Séminaire LIONS

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Electrostatics in electrolytes expressed in an exact formalism reminiscent of the Poisson-Boltzmann picture

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In the PB approximation for electrolyte systems one assumes that the solvent behaves like a dielectric continuum and that the charge of each ion interacts with the average electrostatic potential from other ions in the system, neglecting the correlations. In reality an ion does not “feel” the mean potential since the ions and the solvent molecules in its neighborhood correlate with it—each ion has a local “ion and solvent cloud” of its own where the ion distribution deviate from the average one and where the locations and orientations of solvent molecules are affected. This cloud affects the interactions felt by the ion.

In this treatise it is shown how it is possible to include such effects in an exact manner for the screened electrostatic interactions. Thereby, the exact theory of electrolyte solutions with discrete solvent molecules is reformulated in a manner that has a similar structure as the PB approximation theory. The screened electrostatic interaction between any two particles in the system is then written in terms of the average electrostatic potential due to one of them interacting with an effective charge distribution of the other (rather than with the bare charges as assumed in the PB approximation). This effective charge distribution also has the role as the source of the average electrostatic potential when the latter is expressed in terms of the screened rather than the ordinary (unscreened) Coulomb potential. The resulting exact formalism maintains a large part of the physical transparency of the PB theory.

The primary advantage is conceptual since the formalism separates out the screened electrostatics among complex consequences of the various interactions. Since the theory is exact, the task to obtain numerical results is the same as earlier. To do any numerical work one needs to do computer simulations or use some other approximate analytical or numerical method. One can take such results as input to analyze the behavior of electrolytes using the present formalism. The theory can also be used as a guide to invent new approximations.