pure water from fountains (Dr. Korotkov)

"Holly water", "Energized water" – do they really exist ?

Decorated in Austria



Johann Grander's "revitalized water"

Imported and used in Denmark in farms,
By gardeners, and...

<http://www.johanngrander.com/>

Bread rolls are fresher
Coffee tastes better
Use in air conditioning units
In Austrian Casino

....

Debated Grand water – Topsøe and Danisco also use it ?

- <http://ing.dk/artikel/meta-science-vanvid-om-vand-120253>
- <http://ing.dk/blog/meta-science-uforklarlig-forklaring-126988>
- <http://ing.dk/artikel/dtu-professor-topsoe-og-danisco-til-grin-med-informationsvand-122709>
- <http://ing.dk/artikel/topsoe-og-danisco-jubler-over-rensende-mirakelvand-122331>
- <http://ing.dk/artikel/nysgerrige-danske-forskere-vil-teste-mystisk-vand-117658>
- <http://ing.dk/blog/vand-med-hukommelse-107016>
- <http://ing.dk/artikel/importor-af-mystisk-vandteknologi-kildevand-bliver-behandlet-med-naturmagneter-117616>
- <http://ing.dk/artikel/uforklarlig-vandteknologi-mystificerer-topsoe-og-danisco-117567>
- <http://ing.dk/artikel/ved-stuetemperatur-68350>

Very Amazing Discussions

Theories about water : "The water memory debate"

816

SCIENTIFIC PAPER

NATURE VOL. 333 30 JUNE 1988

Human basophil degranulation triggered by very dilute antiserum against IgE

E. Davenas, F. Beauvais, J. Amara*, M. Oberbaum*, B. Robinzon†, A. Miadonna‡, A. Tedeschi‡, B. Pomeranz§, P. Fortner§, P. Belon, J. Sainte-Laudy, B. Poitevin & J. Benveniste||

INSERM U 200, Université Paris-Sud, 32 rue des Carnets, 92140 Clamart, France

* Ruth Ben Ari Institute of Clinical Immunology, Kaplan Hospital, Rehovot 76100, Israel

† Department of Animal Sciences, Faculty of Agriculture, PO Box 12, The Hebrew University of Jerusalem, Rehovot 76100, Israel

‡ Department of Internal Medicine, Infectious Diseases and Immunopathology, University of Milano, Ospedale Maggiore Policlinico, Milano, Italy

§ Departments of Zoology and Physiology, Ramsay Wright Zoological Laboratories, University of Toronto, 25 Harbord Street, Toronto, Ontario M5S 1A1, Canada

|| To whom correspondence should be addressed.

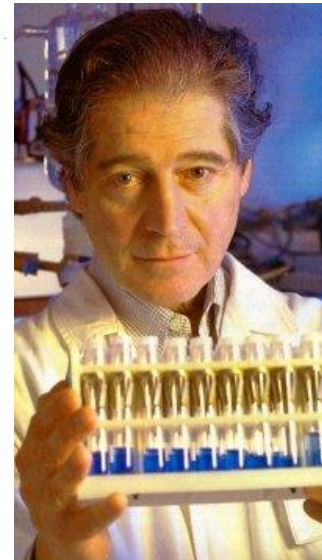
When human polymorphonuclear basophils, a type of white blood cell with antibodies of the immunoglobulin E (IgE) type on its surface, are exposed to anti-IgE antibodies, they release histamine from their intracellular granules and change their staining properties. The latter can be demonstrated at dilutions of anti-IgE that range from 1×10^3 to 1×10^{120} ; over that range, there are successive peaks of degranulation from 40 to 60% of the basophils, despite the calculated absence of any anti-IgE molecules at the highest dilutions. Since dilutions need to be accompanied by vigorous shaking for the effects to be observed, transmission of the biological information could be related to the molecular organization of water.

French scientist Jacques Benveniste (80's)

Water seems to retain information from the molecules it interacted – "water remembers"

Based on experiments with biologically active substances

Water still has biological activity even after all biological molecules have vanished (full dilution + vigorous agitation!)



"The water memory debate" – cont'd. *Nature* is upset

nature

NATURE VOL. 333 30 JUNE 1988

787

When to believe the unbelievable

An article in this week's issue describes observations for which there is no present physical basis. There are good and particular reasons why prudent people should, for the time being, suspend judgement.

INEXPLICABLE observations are not always signs of the supernatural. That is what readers of the remarkable article on page 816 should keep in mind. They should also remember that Avogadro's number, the number of molecules in a gram molecule of material, is roughly 6.23×10^{23} , which naturally implies that most of the experiments with antibody solution reported by Professor J. Benveniste and his colleagues have been carried out in the literal absence of antibody molecules. For what the article shows is that it is possible to dilute an aqueous solution of an antibody virtually indefinitely without the solution losing its biological activity. Or rather, there is a surprising rhythmic fluctuation in the activity of the solution. At some dilutions, the activity falls off; on further dilution, it is restored.

There is no objective explanation of these observations. Nor is there much comfort for anybody in the explanation offered at the end of the article — that antibody molecules once embodied in water leave their internal marks, as ghosts of a kind, on its molecular structure — for there is no evidence of any other kind to suggest that such behaviour may be within the bounds of possibility. Indeed, during the long period since this article was first submitted to *Nature*, it has been plain that Benveniste has been as puzzled as many of those who have read his article by the data he reports. On many occasions, he has responded to referees' suggestions at great inconvenience to himself. When told, for example, that the experiments should be repeated at an independent laboratory, he arranged for this to be done.

One of the purposes that will be served by publishing the article will be to provide an authentic account of this work for the benefit of those, especially in France, who have gathered rumours of it from the popular press. Another is that vigilant members of the scientific community with a flair for picking holes in other people's work may be able to suggest further tests of the validity of the conclusions.

Certainly there can be no justification, at this stage, for an attempt to use Benveniste's conclusions for the malign purposes to which they might be put. There are some obvious dangers. In homeopathic medicine, for example, which works on the principle that very small concentrations of appropriate products may have consequences that far outweigh those expected of them, there will be a natural inclination to welcome Benveniste's article as aid and comfort, but that would be premature, probably mistaken. It will be time for celebrations of that kind only when a lot more water has run underneath this bridge.

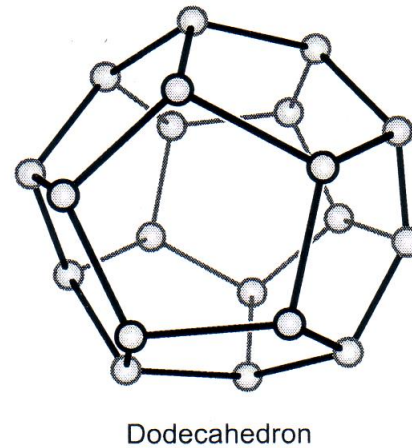
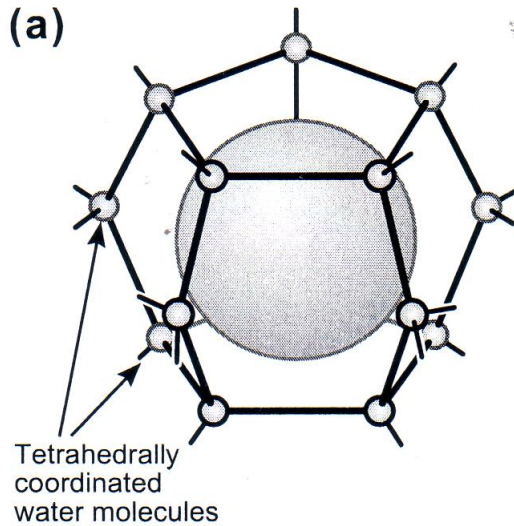
But, those of supernatural inclinations will protest, is it not grossly unfair that science should put aside, even temporarily, some surprising and unexpected observations (such as these) while apparently welcoming others which are no less surprising (such as the recent suggestion that there may be a 'fifth force' between material objects)? The explanation is simple, but, perhaps for that reason, not widely understood. It is entirely possible for physicists to welcome the notion of the fifth force because it would be a novel happening which could nevertheless be accommodated within the accepted framework of science. Benveniste's observations, on the other hand, are startling not merely because they point to a novel phenomenon, but because they strike at the roots of two centuries of observation and

rationalization of physical phenomena. Where, for example, would elementary principles such as the Law of Mass Action be if Benveniste is proved correct? The principle of restraint which applies is simply that, when an unexpected observation requires that a substantial part of our intellectual heritage should be thrown away, it is prudent to ask more carefully than usual whether the observation may be incorrect. □

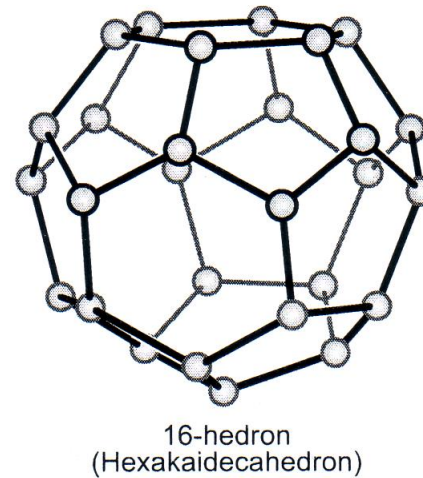
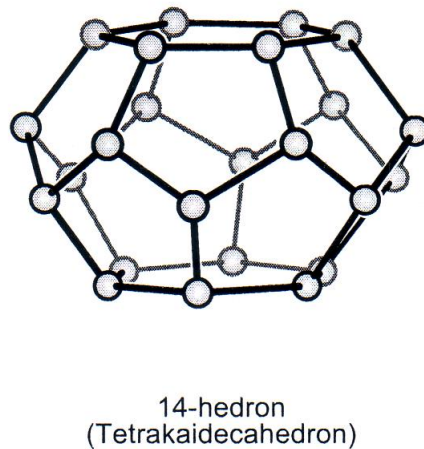
Editorial reservation

READERS of this article may share the incredulity of the many referees who have commented on several versions of it during the past several months. The essence of the result is that an aqueous solution of an antibody retains its ability to evoke a biological response even when diluted to such an extent that there is a negligible chance of there being a single molecule in any sample. There is no physical basis for such an activity. With the kind collaboration of Professor Benveniste, *Nature* has therefore arranged for independent investigators to observe repetitions of the experiments. A report of this investigation will appear shortly. □

"Gas hydrates" by water molecules around small dissolved nonpolar hydrophobic molecules



Water can Participate in up To 4 H-Bonds



More ordered Water than in Bulk liquid

Gas Hydrate Formation and the Memory of Water

” It is widely accepted [1-4] that it is easier (faster) to make hydrates from water that has previously been in hydrate form rather than directly from fresh water – i.e. if you place gas and water under pressure and cycle the temperature up and down to melt and reform hydrates, **each subsequent temperature cycle downwards will form hydrates more quickly. In fact this is used as an experimental technique to run through experiments faster** (this phenomenon is termed “memory water” by researchers in this field, although the term has none of the negative connotations of this idea in other branches of water science)”

Nicolas von Solms

Why on earth does this happen ?

Google: “Water memory in gas hydrates”. 2 million hits – and heated debate !

Ack. Nicolas von Solms

Original Research Papers

Histamine dilutions modulate basophil activation

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Abstract. *Background:* In order to demonstrate that high dilutions of histamine are able to inhibit basophil activation in a reproducible fashion, several techniques were used in different research laboratories.

Objective: The aim of the study was to investigate the action of histamine dilutions on basophil activation.

Methods: Basophil activation was assessed by alcian blue staining, measurement of histamine release and CD63 expression. Study 1 used a blinded multi-centre approach in 4 centres. Study 2, related to the confirmation of the multi-centre study by flow cytometry, was performed independently in 3 laboratories. Study 3 examined the histamine release (one laboratory) and the activity of H₂ receptor antagonists and structural analogues (two laboratories).

Results: High dilutions of histamine (10⁻³⁰–10⁻³⁸ M) influence the activation of human basophils measured by alcian blue staining. The degree of inhibition depends on the initial level of anti-IgE induced stimulation, with the greatest inhibitory effects seen at lower levels of stimulation. This multicentre study was confirmed in the three laboratories by using flow cytometry and in one laboratory by histamine release. Inhibition of CD63 expression by histamine high dilutions was reversed by cimetidine (effect observed in two laboratories) and not by ranitidine (one laboratory). Histidine tested in parallel with histamine showed no activity on this model.

Conclusion: In 3 different types of experiment, it has been shown that high dilutions of histamine may indeed exert an effect on basophil activity. This activity observed by staining basophils with alcian blue was confirmed by flow cytometry. Inhibition by histamine was reversed by anti-H₂ and was not observed with histidine these results being in favour of the

specificity of this effect. We are however unable to explain our findings and are reporting them to encourage others to investigate this phenomenon.

Key words: Basophils – histamine – high dilutions – cimetidine – ranitidine – histidine

Introduction

Human basophils play a key role in allergic diseases. Activation of basophils via cross-linking of membrane bound IgE induces fusion of the cytoplasmic granules with the plasma membrane and the subsequent release of potent mediators including histamine. Histamine itself can inhibit the further degranulation of the basophil by acting on H₂ receptors [1, 2]. A series of investigations, mainly by one group, has demonstrated that high dilutions of histamine are also capable of inhibiting basophil degranulation [3, 4].

Although a biological action of ultra high dilutions has been shown, this is extremely controversial [5–8]. Indeed the paper published by Benveniste and colleagues in 1988 sparked a series of letters and investigations of various degrees of seriousness [7–15]. This group suggested that high dilutions of anti-IgE were able to stimulate human basophils. Ovelgönne et al. and Hirst et al. attempted to repeat these experiments but found no evidence for any periodic or polynomial change of degranulation as a function of anti-IgE dilution [7, 8]. The results did, however, contain a source of variation that could not be explained [8].

Our experiments began in the early 80's and were initially based on examination of the activity of histamine dilutions

Professor
Madeleine Ennis

Tried to disprove
"water memory"
Once and for all
And her results
Showed the exact
Opposite !

"If the results are
Real, she says,
We may need to
Rewrite physics
And chemistry"

Fights about water memory

"Benveniste's idea
sadly makes no sense
It is a kind of desperation

If H.Bonds are lasting
Only a picosecond
Before they break and
Reform, how on earth
Is the shape going to
Be maintained"?

Philip Ball
2011 Talk to
Royal Society of Chemistry



Although individual molecules of water cannot retain any memory of past hydrogen bonding for periods of more than a fraction of a second, the behaviour of water clusters can be entirely different (Figure 1), as shown previously for ice and cationic hydration. Water clusters are proven entities;⁴¹ their size and lifetime dependent on their physical and chemical environment. Liquid water is made up from a mixture of such clusters forming, changing and disappearing.

The lifetime of a particular cluster containing specific water molecules will be not much longer than the life of individual hydrogen bonds (ie nanoseconds) but clusters can continue forever although with constant changing of their constituent water molecules.

SOS
vs
Ball
e
A

Martin F. Chaplin (London South Bank U.)
"The memory of water: an overview
Homeopathy, 2007, 96, 143

Explanations for water memory?

The Memory of Water: an overview *Homeopathy*, 2007, 96, 143
MF Chaplin

Table 1 Possible mechanisms by which water could achieve a 'memory'

<i>Specific mechanisms</i>	<i>Non-specific mechanisms</i>
Remaining material on surfaces Aerosol material reintroduced Bacterial material introduced Imprinted silicates Remaining particle clusters	Silicates, dissolved and particular Nanobubbles and their material surfaces Redox molecules produced from water Natural water clustering Stabilized water clustering Ions, including from glassware Ethanol solution complexity

Four very passionate articles on water memory

Yolene Thomas, 2007. The history of the memory of water. *Homeopathy*, 96, 151

Jose Teixeira, 2007. Can water possibly have a memory? A sceptical view. *Homeopathy*, 96, 158

V. Elia et al., 2007. The "Memory of Water": an almost deciphered enigma. Dissipative structures in extremely dilute aqueous solutions. *Homeopathy*, 96, 163

Four articles, Same year (2007) – Four opinions ?

Article	Main Messages
Martin Chaplin, UK	<p>No such material as pure water exists</p> <p>Liquid water always contains other species such as H⁺ ions In the absence of other materials and surfaces, the HB pattern surrounding a solute does not persist when the solute is removed</p> <p>Numerous "water memory" stories e.g. gas hydrates, etc Many explanations for the phenomenon, see previous slide</p> <p>Glass tubes and dissolved silica is one good explanation</p> <p>The effect of shaking can be significant</p>
Yolene Thomas, France	<p>Very emotional – in favor of J. Benveniste</p> <p>Refers to Eni's work, L. Rey and others who have "proved" water memory</p> <p>Digital Biology story – very exciting story ! But ...</p>

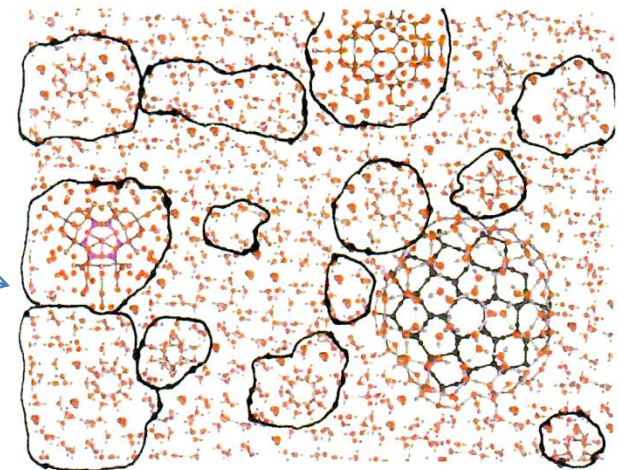
Four articles, Same year (2007) – Four opinions ?

Article	Main Messages
Jose Teixeira, France	<p>Quite critical</p> <p>No water clusters at all ! Except for micelles (surfactants)</p> <p>Any structure has a life of ps order (10^{-12} s)</p> <p>Presence of other molecules or dissolved gases can explain some of the phenomena</p> <p>Water is not pure water – full of impurities, what else is there in the so-called "dilute" solutions ?</p>
V. Elia, E.Napoli, R. Germano, Italy	<p>10 years of experiments proving water memory due to structuring and non-equilibrium status (Also many refs to others' work, "proofs")</p> <p>Impurities have an effect but not the full explanation</p> <p>"within the solutions are molecular clusters of water molecules with HBs far from equilibrium conditions"</p>

Water Memory = 463 mil. Hits in Google !

Water structure – A big mystery

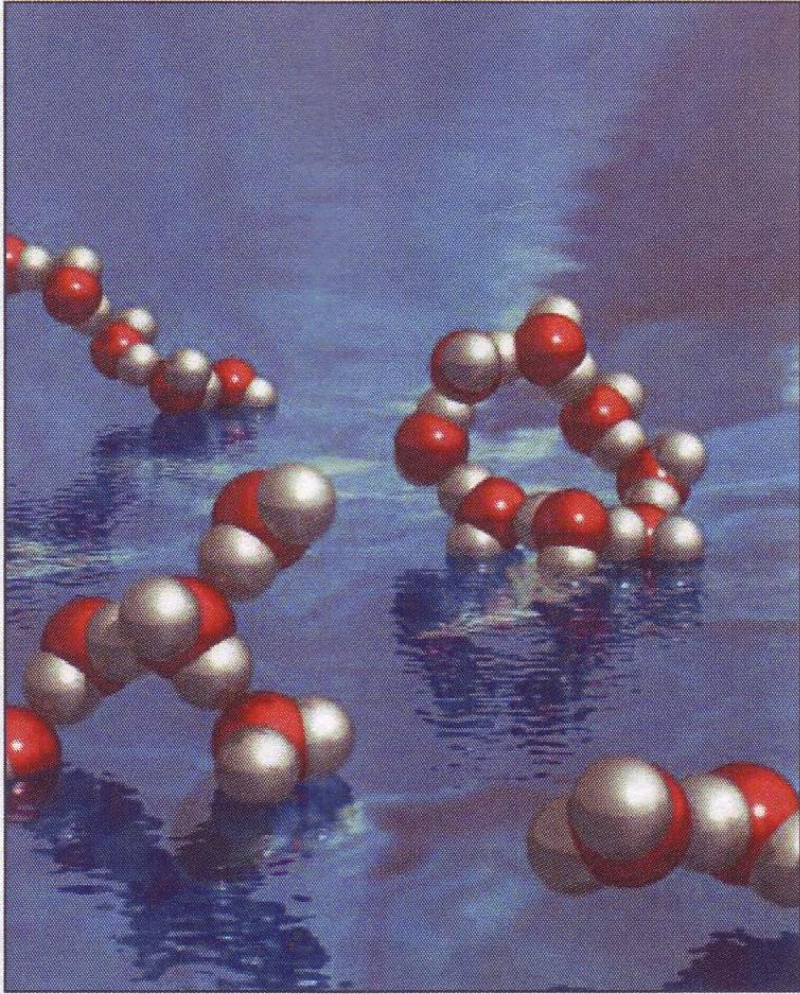
- Diverse models for water structure
- Complex – “even water scientists occasionally have difficulties understanding one another’s theories”
- Most share a common feature: multiple states
- Martin Chaplin (London South Bank U., UK) web-site on water: <http://www.lsbu.ac.uk/water/>
- Rustum Roy et al. model



Water – an enduring mystery

- Article in *Nature* by Philip Ball (2008, 452, 291)
- Lars Pettersson, Anders Nilsson et al. theory in *Science* (2004, 304, 995) :
- *“Molecules in liquid water bind on average to just two others, forming chains and rings” (‘string theory’)*
- *“The tetrahedral structure is not the only way to interpret previous data on water structure from X-ray, neutron scattering and IR. The string model fits the results too, they say”*
- *“Two-state model with both classical tetrahedral structures and chain/rings ones with denser & fewer hydrogen bonds”*
- *“Cold water contains microscopic icebergs in a fluid sea” (Wilhelm Rontgen, 1982) and similar two-state models later (Henry Armstrong in 1920s, Oleg Samoilov in 1940s, Wilse Robinson in 2000)*

How the Sweds see water



Liquid water consists of
Structures with two strong
Hydrogen bonds of each molecule
To its neighbors, resulting in water
Chains and rings

80% form 2-H bonds in Liquid water
Rather than three or four as
Assumed in most water-related
Studies

Liquid water resembles top ice layers

More: *Chemical Physics Letters*
(*cover/frontiers article*), 2008, 460: 387

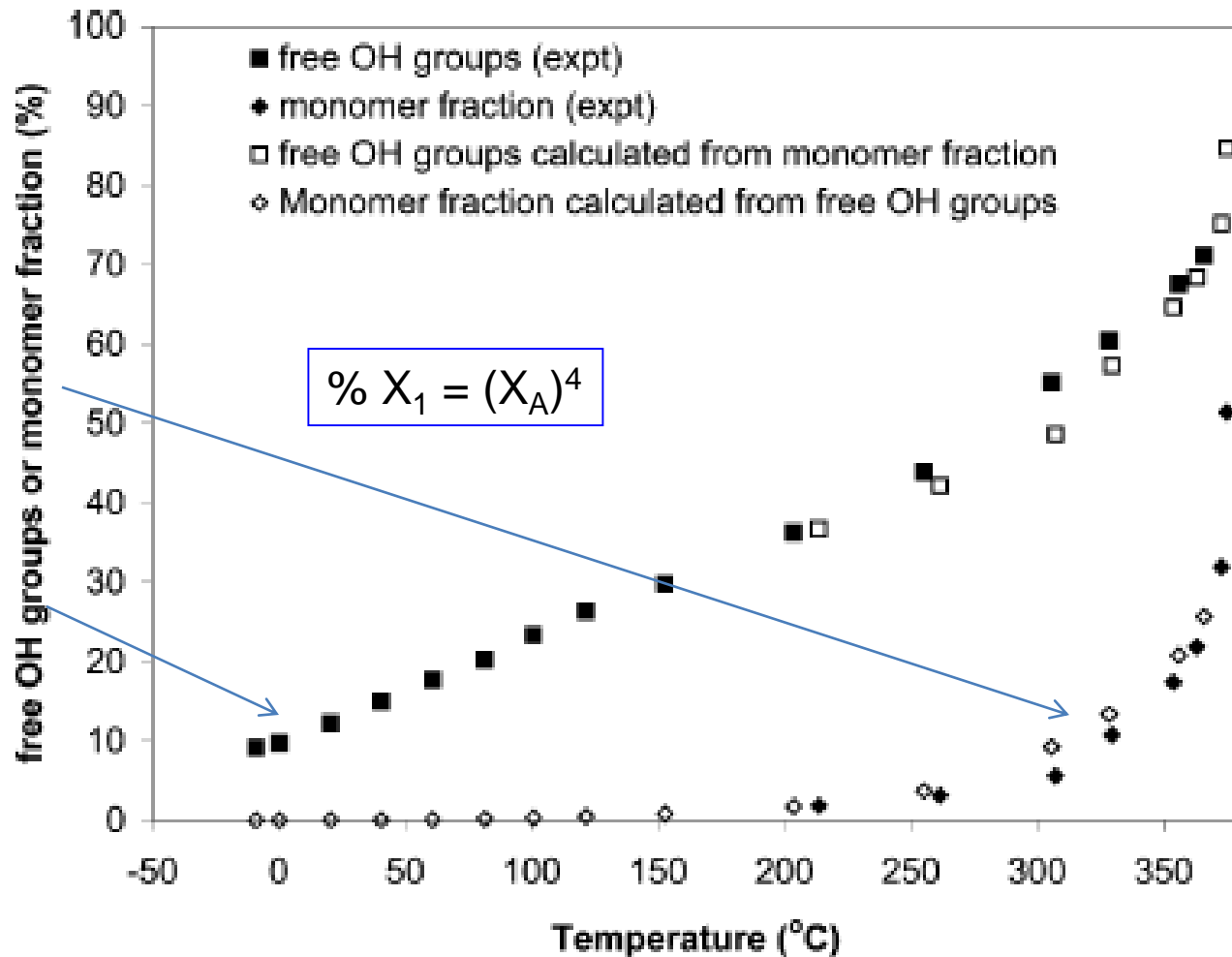
Fights in the pages of *Science*

- Smith et al. [group of Richard Saykally, U.California, Berkeley], October 2004, *Science*, 306, 851 "Energetics of hydrogen bond network rearrangements in liquid water": No way! We have tetrahedra, Only 10% HB broken – they have misintrepreted the data
- Nilsson et al., May 2005, *Science*, 308, 793a. Comment on "Energetics...."
- Smith et al., May 2005, *Science*, 308, 793b. Response to Comment on "Energetics..."
- My conclusion: Different interpretation of the same spectroscopic data ?
- *More evidence for two-component water structure using femtosecond IR spectroscopy (Woutersen et al., 1997, Science, 278, 658)*

1. The experimental (?) monomer fraction data

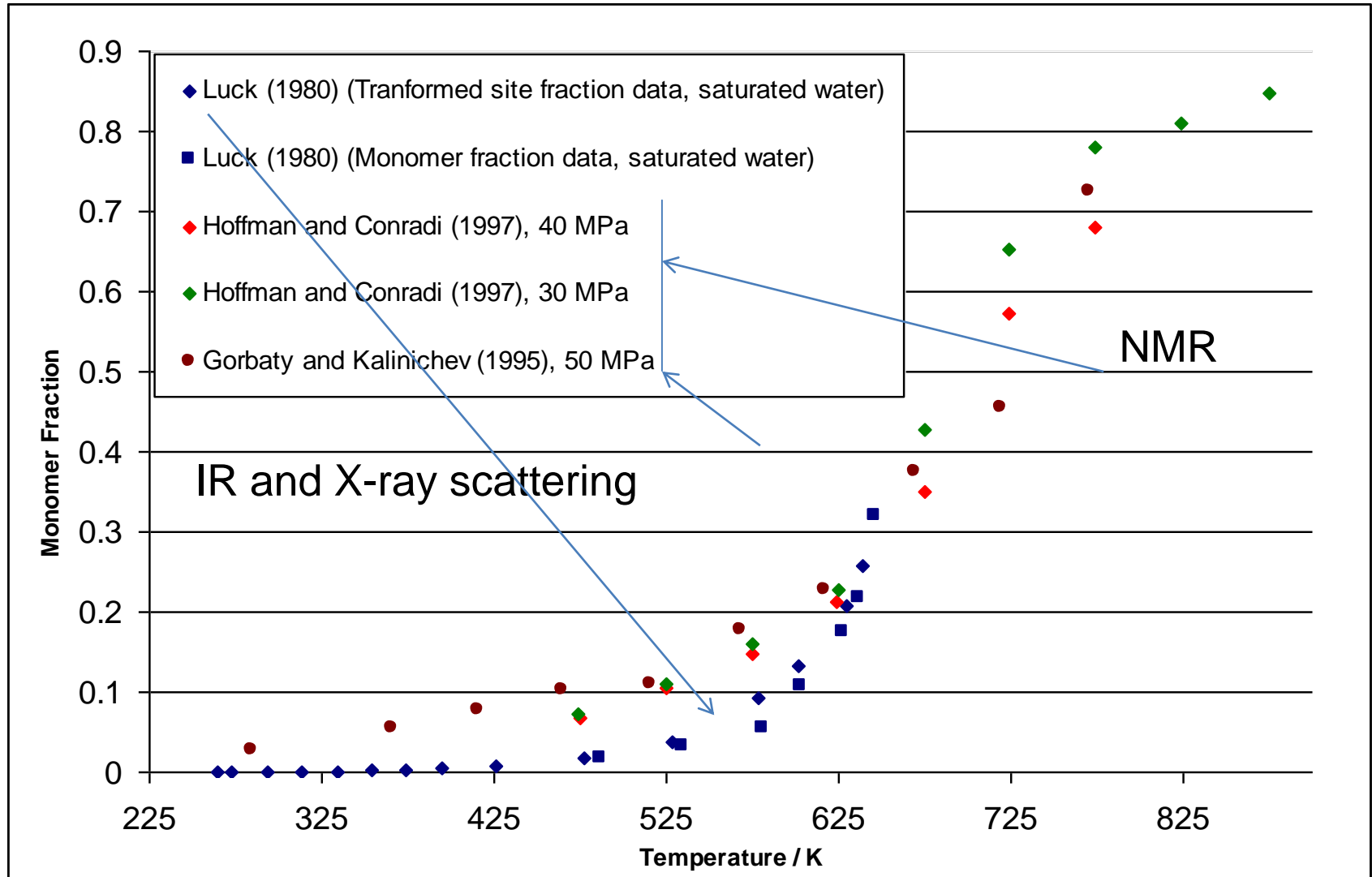
- The data are shown in the next slides:
- Luck's "famous" data (1980)
- More data by other researchers – qualitative agreement with Luck, showing somewhat higher monomer fractions
- "New" data from Mallamace (MIT) showing very high monomer fractions (do we interpret the data correctly?)

Free OH groups and percentage monomer fraction for pure water as a function of temperature [Luck, 1980]



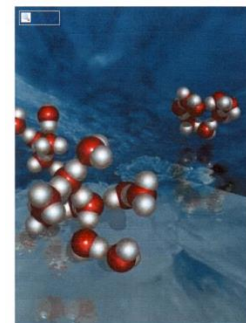
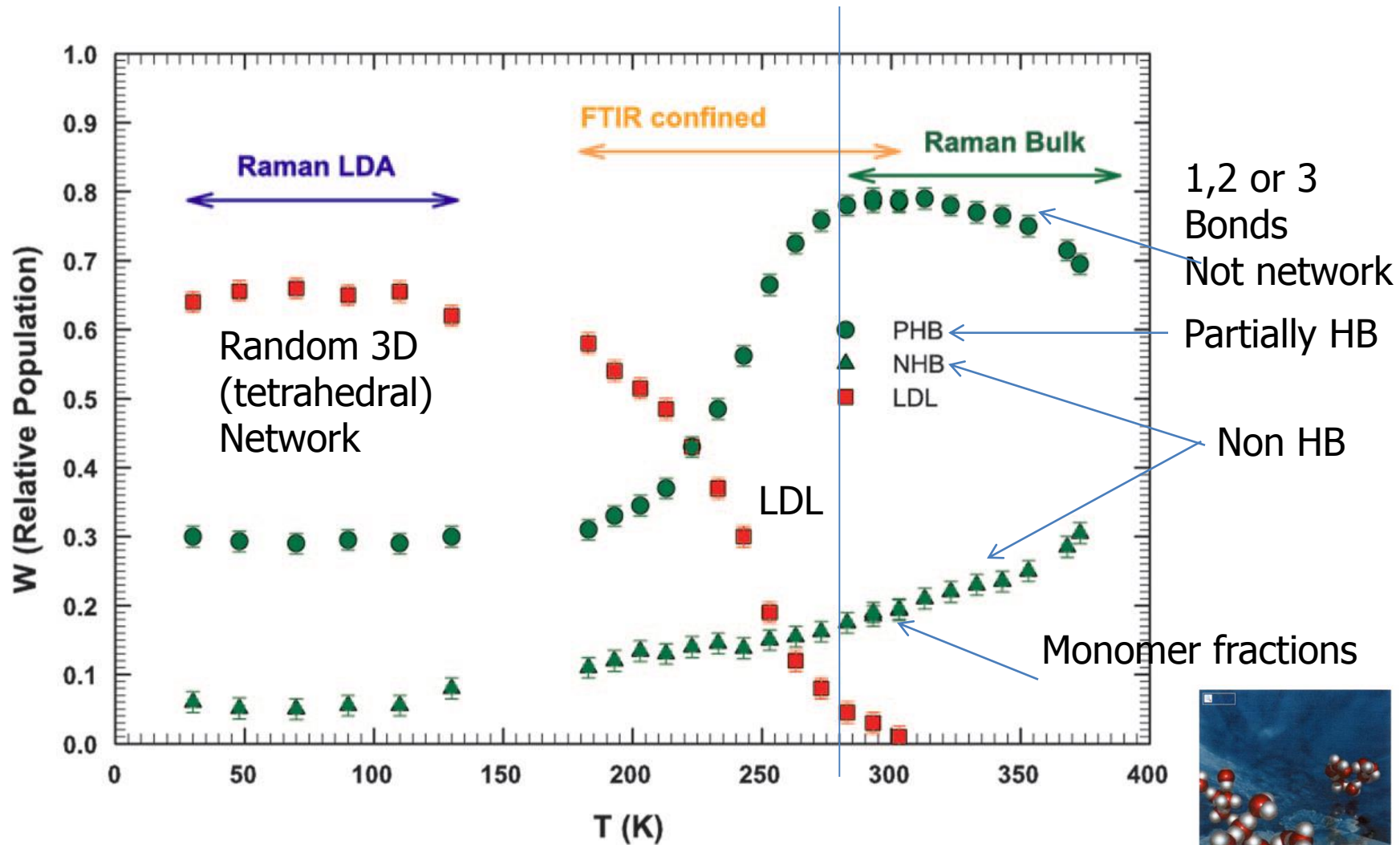
Water monomer fraction data from various sources

Ioannis Tsvintzelis, 2013 (unpublished)



Other than Luck data: Both Liquid and supercritical water

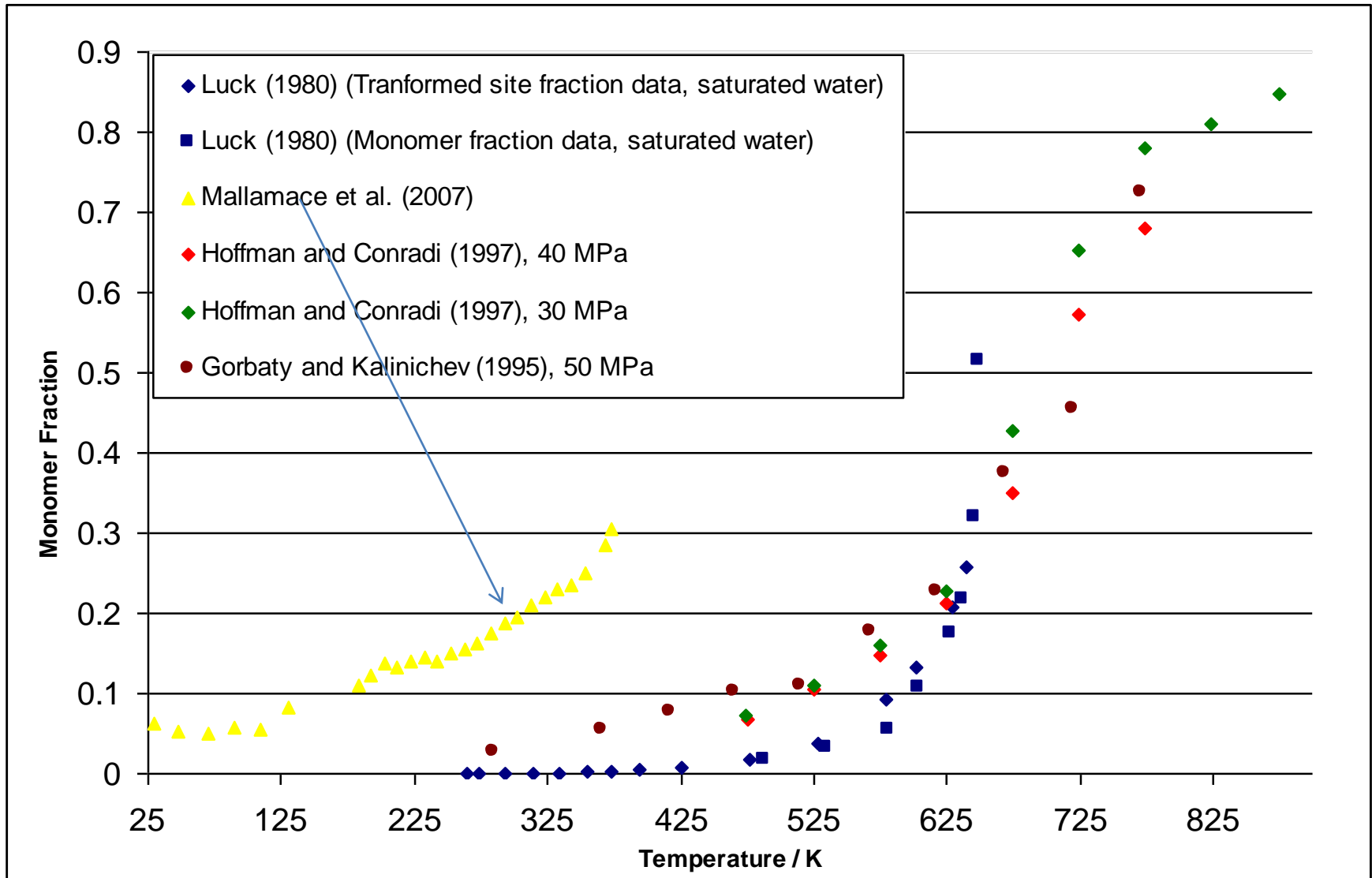
A more recent analysis from MIT



This artist's depiction shows two distinct structures of water: in the foreground, tetrahedral low-density water and in the background, distorted high-density water. (Credit: Image courtesy of Hirohito Ogasawara and Ningdong Huang, SLAC)

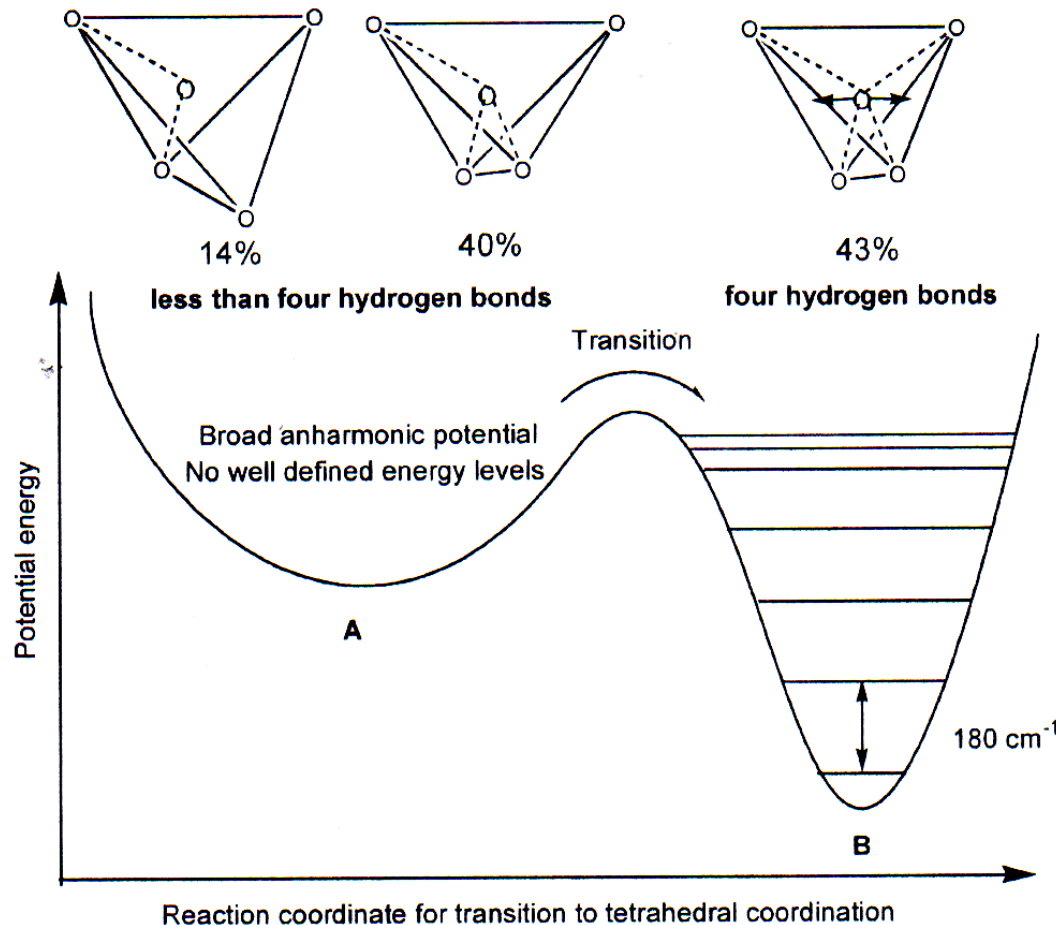
F.Mallamace et al., 2007, Proc.Natl.Acad.Sci., 104(47), 18387 (MIT)

Water monomer fraction data from various sources – cont'd (incl. Mallamace data)



How many sites in water ?

Two-state
Liquid Water
Models



Many more
Controversial
Studies – see later

”Room T: 43% of
water molecules have
4 hydrogen bonds,
the rest have fewer”

Figure 2. A schematic illustration of hydrogen bonding and local water potentials in liquid water.

Answers from molecular simulation ?

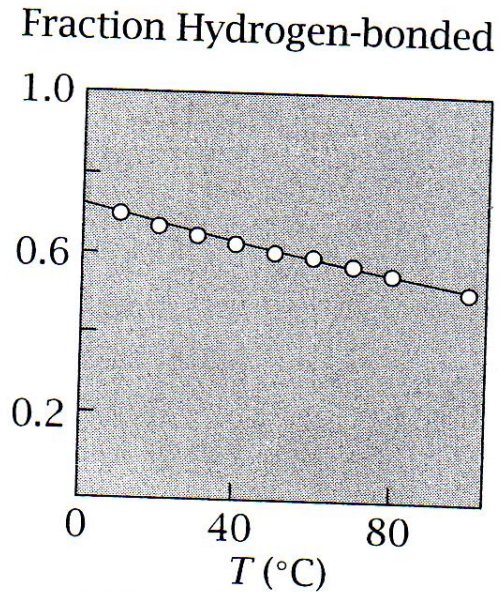


Figure 29.9 Fraction of hydrogen bonds made in liquid water over the liquid temperature range. Sources: DE Hare and CM Sorensen, *J Chem Phys* **93**, 6954-60 (1990); KAT Silverstein, ADJ Haymet, KA Dill, *J Am Chem* **122**, 8037-8041 (2000).

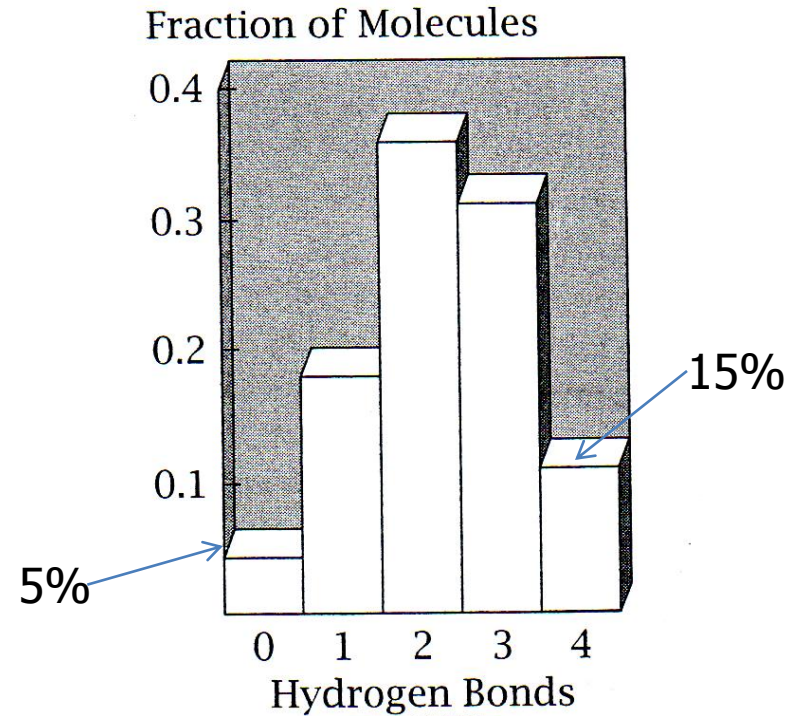
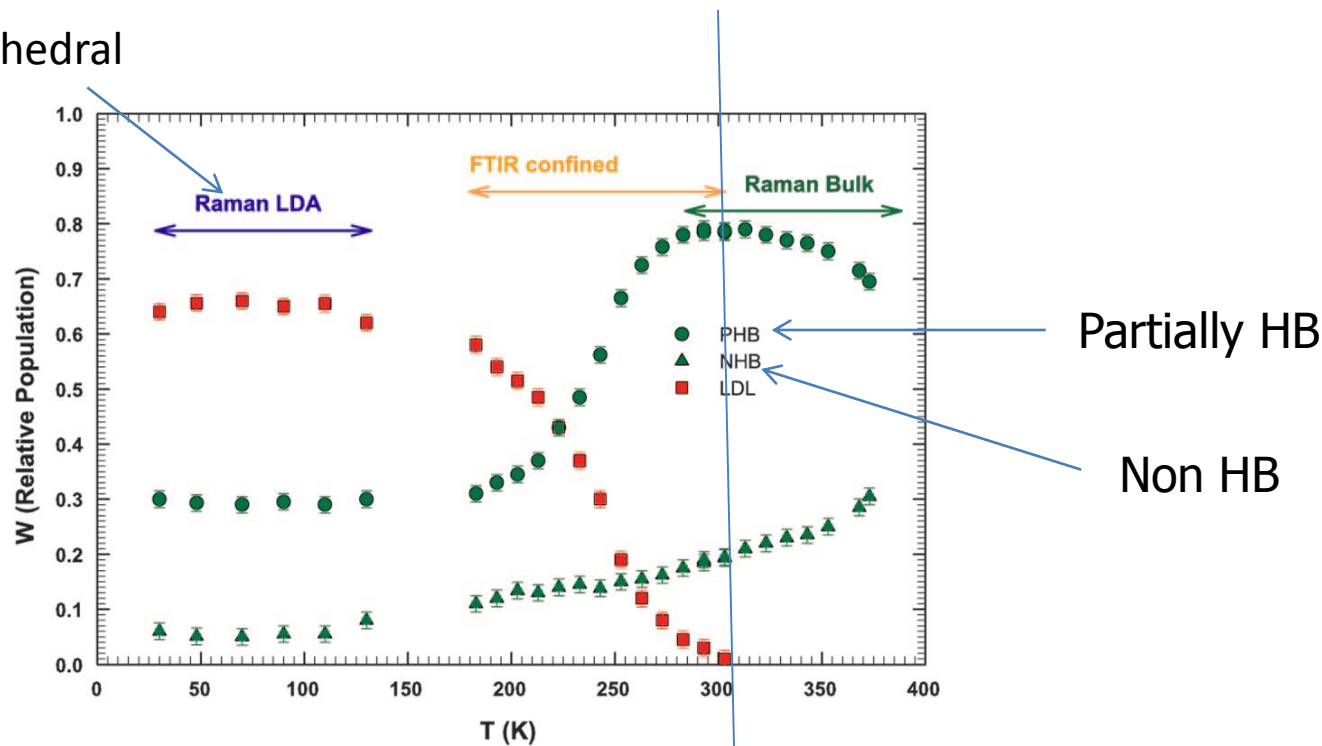


Figure 29.10 Simulated distribution of the number of hydrogen bonds per molecule in liquid water at 25 $^{\circ}\text{C}$. Source: FH Stillinger, *Science* **209**, 451-457 (1980).

More evidence for two-structure liquid water

Tetrahedral



Two different local HB structures: LDA (low density amorphous solid) and HDL (high density liquid)

Two different local structures in liquid water: LDL (like LDA) open "ice like" HB Network and HDL (not fully developed tetrahedral HB network)
HDL = NHB + PHB

Above 303 K (stable liquid) there is NO LDL (No ice-type 3D network!)

Liquid water: 2, 3 or 4 hydrogen bonds – and how much of each one ?

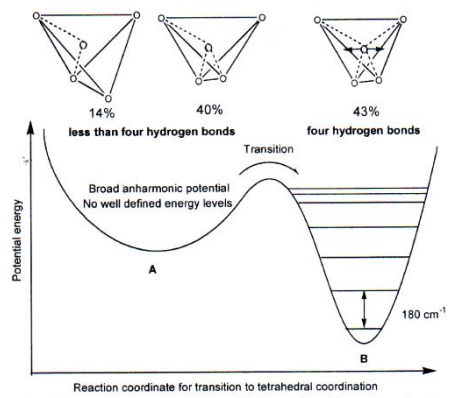
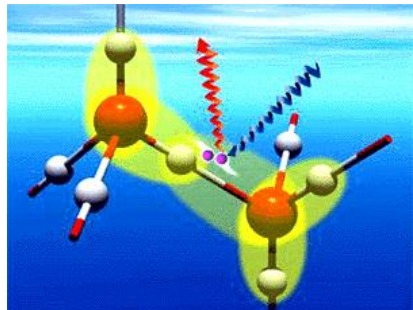
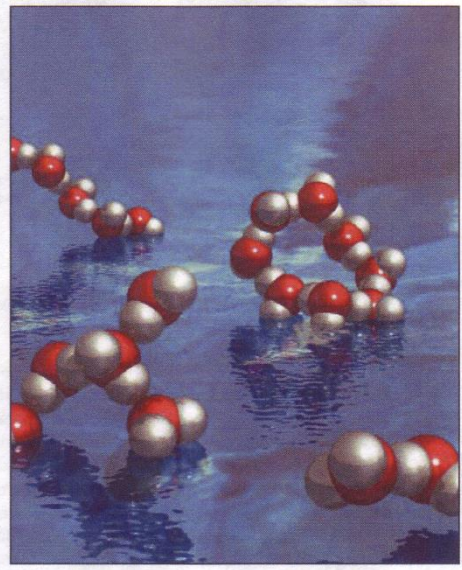
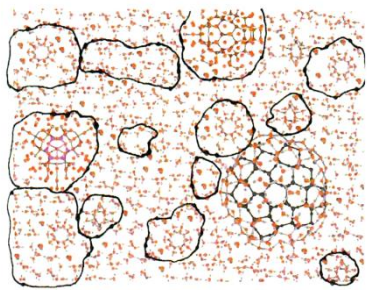
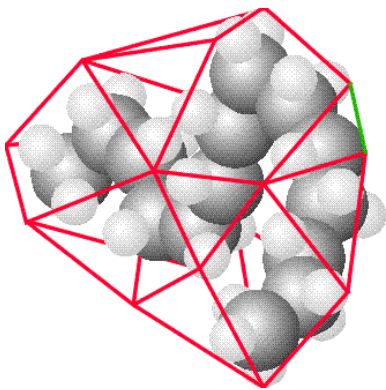


Figure 2. A schematic illustration of hydrogen bonding and local water potentials in liquid water.

More controversies – effect of salts on water structure

% Hydrogen bonds (4 bonds) of water
Increases with salt concentration

$b = \text{free water (NaCl-water)}/\text{free pure water} < 1$

Van't Hoff factor for NaCl dissociation:

$$i = i_d / b = (1+a) / b$$

$a = \text{degree of dissociation}$

Clear change of water structure in presence of ions

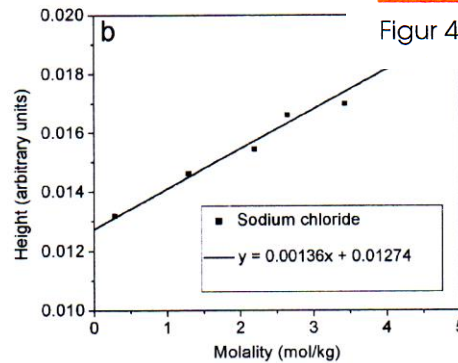
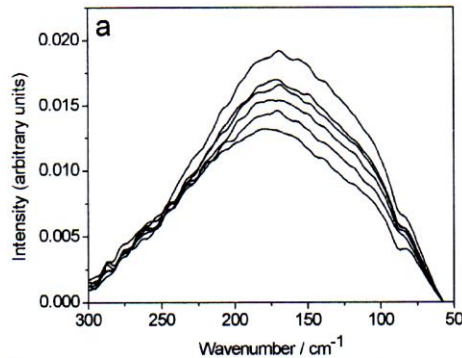
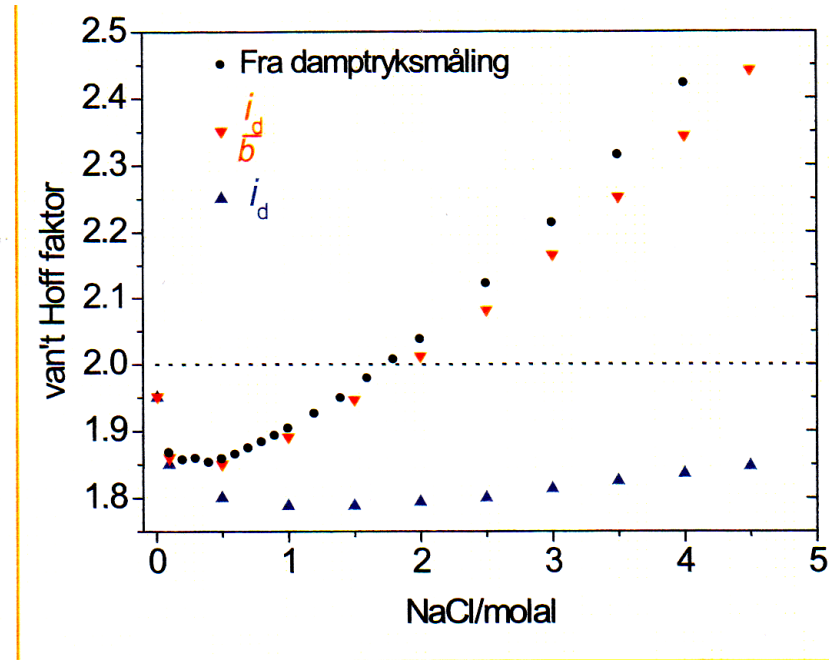


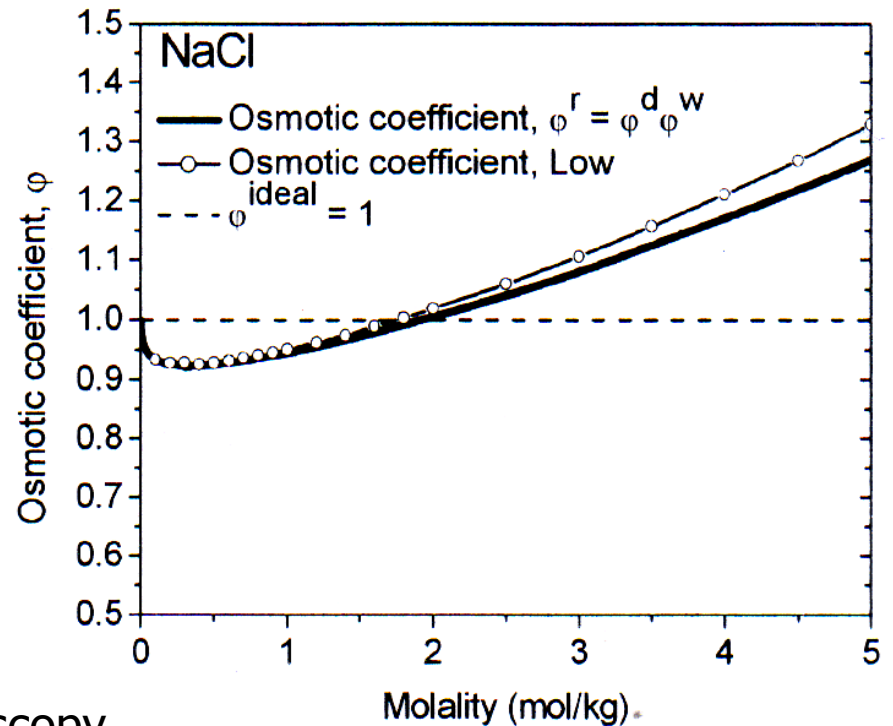
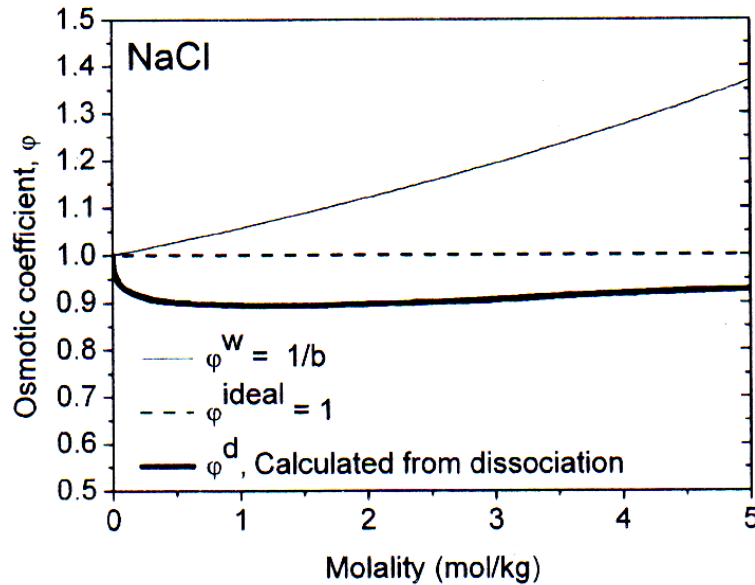
Figure 4. Van't Hoff-faktorer for vandige NaCl-opløsninger.

Figure 4. (a) $R(\bar{\nu})$ representation of the low-wavenumber Raman spectrum of aqueous solutions of NaCl for molalities in the range 0.28–4.55 mol/kg (curves from bottom to top). (b) The heights of the 180 cm^{-1} band as a function of molality of NaCl. The solid line is a linear least-squares fit to the data.

Including change of
Water structure
Brings van't Hoff factors
Close to "independent"
Experimental data

Frosch, M., Bilde, M., Nielsen, O.F., 2010, J.Phys.Chem.A., 114, 11933
& Dansk Kemi, 2011, 92,3, 26 "Vand – en evig gåde"

From water clustering to osmotic coefficients



Osmotic coefficients from Raman spectroscopy

Agree well with thermodynamic ones – when water structure change is accounted for (together with electrolyte dissociation)

Water structure effect crucial at higher concentrations

The minimum explained by considering the dependence of the structure of water on electrolyte - Similar results for other salts

Another opinion...

Negligible Effect of Ions on the Hydrogen-Bond Structure in Liquid Water

Science, 2003, 301: 347

Anne Willem Omta,^{1*} Michel F. Kropman,¹ Sander Woutersen,¹
Huib J. Bakker^{1,2}

The effects of ions on bulk properties of liquid water, such as viscosity, have suggested that ions alter water's hydrogen-bonding network. We measured the orientational correlation time of water molecules in $\text{Mg}(\text{ClO}_4)_2$, NaClO_4 , and Na_2SO_4 solutions by means of femtosecond pump-probe spectroscopy. The addition of ions had no influence on the rotational dynamics of water molecules outside the first solvation shells of the ions. This result shows that the presence of ions does not lead to an enhancement or a breakdown of the hydrogen-bond network in liquid water.

X

X

Y. Zhang and Paul Cremer, 2006, Current Opinion in Chemical Biology, 10: 658
"Ions do not affect the bulk water properties" – numerous evidence for that !!

What's going on ?

- Are Luck's "famous" monomer fraction data for water wrong ?
- Is the tetrahedral structure of water wrong ?
- Do we have many more "free" (monomer) water molecules than originally anticipated ?
- Should we believe in a one or in a two- or in a multi-state structure model for water ?
- What type of structure is consistent with the correct description of the thermodynamic properties of water ?
- ...

2. The theories (SAFT, CPA, NRHB) against monomer fraction data

Results summarized in the next slides:

- Theories in qualitative agreement with each other
- Theories not in very good agreement with Luck, etc data
- All theories predict much "more" hydrogen bonding or less monomer fraction than Luck's data
- If we want to "force" the theories to fit the monomer fraction data it can be done at the cost of getting i) strange parameters ii) poor phase behavior e.g. LLE for water-alkanes

The SAFT model

Michael Wertheim

$$\sigma_i, \varepsilon_i, m_i, (\kappa^{A_i B_i}, \varepsilon^{A_i B_i}) \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij})$$

Chapman, Jackson, Radosz and Gubbins 1990

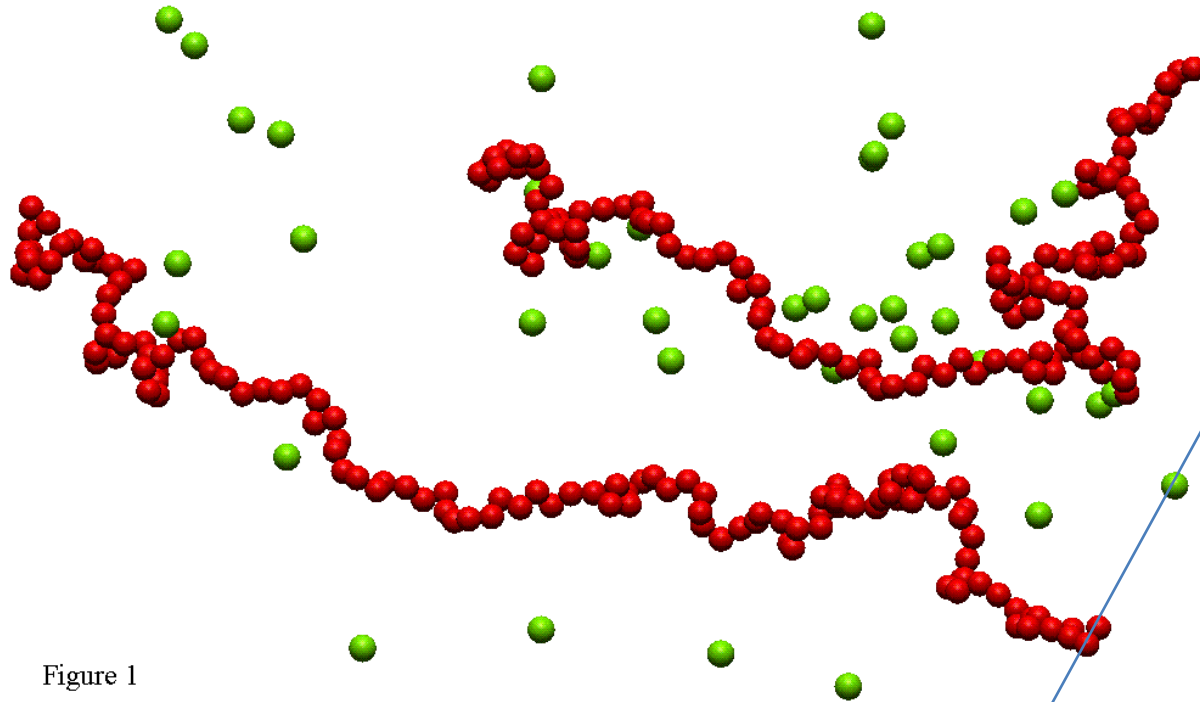


Figure 1

Wertheim's articles in
J. Stat. Physics (1986, 1987)
(over 3000 citations)

"While brilliant are
essentially incomprehensible"
(J.M.Prausnitz)

$$Z = Z^{\text{attr}}(\text{disp}) + Z^{\text{repuls}}(\text{hs}) + Z^{\text{chain}} + Z^{\text{assoc}}$$

SAFT = Statistical Associating Fluid Theory

Dec.10, 2010: 100 year anniversary from J. D. van der Waals Nobel Prize for Physics

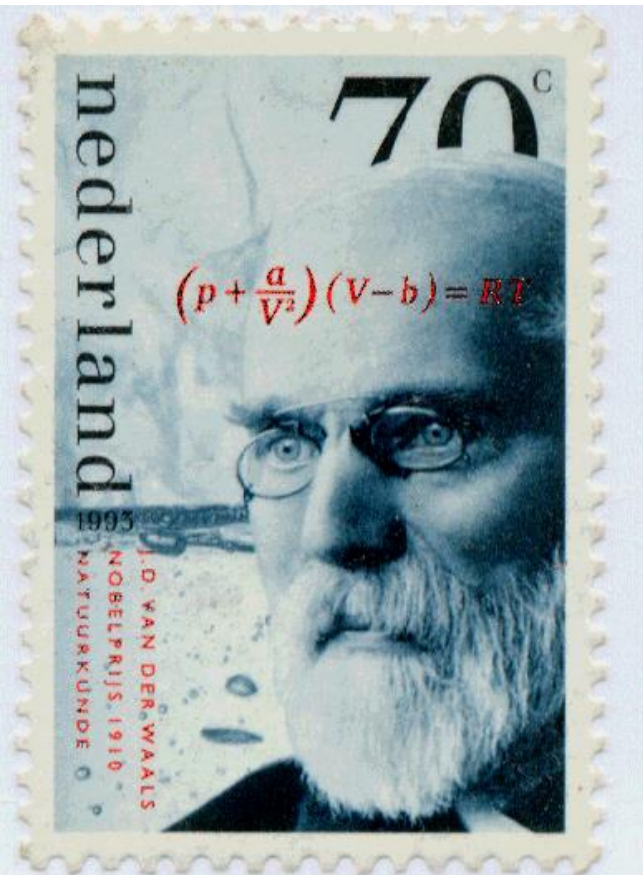
$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

GModel
SUPFLU-2094; No. of Pages 6

ARTICLE IN PRESS

J.O. Valderrama / J. of Supercritical Fluids xxx (2010) xxx-xxx

3



OVER
**DE CONTINUITTEIT VAN DEN GAS- EN
VLOEISTOFTOESTAND.**

ACADEMISCH PROEFSCHRIFT,
TER VERKRIJGING VAN DEN GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE,

AAN DE HOOGESCHOOL TE LEIDEN,

OP GEZAG VAN DEN RECTOR MAGNIFICUS

D^r. M. DE VRIES,

Hoogleraar in de Faculteit der Wisgeerte en Letteren.

OP ZATERDAG DEN 14^{den} JUNI 1873, DES NAMIDDAGS TE 3 UREN.

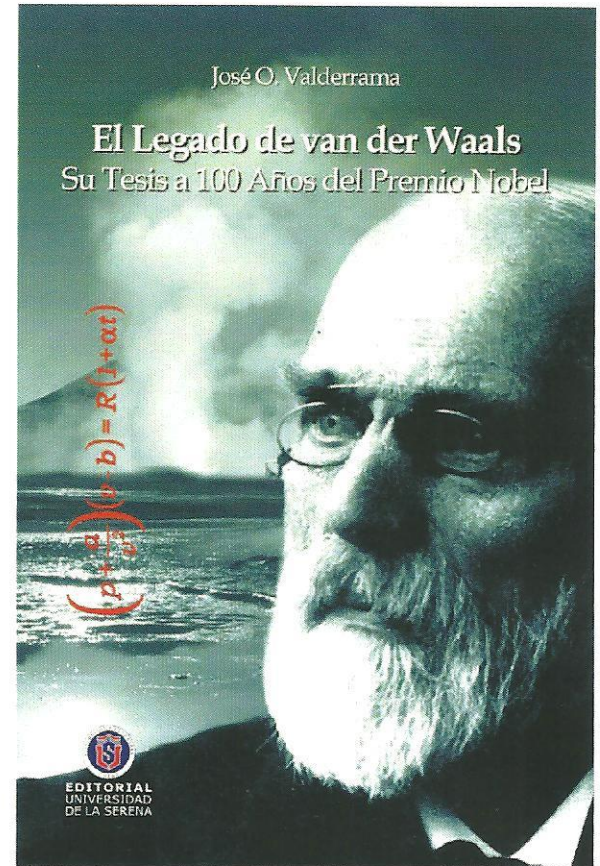
IN HET OPENBAAR TE VERDEDIGEN

DOOR

JOHANNES DIDERIK VAN DER WAAIS,

GEBOREN TE LEIDEN.

LEIDEN,
A. W. SIJTHOFF.
1873.



page of the cover of the original thesis of van der Waals (University of Leiden, Holland, 1873) on the left, and the cover of "The Legacy of van der Waals. His years since the Nobel Prize", the Spanish translation of van der Waals's treatise (Valderrama [32]), on the right.

Jose Valderrama, 2010. The legacy of van der Waals

SAFT – a theoretical concept

- Additive contributions from various effects (attraction, repulsion, chain, association)
- Wertheim theory for chain and association effects
- Segment concept
- Parameters with physical meaning
- Parameters following smooth trends / can be predicted from independent data

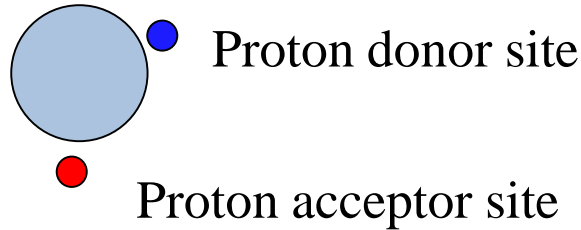
$$Z = Z^{\text{attr}(\text{disp})} + Z^{\text{repuls}(\text{hs})} + Z^{\text{chain}} + Z^{\text{assoc}}$$

SAFT – a family of models

SAFT	Reference	Citations (cit/year)
Original SAFT	Chapman et al., 1990	943 (38)
Original SAFT (II)	Huang and Radosz, 1990	899 (36)
Soft SAFT	Vega and Blass, 1997	164 (7)
SAFT-VR	Jackson et al., 1997	505 (28)
CPA	Kontogeorgis et al., 1996	241 (13)
PC-SAFT	Gross and Sadowski, 2001	755 (54)
sPC-SAFT	Von Solms et al., 2003	88 (7)

Source: Web of Science, July 1, 2014

The concept of association – common in all models



Glue-spot

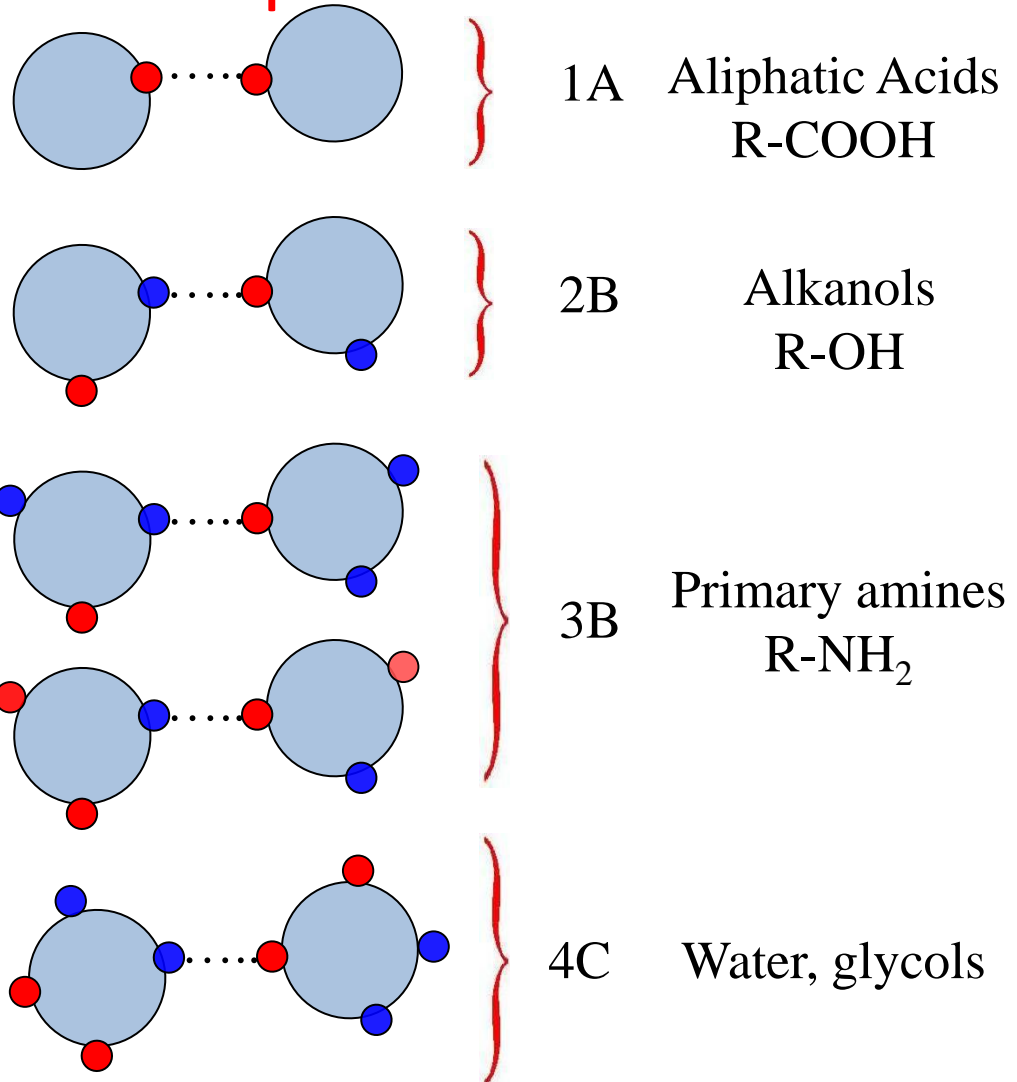
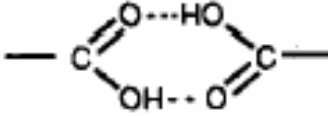
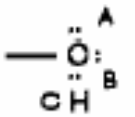
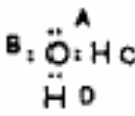
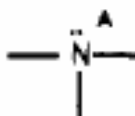
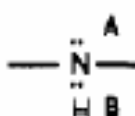
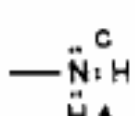
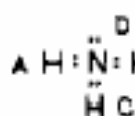


Table 2. Types of Bonding in Real Associating Fluids (Taken from Huang and Radosz, 1990).

species	formula	rigorous type	assigned type
acid		1	1
alkanol		3B	2B
water		4C	3B
amines			
tertiary		1	non-self-associating
secondary		2B	2B
primary		3B	3B
ammonia		4B	3B

The concept and choice of association sites and schemes

Table 2. Types of Bonding in Real Associating Fluids (Taken from Huang and Radosz, 1990).

species	formula	rigorous type	assigned type
acid		1	1
+ amines alkanol		3B	2B
+ glycols alkanolamines		4C	3B
amines			
tertiary		1	non-self-associating
secondary		2B	2B
primary		3B	3B
ammonia		4B	3B

← Dimers

← Oligomers

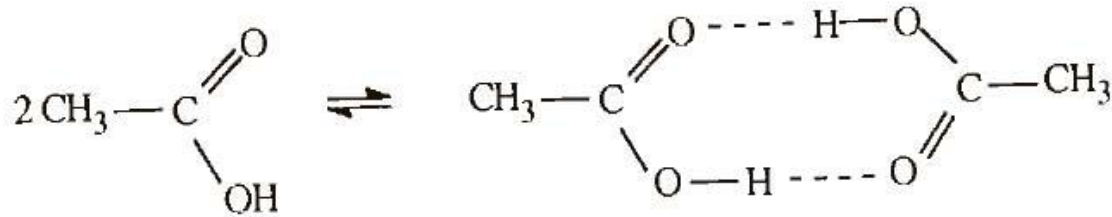
← 3D networks

$H_{1.5} O$

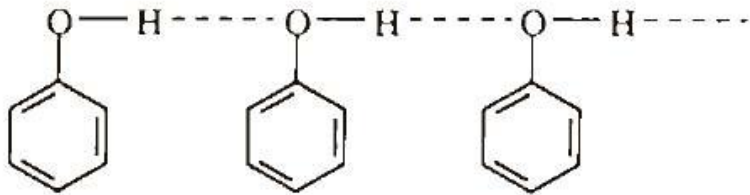
Water: 3.5 sites ?

Dixit et al., 2002 (Nature)
Chatzidimitriou-Dreismann, 2004 (Phys.Rev.Lett.)

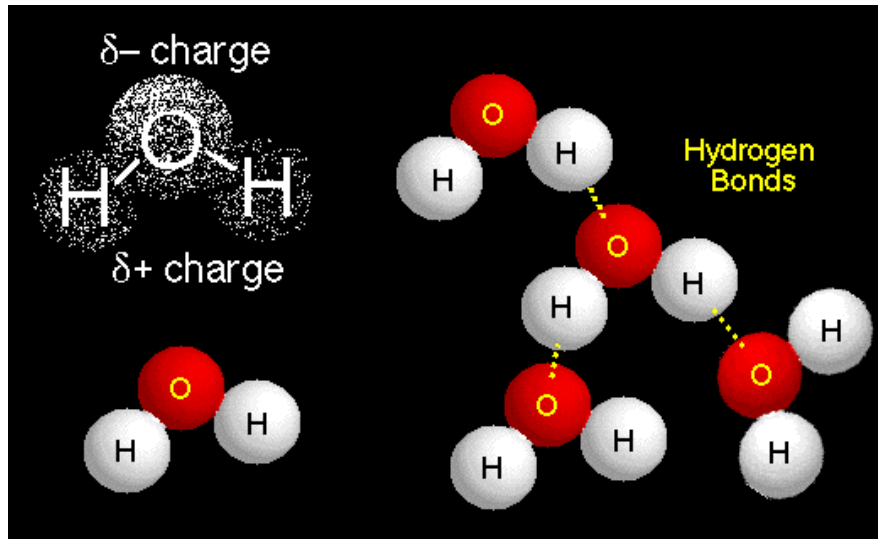
Association models describe well the physics of association (in most cases)



Acetic Acid (dimers)



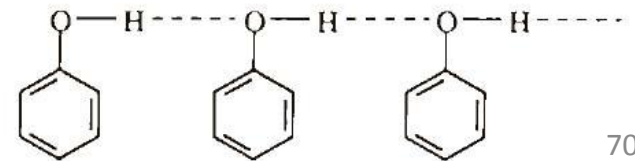
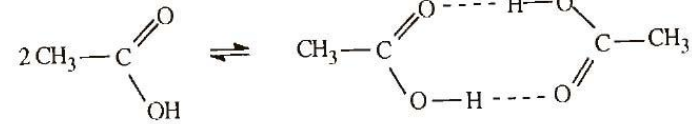
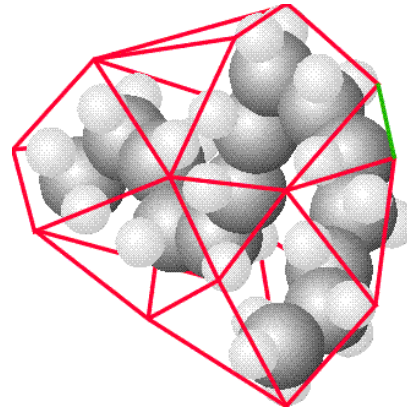
Alcohols, phenols, amines (oligomers)



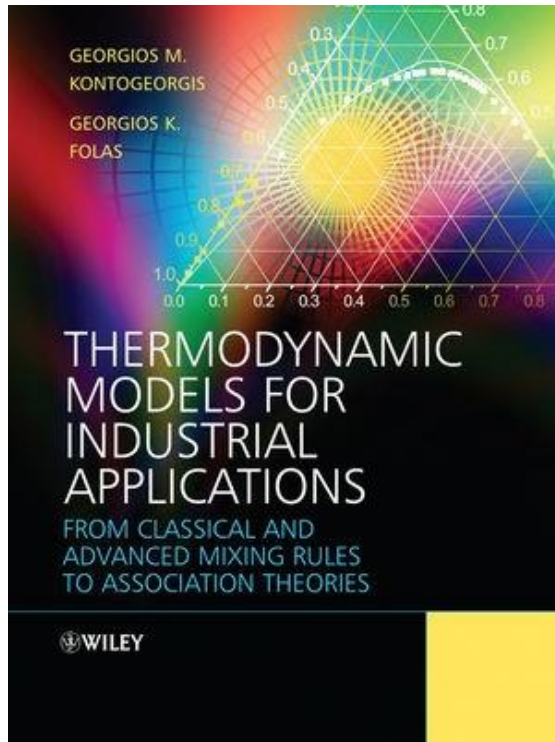
Water – 3D structure
Glycols

Extensive use of the association term – with success

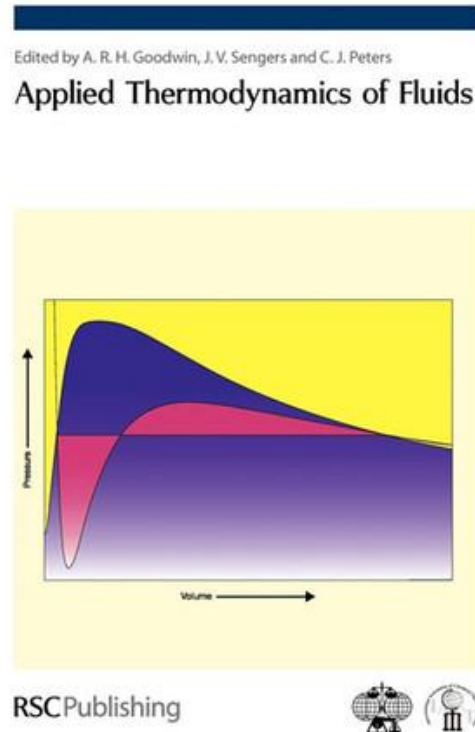
- Water
- Alcohols, glycols
- Amines, organic acids
- Alkanolamines, glycolethers
- Diverse multifunctional (di-acids, polyphenolics)
- Exotic: ionic liquids, asphaltenes



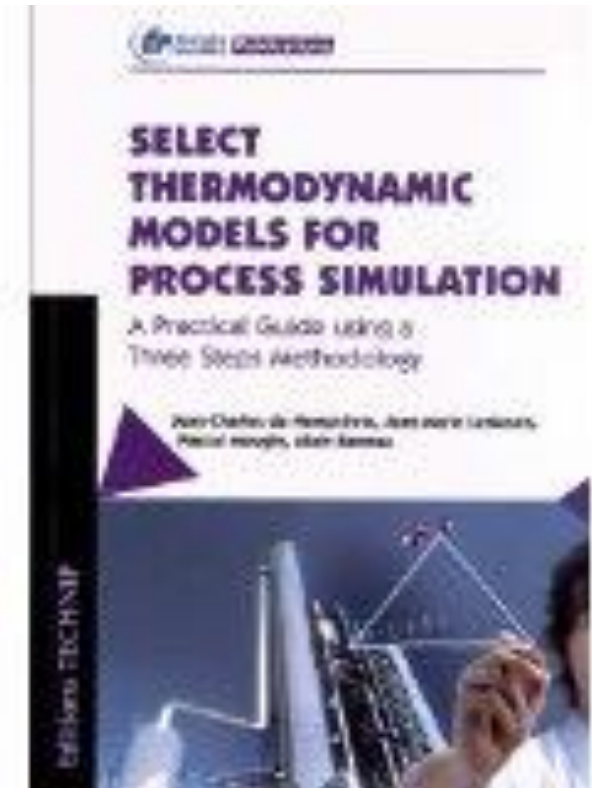
Three Recent Books with Association Models



2010

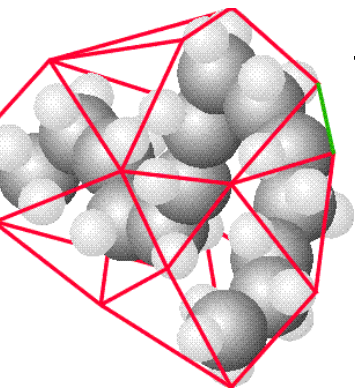


2010

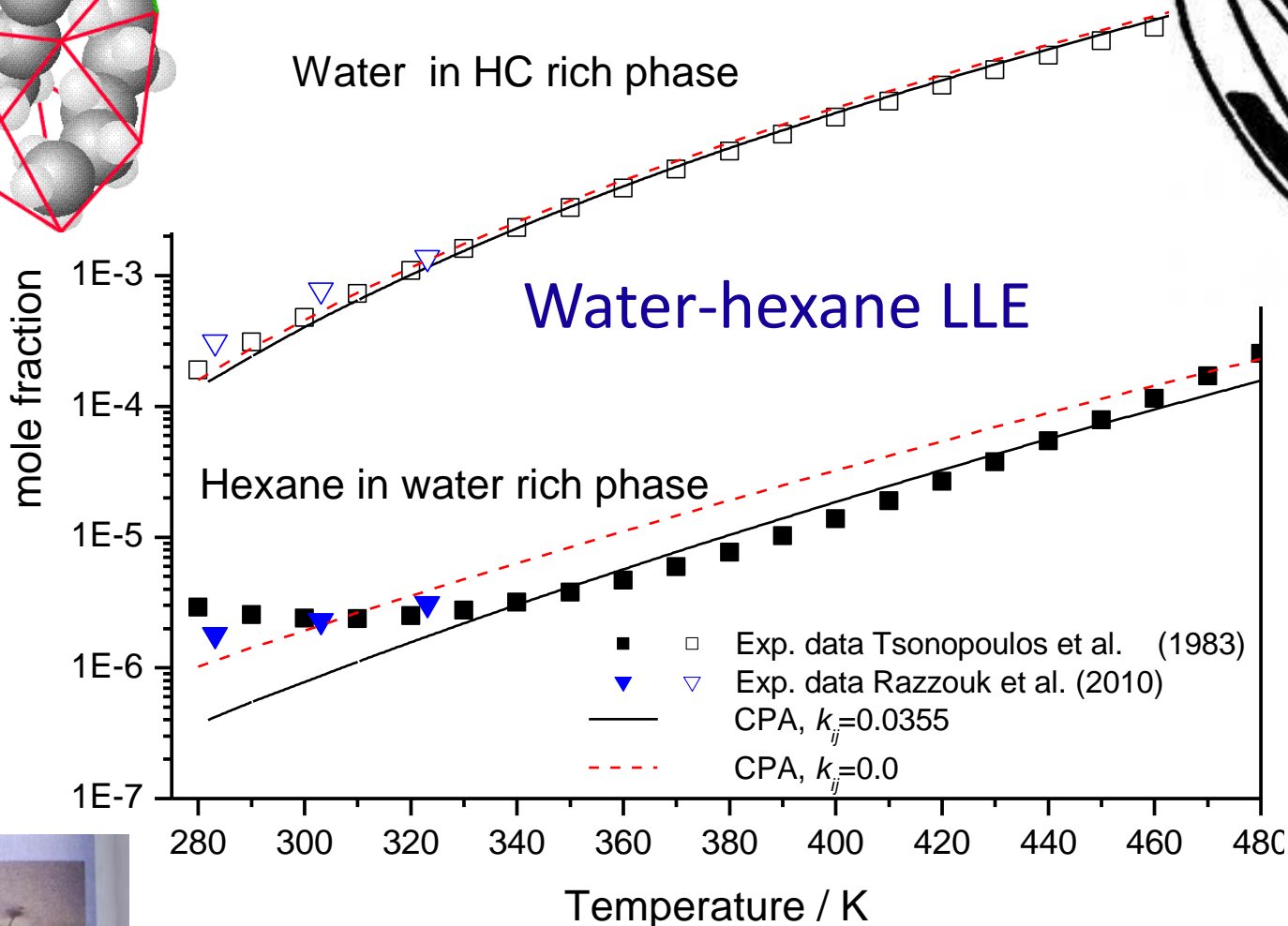


2012

Water-hydrocarbon LLE with CPA

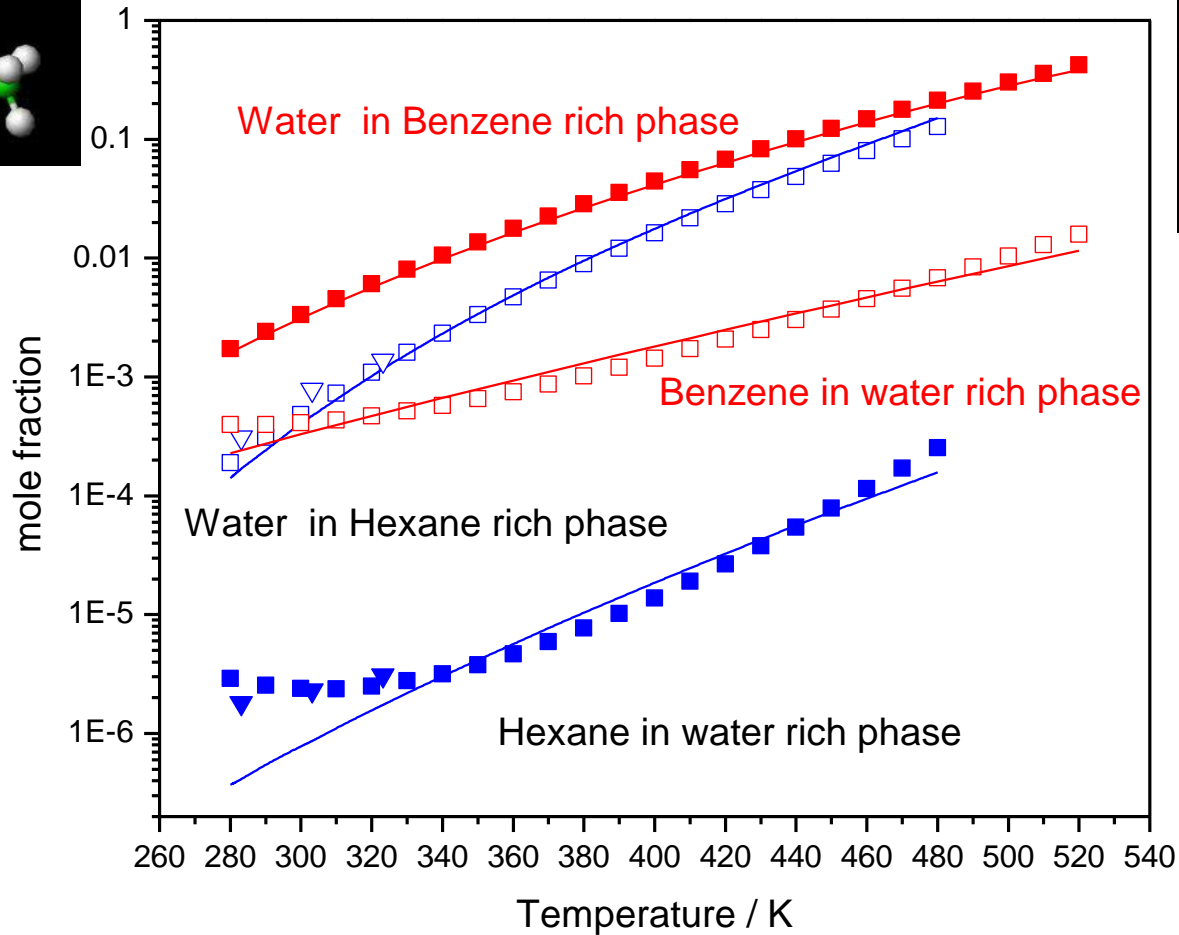
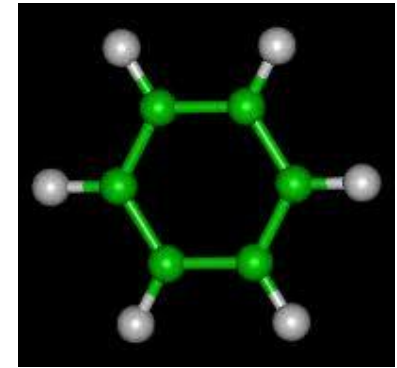
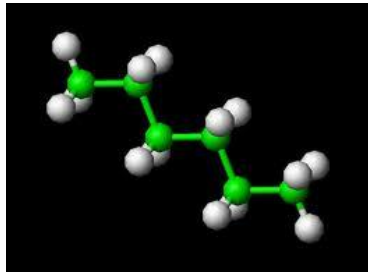


The hydrophobic effect



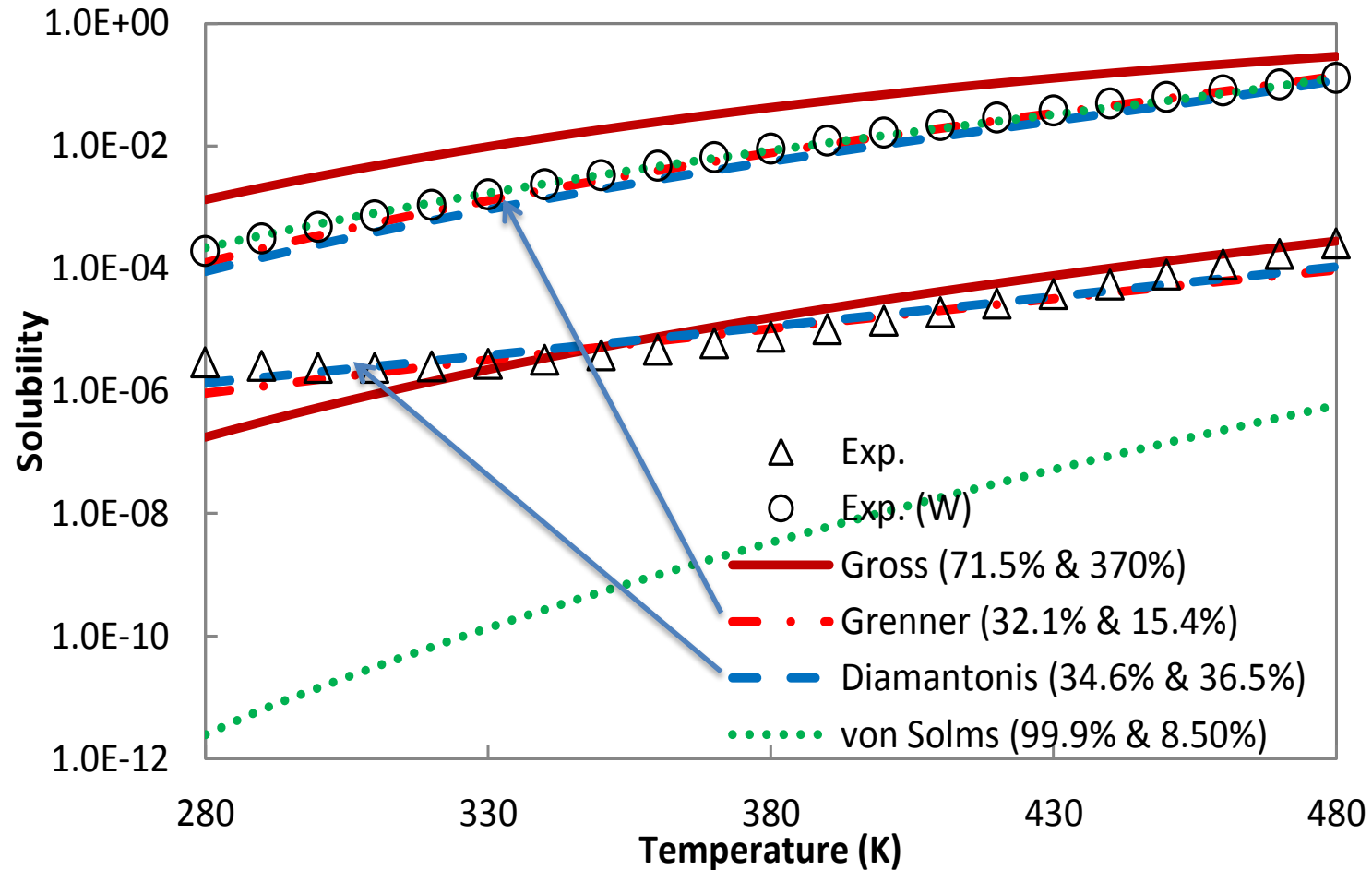
Razzouk et al., 2010
J.Chem.Eng.Data, 55: 1468

Water-hydrocarbon LLE with CPA



LLE with water and nC₆ with PC-SAFT

Using optimum kij



Gross(0.039)

Grenner (0.0571)*

Diamantonis (0.013)

von Solms (0.05)⁺

* taken from Tzivintzelis, I. et. al, *Ind. Eng. Chem. Res.* 2008, 47, 5651

⁺ Arbitrarily set to 0.05

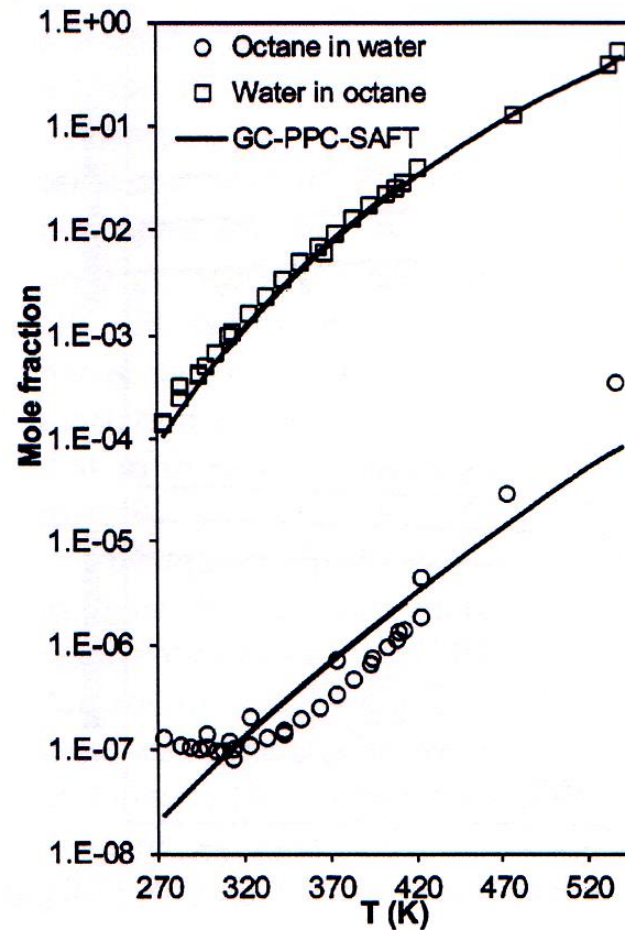
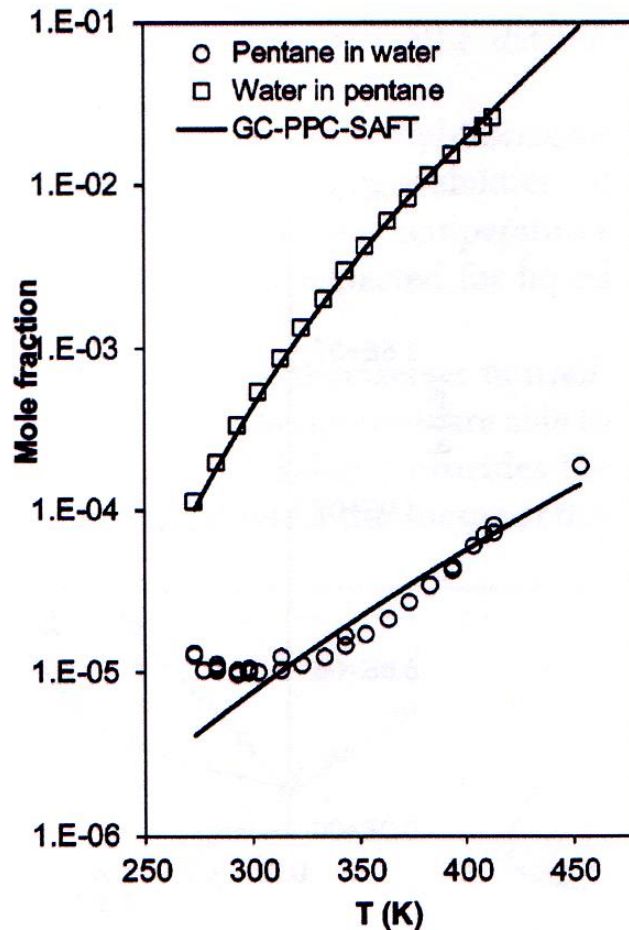
kij

Xiaodong Liang, 2012 (unpublished results)

Good new LLE results for water-alkanes with the GC-PPC SAFT

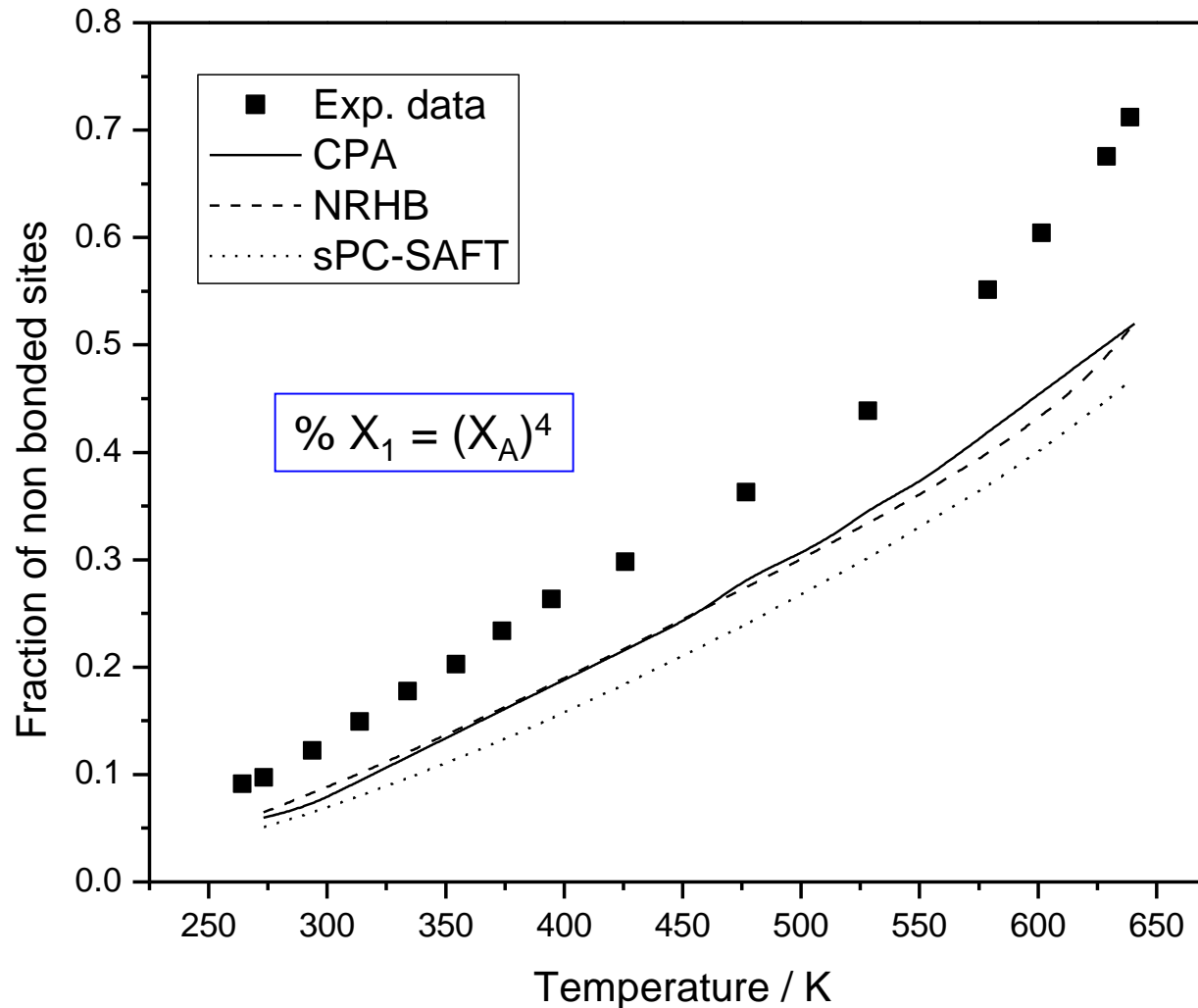
De Hemptinne et al. [2011, IECR, 50: 7467]

Good results due to polarity or "CPA approach"?



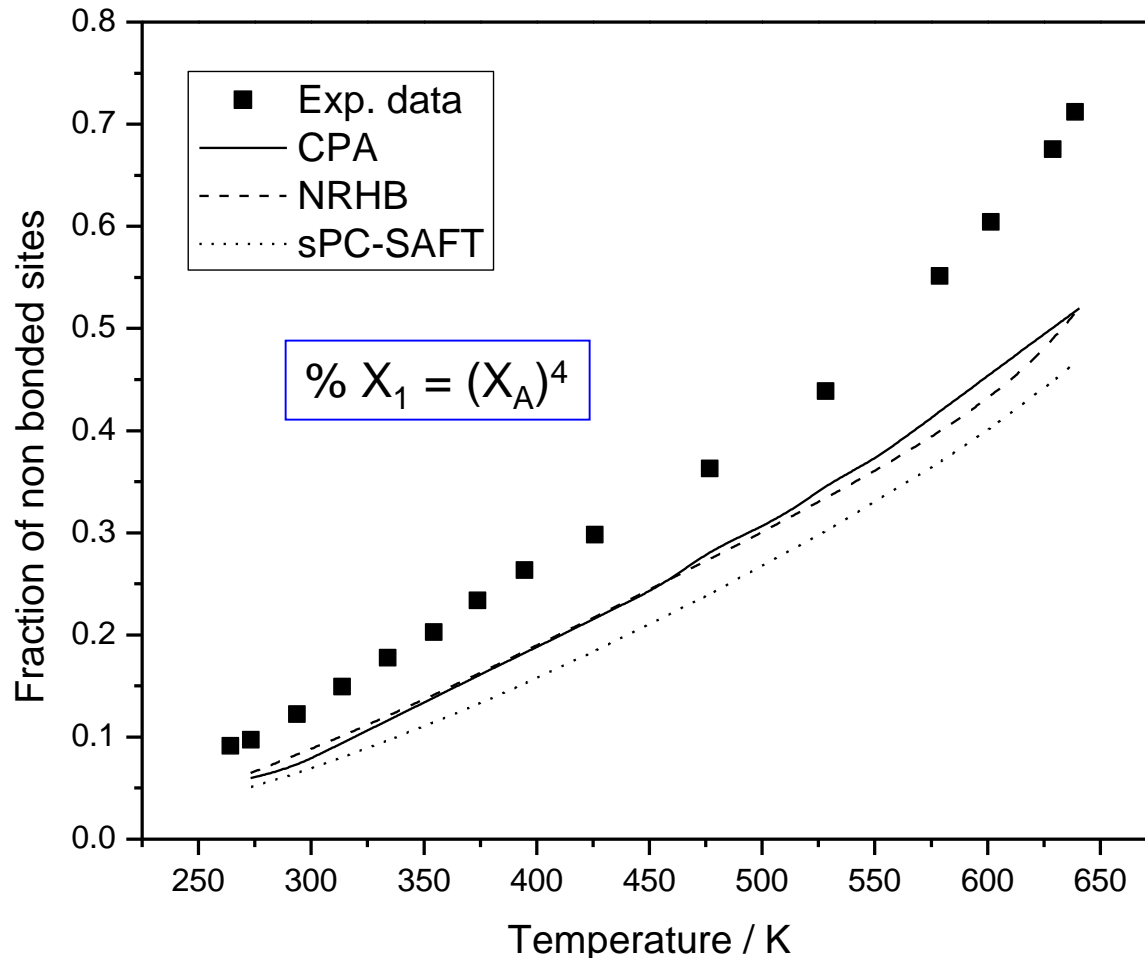
Water (4C), used water/hexane LLE data for "fine tuning" (CPA approach)

X_A – calculations for water with 3 theories (4C)

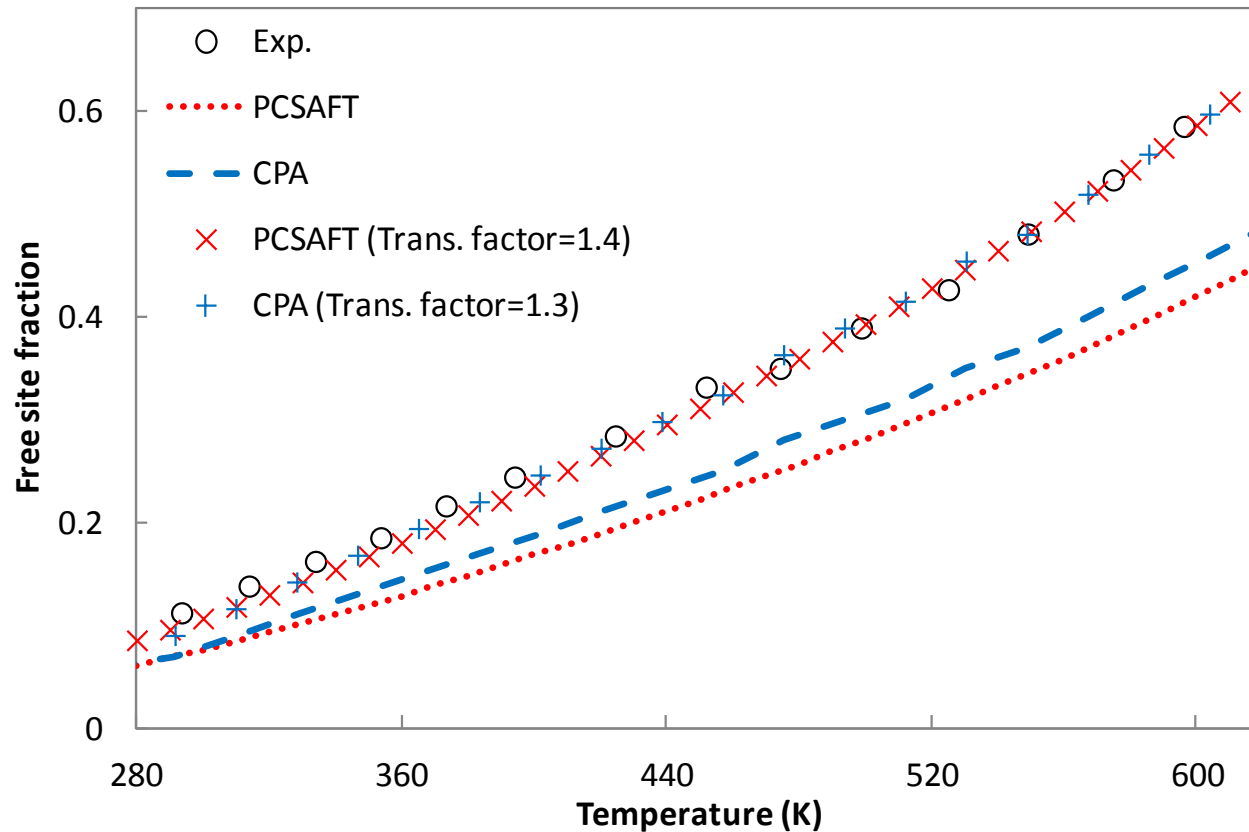


X_A – calculations for water with 3 theories (4C)

All theories predict more H-bonding than Luck's data



X_A – calculations for water with CPA and PC-SAFT (4C)



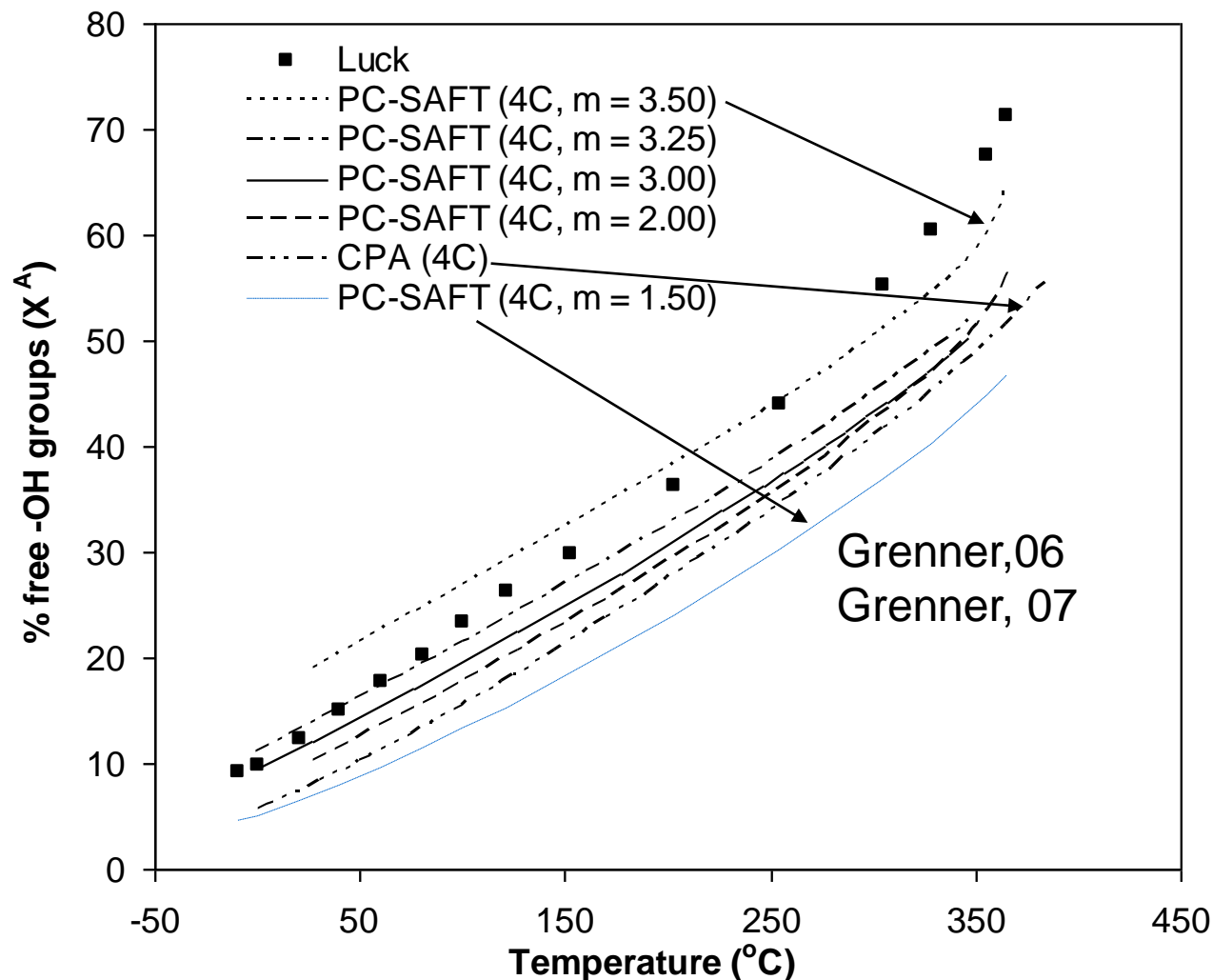
Recent study

Best PC-SAFT
Parameters
(for water-alkane LLE)

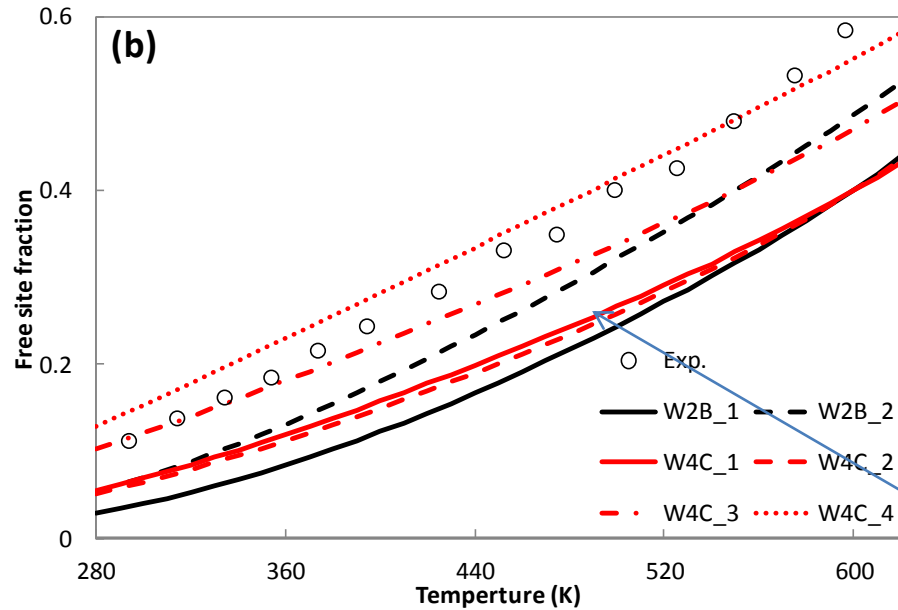
Both models give
Much lower X_A than
Luck

The results can match
The exp. Data by
a multipl. Factor
(artificial)

Best parameters for water are NOT those that reproduce the monomer fraction



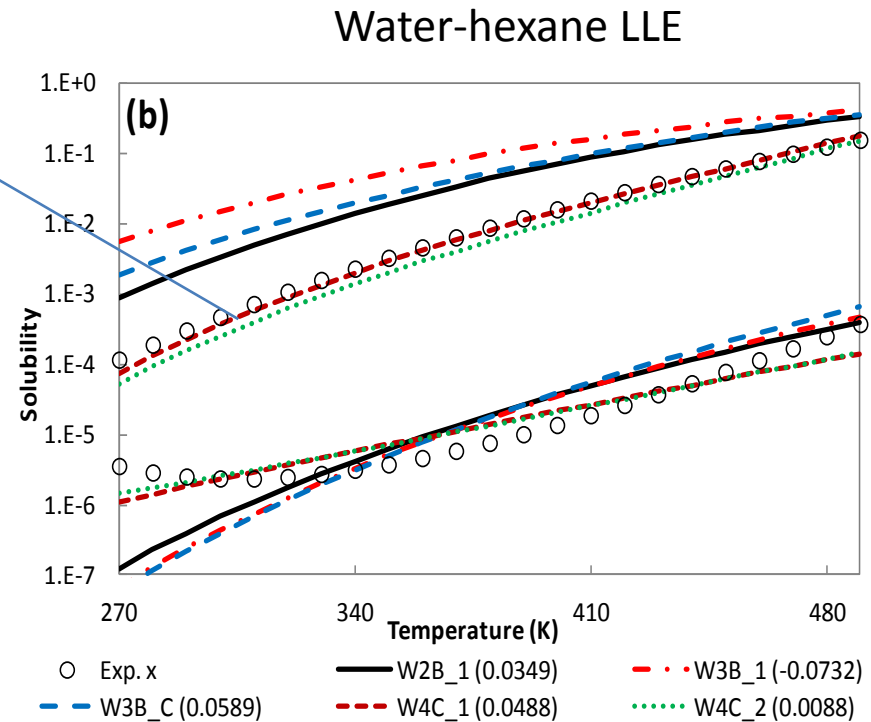
Similar conclusion by recent study



4C-3, 4C-4 Best for X_A but worse for LLE
 4C-1, 4C-2 Best for LLE but worse for X_A

Correlation results/1 kij

	HC in water	Water in HC
4C-1	49.4	13.2
4C-2	46.4	34.6
4C-3	42.3	248
4C-4	58.8	505



3. A new theory links dielectric constant with monomer fraction

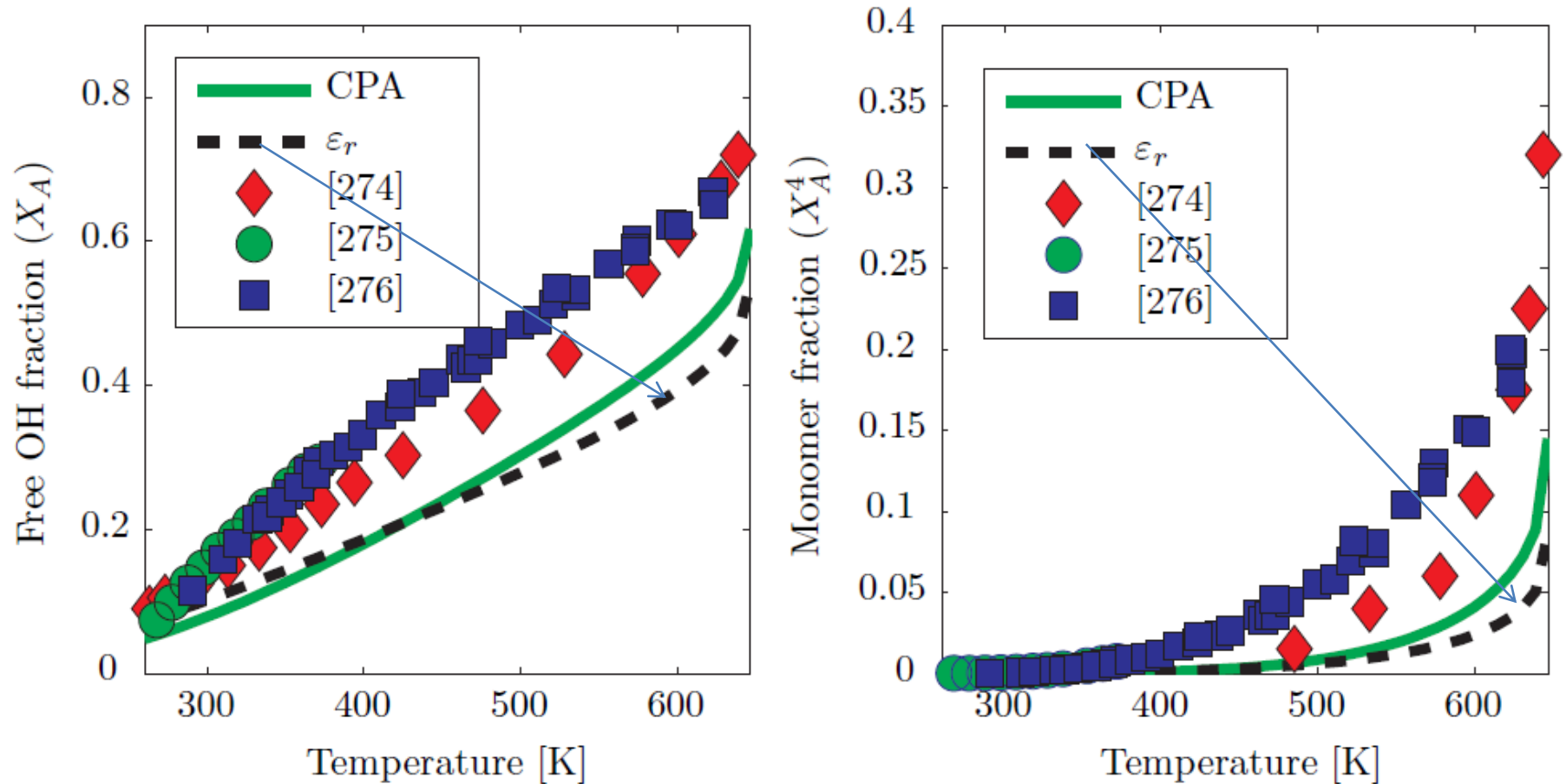
- Theory developed by Bjørn Maribo-Mogensen [J.Phys.Chem.B]
- Theory can be used to estimate dielectric constant using monomer fraction (X_A) from e.g. CPA or SAFT
- Alternatively if dielectric constant and density data are available, the new theory can be used to generate new "exp" monomer fraction (exp if the theory is perfect!)
- Basic equations:

$$(1 - X^A) = \frac{g - 1}{z \cos(\gamma) - (g - 1) \cos(\theta)}$$

$$g = \frac{1}{\mu_0^2} \frac{(2\varepsilon_r + \varepsilon_\infty)(\varepsilon_r - \varepsilon_\infty)}{\varepsilon_r(\varepsilon_\infty + 2)^2} \frac{9\varepsilon_0 k_B T v}{N_A}$$

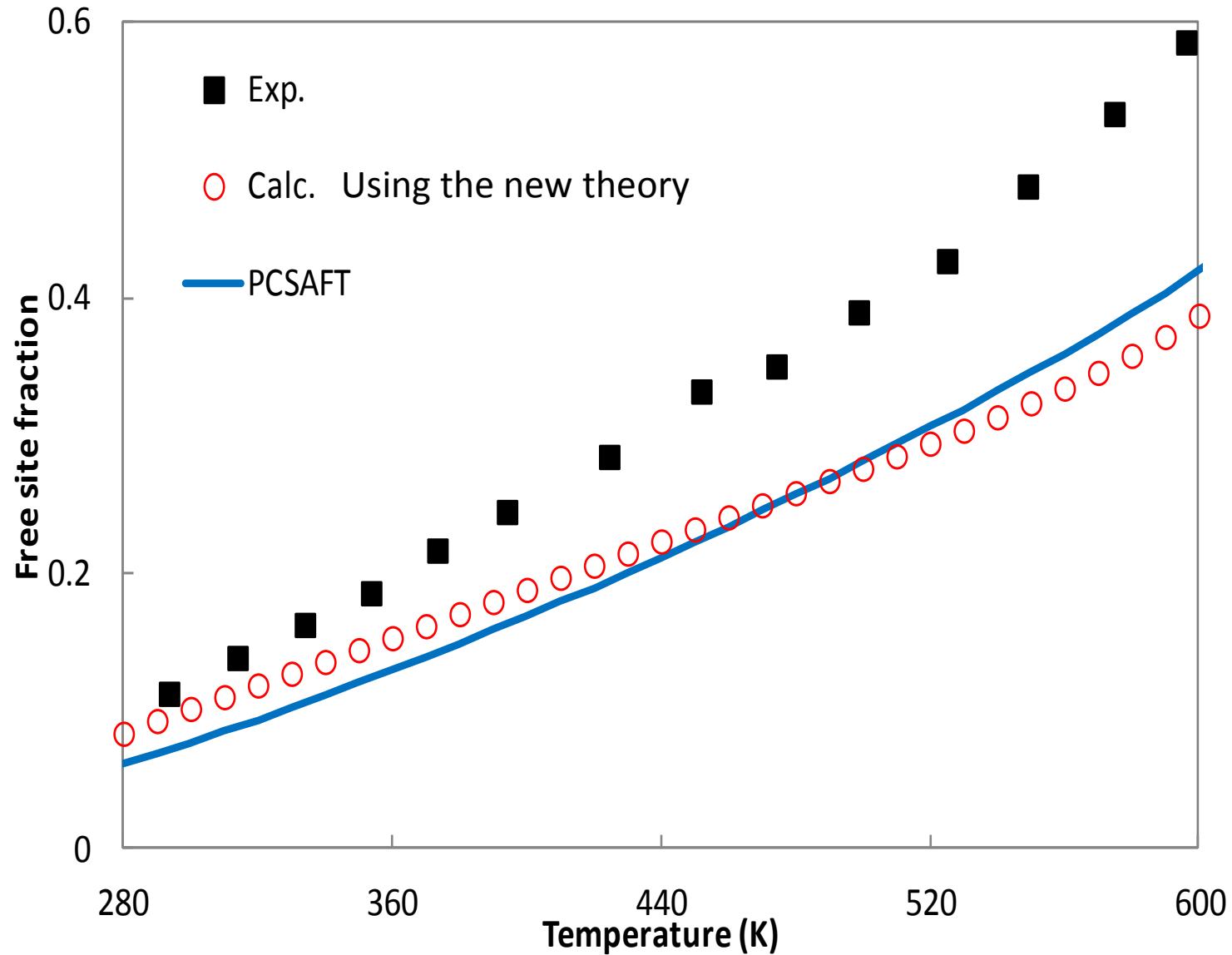
$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{1}{3\varepsilon_0} \frac{N_A}{v} \alpha_0$$

New theory predicts more H-bonding for water – in agreement to Association thermodynamic theories
But *NOT* in agreement to Luck data



Bjørn Maribo-Mogensen, 2014 PhD Thesis

New theory vs. PC-SAFT vs. Luck



Some conclusions from monomer fraction study

- New theory for estimating dielectric constant can be alternatively used for estimating monomer or site fractions
- For methanol & water the theory yields lower X_A values (more H-bonding than Luck); for ethanol it is the opposite
- X_A for water from new theory are in better agreement with CPA + PC-SAFT values than with Luck data
- New theory can be used to obtain monomer fraction data for important compounds e.g. glycols for which no such data is available
- More input to water studies maybe can be obtained from measurements of the hydrophobic effect/free energy of hydration combined also with interfacial energies for water-alkanes

Water – some personal final thoughts

- Monomer fraction data of water could give / could have given an idea about its structure
- I am not sure this is the case! (uncertainties in measurements and interpretation)
- Modern association theories can describe very well many thermodynamic properties of water including phase behavior (e.g. LLE water-alkanes)
- Association theories can predict the monomer fraction of water
- Poor agreement with "published" monomer fraction data using the "best" parameters for phase behavior

Water – some personal final thoughts

- Recent theory relating dielectric constant and monomer fraction provides “more” evidence that association theories and the tetrahedral structure are correct
- Other experimental studies disagree on which water structure is the correct
- Describing phase behavior or some of water properties does not necessarily mean we understand very much the water structure

What have we learnt ?

- Water is a very/far too complex molecule – it should be very hard to describe all properties with one theory
- Water – 4C is "for us" still the best choice (CPA, SAFT association theories) – for phase equilibrium calculations
- (Maybe) No reason to re-think the water parameters "from the practical point of view"
- (Maybe) More advanced water theories can wait...
- (Maybe) Understanding of water structure is far more difficult than previously anticipated ?
- Maybe I have asked more questions than provided answers (about water's structure)

WATERING DOWN SCIENCE?

Unconventional water **STRUCTURE THEORIES** generate criticism, but don't hamper funding

ELIZABETH K. WILSON, C&EN WEST COAST NEWS BUREAU

YOU MIGHT CALL Gerald H. Pollack “the Teflon professor.”

Pollack, a bioengineering professor at the University of Washington, Seattle, has been the subject of savage criticism for his heterodox theories about water—yet he continues to enjoy great success.

In the past decade, Pollack claims to have amassed experimental evidence that in addition to ice, liquid, and gas, water can form a fourth, gel-like or liquid-crystalline phase, as well as store charge—a property that would violate the law of electroneutrality in bulk fluids. Most water and electrochemists dismiss his results, saying they can be entirely explained by invoking basic water chemistry, and the presence of impurities.

These weighty judgments don't seem to have deterred Pollack's supporters, however. Pollack has published numerous papers on his theories in respected journals, including *Physical Review E*, and the ACS journals *Langmuir* and *Journal of Physical Chemistry B*. And this year, he received a \$3.8 million grant from the National Institutes of Health's new Transformative Research Projects Program (T-R01).

Pollack acknowledges that his research is controversial. “It's impossible to break new ground without arousing controversy,” he tells C&EN. But, he adds, “I've somehow managed to stay funded.”

Despite—or perhaps because of—its ubiquity and central importance in biology, chemistry, and physics, water has long been steeped in controversy. In the 1960s, researchers debated the existence of polywater, a polymerized form of liquid water with high boiling point and viscosity. Polywater was eventually debunked, only to be replaced by the concept of water memory in the 1980s. This idea that liquid water can sustain ordered structures for long periods

of time is one of the key tenets of homeopathy, a scientifically suspect concept, in which water supposedly “remembers” features of a solute even after repeated dilutions that remove all solute molecules. Water memory has also been debunked in the pages of *Nature* (1988, 334, 287).

Until the early 2000s, most of Pollack's publications centered on bioengineering topics such as the behavior of muscle proteins. But in 2001, he published the book “Cells, Gels, and the Engines of Life,” in which he dismantled the standard view of cells, including ion pumps and membrane channels. He posited instead that the water inside cells is a structured gel that plays a fundamental role in the organization and action of cellular structures.

Some reviewers took Pollack to task: University of Colorado, Boulder, biology professor Michael W. Klymkowsky criticized the book for an “overall style reminiscent of creationist writings” (*Nat. Cell Bio.* 2001, 3, E213). But some lauded the book's fresh outlook. Harvard University bioengineering professor Donald Ingber described the book as a “nicely sculpted... polemic against complacency in the cell biology establishment” (*Cell* 2002, 109, 688).

IN RECENT YEARS, Pollack has moved outside the confines of the cell to the structure of water in general. In an annual facul-

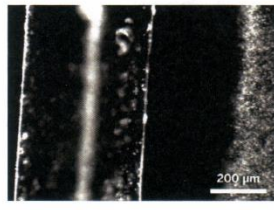
ty lecture at the University of Washington titled “Water, Energy, and Life: Fresh Views From the Water's Edge,” which is also making rounds on YouTube, Pollack describes what he calls an “exclusion zone” where microspheres in a container of water pull away from the surface, while an organized water gel thousands of layers thick forms. Any energy, whether from sunlight or heat, puts energy into the system, helping to increase the phenomenon, he says.

But as Pollack treads further into the territory of chemists, criticisms of his ideas have become more pointed. A recent paper of his in *Langmuir*, titled “Can Water Store Charge?” made the argument that pure water, hooked up to electrodes, will form large pH gradients that persist long after the current is turned off (*Langmuir* 2009, 25, 542). A firestorm ensued.

David G. Whitten, editor-in-chief of *Langmuir*, says the paper readily passed through peer review. “The editing process was completely normal,” he says. But within just a few days of the paper's publication online, Whitten says,

COURTESY OF GERALD POLLACK

MIGRATION According to Pollack, microspheres (right) pull away from a water surface to form an “exclusion zone” (middle) of structured water.



he began receiving complaints from top scientists in Europe and the U.S.

Agustin J. Colussi, a professor at California Institute of Technology, and Horacio R. Corti, a professor at the University of Buenos Aires, published a detailed rebuttal to the paper (*Langmuir* 2009, 25, 6587), which led to a response

from Pollack, followed by a final response from Colussi and Corti. Colussi and Corti pointed out that even “pure” water contains ions, and that charges may migrate, but eventually relax back to equilibrium.

Colussi and Corti were not alone in their criticism of Pollack's paper. Mitch André Garcia, who writes for chemistry-blog.com, also examined the paper in detail. “Claiming macrostructures of water that extend past the picosecond domain is absurd,” he wrote on his website.

“It's a strange thing about the science of water. It attracts some people with unusual ideas.”

David Chandler, UC Berkeley

From C&EN, 14.12.2009 cont'd

Prof. Pavel Jungwirth (Academy of Sciences, Czech Republic):

"The primary problem with Pollack's research is that it employs macroscopic experiments to draw conclusions about water structure. *Instead, microscopic tools such as spectroscopy and molecular simulations are the proper tools for investigating the molecular structure of water*"

From C&EN, 14.12.2009 cont'd

Prof. Pavel Jungwirth (Academy of Sciences, Czech Republic):

"The primary problem with Pollack's research is that it employs macroscopic experiments to draw conclusions about water structure. *Instead, microscopic tools such as spectroscopy and molecular simulations are the proper tools for investigating the molecular structure of water*"

Oh, Really !

Come On Now !!!

We need more collaboration

“It is about time to get real practical answers. This center will provide answers to questions about water’s structure and its implications by (i) bringing together top scientists from Denmark and abroad in water research, working with “conventional” and with “provocative” theories, (ii) allowing ideas to be challenged and (iii) combining a multi-level approach which includes experimental, molecular simulation, theory (statistical mechanics) and modeling research.”

Application to DGF

“The proposed research ideas were not well developed”

Socrates

Ἐν οἶδα ὅτι οὐδὲν οἶδα

"The one thing I know is
that I know nothing"



