

## CPP 16: Modeling and Simulation of Soft Matter II

Time: Tuesday 9:30–13:00

Location: H 0106

CPP 16.1 Tue 9:30 H 0106

**pyMBE: the Molecule Brewer for ESPResSo** — PAOLA B. TORRES<sup>1</sup>, DAVID BEYER<sup>2</sup>, SEBASTIAN P. PINEDA<sup>3</sup>, PETER KOŠOVAN<sup>3</sup>, and PABLO M. BLANCO<sup>4</sup> — <sup>1</sup>Grupo de Bionanotecnología y Sistemas Complejos. Infap-CONICET & Facultad Regional San Rafael, Universidad Tecnológica Nacional, 5600 San Rafael, Argentina — <sup>2</sup>Institute for Computational Physics, University of Stuttgart, D-70569 Stuttgart, Germany — <sup>3</sup>Department of Physical and Macromolecular Chemistry, Charles University, 128 00 Prague 2, Czechia — <sup>4</sup>Department of Physics, NTNU - Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

We introduce pyMBE ([gitlab.com/blancoapa/pyMBE](https://gitlab.com/blancoapa/pyMBE)), a Python-based molecule brewer designed for ESPResSo. pyMBE provides a suite of tools aimed at streamlining the construction of coarse-grained representations for molecules characterized by complex architectures, such as polyelectrolytes, peptides, and globular proteins within the ESPResSo molecular dynamics software. Notably, the tool focuses on automating the setup and simulation of chemical reactions in charge-regulating systems, i.e. ionic soft matter with weak acid/base groups. To accommodate a broad range of systems, pyMBE supports chemical reactions in different ensembles, such as constant-pH and grand-reaction. The versatility of the software is exemplified through three practical applications: weak polyelectrolytes in dialysis, charge-regulating peptides, and globular proteins.

CPP 16.2 Tue 9:45 H 0106

**Flat-histogram Monte Carlo: algorithm parameters optimization and application extension** — TIMUR SHAKIROV — University of Halle, Halle, Germany

Recent developments in flat-histogram Monte Carlo sampling methods have notably expanded our possibility of studying complex physical systems. Despite their decades-long history and established convergence, the problem of optimal parameter selection and the relation between different flat-histogram techniques like Stochastic Approximation Monte Carlo (SAMC) and Multicanonical sampling (MUCA) still present uncharted areas of research. This study proposes general principles for optimizing parameter selection in SAMC, revealing that the optimal convergence achievable is similar to that of MUCA. A significant advancement could be reached by the combination of importance sampling with SAMC or MUCA algorithms, which effectively minimizes the impact of algorithm parameters on the accuracy of estimations. This improvement not only enhances the stability and reliability of simulations but also facilitates an expanded exploration of model parameters within a single flat-histogram simulation run. For example, this approach allows for a more detailed analysis of roles of different energy contributions and enables the estimation of pressure in isochoric Monte Carlo simulations without the need for force or virial computations.

CPP 16.3 Tue 10:00 H 0106

**MAICoS: A toolkit for the Molecular Analysis of Interfacial and Confined Systems** — HENRIK STOOS<sup>1</sup>, PHILIP LOCHE<sup>2</sup>, ADYANT AGRAWAL<sup>3</sup>, MAXIMILIAN BECKER<sup>4</sup>, KIRA FISCHER<sup>3</sup>, SIMON GRAVELLE<sup>5</sup>, MARC SAUTER<sup>3</sup>, PHILIPP STÄRK<sup>1</sup>, SRIHAS VELPURI<sup>1</sup>, and ALEXANDER SCHLAICH<sup>1,3</sup> — <sup>1</sup>SC SimTech, University of Stuttgart — <sup>2</sup>COSMO, EPFL — <sup>3</sup>ICP, University of Stuttgart — <sup>4</sup>Fachbereich Physik, FU Berlin — <sup>5</sup>LIPhy, Université Grenoble Alpes

MAICoS (Molecular Analysis for Interfacial and Confined Systems) is an open-source object-oriented toolkit written in Python tailored to analyse the structural and dynamic properties of interfacial and confined environments derived from molecular simulations. It provides a versatile suite capable of extracting density, orientation, dielectric profiles, structure factors and transport properties from trajectories from a variety of molecular simulation software packages.

The strength of the toolkit lies in its modular design philosophy, which allows analysis in cartesian, cylindrical or spherical coordinates. The use of generic weighting functions extends the adaptability and utility of this software package and illustrates its flexibility and applicability in a wide range of systems. This comprehensive approach facilitates comparative analyses that would prove difficult without a standardised framework. The contribution of MAICoS lies not only in its analytical capabilities, but also in promoting a consistent and

interoperable platform for the advancement of FAIR workflows. Furthermore, users can use the framework with tested basic classes to rapidly implement their own robust workflows.

CPP 16.4 Tue 10:15 H 0106

**Classical and Quantum Molecular Dynamics to Study Open Molecular Systems** — SARA PANAHIAN JAND and LUIGI DELLE SITE — Institute for Mathematics, Freie Universität Berlin, Germany

Open systems that exchange particle and energy with the environment represent a major challenge for theoreticians. Recently, a model has been derived for a system of molecules that continuously, in a dynamical fashion, exchanges energy and particles with the reservoir considering the physical consistency [1]. The idea is based on the Grand Canonical description of a small open subregion treated at high resolution embedded in a large mean-field reservoir. This has been implemented in the latest version of the adaptive resolution scheme (AdResS). As an example, in order to reach a higher efficiency in treating the nuclear quantum effects, the molecular resolution has been switched from being treated by path integral molecular dynamics (PIMD) with high number of degrees of freedom to a non-interacting point particles. Additionally, the quantum effects manifested as delocalization of hydrogen atoms in the aggregation process of two Fullerene molecules have been studied [2]. In a further step, the aforementioned computational protocol has been extended to couple an open quantum system of molecules with a classical environment. The exchange of molecules between QM and MM region occurs under principles based on physical consistency at macroscopic level and at (microscopic) electronic level [3].

References: [1] L. Delle Site, et al., *J. Math. Phys.*, 61, 8 (2020). [2] S. Panahian Jand, et al., *Front. Chem.*, 10 (2022). [3] L. Delle Site, *Comput. Phys. Commun.*, 222 (2018).

CPP 16.5 Tue 10:30 H 0106

**Physical model for magneto-mechanical behavior of magneto-active cylinders** — MEHRAN ROGHANI<sup>1</sup>, DIRK ROMEIS<sup>1</sup>, GASPER GLAVAN<sup>2</sup>, INNA A. BELYAEVA<sup>2</sup>, MIKHAIL SHAMONIN<sup>2</sup>, and MARINA SAPHIANNIKOVA<sup>1</sup> — <sup>1</sup>Institute Theory of Polymers, Leibniz-Institut für Polymerforschung Dresden e. V., Dresden, Germany — <sup>2</sup>East Bavarian Centre for Intelligent Materials (EBACIM), Ostbayerische Technische Hochschule (OTH) Regensburg, Regensburg, Germany

Magneto-Active Elastomers (MAEs) are adaptive composites made of a soft elastomeric matrix with embedded magnetizable micro-particles. Magnetic interactions among the particles enable remote deformation and active modifications of mechanical properties under external magnetic field. This study presents a physically-based model for cylindrical MAE samples that unifies two scales. We use dipolar mean field approach for taking into account the magnetic interactions at micro- and macro-scale. A penalty term is added to the elastic energy due to particle restructuring within the elastomeric matrix. The restructuring causes initially isotropic material to become more and more anisotropic as the magnetic field increases. This transition is taken into account with a transversely isotropic Neo-Hookean material model. The resulting model enables us to explore how microstructure evolution influences the mechanical and magnetic behavior of MAE samples. The model predictions are verified against experiments conducted with different particle volume fractions. The study emphasizes the crucial role of microstructure evolution in modeling MAE deformation, magnetization, and stiffness.

CPP 16.6 Tue 10:45 H 0106

**Mixed-Resolution Force Probe Simulations** — MARCO OESTEREICH, JÜRGEN GAUSS, and GREGOR DIEZEMANN — Department Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

Force probe molecular dynamics (FPMD) simulations are a well-established technique to investigate the conformational transitions in complex molecular systems. In a standard version of these simulations one end of the molecule is fixed in space and the other end is pulled apart with a constant velocity, very similar to the experimental protocols of dynamic force spectroscopy. In order to overcome the problem that the pulling velocities accessible in simulations are much larger than those in experiments usually coarse-graining (CG) methodologies are used to speed up FPMD simulations. In order to

keep atomistic resolution for the solute allowing for a detailed investigation of conformational kinetics we apply the adaptive resolution scheme (AdResS) in our study. In this scheme the solute and the solvent within a well-defined spherical region are treated in an all-atom (AA) manner. Between this region and a CG region outside there is a hybrid region which allows for switching between the two resolutions. We have shown earlier that this setup works well provided the AA region is large enough and the interactions in the CG region are treated via an iterative Boltzmann inversion procedure(1). We present results for two systems undergoing conformational transitions and demonstrate that also a treatment of the CG part of the system employing an ideal gas approximation works extremely well.

### 30 min. break

CPP 16.7 Tue 11:30 H 0106

**Exploring the Role of Ionic Liquids in Polyethylene Terephthalate Glycolysis by Molecular Dynamics Simulations** — ●MOHAMED NOSIR and MANUEL A ORTUÑO — CIQUS, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Recently, ionic liquids (ILs) have been used as environmentally friendly catalysts in the depolymerization of polyethylene terephthalate (PET). We hereby introduce a computational study to understand the function of ILs as a catalyst in the chemical recycling of PET in the presence of ethylene glycol (EG). Our study focuses on the investigation of the roles of cholinium phosphate ( $[Ch]^+$ )<sub>3</sub> [PO<sub>4</sub>]<sup>3-</sup> IL in the glycolytic degradation of PET. For this issue, classical molecular dynamics (MD) simulations were performed to analyze the structure and thermodynamic properties of the IL/EG/PET ternary systems, under a wide range of experimental conditions. After the equilibration of the system, our MD simulation results provide insights into the potential mechanism of PET glycolysis catalyzed by ILs. Our findings demonstrate that anions are primarily responsible for establishing significant hydrogen bonding with EG. Meanwhile, cations interact with the carbonyl oxygen of PET. Our MD simulations exhibit remarkable agreement with the most recent theoretical and experimental investigations. The employed approach for MD simulation in this particular investigation has the potential to be expanded upon in order to explore additional systems consisting of ILs, alcohols, and PET. As a result, valuable knowledge can be gained regarding the underlying mechanism and kinetics of PET depolymerization.

CPP 16.8 Tue 11:45 H 0106

**Universal pairwise interatomic van der Waals potentials from dipolar polarizabilities and  $C_6$  dispersion coefficients** — ●ALMAZ KHABIBRAKHMANOV, DMITRY FEDOROV, and ALEXANDRE TKATCHENKO — Department of Physics and Materials Science, University of Luxembourg, L-1511 Luxembourg

van der Waals (vdW) interactions play an essential role in determining the structure and properties of many molecular and solid-state systems. Classical force fields used in simulations of large systems still mostly rely on empirical Lennard-Jones (LJ) description of vdW interactions. However, LJ potentials are usually prone to large errors and lack physics behind. Therefore, universal and accurate yet non-empirical vdW potentials are strongly desired. Here, we derive the analytical pairwise vdW-QDO potential between atoms, which depend just on two *non-bonded* atomic parameters: static dipole polarizability  $\alpha_1$  and dispersion coefficient  $C_6$ . This makes our potential universal, i.e. applicable to all chemical elements.

Our vdW-QDO potential, based on the coarse-grained quantum Drude oscillator (QDO) model for electronic response, shows excellent accuracy for noble-gas dimers against state-of-the-art *ab initio* and analytical methods. In addition, we demonstrate that the vdW-QDO potential can accurately describe group II atomic dimers. We also apply the vdW-QDO potential to small organic molecules and layered materials. We show that the overbinding error increases with the system size, which emphasizes the growing importance of many-body effects in the extended systems.

CPP 16.9 Tue 12:00 H 0106

**Solvation Shell Thermodynamics of Extended Hydrophobic Solutes** — ●MADHUSMITA TRIPATHY<sup>1</sup>, SWAMINATH BHARADWAJ<sup>1,2</sup>, and NICO VAN DER VEGT<sup>1</sup> — <sup>1</sup>Department of Chemistry, TU Darmstadt, Darmstadt, Germany 64297 — <sup>2</sup>Department of Chemical Engineering, Shiv Nadar University, Delhi-NCR, India 201314

Interfacial solvent density fluctuations play an important role in hy-

drophobic effects, which regulate the functional characteristics of a wide variety of soft matter systems. The loss of water hydrogen bonds near large non-polar solutes leads to enhanced density fluctuations, which make their hydration shells susceptible to small perturbations. Cosolutes can regulate the solute's hydration behavior by enhancing/quenching these fluctuations. To understand the underlying molecular mechanisms, we employ computer simulation to investigate the effect of two adsorbing cosolutes, urea and methanol, on the interfacial thermodynamics of a model extended hydrophobic solute. We find that urea accumulation quenches the interfacial fluctuations, leading to a decrease in the solvation shell compressibility, while methanol accumulation enhances the fluctuations, leading to an increase in compressibility[1]. Analyses on solvation shells energetics indicates that the effect of these adsorbing cosolutes on the density fluctuations, and thereby the stability of the solvation shell, is strongly coupled to their hydration behavior. The observations from this simple model can be discussed in the context of cosolute induced swelling and collapse of polymers in aqueous solutions.

1. M. Tripathy et al. *J.Chem.Phys.* **2022**, 156, 164901

CPP 16.10 Tue 12:15 H 0106

**Thermal dependence of the hydrated proton and optimal proton transfer in the protonated water hexamer** — ●MICHELE CASULA<sup>1</sup>, FÉLIX MOUHAT<sup>2</sup>, MATTEO PERIA<sup>1</sup>, TOMMASO MORRESI<sup>3</sup>, RODOLPHE VUILLEUMIER<sup>4</sup>, and A. MARCO SAIITA<sup>1</sup> — <sup>1</sup>IMPMC, Sorbonne Université, CNRS, MNHN, Paris, France — <sup>2</sup>Saint Gobain Research Paris, Aubervilliers, France — <sup>3</sup>ECT\*-Fondazione Bruno Kessler\*, Trento, Italy. — <sup>4</sup>PASTEUR, École normale supérieure, Paris, France

Water is a key ingredient for life and plays a central role as solvent in many biochemical reactions. However, the intrinsically quantum nature of the hydrogen nucleus, revealing itself in a large variety of physical manifestations, including proton transfer, gives rise to unexpected phenomena whose description is still elusive. Here we study, by a combination of state-of-the-art quantum Monte Carlo methods and path-integral molecular dynamics, the structure and hydrogen-bond dynamics of the protonated water hexamer, the fundamental unit for the hydrated proton. We report a remarkably low thermal expansion of the hydrogen bond from zero temperature up to 300 K, owing to the presence of short-Zundel configurations, characterised by proton delocalisation and favoured by the synergy of nuclear quantum effects and thermal activation. The hydrogen bond strength progressively weakens above 300 K, when localised Eigen-like configurations become relevant. Our analysis, supported by the instanton statistics of shuttling protons, reveals that the near room-temperature range from 250 K to 300 K is optimal for proton transfer.

CPP 16.11 Tue 12:30 H 0106

**On temperature and coordination effects in liquid water in Raman and infrared spectroscopies: Fingerprinting vibrational frequencies via molecular dynamics** — RODOLPHE VUILLEUMIER and ●ARI PAAVO SEITSONEN — Département de Chimie, École Normale Supérieure, Paris

Water is an ubiquitous liquid that has several exotic and anomalous properties. Despite its apparent simple chemical formula, its capability of forming a dynamic network of hydrogen bonds leads to a rich variety of physics. We study [1] the vibrations of water using molecular dynamics simulations, mainly concentrating on the Raman and infrared spectroscopic signatures. We investigate the consequences of the temperature on the vibrational frequencies, and we enter the details of the hydrogen bonding coordination by using restrained simulations in order to gain quantitative insight on the dependence of the frequencies on the neighbouring molecules. Further we consider the differences due to the different methods of solving the electronic structure to evaluate the forces on the ions, and report results on the angular correlations, isotopic mixtures HOD in H<sub>2</sub>O/D<sub>2</sub>O and the dielectric constants in water.

[1] *Vibrational spectroscopies in liquid water: on temperature and coordination effects in Raman and infrared spectroscopies*, Rodolphe Vuilleumier and Ari Paavo Seitsonen; *Condensed Matter Physics* **26**, 30101 (2023); DOI: 10.5488/CMP.26.33301

CPP 16.12 Tue 12:45 H 0106

**Impact of Electrolyte Composition on Reorganization Energies** — ●SOUVIK MITRA, DIDDO DIDDENS, and ANDREAS HEUER — Institut für physikalische Chemie, Universität Münster, Corrensstraße 28/30, 48149 Münster

Reorganization energy plays a pivotal role in Marcus theory, which elucidates the mechanism of electron transfer reactions between redox-active organic molecules such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) in different solvents. This theoretical work[1] reveals that the presence of salt enhances the rate of homogeneous charge transfer reactions by amplifying the reorganization energy. Our study reveals a connection between reorganization energy and local solvation environment surrounding the redox molecule.

This research also underscores the importance of quantum phenomena, including charge delocalization, that contribute to extra stability after redox reactions, a feature not present in conventional classical force fields. As a result, we propose adopting machine learning techniques as a means to reduce reliance on demanding quantum mechanical computations and to accurately estimate reorganization energy in intricate systems.

[1] DOI: 10.26434/chemrxiv-2023-5z186-v2