

CONIN H2020-MSCA-RISE-2016

Action acronym: CONIN

Action full title: "Effects of confinement on inhomogeneous systems"

Grant agreement No 734276

Work Package 2

**Modelling of systems with dominant electrostatic interactions
(Months: 1-66)**

Task 2.4

**Effects of confinement on phase diagram
and concentration profiles of ionic model systems**

Task 2.5

**Experimental study of nanostructured surfaces
by electrochemistry methods.**

(Months:37-66)

Deliverable D2.4

Effects of specific porous structure on ionic liquids

In the period January 2020-June 2022 the planned tasks were:

Task 2.4: Effects of confinement on phase diagram and concentration profiles of ionic model systems.

The effects of disordered porous media on the phase behaviour of model ionic liquids will be studied. New theoretical approaches will be formulated based on the combination of the methods of liquid state theory: the CV method, the SPT and the theory of associative liquids. Matrices of different porosities and topologies as well as several models of ionic liquids will be considered. The effect of orientation anisotropy of a porous medium will be taken into account. A new tool based on the inhomogeneous 3D OZ approximation will be extended for the study of concentration profiles, and charge distributions. The approach will be applied to ionic liquids confined in complex topologies (silica gels, zeolite templated carbons, etc ..) and simple regular pores. The extension of the approach to molecular ionic liquids with both flexible and rigid molecular structures will be one of the key goals of this task.

Lead Participant: CSIC

CSIC, ICMP, CPT, BSTU, IPC will perform analytical, numerical and simulation studies.

Task 2.5: Experimental study of nanostructured surfaces by electrochemistry methods.

We plan experimental study of deposited nanostructured thin films based on nanoparticles as building units on solid surfaces. In particular, nanoparticles production and their assembly during film formation processes will be investigated and the role of different interactions will be pointed out. The relationship between the film architecture and different interactions will be established.

Lead Participant: CPT

CPT and BSTU groups will perform experiments. ESR from BSTU will conduct experiments in the Taleb group from CPT during a long-term visit using the modern experimental facilities, and ER from the CPT will visit BSTU experimental electrochemistry lab.

The activities in WP2 in months 37-66 were the following:

1. Task 2.4: Effects of confinement on phase diagram and concentration profiles of ionic model systems.

- (a) Development of the theory of phase transitions in ionic liquids
- (b) Fluid-fluid phase behaviour in the explicit hard spherocylinder solvent ionic model confined in a disordered porous medium

2. Task 2.5: Experimental study of nanostructured surfaces by electrochemistry methods.

Anti-corrosion coatings formed based on various cationic surfactants with various aliphatic and aromatic ammonium cations.

3. Continuation of tasks 2.1-2.3 and additional tasks associated with WP2:

- (a) Conductivity in three-dimensional lattice models with competing interaction
- (b) Theoretical description of mesoscopic inhomogeneities in concentrated electrolytes
- (c) Charge and electric field distributions in the interelectrode region of an inhomogeneous solid electrolyte

1. Task 2.4: Effects of confinement on phase diagram and concentration profiles of ionic model systems.

1.a Development of the theory of phase transitions in ionic liquids

1.a.1 Ionic-liquid-solvent mixtures

We have used an analytical model developed in our earlier study to investigate the behaviour of ionic liquid (IL)-solvent mixtures in slit mesopores. Our calculations revealed a capillary ionization/deionization transition (i.e., a transition between IL-rich and IL-poor phases) that could be induced by changing applied voltage or temperature (Figs. 1,2). With

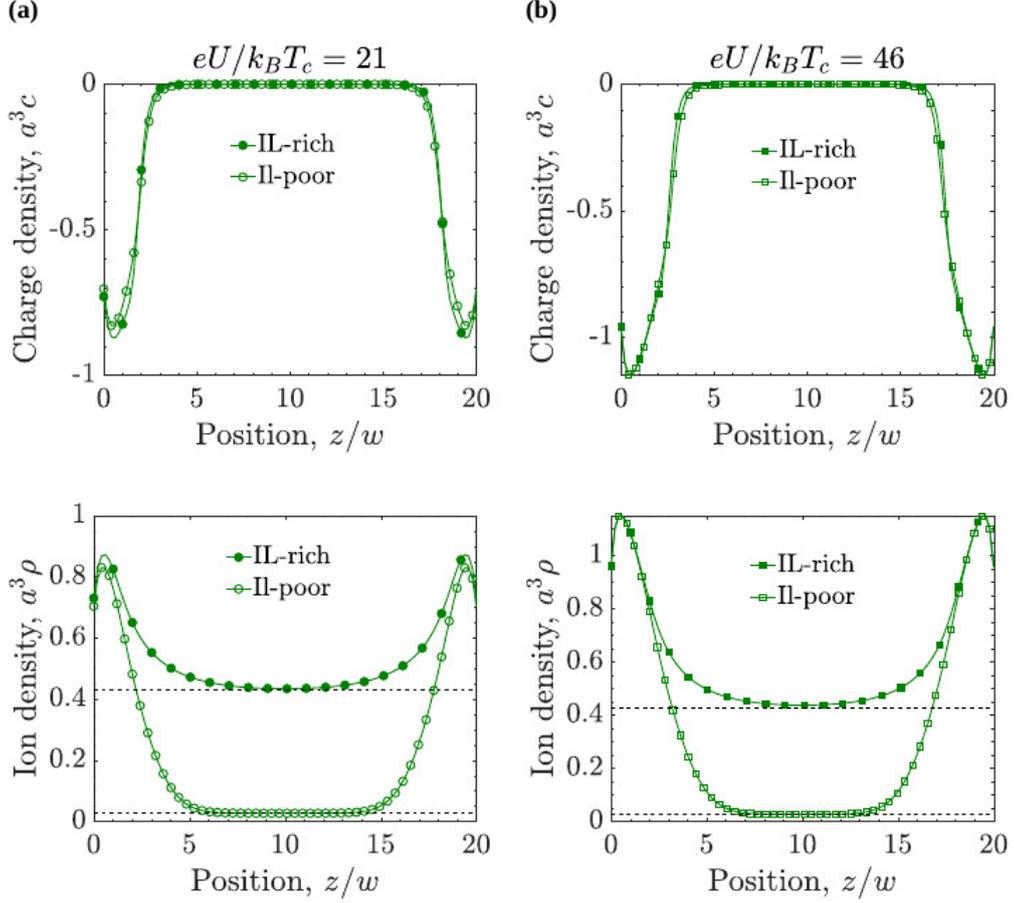


FIG. 1: Capillary ionization transition in a charged slit-shape nanopore for moderate and strong voltage U in the left and right panel, respectively. In the upper row the charge density, and in the lower row the ion density in the two coexisting phases are shown. In all the plots, the chemical potential $\mu/k_B T_c = -4.57$, the temperature $T/T_c = 0.838$, slit width $w = 20a$, and ionophilicity $a^3 h_s/\xi_0 = 0.25$, where T_c is the critical temperature of the demixing transition, ξ_0 is the bare correlation length, h_s measures the hydrophilicity of the walls, and a is the ion diameter. The dashed horizontal lines show the bulk values in the corresponding phases. The filled symbols represent the IL-rich phase while the unfilled symbols denote the IL-poor phase.

general thermodynamic considerations and numerical calculations, we found that a capillary ionization transition is accompanied by a jump in the accumulated charge and stored energy density (Fig. 3). The jump in energy storage may find useful applications in heat-to-energy conversion.

Besides we investigated the concentration fluctuations in a simple model of electrolyte (two positively and negatively charged Lennard-Jones spheres in a solution of an uncharged

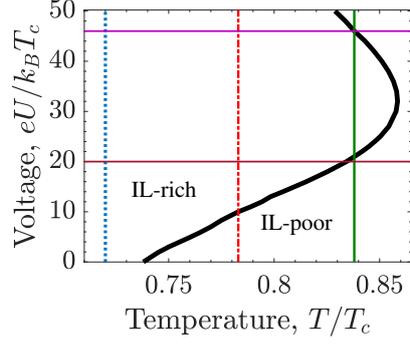


FIG. 2: Phase diagram in the temperature-voltage plane. The thick black line shows a line of first-order transitions between the IL-rich and IL-poor phases. The thin horizontal lines show the values of the voltage used in Fig. 3.

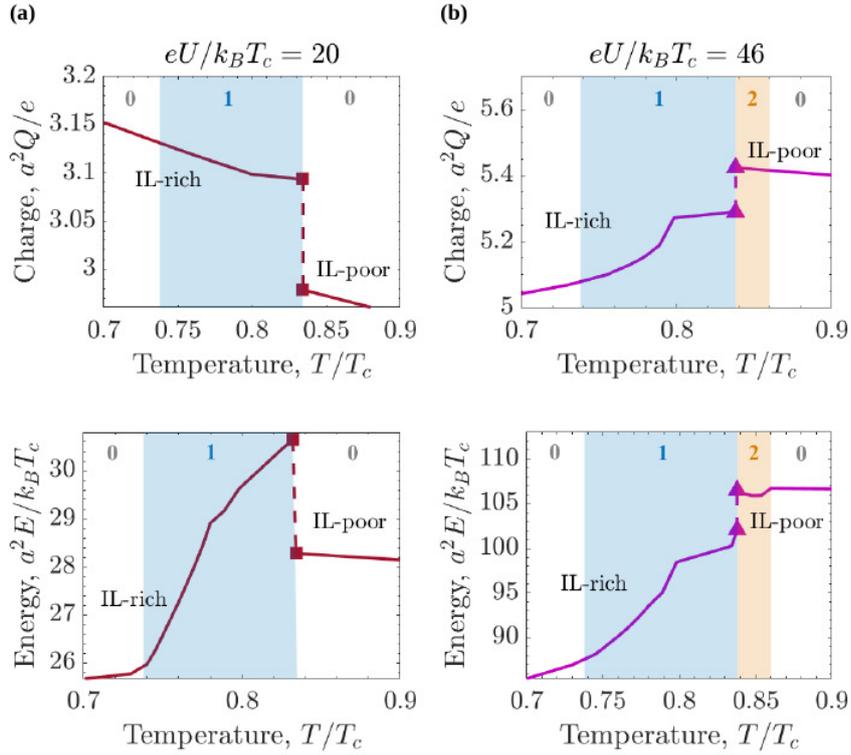


FIG. 3: Accumulated charge and stored energy in equally charged slit-shaped mesopore as a function of temperature. (a) and (b) shows the results for different applied potential differences U . Accumulated charge is shown on top plots and stored energy on the bottom plots. The colored areas show the regions with one and two voltage-induced transitions as indicated by the corresponding numbers (see Fig. 2).

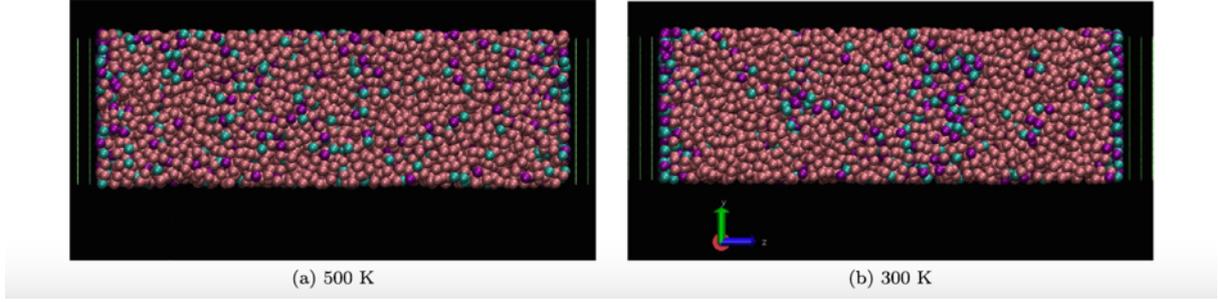


FIG. 4: Effects of clustering when approaching phase separation conditions

Lennard-Jones liquid) confined between electrodes formed by parallel graphene layers. The model can be tuned to reproduce a phase separation between the electrolyte and the solvent by minimal changes in temperature, as seen in Figure 4.

We have first used constant potential molecular dynamics simulations, and determined that below 1V one can safely use constant charge simulations and integrate Poisson equations to determine the potential in a consistent fashion, as long as one is not interested in the differential capacitance, that can only be measured appropriately using the charge fluctuations in the electrodes. After these preliminary studies, we have performed extensive constant charge simulations. The effect of the proximity to the demixing transition on the electric double layers is analyzed and compared to the results of our continuum mean field theory. In agreement with our previous theoretical findings, we observe a considerable enhancement of the capacitance when temperature is lowered approaching the demixing transition for dilute ionic solutions (see Figure 5). This enhancement is less visible when the ionic concentration is increased. Moreover, we observe the new shape of the capacitance, with a maximum at potential of zero charge, and symmetric maxima for positive and negative voltages. In this way we have confirmed previous theoretical findings that suggest that by a careful tuning of the thermodynamic working condition of Electric Double Layer super capacitors it might be possible to enhance their capacitance (and hence their energy storage capacity) by a factor one third.

We continued investigations initiated during the secondments that took place earlier (Alina Ciach and Svyatoslav Kondrat from IPC to BSTU) and continued the collaboration between IPC and CSIC using the internet means of communication

The results dissemination:

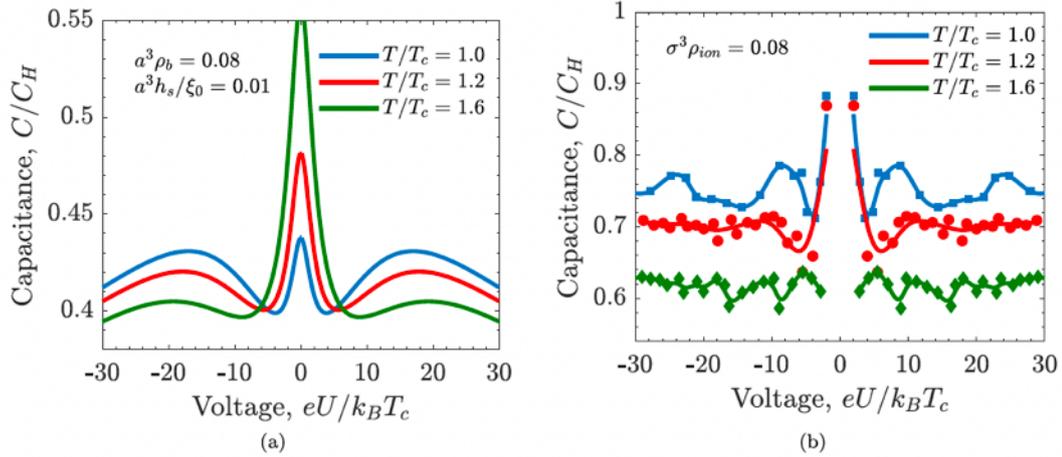


FIG. 5: Theoretical (left) and simulated (right) integral capacitances vs voltage when approaching the demixing temperature

Publications:

- Carolina Cruz, Svyatoslav Kondrat, Enrique Lomba, and Alina Ciach, *Capillary Ionization and Jumps of Capacitive Energy Stored in Mesopores*, J. Phys. Chem. C , **125**, 19, 1024310249, (2021). The results of the publication were presented on the cover page of the journal. DOI:10.1021/acs.jpcc.1c00624
- Carolina Cruz, Enrique Lomba, Alina Ciach, *Capacitance response and concentration fluctuations close to ionic liquid-solvent demixing*, Journal of Molecular Liquids, **346**, 117078, (2022)
- Carolina Cruz and Alina Ciach, *Phase transitions and electrochemical properties of ionic liquids and ionic liquid—Solvent mixtures*, Molecules, **26** (12), 3668 (2021)

Conference presentation:

- Carolina Cruz, Alina Ciach, Enrique Lomba and Svyatoslav Kondrat, *Electrical Double Layers Close to Ionic Liquid-Solvent Phase Transitions*, online conference 11th LIQUID MATTER CONFERENCE 2020/2021 Prague, Czech Republic, July 19-23, 2021 , poster <https://www.lmc2020.cz/>
- Carolina Cruz, Alina Ciach, Enrique Lomba and Svyatoslav Kondrat, *Electrical Double Layers Close to Ionic Liquid-Solvent Phase Transitions*, IV CONIN workshop 'Com-

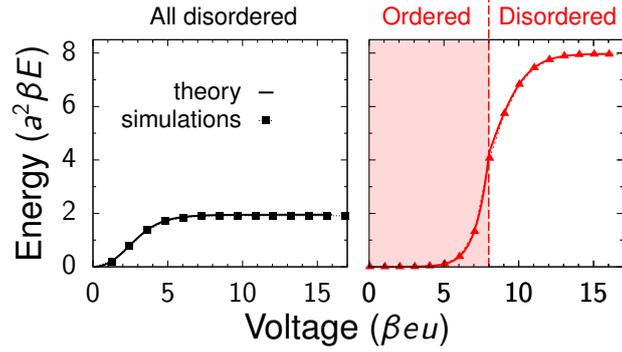


FIG. 6: Stored energy as a function of applied potential. The energy storage is enhanced when an ionic liquid is ordered at zero voltage. Note an excellent agreement between the theory and simulations.

plex interactions, clustering, swarming, and effects of confinement’, 7-10 June 2022, Serock, Poland.

1.a.2. Ionic liquids in ultranarrow slit confinements

To study the behaviour of ions confined to a narrow slit, we considered a two-dimensional lattice model with nearest-neighbour interactions. We solved this model analytically within the Bethe-lattice approach and performed Monte Carlo simulations. The analytical results showed a surprisingly good agreement with the simulations. We also revealed a correlation between the ability to store energy and ordering of ions inside an uncharged pore, see Fig. 6, which may find practical applications. We also studied how the extend of the screened electrostatic interaction between the ions affects the structure and capacitive properties of confined ionic liquids. To this end, we extended our lattice model to include next-nearest and further neighbor interactions. With Monte Carlo simulations and analytical calculations, we found that the next-to-nearest interactions increase the capacity and stored energy density and could significantly affect the phase behavior. In particular, in a certain voltage range, we revealed the appearance of large-scale mesophases (Fig. 7), which have not been previously reported, but which can play an important role in energy storage.

This work was done during the secondments to Warsaw (IPC) of Ya.G. Groda (BSTU) in years 2020-2021.

The results dissemination were:

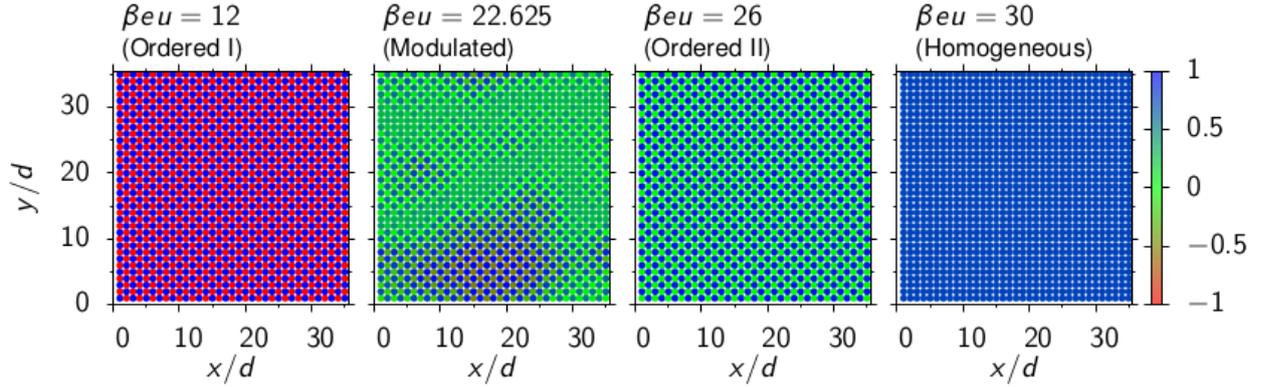


FIG. 7: Sequence of phases as a function of the applied potential u appearing in quasi two-dimensional system of ions confined to a narrow slit pore.

1. Groda Ya., Dudka M., Kornyshev A. A., Oshanin G., Kondrat S. Superionic liquids in conducting nanoslits: insights from theory and simulation *J. of Phys. Chem. C* 125, 4968-4976. (2021); DOI: <https://doi.org/10.1021/acs.jpcc.0c10836>.

2. Groda Ya., Dudka M., Oshanin G., Kornyshev A. A., Kondrat S. Ionic liquids in conducting nanoslits: How important is the extent of the screened electrostatic interactions? // *Journal of Physics : Condensed Matter* 2022, vol. 34. art. no. 26LT01 (8 pp). DOI: <https://doi.org/10.1088/1361-648X/ac6307>

1.b Fluid-fluid phase behaviour in the explicit hard spherocylinder solvent ionic model confined in a disordered porous medium

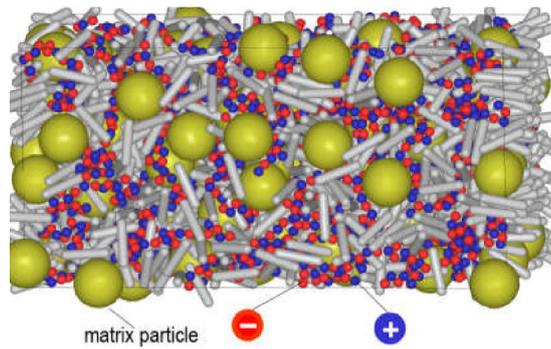


FIG. 8: Schematic presentation of the model under study.

We developed a theoretical approach that takes into account the effects of a disordered porous confinement on the liquid-liquid phase behaviour of the ionic solution modelled by

the restricted primitive model (RPM) with an explicit consideration of the neutral hard spherocylinder (HSC) solvent (Fig. 8). The theory is based on a combination of two approaches: the scale particle theory for the description of the reference system represented by a mixture of hard spheres and hard spherocylinders confined in a disordered hard-sphere matrix and the associative mean-spherical approximation (AMSA) for taking into account Coulomb interactions between ions. Alternatively, the mean spherical approximation is applied for the description of the ionic subsystem for comparison. For the considered solvent explicit model in a matrix, analytical expressions for pressure, free energy and partial chemical potentials are derived for the first time. Using these expressions, the liquid-liquid phase transition is studied, where one phase is enriched with ions and another one – with solvent particles. In the solvent-rich phase, the isotropic-nematic phase transition is observed due to the orientational ordering of the spherocylinder solvent particles at different porosities of a matrix. The effects of the matrix confinement and of the solvent particle elongation on the liquid-liquid and isotropic-nematic phase transitions are studied at different pressures. The role of association phenomena appearing between positively and negatively charged ions in phase behaviour of the considered ionic solutions under confinement is analysed.

A part of the initial stage of this work was done during the secondments of Taras Patsahan and Myroslav Holovko to Minsk. The authors benefited from discussions with George Bokun and Ruslan Lasovsky during their secondments to Lviv.

The results dissemination are:

- M. Hvozd M., O. Patsahan, T. Patsahan, M. Holovko, *Effects of disordered porous media on the phase behavior of the explicit solvent ionic model*, online conference 11th LIQUID MATTER CONFERENCE 2020/2021 Prague, Czech Republic, July 19-23, 2021, poster
- T.M. Patsahan, M.V. Hvozd, O.V. Patsahan, M.F. Holovko, *Effects of disordered porous medium on the phase behaviour in the explicit hard spherocylinder solvent ionic model*, IV CONIN workshop Complex interactions, clustering, swarming and effects of confinement”, Serock, Poland, June 7th-10th, 2022, online talk

Task 2.5: Experimental study of nanostructured surfaces by electrochemistry methods.

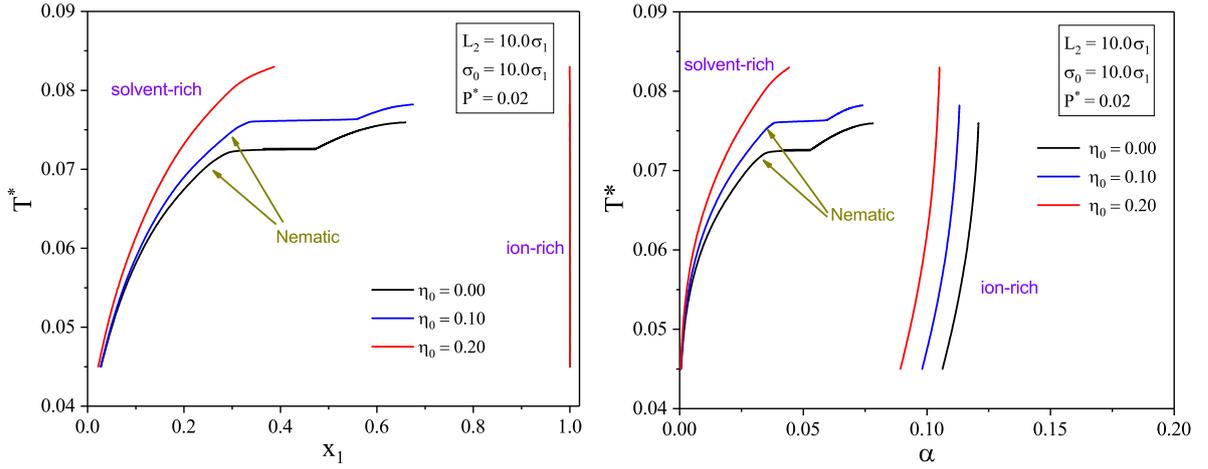


FIG. 9: Liquid-liquid phase diagrams of the RPM-HSC mixture in a disordered hard sphere matrix in the AMSA approximation at the reduced pressure $P^* = 0.02$ for the length of solvent particles $L_2 = 10\sigma_1$. The results are presented in the reduced temperature T^* -concentration x_1 plane (left panel) and in the reduced temperature T^* -degree of dissociation α plane (right panel) for different obstacles packing fraction η_0 : $\eta_0 = 0$ (black), $\eta_0 = 0.1$ (blue) and $\eta_0 = 0.2$ (red). σ_1 and σ_0 are the diameters of the ions and the matrix obstacles, respectively, $x_1 = \rho_1/\rho$ is the concentration of the solute, ρ_1 is the number density of the solute and ρ is the total number density of the solute and solvent particles.

Through the secondments of Hanna Pianka from BSTU to CPT and Abdelhafed Taleb from SU to BSTU we have studied:

Anticorrosive performance for the protection of steel using coatings based on different surfactants with various aliphatic and aromatic ammonium cations.

The effect of the molecular structure of the prepared quaternary ammonium salts, as well as the effect of their Critical Micelle Concentration (CMC), on the structure of their assembly into coatings was established. It has been shown that the formation of a homogeneous and dense surfactant layer with effective anti-corrosion properties depends mainly on the surfactant concentration and the number of voltammetry cycles, and little on its CMC. It has also been shown that the molecular structure of surfactants is a crucial parameter to be considered in the design of inhibitors, to improve the effectiveness of the anti-corrosion coatings they can form. Furthermore, the hydrophobic and barrier properties of the coatings are the consequence of a synergistic effect of the aliphatic and aromatic substituents of the

surfactants.

The results dissemination are:

Hanna Pianka, Sana Falah, Sandrine Zanna, Vladimir Bezborodov, Sergei Mi-khalyonok, Nina Kuz'menok, Alexander Chernik, Yanpeng Xue and Abdelhafed Taleb “Anticorrosion efficiency of inhibitors based on ammonium cation with different substituents: The influence of wettability and molecular structure”, *Coatings* 11 (2021) 1512.

TiO₂ aggregates of controlled size, based on TiO₂ nanoparticles of different sizes as building blocks, were prepared by hydrothermal synthesis. It was shown that the mechanism of aggregate formation depends on the efficiency of the collision and coalescence processes of TiO₂ nanoparticles. In addition, these TiO₂ aggregates were studied as potential negative insertion electrode materials for lithium-ion batteries. The influence of specific surface areas and pore size on capacity enhancement was discussed and conflicting effects were revealed.

The results dissemination:

Saida Mehrez, Wenpo Luo, Jolanta Swiatowska, Bousjema Bezzazi, Abdelhafed Taleb “Hydrothermal synthesis of TiO₂ aggregates and their application as negative electrodes for lithium-ion batteries: the conflicting effects of specific surface and pore size”, *Materials* 14 (2021) 916.

Continuation of tasks 2.1-2.3 and additional tasks associated with WP2:

3.a. Conductivity in three-dimensional lattice models with competing interactions

A three-dimensional model of a solid-state electrolyte with a slab geometry containing grain and intergranular interlayer is considered. The interlayer is described by layers characterized by additional interstitial energy barriers. The interaction between mobile ions consists of long-range electrostatic repulsion and short-range attraction. The system is located between two oppositely charged electrodes. The system is simulated by the Monte Carlo method. The Coulomb energy is determined by Ewald summation with the additional “vacuum regions” on both sides of the slab. The concentration profile of mobile ions was investigated under various conditions.

An increase of a layer with a reduced concentration near a positively charged wall with

an increase of the charge on it wall was noted. This effect becomes more noticeable with a decrease of the average mobile ions concentration.

It is shown that the presence of a grain boundary has practically no effect on the concentration distribution near the walls.

A comparison of the results with analytical calculations shows their quantitative discrepancy of not more than 15%.

In addition, the conductivity in a three-dimensional model, in which the grain boundary was simulated by a layer with segregated immobile ions, was studied. The dependencies of the particles number passing through the boundary, which is proportional to the electric current, on the reciprocal temperature are determined. These dependencies are typical for solid electrolytes. It was noted that an increase in the concentration of mobile ions, as well as an increase in the resistance of the grain boundary, leads to an increase in the activation energy, i.e. to reduce the lability of ions.

This work was done during the secondments to Warsaw (IPC) and Lviv (ICMP) of R.N. Lasovsky (BSTU) in 2021. **The results are summarized in the following publications:**

1. Lasovsky R. N., Gapanjuk D. V., Groda Ya. G. Modeling of three-dimensional solid electrolyte with a slab geometry/ Proceedings of BSTU, issue 3, Physics and Mathematics. Informatics, 2020, no. 1 (230), pp. 26;96;31 (In Russian)

2. Lasovsky R. N., Groda Ya. G., Gapanjuk D. V., Groda N. G. Conductivity in three-dimensional lattice models with competitive interaction. Proceedings of BSTU, issue 3, Physics and Mathematics. Informatics, 2021, no. 2 (248), pp. 28;96;32 (In Russian) DOI: <https://doi.org/10.52065/2520-6141-2021-248-2-28-32>

The results were also presented on:

1. Lasovsky R. N., Patsahan T. M. Monte Carlo Simulation of Solid Electrolyte with Slab Geometry. 84th Scientific and Technical Conference of the Teaching Staff, Researchers and Graduate Students.

2. Lasovsky R. N., Groda Ya. G., Patsahan T. M. Computer simulation of electrical conductivity in a solid ceramic electrolyte. 85th Scientific and Technical Conference of the Teaching Staff, Researchers and Graduate Students. Minsk, BSTU, February 1-13, 2021. Proc. book. P. 236. (in Russian, Lecture).

3. Lasovsky R.N., Groda Ya.G. Electric conductivity in lattice models with SALR-potential. IX International Scientific Conference "Actual problems of solid state physics",

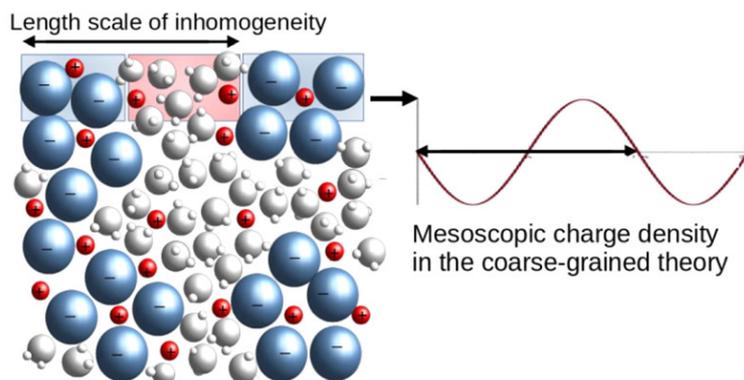


FIG. 10: Schematic representation of the model of water-in-salt electrolytes.

Minsk, Belarus, November 22 ;96j 26, 2021. Book of Abstracts. P. 222. (Lecture).

3.b. Theoretical description of mesoscopic inhomogeneities in concentrated electrolytes

A mesoscopic theory for water-in-salt electrolytes combining density functional and field-theoretic methods is developed in order to explain the unexpectedly large period of the oscillatory decay of the disjoining pressure observed in recent experiments for the LiTFSI (lithium bis(trifluoromethylsulfonyl)-imide) salt [T. S. Groves et. al., J. Phys. Chem. Lett. **12**, 1702 (2021)]. We assumed spherical ions with different diameters, and implicit solvent inducing strong, short-range attraction between ions of the same sign. For this highly simplified model (see Fig. 10), we calculated correlation functions. Our results indicate that mesoscopic inhomogeneities can occur when the sum of the Coulomb and the water-mediated interactions between like ions is attractive at short- and repulsive at large distances. We adjusted the attractive part of the potential to the water-in-LiTFSI electrolyte, and obtained both the period and the decay rate of the correlations in a semiquantitative agreement with the experiment. In particular, the decay length of the correlations increases nearly linearly with the volume fraction of ions (Figure 11).

The results are published in:

O Patsahan, A Ciach, *Mesoscopic inhomogeneities in concentrated electrolytes* ACS Omega **7** (8), 6655-6664 (2022).

O Patsahan, A Ciach, *Mesoscopic inhomogeneities in concentrated electrolytes*, IV CONIN workshop 'Complex interactions, clustering, swarming, and effects of confinement', 7-10 June

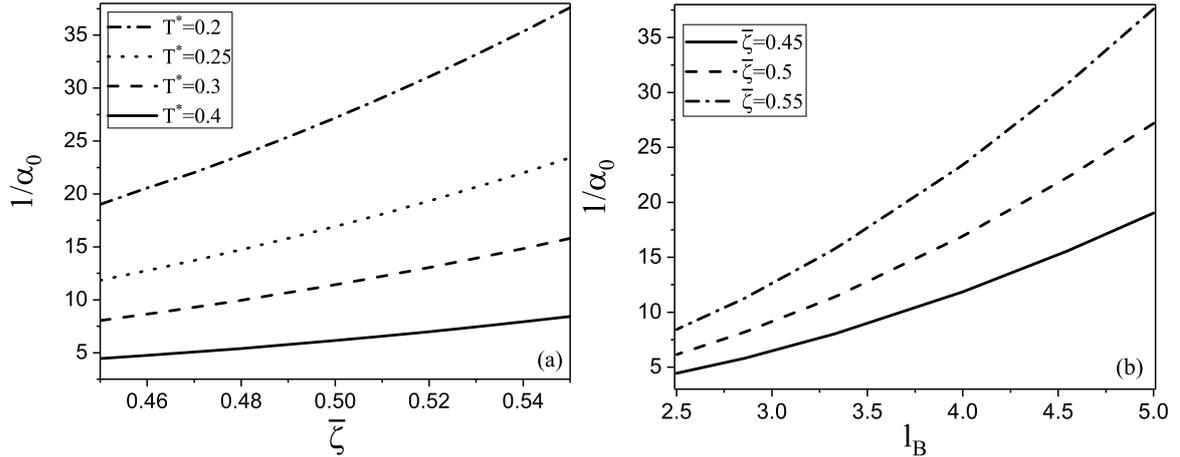


FIG. 11: The decay length $\lambda_s = \alpha_0^{-1}$ of the correlation functions $G_{\alpha\beta}(r)$ as a function of the total volume fraction of ions $\bar{\zeta}$ for $T^* = 0.2, 0.25, 0.3, 0.4$ (from the top to the bottom line) (panel a) and as a function of the Bjerrum length l_B for $\bar{\zeta} = 0.45, 0.5, 0.55$ (from the bottom to the top line) (panel b). $1/\alpha_0$ and l_b are in the a units, $a = (\sigma_+ + \sigma_-)/2 \approx 0.4nm$. The results are for the model with $\delta = 0.5$, $\epsilon_{++}^* = 5$, $\epsilon_{--}^* = 1$.

2022, Serock, Poland.

3.c. Charge and electric field distributions in the interelectrode region of an inhomogeneous solid electrolyte

A solid ionic conductor with cation conductivity in the interelectrode region was studied. Due to their large size, the anions were considered as fixed forming a homogeneous neutralizing electric background. The model can be used to describe properties of ceramic conductors. For a statistical mechanical description of such systems, which are characterized by short-range Van der Waals interactions and long-range Coulomb interactions, an approach combining the collective variables method and the method of mean cell potentials was used. This formalism had been applied in our previous work to a homogeneous state and in the present work was extended to an inhomogeneous case induced by an external electric field. We investigated the solution of this problem in the lattice approximation and studied the charge and electric field distributions in the interelectrode region as functions of plate electrode charges (Fig. 12).

The differential electric capacitance was subsequently calculated and discussed (Fig. 13).

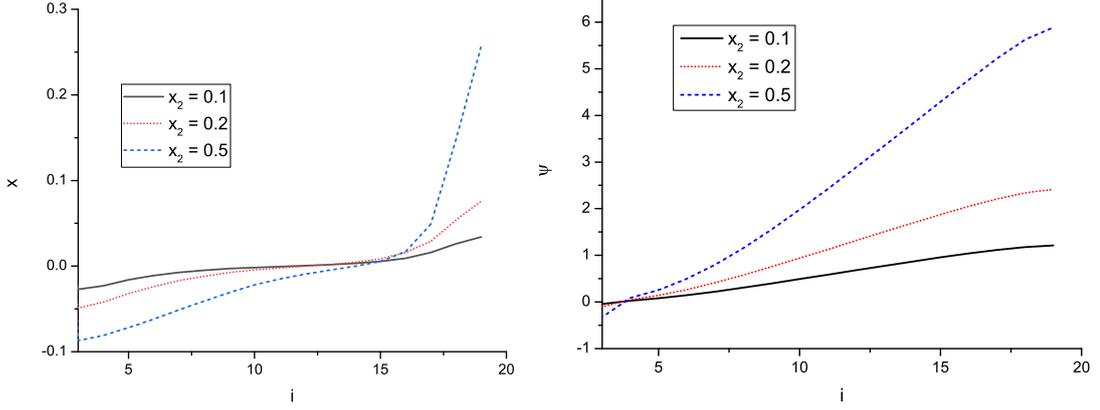


FIG. 12: Charge profile (left) and electric field profile (right) for interacting ions in the interelectrode region of 20 layers at different values of electrode plate charge x_2 .

Notably, we showed that the electric differential capacitance as a function of the electric potential has a typical camel-like shape. At small values of the electric potential the capacitance gradually increases, reaches a maximum, and then falls sharply as the potential is further increased, which is consistent with saturation of the electric charge in the near-electrode region in accordance with the charge distribution. A more gradual change of the capacitance at higher concentrations of mobile ions is due to the fact that this distribution contains an inflection point that expands the region of linear description. This is also the reason for the shift of the curve maxima for higher potentials.

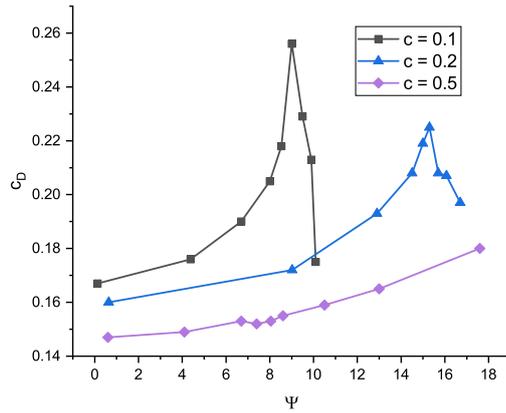


FIG. 13: Differential capacitance as a function of the electric potential at different ion concentrations.

The results dissemination:

I. Kravtsiv, G. Bokun, M. Holovko, N. Prokopchuk, D. di Caprio, Charge and electric field distributions in the interelectrode region of an inhomogeneous solid electrolyte, *Condensed Matter Physics*, **25**, No. 2, 3501:1–15 (2022).