FLUCTUATION ENHANCEMENT OF ION DIFFUSIVITY IN LIQUIDS

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Dependence of ion diffusivity on ion radiu sin liquid is known to have maximum. It is found that there could be multiple maximums on this dependence. A model of ion motion is suggested to describe this effect. It is based on the fluctuations of the ion solvation shell configuration.

Ion motion could be separated into a motion together with solvation shell as a whole and a motion inside the solvation shell. The total diffusivity of the ion is a sum of two diffusivities associated with each of these motions. Motion of the entire solvation shell could be described using Stokes-Einstein relation. It is independent of the ion size. Motion inside the solvation shell is associated with fluctuation of its structure.

Fluctuational change of the solvation shell structure can be described as a motion from one configuration of the shell to another. Every pair of possible configurations adds its impact to ion diffusivity. The total fluctuational diffusivity can be decomposed into diffusivities associated with each pair of configurations. The result of such decomposition are different diffusion components. It can be shown that every such component has maximum. Thus total diffusivity, that is the sum of these components, can have multiple maximums.

A method to compute diffusivity in liquid is presented. It is based on the ideas described above. It is independent of the choice of the interaction potential. In principle, it should not be limited in application to ions. The sufficient conditions for this model are the following. Firstly, solvation shell should have well defined configurations. It means that it is possible to trace configuration fluctuations using some collective variable. Secondly, configuration changes of the solvation shell should be statistically independent.

The model is found to be in a good agreement with direct molecular dynamics calculations of ion diffusivity in liquid. Water and liquid xenon are chosen for demonstration as examples of polar and nonpolar liquids. Theoretical model as well as molecular dynamics are in agreement with experimental data available.

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