Subdiffusion of water and ions at biosurfaces: temporal vs spatial disorder

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Dynamic properties of ions and water in the hydration shells of biomolecules are different from those in bulk water. Simulation studies of hydrated DNA and proteins reveal several anomalous features of the ions and water dynamics. In particular, translational diffusion of water and ions is found to be anomalous under various levels of hydration [1-3]. Water shows anomalous diffusion with exponent $\alpha \approx 0.84$ and 0.8 near DNA and lysozyme, respectively, reflecting mostly a spatial disorder of biological surfaces, which only weakly depends on hydration level. The increase of the exponent α of anomalous diffusion of ions at DNA surface from 0.66 to 0.81 upon hydration correlates with the appearance and growth of the spanning network of hydration water. The anomalous diffusion of ions is governed by the spatial disorder of the surface of hydrated DNA, which is highly sensitive to water clustering and can be seen even under full hydration. Temporal disorder of biosurface causes a "cage effect", which appears as deviation of the time dependence of the mean-square displacement from a power law at short times.

The long-range mobility of hydration water is roughly proportional to the hydration level, whereas the long-range mobility of ions exhibits a stepwise increase at three distinct hydration levels [4]. The first step reflects the onset of the dissociation of ion pairs on the DNA surface probably caused by the increase in the water dielectric permittivity due to the appearance of the spanning H-bonded network [2]. This step coincides with the polymorphic transition from A- to B-form of DNA, indicating a role of intraduplex electrostatic condensation in the low hydration polymorphism of DNA. Protein dynamics strongly affects translational motions of water and this dynamic coupling is maximal at hydration levels, corresponding to the formation of an infinite H-bonded network of hydration water.

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