



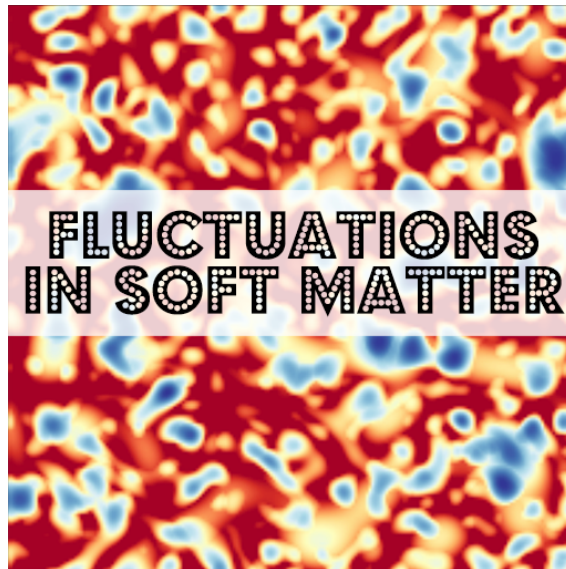
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Fluctuations in Soft Matter: Theory Meets Experiment at Large-Scale Research Infrastructures

ABSTRACTS



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Albano 3: 4204 - SU Conference Room (56 seats)
Albanovägen 29, 114 19, Stockholm

Organizers:

Fivos Perakis, Department of Physics, Stockholm University.

Felix Roosen-Runge, Physical Chemistry, Lund University.

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Anders Nilsson, Stockholm University, Sweden (Invited talk)

Experimental studies of water's second critical point

One hypothesis to explain the apparent divergence of thermodynamic response and correlation functions [1,2] is that there exists a liquid-liquid transition (LLT) with a liquid-liquid critical point (LLCP) at rather high positive pressures [3]. The challenge is that the diverging temperature lies below the homogeneous ice nucleation temperature 232 K, a region of the phase diagram that has been denoted as “no-man’s land”, since ice crystallization occurs extremely fast compared to the experimentally accessible time scale in a typical laboratory setting. Changing the temperature or pressure quickly, followed by probing of the liquid on ultrafast time scales using x-ray lasers have opened-up the possibility of studying water within “no-man’s land” [4]. These experiments have demonstrated the existence of a LLT at positive pressure, one phase behavior at 1 bar at temperatures down to 228 K, and the presence of maxima in several thermodynamic response functions at 1 bar and 230 K [4] consistent with the LLCP hypothesis [3]. However, even after more than 3 decades, since the LLCP hypothesis was proposed, no experiment has yet directly visited the potential critical region of bulk supercooled water. Here we used nano-second IR laser pulses to heat high-density amorphous ice (HDA) to temperatures higher than the previous LLT study [5] and then probe the liquid state at various densities during the decompression with x-ray scattering from the x-ray laser PAL. Here we see signatures of a transition from a two-phase to a one-phase region as the temperature is varied in the first peak of the structure factor simultaneous with high values of the low momentum transfer (q) region, a consistent behavior as expected with the presence of a LLCP. [1] R. J. Speedy, C. A. Angell, J. Chem. Phys. 1976, 65, 851-858. [2] C. Huang et al., J. Chem. Phys. 2010, 133, 134504. [3] P. H. Poole, F. Sciortino, U. Essmann, H. E. Stanley, Nature 1992, 360, 324-328. [4] A. Nilsson, J. Non-Cryst. Solids X 2022, 14, 100095 and references therein. [5] K. H. Kim et al., Science 2020, 370, 978-982.

Beata Ziaja-Motyka, CFEL, DESY, Hamburg & IFJ PAN, Kraków

Distinct transient structural rearrangement of ionized water revealed by XFEL X-ray pump X-ray probe experiment

Authors: Michal Stransky, Thomas J. Lane, Alexander Gorel, Sébastien Boutet, Ilme Schlichting, Adrian P. Mancuso, Zoltan Jurek, and Beata Ziaja

Using X-ray free electron laser (XFEL) radiation to conduct an X-ray pump X-ray probe experiment, we studied strongly ionized water as part of our ongoing work on radiation damage. After irradiance with a pump pulse with a nominal fluence of $\sim 5 \times 10^{15}$ J/cm², we observed for pump-probe delays of 75 fs and longer an unexpected structural rearrangement, exhibiting a characteristic length scale of ~ 9 Å. Simulations suggest that the experiment probes a superposition of ionized water in two distinct regimes. In the first, fluences expected at the X-ray focus create nearly completely ionized water, which as a result becomes effectively transparent to the probe. In the second regime, out of focus pump radiation produces O¹⁺ and O²⁺ ions, which rearrange due to Coulombic repulsion over 10s of fs. Importantly, structural changes in the low fluence regime have implications for the design of two-pulse X-ray experiments that aim to study unperturbed liquid samples. Our simulations account for two key observations in the experimental data: the decrease in ambient water signal and an increase in low-angle X-ray scattering. They cannot, however, account for the experimentally observed 9 Å feature. A satisfactory account of this feature presents a new challenge for theory.

Beatrice Ruta, Researcher at CNRS, Néel Institut, France (Invited talk)

Triggering the pressure response of metallic glasses through the ergodicity of the compressed state glass

The effect of hydrostatic pressure on the vitrification of metallic glass-forming liquids has remained mostly unexplored due to the lack of effective experimental methods [1]. By combining fast scanning calorimetry with synchrotron high energy X-ray diffraction and X-ray Photon Correlation Spectroscopy measurements, we performed a detailed study of the relation between thermal properties, structure and collective atomic motion in a metallic glass former of Pt_{42.5}Cu₂₇Ni_{9.5}P₂₁ under different in situ and ex-situ high pressure and high temperature treatments. By carefully tuning the applied P-T protocol, the system can be driven into different densified glassy states with contrasting thermodynamic stability. While improved kinetic stability can be obtained by quenching the dense liquid, high pressure annealing leads to thermal rejuvenation and is accompanied by the concomitance of negative and positive thermal expansions at different length scales. When heated above their glass transition, these compressed glasses do not convert into the pristine liquid but they transform in several supercooled liquids, challenging the common wisdom of an equilibrium recovery controlled solely by the α -structural relaxation process.

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Nele Striker, DESY

Spatio-temporal correlations to study timescales of higher-order Correlations in liquids and glasses

N. Striker, I. Lokteva, M. Dartsch, F. Dallari, C. Goy, F. Westermeier, V. Markmann, S. C. Hövelmann, G. Grübel, F. Lehmkuhler

When a supercooled liquid approaches the glass transition, its relaxation time increases by several orders of magnitude while the liquid-like structure remains [1]. Although there has been extensive research into the nature of the glass transition, its mechanisms remain mostly unclear. Recent works show that long-living locally favored structures (LFS), such as icosahedral structures forming upon supercooling, may play a key role [2]. In this contribution we show results from a combined X-ray Photon Correlation Spectroscopy (XPCS) and X-ray Cross Correlation Analysis (XCCA) experiment on colloidal hard spheres in the vicinity of the glass transition [3]. We defined a new correlation function g_c probing the timescales of higher-order correlations, which combines both XPCS and XCCA by tracking the time evolution of the structural higher-order correlations within the sample. We observed an increase in the ratio of the relaxation times of g_c and the standard individual particle relaxation time obtained by XPCS from about 0.4 to 0.9. While a value of around 0.5 is expected for free diffusion, the increasing values suggest that the local orders within the sample are becoming more long-lived approaching the glass transition. These results indicate that not only the presence but also the lifetime of LFS grows close to the glass transition. This new correlation approach can in principle be extended to detect structure-dynamics correlations on many length scales, allowing studies of phase transitions or lifetimes of transient structure in liquids and benefits exceptionally from the increased brilliance of diffraction-limited storage rings.

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Anita Girelli, Stockholm University

Anomalous Protein Diffusion and Solvent-mediated interactions in Crowded Solutions with Coherent X-Ray Scattering Using XFELs

Proteins play essential roles in life, for instance serving as carriers, participants in the immune response or for their structural role. In vivo, they exist within crowded environments with protein volume fractions typically ranging as high as 30%. When the environment becomes highly concentrated, the dynamics of proteins deviate significantly from those observed in a dilute system. However, the precise mechanisms influencing these dynamics across different time scales are not yet fully understood. Here we present our recent results [1], where we investigated the effect of self-crowding on protein diffusion in a ferritin solution with varying concentrations using X-ray Photon Correlation Spectroscopy. This technique allows simultaneous monitoring of both the structure, through small angle scattering, and the diffusion, through intensity-autocorrelation functions, of the protein solution, as demonstrated in our previous study [2]. By analyzing the scattering intensity, we observed that the ferritin particles become more densely packed with increasing protein concentration, indicated by a pronounced peak in the structure factor that shifts towards lower momentum transfer values. The protein diffusion, measured at all concentrations, follows a Brownian type of motion, but exhibits deviations at the peak position. This deviation can be attributed to the crowding effect caused by neighboring proteins, which act through hydrodynamic interactions. The hydrodynamic functions, which reflects these interactions, exhibit a peak which coincides with that of the structure factor indicating the connection of the crowding and the hydrodynamic interactions. To elucidate the underlying mechanism, we compare the hydrodynamic functions with estimations based on the $\delta\gamma$ -theory, which considers the non-trivial interactions between particles. The model indicates that the protein diffusion is slower than that of non-interacting hard spheres due to the presence of solvent-mediated interactions and effective local friction between the particles.

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Christian Gutt, University of Siegen, Germany (Invited talk)

Dynamics in dense protein solutions - new insights from XPCS experiments

In this contribution we report on experiments aiming to study the collective dynamics in dense protein solutions on their intrinsic microsecond time and nm length scales. Using the highly coherent X-ray pulses at the European XFEL and the MHz repetition rate we performed XPCS experiments on a variety of protein solutions [1]. We explore the experimental boundary conditions required to study protein dynamics in (quasi) equilibrium conditions. Identifying such windows of opportunity we showcase the influence of crowding on the Q-dependence of the collective diffusion constants for model systems of ferritin and dextrane crowding agents. We observe systematic deviations from the colloidal picture of the short time dynamics in the solutions which can help to understand effects of hydrodynamic interactions on the slow-down of molecular motion in protein solutions. [1] M. Reiser et al. Nature Comm. 13, 5528 (2022)

Martin Weik, Institut de Biologie Structurale, France (Invited talk)

Dynamics of amyloid fibers and their hydration water as studied by neutron spectroscopy

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Protein amyloid fiber formation is the pathological hallmark in various neurodegenerative diseases such as Parkinson's and Alzheimer's. The physico-chemical origin of protein fibrillation, as well as the role that hydration-water might play remain elusive. We combine elastic and quasi-elastic neutron spectroscopy and molecular dynamics simulations on the intrinsically disordered proteins α -synuclein (involved in Parkinson disease) and tau (involved in Alzheimer disease) to investigate both structural and dynamical properties of the protein-hydration water system. One of our findings is an increased water translational diffusion on fiber surfaces, suggesting that hydration-water entropy might be one of the driving forces for amyloid fiber formation. We are now extending our studies to tau and α -synuclein under LLPS.

Mikael Oliveberg, Stockholm University, Sweden

From diffusive protein-protein interactions in live cells to general patterns of functional optimisation across organisms

A striking feature of nucleic acids and lipid membranes is that they all carry net-negative charge, and so is true for the majority of intracellular proteins. It is suggested that the role of this negative charge is to assure a basal inter-molecular repulsion that keeps the cytosolic content suitably 'fluid' for function. This talk focuses on the experimental, theoretical and genetic findings that serve to underpin this idea, and the new questions they raise. Unlike the situation in test tubes, any specific protein-protein interaction in the cytosol is subject to competition from the densely crowded background, i.e. surrounding stickiness. At the non-specific limit of this stickiness is the 'random' protein-protein association, maintaining profuse populations of transient and constantly interconverting complexes at physiological protein concentrations. The phenomenon is readily quantified in studies of the protein rotational diffusion, showing that the more net-negatively charged a protein is, the less it is retarded by clustering. It is further evident that this dynamic protein-protein interplay is under evolutionary control and finely tuned across organisms to maintain optimal physicochemical conditions for the cellular processes. The emerging picture is then that specific cellular function relies on close competition between numerous weak and strong interactions, and where all parts of the protein surfaces are involved. The outstanding challenge is now to decipher the very basics of this many-body system: how the detailed patterns of charged, polar and hydrophobic side chains not only control protein-protein interactions at close- and long range, but also the collective properties of the cellular interior as a whole.

Lars Pettersson, Stockholm University, Sweden, (Invited talk)

Probing Water Structure around Dissolved Argon by Extended X-Ray Absorption Fine Structure (EXAFS) Spectroscopy

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We use Argon dissolved in water as a probe of lower-density local environments in the liquid through EXAFS at the Argon K-edge at 4, 15 and 25 °C. Compared to EXAFS on pure water we find a weaker amplitude and lower frequency in the oscillations, which we ascribe to a longer distance and the lack of protons pointing towards Argon in the hydrophobic cage. We find that simulated EXAFS from MD trajectories give a poor match to the experimental signal and apply the SpecSwap-RMC[1] fitting procedure to elucidate the local structure. We find a somewhat disordered cage with ~20 molecules with structure independent of temperature in the range probed. Argon may be seen as proxy for O₂ and we speculate what such hydrophobic encapsulation entails for the ability of fish to extract similarly dissolved O₂ from water. [1] M. Leetmaa, K.T. Wikfeldt, and L.G.M. Pettersson, J. Phys.: Cond. Mat. 22, 135001 (2010).

Yizhi Liu, Max Planck Institute for polymer research

Nuclear quantum effects on the thermodynamic response functions of a polymorphic waterlike monatomic liquid

Water and hydrogen are examples of substances proposed to exhibit a liquid-liquid critical point (LLCP) at conditions where nuclear quantum effects are relevant. The LLCP is usually accompanied by lines of maxima in density ρ and thermodynamic response functions, such as isothermal compressibility κT and isobaric heat capacity C_P , in the supercritical region of the P-T plane. In the case of water, the ρ - and κT -maxima lines can be accessed in experiments, while, instead, the LLCP has not been observed due to rapid crystallization. In this work, we study the nuclear quantum effects on a monatomic liquid that exhibits waterlike anomalous properties and a LLCP. By performing path-integral Monte Carlo simulations with different values of the Planck's constant h , we are able to explore how the location of the LLCP in the P-T plane and, in particular, the maxima lines in the supercritical region, shift as the system evolves from classical, $h = 0$, to quantum, $h > 0$. We find that as the quantum nature of the liquid (as quantified by h) increases and the atoms in the liquid become more delocalized, the LLCP shifts towards higher pressures and lower temperatures while the LLCP volume remains constant. Similar shifts (towards higher pressures and lower temperatures) are found in the case of the C_P - and κT -maxima lines. Instead, the ρ -maxima line extends towards higher temperatures and expands over a wider pressure interval as the liquid becomes more quantum. It follows that the nuclear quantum effects on the location of the LLCP may be estimated from the shift in C_P - and κT -maxima lines but not on measurements of the ρ -maxima line. Interestingly, nuclear quantum effects considerably alter the slope of the liquid-liquid coexistence line and C_P -maxima line in the P-T plane while the slope of the κT -maxima line along the Widom line is barely affected. We discuss briefly the implications of our results to the case of H₂O/D₂O.

Emanuela Zaccarelli, CNR-ISC and University of Rome, Italy (Invited talk)

Novel insights from computer simulations of microgels

I will report on our recent results obtained by Molecular Dynamics simulations of an ensemble of realistic microgel particles in swollen conditions in a wide range of packing fractions. Through a detailed analysis of single-particle behavior, I will illustrate the different regimes occurring in the suspension: from shrinking to deformation and interpenetration, connecting the simulation results to available experimental observations. I will then link these single-particle features to the collective behavior of the suspension, finding evidence of a structural reentrance, that has no counterpart in the dynamics. Hence, while the maximum of the radial distribution function displays a non-monotonic behavior with increasing packing fraction, the dynamics, quantified by the microgels' mean-squared displacement, always slows down. Even for standard poly(N-isopropylacrylamide) microgels, commonly considered as a prototype of soft colloid, charge effects due to the initiators employed in the chemical synthesis. Hence, I will compare results for neutral and charged microgels, highlighting the key differences between them.

Maddalena Bin, Stockholm University, Sweden

Coherent X-ray Scattering Nanoscale Fluctuations in Supercooled Hydrated Proteins

Hydrated proteins undergo a transition in the deeply supercooled regime around 220 K attributed to rapid changes in hydration water and protein structural dynamics. Here, we present our studies on the structural properties of hydrated proteins using a combination of wide-angle X-ray scattering and molecular dynamic (MD) simulations [1]. Additionally, we examine the nanoscale stress relaxation of the same hydrated proteins stimulated and probed by X-ray Photon Correlation Spectroscopy (XPCS) [2], a technique that utilizes coherent X-rays and can resolve collective nanoscale dynamics in a broad range of soft condensed matter systems, including biomolecular systems [3]. In the former study, we observe that the experimental scattering intensity exhibits a crossover near 230 K. Moreover, the MD simulations allow us to decompose the contributions from protein, which is nearly temperature independent, and water, which displays temperature-dependent changes, indicating that the hydration water is, on average, less tetrahedral than bulk water. The latter approach enables us to access the nanoscale dynamics in the deeply supercooled regime (T=180 K) which is typically inaccessible through equilibrium methods. Our analysis reveals an increase in dynamical heterogeneity upon cooling, as well as enhanced fluctuations observed in the two-time correlation functions and a maximum in the dynamic susceptibility quantified by the normalized variance of the two-time correlation functions. The amplification of fluctuations is consistent with previous studies of hydrated proteins, which indicate the key role of density and enthalpy fluctuations in hydration water. Overall, our studies are consistent with the observed two-state structure of liquid water and the crossing of the so-called Widom line around 230 K at ambient pressure.

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Anna Strander, Lund university, Sweden (Invited talk)

Dynamics of concentrated protein solutions and mixtures

Dynamic properties of protein solutions and mixtures under crowded conditions are difficult to predict and control. An example for a widespread physiological condition based on dynamic properties is presbyopia, or age-related farsightedness, where the pathological stiffening of the eye lens can be related to a liquid-solid transition of the protein mixtures inside the eye lens cells. It is thus essential to achieve a quantitative understanding of inter-protein interactions, and how these interactions influence the stability, dynamics and flow properties of the protein solutions and mixtures up to very high concentrations. Here we use a variety of advanced characterization techniques covering an extended range of time and length scales such as neutron spin echo, x-ray photon correlation spectroscopy, small-angle neutron and x-ray scattering, 3D cross-correlation light scattering and microrheology, combined with state-of-the-art computer simulations to assess and predict interparticle interactions and their impact on the dynamics and flow behavior under crowded conditions. We will address the enormous influence of weak attractive interactions on the solution dynamics and demonstrate the applicability and limits of simple mixing rules to predict solution properties of binary mixtures of two eye lens proteins exhibiting vastly different solution properties.

Felix Roosen-Runge, Lund university, Sweden

Non-uniform slow-down of proteins in the cytosol - a potential mechanism to tune reaction kinetics

Protein diffusion in the crowded solutions of the cellular cytosol is of high relevance for the cellular function by distributing substrates and chaperons throughout the cellular volume. We report that the crowded environment induces a size-specific slow-down factor on the protein diffusion, which occurs already on nanosecond time scales and extends into long-time kinetics. Large proteins are slowed down relatively stronger than expected by the overall volume fraction, while smaller proteins experience an opposite smaller slow-down effect. We observe this effect using quasi-elastic neutron scattering on tracer proteins in deuterated cellular lysate. Using snapshot Stokesian dynamics simulations, we link the effect to hydrodynamic interaction in polydisperse solutions, which for proteins arise on subnanosecond time scales. Measuring interaction rates in Brownian dynamics simulations, we find that the effect of this size-specific slow-down carries on as a general prefactor into the regime of protein transport and reaction kinetics. Our findings imply that the size distributions in the cytosol makes the size of proteins a potential mechanism to tune the reaction kinetics of specific pair-wise protein reactions.

Frank Schreiber, University of Tübingen, Germany (Invited talk)

Proteins under crowding conditions: From phase behavior to dynamics

Proteins are considered the machinery of life. In many cases, not only the behavior of individual proteins needs to be understood, but rather the collective phenomena, which remains a challenge, in particular quantitatively [1-2]. We discuss concepts for controlling and understanding protein phase diagrams, including aggregation pathways and the branching between them in aqueous solution by addition of multivalent ions or depletion agents. The tailoring of the interaction potential is exploited for controlling a) crystallization, b) gelation and amorphous aggregation, c) smaller aggregate formation, as well as d) network formation, with particular emphasis on kinetics and dynamics. We present complementary investigations of the dynamics of these systems using X-ray photon correlation spectroscopy (XPCS) and quasi-elastic neutron scattering (QENS), employing backscattering and spin-echo techniques [1-2]. We show how, via a combination of synchrotron, XFEL, and neutron data, more than 10 orders of magnitude in dynamics can be accessed, connecting internal dynamics of individual proteins to collective dynamics of phase transformations. We discuss how this can be exploited to investigate the questions a) – d) above with their associated dynamics on different time and length scales [3-7]. We also comment on the relationship with theory and simulations and to which extent coarse-grained colloidal or polymeric models can be employed to describe proteins, as well as the specific challenges related to systems in non-equilibrium. Lastly, we comment on the effects of interfaces in these systems [8]. Invaluable contributions by numerous collaborators are gratefully acknowledged as is financial support by BMBF, DFG, and ANR.

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Daria Noferini, European Spallation Source

Hydrogen Dynamics in pHEMA Hydrogels - How Neutron Spectroscopy Can Help in Preserving Precious Artefacts and Designing New Drug Delivery Systems

Hydrogels with tailored release and confining properties for drugs and detergents are pivotal for medical and cultural heritage applications. Notable examples are hydroxyethylmethacrylate (HEMA) based systems. Understanding thoroughly the transport phenomena at the molecular level is essential to enhance delivery properties. To this end, we used quasielastic neutron scattering (QENS) with deuteration to probe the dynamics of the polymer network and the transport properties of the water confined into the hydrogel matrix. Our investigation focused on the effect of crosslinking nature (chemical or physical) and water content. Thanks to the peculiarities of thermal neutrons as a probe, QENS is a very powerful technique to study the dynamics of hydrogenated systems, in time and space ranging from pico- to tens of nanoseconds and from Ångströms to nanometers, respectively. Our findings reveal a distribution of relaxation processes within the polymer network, primarily associated with the side-chains. Water dynamics occur as a hydrogen-bond governed process with a jump-diffusion mechanism. The interaction with the polymer matrix considerably slows the water dynamics with respect to bulk water and water within other confining systems. Such a strong interaction results as well in a fraction of water that appears immobile in the investigated timescale. Higher hydration levels are associated with an increased mobility of both the water and polymer network increases. At the same water content, the physical gel polymer networks present slower relaxation processes and smaller explored space than their chemical gel equivalents. Water mobility is notably diminished in chemical gels, particularly in less hydrated gels, while similarity in mobility is observed at higher hydration levels, albeit with shorter residence times in chemical gels.

Nicolas Giovambattista, City University of New York, Brooklyn College, USA (Invited talk)

The Importance of Fluctuations in Amorphous ice

Amorphous ices at approximately $P < 1$ GPa are usually classified as low-density or high-density amorphous ice (LDA and HDA) with densities $\rho \sim 0.94$ g/cc and $\rho \sim 1.15$ g/cc, respectively. However, a recent experiment crushing hexagonal ice (ball-milling) produced a medium-density amorphous ice (MDA, $\rho \sim 1.06$ g/cc) adding complexity to our understanding of amorphous ice and supercooled water. Motivated by the discovery of MDA, we perform computer simulations where amorphous ices are produced by isobaric cooling and isothermal compression/decompression. We show that, depending on the pressure employed, isobaric cooling can generate a continuum of amorphous ices with densities that expand in between those of LDA and HDA (briefly, intermediate amorphous ices, IA). In particular, the IA generated at $P \approx 125$ MPa has a remarkably similar density and average structure as MDA. Our results imply that MDA is not unique and that it may be possible that MDA is related to liquid water. The IA we obtain are homogeneous but contain LDA nanoscale domains in an HDA background, or vice versa, depending on the cooling pressure. These domains are the result of freezing-in (classical) density fluctuations of the corresponding parent liquid during the isobaric cooling process. By using the potential energy landscape (PEL) formalism, we provide an intuitive understanding of the nature of LDA, HDA, and the IA generated at different pressures. In this view, LDA and HDA occupy specific and well-separated regions of the PEL; the IA prepared at $P = 125$ MPa is located in the intermediate region of the PEL that separates LDA and HDA. In the last part of the talk, I will briefly discuss the role of quantum fluctuations (due to the atoms' quantum delocalization) on LDA, HDA, and the IA.

Esmée Berger, Chalmers University of Technology

Dynasor 2.0: From simulation to experiment through correlation functions

Using correlation functions, the full dynamics of a system can be accessed from atomistic simulations. This is particularly relevant for systems like liquids, where perturbative approaches are not applicable. The dynasor package is a flexible and efficient tool for calculating correlation functions, such as static and dynamic structure factors, both partial and total, as well as current correlation functions. Crucially, correlation functions provide a bridge to experiment, as weighing them with cross sections (or form factors) of, e.g., neutrons, X-rays or electrons, allows for the direct prediction of experimental spectra. Here, we demonstrate the utility of dynasor, which has recently seen a major upgrade to version 2.0 and now features a Python interface, direct support for weighing, and the ability to handle trajectories from more molecular dynamics packages than before. Examples include static and dynamic structure factors, different experimental spectrum predictions, and phonon dispersions for a diverse set of systems.

Paola Gallo, University Roma Tre, Italy (Invited talk)

Molecular dynamics simulations of supercooled aqueous solutions: from ions to biomolecules, the effect of different solutes on water behavior

I will show results from molecular dynamics simulations on the slow dynamics, thermodynamics and structure upon cooling of water in solutions with organic (biological) and inorganic solutes. Upon cooling bulk water dynamics, anomalies, the interplay between high density water and low density water, and the liquid-liquid critical point, can persist in the solutions for concentration from low to moderate. The results that I will discuss are of interest also for atmospheric and outer planets science, and in particular for the research about water on Mars, and for cryobiology and cryoprotection techniques.

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B. V. Ramirez, L. Lupi and P. Gallo, *Mol. Phys.* (2024). DOI: 10.1080/00268976.2024.2315308

Viktor Kurasov, Stockholm University

Fluctuations in the first order phase transition - is the capillary approximation for the critical embryo really suitable for the nucleation rate derivation

The problem of the fluctuation formation of the critical and supercritical embryos in the first order phase transition kinetics is discussed. It is shown that the standard capillary approximation meets several difficulties which are mainly connected with the non-stationarity of the overcoming of the critical barrier in the first order transition. The improvement of the expression for the nucleation rate is suggested and justified. The place of mentioned refinement in the context of the dynamic nature of the first order phase transformation is shown. A special attention is paid to the fluctuation corrections in the determination of the kinetic coefficients and the possible difference in the spectral density of fluctuations in the bulk media and in the small critical embryos.

Kyung Hwan Kim, Chemistry Dept., POSTECH, S. Korea (Invited talk)

Direct Observation of Dynamic Transition in Bulk Supercooled Water using FELs

Most liquids can be classified into two categories, fragile and strong ones, depending on their temperature dependence of the dynamics [1]. A strong liquid obeys the Arrhenius law, whereas the fragile one displays a super-Arrhenius behavior. Water at ambient temperature and modest supercooled conditions is considered to be a fragile liquid whereas it is proposed to be a strong liquid at temperatures close to the glass transition. Thus, it is postulated that there exists a fragile to strong transition of liquid water somewhere in the deeply supercooled regime [2]. However, the fast ice crystallization prevents the direct measurement and thus there has been debates on its existence for many decades due to the lack of direct experimental evidence. Therefore, it is important to determine the dynamic properties in deeply supercooled water to verify the existence of the hypothetical fragile to strong transition and see if this can be related to the divergence observed in thermodynamic and structural properties. By introducing a novel method for achieving deeply supercooled liquid water down to ~227 K [3] in the context of the IR-pump and X-ray-probe experiment at FELs, we were able to investigate the dynamics of water down to deeply supercooled regime. Consequently, we aimed to uncover evidence of a potential transition in water's dynamic properties, such as relaxation time, which may suggest a dynamic transition of water. Our observations revealed that the relaxation time could not be adequately described by either a single fragile liquid or a single strong liquid indicating the presence of a transition in the relaxation dynamics of liquid water at around 230 K.

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Tobias Eklund, Johannes Gutenberg University Mainz, MPI, European XFEL

Ultrafast XFEL pump-probe experiments on vapor deposited amorphous ice

Supercooled liquid water is only stable down to 232 K at ambient pressure. At lower temperatures, water instantly crystallizes to form ordinary hexagonal ice. Water can, however, form metastable non-crystalline states, known as amorphous ices below 160 K. Any investigation into the structure or thermodynamic properties of liquid water at the intermediate temperatures is made difficult by the short lifetime of these states. So much so, that this region of the phase diagram has been deemed experimentally inaccessible, nicknamed "no man's land". In recent years, the truly inaccessible region has shrunk considerably, as faster experimental techniques have been developed. Still, no X-ray experiment was able to probe the structure of liquid water between 205 K to 227 K. In a new setup, We employ an optical-pump-X-ray-probe technique in grazing incidence geometry with in-situ made vapor deposited amorphous ice. The short time window for measurement (less than 100 ns/K) and weakly scattering 10 to 100 nm thin samples leaves only one option for structural probe: the highly brilliant and ultrashort pulses from an X-ray free electron laser. In this presentation, I will outline the scientific background of this project, and discuss first experimental results.

Katrin Amann-Winkel, Max Planck Institute for Polymer Res. (Invited talk)

XPCS at elevated pressures - pressure dependence of glassy dynamics

Since the discovery of two distinct amorphous states of ice with different density (high- and low-density amorphous ice, HDA and LDA) it has been discussed whether and how this phenomenon of polyamorphism at high pressures is connected to the occurrence of two distinct liquid phases (HDL and LDL). The glass-to-liquid transition of the two states is still not fully understood [1]. The almost opposite pressure dependence of the two glass transition temperatures leads to a crossing at elevated pressures. While experimental determination of the glass transition at elevated pressure and cold temperatures is technically difficult to implement, measurements on water and amorphous ices are even more challenging, as the glass-liquid transition is interrupted by crystallization. In my talk I will give an overview about recent X-ray photon correlation spectroscopy (XPCS) measurements on amorphous ice at ambient pressure [2,3], as well as new experiments at elevated pressure using a diamond anvil cell. We also applied the method to investigate the glass transition of a water-glycerol mixture. [1] K. Amann-Winkel et al., *Rev. Mod. Phys.* 88, 0110002 (2016) [2] M. Ladd-Parada, et al., *Environ. Sci.: Atmos.*, 2, 1314 (2022) [3] H. Li et al., *JPCL* 14, 49 (2023)

Lennart Bergström, Stockholm University (Invited talk)

Dynamics and structural diversity of concentrated nanoparticle dispersions

Assembly and interfacial engineering of nanoparticles are essential tools for optimizing and tailoring the structures and properties of nanomaterials. This presentation will give an overview of recent research on how assembly of truncated iron oxide nanocubes and polymers can be followed by time-resolved small-angle X-ray scattering (t-SAXS) while the volume of acoustically levitating droplets decreased due to evaporation. We will give examples how the effect of particle concentration, surfactant concentration, solvation, and the application of weak magnetic fields can control the morphology and the transformation from a disordered colloid to well-ordered mesostructures and mesocrystals. These results gave insight into non-classical crystallization pathways and the rich structural diversity and dynamics of the investigated systems.

Aymeric Robert, MAX IV, Sweden (Invited talk)

Status and Perspective on probing dynamics in disordered matter at MAX IV Laboratory

MAX IV Laboratory [1], a Swedish national research infrastructure, offers scientists access to brilliant X-rays ranging from 4eV to 40keV, catering to diverse research needs encompassing X-ray spectroscopy, scattering, diffraction, and imaging. Presently, MAX IV comprises 16 beamlines providing state-of-the-art analytical tools for researchers across various domains such as materials science, chemistry, life sciences, and soft matter. MAX IV pioneered the first Multi-Bend-Achromat synchrotron source, the first fourth-generation light source. This groundbreaking facility unlocks unprecedented opportunities to leverage X-ray brilliance and coherence to unravel fundamental insights into the structure, dynamics, and kinetics of matter. We will provide an overview of the current status of MAX IV and the opportunities for benefiting from this large X-ray brilliance and coherence. Moreover, we will showcase exemplary research outcomes from our beamlines, highlighting their role in advancing our understanding of soft matter systems. 1] A. Robert., Y. Cerenius, P. Fernandes Tavares, A. Hultin Stigenberg, O. Karis, A.C. Lloyd Whelan, C. Runéus and M-Thunnissen, « MAX IV Laboratory », Eur. Phys. J. Plus 138, 495 (2023)

Helois Nunes Bordallo, University of Copenhagen, Denmark (Invited talk)

Learning a lot from a little: is artificial intelligence magic dust for big-science facilities?

Science is rapidly pushing the frontier of materials research and technology to control atomic and electronic interactions at the 10th of a nm scale. Here quantum effects dominate from the physics of charge transport of quantum materials to the interactions of molecules in complex biological systems. To image these complex interactions, we have constructed multi-billion large-scale research infrastructures such as the European X-ray Free electron laser (XFEL) in Hamburg and next generation neutron source, the European Spallation Source (ESS), in Lund. These facilities operate in a regime where the paradigm of making measurements has shifted from scanning specific regions of k-space to imaging vast volumes of it, providing unprecedented access to information on complex new science that govern functions in materials as well as to the physical laws governing the behavior of complex biological systems. However, with the paradigm shift resulting from the development of these new large-scale facilities, the amounts of data have increased and are reaching the limit of established data handling and processing. Despite these advances serious limiting steps are not only the extensive computational processing of the acquired data that is not yet fully available but also the limitations of human interactions in making timely and appropriate critical experimental decisions within a high speed/high throughout information rich environment. In this talk I will put forward ideas and questions in how experimentalists and theoreticians can contribute to the analysis of quasi-elastic neutron scattering data obtained in systems where confined water plays a crucial role in defining materials properties. This is non-trivial and to achieve such goal collaborations are essential.

[1] Is artificial intelligence magic dust for big-science facilities? Bordallo, H. N., Lioma, C., Taylor, J. & Argyriou, D. N. (2020). IUCrJ 7, 1-2.

Roland Kádár, Chalmers University of Technology

Orientation across length scales in simple shear

We report novel developments on SAXS based rheometry experiments at MAX IV, with a focus on a case study. Elucidating the rheological behavior of hierarchical nanostructured fluids is an ideal study case for combined rheological methods as they have the potential to relate bulk-averaged rheological properties to their hierarchical microstructural dynamics. Here, we report for the first time on simultaneous rheology combined with polarized light imaging (PLI) and small-angle X-Ray scattering (SAXS). We use study mainly aqueous dispersions 1D nanoparticles forming chiral nematic phase (cellulose nanocrystals, CNCs) and nematic (rigid thin wall nanotubes, RTWN). In this presentation, we compare two new setups, one based on a standard parallel-plate glass measuring geometry and a concentric cylinder setup. While rheometry provides a bulk measure of the interaction of all lengthscales in a material, PLI can help distinguish the mesoscale, while SAXS resolves nanoscale particle dynamics. Consequently, in terms of orientation we compare shear thinning, the onset of the latest cross and the onset of anisotropic scattering patterns. We show that the onset of orientation can differ significantly across lengthscales and that only a multiscale approach can truly resolve orientation dynamics in hierarchical materials.

Kristine Niss, Roskilde University, Denmark (Invited talk)

Testing isomorph theory with high pressure experiments on liquids and glasses

When a liquid is cooled (or compressed) to form a glass the time scale of the dynamics rapidly changes many orders of magnitude. The combination of dielectric spectroscopy and quasielastic neutron scattering gives access to time scales from pico- to kilosecond and makes it possible to follow the relaxation dynamics in the liquid from above the melting point and all the way down to the glass transition. Moreover, neutron scattering data give information on the boson peak and fast relaxation in the deeply supercooled liquid. By using a high pressure cell designed for simultaneous dielectric spectroscopy and neutron scattering [1], we have studied the pressure and temperature dependent dynamics in a handful of different glass-forming liquids including van der Waals liquids, hydrogen bonding liquids and a room temperature ionic liquid [2-4]. The data is analyzed in view of the so-called isomorph theory which predicts the existence of lines in the temperature-pressure phase diagram where dynamics is invariant both in terms of time scale and spectral shape. Another prediction from isomorph theory is that the structure is invariant along the isomorph. With molecular dynamics and scattering experiments this prediction is also tested for an ionic liquid [4-6] and a van der Waals bonded liquid [7]. [1] A. Sanz et al.; Review of Scientific Instruments, 89, 023904 (2018). [2] H.W. Hansen et al.; Nature Communications, 9, 218 (2018). [3] H.W. Hansen et al.; Journal of Chemical Physics, 149, 214503 (2018). [4] H.W. Hansen et. al.; Physical Chemistry Chemical Physics, 22, 14169 (2020). [5] P. A. Knudsen et. al.; Journal of Chemical Physics, 155, 054506 (2021). [6] P. A. Knudsen et. al.; Journal of Chemical Physics, 160, 034503 (2024). [7] E. H. Lørup et. al. Work in progress.

Erik Lørup, Roskilde University, Denmark

Experimental evidence for pseudoisomorphs

The fundamental prediction of the isomorph theory is that exist curves in the phase diagram, along which structure, dynamics and excess entropy are invariant, when presented in dimensionless units [1]. This theory has proven powerful in predicting the behavior of computer simulations of model liquids [2] and many of its predictions regarding dynamics are also verified experimentally [3] [4]. For real-world molecular liquid excess entropy is ill-defined, due to the internal degrees of freedom in the molecules. a workaround of this problems are pseudoisomorphs, where structure and dynamics are invariant, but the criteria of excess entropy scaling are neglected. We present results of one of the first experimental test of structural prediction of theories of isomorph theory. The relaxation time is also invariant along isomorphs, making isochrones suitable experimental identifiers for isomorphs. We compare the main diffraction peak along isobars, isotherms, isochors and isochrones, for glass-formers that have shown to obey the dynamical prediction of isomorph. We find that the main diffraction peak collapse along isochrones. The results are to our knowledge the first experimental evidence of pseudoisomorph. [1] J.C. Dyre, J. Phys. Chem. B 118, 10007–10024 (2014). [2] Ingebrigtsen et. al., Phys. Chem. B, 116, 1018–1034 (2012). [3] Hansen et. al. Nature Communications, 9, 518 (2018). [4] Hansen et. al J. Chem. Phys. 149, 214503 (2018).

Minna Patanen, University of Oulu, Finland (Invited talk)

Aqueous clusters and nanoaerosols studied using X-ray spectroscopy and single particle diffraction imaging

Gas phase clusters and nanoaerosols are ubiquitous in nature due to natural and anthropogenic activity but also offer tailored platforms for fundamental studies of matter at nanoscale. We have been interested in studying solvation and precipitation processes at nanoscale, using small water clusters and larger aqueous solution grown particles as platforms. In this talk, I will present some of our recent work on synchrotron radiation excited X-ray photoelectron spectroscopic characterization of unsupported clusters and nanoparticles. Using so-called “pick-up” cluster source, we have created water clusters doped with alkali halide molecules in a more or less controlled way. This has enabled nanoscale solvation studies where chemical shifts of photoelectron signals are interpreted to reflect the state of the solvation, e.g. formation of ion pairs [1,2]. In order to study larger nanoparticles, we have used atomisers producing aqueous droplets which can be dried to different extents and focused using an aerodynamic lens to the interaction region with X-rays in vacuum. We have been especially interested in surface enrichment taking place in these aerosols, as their composition mimic atmospheric aerosols, and the particle surfaces are important for their participation in atmospheric chemistry [3,4,5]. I will also show some preliminary results from European XFEL on coherent diffraction X-ray imaging of real sea spray and model salt aerosol particles. Interestingly, we were observing drastic effects on particle morphology depending on the relative humidity of the particle stream. These systems could offer interesting testbeds for further studies of e.g. water in nanoporous materials.

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Riccardo Mincigrucci, Elettra Sincrotrone Trieste

Structured illumination microscopy with Extreme Ultraviolet Transient Gratings Extreme Ultraviolet

Structured illumination microscopy with Extreme Ultraviolet Transient Gratings Extreme Ultraviolet Transient gratings is now a robust experimental tool, implemented at the FERMI free electron laser facility, that can be used to access nanoscale dynamics (thermal, mechanical, magnetic) of disordered systems manufactured both in bulk or thin film form. Such studies, requires the use of three beams to generate and probe the transient grating, which set some technological limits on the length-scales that can be accessed. An intriguing opportunity is represented by the so-called structured illumination microscopy (SIM), a super-resolution technique, that can reach the sub tens nm scale without the need of third, phase matched pulse to probe them. SIM is a super-resolution technique that exploit the interference of the spatial frequency of an illuminating beam (in the present case the transient grating) with the sample spatial frequencies to generate coarse structures at the frequency difference (moire' fringes) in the emitted fluorescence. The latter, can be used to reconstruct the original image with a resolution beyond the Abbe limit which thanks to the EUV pulses, can hypothetically visualize sub 10 nm objects. The first steps in this direction have already been moved and will be presented in the current contribution. Implications regarding the use of hard X-ray photons to generate the structured beam and X-ray fluorescence together with possible scientific directions will be highlighted.