

CPP 17: Charged Soft Matter, Polyelectrolytes and Ionic Liquids I

Time: Tuesday 9:30–13:00

Location: H 0107

Invited Talk

CPP 17.1 Tue 9:30 H 0107

Dipole-driven Self-assembly and Dynamics in Solutions of Charged Macromolecules — ●MURUGAPPAN MUTHUKUMAR — University of Massachusetts, Amherst, MA, 01003, USA

Control of self-assembled structures of charged macromolecules in aqueous solutions is vital in myriads of natural phenomena. However, a fundamental understanding of the various phenomena exhibited by charged macromolecules is one of the grand challenges in the domains of living matter, biomimicry, and healthcare. The origin of this challenge lies in the simultaneous occurrence of three long-range forces from electrostatics, topology of polymer connectivity, and hydrodynamics. As a result, charged macromolecules exhibit extraordinary behavior unseen in uncharged molecules. Several of these phenomena can be attributed to the dominance of dipole-dipole interaction over monopole-monopole interaction. We will present basic concepts and address structure, dynamics, and transport in a few systems that include biomolecular condensates, polyzwitterions, and intrinsically disordered proteins.

CPP 17.2 Tue 10:00 H 0107

Solvation Behavior of Elastin-like Polypeptides in Divalent Metal Salt Solutions — ●SWAMINATH BHARADWAJ^{1,2}, YANI ZHAO¹, RYAN MYERS³, PAUL CREMER³, and NICO VAN DER VEGT¹ — ¹Technical University of Darmstadt, 64287, Darmstadt, Germany — ²Shiv Nadar Institution of Eminence, Gautam Buddha Nagar, Uttar Pradesh 201314, India — ³Penn State University, University Park, PA 16802, USA

We studied the effects of CaCl₂ and MgCl₂ on the cloud point temperature of two different elastin-like polypeptides (ELPs) sequences. Cloud point measurements of these systems were performed along with molecular dynamics simulations and infrared spectroscopy measurements. Changes in the cloud point for the ELPs in aqueous divalent metal cation solutions were primarily governed by two competing interactions: the cation-amide oxygen electrostatic interaction and the hydration of the cation. In particular, Ca²⁺ cations can more readily shed their hydration shells and directly contact two amide oxygens by forming ion bridges. By contrast, Mg²⁺ cations were more strongly hydrated and preferred to partition towards the amide oxygens along with their hydration shells. Next, the partitioning of the cations was strongly influenced by the presence of triglycine motifs in the ELP sequence. In fact, although the more hydrophilic ELP V₅A₂G₃ was salted-out of solution by low concentrations of MgCl₂, it was salted-in at higher salt concentrations. By contrast, CaCl₂ salted the ELP sharply out of solution at higher salt concentrations because of the bridging effect.

CPP 17.3 Tue 10:15 H 0107

Explaining Giant Apparent pKa Shifts in Weak Polyelectrolyte Brushes — ●DAVID BEYER¹, PETER KOŠOVAN², and CHRISTIAN HOLM¹ — ¹Institute for Computational Physics, University of Stuttgart, D-70569 Stuttgart, Germany — ²Department of Physical and Macromolecular Chemistry, Charles University, 128 00 Prague 2, Czechia

Recent experiments on weak polyelectrolyte brushes found marked shifts in the effective pKa that are linear in the logarithm of the salt concentration. Comparing explicit-particle simulations with mean-field calculations we show that for high grafting densities the salt concentration effect can be explained using the ideal Donnan theory, but for low grafting densities the full shift is due to a combination of the Donnan effect and the polyelectrolyte effect. The latter originates from electrostatic correlations that are neglected in the Donnan picture and that are only approximately included in the mean-field theory. Moreover, we demonstrate that the magnitude of the polyelectrolyte effect is almost invariant with respect to salt concentration but depends on the grafting density of the brush. This invariance is due to a complex cancellation of multiple effects. Based on our results, we show how the experimentally determined pKa shifts may be used to infer the grafting density of brushes, a parameter that is difficult to measure.

CPP 17.4 Tue 10:30 H 0107

Anions and Cations Affect Amino Acid Dissociation Equilibria via Distinct Mechanisms — ●VARUN MANDALAPARTHY,

MADHUSMITA TRIPATHY, and NICO VAN DER VEGT — Department of Chemistry, Technical University, Darmstadt

Salts reduce the pKa of weak acids by a mechanism sensitive to ion identity and concentration that involves charge screening of the deprotonated state. In our recently published study [1], we utilize constant pH molecular dynamics simulations to understand the molecular mechanism behind the salt-dependent dissociation of aspartic acid (Asp). We calculate the pKa of Asp in the presence of monovalent salts and investigate Hofmeister ion effects by systematically varying the ionic radii. We observe that an increase in the anion size leads to a monotonic decrease in Asp pKa. Conversely, changes in the cation size affect the pKa nonmonotonically, interpretable in the context of the law of matching water affinity. The net effect of salt on Asp acidity is governed by an interplay of solvation and competing ion interactions. Our proposed mechanism is rather general and can be applicable to several problems in Hofmeister ion chemistry, such as pH effects on protein stability and ion effects on soft matter interfaces.

[1] Mandalaparth V., Tripathy M., van der Vegt, N.F.A., Anions and Cations Affect Amino Acid Dissociation Equilibria via Distinct Mechanisms, J. Phys. Chem. Lett. 2023, 14, 41, 9250-9256

CPP 17.5 Tue 10:45 H 0107

Influence of salt concentration and PSS molecular weight on PSS diffusion constant in PSS/PDADMA multilayers — ANNEKATRIN SILL, ●PER-OLE HILKEN, and CHRISTIANE A. HELM — Institute of Physics, University of Greifswald, 17489 Greifswald, Germany

We determine the diffusion constant D_{PSS} of polystyrene sulfonate (PSS) during the growth of polyelectrolyte multilayer films from poly(diallyldimethylammonium) (PDADMA) and PSS. Quartz crystal microbalance dissipation (QCM-D), AFM, and ellipsometry are used. The molecular weight of PDADMA was kept constant (117 kDa), and the one of PSS (M_{PSS}) was varied between 10 and 64 kDa. At the beginning of film build-up, the film thickness grows exponentially with the number of deposited PDADMA/PSS bilayers. Eventually, a transition to non-exponential growth occurs. From the film thickness at this transition and the adsorption time, the diffusion constant D_{PSS} is determined. Varying the NaCl concentration c (between 0.1 M and 1 M), one finds $D_{PSS} = A \cdot e^{(-\beta \cdot c)}$ with A as a constant. β decreases linearly on the increase of M_{PSS} . We obtain a power law on varying M_{PSS} : $D_{PSS} = B \cdot M_{PSS}^{-\gamma}$, with γ increasing linearly with c and B increasing exponentially. In conclusion, we found equations to predict D_{PSS} for given preparation parameters. In our experiments, the diffusion constant D_{PSS} varied by four orders of magnitude. The dependence of D_{PSS} on adsorption time, PDADMA molecular weight, and post-preparation treatment are discussed.

CPP 17.6 Tue 11:00 H 0107

Constrained Ion Conductivity in Isolated Polymer Aggregates — ●ALAA YOUSSEF AMIN HASSAN and MARTIN TRESS — Peter Debye Institute, Leipzig University, Leipzig, Germany

Technological progress and environmental concerns propel the popularity of portable electronics and electric vehicles, which demand robust and lightweight energy storage solutions. While polymeric electrolytes are attractive materials for that, a low ionic conductivity and high contact resistance limit their potential. To overcome this, a design based on a comprehensive understanding of structure-property relationships at the molecular level is required, which can be gained through nanoscale and finite-size investigations. We present a novel setup based on broadband dielectric spectroscopy with nanostructured electrodes combined with physicochemical surface modification methods to study the ion conductivity of polymer aggregates containing ~ 900 to 14 polyethylene oxide chains chemically attached to separated binding sites on a surface. Significant deviations from bulk conductivity indicate that ions engage in (slower) motion along the chains instead of (faster) inter-chain hopping, which dominates in bulk. This may be a general phenomenon of polymeric ion conductors at interfaces, which would reduce their performance through a significant increase in interfacial resistance and electrode polarization. The results suggest bottle-brush architectures can reduce this effect, making them promising candidates for enhanced polymeric electrolytes for better solid-state electrolyte batteries and ion-conducting fuel cell membranes

and possibly even improve permeation in polymeric membranes.

15 min. break

CPP 17.7 Tue 11:30 H 0107

Polymerised ionic liquids in solutions: Conformation and rheology — ●CARLOS LOPEZ¹, ATSUSHI MATSUMOTO², TAKAICHI WATANABE³, and WALTER RICHTER⁴ — ¹Materials Science and Engineering Department, The Pennsylvania State University, US — ²Department of Applied Chemistry and Biotechnology, University of Fukui, Japan — ³Department of Applied Chemistry, Okayama University, Japan — ⁴Institute of Physical Chemistry, RWTH Aachen University, Germany, European Union

We investigate the phase behaviour, solution rheology and scattering properties of a polymerised ionic liquid in over 20 different solvents. The polymer is found to be soluble in aprotic solvents of medium or high polarity, but not in protic solvents (e.g. water or ethylene glycol).

In high dielectric constant solvents, the correlation length scales as $\xi \propto C^{-1/2}$, indicating rod-like local conformations. For solvents with modest dielectric permittivities ($\epsilon \simeq 18 - 30$), the correlation length scales as $\xi \propto C^{-1/3}$, suggesting a partially collapsed pearl-necklace conformation. We hypothesise that the collapsed conformation arises from the influence of dipolar attraction from condensed counterions. In THF ($\epsilon = 8$), the scattering pattern follows the Ornstein-Zernike pattern, similar to neutral polymers.

Viscosity data display the exponents predicted by the scaling theory of Dobrynin et al. However, the ratio $\eta_{sp}/(C\xi^3)$ depends on the solvent type, in contradiction to the scaling model. Our results provide a framework to understand the influence of electrostatics and solvation forces on the structure of polyelectrolytes.

CPP 17.8 Tue 11:45 H 0107

Water harvesting by thermoresponsive ionic liquids — ●ROBIN CORTES-HUERTO¹, NANCY C. FORERO-MARTINEZ², and PIETRO BALLONE³ — ¹Max-Planck-Institut für Polymerforschung, Mainz, Deutschland — ²Johannes Gutenberg-Universität, Mainz — ³University College Dublin

Ionic liquids (ILs) whose water solutions are thermoresponsive provide an appealing route to harvest water from the atmosphere at an energy cost that can be accessed by solar heating. IL/water solutions that present a lower critical solution temperature (LCST), i.e., demix upon increasing temperature, represent the most promising choice for this task since they could absorb vapour at night when its saturation is highest and release liquid water during the day. In this talk, we present results for the kinetics of water absorption at the surface and the role of nanostructuring in this process as obtained by atomistic molecular dynamics simulations. We focus on the ionic liquid tetrabutyl phosphonium 2,4-dimethylbenzenesulfonate whose LCST in water occurs at $T_c = 36$ C for solutions of 50/50 wt % composition. The simulation results show that water molecules are readily adsorbed on the IL and migrate along the surface to form thick, three-dimensional islands. On a slightly longer time scale, ions crawl on these islands, covering water and recreating the original surface whose free energy is particularly low. At a high deposition rate, this mechanism allows the fast incorporation of large amounts of water, producing subsurface water pockets that eventually merge into the populations of water-rich and IL-rich domains in the nanostructured bulk.

CPP 17.9 Tue 12:00 H 0107

Microfabricated Poly (Ionic Liquid) Based Electrochemical Oxygen Sensors for Modified Atmosphere Packaging — ●ZOË SIEBERS, ALEXEY YAKUSHENKO, RYAN GUTERMAN, MAKSIM BAH-DANCHYK, STEFAN POPOVIĆ, DEJAN ŠEGAN, PETR VLASOV, and QIANG WANG — FaradaIC Sensors GmbH, Richard-Wagner-Straße 23, 10585 Berlin

The large size and high cost of current state-of-the-art oxygen sensors is the main impediment preventing millions of O₂-sensors entering the Internet of the things (IoT) market. This includes the monitoring of millions of bulk packages of perishable food being transported across the planet under a modified or controlled atmosphere (MAP).

The key to miniaturization and mass fabrication of electrochemical amperometric O₂-sensors is microfabrication. To reach such a goal, new special types of polymerized ionic liquid (poly (ionic liquid), PIL) electrolytes have been developed. These PILs are unique as they maintain high enough ionic conductivity after photopolymerization (up to 5×10^{-5} S/cm (24 °C)) and combine gas sensitivity with photopat-

ternability within a single substance.

With these novel materials, we have developed the first fully micro-fabricated sensor for electrochemical O₂ sensing. With a size of 2 mm x 2 mm x 1 mm it is $> \times 100$ more compact than commercial sensors.

We show that this sensor can be used to reliably measure O₂ concentrations in the specific conditions found in MAP (0-21 % O₂, 0–95 % relative humidity). An optimized readout algorithm is introduced to increase signal stability and sensor regeneration.

CPP 17.10 Tue 12:15 H 0107

Dynamics of ions in confinement: tuning the nanoporous metal-organic framework host for ionic liquids — ●ANEMAR BRUNO KANJ, RUPAL VERMA, MICAELA VAZQUEZ, ZEJUN ZHANG, ABHINAV CHANDRESH, MODAN LIU, WOLFGANG WENZEL, and LARS HEINKE — Karlsruher Institut für Technologie, Karlsruhe, Germany.

Room-temperature ionic liquids (ILs) are molten organic salts. Studying their dynamic properties under nanoporous confinement, such as in metal-organic frameworks (MOFs), is a crucial aspect of fundamental science and can enhance applications like batteries and supercapacitors. Here, we utilize experiments based on MOF thin films and impedance spectroscopy, combined with molecular dynamics simulations. This provides unique insights into their molecular properties: At low IL loadings, the IL cations and anions drift along the electric field in opposite direction. However, at higher concentrations, the ions in the pores mutually obstruct the pathways, leading to a decrease in mobility. This pore blockage results in non-uniform IL density and ion bunching in obstructed pores. By adding lithium in IL, the presence of lithium prevents the formation of Li-anion dimers and the pore blockage and the collapse in conductivity at elevated IL concentrations. The pore size of the MOF confinement also significantly impacts the ion mobility. Smaller pores hinder passage and cause concentration-dependent mobility, while larger pores have minimal interference. We show that the cut-off pore window size corresponds to the diameter of the IL cation-anion dimer. Therefore, optimizing pore size is critical for achieving highly mobile nanoconfined ILs.

CPP 17.11 Tue 12:30 H 0107

Multiscale modeling of ionic liquids under shear — ●ABBAS GHOLAMI¹, SEBASTIAN KLOTH², ZHEN-HAO XU³, MICHAEL VOGEL², KURT KREMER¹, TORSTEN STUHEN¹, and JOSEPH F. RUDZINSKI^{1,4} — ¹Max Planck Institute for Polymer Research, Mainz — ²Institute of Condensed Matter Physics, TU Darmstadt — ³Center for Data Processing, JGU Mainz — ⁴Institut für Physik und IRIS-Adlershof, Humboldt-Universität zu Berlin

Room-temperature ionic liquids (ILs) hold significant promise for various applications thanks to their unique attributes like adjustable physicochemical properties. Molecular Dynamics (MD) simulations provide valuable insights into the behavior of ILs, enhancing our understanding of their properties. Using a coarse-grained representation reduces the computational costs considerably by reducing the intermolecular friction and smoothing the free energy surface while providing detailed information at the molecular level. However, in order to use such models to investigate the transport properties, it is necessary to explore the corresponding time scalings when changing model resolutions.

In this study, the behavior of the C4MIM-PF6 IL is investigated under shear using all-atom and coarse-grained MD simulations. Shearing is introduced accurately utilizing the Lees-Edwards boundary condition while conserving momentum and remaining compatible with periodic boundary conditions. To gain a deeper understanding of the coarse-grained model's behavior under shear, the structure and dynamics of the IL are studied at various shear rates, while assessing the consistency of speed-up factors between the cations and anions.

CPP 17.12 Tue 12:45 H 0107

Effect of Molecular Hydrogen on Surface Tension, Surface Enrichment, and Viscosity of Two Imidazolium-Based Ionic Liquids by Molecular Dynamics Simulations — ●GYÖRGY HANTAL¹, ARSHA CHERIAN¹, CHRISTIAN WICK¹, ZIWEN ZHAI², THOMAS KOLLER², and ANA-SUNCANA SMITH¹ — ¹PULS Group, Department of Physics, Interdisciplinary Center for Nanostructured Films, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany — ²Institute of Advanced Optical Technologies and Thermophysical Properties (AOT-TP), Department of Chemical and Biological Engineering Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany

Ionic liquids (ILs) draw attention for their customizable nature in specific tasks through precise combinations of functionalized cations and

anions. In supported catalytic systems, IL films host the catalyst and reactant, aiming for accumulation to enhance yield. Despite hydrogen's significance in industrial processes, its impact on IL properties remains insufficiently explored. This study uses molecular dynamics simulations to elucidate hydrogen's influence on two ILs across tem-

peratures and pressures. Viscosity and surface tensions decrease with rising temperature and hydrogen pressure, which is confirmed experimentally. Simulations reveal hydrogen surface enrichment, which is more significant at lower temperatures and pressures. Structural analysis provides a molecular-level interpretation of these observations.