Theoretical Models in Biochemical and Related Systems

Solvent–Solute Interactions by Quantum-Mechanical and Statistical Mechanical Simulations

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Quantum-mechanical computations are used to obtain the interaction potentials (two-body, three-body and many-body) between solute–solvent, and between solute–solute for multi-solute, one-solvent systems. *Statistical mechanics simulations* are used to obtain the structure and energy-related parameters of the solute–solvent system at a given temperature. This methodology is applied to a vast number of problems, like the structure of water around DNA, RNA and enzymes, ionic solutions, *etc.* The comparison between simulated and experimental data indicates the need to include temperature parameters, the reaction field, and many-body corrections in order to obtain realistic simulations of quantitative predictive value.

Ion Distributions and Energetics in Lamellar Liquid Crystals. A Comparison between Different Theoretical Approaches

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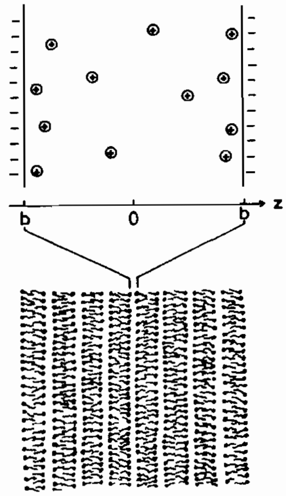

Fig. 1. The amphiphilic molecules form bilayers which are intercalated with aqueous lamellae also containing the counterions. The upper figure shows the schematic model of the aqueous region used in the MC simulations.

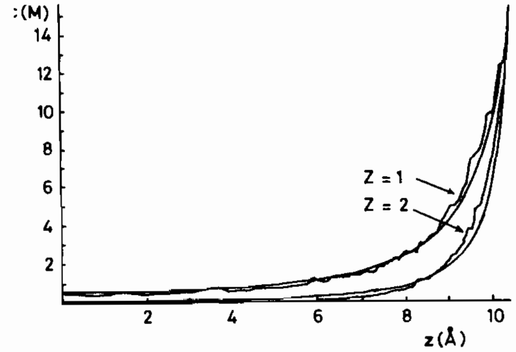

Fig. 2. Concentration profiles between the two charged plates for mono- and divalent ions. The plate distance 2b = 21.0 A. The smooth curves are taken from the PB equation and the two other are obtained from MC-simulations.

Monte Carlo (MC) simultations have been performed for an ionic system between two parallel uniformly charged plates modelling the conditions found in lamellar lyotropic liquid crystals [1] (Fig. 1). The results are used to assess the accuracy of the statistical mechanical approximations leading to the Poisson–Boltzmann (PB) equation. In general there is a good agreement between the MC simulations and results obtained from the PB equation [2], both in the system studied here and in analogous systems [3]. This applies to the ion distribution (Fig. 2) and to a lesser extent to the energy. In particular the PB equation predicts the correct asymptotic behaviour as the distance between the plates is increased. In the MC simulations there is a slight increase in the ion concentration close to the walls compared to the PB solution. This is due to the fact that in the MC simulations one allows for correlations between the ion while the PB equation is derived under assumption that the pair correlation function is constant. It is shown that the accumulation of ions close to the walls is solely due to the repulsions between the ions and it is argued that ion binding in polyelectrolyte system can be understood as caused by the incapability of the bulk solution to sustain a substantial net charge over moderately large distances.

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Successive Approximations in the Quantum-Chemical and Statistical-Mechanical Study of Aqueous Solutions, particularly with Biomolecule Solutes

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The present paper reports Monte Carlo simulation results calculated at room temperature for a variety of aqueous systems, whose interaction potentials had been obtained by fitting quantum-mechanical *ab-initio* calculations, at CI (water–water potential [1]) or SCF-LCAO-MO level [2–4]. Unless otherwise stated, our systems were clusters consisting of one solute molecule and 200–250 water molecules, *in vacuo*; the pairwise additivity approximation was also used.

1) We simulated the two systems glycine–water (neutral molecule and zwitterion) [5]; their solvation structure was elucidated by means of orientational correlation functions (OCF's) and radial distribution functions (RDF's) [5]. The picture obtained by these means was found to be in broad, qualitative agreement with the information one can gain from (orientationally-optimized solute–water) isopotential contour maps.

2) We simulated the systems serine–water (neutral molecule and two conformers of the zwitterion) [6] and calculated RDF's and OCF's, hydrogen- and oxygen-atom probability density (PD) maps, and also investigated the spacial dependence of the average water–water and solute–water interaction energies. We also calculated PD maps for glycine zwitterion, and all the corresponding isopotential contour maps. Some water molecules are strongly hydrogen-bonded to hydrophilic groups (not to the alcoholic one) and, beyond them, there exists a rather rich and complex hydrogen-bonded network, resulting by a subtle balance between solvent–solvent and solvent–solute interactions, which is rather sensitive to conformational effects.

3) We also simulated a system consisting of an Na^+ cation, glycine zwitterion and water. Thermodynamic and structural results showed the Na^+ to be localized in the same plane as the $-COO^-$ group and close to it; no water molecules were found in the neighbourhood of the $COO^- \cdots Na^+$ pair, whereas the solvation of the amino group was not dramatically altered [7,8].

4) One could argue that a cluster *in vacuo* is not a very good approximation to a dilute solution; on the other hand, usage of periodic boundary conditions would probably require an even larger number of solvent molecules, and possibly an Ewald–Kornfeld summation for electrostatic potentials. As an alternative approach, we decided to consider our cluster as contained in a spherical cavity [9] surrounded by a homogeneous and isotropic dielectric continuum, with the same dielectric constant as the pure solvent. The potential energy of the cluster due to the 'dielectric reaction' was evaluated according to classical electrostatics; calculations on two serine zwitterion conformers showed a moderate increase (about 5%) in the solvation energy [10].

5) In order to test the validity of the pairwise additivity approximation, quantum-mechanical calculations were carried out on the $Li^+(H_2O)_2$ system, and two non-pairwise-additive three-body potential functions were extracted from the total interaction energies [11]. One of them appeared to be a short-range repulsive correction; the other one could be interpreted classically, as due to water bond polarization. Both terms were suitably generalized to a system $Li^+ (H_2O)_n$, and Monte Carlo simulation was carried out on clusters with $n \leqslant 6$, both with and without the many-body correction [11]. Comparison with available measured [12] and simulation [13] results showed a significantly improved agreement with experiment.

References

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