

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: 1-48)**

Task 2.3

**Effects of confinement on the structure and diffusion properties
of simple and complex ionic systems
(Months: 25-36)**

Deliverable D2.3

**Effects of confinement on the structure and diffusion properties
of simple and complex ionic systems**

In 2019 the planned task was:

Task 2.3 Effects of confinement on the structure and diffusion properties of simple and complex ionic systems

“We plan to study the effect of grain boundaries in ceramic solid electrolytes and intercalation compounds and electrode/ electrolyte boundaries in solid and liquid electrolytes on the spatial distribution of charge carriers, ion diffusion and electric current. The microscopic models accounting of non-homogeneous character of the systems under consideration will be developed. The gradient contributions in the areas of large concentration gradients will be taken into account. Analytical findings will be compared with Monte Carlo simulation results and available experimental data. Lead Participant: BSTU (V. Vikhrenko). ICMP, IPC, CPT, BSTU, CSIC will perform analytical, numerical and simulation studies”.

The activities in Task 2.3 have been started in 2018. The corresponding deliverables were presented in the report for 2018 (see D2.2: 2a-2g).

The activities in WP2 in 2019 were the following:

1. **Effects of grain boundaries in ceramic solid electrolytes and intercalation compounds and electrode/ electrolyte boundaries in solid and liquid electrolytes.**
 - a. The effect of grain boundaries and electrode/electrolyte boundaries in solid electrolytes and intercalation compounds.
 - b. The effect of short-range interparticle interactions on electrophysical and transport properties of solid electrolytes.
 - c. Distribution of electropotential in the electrode area of a solid state ion electrolyte.
2. **Effect of proximity to ionic liquid-solvent demixing on electrical double layers.**
3. **Fluid-fluid phase behaviour in the explicit solvent ionic model: Hard spherocylinder solvent molecules**
4. **The short-range intermolecular interactions impact on the anticorrosion coating efficiency.**

1. Effects of grain boundaries in ceramic solid electrolytes and intercalation compounds and electrode/ electrolyte boundaries in solid and liquid electrolytes

1a. The effect of grain boundaries and electrode/electrolyte boundaries in solid electrolytes and intercalation compounds

A simple model of ceramic solid electrolyte confined between two oppositely charged walls was suggested and studied. The intergrain boundary is modelled by the corresponding energy landscape of the host system. The mobile cations are considered on the neutralizing background of fixed anions. The mean field approach for the description of density profiles of cations between oppositely charged walls is proposed. This approach is extended by taking into account correlations between cations at short distances.

It is shown that at strong external electric fields (high charge density of the confining walls) a wide depleting zone near the positively charged wall is observed, which gets narrower if the average cation concentration is increased. Besides the Coulomb interaction the effect of short-range attractive potential is introduced. It was found that the cations accumulate near the negatively charged wall, where the short-range interaction leads to a nonmonotonous charge distribution; however, this behavior can be predicted only with taking into account correlations.

The distribution of charge near the walls and intergrain boundary are independent of each other unless the system size is comparable with the width of the depletion zone and the Debye length. Due to positive values of the site energy deviation at the intergrain boundary with respect to the bulk value an essential deficit of charge carriers appears inside this region that results in the excess charge carriers beyond the intergrain boundary. This is a consequence of the total charge neutrality in the system leading to the complicated electric field distribution in the grain boundary region.

The redistribution of the mobile charges in the grain boundary region due to the variations of energetic landscape of the host material results in complicated profiles of the electric potential and field that should significantly affect the current transfer processes in this system. The short-range attractive interactions and correlations considerably change the numerical values of the parameters characterizing the electric field and potential distribution. The results obtained show that alongside with Coulomb interactions the binding energetics

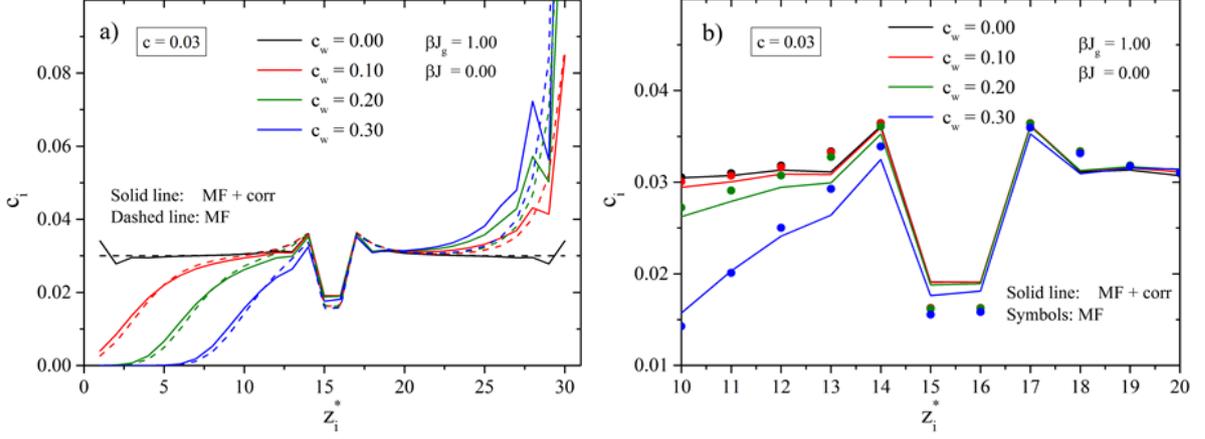


FIG. 1: The concentration profile of cations between the walls of different charges ($c_w=0.0-0.3$) at the lower average concentration ($c=0.03$) and with taking into account the intergrain boundaries ($\beta J_g=1.00$), but with no short-range attraction ($\beta J=0.0$). On the right panel, the intergrain region is shown in a larger scale.

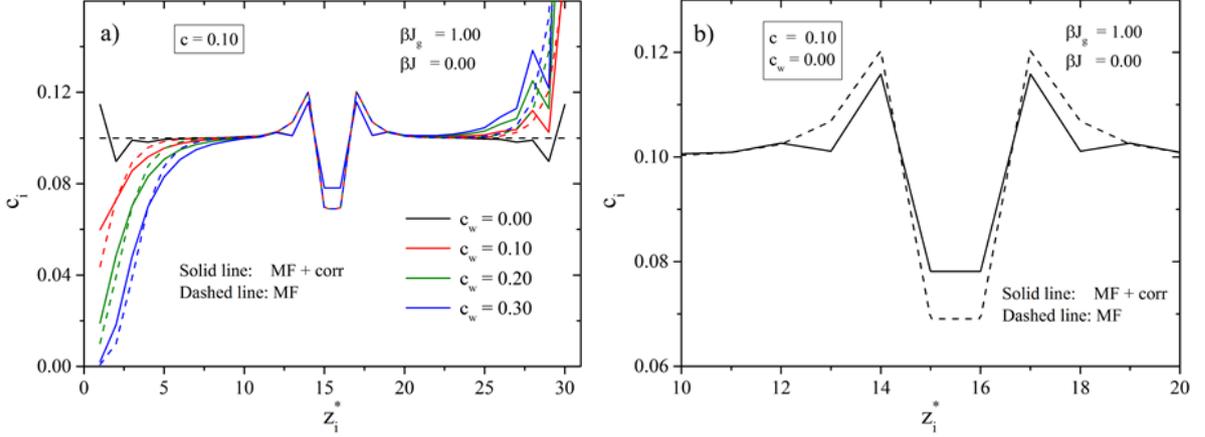


FIG. 2: The same as in Fig. 1, but at the high average concentration of cations ($c=0.10$).

as well as landscape peculiarities can play a crucial role in the charge and electric potential distribution.

This work is a result of a collaboration between ICMP (Taras Patsahan and Myroslav Holovko), CPT (Dung di Caprio), and BSTU (George Bokun and Vyacheslav Vikhrenko). The authors benefited from discussions with Oksana Patsahan during her secondment to Minsk.

The results are published in: T. Patsahan, G. Bokun, D. di Caprio, M. Holovko, and

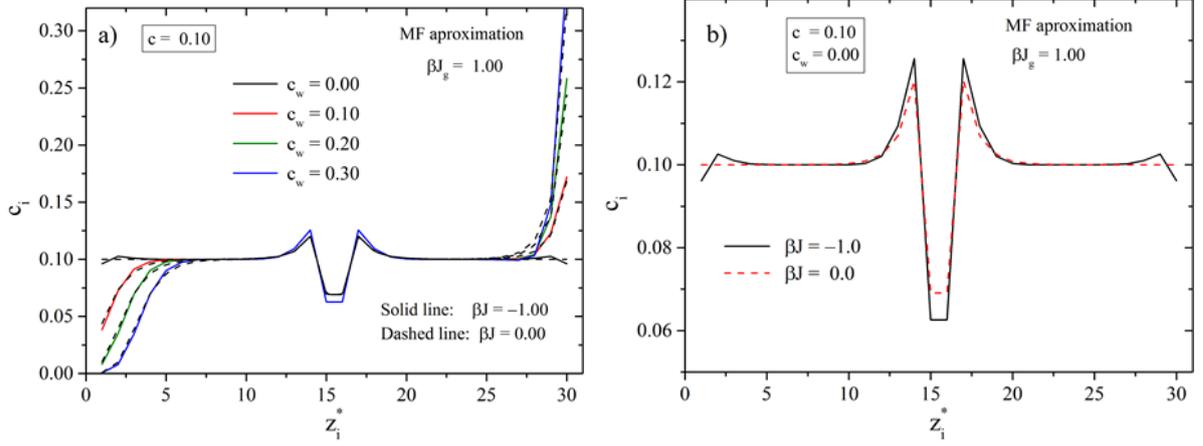


FIG. 3: The concentration profile of cations between the wall of different charges ($c_w=0.0-0.3$), but with taking into account the short-range attraction ($\beta J=-1.0$, solid lines) and the intergrain boundaries presence ($\beta J_g=1.00$) at the average concentration $c=0.10$. For a comparison, the results for cations without the short-range attraction ($\beta J=0.0$) are denoted by dashed lines.

V. Vikhrenko, *The effect of short-range interaction and correlation on the charge and electric field distribution in a model solid electrolyte*, Solid State Ionics, **335** 156-163 (2019), <https://arxiv.org/abs/1903.02736>.

The results are also presented as contributed talks at:

The 5-th Conference “Statistical Physics: Modern Trends and Applications”, 3–6 July 2019, Lviv, Ukraine;

III CONIN workshop: “Systems with competing electrostatic and short-range interactions” July, 1-2 2019 Lviv, Ukraine.

1b. The effect of short-range interparticle interactions on electrophysical and transport properties of solid electrolytes

Condensed ionic systems are described in the framework of a combined approach that takes into account both the long-ranged and the short-ranged interactions. The short-ranged interaction is expressed in terms of mean potentials and the long-ranged interaction is considered in terms of screened potentials. A system of integral equations for these potentials is constructed based on the condition of the best agreement of the system of study with the reference system. In contrast to the description of media with short-ranged interactions, the reference distribution includes not only the field of mean potentials but also Coulomb interaction between particles. A one-component system made of cations in a compensating field of fixed anions is considered. The model can be used to describe solid ionic conductors (ceramics). The free energy functional of a condensed system is generalized to account for the presence of long-ranged interactions. Notably, the approach proposed by L.A. Rott is improved by considering the reference distribution that consists of not only single-particle cell potentials but also of the long-ranged part of inter-molecular interactions. In order to study the movement of cations on the sites of their sub-lattice, the lattice approximation of the theory is employed based on the calculation of the pair distribution function. Using the collective variables approach, a technique improving the starting expression for this function is proposed. Notably, the neglected terms in the expansion of this function are approximated by single-particle terms ensuring that the normalization condition is satisfied. As a result, the applicability of the theory is extended to a wide region of thermodynamic parameters. The chemical potential and the diffusion coefficient are calculated showing the possibility of phase transitions characteristic of the system.

The calculation results for the chemical potential of the system versus concentration at a particular value of the inverse temperature are shown in Fig. 4. The curves show correct symmetry of the chemical potential with respect to the lattice concentration 0.5. The influence of interparticle correlations for different ranges of interparticle correlations on the distribution function is shown in Fig. 5.

Based on the results for the correlation function and compressibility of the system, the concentration dependence of the diffusion coefficient of the charge carriers was calculated (Fig. 6).

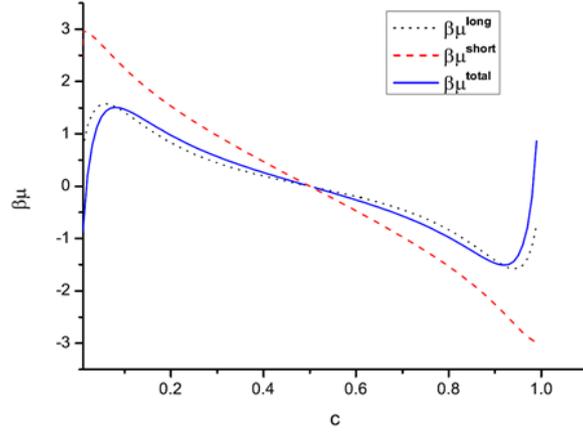


FIG. 4: Different contributions to the chemical potential as functions of the concentration for different numbers of coordination spheres taken into account at reduced inverse temperature 10.

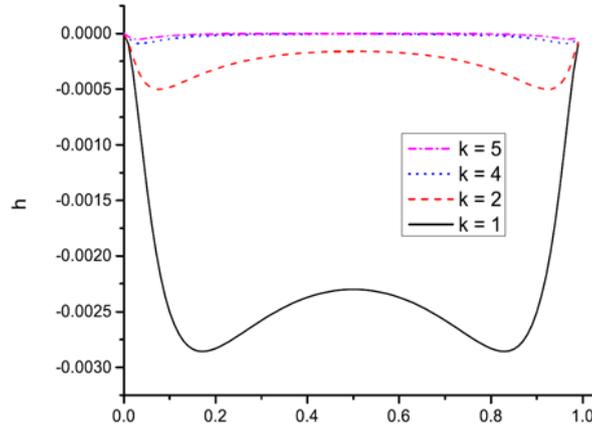


FIG. 5: The pair correlation function as a function of the concentration for different coordination spheres k .

The diffusion coefficient that is proportional to electric conductivity attain small values at high concentration. At small concentration it strongly depends on temperature.

This work is a result of a collaboration between ICMP (Ivan Kravtsiv and Myroslav Holovko), CPT (Dung di Caprio), and BSTU (George Bokun and Vyacheslav Vikhrenko).

The results are published in: G. Bokun, I. Kravtsiv, M. Holovko, V. Vikhrenko, D. di Caprio, *Short- and long-range contributions to equilibrium and transport properties of solid electrolytes*, *Condensed Matter Physics*, **22**, No. 3, 33501:1-14 (2019)

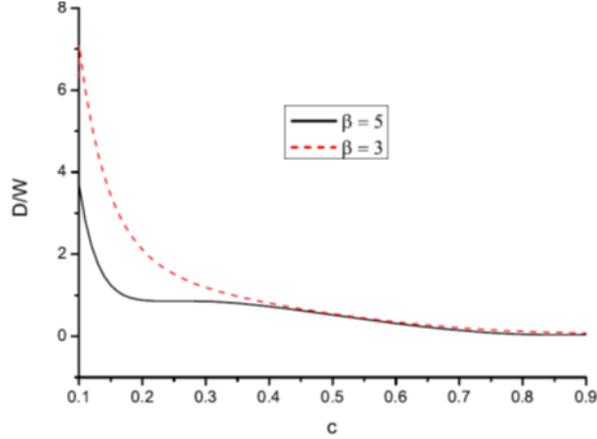


FIG. 6: The diffusion coefficient D as a function of the concentration at two values of the reduced inverse temperature β . W is the frequency factor.

1c. Distribution of electropotential in the electrode area of a solid state ion electrolyte

A solid state electrolyte is considered as a system consisting of cations moving through the volume of a solid body and anions whose mobility can be neglected due to their large size compared to the size of the cations. Accordingly, in the homogeneous case local charge compensation takes place. Under the action of an external electric field, cations create in the near electrode area inhomogeneous redistribution of mobile charges and electric field. The model is used for the statistical-mechanical description of high-temperature ionic conductors and current sources. To obtain the free energy functional of the mobile charge subsystem depending on the distribution of their density, the cluster expansion scheme for the renormalized Mayer functions is used. The Hamiltonian of a system consisting of electric charges moving in the field of single-particle cell potentials of average forces is used as the basis one. The binary function of the host system is expressed in terms of the screened potentials and the potentials of the average forces based on the results of the method of collective variables. The internal energy of the system is calculated taking into account the short- and long-range effects. The Gibbs – Duhem relation was used for calculating the free energy functional of the system. The distribution of the number density of moving particles and the electric potential in the near electrode region were found from the condition of extremity of the free energy. The potentials of average forces are obtained as a result of solving a

system of integral equations in the lattice approximation, with accounting of the short- and long-range effects. The transition from the correlative function to the correlation function allowed us to identify the correlated and uncorrelated parts of the electric potential. The linear contributions of the deviation of the charge concentrations from a uniform distribution to the chemical potential are considered. The calculations take into account the contribution of the correlation between the particles in the first three coordination spheres that leads to attraction of the first, repulsion of the second and third neighbors. The description is carried out using a linear differential equation of the fourth-order with complex values of the roots of the characteristic equation.

This work is a result of a collaboration between ICMP (Myroslav Holovko), CPT (Dung di Caprio), and BSTU (George Bokun).

The results are published in: G.S. Bokun, D. di Caprio, M.F. Holovko, *Distribution of electro-potential in the electrode area of a solid state ion electrolyte*, Journal of the Belarusian State University. Physics, No. 2, P. 73– 83 (2019). <https://doi.org/10.33581/2520-2243-2019-2-73-83> (In Russian).

2. Effect of proximity to ionic liquid-solvent demixing on electrical double layers

We continued to study the mean-field model suitable for the IL-solvent mixtures close to demixing phase transition. The studied system is shown schematically in Fig.7.

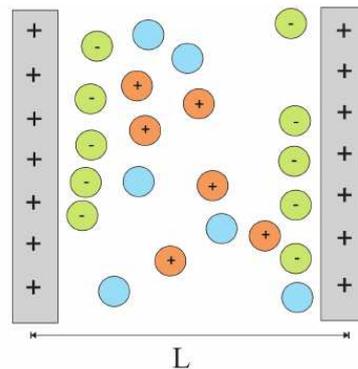


FIG. 7: Schematic representation of the studied system which consists of a mixtures of ionic liquid and solvent molecules.

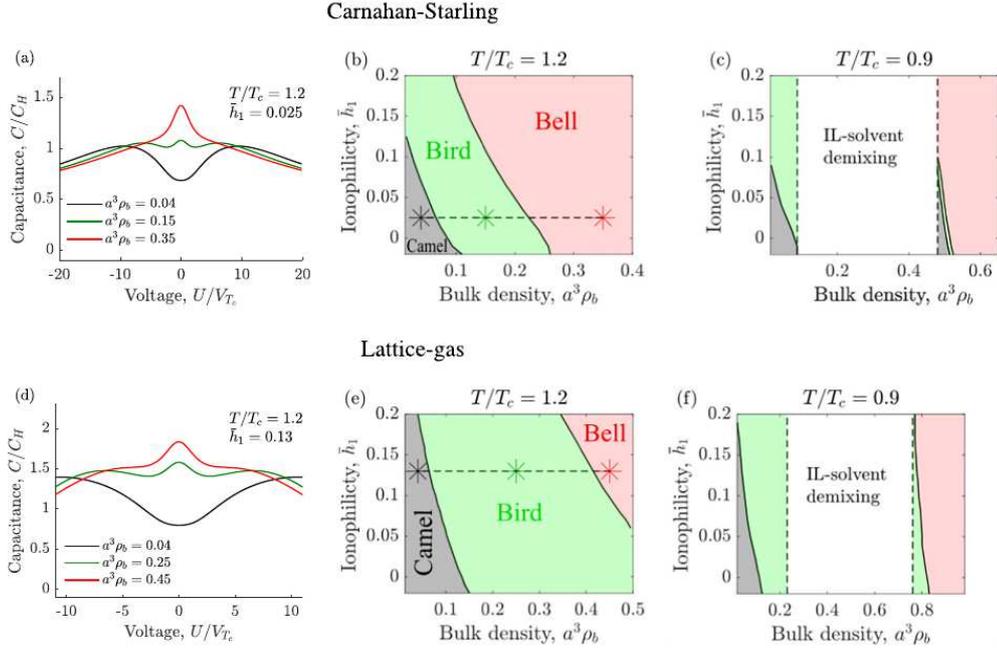


FIG. 8: Capacitance behaviour close to demixing. (a) Differential capacitance for the Carnahan-Starling (CS) entropy as a function of applied potential for constant temperature and for a few ion concentrations, demonstrating the camel, bird, and bell-shaped capacitances. Voltage is expressed in terms of the thermal voltage $V_{T_c} = k_B T_c / e$ taken at the critical temperature of the demixing phase transition, T_c , and the capacitance is measured in units of the Helmholtz capacitance $C_H = \epsilon / 4\pi a$, where a is the ion diameter and ϵ the dielectric constant. (b) Capacitance diagram for the CS model showing the regions of camel, bird, and bell-like capacitances at constant temperature $T/T_c = 1.2$. The dashed horizontal line denotes the value of the ionophilicity \tilde{h}_1 and the symbols mark the bulk densities ρ_b used in (a). (c) Capacitance diagram for the CS entropy for temperature below T_c , $T/T_c = 0.9$. The white region denotes the domain of the IL-solvent demixing. (d) - (f) The same as (a) - (c) but for the lattice-gas entropy.

We compared the Carnahan-Starling (CS) and lattice-gas expressions for the excluded volume interactions in the case of $L \rightarrow \infty$. The model was solved analytically, using perturbation expansion, and numerically. We demonstrated that, besides the well-known camel and bell-shaped capacitances, there is a bird-shaped capacitance, having three peaks as a function of voltage, which emerge due to the proximity to demixing. We found that a transformation between the bell and bird shapes can be caused by varying temperature. This is due to a voltage-induced adsorption of an IL at an ionophilic electrode. Such an

enhanced electrosorption leads to stronger screening and hence to the appearance of wings in the bell-shaped capacitance, giving rise to the bird shape.

In addition, we found that the camel-shaped capacitance, which is a signature of dilute electrolytes, can appear at high IL densities for ionophobic electrodes. The results are summarized in Fig.8.

This work is a result of a collaboration between IPC (Carolina Cruz, Svyatoslav Kondrat and Alina Ciach) and CSIC (Enrique Lomba). A part of the initial stage of this work was done during the secondment of S. Kondrat to Minsk. The authors benefited from discussions with Yaroslav Groda during his secondment to Warsaw.

The results are published in: Carolina Cruz, Svyatoslav Kondrat, Enrique Lomba, and Alina Ciach, “Effect of proximity to ionic liquid- solvent demixing on electrical double layers”, *Journal of Molecular Liquids*, (2019) <https://doi.org/10.1016/j.molliq.2019.111368>.

The results are also presented as a contributed talk at III CONIN workshop: “Systems with competing electrostatic and short-range interactions” July, 1-2 2019 Lviv, Ukraine.

3. Fluid-fluid phase behaviour in the explicit solvent ionic model: Hard spherocylinder solvent molecules

We continue to study the fluid-fluid phase behaviour of the explicit solvent ionic model. Now, we focus on the model in which the solvent molecules are of non-spherical shape. The model is represented as a binary mixture of oppositely charged hard spheres (HS) of equal diameters (RPM) and neutral hard spherocylinders (HSC). To describe the model we propose the approach combining the scale particle theory (SPT) and the associative mean spherical approximation (AMSA). More specifically, thermodynamic properties of the reference system represented as a binary mixture of neutral HS and neutral HSC are obtained using the SPT approach. For an ionic subsystem, we use the SIS-AMSA theory, which corresponds to the Wertheim first-order thermodynamic perturbation theory. For a comparison, the ionic subsystem is also treated within the MSA theory.

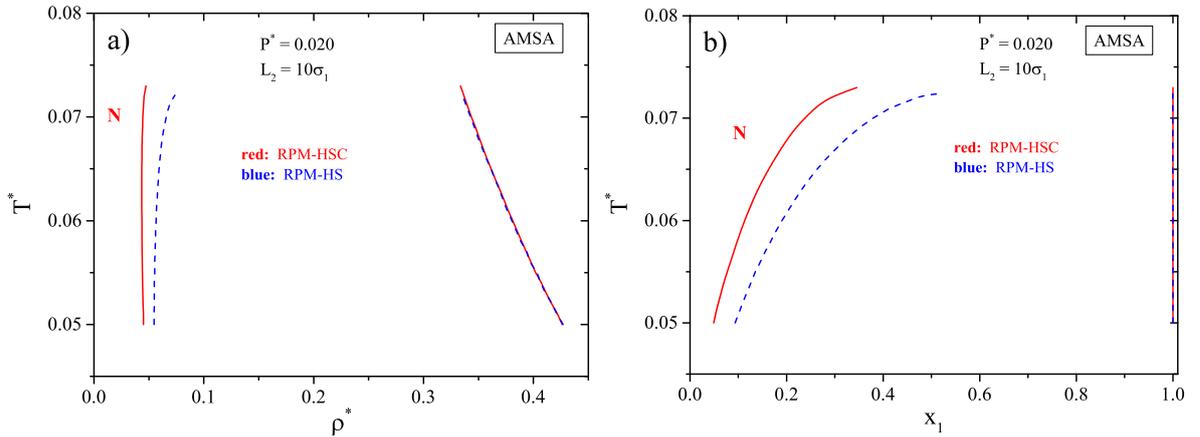


FIG. 9: Coexistence curves of the RPM-HSC mixture with $L_2/\sigma_1 = 10$ and its equivalent RPM-HS mixture in $T^* - \rho^*$ (a) and $T^* - x_1$ (b) planes obtained at the constant pressure $P^* = 0.02$ using the AMSA approximation. Symbol “N” indicates the nematic phase location ($T^* = k_B T \varepsilon \sigma_1 / e^2$, $P^* = P \varepsilon \sigma_1^4 / e^2$, $\rho^* = \rho \sigma^3$, $\rho = \rho_s + \rho_i$, $x_1 = \rho_i / \rho$).

We consider two models: the RPM-HSC mixture and an “equivalent” RPM-HS mixture. In the former case, we restrict our attention to the HSC with aspect ratios $L_2^* = L_2/\sigma_2 = 5$ and 10, provided the diameter of RPM particles is set to $\sigma_1 = \sigma_2$. In the latter model, the solvent is represented as HS particles with the volume equal to the volume of the HSC particles of the former case. In this way, we have studied the effect of solvent particles asphericity on the fluid-fluid phase behaviour in the RPM-HSC system.

An increase of the solvent particle length L_2 broadens the region of phase coexistence presented in the $T^* - \rho^*$ plane for $L_2^* = 5$ and 10. In the case of $L_2^* = 10$, this effect is even more essential due to the formation of a nematic phase of HSC solvent in the ion-poor phase. It results from both the MSA and AMSA approximations. However, it has been noticed that the MSA significantly shifts the coexistence region of the RPM-HSC system towards higher temperatures in comparison with the equivalent RPM-HS system whereas this shift is minor in the AMSA. Unlike the MSA, the AMSA phase diagrams show that the high-density phase mostly consists of the ions for all pressures considered in this study. We explain the above discrepancies by a poorer description provided by the MSA approximation which does not take into account the association effects between ions and, as a result, leads to an overestimate of temperatures and to less reliable results for densities than in the AMSA.

A part of this work was done during the secondments of M. Holovko, T. Patsahan, O. Patsahan and M. Hvozď to Minsk. The authors benefited from discussions with George Bokun during his secondment to Lviv.

The results are presented as a poster at The 5-th Conference “Statistical Physics: Modern Trends and Applications” 3–6 July 2019, Lviv, Ukraine.

4. The short-range intermolecular interactions impact on the anticorrosion coating efficiency

Different cationic surfactants based on various aliphatic and aromatic ammonium cations were synthesized and characterized by different techniques such as IR spectroscopy and NMR. Their anticorrosion properties were evaluated in different medias (HCL, H2SO4 and NaCL solutions), after their electrografting on steel surface. Electrochemical techniques, such as potentiodynamic polarization, were used to study the inhibition efficiency of synthesized surfactants. The interdependence of the wetting properties of electrografted layer and its homogeneity, on the molecular structure of the prepared surfactants, was studied. A particular attention was paid to the relationship between these surfactant properties and their anticorrosion efficiency. It was demonstrated that the inhibitor properties, in terms of surfactants structure, and the interactions between them, play a major role in their anticorrosion efficiency.

The wetting properties of the steel electrodes surface have being shown to change after the electrografting process. Among the synthesized molecules, the surfactants with enhanced

hydrophobic properties, provide the coating with the best efficient anticorrosion properties. In addition, the influence of critical micelles concentration on the homogeneity of surfactant coating was investigated. When the surfactant concentration is within the post-micellar region, the competition between the surfactant adsorption on the steel surface and the micelles formation takes place; which makes the surfactant coating inhomogeneous with weak barrier properties, and in turn worse anticorrosion efficiency. The obtained results show clearly that the anticorrosion properties of the prepared coating is connected to the interactions and structure of the surfactants within their assembly into a thin coating.

This work is achieved by the PhD student Hanna Pianka during her training in our lab from 01/02/2019 to 30/06/2019, and it is a result of a collaboration between BSTU (Hanna Pianka, Vladimir Bezborodov, Sergei Mikhalynok, Nina Kuz'menok, Alexander Chernik) and the Sorbonne University (Abdelhafed Taleb).

The results were presented at the International scientific and technical conference "MODERN ELECTROCHEMICAL TECHNOLOGIES AND EQUIPMENT – 2019", May 13-17, 2019, Minsk Republic of Belarus (Oral Contribution).

Now two papers are in preparation:

1. Hanna Pianka, Sana Falah, Sandrine Zana, Vladimir Bezborodov, Sergei Mikhalynok, Nina Kuz'menok, Alexander Chernik, Abdelhafed Taleb, *The synthesis and anticorrosion efficiency of inhibitors based on ammonium cation with different substituents: The influence of wettability and molecular structure.*
2. Hanna Pianka, Sana Falah, Sandrine Zana, Vladimir Bezborodov, Sergei Mikhalynok, Nina Kuz'menok, Alexander Chernik, Abdelhafed Taleb, *Smart coating based on TiO₂, Ni and inhibitors based on N-Dodecylpyridinium bromide for corrosion protection of steel.*

DISSEMINATION AND PUBLICATION ACTIVITIES

Activity 1.

T. Patsahan, G. Bokun, D. di Caprio, M. Holovko, and V. Vikhrenko, *The effect of short-range interaction and correlation on the charge and electric field distribution in a model solid electrolyte*, Solid State Ionics, **335** 156-163 (2019), <https://arxiv.org/abs/1903.02736>.

Activity 2.

G. Bokun, I. Kravtsiv, M. Holovko, V. Vikhrenko, D. di Caprio, *Short- and long-range contributions to equilibrium and transport properties of solid electrolytes*, Condensed Matter Physics, **22**, No. 3, 33501:1-14 (2019).

Activity 3.

Carolina Cruz, Svyatoslav Kondrat, Enrique Lomba, and Alina Ciach, *Effect of proximity to ionic liquid- solvent demixing on electrical double layers*, Journal of Molecular Liquids, **294**, 111368 (2019), <https://doi.org/10.1016/j.molliq.2019.111368>.

Activity 4.

G.S. Bokun, D. di Caprio, M.F. Holovko, *Distribution of electro-potential in the electrode area of a solid state ion electrolyte*, Journal of the Belarusian State University. Physics, No. 2, P. 73– 83 (2019). <https://doi.org/10.33581/2520-2243-2019-2-73-83> (In Russian).

Activity 5.

Hanna Pianka, Sana Falah, Sandrine Zana, Vladimir Bezborodov, Sergei Mikhalynok, Nina Kuz'menok, Alexander Chernik, Abdelhafed Taleb, *The synthesis and anticorrosion efficiency of inhibitors based on ammonium cation with different substituents: The influence of wettability and molecular structure* (paper in preparation).

Activity 6.

Hanna Pianka, Sana Falah, Sandrine Zana, Vladimir Bezborodov, Sergei Mikhalynok, Nina Kuz'menok, Alexander Chernik, Abdelhafed Taleb, *Smart coating based on TiO₂, Ni and*

inhibitors based on N-Dodecylpyridinium bromide for corrosion protection of steel(paper in preparation).

Activity 7.

V. S. Vikhrenko, G. Bokun, T. Patsahan, D. di Caprio, M. Holovko, I. Kravtsiv, *Influence of interparticle correlations on electrophysical properties of solid electrolytes*. The 5-th Conference “Statistical Physics: Modern Trends and Applications” Programme and Abstracts 3–6 July 2019, Lviv, Ukraine. P. 63. (Contributed talk).

Activity 8.

Carolina Cruz, Alina Ciach, Enrique Lomba, and Svyatoslav Kondrat *Electrical double layers close to ionic liquid-solvent demixing*, III CONIN workshop: “Systems with competing electrostatic and short-range interactions” July, 1-2 2019 Lviv, Ukraine (Contributed talk).

Activity 9.

V. Vikhrenko, G. Bokun, D. di Caprio, M. Holovko, R. Lasovsky, T. Patsahan, *Electric field and charge distribution in near electrode and intergrain regions of solid electrolytes*, III CONIN workshop: “Systems with competing electrostatic and short-range interactions” July, 1-2 2019 Lviv, Ukraine (Contributed talk).

Activity 10.

T. Patsahan, M. Hvoz, O. Patsahan, M. Holovko, *Recent progress in the theoretical description of fluid-fluid phase behaviour in the explicit solvent ionic model*, III CONIN workshop: “Systems with competing electrostatic and short-range interactions” July, 1-2 2019 Lviv, Ukraine (Contributed talk).

Activity 11.

Alina Ciach, “Theory for Charge Distribution in Ionic Liquids Near a Charged Wall”, III CONIN workshop: “Systems with competing electrostatic and short-range interactions” July, 1-2 2019 Lviv, Ukraine (Poster).

Activity 12.

Alina Ciach, “Theory for Charge Distribution in Ionic Liquids Near a Charged Wall”, “XXII International Conference on Chemical Thermodynamics in Russia”, Petersburg, 19-23.06.2019 (Poster).

Activity 13.

V. Vikhrenko, R. Lasovsky, and T. Patsahan, *Monte Carlo simulation of a 3D solid electrolyte on a simple cubic lattice: concentration and electric field distribution at and without an external field*. The 5-th Conference “Statistical Physics: Modern Trends and Applications” Programme and Abstracts 3–6 July 2019, Lviv, Ukraine. P. 169. (Poster)

Activity 14.

M. Hvozď, T. Patsahan, O. Patsahan and M. Holovko, *Fluid-fluid phase behaviour in the explicit solvent ionic model: Hard spherocylinder solvent molecules* The 5-th Conference “Statistical Physics: Modern Trends and Applications” Programme and Abstracts 3–6 July 2019, Lviv, Ukraine. P. 116. (Poster)

Activity 15.

Hanna Pianka, Sana Falah, Sandrine Zana, Vladimir Bezborodov, Sergei Mikhailynok, Nina Kuz'menok, Alexander Chernik, Abdelhafed Taleb, *Preparation and Characterization of Diazonium functionalized TiO₂ Nanoparticles deposited on Steel Surface*, Proceedings of the international scientific and technical conference “MODERN ELECTROCHEMICAL TECHNOLOGIES AND EQUIPMENT – 2019”, 323-326, 2019.