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Perspective

Perspective on "Molecular dynamics study of liquid water"

Rahman A, Stillinger FH (1971) J Chem Phys 55: 3336–3359

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Abstract. The first molecular dynamics simulation of liquid water by Rahman and Stillinger was the cornerstone of much subsequent research, including molecular dynamics of proteins and other biological systems

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The paper by Rahman and Stillinger was the first molecular dynamics simulation of a polar molecule: the single most important one for sustaining life, water. It built on the technique for classical molecular dynamics introduced for hard spheres by Alder and Wainwright [1]. A Monte Carlo study of the structural properties of the liquid appeared around the same time [2]. This paper signaled the beginning of classical molecular dynamics studies of molecules of biological interest and also provided great insight into the structure and dynamics of liquid water. Rahman was subsequently a key member in the CECAM workshop on molecular dynamics in France which facilitated the application of molecular dynamics methods to proteins and led to the first molecular dynamics study on a protein, which was reported by McCammon et al. [3].

Rahman and Stillinger used a four-point-charge model and Lennard-Jones parameters, noting that their model gave a reasonable representation of water dimer energy and structure, which were being first studied by ab initio quantum mechanical calculations around the same time. They used a 0.4-fs time step and carried out 2-ps of production dynamics at an average temperature of 34°C. By integrating the equations of motion in dimensionless form they were able to suggest a scale factor of 1.06 for the potential energy that would improve the agreement with experiment for the average energy and diffusion coefficient and that would correspond to a temperature of 52°C. They also carried out a more limited simulation at −8°C. The simulations were carried out at a constant density of 1 gr/cm^3 and the dynamical equations used rigid water monomers and a fifth-order integration algorithm for translation and a fourth-order one for rotation.

The results were analyzed for a large number of structural and dynamical properties of the liquid and quite good agreement with available experimental results was achieved for all properties. These included average liquid energy, diffusion coefficients, radial distribution functions and their relation to experimental X-ray scattering intensities, the Kirkwood *g* factor, hydrogen-bond energy distribution, dipole-direction relaxation, dielectric relaxation, and proton motion and neutron scattering.

Most interestingly, this article contributed to the appreciation of the usefulness of computer graphics visualization of molecular structures and dynamics for complex molecular systems [4]. Rahman and Stillinger saved ten intermediate structures and then viewed them in stereo. Equally important as the quantitative analysis noted above were the qualitative insights into the water structure they found this way, as noted on pages 3348–3349:

> (1) There is a very clear tendency for neighboring molecules to be oriented into rough approximations to tetrahedral hydrogen bonds, but the average degree of bending away from bond linearity and ideal approach directions is considerable.
> (2) Except on the smallest scale, the random molecular configurations are rather homogenous in density. No large "clusters" of anomalous density seem to occur.
> (3) No recognizable patterns characteristic of the known ices or clathrates appear, beyond occasional polygons of hydrogen bonds. Such polygons occur with 4, 5, 6, 7 (and perhaps more) sides, but they tend to be distorted out of their most natural conformations.
> (4) Dangling OH bonds exit, which are not included in hydrogen bonds. These entities persists far longer than water molecule vibrational periods, and hence may hold the key to the structurally sensitive band shapes that arise in infrared and Raman spectroscopy of water and its solutions.
> (5) No obvious separation of molecules into "network" vs "interstitial" types suggests itself. This fact is consistent with the single-peak character of the hydrogen-bond coordination number distributions exhibited in Fig. 19. It also seems to diminish the validity of the interstitial models that have been proposed to explain liquid water.
> (6) In the case of moderately well-formed (i.e., undistorted) hydrogen bonds, all angles of rotation of the molecules about the bond axis seem to be frequently represented. This behavior may have direct relevance in study of nonelectrolyte solvation,

where the geometric requirements attendant upon formation of a hydrogen-bonded solvation cage forces the rotation angles into "eclipsed" configurations only, thus lowering configurational entropy.

(7) No significant examples of network interpenetration were found, analogous to the interpenetration known to obtain in ice VII and ice VIII.

These insights enabled one to discriminate among the many phenomenological models of liquid water that had been proposed and to argue both against the presence of "ice-bergs" and the validity of "mixture" models. Their conclusions were further supported by subsequent simulations of liquid water as well.

In their discussion, Rahman and Stillinger anticipated further studies on molecular dynamics of water solutions under various conditions, including studies of the hydration of macromolecules and membranes.

Thus, in summary, the article by Rahman and Stillinger provided the first accurate description of liquid water and that description holds today; their study laid the ground-work for molecular dynamics studies of macromolecules in aqueous solution and thus is the cornerstone of a large body of subsequent research, which is becoming ever more powerful and useful, and their use of computer graphics visualization anticipated the exciting insights such methods could give in understanding structures and dynamics of liquids and complex biological molecules.

References

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