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Report on the PhD thesis of Carolina Cruz Cardona
„Effects of confinement on ionic liquids"

The PhD Thesis of Carolina Cruz Cardona analyzes the behavior of ionic liquids-solvent mixtures. Ionic liquids are very important materials from the application point of view – they are new electrolyte media for the future. They already are and will be progressively more used in fuel cells, batteries, and supercapacitors. In these applications, ionic liquids are confined within porous matrix, hence understanding of how confinement affects the properties of the ionic liquid is of the utmost importance. And this is precisely the question that Carolina Cruz Cardona tackles in her Thesis. The task at hand is a difficult one, due to the interplay of several factors: the presence of long-range-forces, strong interactions with the walls, entropic effects and relatively complicated phase behavior close to the demixing transition.

The Thesis is structured in a clear logical manner. The first three chapters are introductory, discussing the goal and structure of the Thesis (Chapter 1), the properties of ionic liquids (Chapter 2) and physics of phase transitions (Chapter 3). They are written in a lucid manner, well balancing the clarity and scientific content, although there are a couple of typos. For example, the valencies of the ions are missing in the exponent in 2.4 (or at least – if they are monovalent, there should still be +/- depending on whether these are cations or anions), as otherwise *sinh* in Eq. 2.6 cannot be recovered. Additionally, the minus sign seems to be missing in the exponent of Eq. 2.9.

The main elements of the model are then introduced in Chapter 4. The model is formulated on the mean field level. First, the grand thermodynamic potential is constructed with the contributions from the electrostatic energy, the internal energy associated with van der Waals-like dispersion (non-Coulombic) interactions, the energy associated with the pore walls, and

the entropy respectively. Next, there is coarse-graining of the short-range interactions carried out, accompanied by the Taylor expansion of the density. Eventually, the vdW forces are described in terms of their mean strength (parameter K) and characteristic length (parameter ξ_0). The interaction with the walls is characterized by introducing ionophilicity parameter (denoted by h_s) describing the preference of the electrode for ions or solvent. Finally, the entropy of mixing is taken into account as well as of the excess free energy associated with the excluded volume interactions. There are two approximations used in the Thesis to characterize the latter – either Carnahan–Starling approximation, coming from the hard-sphere models, or the expression originating from the lattice-gas model. The former can be used when there is a size separation between the ions and solvent molecules, the latter is more appropriate if they are of the same size.

Next, the grand potential constructed in this way is minimized which leads to the Euler-Lagrange equations for the electrostatic potential and for the order parameter ϕ (corresponding to the difference between the density and its equilibrium bulk value). The Euler-Lagrange equations are then solved, analytically and numerically, in Chapter 5. The analytical solution is obtained by using a perturbation expansion with the wall interaction potential as a small parameter. In the first-order approximation, the electrostatic potential u and the order parameter ϕ are fully decoupled; the coupling first appears in the second-order approximation. This coupling is responsible for the nonlinear behavior of the system as it approaches demixing. The Euler-Lagrange equations are also solved numerically (with the details of the procedure presented in the second part of Chapter 5).

In Chapter 6 these solutions are analyzed in detail for the case when an ionic liquid solution is in contact with a planar metallic electrode. Ion density and charge density profiles are plotted both for numerical and analytical solution (based on the perturbation expansion). As expected, both agree for low applied potentials and diverge as potential increases. Interestingly, the perturbation expansion seems to work much better for the charge density than for the ion density – it would be good to have a more in-depth discussion of this observation in the Thesis. The differences between the perturbative solutions and the full numerical ones are particularly pronounced on the differential capacitance demonstrating that – particularly for large densities – even the qualitative shape of the voltage dependence of capacitance can be completely different. The Author then switches to the numerical solutions for a more in-depth analysis of the differential capacitance in Sec. 6.2. This section contains perhaps the most

important results in the Thesis, showing the appearance of the bird-shaped capacitance curve that exhibits three peaks as a function of voltage, which emerges due to the proximity to demixing. Such a shape has not been predicted before. In a sense, it sits between the bell-shaped and camel-shaped capacitance as defined by Kornyshev. This is confirmed by the capacitance diagrams (Fig. 6.6) in the ionophilicity-bulk density plane where we indeed find that the region corresponding to the bird-shaped capacitance is located in between the bell-shaped and camel-shaped region. The transitions between the different regions can be induced by either changing the density of the ionic liquid or the temperature. Such a transition is also associated with dramatic changes in the charging parameter, which shows a strong peak at a non-zero voltage. The energy stored in the system also shows a temperature dependence, increasing as we approach demixing. This can be used to boost the efficiency of supercapacitor-based devices which generate electricity from waste heat.

Another important set of results is found in Chapter 7, devoted to the analysis of the behavior of ionic liquid solutions in slit-shapes nanopores, i.e. in between two electrodes. It is demonstrated that the pores can become spontaneously ionized or deionized in response to relatively small temperature changes or potential differences applied to the electrodes. The phase diagram in voltage-temperature plane turns out to be nontrivial, with an interesting reentrant behavior characterized by the bending of the capillary ionization line at higher voltages. This behavior is then analyzed in detail and it is established that at high voltages the charge density as well as the ion density near the pore walls become identical in both phases. Thus the thermodynamic state is then determined by the bulk region, which favors the IL-poor phase. The phase transitions result in the associated jumps in the accumulated charge and stored energy which can be used in the practical applications.

Finally, in Chapter 8, a completely different approach of studying the system's behaviour is used, viz. molecular dynamics simulations. These are performed using the LAMMPS package, with both the ions and the solvent represented as equal-sized spheres. The ions interact with Coulombic forces whereas the dispersion interactions are represented by truncated Lennard-Jones potentials. The goal here was to confirm the behavior predicted by the mean-field theory. This was successful to some extent only, as evidenced by Fig. 8.5. There is a qualitative agreement between the theory and MD results, but a more detailed comparison is hindered by large fluctuations of the MD data. In my opinion, these fluctuations may even make it impossible to state unequivocally that a bird-shape dependence

is indeed observed – the curves in Fig. 8.5 seem to have several maxima, and not just three as predicted by the theory, whereas the bell-shaped curve in Fig. 8c at $T/T_c=2.2$ is not reproduced in the MD data. Clearly, longer trajectories with more averaging are needed here. I also miss the simulation corresponding to the conditions characterized by the camel-shape, which could allow one to see if it can be reproduced numerically.

The last chapter of the Thesis contains the summary and conclusions. The main text is then followed by four appendices and bibliography.

Notwithstanding some critical remarks which I have formulated above, I assess the PhD dissertation presented by Carolina Cruz Cardona very favorably. I really enjoyed reading this excellent and well-written thesis. The scientific results in the Thesis are of a high quality and offer a deep and complete investigation of the ionic liquid solutions close to demixing. Importantly, the results are already published in five papers in leading journals in the field, with Carolina Cruz Cardona being the first author of each publication. Overall, the Thesis presents a significant amount of work that demonstrates that the candidate has excellent theoretical knowledge of the scientific field, methodological rigor, and understanding of the methods used.

I am fully convinced that the Thesis fulfills all the statutory and customary requirements posed on theses aimed for obtaining the PhD degree and I recommend the admittance of MSc Carolina Cruz Cardona to the next stages of the doctoral process. It is also my pleasure to ask for a distinction of the doctoral dissertation of Carolina Cruz Cardona due to its scientific novelty, in particular the discovery of bird-shaped capacitance curve, which emerges due to the proximity to demixing, and a detailed and comprehensive analysis of the phase behavior of ionic liquid – solvent mixtures in confinement.