

**Action acronym: CONIN**

**Action full title: “Effects of confinement on  
inhomogeneous systems”**

**Grant agreement No: 734276**

**Funded by European Union’s Horizon 2020 research and innovation  
programme under the Marie Skłodowska-Curie  
Report on the II CONIN workshop  
Lviv, 1-2 July 2019**

**III CONIN Workshop:  
Systems with competing electrostatic  
and short-range interactions**



**July 1-2, 2019, Lviv, Ukraine**

[www.icmp.lviv.ua/statphys2019/conin.html](http://www.icmp.lviv.ua/statphys2019/conin.html)



The III CONIN workshop was organized in Lviv on July 1-2 2019. The aim of this workshop was to summarize the recent progress in colloidal and amphiphilic self-assembly and in the room temperature ionic liquids, both in the bulk and in confinement, as well as in mobile ions in intercalation compounds and on solid surfaces. Besides experienced researches from the consortium, seven outstanding theoreticians and experimentalist lectures were invited. Our intention was to provide an overview of the research done in the CONIN project but also get an actualized view of the field in general.

There were 27 inscribed participants in the workshop, 20 researchers from the consortium and 7 guest lecturers. The guest lecturers were:

- Dezső Boda, University of Pannonia, Veszprém, Hungary
- Christian Holm, Stuttgart University, Germany
- Alexandr Malijevský, Czech Academy of Sciences, Prague, Czech Republic
- Aurélien Perera, Sorbonne Université, Paris, France
- Davide Pini, University of Milan, Italy
- Mykola Tasinkevych, University of Lisbon (CFTC), Portugal
- Vojko Vlachy, University of Ljubljana, Slovenia

Professors Davide Pini, Mykola Tasinkevych and Alexandr Malijevský delivered lectures related to WP1 (systems with competing short-range attraction long-range repulsion). Prof. Pini presented the results on self-assembly in soft- and hard-core fluids based on a numerical implementation of mean-field density-functional theory tailored to periodic phases. Prof. Tasinkevych talked about self-phoretic colloids in confined geometries. Prof. Malijevský summarised the recent advances in the theory of wetting and related phenomena that are induced by geometric heterogeneity of adsorbing substrates. The guest lectures of Professors Vojko Vlachy and Aurélien Perera were related to WP2 (systems with electrostatic interactions) as well as to WP1. Prof. Vlachy provided a nice overview of both experiments and the theory on protein solvation and self-assembly in aqueous electrolyte solutions. Prof. Perera discussed the capability of the liquid state integral equation theories to describe charge ordering in the system with competing electrostatic and short-range interaction. The guest lectures of Professors Dezső Boda and Christian Holm were related to WP2. Prof. Holm reported on charge dynamics and structure of ionic liquids in nanoporous

supercapacitors. Prof. Boda presented computational results for homogeneous and inhomogeneous ionic systems as well as for equilibrium and non-equilibrium framework.

Researchers from the five institutions involved in the consortium attended the III CONIN workshop. The complete list of participants from the consortium is:

- Alina Ciach, Warsaw
- Wojciech Gozdz, Warsaw
- Svyatoslav Kondrat, Warsaw
- Jakub Pękalski, Warsaw
- Marek Litniewski, Warsaw
- Carolina Cruz Cardona, Warsaw
- Dung di Caprio, Paris
- Abdelhafed Taleb, Paris
- Vyacheslav Vikhrenko, Minsk
- Ivan Narkevich, Minsk
- Yaroslav Groda, Minsk
- Ruslan Lasovsky, Minsk
- Eldar Bildanov, Minsk
- Vera Grishyna, Minsk
- Myroslav Holovko, Lviv
- Ihor Mryglod, Lviv
- Oksana Patsahan, Lviv
- Taras Patsahan, Lviv
- Ivan Kravtsiv, Lviv
- Marta Hvozd, Lviv

There was a total of 14 lectures, whose titles can be seen in the agenda provided in the annex. Besides, young researchers presented posters. The topics covered in the workshop included:

**1. Systems with short-attraction long-range repulsion interactions:**

- Experiments and the theory on protein solvation and self-assembly in aqueous electrolyte solutions.
- Theoretical description and simulations of self-assembly in soft- and hard-core fluids.
- Complex phase and critical behaviour of the adsorbed fluid.

- Active colloids at structured surfaces.
- Structural transitions in closed systems with competing interactions.

## 2. Ionic systems:

- Experiments and the theory on protein solvation and self-assembly in aqueous electrolyte solutions.
- Charge distribution in near electrode in solid electrolytes.
- Electrical double layers close to ionic liquid-solvent demixing.
- Electrolytes in confinement: nanopores, ion channels, and double layers.
- Charge ordering in ionic liquids
- Theoretical description of phase behaviour in the explicit solvent ionic model.

Besides getting an overview of the field, the workshop served both to discuss joint work that is carried out between members of different institutions of the consortium, and to establish new collaborations, not only with members of CONIN but also with the guest lectures.

The workshop was advertised in the IIICONIN workshop webpage: <http://www.icmp.lviv.ua/statphys2019/conin.html> and in the webpage of the 5-th Conference “Statistical Physics: Modern Trends and Applications”: <http://www.icmp.lviv.ua/statphys2019/>, as well as in local mailing lists. As a result, we had a few participants from the Institute for Condensed Matter Physics of the National Academy of Sciences, two participants from University of Ljubljana and a participant from Institute of Chemistry, UNAM (Mexico).



## Annex 1. Workshop agenda

## Programme

### June 30

16.00–18.00	Registration (UCU)
18.00	Dinner

### July 1

Chair: Myroslav Holovko

9.30–9.40	Workshop opening
9.40–10.20	<b>Vojko Vlachy:</b> Protein solvation and self-assembly in aqueous electrolyte solutions
10.20–11.00	<b>Davide Pini:</b> An unconstrained DFT study of self-assembly in soft- and hard-core fluids
11.00–11.30	Coffee break

Chair: Dung di Caprio

11.30–12.10	<b>Mykola Tasinkevych:</b> Self-phoretic active colloids in confined geometries
12.10–12.40	<b>Jakub Pękalski:</b> Structural transitions in closed systems with competing interactions
12.40–14.30	Lunch

Chair: Wojciech Gózdź

14.30–15.00	<b>Yaroslav Groda:</b> Equilibrium properties of three-dimensional lattice fluids with SALR interactions
15.00–15.30	<b>Ivan Kravtsiv:</b> Soft-particle system with competing interactions: field theory treatment
15.30–16.00	Poster session/Coffee break
16.00–19.00	Excursion
19.00	Dinner

July 2

Chair: Alina Ciach

- 9.30–10.10      **Dezso Boda:** Electrolytes in confinement: ionic competition based on the balance of long- and short-range forces in nanopores, ion channels, and double layers
- 10.10–10.50      **Christian Holm:** Charging dynamics and structure in Nanoporous Supercapacitors
- 10.50–11.20      Coffee break

Chair: Vyacheslav Vikhrenko

- 11.20–12.00      **Aurélien Perera:** Exploring systems with competing electrostatic and short range interaction with the liquid state integral equation theories
- 12.00–12.40      **Alexandr Malijevský:** Wetting phenomena at structured surfaces: the role of microscopic forces
- 12.40–14.30      Lunch

Chair: Ihor Mryglod

- 14.30–15.00      **Vyacheslav Vikhrenko:** Electric field and charge distribution in near electrode and intergrain regions of solid electrolytes
- 15.00–15.30      **Carolina Cruz Cardona:** Electrical double layers close to ionic liquid-solvent
- 15.30–16.00      Coffee break

Chair: Yaroslav Groda

- 16.00–16.30      **Dung di Caprio, Abdelhafed Taleb:** Effect of adatom diffusion and reaction on the morphology and the porosity of electrodeposited films
- 16.30–17.00      **Taras Patsahan:** Recent progress in the theoretical description of fluid-fluid phase behaviour in the explicit solvent ionic model
- 18.00              Dinner

**July 3**

8.00–9.30

Breakfast

Departure

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**Book of Abstracts**

Lviv – 2019

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- 18.00 Dinner

July 3

8.00–9.30

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Departure

## Protein solvation and self-assembly in aqueous electrolyte solutions

Vojko Vlachy

*Faculty for Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia*

As examples of the system of competing long- and short-range interactions we present our studies of protein and polyelectrolyte solutions. We start with an aqueous protein-buffer mixture, being soluble at room temperature. By cooling down the solution we may arrive at the cloud-point temperature,  $T_c$ , where first cloudiness indicates that solubility limit is reached [1]. This temperature depends on ionic strength of the added buffer; higher buffer content causes an increase of  $T_c$ , reflecting a stronger destabilization of the solution. Interestingly, there exist a limiting buffer concentration after which  $T_c$  does not rise any more – the long-range electrostatic interaction appears to be screened. In the second part of the experiment, we replace a certain amount of the buffer by a low-molecular-mass salt, keeping the total ionic strength constant. This way we change the composition of the buffer-protein-salt mixture. As a result we observe an additional destabilization of the protein solution. The  $T_c$  increase depends on the nature of added salt and is well correlated with the enthalpy of solvation of the salt anions, following the inverse Hofmeister series. The results suggest that dehydration of salt ions interacting with charged groups on the protein surface are responsible for these effects. We assume that under such conditions interaction among proteins is of short range, so we model proteins either as hard spheres [2], dumb-bells [3] or in case of monoclonal antibodies as Y-shaped molecules [4]. Model proteins possess attractive square-well sites on the surface to allow aggregation. Using the thermodynamic perturbation theory of Wertheim [5] we calculated the liquid-liquid phase diagram, the second virial coefficient, and correlated the solution viscosity with protein aggregation [2–4].

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## An unconstrained DFT study of self-assembly in soft- and hard-core fluids

Davide Pini

*Dipartimento di Fisica "A. Pontremoli", Università degli Studi di Milano, Via Celoria 16,  
20133 Milano, Italy*

Among several mechanisms leading to self-assembly in fluids, one which has been under the spotlight for quite some time is the formation of mesoscopic aggregates of particles interacting via potentials whose Fourier components display a negative absolute minimum at non-vanishing wave vector  $q$  [1]. While this will favor modulations of the density profile with wavelength  $\lambda \approx 2\pi/q$ , several different scenarios may arise, depending on the additional features of the interaction.

Here we will present some results on self-assembly for this class of potentials based on a fully numerical implementation of mean-field density-functional theory tailored to periodic phases, which does not rely on any additional assumption on the functional form of the density profile. Specifically, we will discuss the phase diagram of hard-core fluids with competing attractive and repulsive interactions [2], and compare it with the scenario observed in cluster-forming soft-core fluids. The main qualitative differences between the two cases can be accounted for by a simple model, which yields rather general predictions for the size and density of the mesophases at coexistence [3].

The behavior of soft- and hard-core self-assembling fluids will be further examined by considering the formation of mesophases of systems confined on a spherical surface [4]. Here the scenario is further enriched by two new ingredients, namely, the finite size of the system and the topological frustration. We will examine how these constraints combine with the intrinsic length scale of the density modulations characteristic of this kind of interactions.

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## Self-phoretic active colloids in confined geometries

Mykola Tasinkevych

*Department of Physics, The University of Lisbon, Portugal*

Autonomous microscopic agents moving through confined, liquid-filled spaces are envisioned as a key component of future lab-on-a-chip and drug delivery systems. Chemically active Janus particles offer a realization of such agents. Depending on the systems, various self-propulsion mechanisms emerge, such as bubble propulsion, self-electrophoresis or self-diffusiophoresis. Here, we discuss the self-propulsion of a Janus spheroidal particle. First, we describe how the swimming velocity depends on the particle's aspect ratio and on the catalyst coverage. Next we analyse how such active particles can be used as carriers of micro-cargo, and show that the velocity of the carrier-cargo composite strongly depends on the relative orientation of the link between the active and passive particles.

Near a hard wall, a Janus active particle reveals a very interesting behavior, including novel sliding and hovering steady states. The sliding steady state provides a starting point to engineer a stable and predictable motion of microswimmers. For example, at topographically patterned walls, novel states of guided motion along the edges of the geometrical patterns can emerge. We also predict that the trajectories of chemical microswimmers can be efficiently controlled by using chemically patterned walls. The induced chemi-osmotic flows at the wall can cause particles to either “dock” at the chemical step or to robustly follow a thin chemical stripe.

Finally, we demonstrate that platinum microparticles move spontaneously in solutions of hydrogen peroxide and that their motions can be rationally designed by controlling particle shape. The observed relationships between particle shape and motion provide evidence for a self-electrophoretic propulsion mechanism, whereby anodic oxidation and cathodic reduction occur at different rates at different locations on the particle surface.

**Acknowledgement.** We acknowledge financial support from the Portuguese Foundation for Science and Technology (FCT) under Contracts No.IF/00322/2015 and UID/FIS/00618/2019.

## Electrolytes in confinement: ionic competition based on the balance of long- and short-range forces in nanopores, ion channels, and double layers

Dezső Boda

*Department of Physical Chemistry, University of Pannonia, Veszprém, Hungary*

I will present computational results for homogeneous (bulk) [8,14,15] and inhomogeneous ionic systems as well as for equilibrium and non-equilibrium [12,13,6,17,19–21] systems for electrolytes modeled in the continuum solvent framework (the ill-named “primitive” model). Short range forces are ion-diameter dependent hard sphere-exclusions and the square-well potential representing selective binding sites in nanopore sensors [17,20]. Long-range forces are screened Coulomb interactions between ions, between ions and surface charges, and between ions and external fields. Non-additive interactions between ions and polarization charges induced on dielectric interfaces [4–7,9,10,12] are of special importance because they include the effect of solvation [8,10,14,15].

Results will be shown for bulk electrolytes, where the concentration dependence of the activity coefficient was studied on the basis of the II+IW (ion-ion and in-water interactions) model that uses the concept of a concentration dependent dielectric constant of the electrolyte [8,14,15].

At charged surfaces, electrical double layers are formed, where the competition between short- and long-range forces determines the competitive adsorption of ions at highly charged interfaces [2,3,18] and in slits [11]. The the point-of-zero-charge potential [1,2,18] is also sensitive to this competition. An extended study for a large variety of parameters (ion sizes, ion valences, surface charge, concentration) has been performed and the database made public [18].

Ion channels whose selectivity filters are crowded with charged amino acid groups ( $\text{COO}^-$ ) also exhibit a selectivity behavior based on the competition of “entropic” hard sphere exclusion and “energetic” electrostatic attraction (the “charge-space competition” mechanism). This mechanism is strongly enhanced by the presence of dielectric boundaries. Grand canonical MC (GCMC) simulations have been performed for the L-type calcium channel [5–7,9,10,12], the Ryanodine Receptor calcium release channel [12], and the neuronal sodium channel [4]. An energetic analysis of the selectivity in terms of various components of the excess chemical potential (these components correspond to the various short- and long-range forces) has been provided [9,10].

Beyond equilibrium adsorption selectivity studies, non-equilibrium calculations for ionic transport through ion channels [12], transporters [13], and nanopores [16,17,19–21] have been performed. Various methods in the framework of a multiscale approach are used including molecular dynamics [16,21], Dynamic MC [13], and Poisson-Nernst-Planck (PNP) [19,21]. Our main method — developed by us — is a non-equilibrium adaptation of the GCMC technique (the Local Equilibrium MC with spatially varying chemical potential) coupled to the Nernst-Planck transport equation [16,17,19–21]. The studied phenomena in the case of nanopores are rectification [16,21], control of ionic current [19], and sensing [17,20]. While mean-field electrostatics (PNP) properly reproduces phenomena where long-range electrostatics are the dominant interaction type (bipolar diodes [16,21], transistors [19]), ionic sizes and computer simulations become important in cases, where ion competition is a central phenomenon (sensors [17,20]).

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## Charging dynamics and structure of ionic liquids in nanoporous supercapacitors

Christian Holm<sup>1</sup>, Konrad Breitsprecher<sup>1</sup>, Slava Kondrat<sup>2</sup>

<sup>1</sup>*Institute for Computational Physics, Universität Stuttgart, Germany*

<sup>2</sup>*Warsaw, Poland*

Ionic liquid based nanoporous supercapacitors have attracted much attention recently as energy storage devices with remarkable cyclability and high power and energy densities. However, their use in high-frequency applications might be limited by a relatively slow charging process. In this talk we will first discuss the fluid structure within a slit-pore capacitor system [1] and report on the physics and optimization of charge/discharge cycles [2,3]. We will see that step-voltage charging is slow because the ions become trapped in narrow pores of the supercapacitor electrodes. To avoid such trapping, a slow voltage-sweep charging is considered, which allows to accelerate the overall charging process substantially. We furthermore examine in detail the discharging process, as well. At the end we will report on the effect of nonlinear charging functions.

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## Exploring systems with competing electrostatic and short range interaction with the liquid state integral equation theories

Aurélien Perera

*LPTMC, Sorbonne Université, Paris, France*

Disorder in liquids comes into two categories, simple and complex. Generally, short range Lennard-Jones type interactions generate simple disorder, while Coulomb interactions generate a special form of disorder called charge order. When molecules are made of a combination of both type of atomic interactions, then complex disorder is found, which ranges from solutions to soft-matter systems. Liquid state integral equation theories are relatively good for simple disorder. They are generally incapable of describing complex disorder. Many body correlations involving higher than pair correlations — the so-called bridge function, are essential to describe this type of disorder, as will be outlined in this talk through several examples.

## Wetting phenomena at structured surfaces: the role of microscopic force

Alexandr Malijevský<sup>1,2</sup>

<sup>1</sup>*Department of Physical Chemistry, University of Chemical Technology Prague, Praha  
166 28, Czech Republic*

<sup>2</sup>*Department of Molecular and Mesoscopic Modelling, ICPF of the Czech Academy  
Sciences, Prague, Czech Republic*

In this talk, I will summarise the recent advances in the theory of wetting and related phenomena that are induced by geometric heterogeneity of adsorbing substrates. These includes rough, patterned or sculpted solid surfaces with microscopic length scales characterizing their non-planar structure. Particular emphasis will be placed on an intricate interplay between microscopic forces, surface and/or line tension, fluctuation effects and wall geometry which generates very complex phase and critical behaviour of the adsorbed fluid involving phenomena absent in bulk and simple planar systems. Macroscopic, mesoscopic and microscopic approaches to a description of such phenomena will be discussed in some detail and strong and weak points of the theoretical treatments will be highlighted. Repercussions of the recent findings for technological applications dealing with fabrication of superhydrophobic materials will also be briefly mentioned.

## Structural transitions in closed systems with competing interactions

Jakub Pękalski<sup>1</sup>, Eldar Bildanov<sup>2</sup>, Alina Ciach<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52,  
01-224 Warszawa, Poland*

<sup>2</sup>*Belarusian State Technological University, 13a Sverdlov Str., 220006 Minsk, Belarus*

Self-assembly of isotropic nanoparticles that interact *via* nonmonotonic pair potentials results in formation of highly symmetric structures if the system is unconfined. In particular, in a two-dimensional (2d) system of particles which effectively attract each other at short distances, and repulse at longer separations (SALR interactions), spontaneous formation of either hexagonally ordered clusters or stripes with two-fold symmetry can occur. When the system is closed, the imposed confinement can break the symmetries and give rise to new ordered patterns. In this talk, we present results for the 2d SALR model in a hexagonal confinement. We show that at low temperatures the hexagonal geometry induces self-assembly of concentric rings that have no topological defects regardless of the size of the hexagon. Moreover, melting of the rings induced by heating of the system may result in formation of spiral patterns, previously observed experimentally in diblock copolymer systems. We present a way to induce the equilibrium spiral formation with desired chirality by breaking the symmetry of the system by a tiny triangular wedge attached to one vertex of the hexagon. The formation of equilibrium spirals in both SALR and copolymer systems is explained by simple phenomenological reasoning. Our results show that isotropic particles can form globally chiral two-dimensional patterns, which are expected to have interesting optic properties, and that a small wedge can induce striking topological transitions in the stripe forming systems.

## Equilibrium properties of three-dimensional lattice fluids with SALR interactions

Ya.G. Groda<sup>1</sup>, D. di Caprio<sup>2</sup>, A. Ciach<sup>3</sup>, V. S. Vikhrenko<sup>1</sup>

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The lattice models with competing interparticle interactions (short-range attractive and long-range repulsive, so-called SALR-systems) on a three-dimensional lattice is studied as models of the biological objects like colloids or ensembles of protein molecules. In such systems, the attraction between the structural elements of the system ensures the phase separation and the repulsion can lead to the formation of clusters.

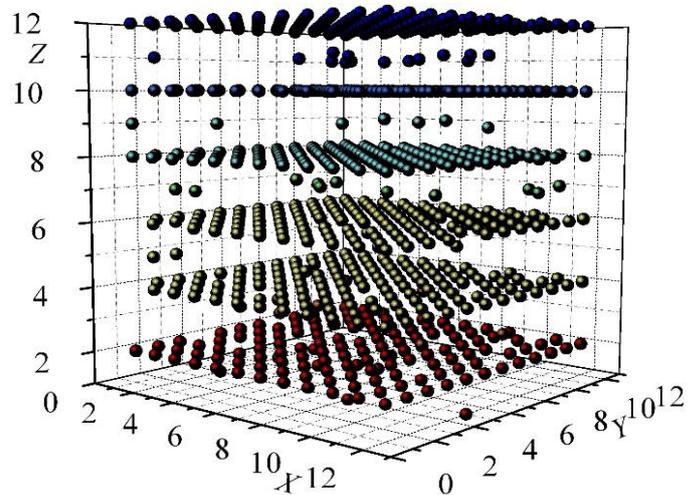
The lattice fluid with attractive interaction between the nearest neighbors and repulsive interaction between the next-next-nearest neighbors on a simple cubic lattice is investigated, as well as the lattice fluid with attractive interaction between nearest and repulsive interaction between fourth neighbors on the same lattice.

It was established that in the first case at the low temperature and the concentration of 0.5, the ordered phase corresponds to the alternation of almost completely filled and almost completely empty lattice layers (see fig. 1). In the second case, the ordered state corresponds to the fact that each lattice layer is in one of the ordered states characteristic for the square lattice and described in [1].

The geometric order parameters for localizing the second-order phase transition points are introduced for both models. With their help, the critical values of the interaction parameters were established, and the phase diagrams of the systems were constructed.

The Monte Carlo simulation data of equilibrium properties of the models are compared with the results of a quasi-chemical approximation. It is shown that the quasi-chemical approximation provides reasonable semiquantitative results for the systems studied.

In a similar way, the lattice fluid with attractive interaction between the nearest neighbors and repulsive interaction between the next-next-nearest neighbors on a body centered cubic lattice was investigated.



**Fig. 1.** The ordered phase of lattice fluid with attractive interaction between nearest neighbors and repulsive interaction between next-next-nearest neighbors on simple cubic lattice at  $\mu=9J$  ( $c = 0.5$ ) and  $J/(k_B T) = 0.25$ .

[1] Ya.G. Groda, V.S. Vikhrenko, D. di Caprio, Equilibrium properties of the lattice system with SALR interaction potential on a square lattice: quasi-chemical approximation versus Monte Carlo simulation. *Condens. Matter Phys.*, **21** (2018) 43002:1–10.

## Soft-particle system with competing interactions: field theory treatment

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We study of a system of soft particles interacting with the three-Yukawa pair potential (3Y potential). The parameters of this potential are adjusted to make it attractive at short distances and repulsive at long distances. Therefore, the potential used in this study is another example of the so-called SALR potentials [1-5], which are known for being capable of describing a specific solvent-mediated interaction between particles in m of complex molecules and charged colloids. However, contrary to most known SALR models, the particles in such systems can be rather soft, as they are, for instance, in star-polymer blends, dispersions of polymer-grafted nanoparticles, solutions of proteins, or microgel suspensions. This peculiarity can effectively be taken into account with the 3Y potential containing a soft-core repulsion. Also, the choice of this potential is motivated by the convenience of using it in an analytical theory development. In our study we present the results of both simulations and a theoretical approach for the description of structural properties of a 3Y fluid in the bulk and near a hard wall.

Using the computer simulations, we have examined the considered systems in wide ranges of densities and temperatures. We show that at low temperatures the self-assembly phenomena appear and different well-known mesostructures, such as lamellar and gyroidal phases, hexagonally packed cylindrical phases, cubically ordered and disordered clusters [1-5], are formed. Based on this, a corresponding phase diagram is built for the bulk case. In the case of the system confined between two hard walls the self-assembly effects in a 3Y fluid become even more essential and may also be observed at temperatures that are noticeably higher than in the bulk. A further increase of the temperature leads to the disappearance of mesostructures; however, a strong inhomogeneity near the wall still persists and is characterized by the split of the first maximum of the density profile. We relate this splitting to the competing nature of the pair potential between particles, because this specific behavior has not been observed earlier in a simple attractive 2 Yukawa fluid [6].

To describe structural properties of a 3Y fluid at high temperatures and reproduce density profiles obtained from our simulations, a classical field theory [6, 7] is applied. As a first step, we present theoretical results for the homogeneous phase in contact with a hard wall. We derive mean field analytical expressions for the interfacial properties, notably the density profile and the adsorption. Subsequently, we take into account Gaussian fluctuations of the density and study their effect on the structure of the fluid close to the wall for different values of the temperature and the bulk density. To this end, explicit expressions for the correlation function, the free energy, and the pressure are calculated. The results found are tested against the simulation data and the exact contact theorem for the density profile.

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## Electric field and charge distribution in near electrode and intergrain regions of solid electrolytes

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Solid electrolytes important for industrial applications are frequently ceramic objects that consist of grains connected by intergrain regions and are subject to confining effects. The long-range Coulomb interactions and inhomogeneities in the near electrode and intergrain regions considerably complicate their theoretical analysis. These complications can be taken into account on the basis of lattice models.

The lattice model of a one-component electrolyte with neutralizing background is considered. The system of equations for ion concentration distribution is formulated. The short-range Van der Waals interactions of the first neighbors are taken into account as well. The equations were numerically solved at various conditions. The interparticle correlations up to third neighbors are taken into consideration as well. The influence of correlations and short-range interactions on charge and electric field distribution is investigated.

The short-range interactions and correlations result in non-monotonic oscillating decaying of the charge distribution in the near electrode regions. At large surface charge of the same sort as the mobile ions the depletion near electrode zone appears. At zero surface charge density and not too small concentration of mobile ions, the short-range interactions cause wave-like charge distribution in the bulk that is characteristic for competing effects of long-range Coulomb repulsion and short-range Van der Waals attraction. The intergrain regions are modelled by variations of the energetic landscape created by the host system on which the mobile ions can perform thermally activated moves. This landscape results in redistribution of mobile ions and creation of double layer like charge distribution in the intergrain regions.

At small mobile ion concentration and in a weak external electric field the equations for charge distribution can be analytically solved. Again, the oscillating decaying of the charge distribution in the near electrode region is observed. The dependence of the decaying constant and oscillation period on thermodynamic parameters is established.

Monte Carlo simulation of 3D Coulomb lattice model with and without short-range interactions is performed. The Ewald method is used for summation of the Coulomb interactions. The results are compared with the analytical and numerical solutions of the model.

## Electrical double layers close to ionic liquid-solvent demixing

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In recent years, much work has been headed towards understanding the properties of ionic liquids (ILs) at metallic interfaces. The main focus so far has been on electrical double layers (EDLs) with ILs far from phase transitions, while EDLs with ionic liquid-solvent mixtures (ILSMs) in the proximity of their phase separation received virtually no attention. In this talk, I will describe a mean-field model suitable for IL-solvent mixtures close to demixing. In this model, we took into account dispersion interactions [1], which are often neglected in theoretical approaches, and we combine it with the Carnahan-Starling and Bikerman-Kornyshev expressions for the excluded volume interactions. We demonstrate the emergence of a new type of the capacitance shape, a “bird” shape, in addition to the extensively studied camel and bell shapes. Remarkably, we reveal that the camel-shaped capacitance, which is a signature of dilute electrolytes, can be observed also at high concentrations in the vicinity of demixing [2]. We also find that the energy stored in an EDL increases appreciably as the system approaches demixing, which can be utilized for generating electricity from waste heat [1, 2].

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## Effect of adatom diffusion and reaction on the morphology and the porosity of electrodeposited films

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In the fields of material science, there is a tremendous interest in designing micro/nano structures, with desired morphology and roughness, allowing the preparation of materials with properties on demand. Among studied micro/nano structures, dendrites offer various morphologies with potential applications in different fields.

In this presentation, results dealing with the formation of electrodeposited films with dendritic morphology and controlled porosity using a simple lattice model will be discussed. The model takes into account a diffusive flux of cations in solution, the instantaneous adsorption and reaction in contact with the film surface, and a relaxation modelled by random walks of mobile atoms on that surface, with a maximum of  $G$  hops per atom and a detachment probability  $\epsilon$  per neighbor at the current position. The simulations highlight the formation of a compact layer followed by the formation of branched morphologies, dendrites with given porosity. The instability onset for the transition is analysed and a scaling approach is applied to predict the crossover. It is also shown that the dendritic morphology depends on the interplay between the energetics of the crystal and the electric current. Furthermore, assuming that the adsorbate diffusion is thermally activated, we suggest that the average dendrite size is a ratio between an Arrhenius factor and a power law of the current.

The simulation results are compared to experimental results of electrodeposition and a good agreement is found.

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## Recent progress in the theoretical description of fluid-fluid phase behaviour in the explicit solvent ionic model

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The description of the thermodynamic behaviour of ionic solutions including their phase separation is important in many fields such as biology, electrochemistry, and material science. The simplest model capable of capturing the main features of the systems with electrostatic interactions is the restricted primitive model (RPM). In this model, the ionic fluid is modelled as an electroneutral binary mixture of charged hard spheres (HS) of equal diameter and valency immersed in a structureless dielectric continuum. A major drawback of this model is the use of the solvent continuum assumption in which the effects of solvent structure are totally neglected. The simplest possible model which treats the solvent explicitly is a mixture of the RPM fluid and neutral hard spheres (the RPM-HS mixture). In such a model, the polar nature of the solvent is represented implicitly by a continuum background with a dielectric constant. The RPM-HS mixture undergoes a demixing phase transition in the phases of different ion concentrations. This problem was considered by us recently using the associative mean spherical approximation (AMSA) [1].

Now, we present a study of the fluid-fluid phase behaviour of an ionic solution model in which the solvent molecules are of non-spherical shape. More precisely, we focus on the mixture of the RPM and uncharged hard spherocylinders (HSC) and refer to this system as the RPM-HSC mixture [2]. To this end, we combine two theoretical approaches, i.e., the scale particle theory (SPT) and the AMSA. The SPT is sufficient to provide a rather good description of a reference system taking into account hard-core interactions not only for the bulk, but also for the systems confined in disordered matrices [3-5]. Therefore, we extend our theoretical approach for the description of the thermodynamic properties of mixtures consisting of model ionic liquids and neutral elongated solvent molecules in disordered porous materials. Based on this, the fluid-fluid phase diagrams of the RPM-HSC mixtures are calculated in the temperature-density and temperature-concentration coordinates at different pressures. In the model, we set diameters of HSC particles  $\sigma_2$  equal to the diameter of RPM particles  $\sigma_1$ , while the length of HSC particles is chosen  $L_2/\sigma_2 = 5$  or  $10$ . From the results we have noticed a formation of nematic state in the HSC-rich phase for  $L_2/\sigma_2 = 10$  in a wide range of considered pressures, while for  $L_2/\sigma_2 = 5$  the nematic phase is found only at high pressures. It is shown that in a disordered matrix the region of coexisting phases gets narrower and shifts towards lower densities in comparison with the bulk case. Moreover, the confinement effect of matrix favors a formation of the nematic state in a HSC-rich subsystem. The AMSA results are also compared with the mean spherical approximation (MSA). It is found that in general both approximations lead to similar qualitative results for the phase diagrams. However, the AMSA and the MSA produce different concentration dependences, i.e., contrary to the MSA, the AMSA phase diagrams show that the high-density phase mostly consists of the ions for all pressures considered. To demonstrate the effect of asphericity of solvent molecules on the

fluid-fluid phase transition, we consider an “equivalent” mixture in which the HSC particles are replaced by HS particles of the same volume. It is observed that in the case of HSC solvent, the region of phase coexistence is wider than for the solvent molecules being of spherical shape. It is also noticed that the critical temperature is higher in the RPM-HSC model than in the equivalent RPM-HS model, though it becomes the same at higher pressures in the MSA, while in the AMSA this difference remains considerable.

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## Theory for charge distribution in ionic liquids near a charged wall

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The mesoscopic field theory for ionic systems [1] is extended to the system with charged boundaries. A very simple expression for the excess grand potential functional of the charge density is developed. The size of hard-cores of ions is taken into account in the expression for the internal energy. The functional is suitable for a description of a distribution of ions in ionic liquids and ionic liquid mixtures with neutral components near a weakly charged wall. The Euler-Lagrange equation is obtained, and solved for a flat confining surface. An exponentially damped oscillatory charge density profile is obtained. The electrostatic potential for the restricted primitive model agrees with the simulation results on a semiquantitative level.

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## Ground state of a system with SRLA interaction

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Self-assembly of soft shell-hard core (SSHC) particles on fluid-fluid interfaces can be driven by competition between isotropic repulsive and attractive forces. If the repulsion dominates at short distances and attraction at larger separation, the effective interaction potential takes form of the so called SRLA potential. So far, SSHC particles were shown to form only hexagonally ordered structures when exposed to lateral pressure. We present a lattice model for the SSHC particles that shows stability of ordered phases with different symmetries.

In our model, the particles repulse each other when they are nearest or next-nearest neighbors and attract each other at longer distances. The thermodynamic Hamiltonian of the system has the following form:

$$H = \frac{1}{2} \sum_{k=1}^{k_{\max}} \sum_{ki=1}^{z_k} \sum_{i=1}^M J_k \hat{n}_i \hat{n}_{ki} - \mu \sum_{i=1}^M \hat{n}_i$$

where  $M$  is the total number of lattice sites,  $ki$  numerates the sites of the  $k$ -th coordination sphere around site  $i$ ,  $z_k$  is the coordination number,  $J_k$  is the interaction constant for  $k$ -th coordination sphere,  $\hat{n}_i$  is the occupation number (0 or 1),  $\mu$  is the chemical potential.

We found that at zero temperature, where the value of the Hamiltonian determines the stability of the structure, depending on the chemical potential a vacuum, condensed phase or ordered states were found stable. Apart from the ordered states with hexagonal symmetry, a lamellar phase and a number of different ordered structures were found. Our results indicate that the range of the attractive and repulsive parts of interaction significantly influence the pattern formation. At positive temperature the chemical potential versus concentration, order parameter, number of particles and energy fluctuations were investigated.

## Effect of aggregation on adsorption phenomena

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Adsorption at an attractive surface in a system with particles self-assembling into small clusters is studied by Molecular dynamics (MD) simulation. We assume Lennard-Jones plus repulsive Yukawa tail interactions, and focus on small densities. The relative increase of the temperature at the critical cluster concentration near the attractive surface (CCCS) shows a power-law dependence on the strength of the wall-particle attraction. At temperatures below the CCCS, the adsorbed layer consists of undeformed clusters if the wall-particle attraction is not too strong. Above the CCCS, or for strong attraction leading to flattening of the adsorbed aggregates, we obtain a monolayer that for strong or very strong attraction consists of flattened clusters or stripes respectively. The accumulated repulsion from the particles adsorbed at the wall leads to a repulsive barrier that slows down the adsorption process, and the accession time grows rapidly with the strength of the wall-particle attraction. Beyond the adsorbed layer of particles, a depletion region of a thickness comparable with the range of the repulsive tail of interactions occurs, and the density in this region decreases with increasing strength of the wall-particle attraction. At larger separations, the exponentially damped oscillations of density agree with theoretical predictions for self-assembling systems. Structural and thermal properties of the bulk are also determined. In particular, a new structural crossover associated with the maximum of the specific heat, and a double-peaked histogram of the cluster size distribution are observed.

## Synthesis of porous TiO<sub>2</sub> aggregates for Li-ion batteries application

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During the past few years, there have been enhanced interest in controlling the properties of thin films regarding desired application. Among the strategies reported, nanoparticles agglomeration appear to be a promising approach to obtain materials with controlled architectures and desired properties. Furthermore, for achieving a higher integration level, deposited thin film should provide one or more function.

In this work, porous TiO<sub>2</sub> aggregates of controlled size and porosity have been successfully prepared hydrothermally. Different techniques were used to characterize prepared porous TiO<sub>2</sub> aggregates such as DRX, BET, FEGSEM and electrochemical measurements. It was illustrated that the size of prepared TiO<sub>2</sub> aggregates is ranged from 10 nm to 100 nm and their pores size from 5.6nm to 12nm. In addition, it was demonstrated that the properties of prepared aggregates in terms of size and porosity were influenced by the synthesis temperature. The aggregate formation and properties were discussed in terms of efficient collision and coalescence processes. Furthermore, prepared porous TiO<sub>2</sub> aggregates have been investigated as a negative insertion electrode material for the lithium-ion batteries application and the role of the aggregates properties on its performance are discussed.

## **The effect of electric field on the productivity of lithium cell with porous anode**

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By means of computer simulation, the potentiodynamic cycling and galvanostatic discharge curves have been obtained for lithium cell with nanoporous carbon anode. Predictions of the three types of models describing the intrusion of positive lithium ions into anode have been considered and compared with experimental data and with each other: purely diffusive model, the model of chemical potential and the electrodynamic one. Our investigation suggests that all the interactions — both direct and indirect — between ions in the bulk of carbon anode could be reduced to mere electrostatic.

## INFORMATION ABOUT THE HOST INSTITUTION



The Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine (ICMP of NAS of Ukraine) was founded in 1990. It became the first academic center for fundamental investigations in physics in western Ukraine. The principal directions of scientific research in ICMP include

- statistical theory of solid state and soft matter;
- computer simulations of physical and chemical processes and calculations of the main characteristics of condensed matter;
- physics of complex systems.

However, an actual chronicle of ICMP started on April 1969 with the foundation of the Lviv Department for Statistical Theory of Condensed States of the Kyiv Institute for Theoretical Physics (ITP) of the Academy of Sciences of Ukrainian SSR (now – The Bogolyubov Institute for Theoretical Physics of NAS of Ukraine). The department was founded by a young and active professor Ihor Yukhnovskii, head of the Chair of Theoretical Physics of the Ivan Franko Lviv State University. An idea to establish this department was a natural continuation of scientific collaboration between I.R. Yukhnovskii and academician N.N. Bogolyubov who was a director of ITP at that time. From the time of foundation and till May 2006, the Institute was headed by academician Ihor Yukhnovskii. Since 2006 the Institute is headed by academician Ihor Mryglod, the former student of I. Yukhnovskii.

In 1992, a new project UARNet (Ukrainian academic and research network) was established and, within its framework, the first in Ukraine satellite channel connected to global information network was built in 1993. Later (1995), a separate laboratory for information technologies and computer networks was founded in ICMP, known since 1999 as independent state enterprise “Research and Telecommunication Centre “Ukrainian Academic and Research Network” of ICMP.

In 2001, the first in Ukraine computational cluster was launched. In 2007, the cluster was connected to GRID network of NAS of Ukraine, and in 2009 the western regional GRID node of the academic GRID-network was created on its base. ICMP cluster is among five biggest clusters of all-national grid infrastructure.

Since 1993 the Institute issues a quarterly journal “Condensed Matter Physics”, which publishes both original and review papers on statistical physics and theory of condensed matter. Since 2005 it is included into the list of the main scientific editions, created by the American Institute for Scientific Information, and in 2008 it was the first in independent Ukraine to be evaluated by an impact-factor.

Nowadays, the organizational structure of ICMP consists of four departments and a laboratory: Department for Statistical Theory of Condensed Systems, Department for

Quantum Statistics, Department of Soft Matter Theory, Department for Computer Simulations of Many-Particle Systems and Laboratory for Statistical Physics of Complex Systems. The research staff includes two Full Members and three Corresponding Members of the Academy, 23 Doctors and 37 Candidates (Ph.D) of Sciences in Physics and Mathematics. Currently we supervise seven Ph.D students, and three doctorants are seeking for full habilitation (the degree of Doctor of Sciences). We have certain experience of scientific collaboration with more than 50 research centers throughout the world, among them institutes and universities of Poland, France, Austria, Great Britain, USA, Slovakia, Czech Republic, Germany, Italy, Slovenia, Spain, Sweden, Japan, etc.

The main institute building, located at Svientsitski Street 1 (the former Instytutaska Street), was built in 1900 according to the project of Ludvig Verzhbitsky – a well-known architect, a public figure and a designer of many municipal buildings in Galychyna. Previously, the Society for Scientific Assistance was located here. In Soviet times, the building belonged to Lviv Committee of Communist Party. The Institute for Condensed Matter Physics of NAS of Ukraine moved into this building in 1991.

# Structural transitions in closed systems with competing interactions

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Marie Skłodowska-Curie  
Actions

# Outline

## **Introduction:**

Pattern forming systems in the bulk.

## **Scope:**

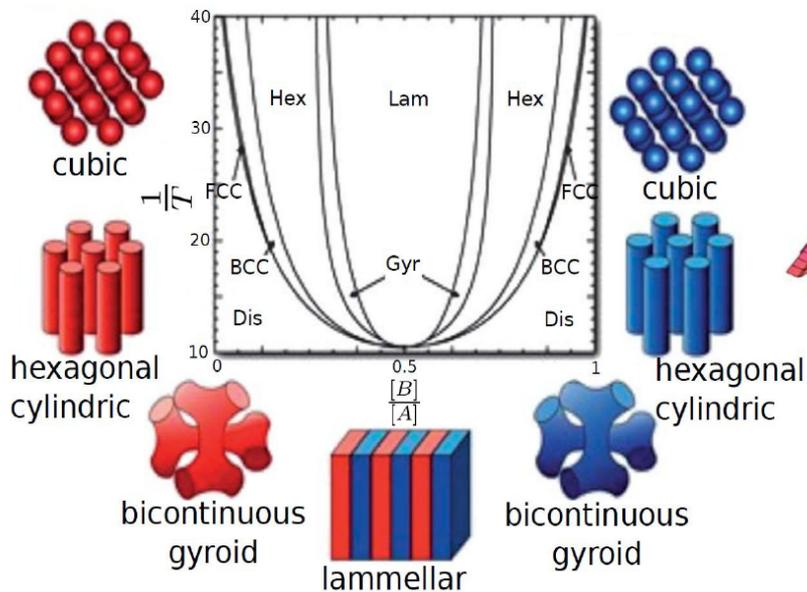
Pattern self-assembly in confinement

## **Plans:**

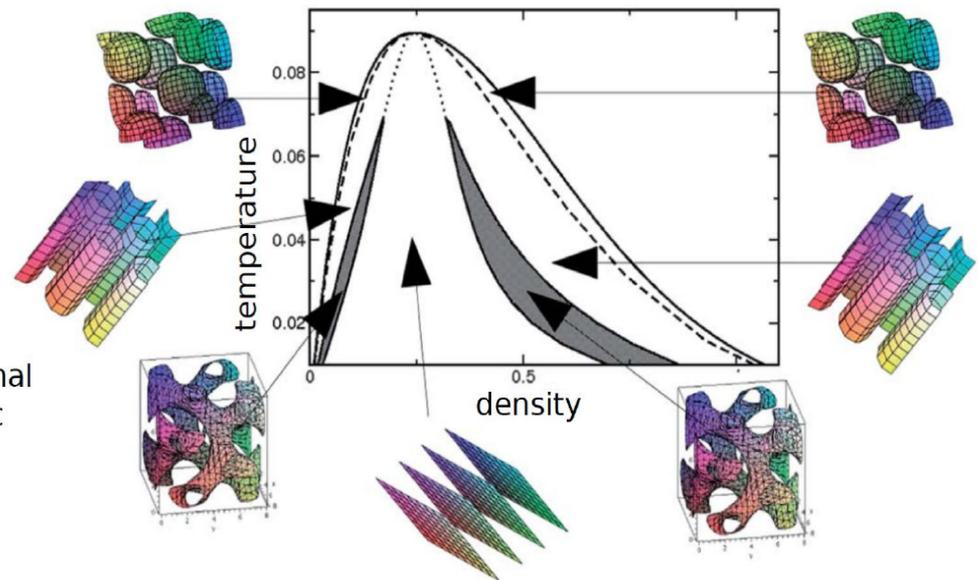
Shear impact on disordered states

# Universality among 3D pattern forming systems

## DiBlock Copolymers

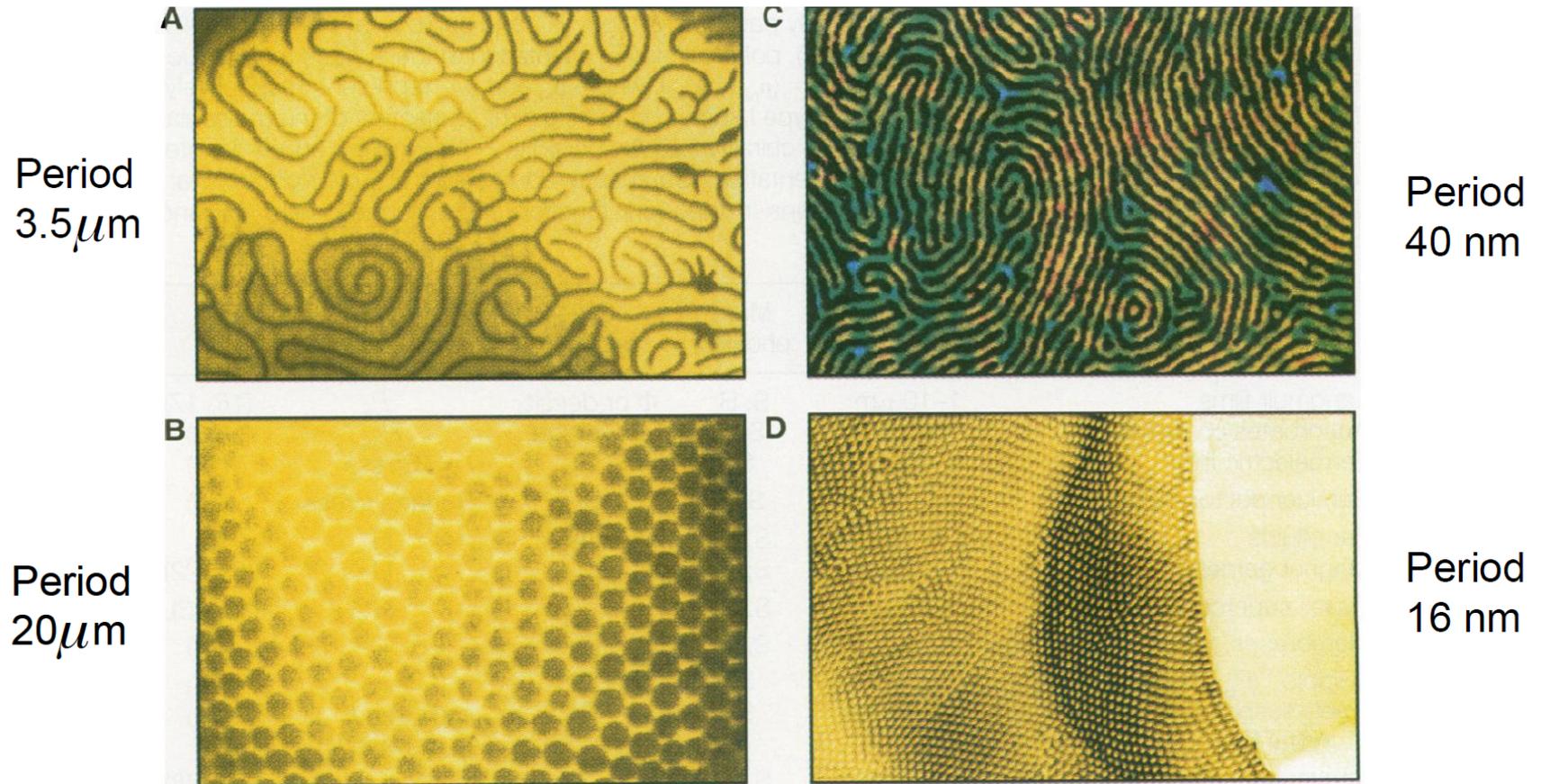


## Isotropic SALR particles



Both systems can be described by Landau-Brazovskii functional of the same form.  
(A. Ciach, J. Pekalski and W. T. Gozdz *Soft Matter* **9** 6301 (2013))

# Pattern formation in 2D bulk

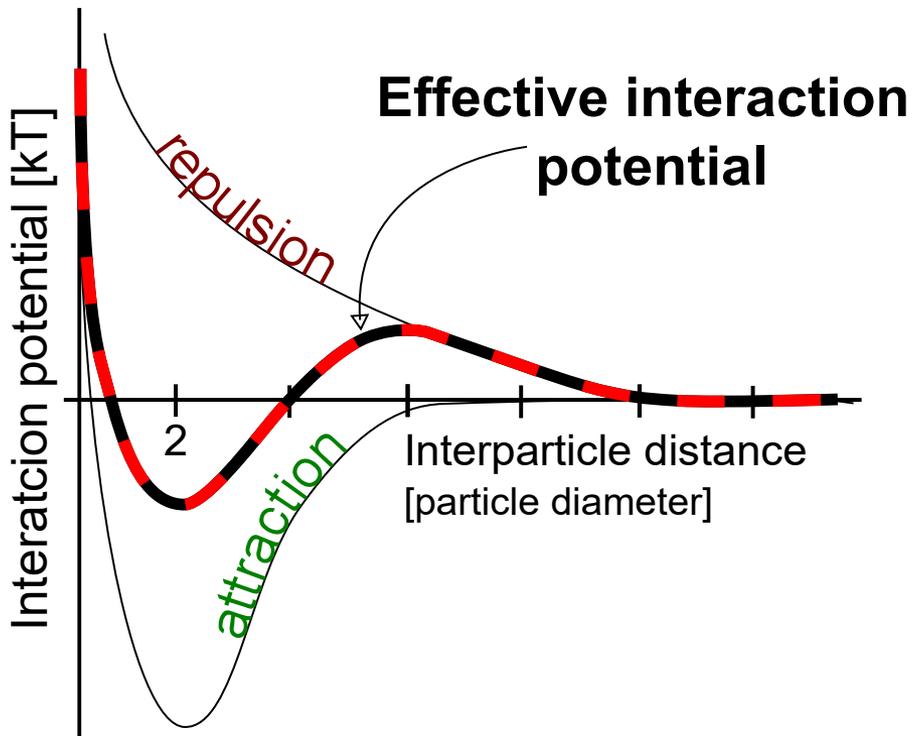


Panels A, B: organic Langmuir films seen by fluorescence microscope.  
Panels C, D: solvent-cast film of block copolymers imaged by TEM.

M. Seul and D. Andelman, *Science* 267:476 (1995)

# SALR particles

Isotropic particles with competing attractive and repulsive interactions.



Origin of **attraction**:

- Van der Waals interactions
- Entropic depletion interactions
- Solvophobic forces

Origin of **repulsion**:

- Electrostatic interactions
- Surface curvature effects

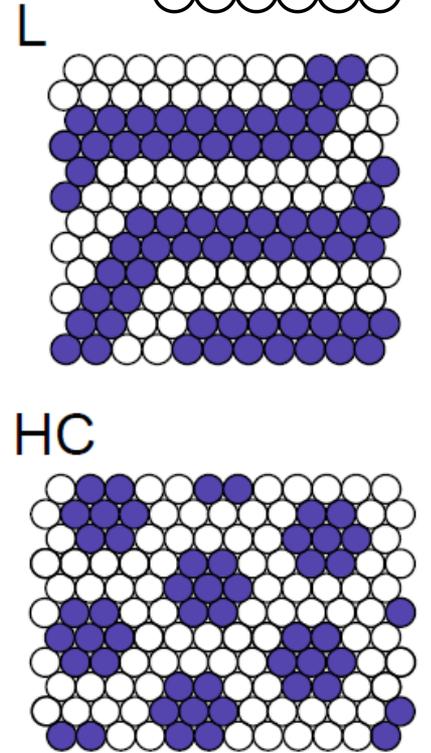
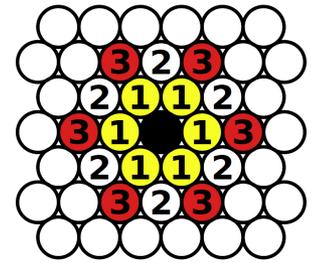
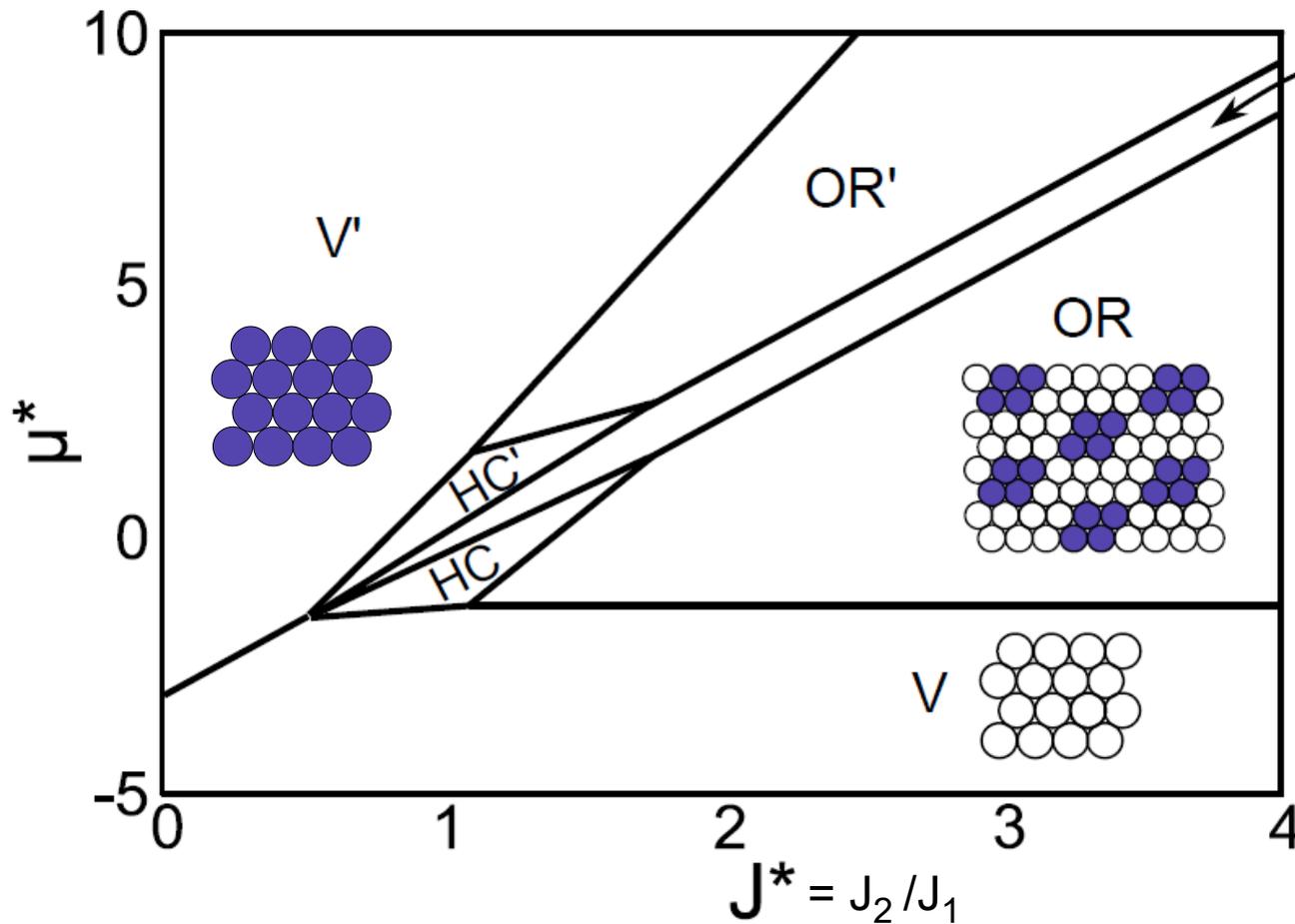
**Effective interaction:**

**Short-range Attraction and Long-range Repulsion (SALR)**

Examples: colloidal suspensions, protein solutions, quantum dots, nanoparticles covered with polymeric brushes.

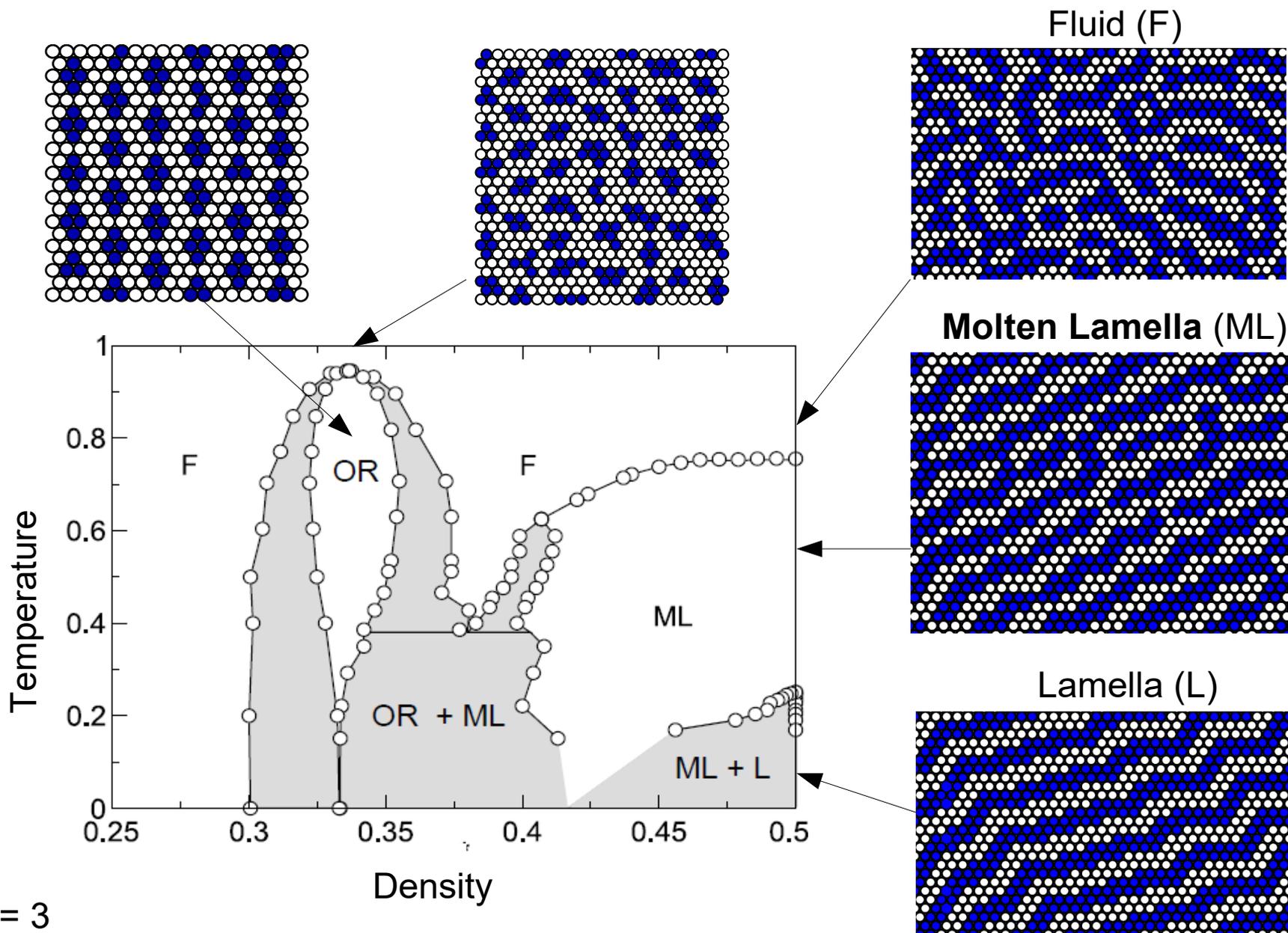
$$U_{\text{SALR}} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{2\alpha} - \left( \frac{\sigma}{r_{ij}} \right)^\alpha \right] + D \frac{e^{-r_{ij}/\xi}}{r_{ij}/\xi}.$$

# Bulk Ground State ( $T = 0$ K)



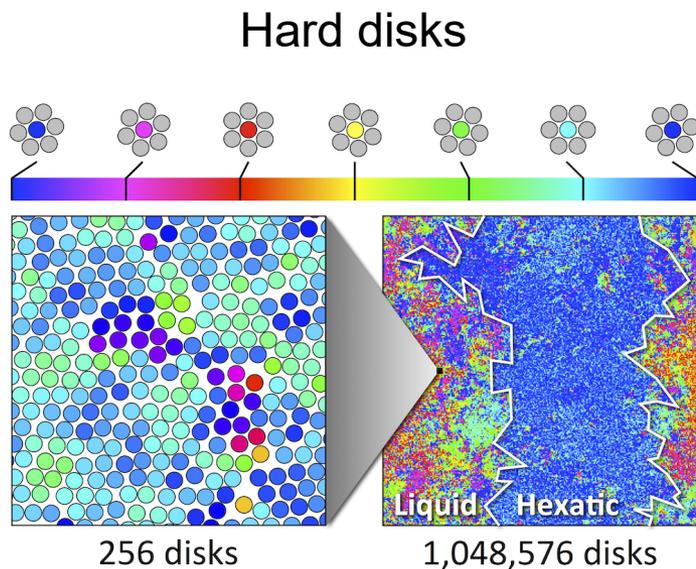
$\mu^*$  - the dimensionless chemical potential,  $J^*$  - ratio of repulsion to attraction energy

# Phase diagram ( $T^* > 0$ and $J^* = 3$ )

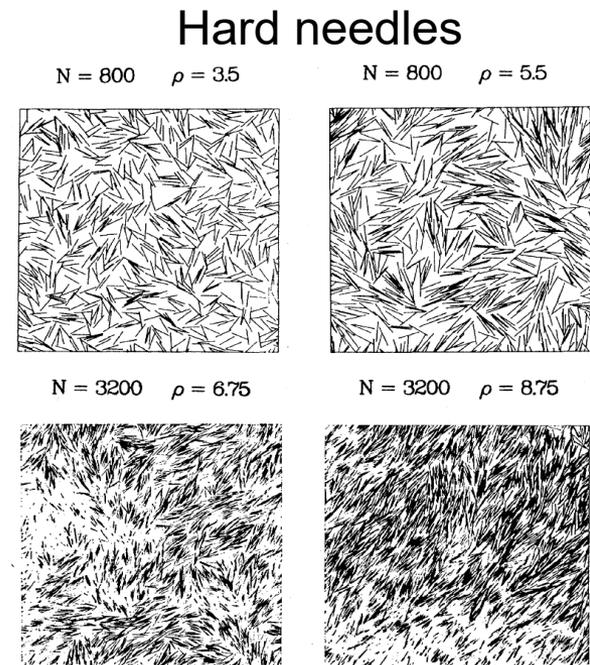


# Take home message 1:

Particles with isotropic interactions can have **orientational order**.



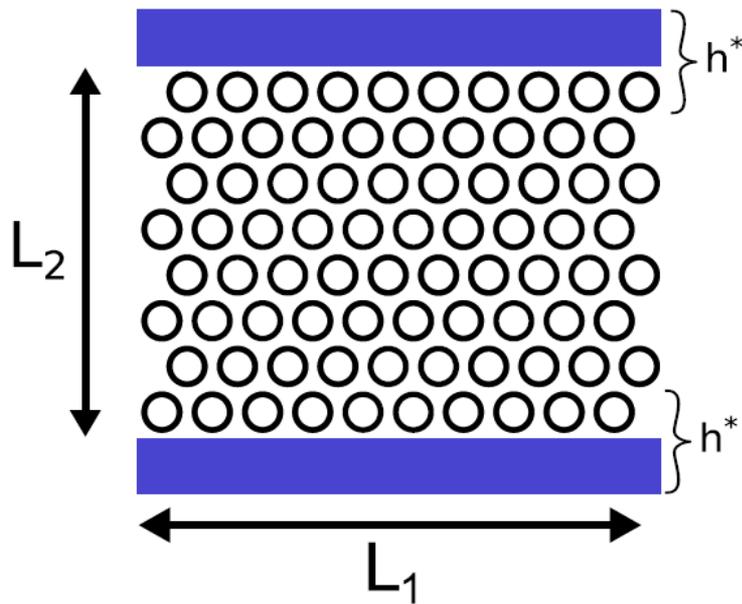
M. Engel et. al *Phys. Rev. E* **87**, 042134 (2013)



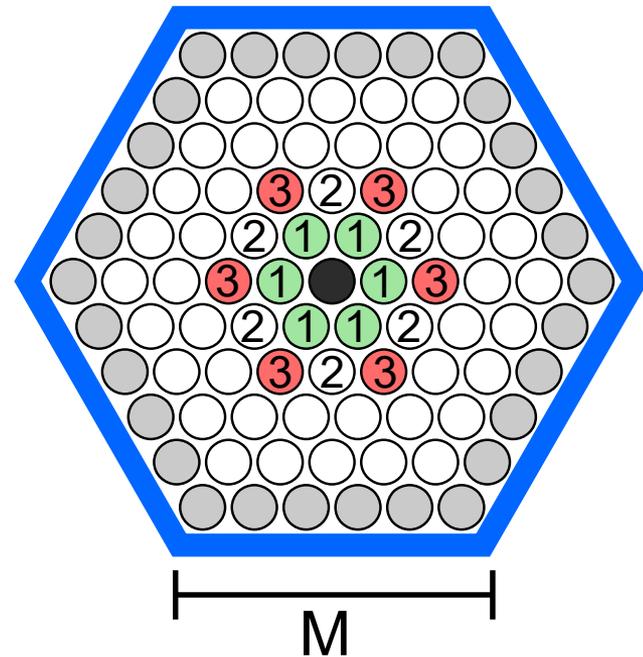
D. Frenkel, R. Eppanga, *Phys. Rev. A*, **31**(3), 1776 (1985)

# Structural transitions in confined stripe-forming systems

A. Slit



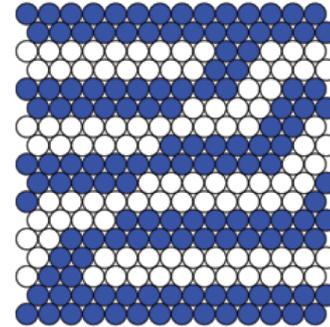
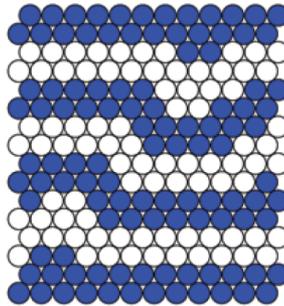
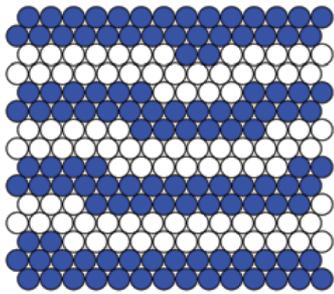
B. Hexagon



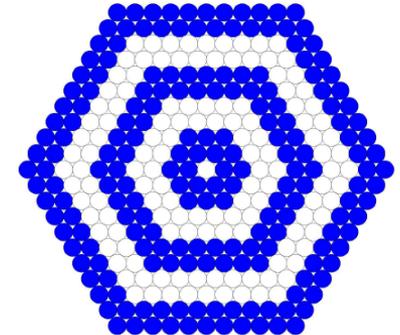
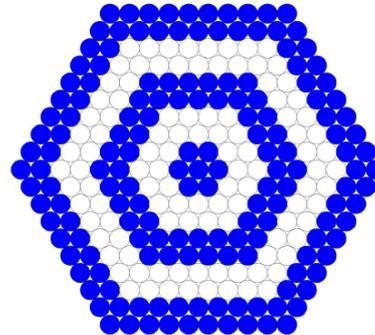
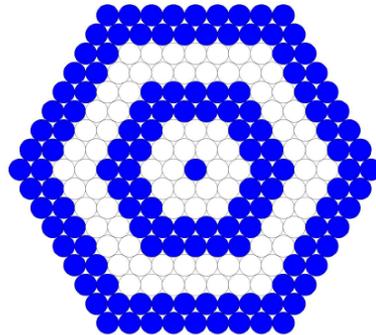
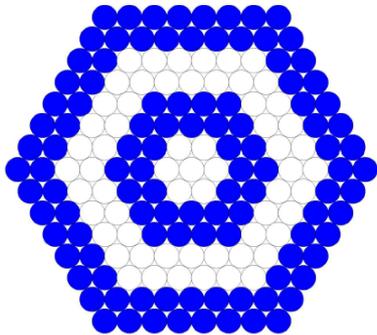
Question: can geometry induce formation of new structures?

# Ground State ( $T=0$ )

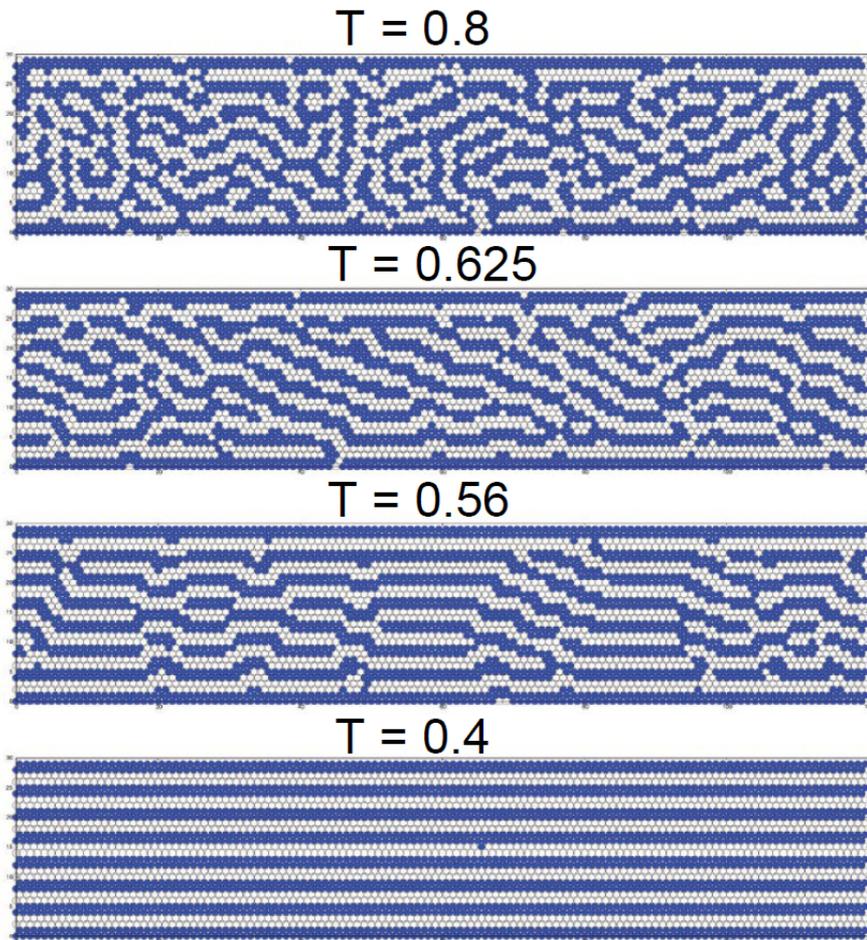
**Slit:** Periodic corrugations appear if the wall-wall distance is not fitted to the period of the bulk structure.



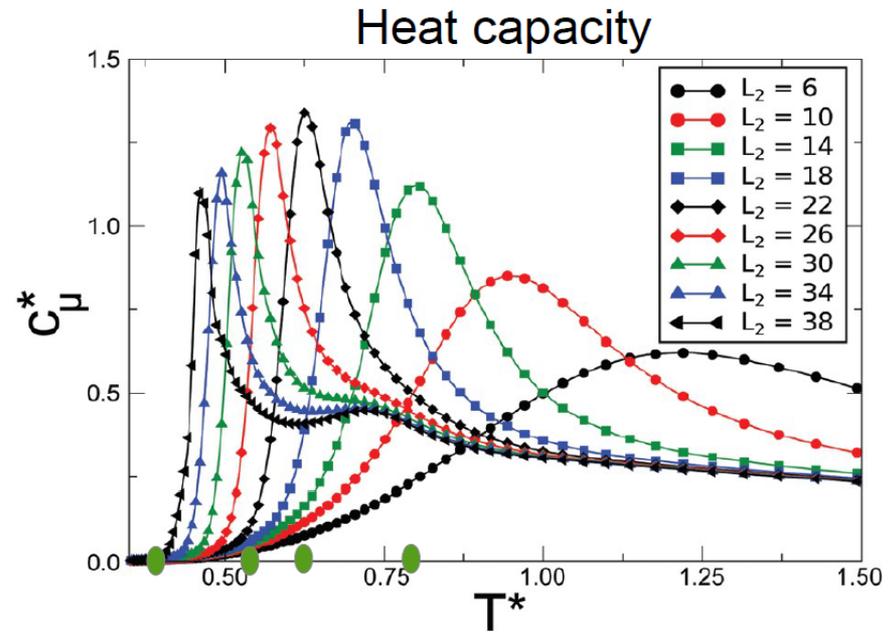
**Hexagon:** for any system size concentric rings are formed.



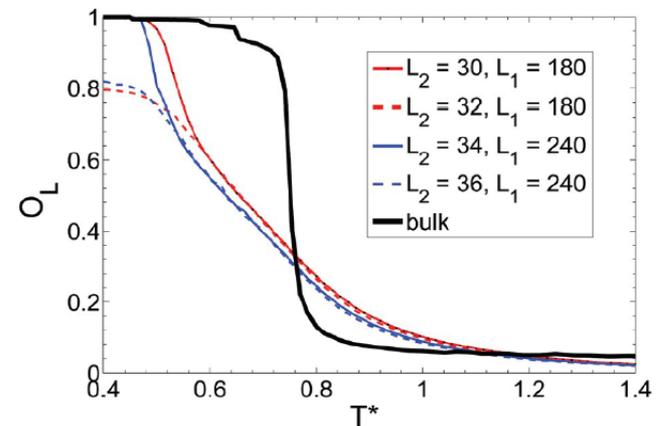
# What happens at $T > 0$ inside the **slit**?



$L_2 = 30$

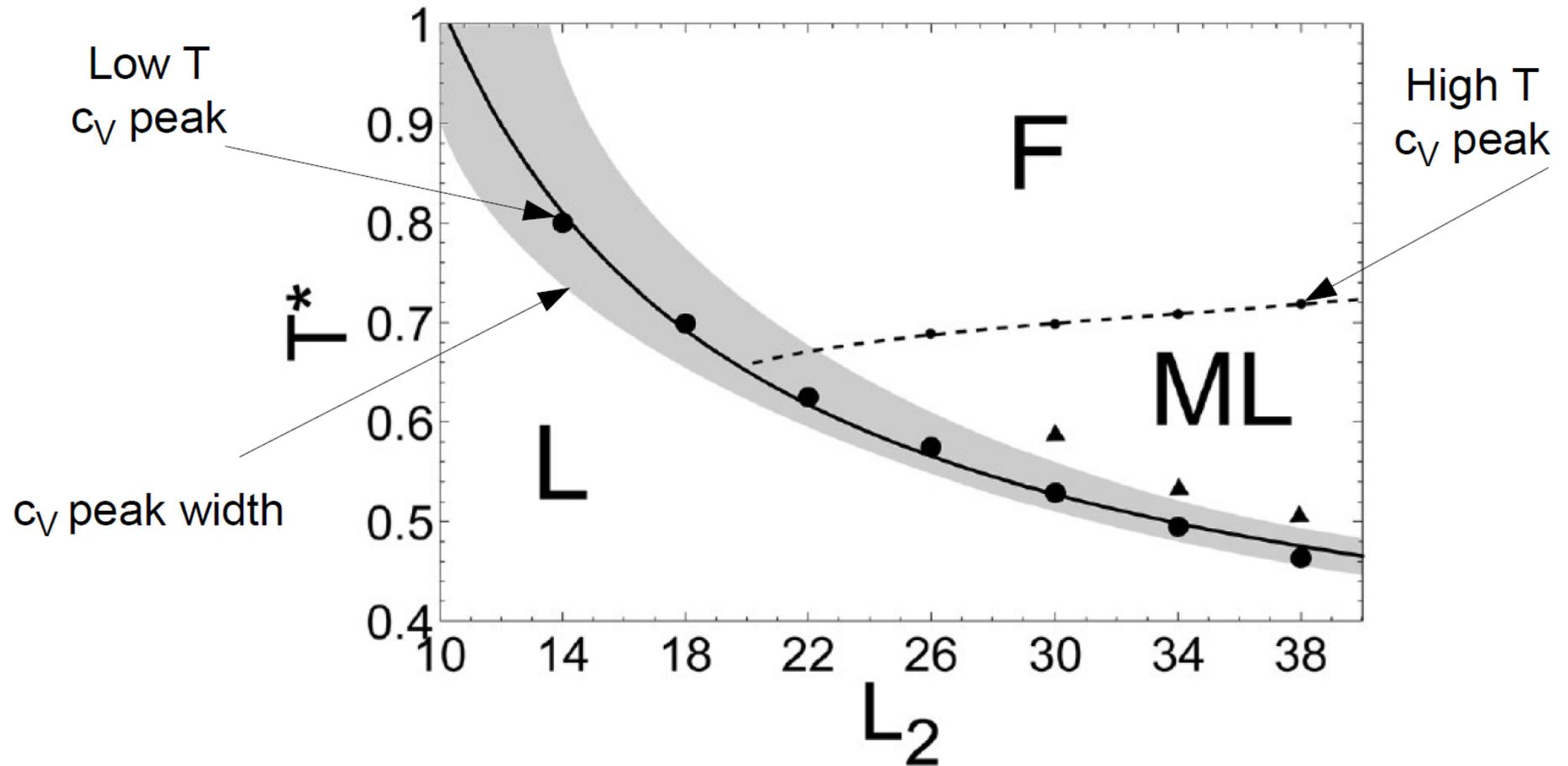


## Orientational Order Parameter



# What happens at $T > 0$ inside the **slit**?

Heat capacity based structural diagram



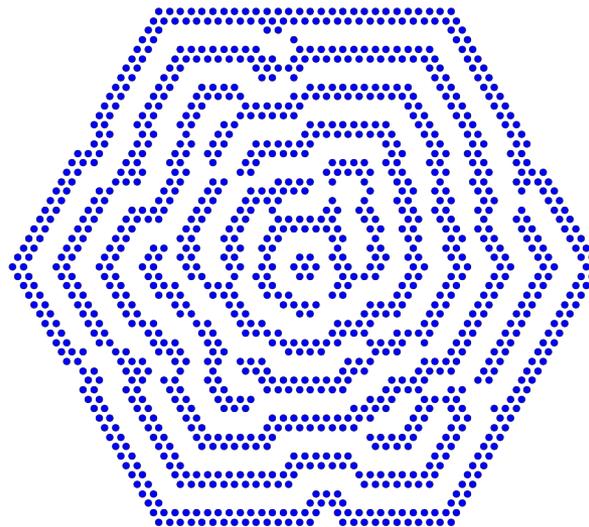
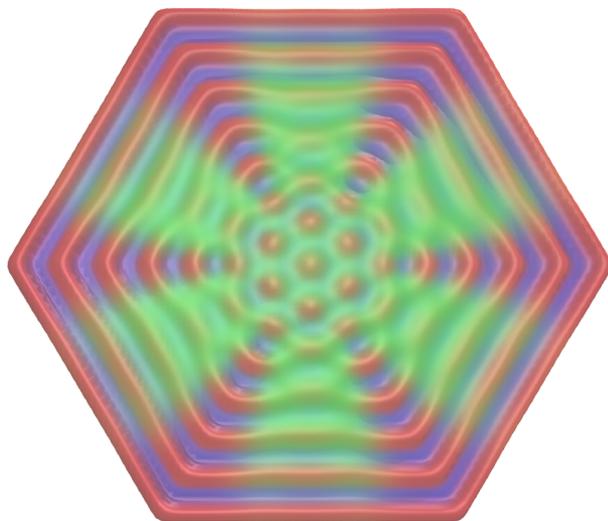
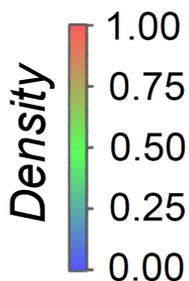
In the bulk  $L \rightarrow ML$  transition is at  $T^* = 0.245$  !

The solid line is the best fit to the equation:  $T_K^*(L_2) = T_b^* + a/L_2$ .

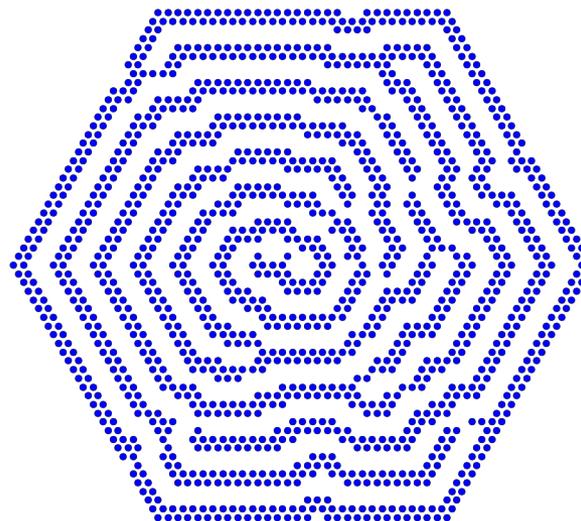
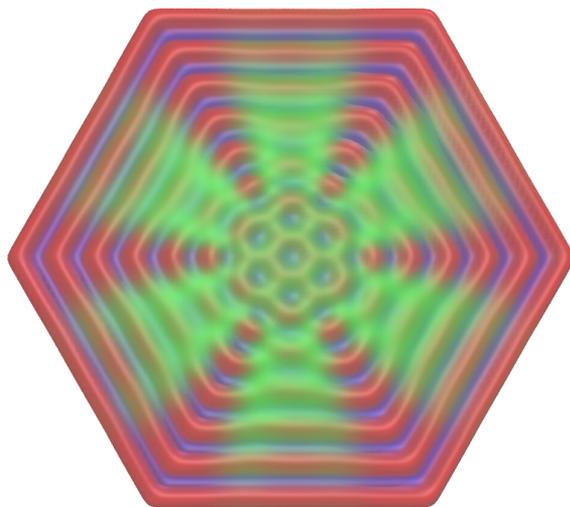
More details: N. G. Almarza, J. Pękalski, A. Ciach, *Soft Matter* **12** 7551 (2016)

# What happens at $T > 0$ inside the **hexagon**?

$M = 28$   
 $T = 0.49$



$M = 30$   
 $T = 0.47$



(density map)

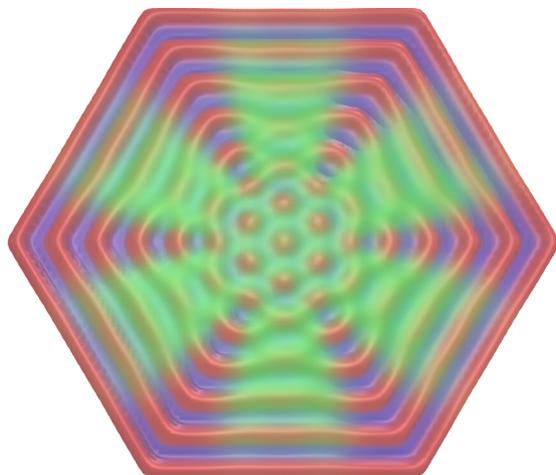
(single snapshot)

Note: ordering occurs only at the level of average densities

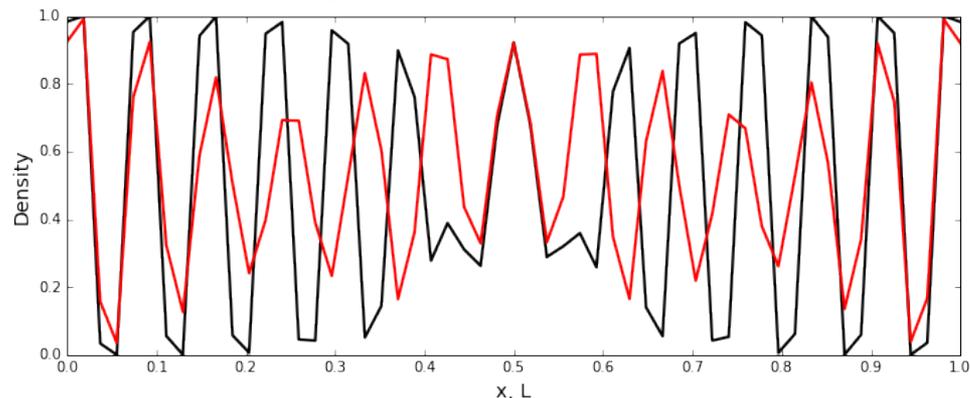
# Pattern origin

„Inteference” of density waves

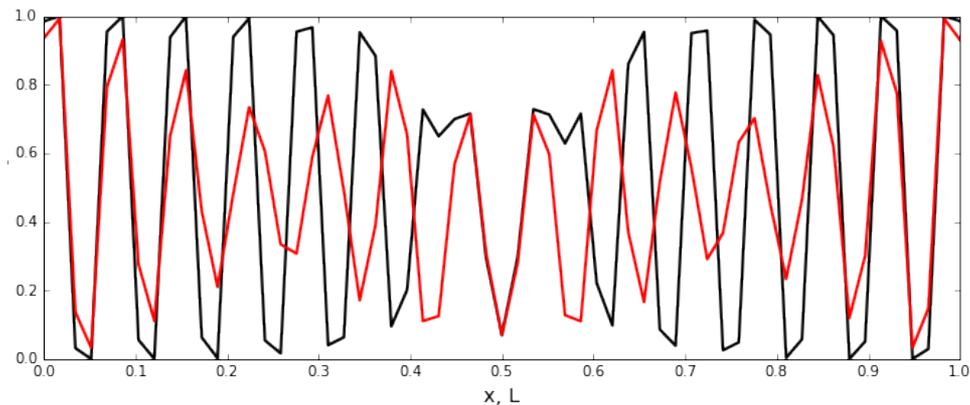
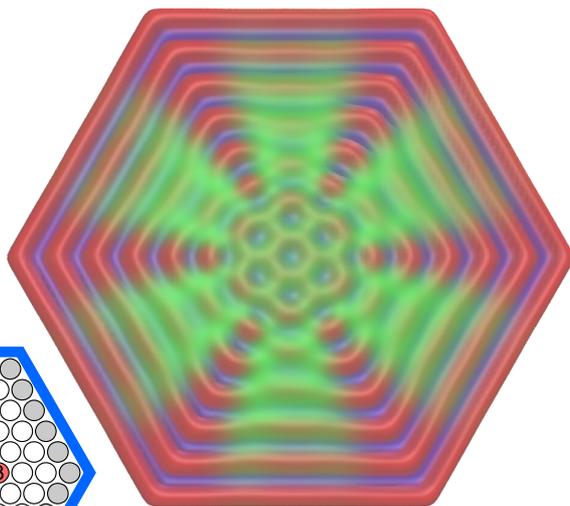
$M = 28$   
 $T = 0.49$



Density profiles along different axes



$M = 30$   
 $T = 0.4$

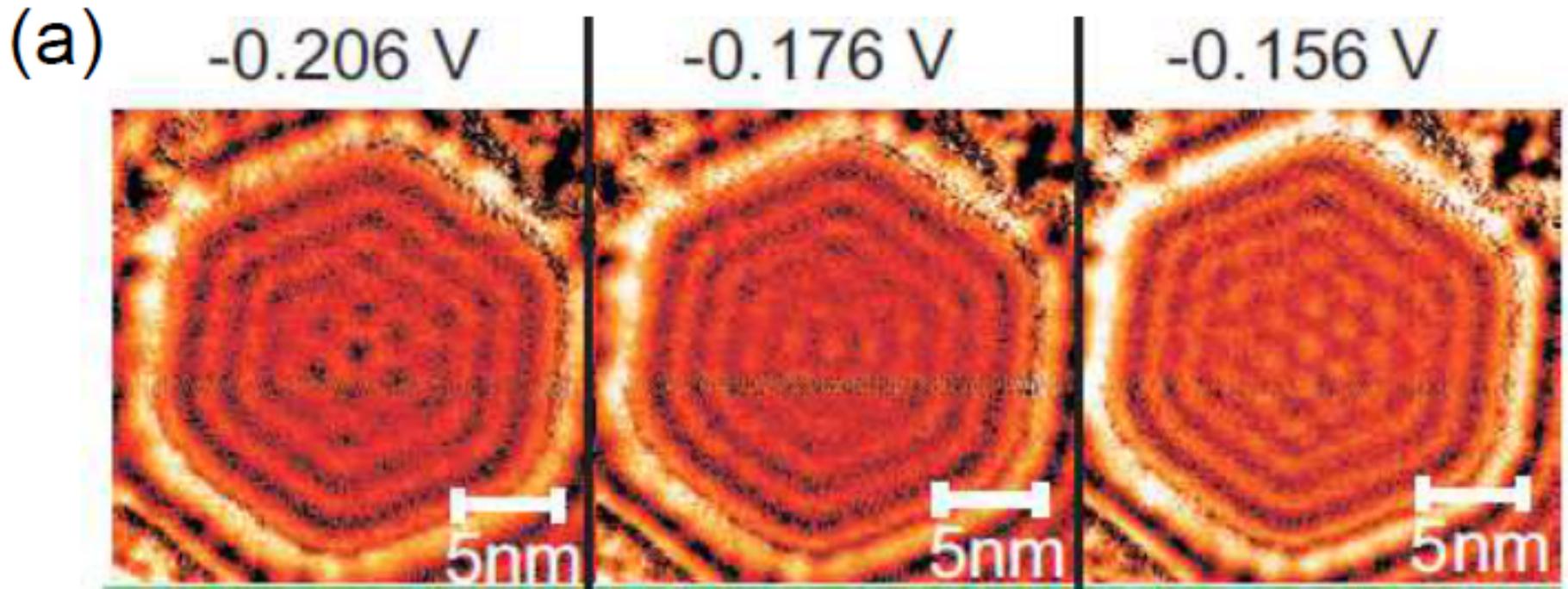


 side center     diagonal

# Pattern origin

„Inteference” of density waves

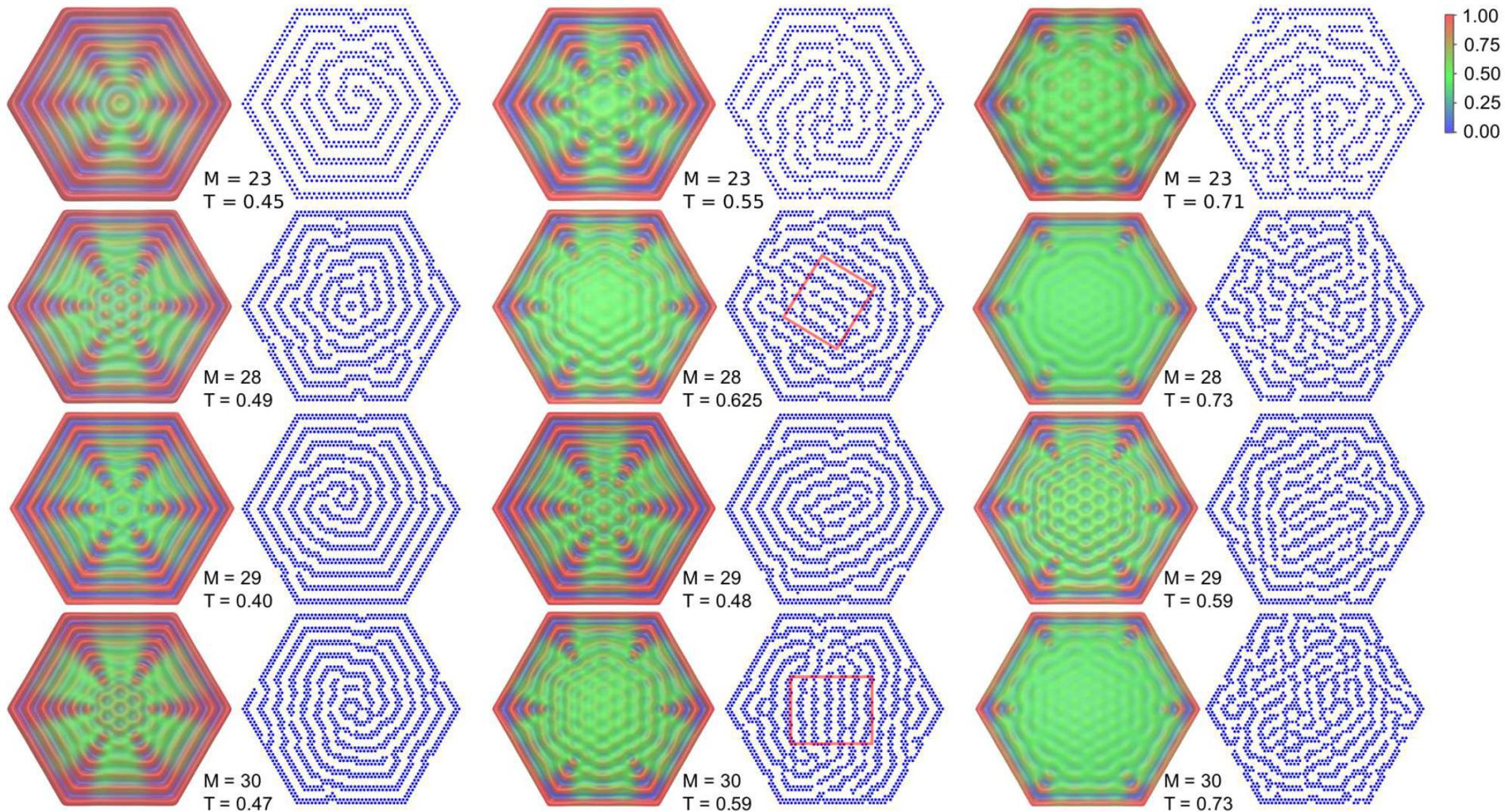
Electron Local Density of States exhibit similar patterns when confined in hexagonal nanostructure.



# Highly complex structural behavior

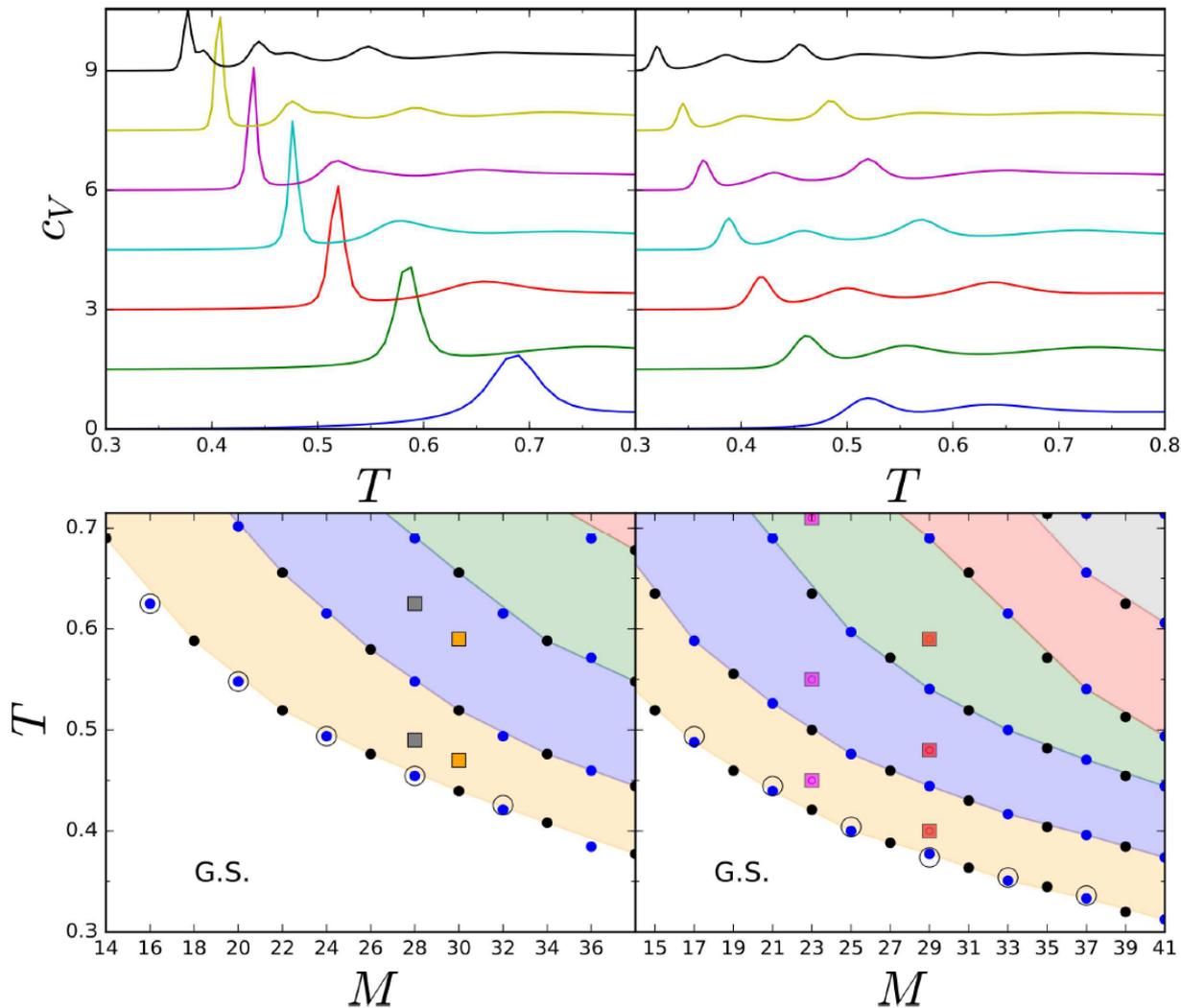
Average density maps vs. single snapshots

M \ T

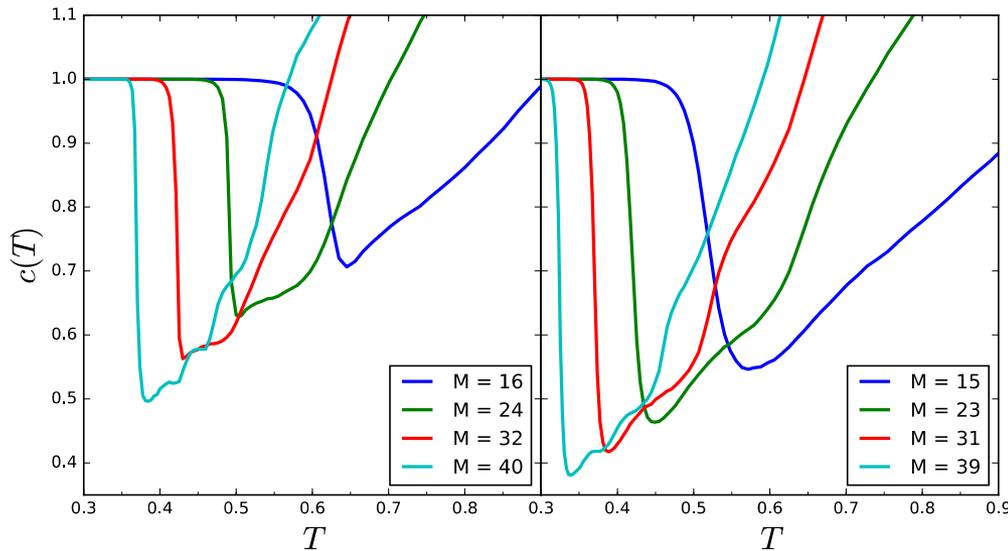


Temperature

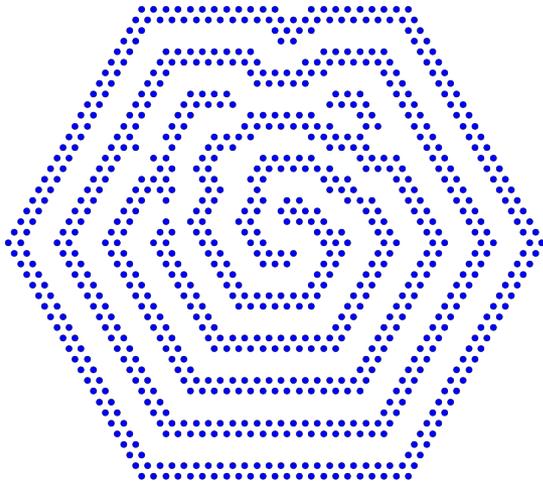
# Heat Capacity Based Structural Diagram For hexagonal confinement



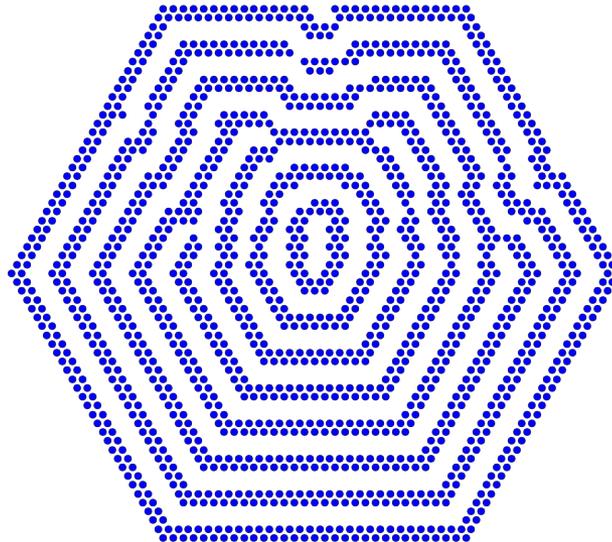
# Average cluster size change with temperature



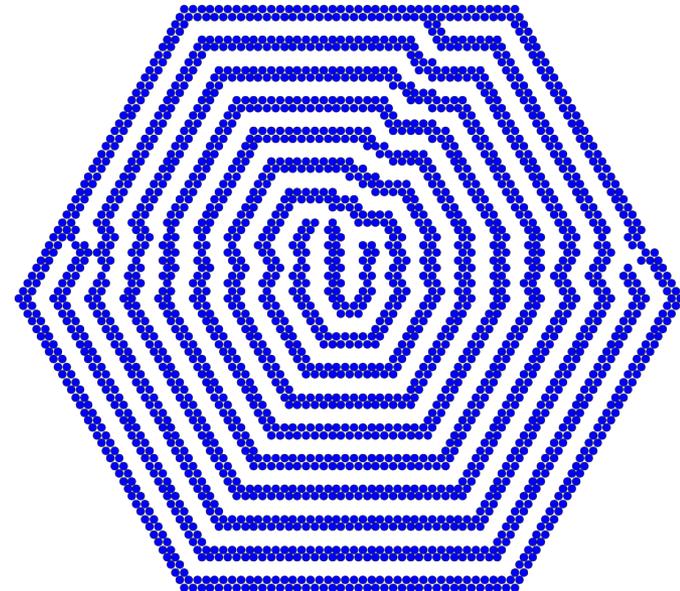
- Heating up the ground state results in merging of the rings.
- The larger the system the less clusters are present.



$M = 23, T = 0.45$



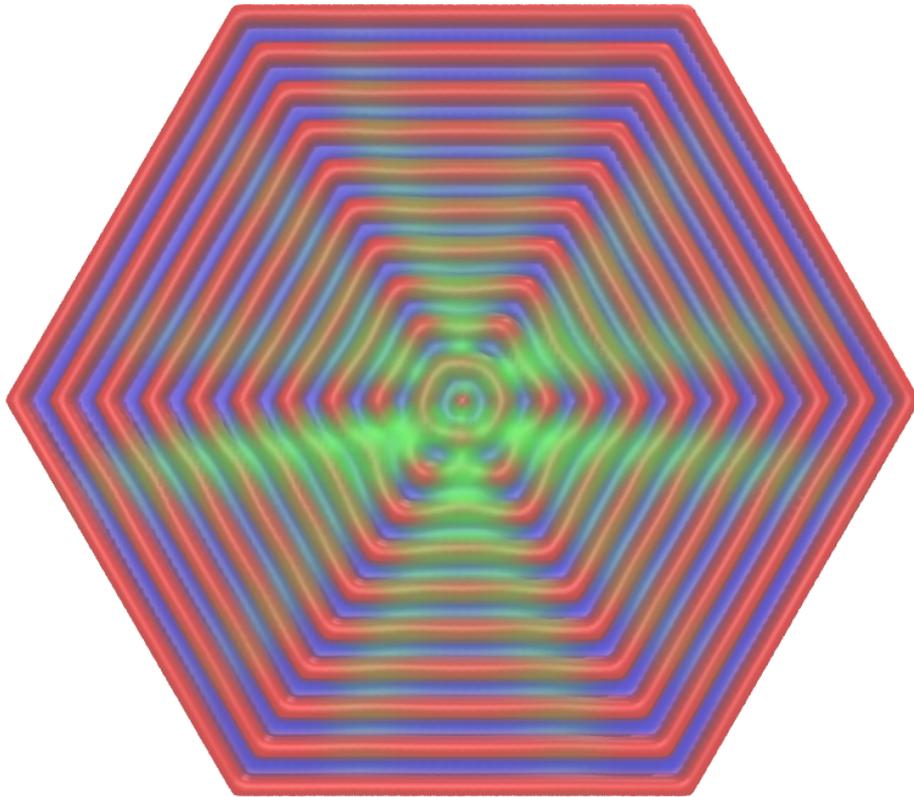
$M = 31, T = 0.39$



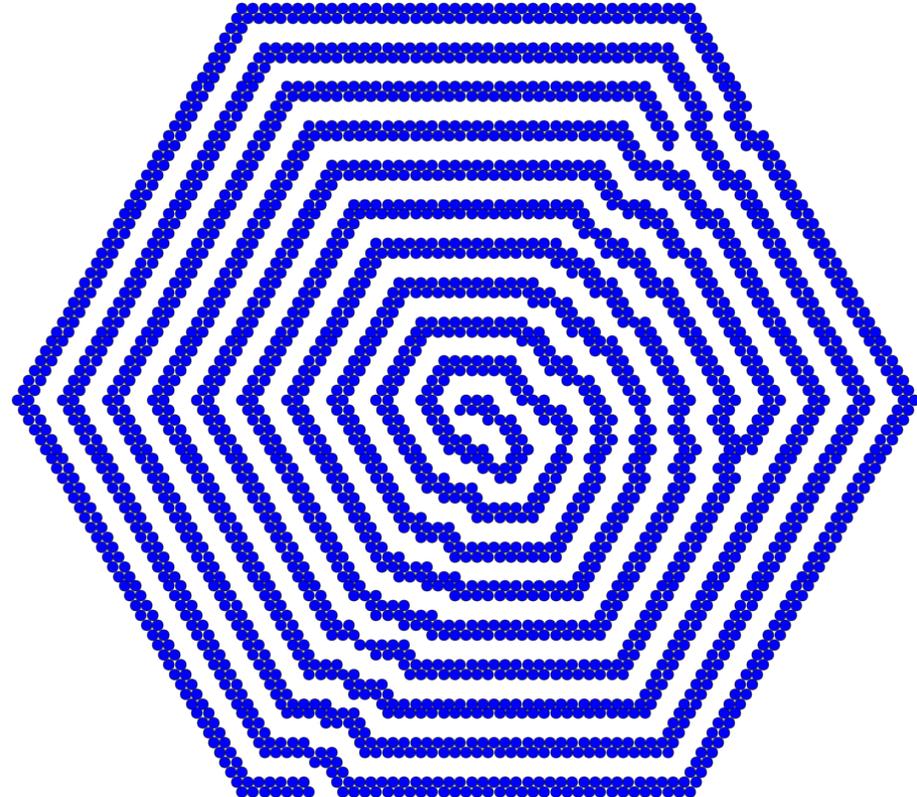
$M = 39, T = 0.34$

# Spiral for large systems

Merging of concentric rings can result in formation of a chiral structure – a spiral.



(density map)

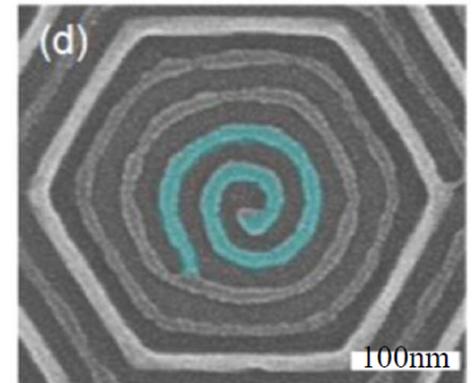
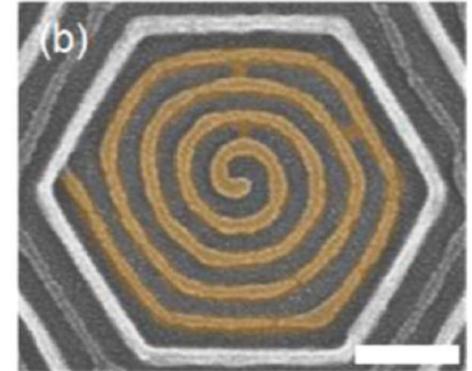
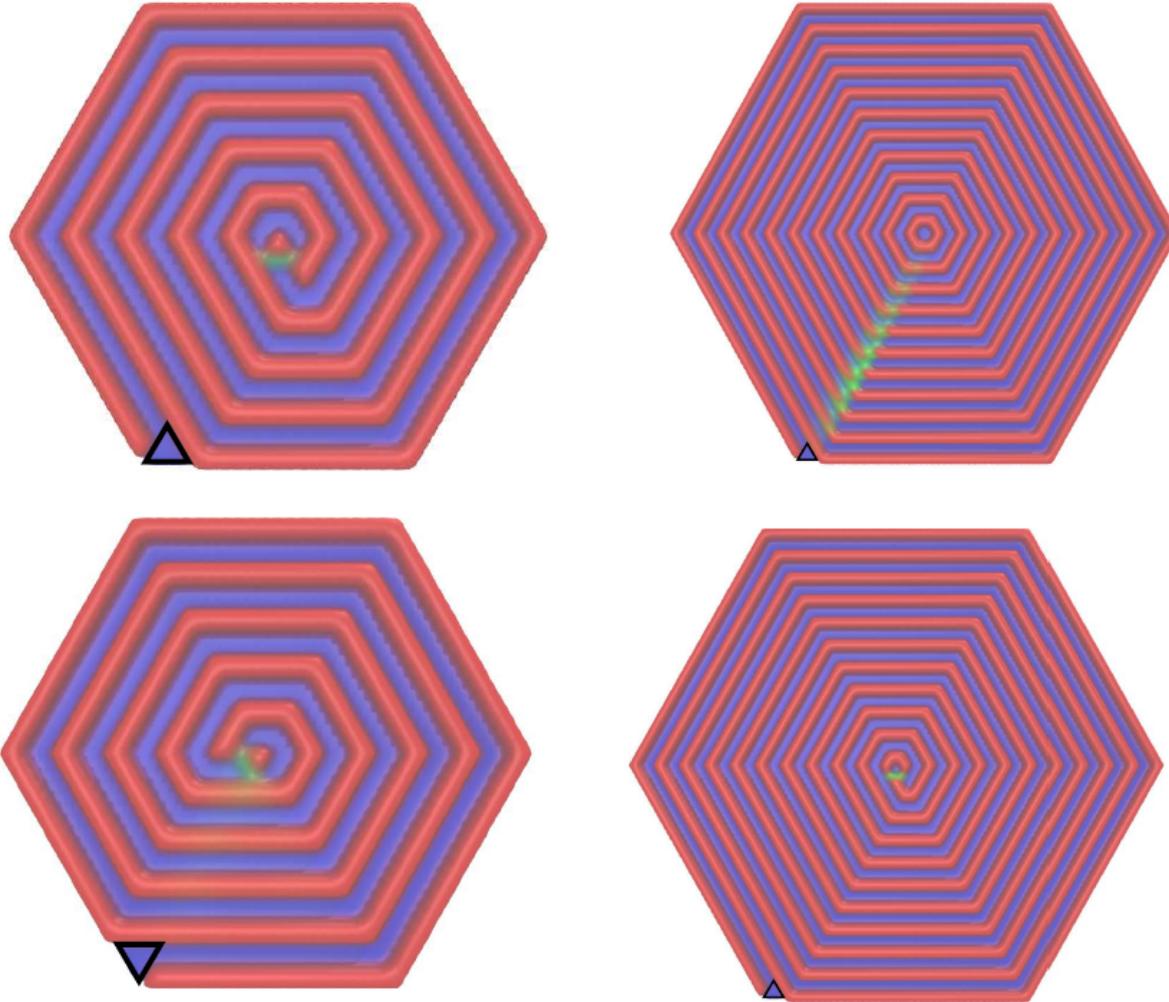


(single snapshot)

$$M = 41, T = 0.35$$

# Can we induce a spiral?

Yes we can!



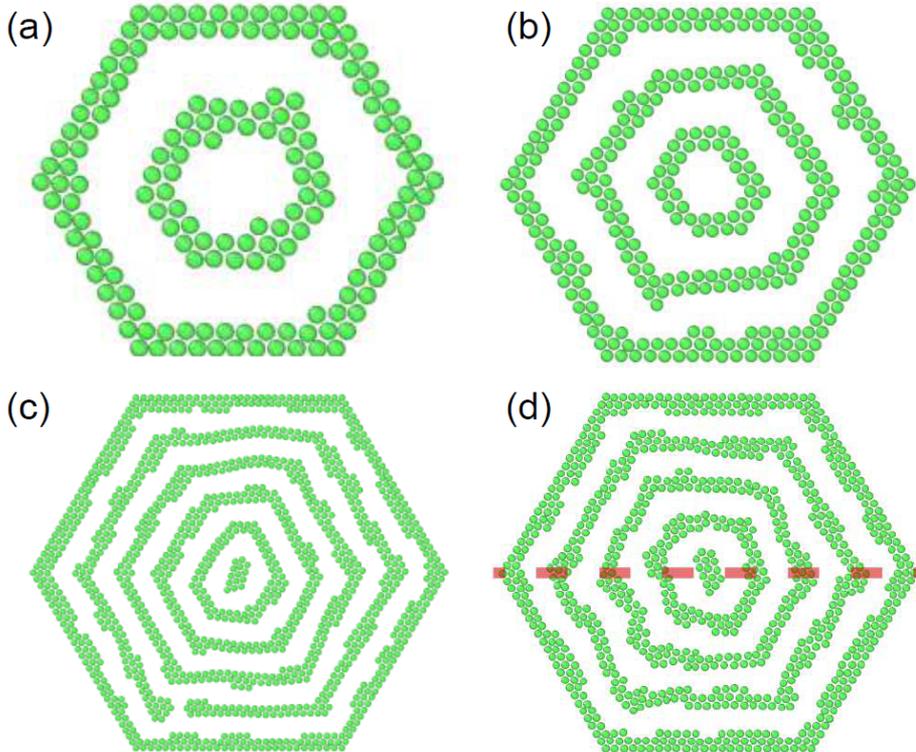
SEM image of diblock copolymers  
from H. K. Choi *et al.* Nano Futures 2017

Spiral with controlled chirality can be induced by a wedge.

# How general are those results?

1. Off-lattice MD simulations also show stability of concentric rings

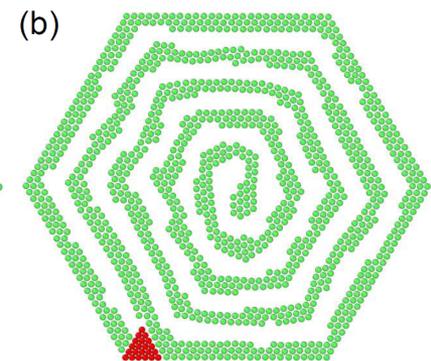
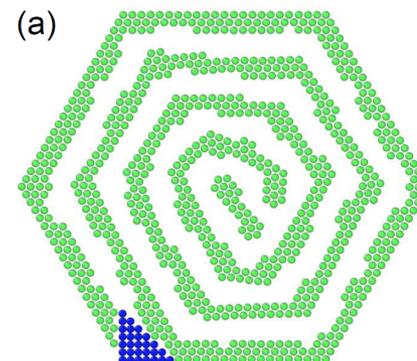
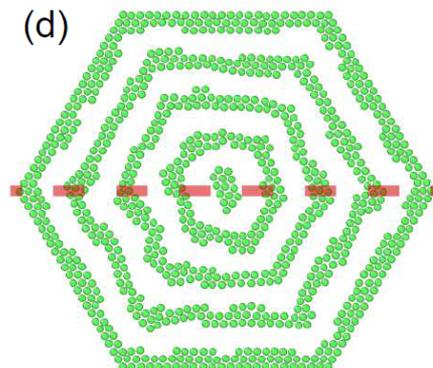
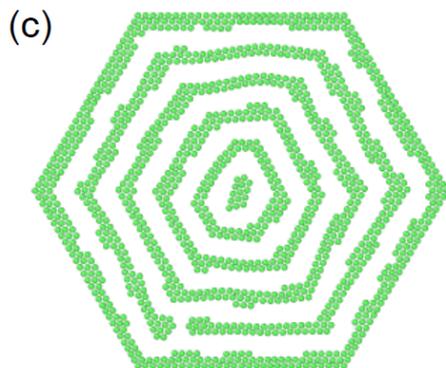
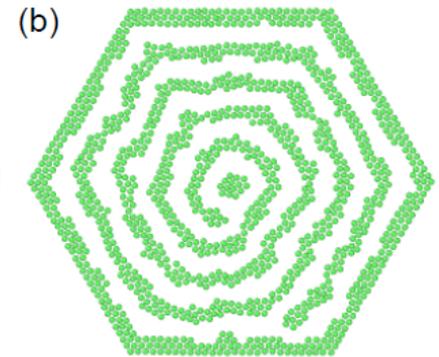
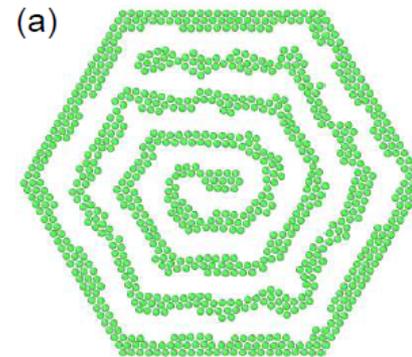
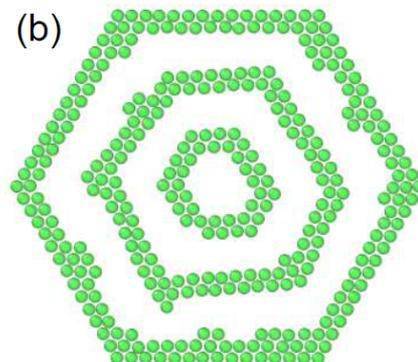
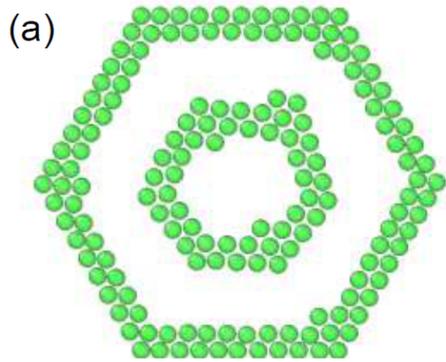
$$U_{\text{SALR}} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{2\alpha} - \left( \frac{\sigma}{r_{ij}} \right)^\alpha \right] + D \frac{e^{-r_{ij}/\xi}}{r_{ij}/\xi}.$$



# How general are those results?

1. Off-lattice MD simulations also show stability of concentric rings and spirals.

$$U_{\text{SALR}} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{2\alpha} - \left( \frac{\sigma}{r_{ij}} \right)^\alpha \right] + D \frac{e^{-r_{ij}/\xi}}{r_{ij}/\xi}.$$



# How general are those results?

2. Model-independent thermodynamic reasoning shows that concentric rings and spiral should be formed in many stripe forming systems.

$$\Omega = \omega_b A + (\Gamma_w + \Gamma_{db})M + D$$

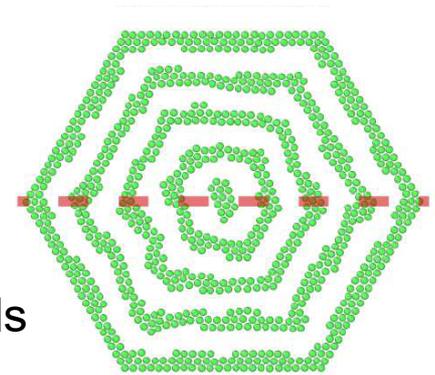
$A$  - area of the hexagon

$\omega_b$  - grand potential per surface area

$\Gamma_w$  - sum of the surface tensions at all the confining walls

$\Gamma_{db}$  - sum of the surface tensions at the boundaries between domains with different stripe-orientation

$D$  - contribution of the point-like defects



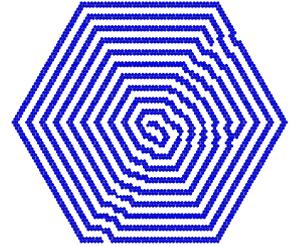
Condition for stability of concentric rings:

$$4(\gamma_t - \gamma_{||}) - 6\gamma_{db} - d_c/M > 0$$

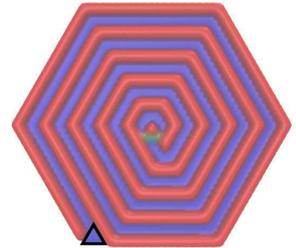
$$\Gamma_w = 6\gamma_{||}, \Gamma_{db} = 6\gamma_{db} \quad D = d_c$$

## Conclusions

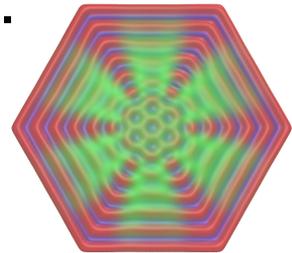
- Isotropic particles can form chiral patterns.



- A tiny wedge can induce topological transitions.



- Order can occur only at the level of density maps.

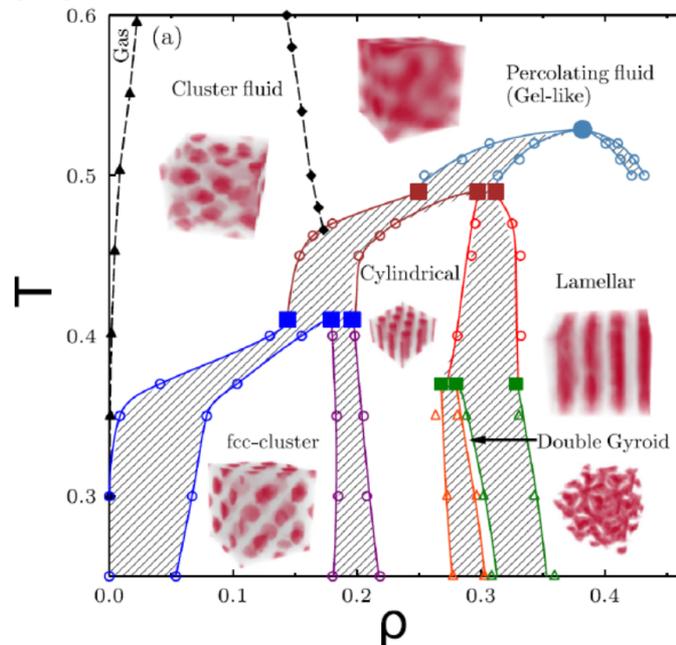


- Different stripe-forming systems can form similar patterns.

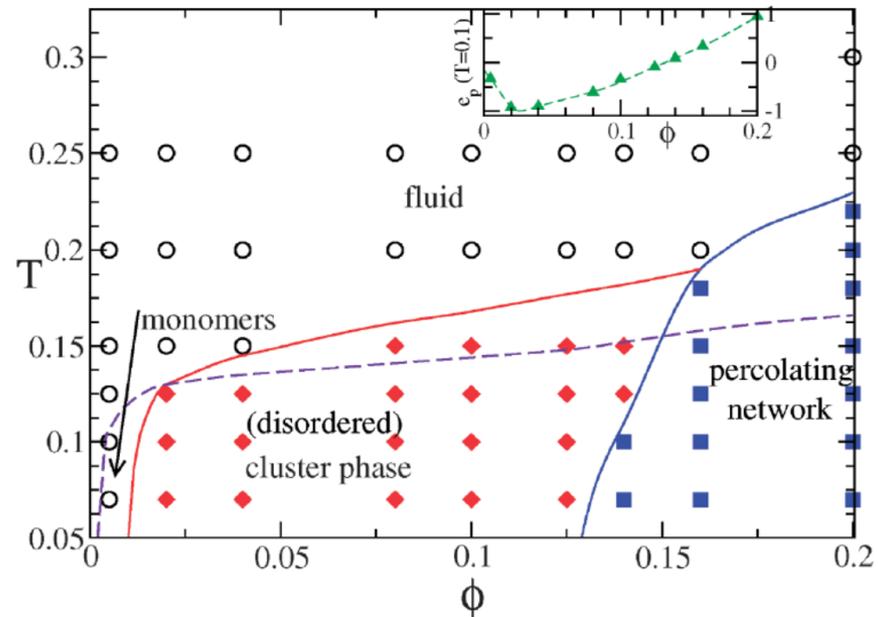
# Current project

Depending on the shape of the effective potential SALR particles exhibit ordering or not

(a) Ordered structures



(b) Disordered structures



Attraction range: (a)  $1.5\sigma$ , (b)  $0.02\sigma$ , where  $\sigma$  is the particle diameter.

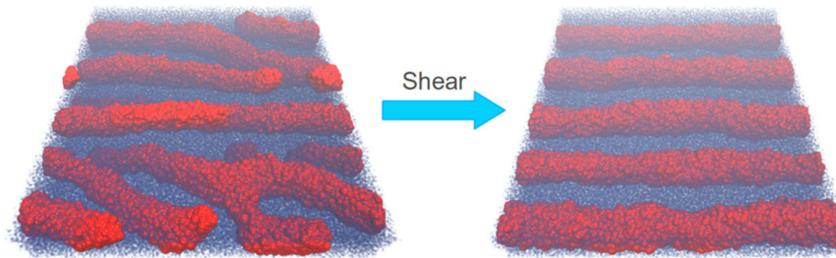
(a) Y. Zhuang et al. *Phys. Rev. Lett.* **116** 098301 (2016)

(b) J. Toledano, F. Sciortino, E. Zaccarelli *Soft Matter* **5** 2390 (2009)

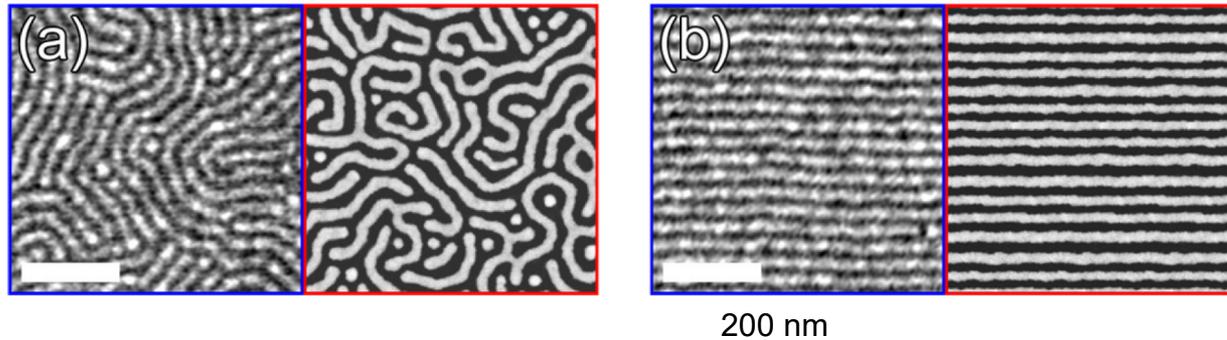
# Percolated network under shear

- In the case of Diblock Copolymers shear was shown to induce long range order.

By simulations...



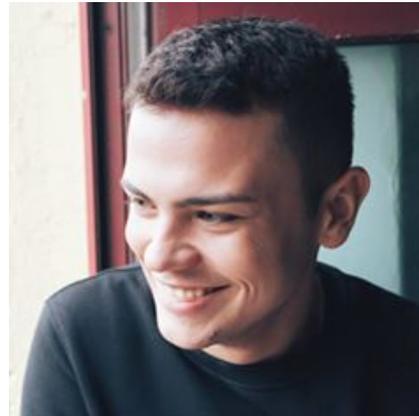
... and experiment.



The presented work on SALR system was done with



Prof. Alina Ciach  
Polish Academy of Sciences



Eldar Bildanov  
Belarusian State University



Dr Noé G. Almarza  
CSIC, Madrid

and founded by:



*Foundation for Polish Science*



NATIONAL SCIENCE CENTRE  
POLAND



Marie Skłodowska-Curie  
Actions

Thank you



HR EXCELLENCE IN RESEARCH



CSIC

# Electrical double layers close to ionic liquid-solvent demixing

Carolina Cruz

III CONIN Workshop

Lviv, Ukraine

July 2019



Horizon 2020  
European Union Funding  
for Research & Innovation



# Outline

Introduction

Model

IL-solvent phase behaviour

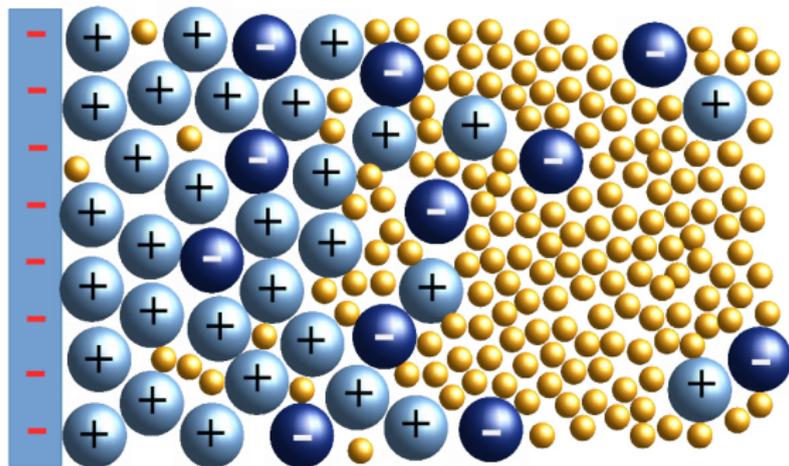
Charging close to demixing

Conclusions

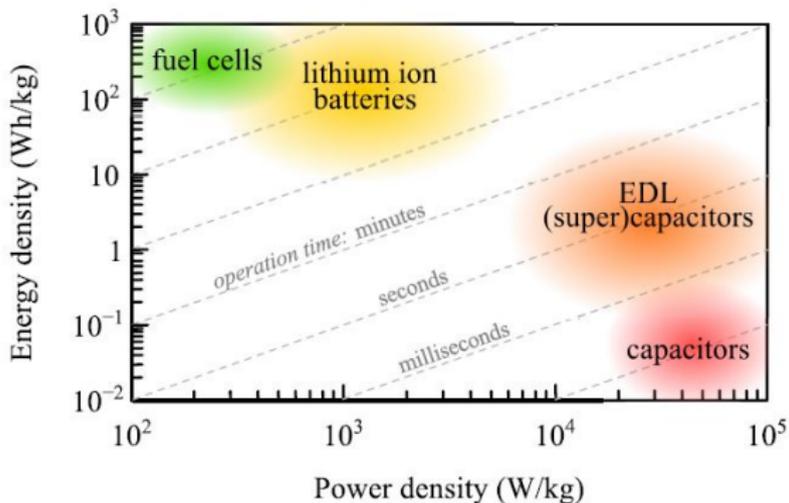


NaMeS

# Electrical double layers (EDL)



# Ragone plot

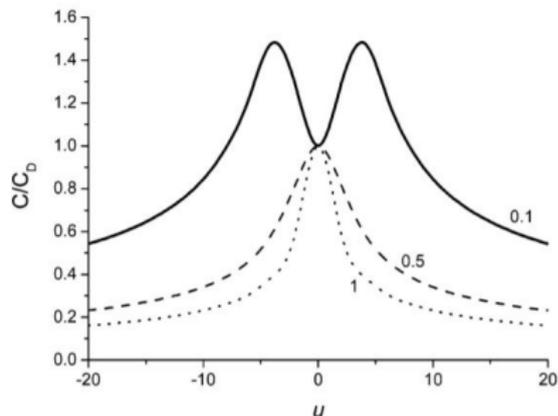
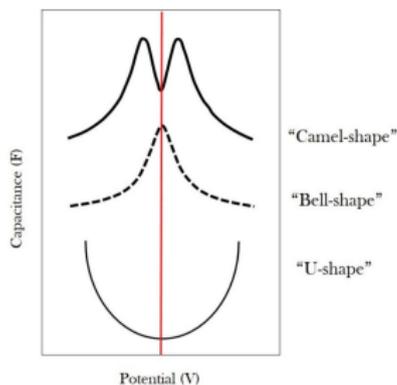


Fedorov, M. V.; Kornyshev, A. A. *Chem. Rev.* **2014**, 114, 2978.



# EDL Capacitance

Capacitance shapes: signature of how dense the system is

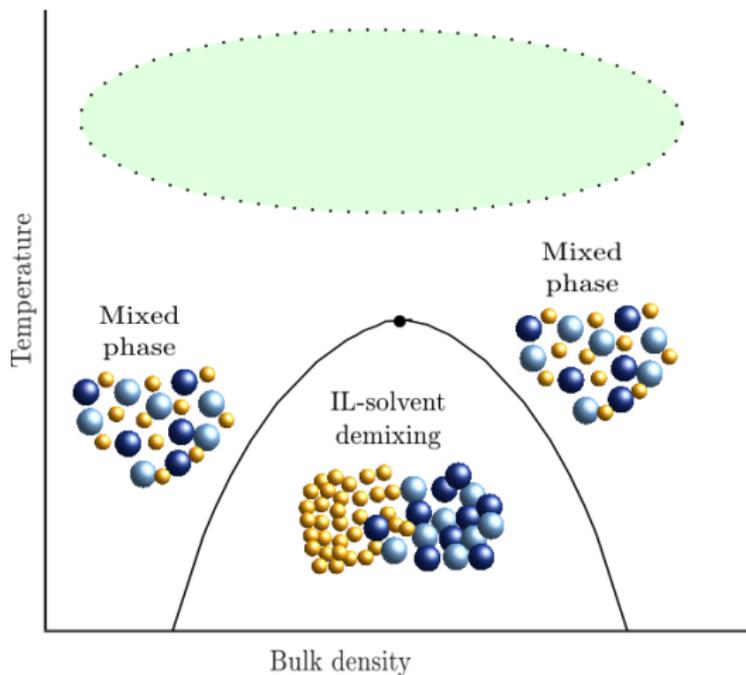


Hailu, A.; Horvath, A.; Shaw S. K. *ECS* **2018**.

Kornyshev, A. A. *J. Phys. Chem. B* **2007**, 111, 5545.



# IL-solvent mixtures



What is the effect of approaching demixing on the EDL properties?

# Model

The grand canonical thermodynamic potential of the system:

$$\begin{aligned}\Omega/A &= K \left[ \int_0^\infty dz \left( \frac{\xi_0^2}{2} \left( \frac{\partial \rho}{\partial z} \right)^2 - \frac{1}{2} \rho^2(z) \right) + \frac{\xi_0}{2} \rho^2(z=0) - h_1 \rho(z=0) \right] \\ &+ \int_0^\infty dz \left[ c(z) u(z) - \frac{1}{8\pi\lambda_B} \left( \frac{\partial u}{\partial z} \right)^2 \right] \\ &+ k_B T \int_0^\infty dz \left[ \rho_+(z) \ln \rho_+(z) + \rho_-(z) \ln \rho_-(z) + \beta f_{ex}(\rho(z)) \right] \\ &- \bar{\mu} \int_0^\infty dz \rho(z)\end{aligned}$$

$u$  Electrostatic potential       $\rho = \rho_+ + \rho_-$  Ion density       $c = \rho_+ - \rho_-$  Charge density       $\lambda_B$  Bjerrum length



NaMeS

# Model

The grand canonical thermodynamic potential of the system:

$$\begin{aligned}\Omega/A &= K \left[ \int_0^\infty dz \left( \frac{\xi_0^2}{2} \left( \frac{\partial \rho}{\partial z} \right)^2 - \frac{1}{2} \rho^2(z) \right) + \frac{\xi_0}{2} \rho^2(z=0) - h_1 \rho(z=0) \right] \\ &+ \int_0^\infty dz \left[ c(z)u(z) - \frac{1}{8\pi\lambda_B} \left( \frac{\partial u}{\partial z} \right)^2 \right] \\ &+ k_B T \int_0^\infty dz \left[ \rho_+(z) \ln \rho_+(z) + \rho_-(z) \ln \rho_-(z) + \beta f_{ex}(\rho(z)) \right] \\ &- \bar{\mu} \int_0^\infty dz \rho(z)\end{aligned}$$

Van der Waals  
interactions

Electrostatic  
energy

Entropic  
contribution

Chemical  
potential



NaMeS

C. Cruz; A. Ciach; E. Lomba; S. Kondrat. *J. Phys. Chem. C*  
2019, 123, 1596.

# Model

The grand canonical thermodynamic potential of the system:

$$\begin{aligned}\Omega/A &= K \left[ \int_0^\infty dz \left( \frac{\xi_0^2}{2} \left( \frac{\partial \rho}{\partial z} \right)^2 - \frac{1}{2} \rho^2(z) \right) + \frac{\xi_0}{2} \rho^2(z=0) - h_1 \rho(z=0) \right] \\ &+ \int_0^\infty dz \left[ c(z)u(z) - \frac{1}{8\pi\lambda_B} \left( \frac{\partial u}{\partial z} \right)^2 \right] \\ &+ k_B T \int_0^\infty dz \left[ \rho_+(z) \ln \rho_+(z) + \rho_-(z) \ln \rho_-(z) + \beta f_{ex}(\rho(z)) \right] \\ &- \bar{\mu} \int_0^\infty dz \rho(z)\end{aligned}$$

Van der Waals  
interactions

Electrostatic  
energy

Entropic  
contribution

Chemical  
potential



NaMeS

C. Cruz; A. Ciach; E. Lomba; S. Kondrat. *J. Phys. Chem. C*  
2019, 123, 1596.

# Model

The grand canonical thermodynamic potential of the system:

$$\begin{aligned}\Omega/A &= K \left[ \int_0^\infty dz \left( \frac{\xi_0^2}{2} \left( \frac{\partial \rho}{\partial z} \right)^2 - \frac{1}{2} \rho^2(z) \right) + \frac{\xi_0}{2} \rho^2(z=0) - h_1 \rho(z=0) \right] \\ &+ \int_0^\infty dz \left[ c(z)u(z) - \frac{1}{8\pi\lambda_B} \left( \frac{\partial u}{\partial z} \right)^2 \right] \\ &+ k_B T \int_0^\infty dz \left[ \rho_+(z) \ln \rho_+(z) + \rho_-(z) \ln \rho_-(z) + \beta f_{ex}(\rho(z)) \right] \\ &- \bar{\mu} \int_0^\infty dz \rho(z)\end{aligned}$$

Van der Waals  
interactions

Electrostatic  
energy

Entropic  
contribution

Chemical  
potential



NaMeS

C. Cruz; A. Ciach; E. Lomba; S. Kondrat. *J. Phys. Chem. C*  
2019, 123, 1596.

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2019, 123, 1596.

# Model: Van der Waals interactions

$$\begin{aligned}\Omega/A &= K \left[ \int_0^\infty dz \left( \frac{\xi_0^2}{2} \left( \frac{\partial \rho}{\partial z} \right)^2 - \frac{1}{2} \rho^2 \right) + \frac{\xi_0}{2} \rho^2(0) - h_1 \rho(0) \right] \\ &+ \int_0^\infty dz \left[ cu - \frac{1}{8\pi\lambda_B} \left( \frac{\partial u}{\partial z} \right)^2 \right] \\ &+ k_B T \int_0^\infty dz \left[ \rho_+(z) \ln \rho_+(z) + \rho_-(z) \ln \rho_-(z) + \beta f_{ex}(\rho(z)) \right] \\ &- \bar{\mu} \int_0^\infty dz \rho(z)\end{aligned}$$

$K$ : VdW  
interactions

$\xi_0$ : Spatial  
extension

$h_1$ : Electrode's  
ionophilicity



## Model: Van der Waals interactions

$$\begin{aligned}\Omega/A &= K \left[ \int_0^\infty dz \left( \frac{\xi_0^2}{2} \left( \frac{\partial \rho}{\partial z} \right)^2 - \frac{1}{2} \rho^2 \right) + \frac{\xi_0}{2} \rho^2(0) - h_1 \rho(0) \right] \\ &+ \int_0^\infty dz \left[ cu - \frac{1}{8\pi\lambda_B} \left( \frac{\partial u}{\partial z} \right)^2 \right] \\ &+ k_B T \int_0^\infty dz \left[ \rho_+(z) \ln \rho_+(z) + \rho_-(z) \ln \rho_-(z) + \beta f_{ex}(\rho(z)) \right] \\ &- \bar{\mu} \int_0^\infty dz \rho(z)\end{aligned}$$

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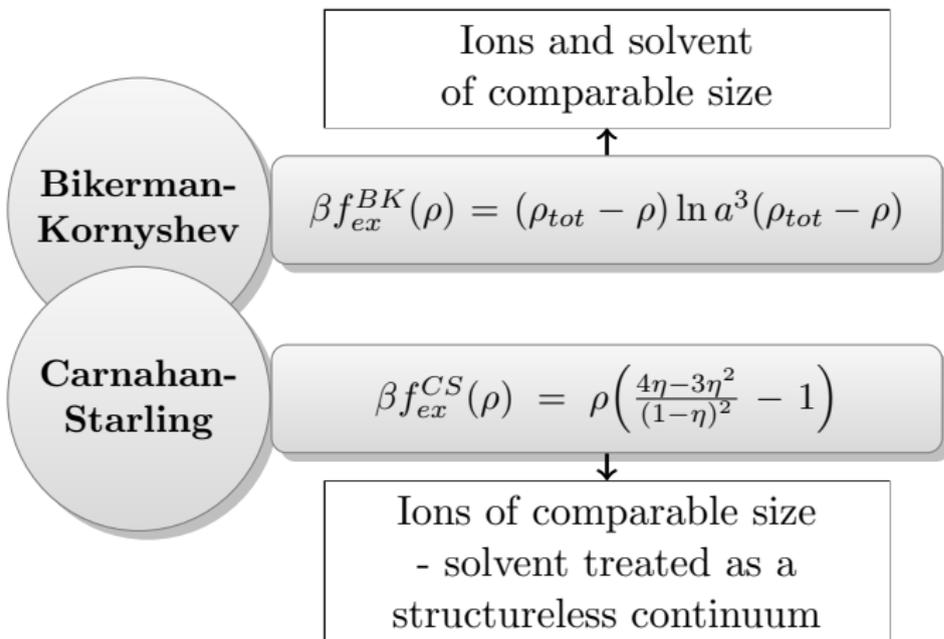
$K$ : VdW  
interactions

$\xi_0$ : Spatial  
extension

$h_1$ : Electrode's  
ionophilicity



# Model: Excluded volume interactions

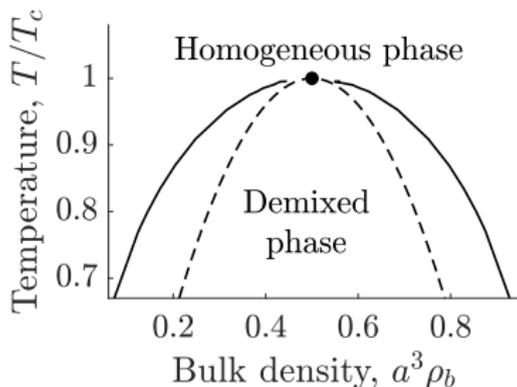


Kornyshev, A. A. *J. Phys. Chem. B* **2007**, 111, 5545.

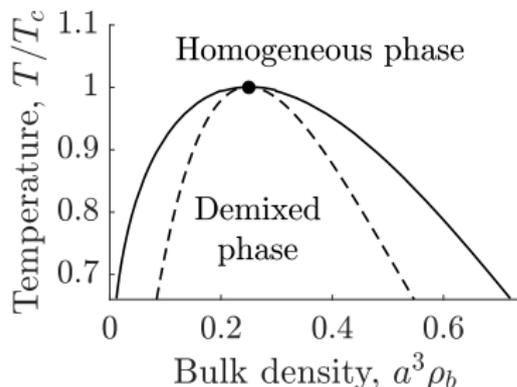
Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, 51, 635.

# Bulk phase diagram

## Bikerman-Kornyshev



## Carnahan-Starling

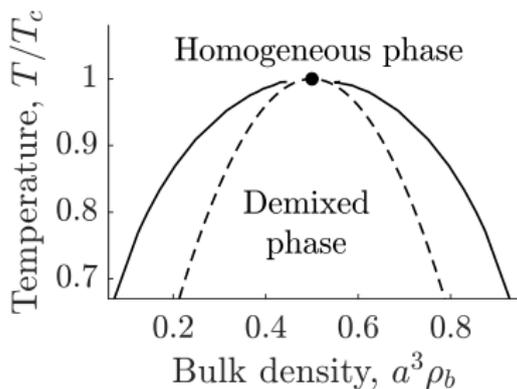


C. Cruz; S. Kondrat; E. Lomba; A. Ciach. 2019 Submitted to J. Mol. Liq.

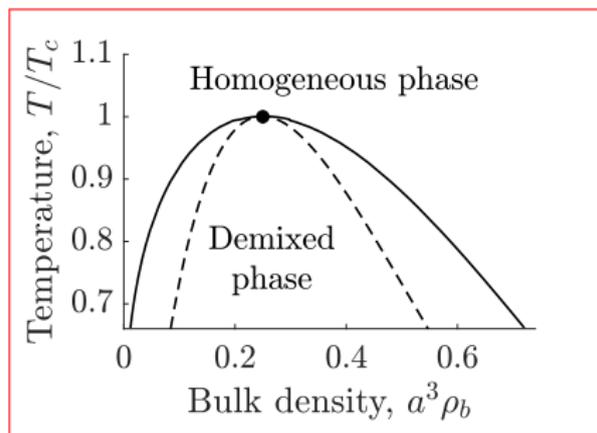


# Bulk phase diagram

## Bikerman-Kornyshev



## Carnahan-Starling



C. Cruz; S. Kondrat; E. Lomba; A. Ciach. 2019 Submitted to J. Mol. Liq.



# Differential capacitance

The differential capacitance is:

$$C = \frac{\partial Q}{\partial U}.$$

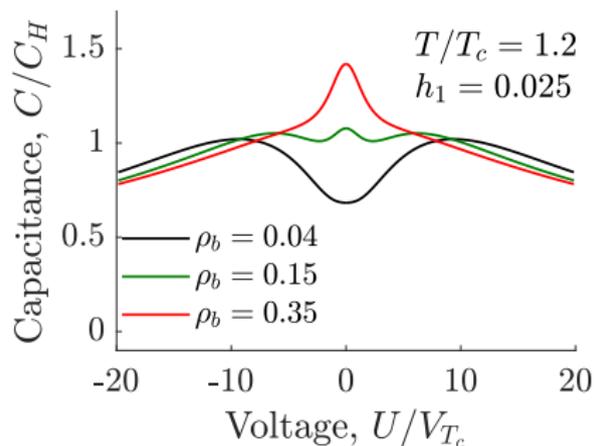
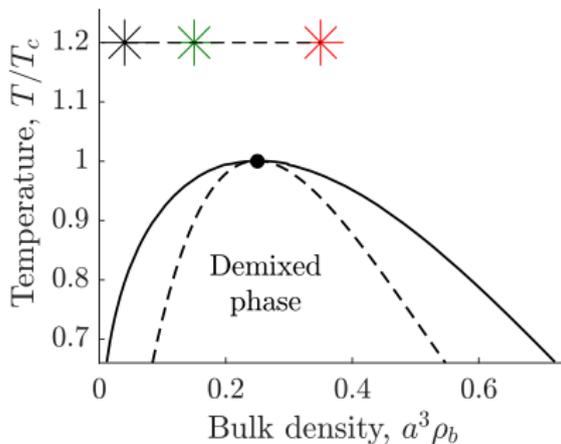
where the total charge,  $Q$ , stored in an EDL is

$$Q = -e \int_0^{\infty} cdz = \frac{4\pi}{\epsilon} \frac{du}{dz} \Big|_{z=0}.$$



# Differential capacitance

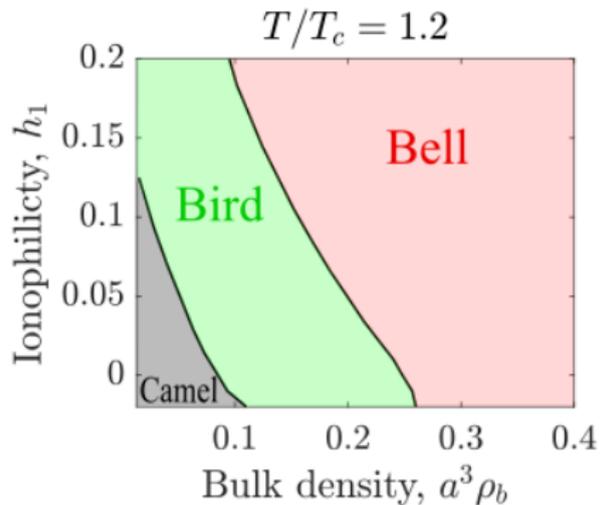
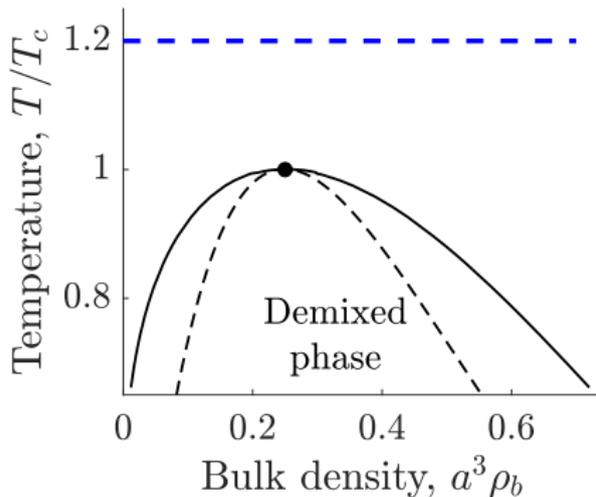
Capacitance curve having three peaks



C. Cruz; A. Ciach; E. Lomba; S. Kondrat. *J. Phys. Chem. C* **2019**, 123, 1596.



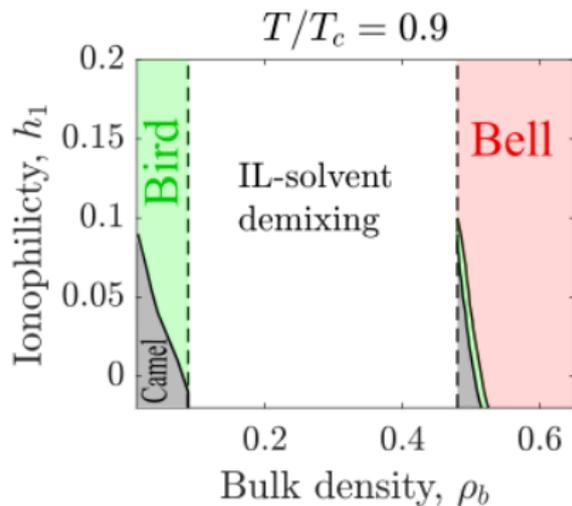
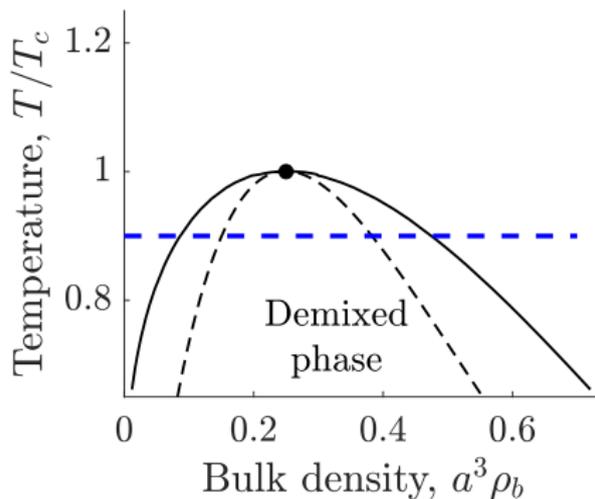
# Capacitance diagram



C. Cruz; S. Kondrat; E. Lomba; A. Ciach. 2019 Submitted to J. Mol. Liq.



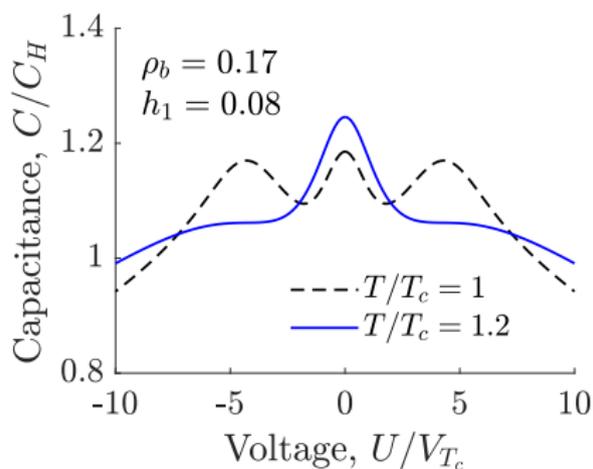
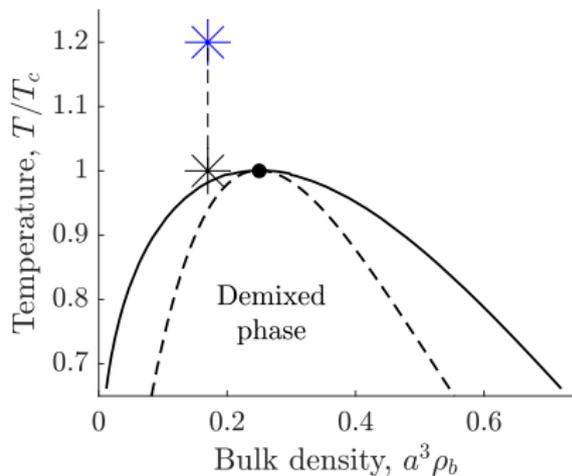
# Capacitance diagram



C. Cruz; S. Kondrat; E. Lomba; A. Ciach. 2019 Submitted to J. Mol. Liq.



# Appearance of 'wings'



C. Cruz; S. Kondrat; E. Lomba; A. Ciach. **2019** Submitted to J. Mol. Liq.



# Charging parameter

The charging parameter

$$X_D = \frac{e}{C(U)} \frac{d\Gamma}{dU},$$

where  $\Gamma = \int_0^\infty (\rho - \rho_b) dz$  is the surface coverage by IL.

Forse, A. C.; Merlet, C.; Griffin, J. M.; Grey, C. P. *J. Am. Chem. Soc.* **2016**, 138, 5731.  
Breitsprecher, K.; Abele, M.; Kondrat, S.; Holm, C. *J. Chem. Phys.* **2017**, 147.



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# Charging parameter

$$X_D = \frac{e}{C(U)} \frac{d\Gamma}{dU}$$

$X_D = 0 \implies$  Swapping coions for counterions

$X_D = 1 \implies$  Counterions electrosorption

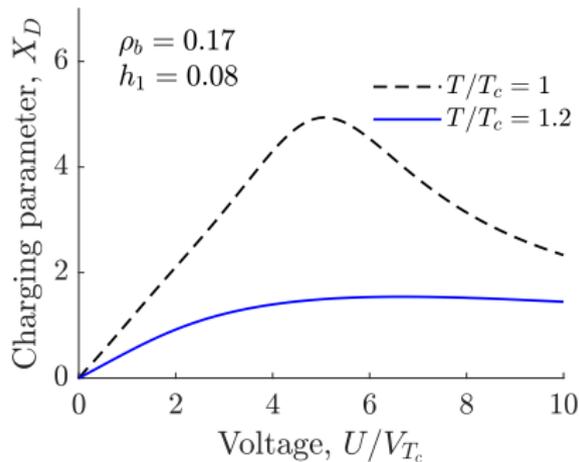
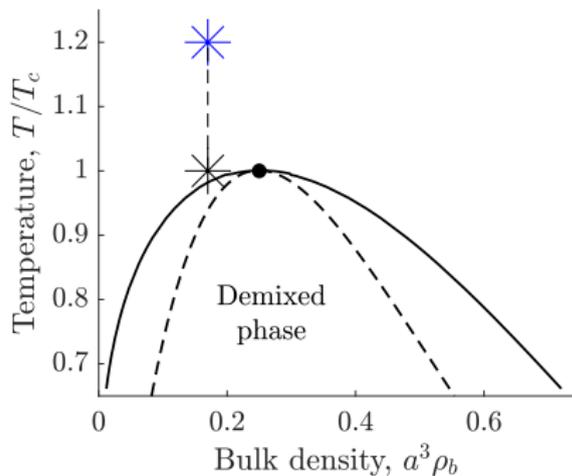
$X_D > 1 \implies$  Counterions and coions adsorbed

Forse, A. C.; Merlet, C.; Griffin, J. M.; Grey, C. P. *J. Am. Chem. Soc.* **2016**, 138, 5731.  
Breitsprecher, K.; Abele, M.; Kondrat, S.; Holm, C. *J. Chem. Phys.* **2017**, 147.



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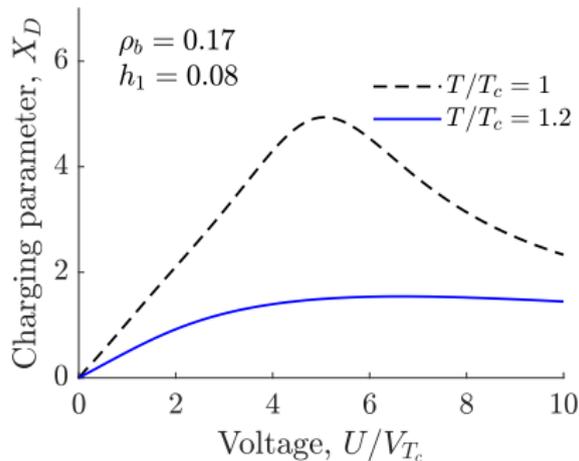
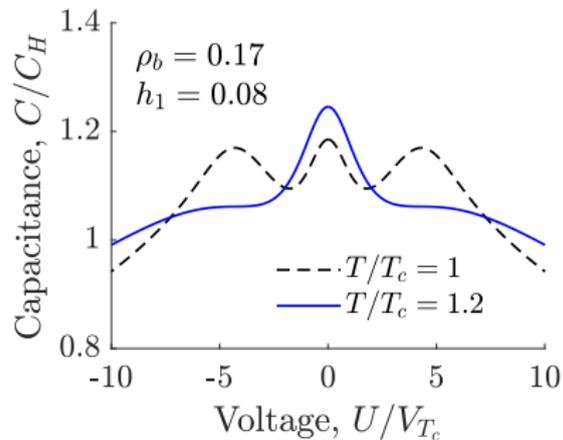
# Charging parameter



C. Cruz; S. Kondrat; E. Lomba; A. Ciach. **2019** Submitted to J. Mol. Liq.



# Charging parameter



C. Cruz; S. Kondrat; E. Lomba; A. Ciach. **2019** Submitted to J. Mol. Liq.



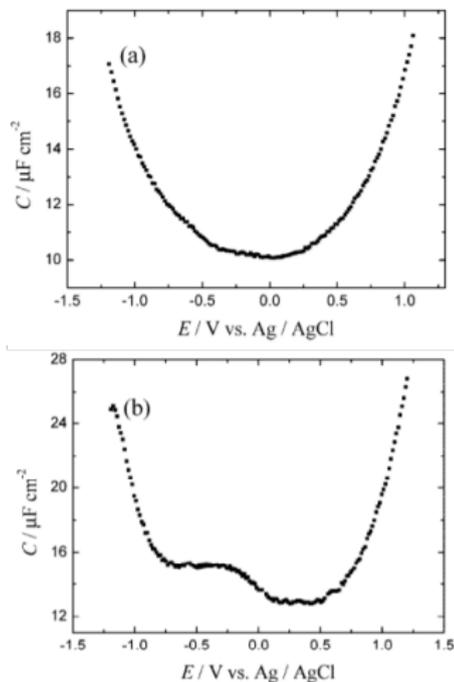
# Bird-shaped capacitance?

## Experiments

Appearance of humps for some  $N_2$ -saturated ILs

“The cause is unknown”

Alam, M. T.; Islam, M. M.; Okajima, T.; Ohsaka, T. *J. Phys. Chem. C* **2008**, 112, 16600.



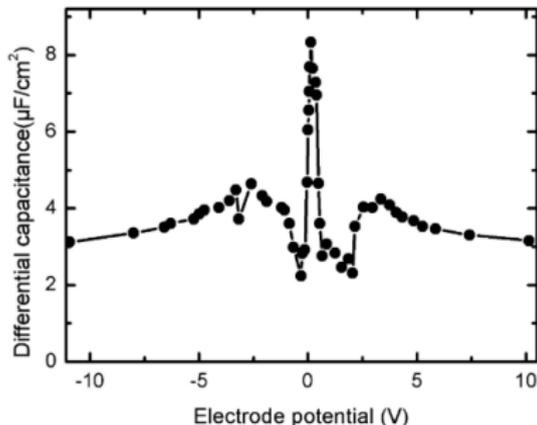
# Bird-shaped capacitance?

## MD simulations

Au(100) electrodes in 1-butyl-3-methyl-imidazolium hexafluorophosphate

Adsorption on the electrode surface

Sha, M.; Dou, Q.; Luo, F.; Zhu, G.; Wu, G. *ACS Appl. Mater. Interfaces* **2014**, 6, 12556.



“Bell-shaped curve with two declining wings”

# Energy storage

Energy density stored in EDL

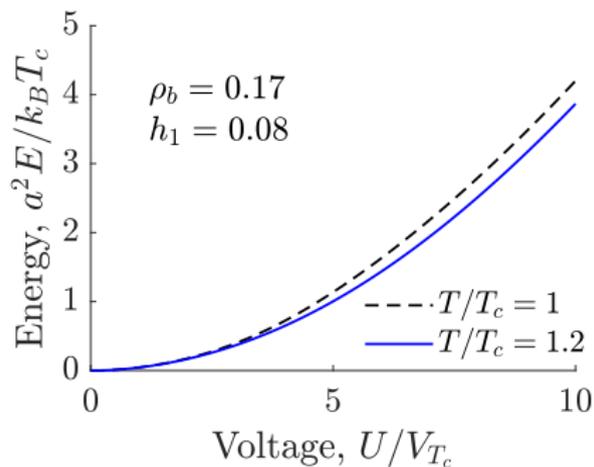
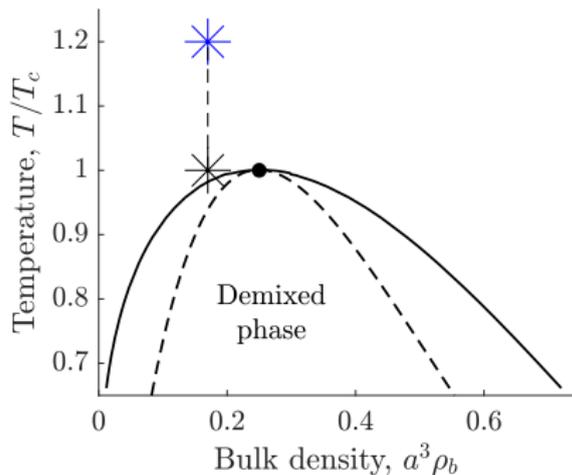
$$E(U) = \int_0^U C(u)u du.$$

where  $C$  is the differential capacitance

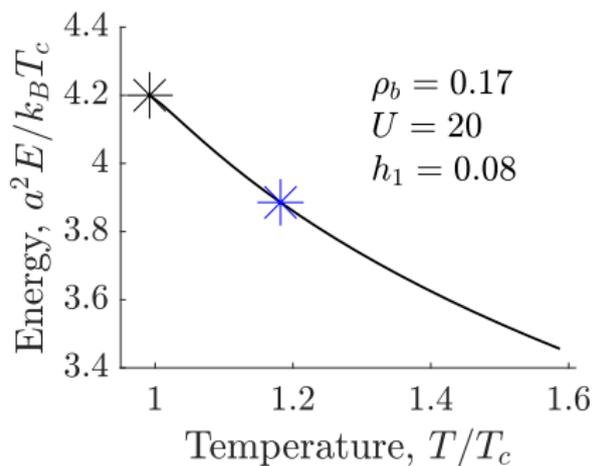
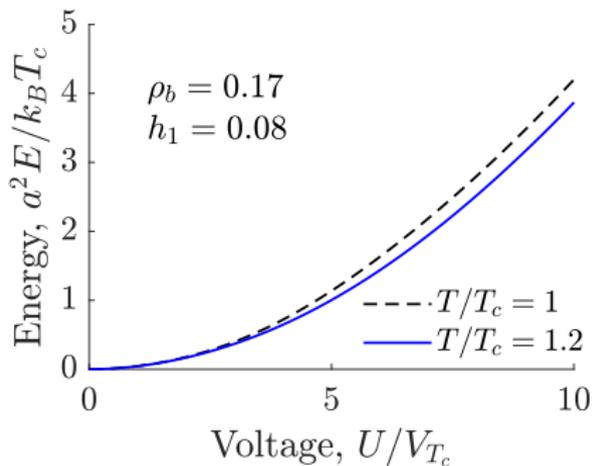


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# Energy storage



# Energy storage



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# Conclusions

- Model for description of EDLs with IL-solvent mixtures.
- Emergence of a new type of the capacitance shape, a “bird” shape, in addition to the extensively studied camel and bell shapes.
- The camel-shaped capacitance, which is a signature of dilute electrolytes, can be observed also at high concentrations in the vicinity of demixing.
- The energy stored in an EDL increases appreciably as the system approaches demixing, which can be utilized for generating electricity from waste heat.



NaMeS

# Acknowledgments

- prof. Alina Ciach
- prof. Enrique Lomba
- Dr. Svyatoslav Kondrat



This work was supported by the European Unions Horizon 2020 research and innovation programmes under the Marie Skłodowska-Curie grant agreement No. 711859 to C.C and No. 734276 to A.C. and S.K. Additional funding was received from the Ministry of Science and Higher Education of Poland for the project No. 734276 in the years 2017-2018 (agreement No. 3854/H2020/17/2018/2) and for the implementation of the international co-financed project No. 711859 in the years 2017-2021.





3<sup>rd</sup> CONIN workshop,  
1 – 3 July 2019, Lviv, Ukraine

# Electric field and charge distribution in near electrode and intergrain regions of solid electrolytes

George Bokun, Dung di Caprio, Myroslav Holovko,  
Ruslan Lasovsky, Taras Patsahan, Vyacheslav Vikhrenko

Belarusian State Technological University (Belarus)  
Institute for Condensed Matter Physics (Ukraine)  
Chimie ParisTech (France)

[vvikhre@gmail.com](mailto:vvikhre@gmail.com)

Solid electrolytes important for industrial applications (electrical energy sources, Capacitors, etc.) are frequently ceramic objects that consist of grains connected by intergrain regions and are subject to confining effects. The long-range Coulomb interactions and inhomogeneities in the near electrode and intergrain regions considerably complicate their theoretical analysis. These complications can more easily be taken into account on the basis of lattice models.

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We would like to answer the questions about the influence of **a strong external electric field** on the charge density distribution in the near electrode regions,  
the influence of **the potential energy landscape** on the charge distribution in the vicinity of intergrain boundaries,  
the effect of **short-range Van der Waals interactions** in Coulomb systems.

# The model

consists of  $N$  cations on a simple cubic lattice on the background of uniformly distributed anions and the potential relief of the host system. The system is confined between two oppositely charged walls. The potential relief can be used for modelling specific interactions at the system boundary or the presence of the grain structure and intergrain regions in ceramic electrolytes. The free energy functional with accounting of various interactions can be constructed. Its minimization with respect to the ion concentration in lattice plains parallel to the walls leads to the equilibrium condition for the chemical potential of a nonhomogeneous medium in the direction perpendicular to the walls

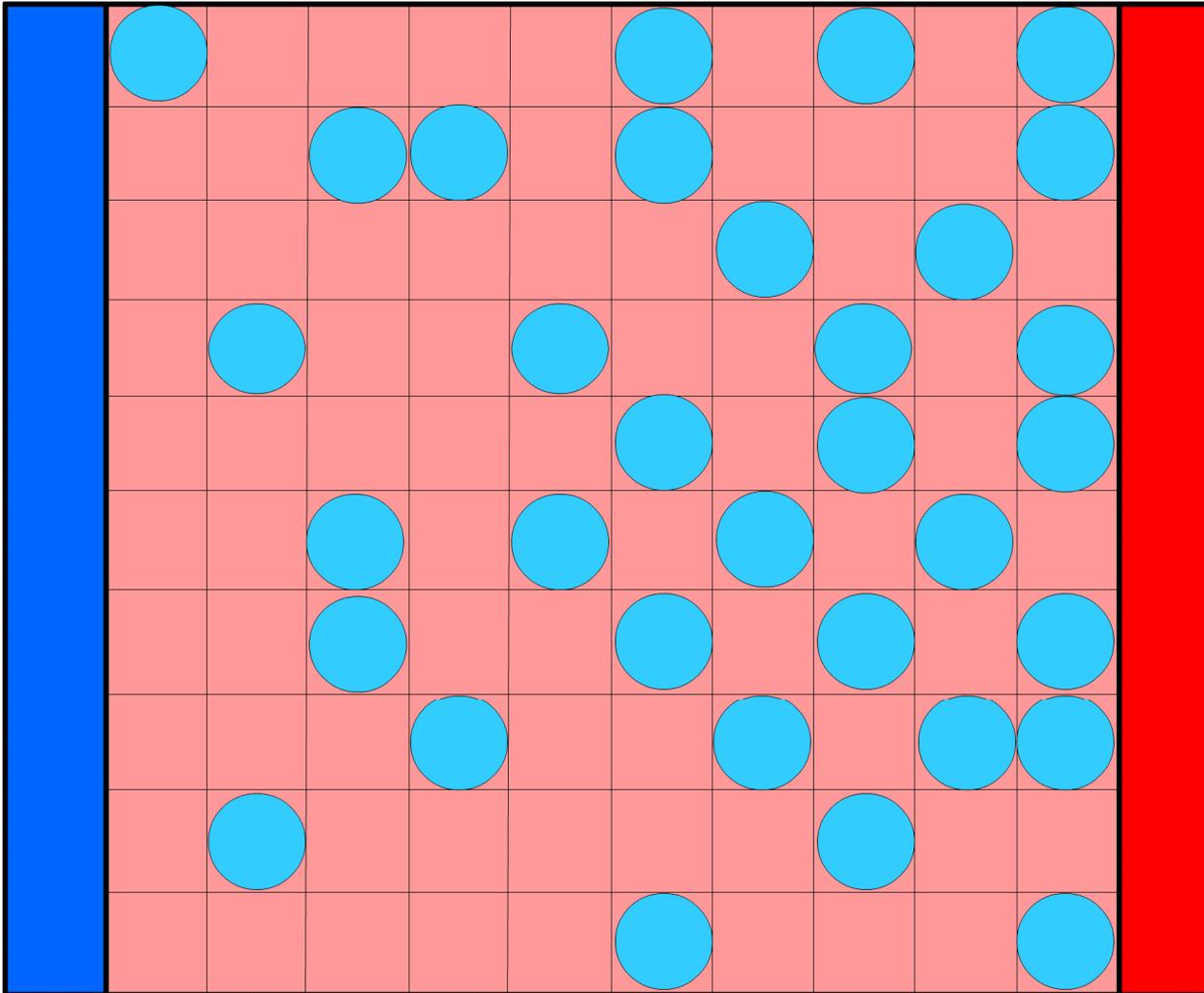
$$\beta\mu_i = \beta\mu_b$$

where  $\mu_b$  is the chemical potential of the homogeneous system with the same interactions. The subscript  $i$  designates the lattice plains parallel to the walls.

Bokun G., Di Caprio D., Holovko M., Vikhrenko V., *J. Mol. Liquids*, The system of mobile ions in lattice models: Screening effects, thermodynamic and electrophysical properties, 270 (2018) 183-190.

Patsahan T., Bokun G., Di Caprio D., Holovko M., Vikhrenko V., *Solid State Ionics*, The effect of short-range interaction and correlations on the charge and electric field distribution in a model solid electrolyte, 335 (2019) 156-163

# Schematic representation of the model



Parameters  
 $n_z=30$ ,  $a=0.4$  nm

The chemical potential contains contributions from various interactions

$$\beta\mu_i = \beta\mu_i^{\text{id}} + \beta\mu_i^{\text{sr}} + \beta\mu_i^{\text{el,mf}} + \beta\mu_i^{\text{el,corr}} + \beta\mu_i^f + \beta\mu_i^g$$

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$$\beta\mu_i = \beta\mu_i^{\text{id}} + \beta\mu_i^{\text{sr}} + \beta\mu_i^{\text{el,mf}} + \beta\mu_i^{\text{el,corr}} + \beta\mu_i^f + \beta\mu_i^g$$

The ideal entropy contribution

$$\beta\mu_i^{\text{id}} = \ln \frac{c_i}{1 - c_i} \quad \beta = 1 / k_B T \quad c_i = \rho(z_i) a^3$$

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The ideal entropy contribution

$$\beta\mu_i^{\text{id}} = \ln \frac{c_i}{1 - c_i} \quad \beta = 1 / k_B T \quad c_i = \rho(z_i) a^3$$

The contribution of short-range Van der Waals interactions is split into the mean field and correlation contributions

$$\begin{aligned} \beta\mu_i^{\text{sr}} &= \beta\mu_i^{\text{sr,mf}} + \beta\mu_i^{\text{sr,cor}} \\ &= \beta J c_{i-1} (1 + h_{i,i-1}^{(1)}) + 4\beta J c_i (1 + h_{i,i}^{(1)}) + \beta J c_{i+1} (1 + h_{i,i+1}^{(1)}) \end{aligned}$$

The correlation contribution is designated by the  $h$  functions and concerns the nearest neighbor contributions only with the intensity  $J$

The chemical potential contains contributions from various interactions

$$\beta\mu_i = \beta\mu_i^{\text{id}} + \beta\mu_i^{\text{sr}} + \beta\mu_i^{\text{el,mf}} + \beta\mu_i^{\text{el,corr}} + \beta\mu_i^f + \beta\mu_i^g$$

The mean field contribution of the electrostatic interactions is taken into account through the Poisson equation

$$\nabla^2\psi(z_i) = -\frac{q}{\epsilon_0\epsilon}(c(z_i) - c) \quad c = \frac{1}{n_z} \sum_{k=1}^{n_z} c_k$$

and in the approximation of homogeneous plains it can be written

$$\beta\mu_i^{\text{el,mf}} = \beta\psi_i q = -\frac{2\pi\lambda_B}{a} \sum_{j=1}^{n_z} \langle c_j - c \rangle |j - i|$$

where the Bjerrum length

$$\lambda_B = q^2 / (4\pi\epsilon_0\epsilon k_B T)$$

The correlation electrostatic contribution is accounted for the three lowest coordination spheres

$$\begin{aligned} \beta \mu_i^{\text{el,corr}} = & - \frac{2\pi\lambda_B}{a} \left( c_{i-1} h_{i,i-1}^{(1)} + 4c_i h_{i,i}^{(1)} + c_{i+1} h_{i,i+1}^{(1)} \right) \\ & - \frac{2\pi\lambda_B}{a\sqrt{2}} \left( 4c_{i-1} h_{i,i-1}^{(2)} + 4c_i h_{i,i}^{(2)} + 4c_{i+1} h_{i,i+1}^{(2)} \right) \\ & - \frac{2\pi\lambda_B}{a\sqrt{3}} \left( 4c_{i-1} h_{i,i-1}^{(3)} + 4c_{i+1} h_{i,i+1}^{(3)} \right), \end{aligned}$$

The correlation contributions are taken into account in the lowest approximation of the method of collective variables

$$h_{ij}^{(k)} = g_{ij}^{(k)} - 1 = \exp(-\beta w_{ij}^{(k)}) - 1 \quad w_{ij}^{(k)} = J\delta_{1k} + \frac{\lambda_B}{a\sqrt{k}} e^{-\kappa a\sqrt{k}}$$

$$\kappa = \sqrt{4\pi\lambda_B c(1-c) / a^3} \quad \text{is the inverse Debye length, } k=1, 2, 3$$

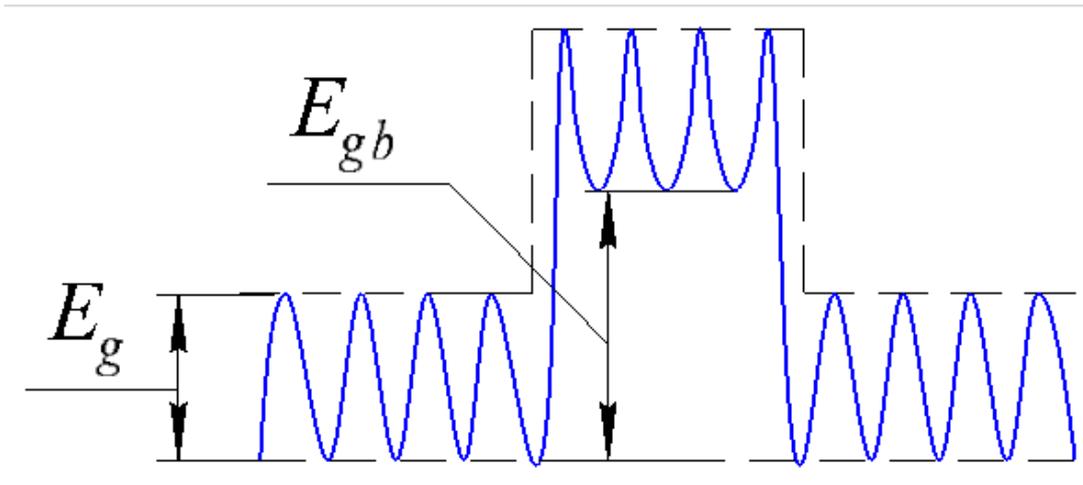
Yukhnovskii I.R., Holovko M.F., *Statistical Theory of Classical Equilibrium Systems*, Naukova Dumka, Kiev, 1980 (in Russian).

Golovko M.F., Yukhnovskii I.R., *Approaches to the many-body theory of dense ion-dipole plasma, Application to ionic solvation*, In: *The Chemical Physics of Solvation, Part A.*, Eds. R.R. Dogonadze, E. Kalman, A.A. Kornyshev, J. Ulstrup, Amsterdam, North Holland, Elsevier, 1985, 207.

The intergrain regions were modelled by the deviation of the energetic relief from the bulk value

$$\beta\mu_i^g = E_{gb} \quad \text{for } i=n_z/2 \text{ or } n_z/2+1$$

The model of the intergrain domain



The chemical potential contains contributions from various interactions

$$\beta\mu_i = \beta\mu_i^{\text{id}} + \beta\mu_i^{\text{sr}} + \beta\mu_i^{\text{el,mf}} + \beta\mu_i^{\text{el,corr}} + \beta\mu_i^g + \beta\mu_i^f$$

The last contribution is the external electric field of the charged walls

$$\beta\mu_i^f = - \frac{4\pi\lambda_B c_w}{a} \left( i - \frac{n_z + 1}{2} \right)$$

**Altogether** this produces  $n_z$  transcendental equations for the charge distribution in different lattice plains at various boundary and thermodynamic conditions

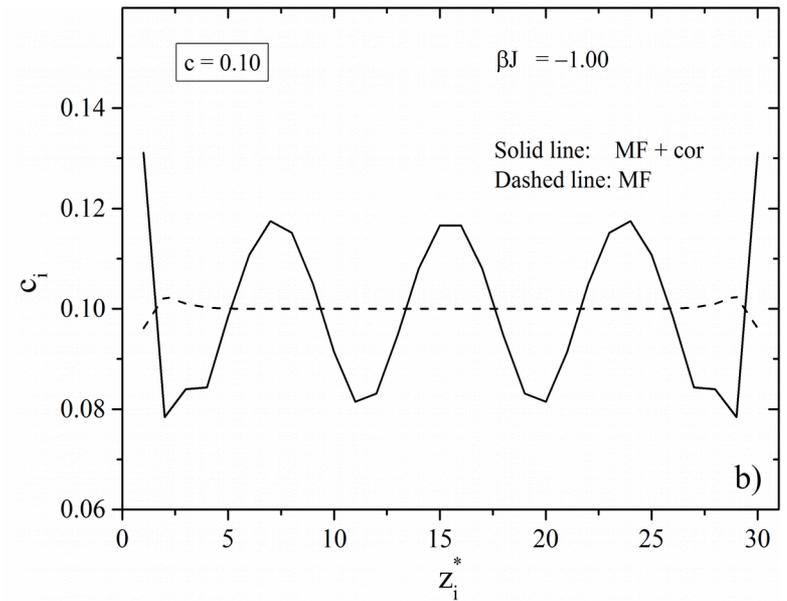
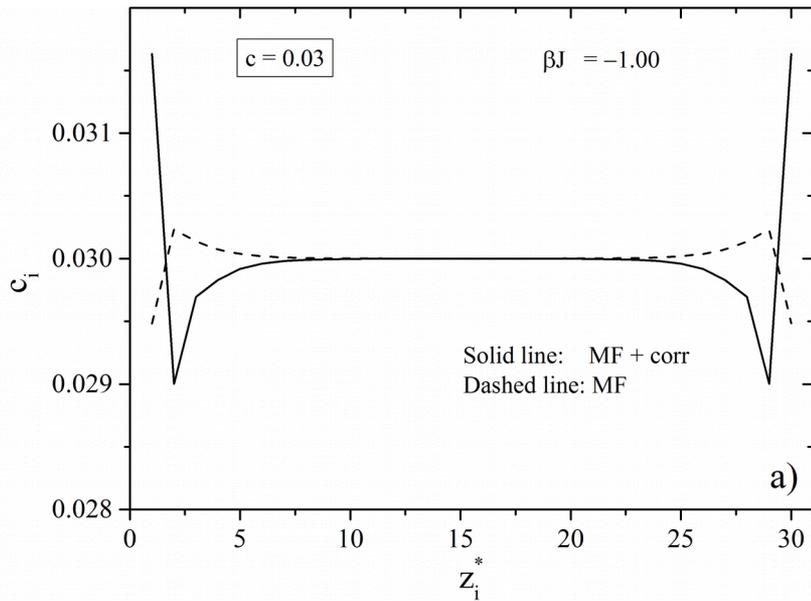
The Monte Carlo simulation method was planned to check the adopted approximations and the results obtained from the numerical solution of the transcendental equations. The Coulomb interaction contribution was split into two parts in the direct and inverse spaces in accordance with the Ewald's summation method

$$U_{\text{Coul}} = \frac{1}{2} \sum_{i=1}^N \left( \sum_{|\mathbf{n}|=0}^{\infty} q_i q_j \frac{\text{erfc}(\alpha |\mathbf{r}_{ij}|)}{|\mathbf{r}_{ij}|} \right. \\ \left. + \frac{1}{\pi V} \sum_{\mathbf{k} \neq 0} q_i q_j \frac{4\pi^2}{\alpha^2} \exp\left(-\frac{k^2}{\alpha^2}\right) \cos(\mathbf{k} \cdot \mathbf{r}_{ij}) \right) + \frac{2\pi}{3L^3} \left| \sum_{j=1}^N q_i \mathbf{r}_i \right|^2$$

The last term appears due to the slab geometry with periodic boundary conditions in the directions parallel to the confining walls.

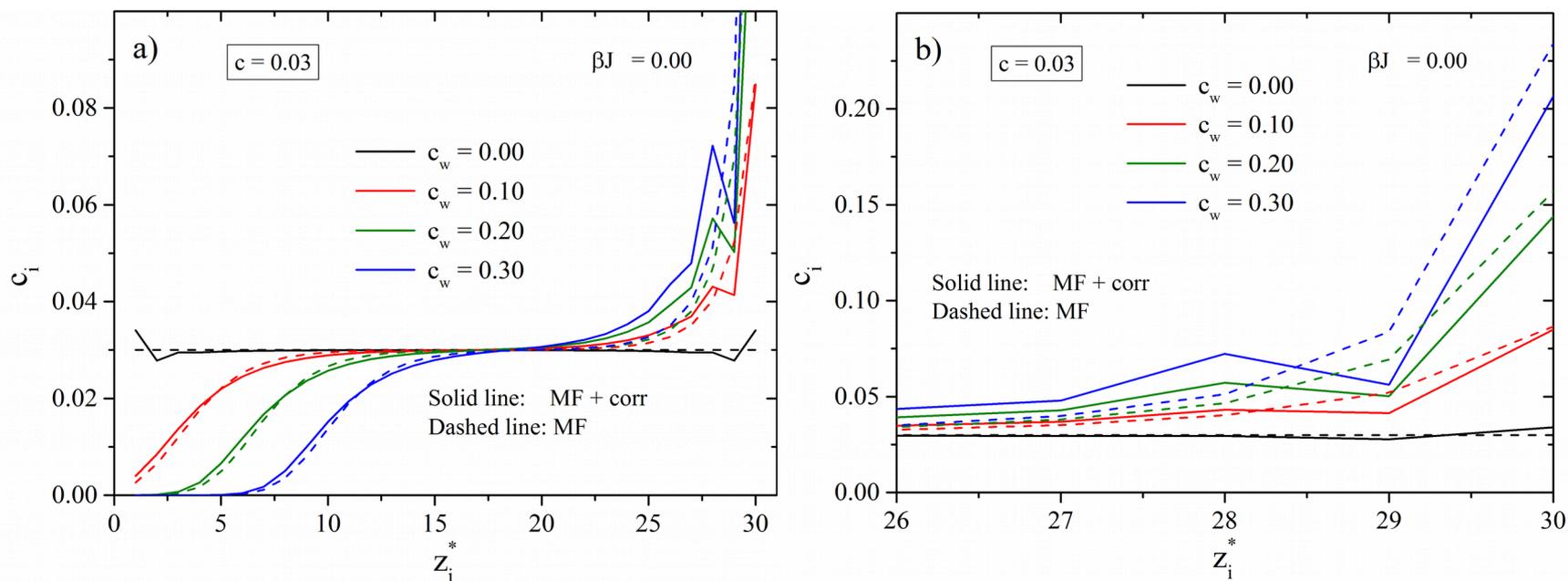
In-Chul Yeh and Max L. Berkowitz, Ewald summation for systems with slab geometry, J. Chem. Phys. 111 (1999) 3155.

A.P. dos Santos, M. Giroto, and Y. Levin, Simulations of Coulomb systems with slab geometry using an efficient 3D Ewald summation method. JCP, 144 (2016) 144103.

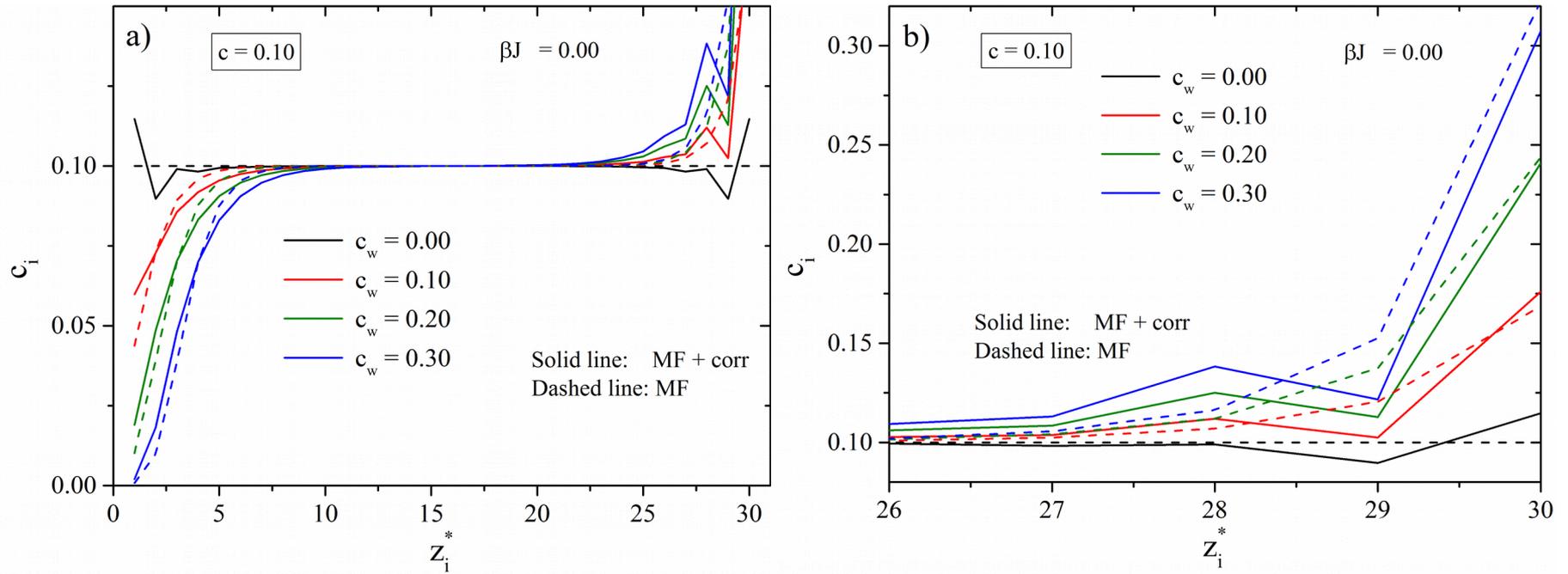


**Fig. 1.** The concentration profile of cations between uncharged walls ( $c_w=0.0$ ), but with taking into account the short-range attraction ( $\beta J=-1.0$ ) at the low (left panel,  $c=0.03$ ) and high (right panel,  $c=0.10$ ) average concentrations. Comparison between the MF (dashed line) and MF+corr (solid line) approximations.

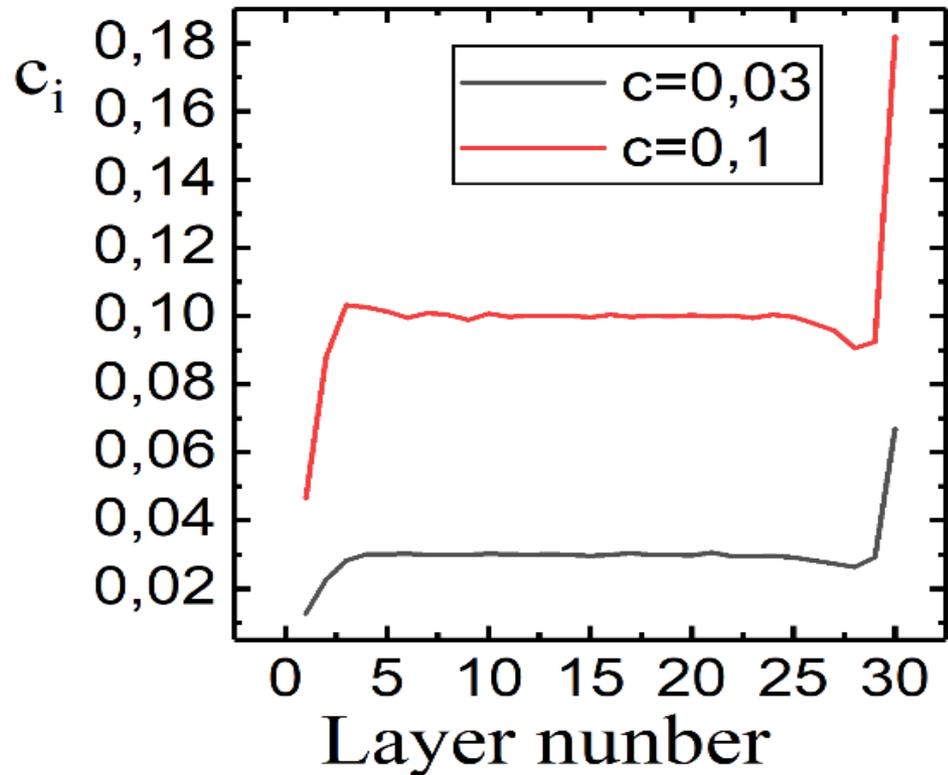
Patsahan T., Bokun G., Di Caprio D., Holovko M., Vikhrenko V., The effect of short-range interaction and correlations on the charge and electric field distribution in a model solid electrolyte, *Solid State Ionics*, 335 (2019) 156-163



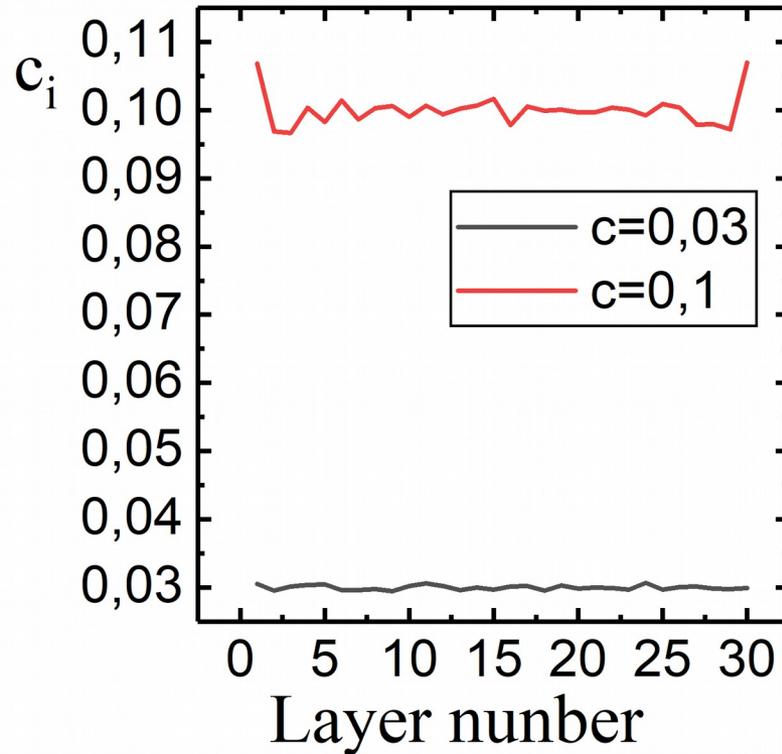
**Fig. 2.** The concentration profile of cations between the walls of different charges ( $c_w=0.0-0.3$ ) at the lower average concentration ( $c=0.03$ ). Dashed lines correspond to the results obtained within the mean field (MF) approximation and solid lines obtained with taking into account correlations (MF+corr). On the right panel, the region near the right wall is shown in a larger scale.



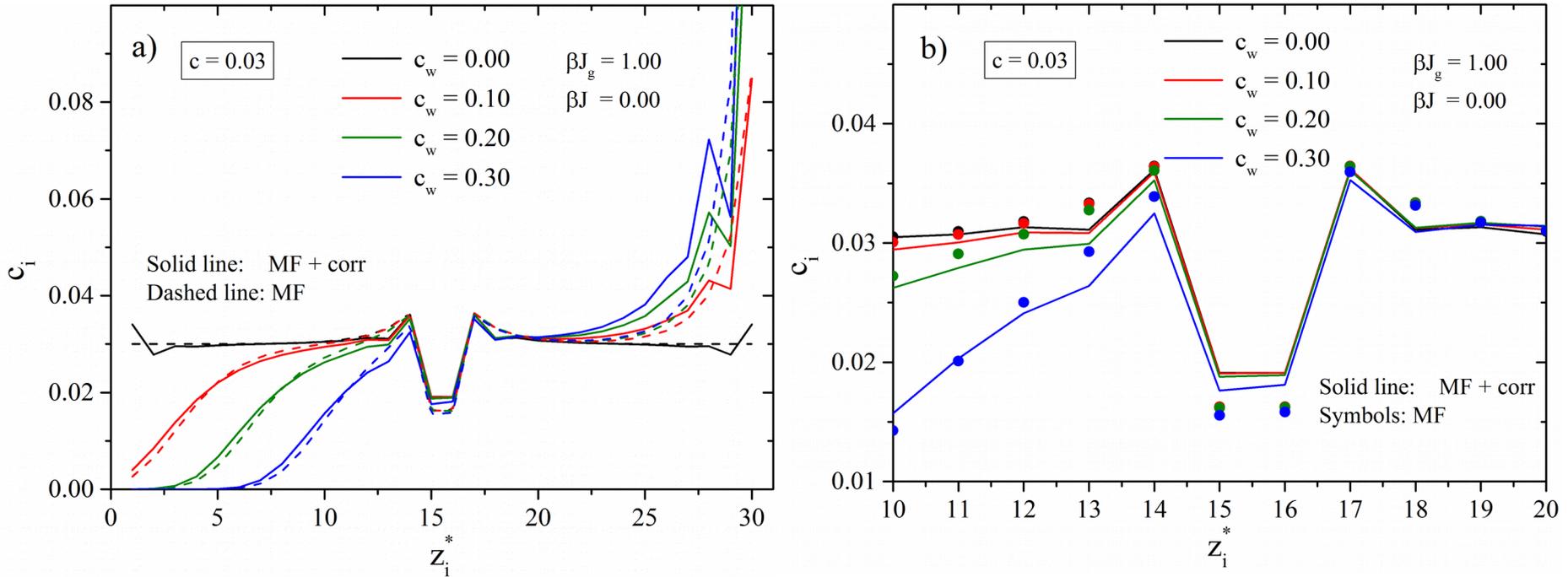
**Fig. 3.** The concentration profile of cations between the walls of different charges ( $c_w=0.0-0.3$ ) at the larger average concentration ( $c=0.10$ ). Dashed lines correspond to the results obtained within the mean field (MF) approximation and solid lines obtained with taking into account correlations (MF+corr). On the right panel, the region near the right wall is shown in a larger scale.



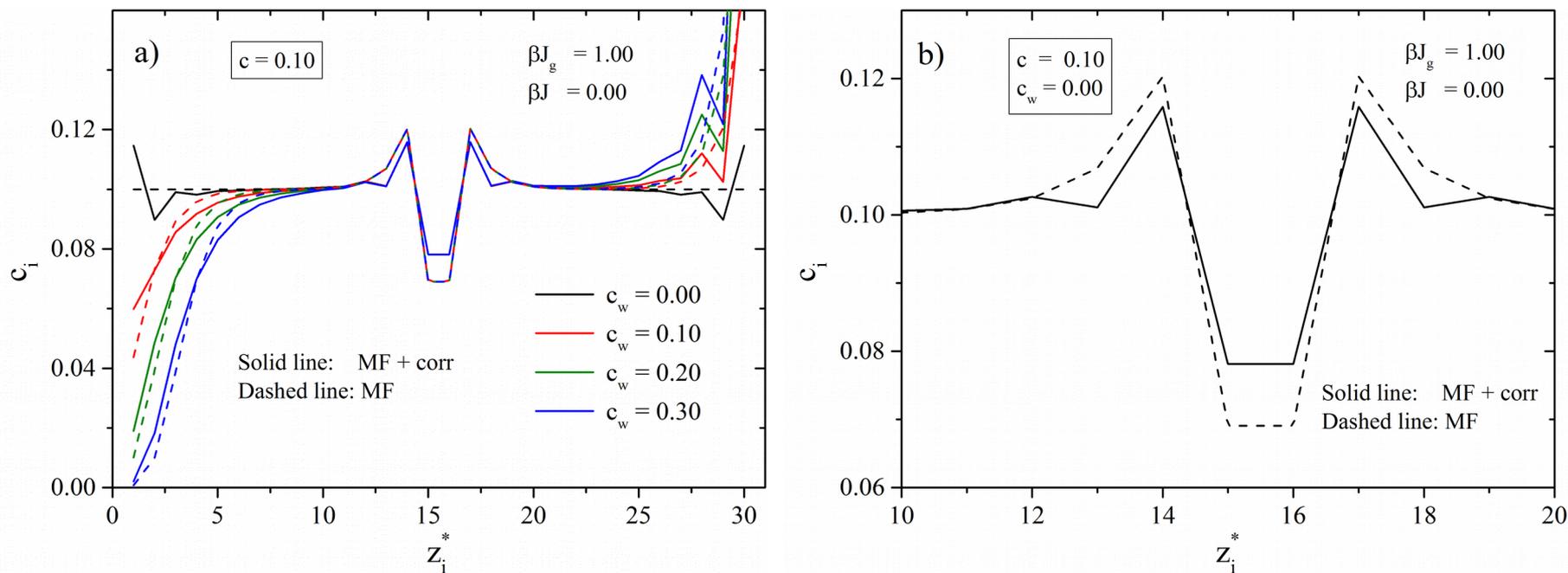
**Fig. 4.** The Monte Carlo simulation results for the concentration profiles of cations between the walls at  $c_w=0.2$  and the average concentrations  $c=0.03$  and  $0.10$ . The concentration at the right wall is  $0.18$  and  $0.064$  that can be compared to  $0.24$  and  $0.14$  that follows from the solution of the equations.



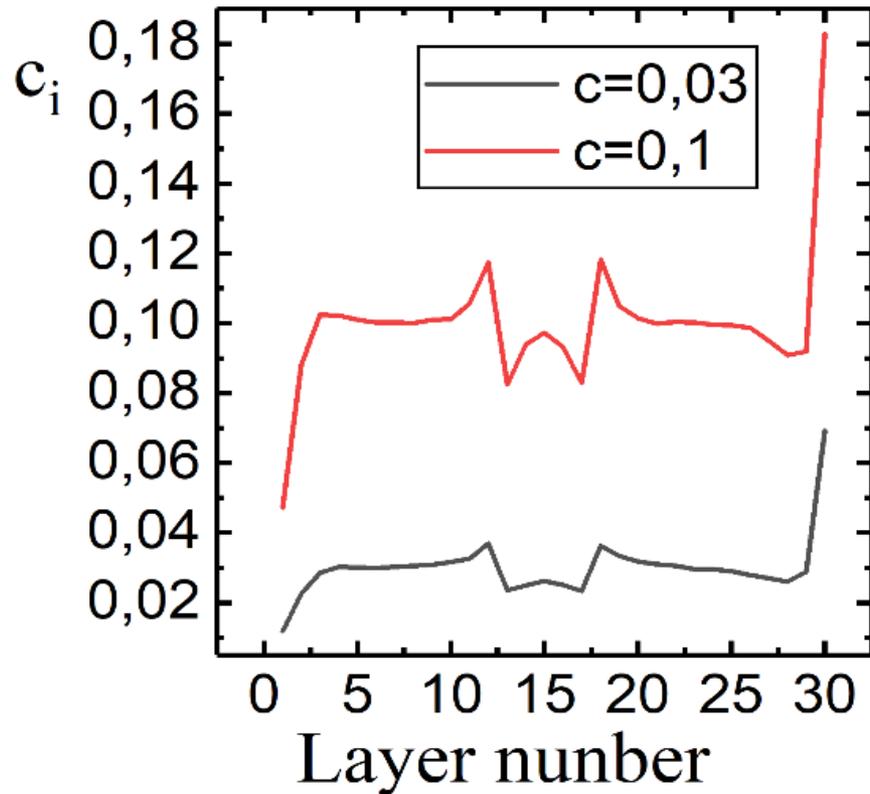
**Fig. 5.** The Monte Carlo simulation results for the concentration profiles of cations between the walls at  $c_w=0$  and the average concentrations  $c=0.03$  and  $0.10$ .



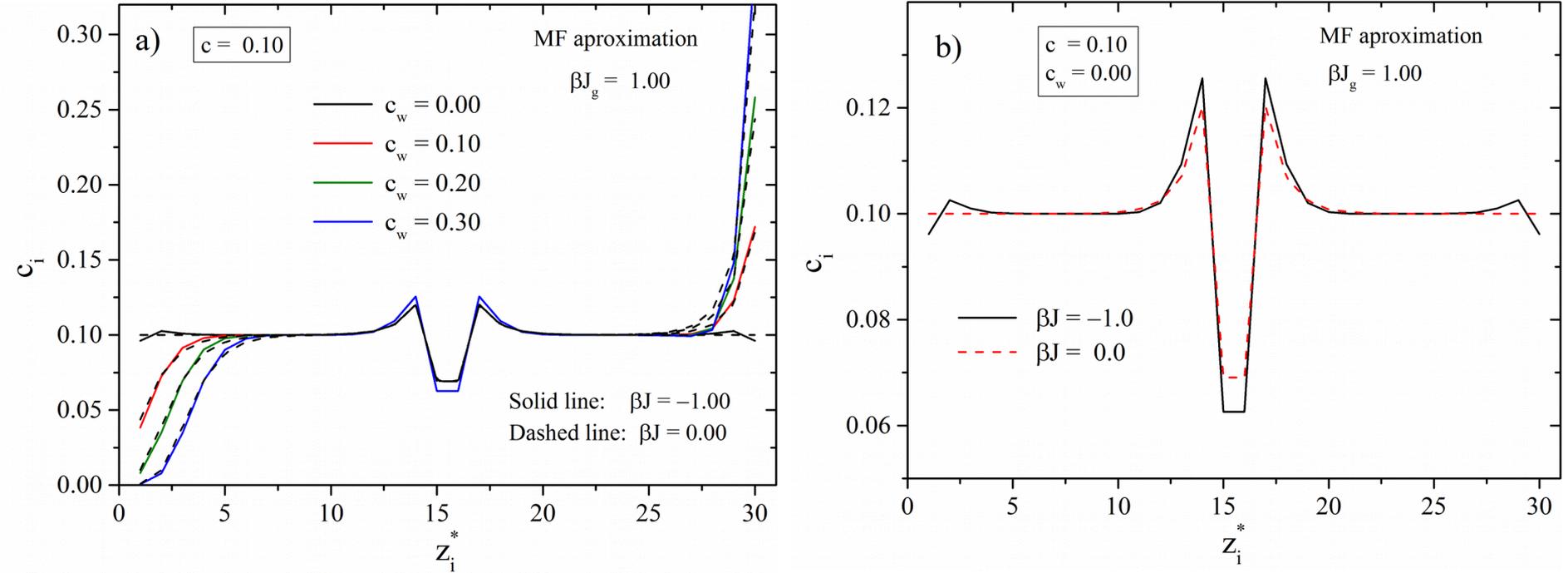
**Fig. 6.** The concentration profile of cations between the walls of different charges ( $c_w=0.0-0.3$ ) at the lower average concentration ( $c=0.03$ ) and with taking into account the intergranular boundaries ( $\beta J_g=1.00$ ), but without short-range attraction ( $\beta J=0.0$ ). On the right panel, the intergranular region is shown in a larger scale.



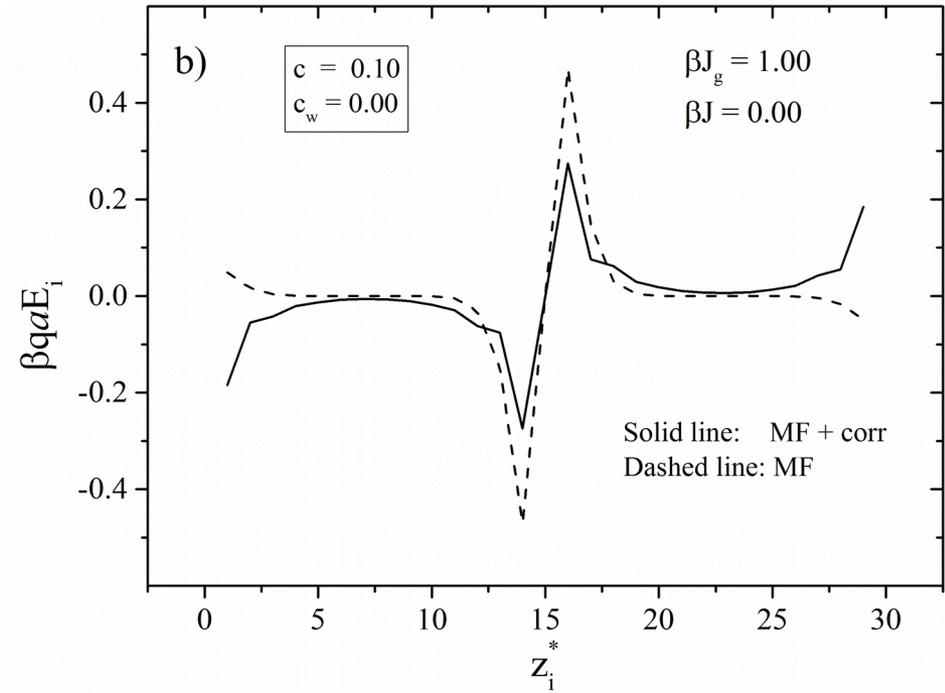
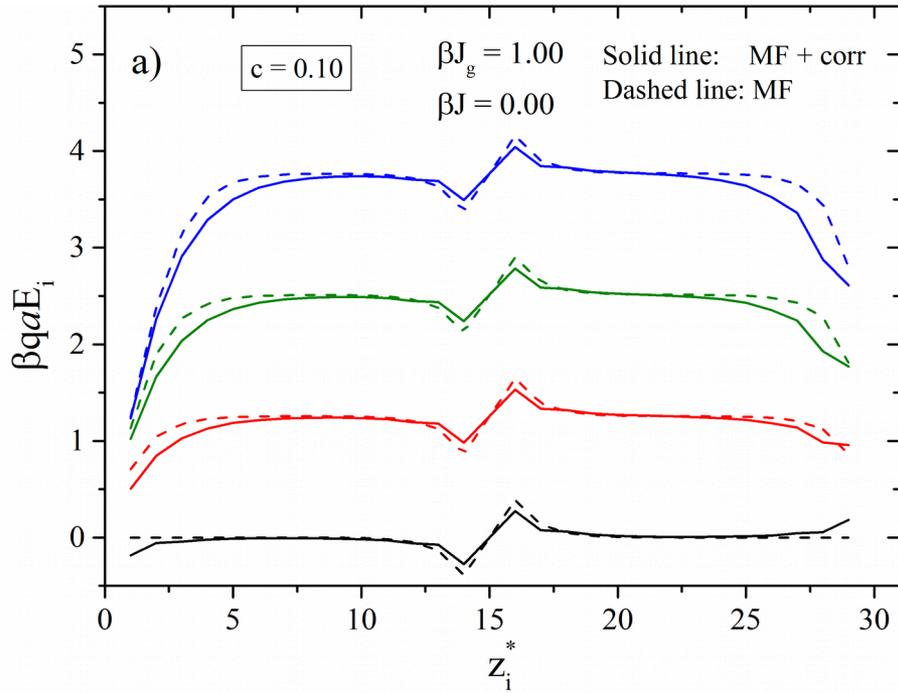
**Fig. 7.** The concentration profile of cations between the walls of different charges ( $c_w=0.0-0.3$ ) at the larger average concentration ( $c=0.10$ ) and with taking into account the intergrain boundaries ( $\beta J_g=1.00$ ), but without short-range attraction ( $\beta J=0.0$ ). On the right panel, the intergrain region is shown in a larger scale.



**Fig. 8.** The Monte Carlo simulation results for the concentration profiles of cations between the walls at  $c_w=0.2$  in presence of the intergrain boundary and the average concentrations  $c=0.03$  and  $0.10$ . The concentration distribution in the region of the intergrain boundary within approximately 10 per cent corresponds to that follows from the solution of the equations.



**Fig. 9.** 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.



**Fig. 10.** The electric field profile of cations between the walls of different charges ( $c_w=0.0-0.3$ ) at the higher average concentration of cations  $c=0.10$  and with taking into account the intergrain boundaries ( $\beta J_g=1.00$ ), but without short-range attraction ( $\beta J=0.0$ ). The colors denote the same values of  $c_w$  as in the previous figures. On the right panel, the intergrain region is shown in a larger scale.

# Conclusion

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

Thank you very much  
for your attention