WATER SPECIFICALLY STRUCTURED WITH HYDRATED PRISTINE FULLERENES AS A UNIVERSAL REGULATOR OF BIOLOGICAL PROCESSES

(Hydrated fullerenes - the unique scientific tool for knowledge of water mysteries)

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In the present report the following positions will be considered:

1. Hydrated C_{60} fullerene (HyFn) - $C_{60}@\{H_2O\}_n$- the unique symbiosis of the molecular form of pure carbon and waters structures. About similarity of water structures of M. Chaplin's icosahedral clusters and HyFn. Cluster nanostructures of water of higher order (with the size approx 3.4, 7.1, 10.9, 14.5, 18.1, 21.8, 25.4, 28.8, 32.4, 36.0 nm).
2. What is the common between cluster organization of water at HyFn, at Coherence Domain of E. Del Giudice and G. Pollack's Exclusion Zone Water (EZ-water)" .
3. Water nanoclusters "collisions" can generate on/in their diffusive surface redox reactions between water molecules (V. Voeikov) as well as produce the radical forms of oxygen (Probable explanations of reasons of the water sonoluminescence and strong absorption of EZ-water in UV-region at 270 nm).
4. Hydrated fullerenes create in water medium the ordered, heterogeneous environment in which chemical and biochemical processes go differently than in pure (unordered) water. Some facts about catalytic and antiradical properties of cluster water ordered by C_{60} fullerene molecule.
5. HyFn reveal only positive biological activity in experiments *in vitro* and in *vivo* (brief review).
6. HyFn accelerate growth of plants and animals (on an example of two-day chickens).
7. The facts about antitumor, ant atherosclerotic, antineurodegenerative, radioprotective, antidiabetic activity of HyFn water solutions. About biological efficacy of super small concentrations and doses of HyFn.
8. About antioxidant properties of HyFn *in vitro* and *in vivo* systems. The mechanism of free radicals recombination (self-neutralization) caused by properties of specific structures of the water ordered by fullerenes. What is "wise" antioxidant activity of HyFn? (Aphorism: *THERE CAN NOT BE MORE UNIVERSAL ANTIOXIDANTS, NAMELY FREE-RADICAL PROCESSES REGULATORS, THAN THE WATER STRUCTURES ORDERED QUITE SPECIFICALLY*, which, at the first stage of the primary evolution of biological molecules, served them as "defenders" from free-radical cleavage at action of radioactive radiation, hard ultra-violet rays, oxygen radical forms, etc.).
9. About universalism of HyFn biological activity as the confirmation of hypothesis that "$C_{60}.H_2O$" systems might be the matrix for primary biological matter (substance) formation. (Aphorism: In the words of Nobel Laureate Albert Szent-Gyorgyi, "LIFE IS WATER DANCING TO THE TUNE OF SOLIDS", but studying the remarkable and versatile bio-activity of hydrated fullerenes I incline to believe that *"LIFE IS THE CARBON-CONTAINED SOLIDS DANCING TO THE TUNE OF ORDERED STRUCTURES OF WATER"*).
10. Suggestion: A*s for Life, we should not try to structure water by means of some speculative influences. In fact, we should purposefully increase and support in water an amount of quite specific cluster structures that water forms into itself naturally*!

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14. ABSTRACT

The 3rd Annual Conference on the Physics, Chemistry and Biology of Water was held in West Dover, Vermont October 16th thru 19th, 2008. The conference was organized by Vermont Photonics Technologies Corporation of Bellows Falls, Vermont, and was attended by an international group of 51 scientists who presented 31papers during the 4 days. The cost of organizing this event was approximately $43,000, offset by attendance fees, sponsorship by 2 commercial companies, and a grant from the Office of Naval Research (ONR). Subsidies were paid to 31 speakers to offset their travel expenses in the amount of $23,400. All speakers who received travel subsidies from ONR support were so notified in writing. The consensus of the attendees was that the conference was very informative, having offered a wide range of papers presented by scientists with varied interests and backgrounds.

15. SUBJECT TERMS
Interfacial water, quantum electrodynamical coherence, homeopathic medicine, peroxy, protein reactivity, osmolytes, nanomechanics of exclusion-zone water, carbon nanotube confinement, photocatalytic water splitting, recyclable hydrogen, thermoluminescence, nanofluids, nanochannels, aqueous hydroxide ion transport, IR spectrometry

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SCHEDULE & SPEAKERS FOR THIRD ANNUAL CONFERENCE ON THE PHYSICS, CHEMISTRY AND BIOLOGY OF WATER 2008

Thursday October 16

Session TH-I
Water: Global Considerations
Chairs: Julie McGeoch & Friedemann Freund

14:00	**Vladimir Voeikov/ Thomas Lowell**	Welcome
14:15	**Gerald Pollack** Univ. of Washington	Long-range water structuring at hydrophilic interfaces
15:25	**Emilio DelGiudice** INFN, Milan	Quantum ElectroDynamical (QED) Coherence and interfacial water
16:00	**REFRESHMENTS**	
16:30	**Sergey Pershin** Prokhorov Inst. of General Physics	Four-photon laser spectroscopy of rotational lines in water: observation of protein/DNA selective interaction with H_2O para-isomer in aqueous solutions
17:05	**Konstantin Korotkov** ITMO St. Petersburg	Dynamic Electrophotonics Analysis of Water and Liquids
18:00	**Reception (hearty hors d'oeuvres and beverages served)**	

TH-II
Water: Interfacial Structures
Chairs: David Anick & Ivan Cameron

19:30	**Eugene Khizhnyak** ITEM, Puschino	Unusual diffusion processes associated with interfacial layers of water
20:05	**Grigoriy Andrievskiy** Natl. Academy of Sciences, Ukraine	Water Specifically Structured with Hydrated Pristine Fullerenes as a Universal Regulator of Biological Processes

Friday October 17

Session F-I
Short-range Interactions: water in confined spaces-1
Chairs: Chaim Frenkel & Glenn Edwards

09:00	**Joel Friedman** Albert Einstein Coll. of Medicine	The Mechanisms of Hydration-Dependent Modulation of Protein Reactivity through Confinement and Addition of Osmolytes
09:35	**Gerhard Artmann** Univ. of Applied Sciences Aachen	The Crucial Role of Water in a Phase Transition of Hemoglobin at Body Temperature
10:10	**Deborah Ortiz** Georgia Tech.	Strain-dependent relaxation time in confined wetting liquids
10:45	**REFRESHMENTS**	
11:15	**Jose Teixeira** CEA/CNRS	Hydrogen bonds as a possible explanation of the unusual behavior of water and aqueous solutions
11:50	**Andrei Tokmakoff** MIT	The dynamics of aqueous hydroxide ion transport from 2D IR spectroscopy
12:25	**Lunch TOGETHER**	

Session F-II
Short-range Interactions: water in confined spaces - 2
Chairs: Nadezda Palmina & Giuseppe Vitiello

14:00	**Alexander Kolesnikov** Oak Ridge Natl Lab	Structure and Dynamics of Water in Carbon Nanotube Confinement.
14:35	**Wilson Quevedo** Max-Planck Inst.	Structural and Dynamical Behaviour of Water in (and on) Nano-confined Systems
15:10	**Paul Cremer** Texas A&M	Investigating the Role of Ion Specificity on Water Structure and Hydrophobic Collapse
15:45	**REFRESHMENTS**	
16:15	**Ivan Brovchenko** Dortmund Univ.	Which "anomalies" of aqueous systems cannot be explained by the general laws of the statistical physics of fluids?
16:50	**Elmar Fuchs** WETSUS	Experiments with the Floating Water Bridge
17:25	**Lorenzo Cordone** Univ. of Palermo	Water mediated HB networks couple the embedded protein with surroundings in trehalose-water but not in sucrose-water matrixes **DINNER (on your own)**
19:30-21:30	**POSTER SESSION** **Beverages and Wine Served**	

Saturday October 18

Session Sat-I
Long-range and Subtle Interactions
Chairs: Konstantin Korotkov & Benny Johansson

09:00	**Giuseppe Vitiello** Univ. of Salerno	Quantum fluctuations, gauge freedom and mesoscopic/macroscopic stability
09:35	**Louis Rey** Conseiller Scientifique	Thermoluminescence as an experimental tool to investigate the ' structure ' of high dilutions
10:10	**Vittorio Elia** Univ. of Naples	Dissipative structures in extremely diluted aqueous solutions of homeopathic medicine
10:45	**REFRESHMENTS**	
11:15	**Nadezhda Palmina** Inst. of Biochemical Physics, RAS	Water and effect of chemical agents in ultra low concentrations
11:50	**Eran Gabbai**	Induced long range order in water – A Myth or over-looked reality (Eshel Ben-Jacob talk)
12:25	**Lunch together**	
13:30	**Free Time until 16:00**	

Session Sat-II
Water and Energy
Chairs: John Swain & Bernhard Pollner

16:00	**Akihiko Kudo** Tokyo U. of Science	Photocatalytic water splitting to generate clean and recyclable hydrogen
16:35	**Friedemann Freund** NASA SETI Inst.	How Water Helped Oxidize the Earth - the Peroxy Way
17:10	**Miklos S.Z. Kellermayer Jr.** University of Pécs	Nanomechanics of exclusion-zone water
17:45	**Vladimir Voeikov** Lomonosov Moscow State Univ.	Water -- the Base of the Living State and Vital Functions
19:00	**Dinner and Entertainment**	

Sunday October 19

Session Sun-I
Biology of Water
Chairs: Eshel Ben-Jacob & Gerald Pollack

09:00	**David Anick** Harvard Medical School	Aqueous hydroperoxide: A theoretical study and a provocative hypothesis
09:35	**Galina Zubareva** Tver Medical Acad.	IR spectrometry of water base of biologically active solution
10:10	**Ivan Cameron** U. of Texas Health Ctr. at San Antonio	Solute exclusion from cells, gels and proteins: relevance to drug delivery
10:45	**REFRESHMENTS**	
11:15	**Ryszard Grygorczyk** Univ. of Montreal	The cytoplasm's gel-like behavior contributes to human cell osmosensitivity
11:50	**Alex Kaivarainen** H-Systems	Hierarchic theory of liquids and solids and its application to biosystems

The Crucial Role of Water in a Phase Transition of Hemoglobin at Body Temperature

Gerhard M. Artmann[‡], A. M. Stadler*[†], J. P. Embs[§¶], G. Zaccai*, G. Bueldt[†], A.Artmann and I. Digel[‡]

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The laboratories of Prof. Shu Chien and Paul Sung, the Whitaker Institute of Biomedical Engineering, UC San Diego, were the birth places of the observation of a temperature transition occurring at a critical temperature close to body temperature. The observation was found randomly and caused a series of experiments which we performed subsequently around the globe. We will present results of a couple of quite unusual experiments performed with red blood cells and hemoglobin of different species and we will work on answering the question whether or not and how hemoglobin can "sense" a species body temperature.

When aspirating human red blood cells (RBCs) into 1.3 μm pipettes (ΔP=-2.3kPa), a transition from blocking the pipette below Tc=36.3±0.3°C to passing it above occurred (micro pipette passage transition). With a 1.1 μm pipette no passage was seen and RBC volume measurements were possible. With increasing temperature RBCs lost volume significantly faster below than above a T_c=36.4±0.7 (volume transition). Colloid osmotic pressure (COP) measurements of RBCs in autologous plasma (25°C≤T≤39.5°C) showed a Tc at 37.1±0.2°C above which the COP rapidly decreased (COP transition). In NMR T1-measurements, the T1 of RBCs in autologous plasma changed from a linear (r=0.99) increment below Tc=37±1°C at a rate of 0.023 s/K into a parallel to the temperature axis above Tc (RBC T1 transition). Lately, incoherent quasielastic neutron scattering (Stadler, Zaccai, [†]Bueldt; Institut Laue-Langevin, Grenoble, France; [†]Research Centre Juelich, Juelich, Germany); experiments were performed to measure the temperature dependence of hemoglobin dynamics in human red blood cells. The technique probed average protein dynamics in the picosecond time range and Ångstrom length scale between 16.9 °C and 45.9 °C in heavy water buffer. Besides many interesting results, we found that the geometry of internal haemoglobin motion changed at 36.9 °C (Neutron scatter transition).

In conclusion: In the micropipette experiments, an amorphous hemoglobin-water gel forms within the spherical trail of the aspirated RBC. At Tc, a sudden fluidization of the gel occurs at which non-covalent bonds brake down. We suggest that this is initiated by a sudden phase transition occurring at Tc in the hemoglobin molecules entropy. All changes mentioned above happen at a distinct Tc close to body temperature. A Tc was found in hemoglobin of different species as well and all occurred at the species`body temperature. Thus, we concluded that Tc marks the set point of a normal body temperature which is inscribed in the primary structure of hemoglobin and possibly other proteins. A potential physical-biological mechanism will be presented.

Which "anomalies" of aqueous systems can not be explained by the general laws of the statistical physics of fluids?

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Various properties of water and aqueous systems seem to be "anomalous" in comparison with the propeties of other fluid systems. To understand specfic behavior of aqueous systems, it is necessary to distunguish those properties, which are universal for all fluid systems. This can be done by application of the laws of the statistical physics of fluids, which describe how fluid properties are affected by the phase transitions and respective percolation transitions. Our simulation studies of the phase diagram and properties of various aqueous and non-aqueous systems (bulk fluids, confined fluids, fluid mixtures) evidence high universality in the behavior of fluids, including water. When the universal features in the behavior of aqueous systems are known, we can distinguish specific properties of aqueous systems and to consider their origins. Below, some examples are presented.

a) The specific properties of **bulk water** originate mainly from the proximity of the liquid-liquid phase transitions, which are located in supercooled region. These transitions are caused by the variety of the local ordering in water. The specificity of water is the location of the liquid-liquid transitions not very far from the freezing temperature; thus, their distant effect on the properties of liquid water is noticeable in a wide temperature-pressure range. **b**) Behavior of liquid water near **hydrophobic surfaces** is essentially the same as behavior of other fluids near weakly-attractive surfaces. In both cases, disordering effect of a surface causes density depletion near a surface. Solvent-mediated attraction between extended weakly-attractive surface ("**hydrophobic attraction**" in water) is a phenomenon universal for all fluids. The specificity of water is in abundance of hydrohpobic surfaces on the Earth. **c**) Near **hydrophilic surfaces**, liquid water forms two highly orientationally ordered layers, whose properties noticeably differ from water properties in third and subsequent layers. This specific water behavior is due to the rearrangement of H-bonds near a hydrophilic surface. **d) Clustering** of water and solute molecules in aqueous solutions and its changes upon varying thermodynamic conditions follow the laws general for lattices and fluids. **e**) Many solutes have an extremely **low solubility** limit in liquid water (for example, it is about 10^{-12} for amyloidogenic peptides). In oversaturated solution of such solutes, a lag time of aggregation (precipitation) may take years. **f)** The crucial **role of hydration water in biofunctions** is the most intriguing problem, which should be solved. Our simulation studies of hydration water evidences, that there is an area in the temperature-pressure diagram, where a surface is covered by a spanning network of normal (fragile) hydration water. This area is bounded by liquid-liquid transition to strongly tetrahedral water at low temperatures, by transition to weakly tetrahedral water at high pressures and by thermal break of a spanning water network via a percolation transition at high temperatures. Interestingly, this area approximately maps the thermodynamic range, where biomolecules exhibit activity and living organisms may function.

I. Brovchenko and A. Oleinikova: Interfacial and Confined Water, Elsevier, 2008, 320 p.

Solute exclusion from cells, gels and proteins: relevance to drug delivery

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A vital dye exclusion test is the most commonly used method for determination of living vs. dead cells. Cell death is thought to disrupt the vital dye (i.e. methylene blue, trypan blue, nigosin, propidium iodide and others) exclusion function of the cell membrane and this allows the dye to enter and stain the intracellular contents. An alternate dye excluding mechanism is that most if not all of the water in the cytoplasm of a living cell is structured in such a way as to be non-solvent for the vital dye. As proteins are, by dry mass, the most abundant material in the cell it seems logical to think that proteins are the likely source of water structure. According to this idea, death of the cell causes decrease in water structure and its dye excluding properties.

It is difficult to get enough cytoplasm to study its solute exclusion and other physical properties. As reported here, hen egg white has provided a useful surrogate for cytoplasm and can be separated into thin and thick albumen fractions that remain non-miscible. Thick albumen without a membrane is vital dye excluding, demonstrates osmotic behavior and has the ability to transform from a dye excluding gel to a non-dye excluding more fluid sol by pressure agitation a gentle shear force. The sol phase does, with time, transform back to a dye excluding gel. Thin albumen is also shown to have a dye excluding shell of water that can be removed by centrifugal pressure.

It seems likely that protein rich living cells, like thick albumen, would have a proclivity to exist in a vital dye excluding gel state that can transform to a more fluid non-dye excluding sol state upon physical perturbations or death.

It may be that structured cell water excludes drugs from interaction with their cellular target molecules and that physical means could be used to help destructure water and therefore allow access of drugs to their target molecules at specific sites in the body.

Water-Mediated HB Networks Couple the Embedded Protein with Surroundings in Trehalose-Water but not in Sucrose-Water Matrixes

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Trehalose is a non-reducing disaccharide of glucose found in organisms, which can survive adverse conditions such as extreme drought and high temperatures. Furthermore, isolated structures, as enzymes or liposomes, embedded in trehalose are preserved against stressing conditions[1]. Analogous protective effect is also accomplished by other saccharides, but with a lower efficiency. Among other hypotheses, the protective effect of trehalose has been suggested to stem from the formation of a water-mediated, hydrogen bond network, which anchors the biomolecule surface to the water-sugar matrix[2]. Here it will be reported:

i) on the recombination kinetics of the primary, light-induced charge separated state ($P^+Q_A^-$), and the thermal stability of the photosynthetic reaction centre (RC) of *Rhodobacter sphaeroides*, in trehalose-water and in sucrose-water matrixes of decreasing water content, and

ii) on the structural an dynamic effects that *carboxy-myoglobin* embedded in saccharide-water matrixes of very low water content, causes on the water-sugar matrix.

Data show that, in sucrose, at variance from trehalose, the system undergoes a "*nano phase-separation*" at very low water/sugar ratios. We rationalise this result assuming that the hydrogen bond network, which anchors the protein surface to its surroundings is formed in trehalose but not in sucrose. Furthermore, we suggest that both the coupling, in the case of trehalose, and the "*nano phase-separation*", in the case of sucrose, start at very low water content when the components of the system enter in competition for the residual water.

1. Crowe LM (2002) *Comp Biochem Physiol A* 131:505-513
2. Giuffrida S, *et al.* (2003) *J Phys Chem B* 107:13211-13217

Investigating the Role of Ion Specificity on Water Structure and Hydrophobic Collapse

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The presence of various salts in aqueous solution influences processes ranging from enzyme turnover rates and protein folding to colloidal assembly and macromolecular precipitation. The ordering of the anions with respect to their influence on a particular physical property generally follows a recurrent trend. The trend, known as the Hofmeister series, has been known since the late nineteenth century. The series is as follows:

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > NO_3^- > Br^- > I^- > ClO_4^- > SCN^-$$

The underlying mechanism of this phenomenon has remained unclear for over one hundred years. Two competing hypotheses have been put forth. One involves the relative influence of the anions on bulk water structure, while newer theories claim that dispersion effects and specific interactions with macromolecules are more important. Using a combination of vibrational sum frequency spectroscopy, microfluidic technologies, and light scattering techniques we have been able to test these theories in a variety of interfacial and colloidal systems. The results clearly indicate that direct anion/macromolecular interactions play a key role. On the other hand, indirect effects on water structure are not necessarily of paramount importance.

QUANTUM ELECTRODYNAMICAL (QED) COHERENCE AND INTERFACIAL WATER

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It has been shown in the last 20 years in the conceptual framework of QED that liquids are two-fluid system.The first fluid is an ensemble of Coherence Domains (CD),where the component molecules oscillate in unison between two configurations of their electron cloud in tune with an e.m. field self-trapped in the CD. The second fluid is a dense gas of independent molecules, put out of tune by the thermal fluctuations, which is trapped in the interstices among CDs. The interplay between e.m. and thermal fluctuations produces a flickering mixture of the coherent and noncoherent fractions of the liquid.
Water is peculiar since the coherent oscillation in the CDs raises the component molecules up to the threshold of ionization, so that in each CD there is a plasma of quasi-free electrons , whose excitations give rise to a spectrum. It is this possible to induce CD oscillations able to produce a coherence among CDs , that can reach macroscopic sizes.
A surface is able to interact with water CDs producing a further stabilization that shields water CDs at the interface from thermal fluctuations. Interfacial water is thus almost fully coherent and exhibits the corresponding properties:
i) the exclusion of the noncoherent fraction prevents solutes from entering interfacial water (exclusion zone)
ii) the presence of a plasma of quasi-free electrons in the CDs makes interfacial water a donor of electrons , so that it becomes a reducing agent.
CDs , as all coherent systems, are able to add to their chemical potential any externally applied e.m. potential (Boehm-Aharonov effect) . Then a negatively charged surface lowers the CD chemical potential , producing the crowding of many CDs and the formation of an exclusion zone, whereas the opposite result is produced by a positively charged surface. The emerging QED picture of the interfacial water supports the findings of the Pollack group. An independent electrochemical evidence is presented, that supports such findings.

Abstract

Dissipative structures in extremely diluted aqueous solutions of Homeopathic Medicine

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In the last decade, we have investigated, from physicochemical point of view , whether water treated by the procedure of homeopathic medicine(leading inexorably to systems without any molecule different from the solvent) results in water different from the initial water.
The answer, unexpectedly , but strongly supported by many experimental results is positive. We used well established physicochemical methodology : flux calorimetry, conductometry, pHmetry and galvanic cells electrodes potential. unexpectedly, the physicochemical parameters evolve in time .
The water solvent exhibits large changes in measurable properties as a function of its history, the solute previously dissolved, and time. In particular we found evidence of two new phenomena, both totally unpredicted, in homeopathic dilutions: the presence of a maximum in the measured physicochemical parameters vs sample age, and their dependence on the volume in which the dilution is stored. These new experimental results strongly suggest the presence of an extended and ordered dynamics involving liquid water molecules

How Water Helped Oxidizing the Earth – the Peroxy Way

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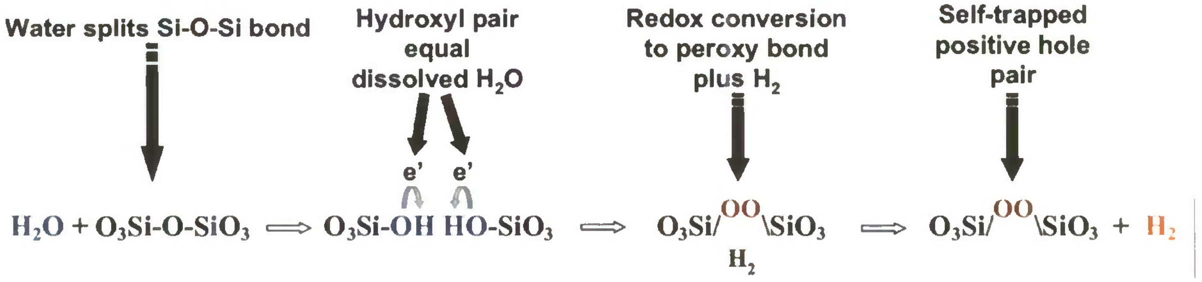
We live on a planetary body with an oxygen-rich atmosphere. We forget that this is an anomaly in the solar system and beyond. Originally, accreting out of the H-dominated solar nebula, the entire Earth was thoroughly reduced. However, over the course of Earth's first 1.5 to 2 billion years, oceans and the surface environment became slowly, but inextricably ever more oxidized. Still there was little or no free O_2 in the atmosphere. About 2.4 billion years ago the global oxidation accelerated, leading to what is known as the "Great Oxidation Event". After that remarkable event, the Earth's atmosphere acquired the 21 vol-% of free O_2, which we now enjoy.

Most likely the "Great Oxidation Event" marks the rise of oxygenic photosynthesis: Life's capacity, with the help of sunlight, to split H_2O and CO_2 into H and organic C plus O_2. By contrast, the cause for the slow but seemingly unstoppable early global oxidation remains essentially unexplained.

It now appears that water had something to do with it, although in a somewhat unexpected way.

When rocks crystallize from magmas or recrystallize deep in the Earth's crust most of their minerals are nominally anhydrous, meaning that their crystal structures do not provide any regular sites for hydroxyl, OH^-.Nonetheless nominally anhydrous minerals invariably incorporate small amounts of H_2O, generally in the form of hydroxyl, Si-OH, commonly Si-OH OH-Si pairs. During cooling, many of these "impurity" Si-OH HO-Si pairs, if not most, rearrange electronically splitting off H_2 and forming peroxy bonds, Si-OO-Si. Chemists call this a redox reaction:



With H_2 being diffusively mobile and capable of escaping over time, terrestrial rocks retain peroxy as a memory of a former solute H_2O content. On the tectonically active early Earth the presence of peroxy in essentially all crustal rocks has far-reaching consequences (even if some H_2 lingers on). During weathering peroxy hydrolyzes to H_2O_2 (hydrogen peroxide). Peroxy bonds under tectonic stresses, break. They generate an electric current carried by defect electrons in the O^{2-} sublattice (positive holes), equivalent to O^- radicals, which oxidize water to H_2O_2 at rock-water interfaces.

Peroxy in rocks may have provided enough oxidation power to change the course of history, forcing the early Earth to slowly oxidize over the course of her first 1.5 to 2 billion years. Along the way reactive oxygen species (ROS), released during the break-up of peroxy, provided a "training ground" for primitive early Life to evolve toward the more advanced eukaryotic life forms. The eukaryots were able to cope with and eventually take advantage of free O_2 in Earth's atmosphere by "learning" how to do oxygenic photosynthesis.

The Mechanisms of Hydration-Dependent Modulation of Protein Reactivity through Confinement and Addition of Osmolytes. Joel M. Friedman, Professor, Dept of Physiology and Biophysics, Albert Einstein College of Medicine, Bronx, New York 10461. Tel.718 430 3591. Email jfriedma@aecom.yu.edu

Understanding the molecular mechanisms through which environmental factors modulate protein reactivity and stability is a core issue for biophysics and biotechnology. Both reactivity and stability are directly connected to protein dynamics which in turn are strongly coupled to the dynamical properties of the surrounding water. We have adopted a two pronged approach to this issue. First we expose how different categories of functionally important dynamics are coupled to specific water dynamics. Second we expose how different environmental factors including confinement in either sol-gels or glassy matrices and addition of osmolytes perturb properties of water in the hydration layer that are linked to the modulation of protein dynamics. The framework for organizing and studying hydration-sensitive protein dynamics is the Protein Dynamic State Model(Samuni and others 2007a; Samuni and others 2007b) which is based on the concept of solvent slaved protein motions(Fenimore and others 2002; Fenimore and others 2004). Using this model we can directly monitor how specific categories of functionally important protein dynamics respond to environmentally-induced specific changes in hydration waters. In parallel we use a range of spectroscopic tools to probe the changes in the hydration waters as a function of these same environmental perturbations. These tools include: i) fluorescence from hemoglobin-associated pyranine (HPT) to monitor changes in water activity/mobility(Roche and others 2006); ii) fluorescence from BADAN coordinated to proteins and peptides to monitor changes in polarity within the hydration layer; and iii) Gd(+3) vibronic luminescence spectroscopy(Iben and others 1991; Roche and others 2006; Stavola and others 1981) to monitor changes in the hydrogen bonding between first and second shell hydration waters on the surface of calcium binding peptides, chelates and proteins.

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The cytoplasm's gel-like behavior contributes to human cell osmosensitivity

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Current models of cell volume regulation are almost exclusively based on the concept of free diffusion in the aqueous cytoplasm surrounded by a semi-permeable membrane, which controls solute fluxes with an array of channels and pumps. However, the cytoplasm is a matrix of large, crosslinked, charged polymers, making it a viscous, gel-like structure that restricts diffusion, retains water and, like non-living hydrogels, may have distinct swelling properties. The gel-like nature of the cytoplasm has not been fully documented for mammalian cells, and its impact on cellular processes, such as volume-sensing, remains unclear. Here, we demonstrate that gentle perforation of the surface membrane with digitonin preserves the gel-like character of the cytoplasm, enabling us to examine its biophysical properties at the single-cell level. Volume changes of intact and permeabilized, substrate-attached human epithelial cells were investigated by a light microscopy, 3D imaging technique developed in our laboratory. Upon membrane permeabilization, the cells swelled 2.2-fold due to the Donnan effect. In response to subsequent external osmolarity changes, permeabilized cells behaved like a highly-sensitive osmometer showing reversible volume alterations that were several-fold larger than those in intact cells, indicating the cytoplasm's high water-binding capacity. Binding or release of large amounts of water may allow rapid modulation of local fluidity, macromolecular crowding and activity of the intracellular environment, consistent with the cytoplasm's function as osmosensor. Permeabilized cell volume also displays bell-shaped pH-dependency, with a maximum at pH 7.4, similar to that observed in intact cells. Isoosmotic replacement of K^+ by Mg^{2+} resulted in significant shrinkage of permeabilized cells, likely due to increased charge screening and ionic crosslinking effects. Our study demonstrates that the cytoplasm of single human cells behaves like a hydrogel, and its swelling properties contribute to intact cell volume responses. These findings are of fundamental importance in our understanding of cell osmosensitivity and volume regulatory processes.

Hierarchic Theory of Liquids and Solids & its Application to Biosystems

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Basically new quantitative Hierarchic theory of matter general for liquids and solids will be discussed (http://arxiv.org/abs/physics/0102086). This theory is proved to be more advanced than well known basic models of Einstein and Debye of condensed matter and can be reduced to them only after number of simplifications. In our approach the condensed matter is considered as a system of three-dimensional (3D) superposition of standing waves of following types:
a) the most probable de Broglie waves, related to molecules translation and librations in composition of condensed matter; b) the acoustic waves (thermal phonons); c) the electromagnetic waves (IR photons).

The existence of ambient (high-T) *mesoscopic* Bose condensation (mBC) in composition of liquids and solids in form of coherent molecular clusters with volume of 3D de Broglie waves of molecules, has been discovered as a result of computer simulations, using software, based on Hierarchic theory (copyright, 1997, USA, Kaivarainen).
Strongly interrelated collective excitations (quasiparticles), named the *effectons, convertons, transitons and deformons and their different combinations* are introduced in hierarchic model of condensed matter. They represent a mesoscopic scale of matter, intermediate between microscopic and macroscopic ones.

Our Hierarchic theory of condensed matter got a lot of convincing computerized verifications on examples of water and ice from comparison of calculated and experimental physical parameters, like heat capacity, thermal conductivity, surface tension, vapor pressure, viscosity and self-diffusion. The new quantitative theories of refraction index, Brillouin light scattering, Mössbauer effect and others, based on the same hierarchical model, are also in good correspondence with experiment. New optoacoustic device: "Comprehensive Analyzer of Water Properties (CAMP)", based on Hierarchic theory and corresponding computer program, has been proposed (http://arxiv.org/abs/physics/0207114).
It is shown, that the dimensions and dynamics of water clusters (mesoscopic Bose condensate) are crucial factors in evolution of biopolymer's spatial and dynamic structure.

Number of new phenomena where revealed:
- Solvent - mediated remote interaction between different kinds of proteins in the process of their large - scale dynamics (flexibility) change, induced, respectively, by ligand binding to the active sites, by temperature or by variation of solvent composition;
- Solvent-mediated distant interaction between protein and cells, accompanied by cells swelling or shrinking, correlated with change of protein flexibility and water activity, enhancing or triggering the passive osmosis via membranes of cells.

A new kind of interaction of water clusters, containing 30 - 70 molecules, with the open inter-domain and inter-subunit cavities of macromolecules/proteins, named *clusterphilic interaction,* was introduced (http://arxiv.org/abs/physics/0105067). Such interaction can be considered, as the intermediate one between the hydrophobic and hydrophilic ones. It follows from our

dynamic model of protein behavior in water, that intramolecular *clusterphilic interaction* stands for remote signal transmission, allosteric properties in multi-domain and oligomeric proteins.
Related papers online: http://arxiv.org/find/physics/1/au:+Kaivarainen_A/0/1/0/all/0/1

Nanomechanics of exclusion-zone water

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Intra- and extracellular space is rich in charged biopolymeric surfaces. A vast array of previous studies suggest that the properties of water at and near these surfaces are quite different from that of ordinary bulk water: the ordering of water molecules in co-ordinated multiple layers results in the exclusion of solutes, and thereby leads to the formation of an exclusion zone near the surface. Recent experiments revealed that even large, micron-sized charged particles can be excluded from the vicinity of charged polymeric surfaces to distances reaching hundreds of microns. The exclusion is probably driven by long-range forces, the nature and origin of which remain to be understood.

To investigate the mechanisms of solute exclusion, we combined microfluidics with optical trapping nanomechanics. We followed the collective motion of latex beads (0.5 - 2.0 μm diameter) suspended in aqueous solutions and introduced near the surface of Nafion (synthetic, perfluorinated teflon) in a vertically-mounted sample chamber. Following the entry of the suspension in the chamber, the beads began to rise and move collectively away from the Nafion surface, driven by the vectorial sum of gravitational, buoyancy, frictional and exclusion forces. The velocity of the bead phase boundary decayed exponentially as a function of time. In pure water the time constant of velocity decay was ~100 s, and the exclusion zone grew to a width of ~200 μm. From the initial velocity of ~2.3 μm/s we calculated an exclusion force of ~35 fN acting on a single, 1 μm bead. Replacing Nafion with Parafilm completely abolished bead exclusion. Replacing pure water with ethanol solution reduced the width of the exclusion zone. We tested four possible mechanisms that may lead to the generation of the exclusion force: 1) direct pressure by polymer strands dissociating via reptation, 2) direct pressure by entropic polymer brush, 3) direct force applied by moving phase boundary, and 4) physical-chemical gradient that manifests in force. We excluded the reptation and entropic brush mechanisms by imaging and mechanically tapping the Nafion surface with atomic force microscopy. To distinguish between the moving phase boundary versus gradient mechanisms, we trapped beads with optical tweezers in order to relocate them between phases. When beads held, with optical tweezers, in the exclusion zone were released by turning the laser off, they started moving away from Nafion and soon caught up with the the bulk of the beads. Thus, it is not a translocating phase boundary that pushes the beads away from the polymer surface. Rather, a physical-chemical gradient is present within the exclusion zone that sustains a distance-dependent force. In sum, the properties and dynamics of water in the vicinity of biolymer surfaces may have direct mechanical consequences. How they might influence biologically important processes such as molecular recognition, enzymatic activity and motor protein function, remain to be resolved.

“Unusual diffusion processes associated with interfacial layers of water”

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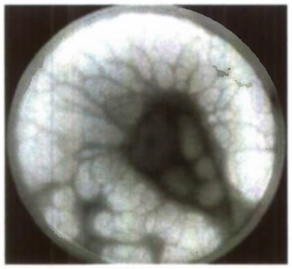
Open water surface in contact with the air is one of the most interesting cases of interfacial water. Largest part of the surface of our planet is covered by water in contact with the air. Many biological experiments are performed in physiological (water based) solutions with open surfaces. Previously we have demonstrated the formation of non-uniform structures in superficial layers of water and multi-component water solutions. Such structures are invisible in visual spectral range but they could be visualized using the method of real-time infrared imaging.

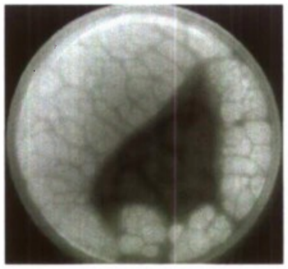
Mechanism of such structures formation is associated with convective and diffusion processes in thin superficial layer of water caused by thermal gradient, which appears due to evaporation and components mixing. Our future studies show that the time-dependent behavior of such structures could provide us with unique information concerning diffusion processes in very thin superficial interfacial layer of water. Open surface of the water allows us to directly observe diffusion processes in superficial layers using the technique of infrared imaging.

Experimental studies were performed using infrared (IR) camera with 3-5 micron spectral window of sensitivity and better than 15 mK temperature sensitivity at 200 frames per second acquisition rate. Such method makes it possible to visualize the difference between free and bounded water and to observe the dynamics of non-uniform structures in superficial layers of water and multi-component water solutions.

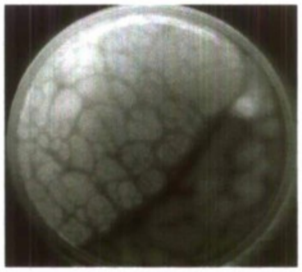
The separation of real multi-component water solutions in thin superficial layer has been observed. Examples of IR patterns in superficial layers of multi-component water solutions (10% ethanol and 5 % glycerin) are presented below.



a



b



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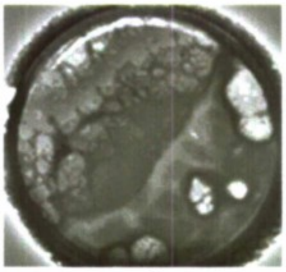
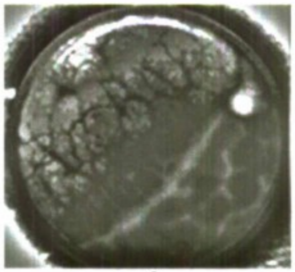
d



e



f

The darker structure in the middle areas of pictures **a** and **b** and in lower right area of picture **c** is the area of pure water without solution components. Pictures **d, e** and **f** are representing the evolution of IR pattern leading to picture **c**.

The mechanism of self separation in the thin superficial area of true multi-component water solutions will be discussed.

Structure and Dynamics of Water in Carbon Nanotube Confinement

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Abstract. The incorporation of water into carbon nanotubes provides a simple analogue of biologically important trans-membrane channels and so is of large interdisciplinary scientific interest. Recently quasi-one-dimensional water encapsulated inside carbon nanotubes (*nanotube-water*) at different temperatures (4-300 K) and pressures (1-3700 atm) were studied by means of neutron diffraction, quasielastic, inelastic and deep inelastic neutron scattering and observed extremely soft dynamics of nanotube-water at low temperatures were explained by molecular dynamics (MD) simulations. Application of a 'parallel tempering' MD algorithm allowed to calculate the structural and dynamical properties of nanotube-water simultaneously for different temperatures and revealed the phase transitions in temperature - pressure nanotube-water phase diagram, which were really observed in neutron scattering experiments.

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Dynamic Electrophotonic Analysis of Water and Liquids

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Computerized Dynamic Electrophotonic Analysis (DEPA) is based on Gas Discharge Visualization (GDV) technique which have found a lot of applications in medicine and biology [1,2].

The DEPA method is based on the stimulation of photon and electron emissions from the surface of the object whilst transmitting short electrical pulses – 5-7 mcs. In other words, when the object is placed in high intensity electromagnetic field, it is primarily electrons, and to a certain degree photons, which are 'extracted' from the surface of the object. This process is called 'photo-electron emissions' and it has been quite well studied with physical electronic methods. The emitted particles accelerate in the electromagnetic field, generating electronic avalanches around the subject (water drop). The discharge causes glow due to the excitement of molecules in the surrounding gas, and this glow is what are being measured by the DEPA method. Therefore, voltage pulses stimulate optoelectronic emission whilst intensifying this emission in the gas discharge, owing to the electric field created. Commercially available device "GDV Camera" produced by Russian company KTI (www.kti.spb.ru) is being used in the technique.

Informativity of DEPA method for studying liquid-phase subjects has been demonstrated during research of glow of microbiological cultures [3] blood response to allergens [4], ultra-low concentration of different salts [5] comparison of natural and synthetic, organic and ordinary, clockwise and counterclockwise rotating samples of essential oils [6], homoeopathic preparations of 30C potency [7],. In particular, ddifference of solutions and distilled water glow parameters stays up to 2^{-15} dilution, though dynamic trends of 2^{-15} dilution and distilled water show different directions in this case as well. The works on revealing differences in glow of natural and synthetic essential oils of the same composition [9] have aroused great interest.

The DEPA method was found to be highly reproducible, sensitive and relatively simple in use. Data collected in several laboratories demonstrate that DEPA method has high selectiveness and sensitivity if applied to study of liquid-phase subjects and different types of water in particular. The information being obtained depends on chemical composition of water but determinative and most interesting is the dependence on structural composition of liquid. DEPA glow parameters are determined by emissive activity of liquid surface layer, which depends on availability of surface-active valences. Obviously, this feature is determined by structure of the near-surface clusters, i.e. DEPA method is one of the informative methods of structural and informational liquid properties research. At present time there is every reason to include DEPA method into the set of integrated tests of liquid and water properties.

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PHOTOCATALYTIC WATER SPLITTING TO GENERATE CLEAN AND RECYCLABLE HYDROGEN

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Energy and environmental issues in a global level are important topics. It is indispensable to construct clean energy systems in order to solve the issues. Hydrogen will play an important role in the system because it is an ultimate clean energy. It can be used for a fuel cell. Moreover, hydrogen is used in chemical industries. At present, hydrogen is mainly produced from fossil fuels such as a natural gas by steam reforming. In this process, fossil fuels are consumed and CO_2 is emitted. Hydrogen has to be produced from water using natural energies such as sunlight if one thinks energy and environmental issues. Therefore, achievement of the solar hydrogen production from water has been urged. Photocatalytic water splitting is one of the methods for solar hydrogen production from water in the future. Sunlight shines at photocatalyst powders dispersed in a pool with water, and then hydrogen is readily obtained. So, photocatalytic water splitting is an attractive reaction and will contribute to an ultimate green sustainable chemistry and solving energy and environmental issues resulting in bringing an energy revolution. New photocatalyst materials for water splitting have recently been discovered one after another. For example, a highly efficient water splitting was achieved using a powdered photocatalyst of $NiO/NaTaO_3$:La under UV irradiation. The finding has proven that highly efficient water splitting is actually possible using powered photocatalysts. New powdered photocatalyst systems of oxynitrides such as $Cr_xRh_{2-x}O_3$/GaN:ZnO and Z scheme such as $Ru/SrTiO_3$:Rh-$BiVO_4$ have been developed for overall water splitting under visible light irradiation. Solar water splitting is confirmed using the $Ru/SrTiO_3$:Rh-$BiVO_4$ photocatalyst system. Moreover, in the presence of sulfur compounds of electron donors, the sulfide solid solution photocatalysts $AgInS_2$-$CuInS_2$-ZnS are highly active for H_2 evolution under solar light irradiation. H_2 is realistically obtained under sunlight irradiation. Thus, the library of photocatalyst materials becomes plentiful. Although the photon energy conversion using powdered photocatalysts is not at the stage of practical use, the research in photocatalytic water splitting is being advanced. The photocatalytic water splitting is still a challenging reaction even if the research history is long. In the present paper, heterogeneous photocatalyst materials for water splitting are introduced.

"Water and effect of chemical agents in ultra low concentrations".

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Ample experimental data accumulated to date provide evidence for the effect of various classes of biologically active compounds (BAC) at ultra low concentrations (< 10^{-13}M) (ULC) at different organizational levels of biological systems – from macromolecules, cell membranes, organs and tissues to animals, plants and even populations. There are similarities in the effect of all compounds at ultra low concentrations; the most important of them is nonlinear polymodal concentration-effect dependence.

A number of our studies showed that the introduction of different BAC (antioxidants, phorbol esters, peptides) in ULC in model system containing membrane suspension was always accompanied by changes in lipid peroxidation process and structural characteristics of lipid bilayer of membranes (microviscosity and order parameter). We have found that there were three areas of concentrations for all of the investigated BAC:1) the area of physiological concentrations (10^{-3}-10^{-8}M); 2) the area of BAC interaction with specific sites on cell membranes (10^{-9}-10^{-15}M); 3) the area of apparent concentrations (10^{-16}-10^{-25} M).

Our experiments indicate that effect of BAC in concentrations 10^{-16}-10^{-25} M was observed only in polar solvents (water, alcohol-water mixture), but in non-polar solvent (petrolatum oil) it disappeared. To reveal the contribution of water dynamic parameters to the mechanism of BAC action at ULC, the effect of some of them in a wide range of concentrations on the fluctuations of transmission indexes, measured using Fourier transform infrared spectroscopy in 9 narrow infrared-bands (4000-500cm^{-1}) for the corresponded water dilutions taken as a standard, was studied. As a characteristic of water structure modifications in the presence of different BAC doses the Mahalonobis criterion was used. It allows considering the correlation between infrared indexes of the sample and standard and is very sensitive to its dispersions. As a result, significant changes in the structural dynamic state of water have been observed under the effect of BAC at the 10^{-9}-10^{-25} M concentration range which has induced statistically reliable modifications of membrane structure. The same kind of experiments carried out with peptides in near range of infrared area (5200-14000 cm^{-1}) have shown the big changes in these specters of water under the effect of several doses BAC. The greatest deviations have been observed at the wave 9500 cm^{-1}. High concentrations of BAC (10^{-4}-10^{-7}M) had the strongest impact on the absorbtion (decreasing up to 10%) but there was a statistically reliable maximum (increasing up to 6%) at the concentration 10^{-15} M also. Taking together these results indicate that BAC change a structure of water system, probably, inducing the formation of new types of water microdomains which can influence on absorbtion parameters in a great scale. So, the biological effect of BAC at 10^{-15}-10^{-25} M can be explained on the basis of this data.

Four-photon laser spectroscopy of rotational lines in water: observation of protein/DNA selective interaction with H_2O para-isomer in aqueous solutions

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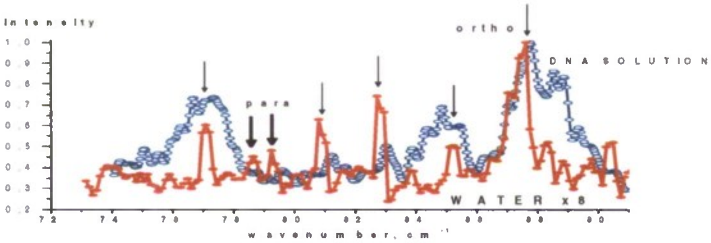
KEY WORDS: four-wave mixing, biopolymer terahertz spectroscopy, *ortho/para* H_2O isomers

The four-wave mixing (FWM) spectra have been recorded in the microwave range (0.1-100 cm^{-1}, 3GHz-3THz) for distilled water, aqueous solutions of DNA, α-chymotrypsin protein and single wall carbon nanotubes (SWNT) suspension. The method is based on mixing of two laser waves at frequencies ω_1 and ω_2, whose difference $\pm(\omega_1-\omega_2)$ is scanned in the microwave range (both, in positive and negative detuning value). The parameter to be measured is the depolarization of radiation at the frequency $\omega_s=\omega_1-(\omega_1-\omega_2)$, whose nonlinear source is given by:

$$P_i^{(3)}=6\chi_{ijkl}^{(3)}(\omega_s;\omega_1;\omega_2;-\omega_1)\,E_j^{(1)}E_k^{(2)}E_l^{(1)*}\ ,$$

where $\chi^{(3)}$ is the cubic susceptibility of the medium, proportional to the correlation function of optical anisotropy fluctuations, and $E^{(1)}$ and $E^{(2)}$ are the amplitudes of the interacting fields and $I_S\propto\left|\chi^{(3)}\right|^2 I_1^2 I_2$ is the intensity of coherent signal.

The experiments shown that FWM[1,2] signal of distilled water in the range 0.1-100 cm^{-1} involves the known gas-like rotational spectrum of H_2O *ortho/para* spin-isomer molecules. It was established that in the biopolymer's (protein, DNA) aqueous solutions the *ortho* isomer rotational lines intensity increases by factor of ~10. In contrary, the *para* isomer's lines are suppressed considerably. Thus, the selective interaction of H_2O spin isomers with biopolymers was observed for the first time to our knowledge in aqueous solution. We suggest that the biological macromolecules are able to selective influence on the concentration of H_2O spin isomers at the nearest surrounding layers. Remarkably, the interaction DNA-H_2O efficiency in the interface layers is reducing substationally due to DNA denaturing at 95 ^{0}C for the 30 minutes. The Figure demonstrates the FWM spectra in the range 73-91 cm^{-1} of DNA aqueous solution (concentration 15mg/ml, open circles) and *Milli-Q* water (multiply by factor of x8), full circles. The rotational resonances of *ortho-* and *para-* isomers are marked by thin and thick arrows, respectively.



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Unexpectedly Critical Role of Hydrophilic Surfaces on Nearby Water

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The impact of surfaces on the contiguous aqueous phase is generally thought to extend no more than a few water-molecule layers. We find, however, that colloidal and molecular solutes are profoundly excluded from the vicinity of various hydrophilic surfaces, to distances typically several hundred micrometers. Such large exclusion zones have been observed next to many surfaces, including hydrogels, biological tissues, hydrophilic polymers, monolayers, and ion-exchange beads. And, many diverse solutes are excluded. Hence, the exclusion phenomenon appears to be quite general.

Several methods have been applied to test whether the physical properties of the exclusion zone differ from those of bulk water. NMR, infrared, and birefringence imaging, as well as measurements of electrical potential, viscosity, and UV-VIS absorption spectra, reveal that the solute-free zone is a physically distinct, less mobile, ordered, phase of water that can co-exist essentially indefinitely with the contiguous solute-containing phase. Indeed, this unexpectedly extensive zone may be a candidate for the long-postulated "fourth phase" of water.

The energy responsible for building this charged, low entropy zone may come from sunlight. We found that incident radiant energy including all visible and near-infrared wavelengths induce exclusion-zone growth in a spectrally sensitive manner. IR is particularly effective. Ten-minute exposure to LED radiation at 3.1 μm (corresponding to OH stretch) causes exclusion-zone-width increase up to four times. Apparently, incident photons cause some change in bulk water that predisposes constituent molecules to reorganize and build the charged, ordered exclusion zone.

Photons from ordinary sunlight, then, may have an unexpectedly powerful effect that goes beyond mere heating. It may be that solar energy builds order and separates charge between the exclusion zones next to hydrophilic surfaces and the bulk waters beyond — each separation creating a battery. The resemblance to photosynthesis is evident. Indeed, this light-induced action would seem relevant not only for photosynthesis but also for all realms of nature involving water and interfaces. The implications are amply discussed in: http://uwtv.org/programs/displayevent.aspx?rID=22222 and will be presented.

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Thermoluminescence as an experimental tool to investigate the " structure " of High Dilutions

: Glimpses into the potential role of the gas phase during succussion

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It has been known for a long time that water, a most simple chemical, shows however many abnormal properties. Most scientists do believe that this is due to the fact that polar water molecules are able to build complex 3-D structures around foreign compounds and between themselves thanks to what has been called " hydrogen bonds ". Generally combined in tetrahedric arrays around a single central molecule, these bonds maintain together large " clusters " or " reference domains " which are specific of their initial history . Another interesting feature is that, though their life-time is only of a few tens of picoseconds and that, accordingly, they do not constitute permanent features, they are able to reconstitute almost continuously within a given identical pattern giving, thus, to the liquid some kind of a statistical " finger-print". This looks to be particularly true for ultra-high dilutions because it is felt that, during the very violent mechanical stirring (succussion), an essential part of their preparation process, the gas phase overlying the liquid is dispersed into trillions of "nano-bubbles" surrounded by successive shells of water molecules which might very well bear the identity of the dilution.

Since water, as an ever moving fluid, is very difficult to observe, we thought that by turning it into a stable solid by low-temperature freezing (in liquid Nitrogen -196°C) the " statistically structured " areas would be converted into corresponding "permanent defects" within the crystalline lattice. These "odd points" could, then, be further "activated" by low-temperature irradiation and become light emission centers during controlled rewarming in a process of thermally activated luminescence . Our experiments, during the last 10 years, did confirm that hypothesis and showed that ultra-high dilutions (even beyond the Avogadro number) could be discriminated between themselves as well as from their dilution fluid, thus giving a credible physical basis to the long-lasting claims of the practictioners of homeopathic remedies.

Nanofluids and Nanochannels

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Understanding and manipulating liquids and solids at the nanoscale is a matter of continuously growing scientific and technological interest. The study of solid and liquid nanoscale systems not only presents beautiful and sometimes unexpected new physics but it is also relevant for applications such as micro-electro-mechanical systems, organic electronics, nano-electronics, tribology, micro/nano-fluidics, and biology. During this seminar I will address two topics: the viscoelastic behavior of nano-confined fluids and the development of a new chemical nanolithography technique for nanofluidics and biological applications.

The viscoelastic dynamics of nano-confined wetting liquids is studied by means of atomic force microscopy (AFM) (1, 2). We observe a nonlinear viscoelastic behavior remarkably similar to that widely observed in metastable complex fluids. We show that the origin of the measured nonlinear viscoelasticity in nano-confined water and silicon oil is a strain rate dependent relaxation time and slow dynamics. By measuring the viscoelastic modulus at different frequencies and strains, we find that the intrinsic relaxation time of nano-confined water is in the range 0.1-0.0001 s, orders of magnitude longer than that of bulk water, and comparable to the dielectric relaxation time measured in supercooled water at 170-210 K.

AFM technologies have become of increased importance due to their potential for low cost nanofabrication. By using new polymer materials we have demonstrated the ability to thermally activate a chemical reaction at the nanometer scale by means of a hot AFM tip. This methodology allows us to write chemical and topographical features at a rate of mm/s with sub-15 nm resolution (3, 4).

1. Li et al., Phys. Rev. B 75, 115415 (2007)
2. Li et al., Phys. Rev. Lett. 100, 106102 (2008)
3. Szoszkievicz et al., Nano Lett. 7, 1064 (2007)
4. Wang et al., Appl. Phys. Lett. 91, 243104 (2007)

Structural and Dynamical Behaviour of Water in (and on) Nano-confined Systems

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Time-resolved spectroscopic investigations as well as investigations based on time-resolved x-ray diffraction techniques reveal new insides into the structural dynamics of matter. In this contribution we will present our studies on nanoconfined media like ternary liquid crystal systems (as membrane model systems), or proteins. We will discuss how water solvation shells (in the case of proteins) or the water (structure) itself influences the kinetics and dynamics of the systems mentioned.

Special emphasis will be focused on the ultrafast structural response function of water as been investigated at the Free Electron Laser Facility FLASH at DESY. The remarkable coherent and brilliant properties of this source (100 % transversal coherence, up to 10^{12} photons / pulse) - combined with its time resolution (30 – 100 fs) provide a unique opportunity to elucidate short living structural intermediates and states. The experiments carried out were based on a pump / probe scheme where a femtosecond optical laser excites the system of investigation and the FLASH soft x-ray pulse (7 nm) probes its structural response function by XUV diffraction techniques. The available energy range (EUV-Soft X-rays) makes it furthermore possible to investigate fundamental processes, such as inner shell photon ionization or the structural response function of matter under extreme laser fields. Early intermediates of radiation chemistry (like solvated electrons) have been observed by applying the experimental scheme of FLASH pump / optical laser probe in the ultrafast time domaine.

Hydrogen bonds as a possible explanation of the unusual behaviour of water and aqueous solutions

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Since more than 30 years the puzzle of the anomalous properties of liquid water remains object of debate. The more recent developments have been achieved almost exclusively by computer simulations of the molecular dynamics using different "effective" potentials. Some of them demonstrate the existence of liquid-liquid phase transitions and of a critical point under temperature-pressure conditions not accessible to real experiments. It is not obvious that such results apply to liquid water. We focus our attention on the role of hydrogen bonds formed between neighbouring molecules. Their fast dynamics and ability to create short lived networks with structures similar to ices must be taken into account in theories to be developed at the molecular level. We will present recent experimental results that use coherent quasi-elastic neutron scattering in an original way that partly discriminates the dynamics of different partial components of the scattering law. The results confirm that the dynamics of hydrogen bonds follows an Arrhenius behaviour. We argue that the dynamics of supercooled water between the homogeneous nucleation temperature (not accessible to simulations) and the glass transition is determined by the dynamics of the bonds similarly to beta relaxation in polymer melts.

The Dynamics of Aqueous Hydroxide Ion Transport from 2D IR Spectroscopy

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Compared to ions of similar size and charge density, the hydroxide ion is able to move through liquid water extremely rapidly. It is believed that this anomalously fast diffusion constant arise from its ability to accept a proton from a neighboring water molecule, leading to translocation of the ion. Despite the seeming simplicity of this reaction, the exact mechanism by which it proceeds remains highly controversial. Central to the debate is how the coordination number about the hydroxide ion and its first solvation shell change over the course of the reaction as well as how strong of a role the remaining solvent plays in guiding the reaction. We have used femtosecond two-dimensional infrared spectroscopy (2D IR) to investigate this process through the vibrational dynamics of the OH stretching vibration in isotopically dilute NaOD/D_2O solutions. Our experiments separate the dynamics of the hydroxide from those of its first solvation shell, characterize the kinetics for proton exchange and show signatures of the intermolecular proton transfer dynamics.

Title: Quantum fluctuations, gauge freedom and mesoscopic/macroscopic stability

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Motivated by the study of the problem of defect formation during the process of phase transition, we discuss [1], in the framework of quantum field theory, the formation of extended domains exhibiting in their fundamental states non-vanishing order parameters.

[1] E. Del Giudice and G. Vitiello, Phys. Rev. A 74 (2006) 022105

Water -- the Base of the Living State and Vital Functions

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The dominant substance in all the organisms is water. Some hydrobionts where it represents more then 99% by their mass may be considered "living water". However, to elicit most basic properties of this water making it so special one needs to define what a "living state" is.

More than 70 years ago Russian-Hungarian biologist Ervin Bauer formulated the fundamental principle of Stable Non-Equilibrium to differentiate between animate and inanimate systems: *"All and only living systems are never at equilibrium. At the expense of their free energy* ***they ceaselessly perform work against equilibrium****, demanded by the physical and chemical laws appropriate to the actual external conditions"*. Stable non-equilibrium (excited) state of matter is displayed at all the levels of a living system organization, including the molecular one. Inasmuch as the structure of matter in an excited state differs from structure of the same matter in the equilibrium (ground) state Bauer defined free energy of EXCITED structural elements of the living system ("living matter") as "structural energy". Growth and development of a living system goes on due to assimilation of food – conversion of its potential energy into structural energy of "living matter" and transformation of the consumed matter into a non-equilibrium state characteristic of living matter. All forms of work including assimilation of food as are performed by a living system at the expense of structural energy of living matter. To retard spontaneous relaxation of excited state of workable structural elements they should be so interdependent, that a living system may be considered a multilevel coherent system. All vital functions: metabolism and assimilation, multiplication, adaptability, excitability and even evolution may be derived from this principle.

However, Bauer's theory of a living state does not consider how it could primordially emerge. Besides no conclusive answer is given to the question of what particular substance may stably reside in a non-equilibrium state and return back to it when it releases structural energy for the performance of useful work providing for the continuity of "living matter".

We'll reason here that unique properties of interfacial water (EZ-water after G. Pollack) fully meet all the requirements of the Principle of Stable Non-Equilibrium. Most important property of EZ-water is its electron-donating capacity due to much higher state of excitation of electrons in it in comparison to "bulk" water. The natural electron acceptor always present in water is oxygen. If energy of activation even in a form of a triggering stimulus is available EZ-water may donate electrons to oxygen, and the overall reaction of full oxygen reduction may proceed:

$$\mathbf{2H_2O} + O_2 \rightarrow \mathbf{O_2} + 2H_2O + n*hv \text{ (Energy)}$$

Though the molecular species at the left and right sites of this equation are the same (water and oxygen) up to 8 eV of energy may be donated by this reaction. It is structural energy (in Bauer's sense) of EZ-water residing in the stable non-equilibrium state that is released when two water molecules belonging to it (left side of the equation) convert into the ground state water molecules (right side of the equation).

Part of this energy may be used for the restoration of EZ-water. If CO_2 and N_2 are present in water some part of energy may be used for their excitation and chains of chemical reactions in the course of which complex organic molecules are produced may be initiated. New surfaces turning water into EZ-water appear and the overall stock of structural energy of such aqueous system increases. Thus its ability to perform work against equilibrium enhances.

The necessary condition for this scenario to realize is availability of sufficient energy to keep enough water in a liquid state in which EZ-water (or coherent domains according to E. Del Giudice) and ground state water coexists. This is the necessary condition for spontaneous emergence and sustainability of living systems in all the forms known to us.

IR-SPECTROMETRY OF WATER BASIS OF BIOLOGICALLY ACTIVE SUBSTANCES

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Water researches have clearly shown that even ideally pure water represents like difficult arranged system. In what direction as a whole there is a water researching?

From the ecological point of view the water research is directed on studying of its qualitative and quantitative structure. However on a question, whether it is possible to drink water of such structure, we do not receive the answer. It is established, that in the presence of numerous impurity in water their total biological effect surpasses the maximum permissible concentration of separate components established by statutory acts. Thus, it is important to define not only the maintenance of separate substances, but also to register effect of their influence on biological objects, more exact for water component.

The human body almost on 80 % consists of water. However, at studying of pathological conditions arising in a human body, scientists try to find out, what of biochemical tests bears responsibility for it. And again we see, that scientists try to dismember difficult system to the simple parts. And can, it is necessary to reflect, what occurs during this moment to the aqueous component?

Our scientific interest is study the modelling solutions and biological systems. In the researches we have applied the phenomenological approach to studing object that assumes substance studing as a single whole, without separation of primary elements. Novelty of such approach is defined by this: water systems are analyzed as a unit, and their dynamic features are considered. It became possible with introduction in research practice developed infra-red (IR) spectrometer «IKAR» and application the multidimensional analysis of databases by criteria Machalanobis and Bartlett. Such approach to the analysis of the water systems reflecting their complete condition, has allowed us to be engaged in researches of properties of high dilution by pure water the solutions of biologically active compounds.

In the message we will speak on features of the device and application possibilities «IKAR» in researches of a water basis of modelling solutions of biologically active substances and biological liquids. We will present results of experiments. The obtained data will promote clearing-up of mechanisms of participation endogenous waters in functioning of biological systems.