

Revised central force potentials for water^{a)}

F. H. Stillinger

Bell Laboratories, Murray Hill, New Jersey 07974

A. Rahman

Argonne National Laboratory, Argonne, Illinois 60439

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Computer simulation by the molecular dynamics technique has been used to investigate a modification of the previously introduced "central force model" for liquid water. The simulation involved 216 molecules, with periodic boundary conditions and Ewald summation, at 29.5°C and 1 g/cm³. In all respects considered (pressure, energy, pair correlation functions, self-diffusion rate) the revised set of interactions represents water more accurately than the earlier set.

I. INTRODUCTION

In the interests of conceptual and theoretical simplicity, a "central force model" has been introduced to describe structure and dynamics in liquid water.^{1,2} This model treated the constituent oxygen and hydrogen atoms as dynamically distinct mass points which have suitable electrostatic charges, and which are subject to strictly additive pair potentials. The three pair potentials were chosen to be consistent with formation of stable H₂O molecules with the proper nonlinear geometry, to permit vibrational motions about that geometry, and to produce hydrogen bonding of approximately correct energy and geometry between neighboring H₂O molecules. Interactions within a molecule and those between molecules were regarded as indistinguishable, and as a result it has been possible to apply standard integral equation methods to the central force model.³

A molecular dynamics study of the central force model for water has been reported.⁴ The results of this study were encouraging; liquid water at 22 °C and 1 g/cm³ appeared to consist of intact molecules arranged in roughly the sort of random hydrogen-bond network thought to be present in real water. It was clear, nevertheless, that this original version was quantitatively somewhat deficient. In particular the pressure was too high, the self-diffusion rate was too low, and the three independent atom-pair static correlation functions seemed too highly structured.

Evidently changes in the central force interactions were warranted. It is the purpose of the present paper to report an improved set of interactions and to document its superiority. It was not obvious at the outset that substantial improvement was possible, but trial and error (using molecular dynamics as the evaluation instrument) eventually produced satisfactory progress.

II. INTERACTION MODIFICATION

The old and new sets of central potentials V_{HH} , V_{OH} , and V_{OO} are presented in the Appendix. In gross graphical appearance the functions remain unchanged. $V_{\text{OO}}(r)$ continues to be monotonically decreasing with r , $V_{\text{OH}}(r)$

has single deep minimum at the stable OH bond length in water, and $V_{\text{HH}}(r)$ remains non-negative and continues to have a relative minimum at the molecular HH separation. The reader can refer to Fig. 1 in Ref. 4 for a graph of the old set.

In order to stress the relatively subtle changes being imposed, we have plotted the differences

$$\Delta V_{\alpha\beta}(r) = V_{\alpha\beta}^{\text{new}}(r) - V_{\alpha\beta}^{\text{old}}(r) \quad (2.1)$$

in Fig. 1. Since virtually all pairs of oxygen atoms in liquid water under ordinary conditions will be further apart than 2.5 Å, the modification $\Delta V_{\text{OO}}(r)$ for $0 < r < 2.5$ Å is essentially irrelevant. Similarly the values of $\Delta V_{\text{OH}}(r)$ for $0 < r < 0.8$ Å and $\Delta V_{\text{HH}}(r)$ for $0 < r < 1.3$ Å are essentially irrelevant. But we shall see that important structural changes in the model liquid result from the remainder of the $\Delta V_{\alpha\beta}$.

III. MOLECULAR DYNAMICS RESULTS

In the interests of providing a reasonably clear comparison, the present study involved 216 water molecules at density 1 g/cm³, just as did the earlier work reported in Ref. 4. We have likewise employed the same periodic boundary conditions and Ewald summation to account for the infinite array of point-charge images. After lengthy equilibration, a molecular dynamics run comprising 7487 steps of size

$$\Delta t = 2.5 \times 10^{-16} \text{ sec} \quad (3.1)$$

was generated to provide statistical averages. The temperature for the run was 29.5 °C; this is close enough to the preceding 22 °C study that identical quantities from the two investigations can meaningfully be compared.

In the present case, the mean interaction energy in the liquid was found to be -9.478 kcal/mole, compared to the experimental value -9.89 kcal/mole for real water at 29.5 °C and atmospheric pressure. The previous molecular dynamics study obtained -9.201 kcal/mole at 22 °C compared with -9.96 kcal/mole for the experimental value,⁴ so that indeed some improvement has been effected.

The dimensionless compressibility factor $p/c_0 k_B T$, where p is pressure and c_0 is number density of water

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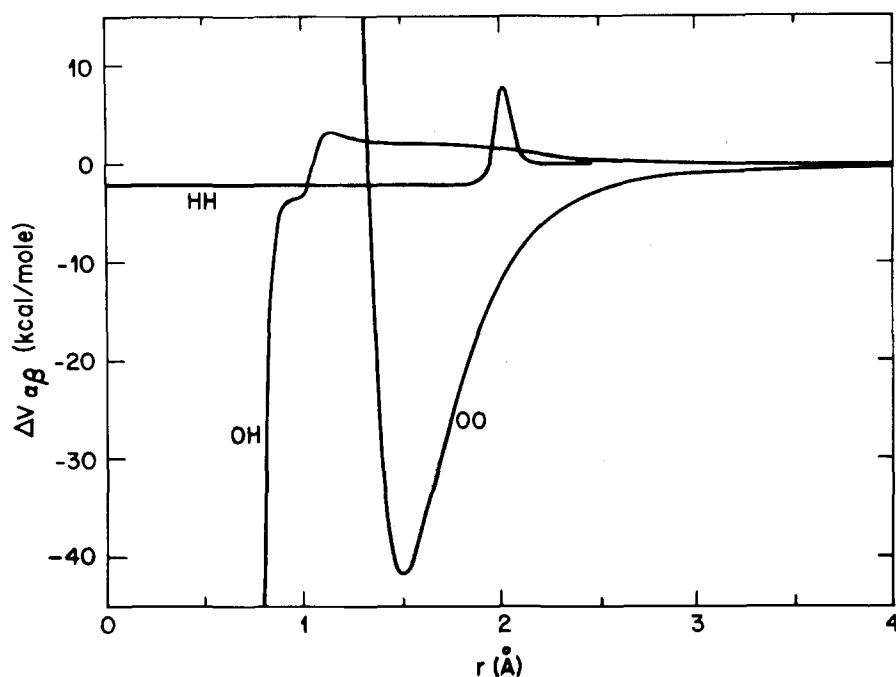


FIG. 1. Changes $\Delta V_{\alpha\beta}$ introduced into the prior set of central force interactions $V_{\alpha\beta}$, employed in the molecular dynamics study of Ref. 4.

molecules, measures the extent to which a model successfully reproduces the equation of state. Under the conditions which prevail in our calculations, this dimensionless quantity should be 0.070. Results obtained in the two studies are as follows

$$p/c_0 k_B T = 2.6 \pm 0.1 \text{ (old) ,} \quad (3.2)$$

$$p/c_0 k_B T = 0.1 \pm 0.1 \text{ (new) .}$$

Obviously there has been a dramatic improvement. The desire to cause a reduction in this quantity was one of our primary motivations in seeking revision of the old central force potential set.

At 29.5 °C and 1 atm, the self-diffusion constant in water is experimentally⁵ found to be about 2.4×10^{-5} cm²/sec. By monitoring motions of oxygen nuclei in the present molecular dynamics study, we find the value 1.12 cm²/sec. Although this is small by comparison with experiment, it still represents an improvement over the result 0.73×10^{-5} cm²/sec reported in Ref. 4 for the earlier version of the central force model (for which the corresponding experimental value was 2.1×10^{-5} cm²/sec).

Figure 2 compares the oxygen-oxygen pair correlation functions $g_{OO}(r)$ calculated for the old and the new versions of the central force model. Both functions dis-

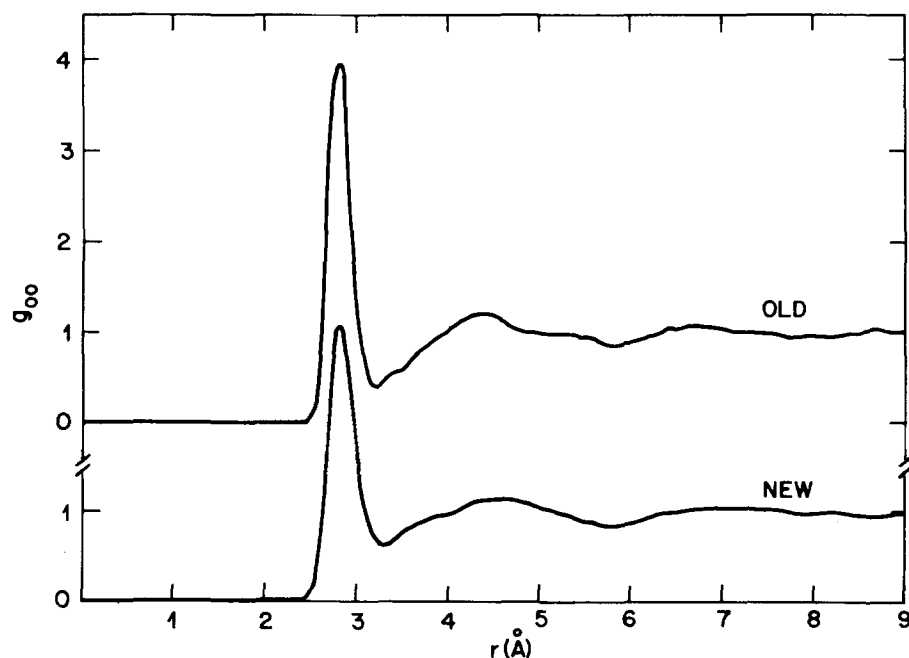


FIG. 2. Comparison of oxygen-oxygen pair correlation functions $g_{OO}(r)$ at 1 g/cm³. "Old" refers to results at 22 °C from Ref. 4, "new" refers to the present calculations at 29.5 °C.

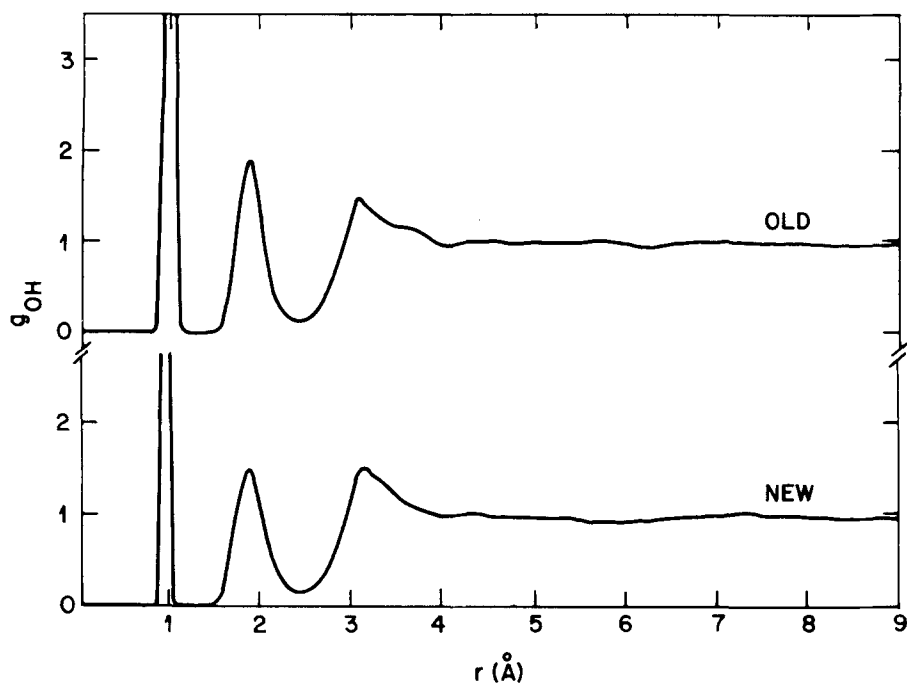


FIG. 3. Comparison of oxygen-hydrogen pair correlation functions, $g_{OH}(r)$ at 1 g/cm^3 .

play a prominent first-neighbor peak centered at approximately 2.85 \AA ; however this peak is not as narrow or high in the present version as in the predecessor. In both cases the average number of nearest neighbors (obtained by integration to the first minimum in g_{OO}) is approximately 4.5. Both as regards the maximum value of the first peak and the shape and position of the second peak around 4.5 \AA , the new version agrees more closely with $g_{OO}(r)$ measured experimentally by x-ray diffraction.^{6,7}

The respective results for the oxygen-hydrogen pair correlation function $g_{OH}(r)$ have been plotted in Fig. 3.

This function includes a narrow and isolated contribution centered around 0.96 \AA , that is strictly due to intramolecular OH bonds. This intramolecular peak is definitely narrower in the new version than it was in the old version. No molecular dissociation occurs under the prevailing temperature and density (although in principle it can do so within the central force model framework); the intramolecular peaks thus correspond to exactly two OH pairs per molecule. The second g_{OH} peak (maximum near 1.85 \AA in both calculations) corresponds to H and O connected directly by a hydrogen bond. This intermolecular contribution is broader and lower in the present calculation than it was before,

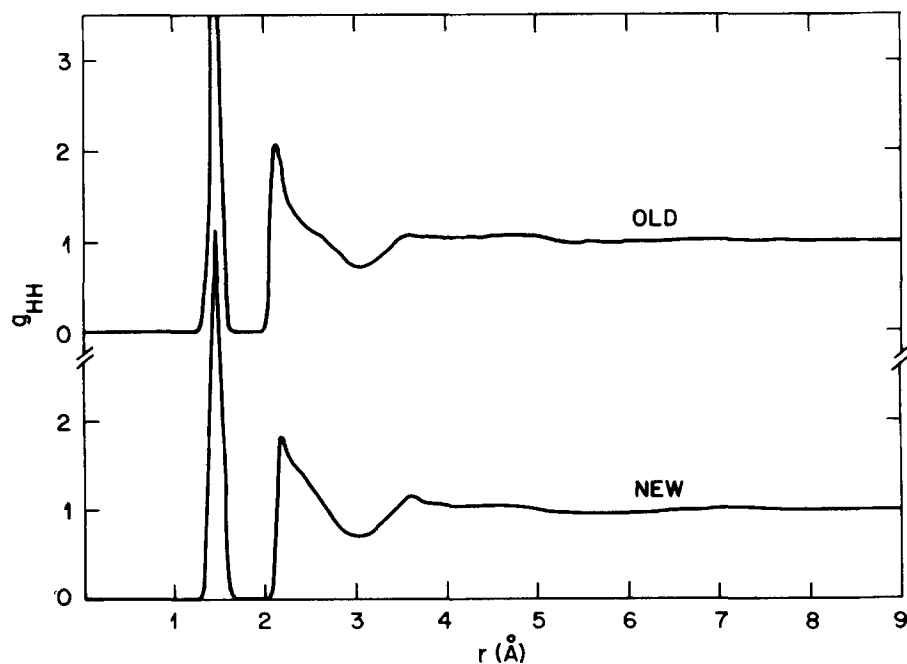


FIG. 4. Comparison of hydrogen-hydrogen pair correlation functions $g_{HH}(r)$ at 1 g/cm^3 .

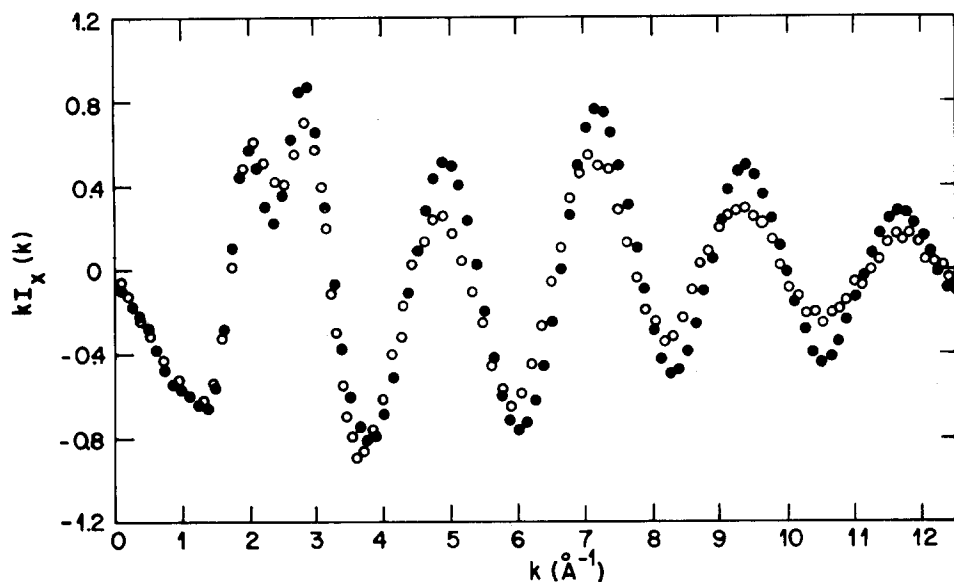


FIG. 5. Comparison of X-ray diffraction intensities. The present simulation results are denoted by dots; Narten's experimental results for 25 °C (Ref. 11) are denoted by open circles.

which is what must be expected from the spatial delocalization of the first $g_{OO}(r)$ peak already discussed. Changes induced in $g_{OH}(r)$ by the change in interactions cause improved agreement with results for this function that have emerged from previous rigid water molecule simulations,^{8,9} and with results inferred from combined x-ray and neutron diffraction measurements.¹⁰

The calculated values for $g_{HH}(r)$, the hydrogen-hydrogen pair correlation function, appear in Fig. 4. The intramolecular peak, comprising exactly one HH pair per molecule, is virtually unchanged. However the intermolecular contributions which occur at larger distance are in somewhat better accord with other simulations^{8,9} and with Narten's "experimental" result.¹⁰

In addition to examining the pair correlation functions themselves, it is also instructive to examine the x-ray and neutron diffraction patterns that they imply. This

was done in Ref. 4, and has been repeated here for the new version of the model. Figure 5 exhibits the results for x-ray intensity $I_x(k)$, prepared according to accepted procedure with standard atomic scattering factors.⁴ Figure 5 also contains Narten's experimental results¹¹ at 25 °C, the nearest available temperature. Figure 6 shows the calculated neutron diffraction pattern $I_n(k)$ for D_2O^{16} (using known scattering lengths¹⁰), along with Narten's experimental result¹⁰ for the same heavy water at 25 °C.

Although Fig. 5 and 6 reveal some discrepancies between the present model results and the corresponding measurements, the principal qualitative features are preserved. By checking analogous figures in Ref. 4 the reader will verify that revising the central force potentials has improved agreement with both types of diffraction experiments.

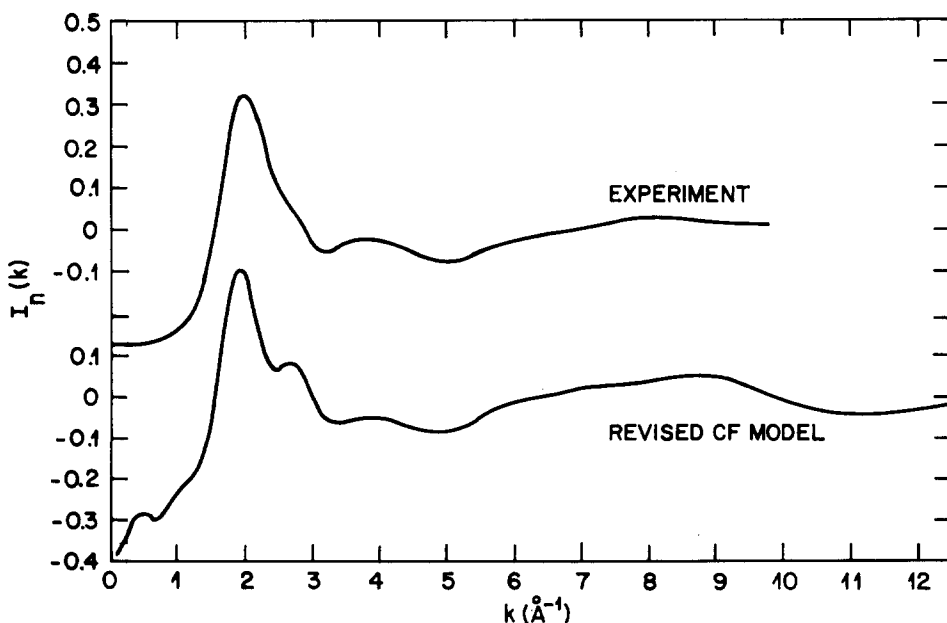


FIG. 6. Comparison of neutron diffraction patterns for D_2O^{16} . The experimental results (for 25 °C) have been taken from Narten, Ref. 10.

IV. CONCLUSIONS

In all essential aspects examined, the modifications applied to the central force model have improved its ability to represent real water. Evidence suggests that the model possesses a liquid phase consisting of intact molecules arranged in a random, defective, and roughly tetrahedral hydrogen-bond network of the type thought to exist in pure water. The new version of the model ought to be useful for the study of water by established analytical techniques of liquid state theory.³

It is possible that further refinements to the model could improve it even more. However there must always remain an irreducible level of error. This error stems from the several mathematical restraints placed on the model, specifically: (a) common additive central potentials for all nuclei; (b) mechanical stability for single water molecules at the known nonlinear C_{2v} geometry; and (c) fixed molecular dipole moment and force constants. To create major improvement while leaving (a) intact would surely require compromising (b) and (c).

It is our belief that water and its solutions need to be studied theoretically with a variety of models. The lattice models are perhaps the simplest.^{12,13} The central force model stands at a higher level of sophistication and complication. Probably some attention should be devoted in the near future to development of even more sophisticated models that incorporate many-body polarization effects in order at least to produce a quantitative theory of the dielectric properties of water.

APPENDIX: UNITS FOR EXPRESSING CENTRAL INTERACTIONS

Convenient units for expressing the central interactions are kcal/mole for energy and Å for length. In these units the old set of potentials (used in Ref. 4) is

$$\begin{aligned}
 V_{\text{HH}}(r) &= \frac{36.1345}{r} + \frac{20}{1 + \exp[40(r-2)]} \\
 &\quad - 17.03002 \exp[-7.60626(r-1.4525)^2], \\
 V_{\text{OH}}(r) &= -\frac{72.269}{r} + \frac{2.6677}{r^{14.97}} - \frac{6}{1 + \exp[5.49305(r-2.2)]} \\
 V_{\text{OO}}(r) &= \frac{144.538}{r} + \frac{23401.9}{r^{8.3927}}. \quad (\text{A1})
 \end{aligned}$$

Using the same units, the new and improved set appears as follows

$$\begin{aligned}
 V_{\text{HH}}(r) &= \frac{36.1345}{r} + \frac{18}{1 + \exp[40(r-2.05)]} \\
 &\quad - 17 \exp[-7.62177(r-1.45251)^2], \\
 V_{\text{OH}}(r) &= -\frac{72.269}{r} + \frac{6.23403}{r^{9.19912}} - \frac{10}{1 + \exp[40(r-1.05)]} \\
 &\quad - \frac{4}{1 + \exp[5.49305(r-2.2)]}, \\
 V_{\text{OO}}(r) &= \frac{144.538}{r} + \frac{26758.2}{r^{8.8591}} - 0.25 \exp[-4(r-3.4)^2] \\
 &\quad - 0.25 \exp[-1.5(r-4.5)^2]. \quad (\text{A2})
 \end{aligned}$$

In both sets V_{OH} has an absolute minimum at $r = 0.9584$, and V_{HH} has a relative minimum at $r = 1.5151$. Furthermore, the curvatures at these minima are identical in the two sets

$$\begin{aligned}
 V''_{\text{OH}}(0.9584) &= 1147.6, \\
 V''_{\text{HH}}(1.5151) &= 257.3. \quad (\text{A3})
 \end{aligned}$$

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