

## Application of hypernetted-chain integral equations to a central-force model of water

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Hypernetted-chain (HNC) integral equations have numerically been integrated to give atom-pair correlation functions for supercritical water. The classical model employed postulates additive central interactions for each pair of H and O particles. At low temperature these interactions are known to cause separate non-linear H<sub>2</sub>O molecules to form spontaneously, and then to engage in hydrogen bonding. The high-temperature, low-density fluid structure found in this study also exhibits formation of intact molecules (though incompletely), accompanied by substantial molecular distortion. The direct iterative solutions constructed here pave the way for efficient variational extension toward room temperature.

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### 1. INTRODUCTION

A vast amount of scientific effort has been expended in theoretical investigation of the equilibrium structure and thermodynamic properties of liquid water [1]. While many recent advances stem from direct numerical simulation of hamiltonian models of water [2-5], the formulation of an analytical approach to the full statistical mechanics of water remains an important and largely unresolved issue. We report in the present paper an exploratory study aimed at partial resolution of the problem.

The models of water that have received most serious attention to date have been based upon a representation of the molecules by rigid arrays of unpolarizable force centres [6]. On account of molecular rigidity, the interaction between two molecules, consisting of coulombic and non-coulombic terms, depends strongly on relative molecular orientation as well as on the separation of the centres of mass. This non-central component of the energy of interaction is sufficiently complicated to make the development of an approximate analytical theory of liquid water a formidable task indeed.

In a previous paper [7] the present authors have described an approach which attempts to circumvent this difficulty. A class of models for water is defined which is based upon central-force interactions operating between point-charge ions that move separately. Three potential functions are required to specify the interactions between 'oxygen ions' and 'hydrogen ions'; as shown in reference [7], a set of potentials may be constructed which constrains two hydrogen ions and one oxygen ion to assume the known monomer geometry (bond length

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0.9584 Å, bond angle 104.45°), and which also enforces linear hydrogen bonding between two neighbouring molecules. The following set of functions was explored in reference [7]:

$$v_{OO}(r)/\text{kcal mol}^{-1} = \frac{144.538}{(r/\text{Å})} + \frac{1.69712 \times 10^6}{(r/\text{Å})^{12}} - \frac{4.03939 \times 10^3}{(r/\text{Å})^6}, \quad (1.1 a)$$

$$v_{OH}(r)/\text{kcal mol}^{-1} = -\frac{72.269}{(r/\text{Å})} + \frac{2.66366}{(r/\text{Å})^{14.9797}}, \quad (1.1 b)$$

$$v_{HH}(r)/\text{kcal mol}^{-1} = \frac{36.1345}{(r/\text{Å})} + \frac{30}{1 + \exp [21.9722(r/\text{Å} - 2.125)]} - 26.51983 \exp [-4.728281 (r/\text{Å} - 1.4511)^2]. \quad (1.1 c)$$

These functions are displayed graphically in figure 1.

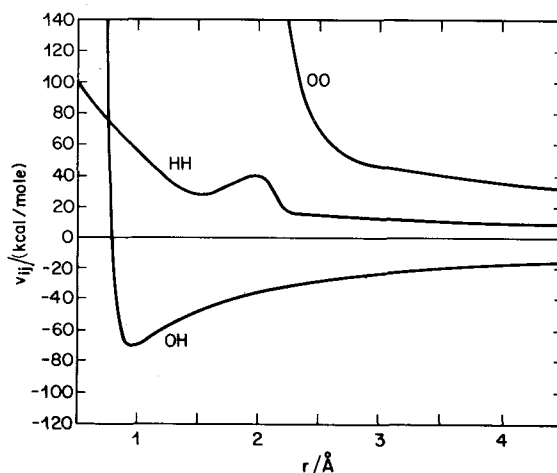


Figure 1. Additive central interactions used to model water.

An important justification for a central-force approximation to water interactions is the extent to which the evaluation of the liquid's equilibrium structure is facilitated. In the present paper we report some highly encouraging results from solution of the hypernetted-chain (HNC) equations [8] for central-force water. A molecular dynamics investigation reported separately [9] (for a set of potentials similar to (1.1 a)–(1.1 c)) has firmly established that central forces alone can account for hydrogen bonding and nearly tetrahedral order in liquid water. Because the interactions are independent of angular degrees of freedom, these computations proceeded somewhat more rapidly than comparable calculations with the BNS reference [2] or ST2 reference [4] potentials.

By focusing attention on spherically symmetric ions instead of complete molecular units, the central-force representation of water molecule interactions considerably simplifies the statistical mechanical description of water. Thus, each pair distribution function (for ions) is dependent on a single distance variable; the internal energy, virial pressure, and dielectric response are among numerous physical properties that can be expressed in relatively compact form

for the model [7]. In addition, the central-force formulation treats intra- and intermolecular forces from a unified point of view, and makes possible, for the first time, some study of the consequence of molecular non-rigidity, as well as dissociation.

Some comment seems in order regarding the choice of hypernetted-chain theory in this paper. From the integral equation studies that have been pursued in recent years, one may fairly conclude that different approximate integral equations (HNC, Percus–Yevick [10], Born–Green [11], etc.) are appropriate for different fluid systems. Thus, the Percus–Yevick theory appears to encompass those classes of cluster diagrams which are important for systems dominated by repulsive interactions. The HNC approximation, on the other hand, provides a more realistic treatment of systems with strong attractive forces and with long-range coulombic forces. The HNC work of Friedman and his collaborators [12], for example, stands as a significant contribution to the theory of electrolyte solutions. More recently, Hansen and McDonald [13] have successfully solved HNC equations for symmetrical models of a dense molten salt. We wish to establish in the present paper that the HNC approximation may also be fruitfully applied to the study of polyatomic liquids. Water, anomalous in many respects, probably presents the most severe test for such an investigation.

## 2. HNC INTEGRAL EQUATIONS

As modelled by central forces, water consists of a binary mixture of positive (hydrogen) and negative (oxygen) ions, bearing charges  $q$  and  $-2q$ , which interact in a pairwise manner. A complete set of integral equations for such a system is most compactly expressed in a  $2 \times 2$  matrix representation. With pair correlations  $g_{ij}$  defined in the usual fashion (see reference [14]), one constructs a matrix  $\mathbf{H}(r)$  of indirect correlation functions with elements  $h_{ij}(r) = g_{ij}(r) - 1$ . The Ornstein–Zernike (OZ) relation then determines a matrix  $\mathbf{T}(r)$  of direct correlation functions (dcf's)  $t_{ij}(r)$  by

$$\mathbf{T}(r) = \mathbf{H}(r) - (\mathbf{H} \star \mathbf{T} + \mathbf{T} \star \mathbf{H})/2. \quad (2.1)$$

The asterisks in (2.1) denote a matrix product and convolution operator in which each term is weighted by an appropriate concentration variable  $c_k$ :

$$(\mathbf{H} \star \mathbf{T})_{ij} = \sum_k c_k \int d\mathbf{r}' H_{ik}(|\mathbf{r}'|) T_{kj}(|\mathbf{r} - \mathbf{r}'|). \quad (2.2)$$

Equation (2.1) has been expressed in a symmetrized form to emphasize the fact that the matrix OZ relation comprises only three independent scalar equations for the binary mixture.

In order to obtain a complete set of integral equations for the liquid structure, a second set of relations between sets  $\{h_{ij}(r)\}$  and  $\{t_{ij}(r)\}$  must be chosen. For reasons discussed in the Introduction, the HNC approximation was adopted for study in the present efforts. In terms of the correlation functions defined above, the HNC equations may be expressed as

$$h_{ij}(r) = \exp [h_{ij}(r) - t_{ij}(r) - \beta v_{ij}(r)] - 1, \quad (2.3)$$

$$i, j = \text{O, H}$$

where  $\beta = 1/k_B T$  and  $v_{ij}(r)$  is the potential energy of interaction between particles of species  $i$  and  $j$  which are separated by distance  $r$ .

Although the HNC approximation gives rise to some inconsistencies when the integral equation solutions are employed to evaluate thermodynamic quantities (such as internal energies and pressures from virial and compressibility expressions), for an ionic system the equations are fully consistent with fundamental physical requirements on the zeroth and second moments of the pair correlation functions [15]:

$$c_O \int [g_{OH}(r) - g_{OO}(r)] d\mathbf{r} = 1, \quad (2.4 a)$$

$$c_H \int [g_{OH}(r) - g_{HH}(r)] d\mathbf{r} = 1, \quad (2.4 b)$$

$$\int [2g_{OH}(r) - g_{OO}(r) - g_{HH}(r)] r^2 d\mathbf{r} = 3k_B T / 8\pi c_0^2 q^2. \quad (2.4 c)$$

The first two of these equations express the electroneutrality of a system of  $N$  oxygen and  $2N$  hydrogen ions in the thermodynamic limit ( $N, V \rightarrow \infty, c_0 = N/V$  constant), whereas (2.4 c) summarizes the way in which dielectric screening affects the long-range correlations between essentially ionic particles.

In addition to conditions (2.4), a satisfactory treatment of water by means of integral equations should be consistent with known data on molecular stoichiometry and structure. Thus, at low temperatures ( $\approx$  room temperature), two hydrogen ions should be bonded to each oxygen ion, with OH bond distances  $\approx 0.96 \text{ \AA}$  and an unbonded HH distance of  $\approx 1.52 \text{ \AA}$  (corresponding to the equilibrium HOH angle of  $104.5^\circ$ ). A reasonable approach to the structure and properties of liquid water should therefore exhibit *saturation* of the extremely strong attractive forces which are entailed by (1.1 b). On a quantitative level, these structural restrictions on the monomer are best stated in terms of a separation of intra- and intermolecular distance scales. At ordinary temperatures this separation will be nearly exact (except for the one molecule in roughly  $10^8$  which dissociates); as a consequence, the correlation functions  $g_{OH}(r)$  and  $g_{HH}(r)$  should assume values very close to zero within intervals around  $r = 1.3 \text{ \AA}$  and  $1.9 \text{ \AA}$ , respectively. The stoichiometric conditions can then be written as

$$c_H \int_0^{L_{OH}} g_{OH}(r) d\mathbf{r} = 2, \quad (2.5 a)$$

and

$$c_H \int_0^{L_{HH}} g_{HH}(r) d\mathbf{r} = 1, \quad (2.5 b)$$

where  $L_{OH} \approx 1.3 \text{ \AA}$  and  $L_{HH} \approx 1.9 \text{ \AA}$ .

At high temperatures and pressures, significant molecular distortion and/or dissociation may occur. Under these circumstances (2.5 a) and (2.5 b) may not hold exactly. The left-hand sides retain an instructive physical content, nonetheless, if we define  $L_{OH}$  and  $L_{HH}$  as locations of the first minima in  $g_{OH}(r)$  and  $g_{HH}(r)$ , and interpret the integral expressions as the number of OH and HH pairs per molecule. In spite of the imperfect separation of distance scales at elevated temperatures and pressures, saturation of the attractive forces should be manifest in the relatively small number of OH pairs which populate the region  $r \lesssim L_{OH}$ , and HH pairs which populate  $r \lesssim L_{HH}$ .

3. METHOD OF SOLUTION

To expedite numerical solution of (2.1) and (2.3), the equations were reformulated. Because of the convolution operator in (2.1), this equation is most conveniently written in terms of Fourier-transformed correlation matrices

$$\left. \begin{aligned} \hat{\mathbf{T}}(k) &= \int d\mathbf{r} \mathbf{T}(r) \exp [i\mathbf{k} \cdot \mathbf{r}], \\ \hat{\mathbf{H}}(k) &= \int d\mathbf{r} \mathbf{H}(r) \exp [i\mathbf{k} \cdot \mathbf{r}], \end{aligned} \right\} \quad (3.1)$$

as

$$\hat{\mathbf{T}}(k) = \hat{\mathbf{H}}(k) - (\hat{\mathbf{H}}(k)\mathbf{C}\hat{\mathbf{T}}(k) + \hat{\mathbf{T}}(k)\mathbf{C}\hat{\mathbf{H}}(k))/2. \quad (3.2)$$

$\mathbf{C}$  is a diagonal matrix of number concentrations ( $C_{ij} = c_i \delta_{ij}$ ).

The direct correlation functions are next re-expressed in terms of their short-ranged components by defining

$$t_{ij}^s(r) = t_{ij}(r) + \frac{\beta q_i q_j}{r} [1 - \exp(-ar)]. \quad (3.3)$$

Addition of the Coulomb potential times  $1/k_B T$  cancels the long-range tail in the full dcf, while the exponential correction ensures that all  $t_{ij}^s(r)$  remain well behaved near  $r=0$ .

Using the matrix  $\mathbf{T}^s(r)$  of short-ranged functions  $t_{ij}^s(r)$ , the OZ relations can be written in terms of functions which are well behaved both in real space and in the space of transform variable  $k$ . We first define  $\hat{\mathbf{Q}}(k)$ , the matrix Fourier transform of 'excess terms' in (3.3):

$$\hat{Q}_{ij}(k) = \frac{\beta q_i q_j a^2}{k^2(k^2 + a^2)}; \quad (3.4)$$

then equation (3.3) becomes

$$\hat{\mathbf{T}}^s(k) = \hat{\mathbf{H}}(k) + \hat{\mathbf{Q}}(k) - \hat{\mathbf{H}}(k)\mathbf{C}(\hat{\mathbf{T}}^s(k) - \hat{\mathbf{Q}}(k))/2 - (\hat{\mathbf{T}}^s(k) - \hat{\mathbf{Q}}(k))\mathbf{C}\hat{\mathbf{H}}(k)/2. \quad (3.5)$$

If we next define a short-ranged potential energy component  $v_{ij}^s(r)$  by

$$v_{ij}^s(r) = v_{ij}(r) - \frac{q_i q_j}{r} [1 - \exp(-ar)], \quad (3.6)$$

the HNC approximation may be represented as

$$h_{ij}(r) = \exp [h_{ij}(r) - t_{ij}^s(r) - \beta v_{ij}^s(r)] - 1. \quad (3.7)$$

Equations (3.5) and (3.7) are the forms that were used for numerical work.

Solution of the equations was attempted by an iterative method which relied upon the Cooley-Tukey Fast Fourier Transform [16], and which employed molecular dynamics results for initial estimates of  $h_{ij}(r)$  and  $t_{ij}^s(r)$ . Matrix transforms from step  $n$  were used in (3.5) to generate approximation  $n+1$  for  $\mathbf{t}^s(k)$ ; after Fourier inversion, the new dcf's were inserted in (3.7) to obtain an improved set of  $h_{ij}(r)$ . To ensure stability of the algorithm, linear combinations of approximate solutions  $n-1$  and  $n$  were constructed and used as input at the  $(n+1)$ st iteration step.

Numerical investigations were started at high temperatures and low densities,

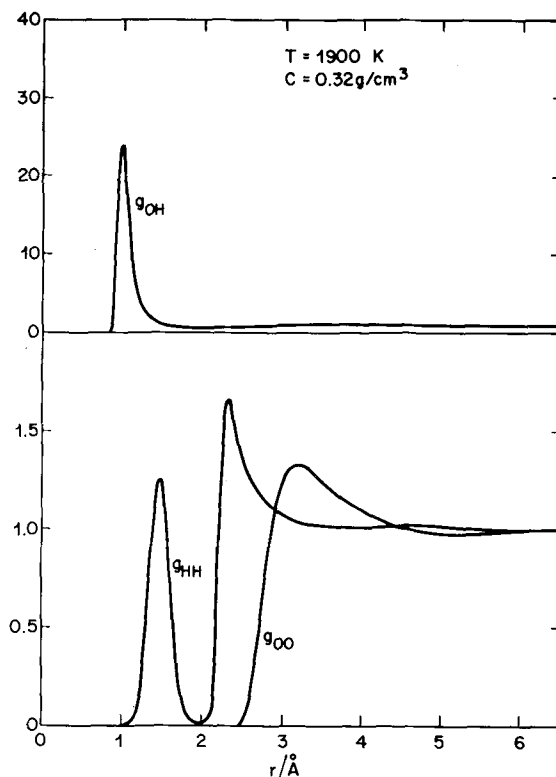


Figure 2. Atom-pair correlation functions for water at 1900 K, 0.32 g/cm<sup>3</sup>. These are solutions to the HNC equations (3.5) and (3.7) obtained by direct numerical iteration.

the physical regime in which (3.5) and (3.7) should yield most readily to solution. 'High temperature', in this context, refers to thermal energies which are comparable to the depth of the OH potential well entailed by (1.1 *b*),  $\approx 3 \times 10^4$  K, the largest relevant energy parameter characterizing interactions in the system. Just as one intuitively expects, the correlation functions are relatively featureless under such conditions, except for nearest-neighbour peaks, on account of extreme thermal disorder.

As temperature is lowered, however, the correlation functions begin to develop features which reflect the water's distinctive liquid-state structure. At 1900 K and a density of 0.32 g/cm<sup>3</sup> (close to the critical density of real water),  $g_{OO}$  has a maximum at 3.18 Å (see figure 2), reasonably close to the optimal OO separation for hydrogen-bonded molecules near room temperature (2.86 Å). A prominent OH peak centred at 0.98 Å reflects the strong attractions which are responsible for intramolecular OH bonds in the model, but  $g_{OH}$  exhibits little additional structure at this temperature.

The HH correlations provide support for the feasibility of the present approach and deserve somewhat more extended discussion. Even at 1900 K,  $g_{HH}$  divides into distinct intra- and intermolecular regions: the HH correlation function plunges to a minimum of  $\approx 10^{-2}$  at 2.00 Å which is bracketed by two well-developed maxima. The peak at 1.46 Å corresponds to an equilibrium

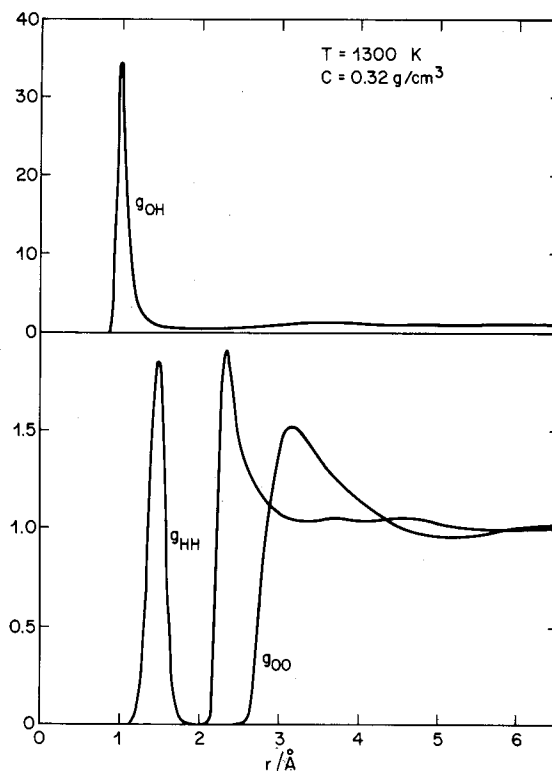


Figure 3. Atom-pair correlation functions for water at 1300 K, 0.32 g/cm<sup>3</sup>.

distance of 1.52 Å in the free molecule; the decrease in unbonded HH distance parallels similar molecular dynamics results [9]. A second HH maximum at 2.32 Å is consistent with linear hydrogen bonding (for the most probable OO and OH separations) in which acceptor molecules are oriented at angles somewhat greater than the value which produces ideal tetrahedral coordination.

As temperature is decremented from 1900 K, one expects decreasing thermal disorder to be manifested in more effective localization of particles in potential energy wells. Correlations between particles should therefore extend to large separations, as the equilibrium structure for second-, third-, . . . neighbour distances reflects the propagation of favoured near-neighbour geometries throughout the liquid. Figure 3, which depicts the three pair correlation functions at 1300 K and 0.32 g/cm<sup>3</sup>, supports these expectations. All three are more highly structured than at 1900 K.

At this lower temperature,  $g_{OO}$  shows a more pronounced peak at 3.16 Å, along with a number of subsidiary extrema that were barely perceptible at 1900 K. An OH maximum is again observed at 0.98 Å, but is now about 25 per cent higher than the maximum in figure 2. Intermolecular correlations are significantly enhanced at 1300 K, as measured by  $g_{OH}$ ; the secondary local maxima and minima have shifted in magnitude and position in ways that suggest a more highly ordered liquid.

Most encouraging for the present study is the fact that the first minimum in  $g_{OH}$  has decreased in magnitude and has shifted to a smaller distance, both of

which imply a growing separation of intra- and intermolecular distances. This fact is all the more impressive when one recognizes that near the minimum, the bare potential  $v_{OH}$  assumes values  $\approx -40$  kcal/mole, corresponding to Boltzmann factors of about  $\exp(15)$  at 1300 K. The HNC equations apparently produce a potential of mean force which has correctly saturated the strong attractions of  $v_{OH}$ .

Finally, we observe the change in  $g_{HH}$  as  $T$  is lowered. The two correlation regions are more rigorously segregated at the lower temperature, for  $g_{HH}$  is an order of magnitude smaller at the minimum ( $r=2.00$  Å) at 1300 K.

The direct correlation functions, corresponding to the  $g_{ij}$ 's in figures 2 and 3, are presented in figures 4 and 5, respectively. They develop enhanced structure as temperature declines, in parallel with the  $g_{ij}$ 's. The specific features exhibited by the  $t_{ij}$ 's obviously stem from the unusual interactions in the model,

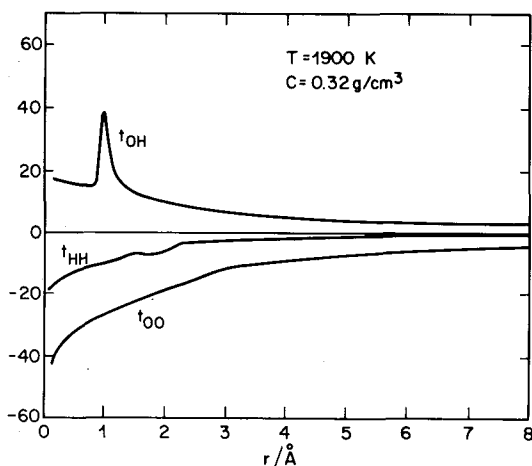


Figure 4. Direct correlation functions for water at 1900 K, 0.32 g/cm<sup>3</sup>. These results correspond to the  $g_{ij}$  shown in figure 2.

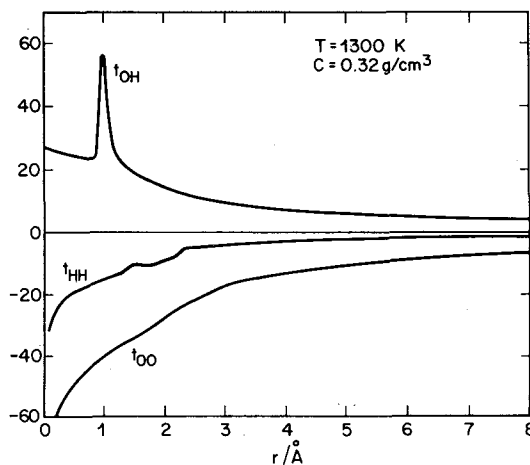


Figure 5. Direct correlation functions for water at 1300 K, 0.32 g/cm<sup>3</sup>.



but the detailed shapes and magnitudes obtained for the curves in figures 4 and 5 seem to have no simple explanations.

Self-consistency of the numerical solutions reported above was judged by the extent to which electroneutrality and second moment conditions (2.4 *a*)–(2.4 *c*) were satisfied. Although the equations are integral constraints only, the three together provide a good qualitative measure of errors in the calculations. Since the integrals weight errors in the correlation functions especially heavily at large distances, even minor inaccuracies in the long-range structure will be enormously magnified.

At 1900 K the triplet of pair correlation functions corresponds to a model fluid which is very nearly electrically neutral, the mean deviation being about 0.4 per cent. The second moment relation is satisfied to within 4.0 per cent. For the lower temperature 1300 K, where there is appreciably greater structure in the correlation functions, self-consistency is slightly less satisfactory. The two sides of (2.4 *a*) and (2.4 *b*) agree to within 1.2 per cent, while the exact expression in (2.4 *c*) is reproduced to within 6.7 per cent. The errors, it should be noted, do not reflect inadequacies of the HNC approach, but are algorithm-dependent. Additional refinement of the results by more rapidly converging non-iterative methods will undoubtedly improve the degree of self-consistency.

#### 4. DISCUSSION

It is our ultimate goal to examine liquid water in the neighbourhood of 300 K and 1.00 g/cm<sup>3</sup> as a dual test of HNC theory and of the central-force approach to the statistical mechanics of polyatomic liquids. Because the rate of convergence of the numerical scheme outlined above decreases substantially as one proceeds towards this physically interesting state, we have limited the results reported here to the high-temperature, low-density regime in which numerical solutions are readily obtained.

More extensive studies will be reported in a later paper. In this connection we point out that numerical solution to coupled equations (3.5) and (3.7) can be cast into a variational format, with the  $t_{ij}$  serving as variational functions. With a small number of adroitly chosen variational parameters this can be an efficient process. In the present case with highly structured  $t_{ij}$ 's, it is clearly necessary to have first established the qualitative forms required for these functions by a direct iterative solution of the integral equations. The results obtained in the present study thus serve as a natural prerequisite to variational extension to those lower temperatures where direct iteration converges too slowly (if at all) to be practical.

We believe that the present preliminary report depicts trends which are very encouraging for the development of an analytical approach to the theory of polyatomic liquids. The separation of intra- and intermolecular correlations for central-force water, in particular, is an unprecedented finding in integral equation studies. Although not conclusive, the results reported here strongly suggest that hypernetted-chain theory offers a promising microscopic blueprint for understanding water's unusual liquid state architecture.

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## REFERENCES

- [1] STILLINGER, F. H., 1975, *Adv. chem. Phys.*, **31**, 1. PERRAM, J. W., and LEVINE, S., 1974, *Adv. molec. relax. Proc.*, **6**, 85.
- [2] RAHMAN, A., and STILLINGER, F. H., 1971, *J. chem. Phys.*, **55**, 3336.
- [3] STILLINGER, F. H., and RAHMAN, A., 1972, *J. chem. Phys.*, **57**, 1281.
- [4] STILLINGER, F. H., and RAHMAN, A., 1974, *J. chem. Phys.*, **60**, 1545.
- [5] SARKISOV, G. N., DASHEVSKY, V. G., and MALENKOV, G. G., 1974, *Molec. Phys.*, **27**, 1249.
- [6] BERNAL, J. D., and FOWLER, R. H., 1933, *J. chem. Phys.*, **1**, 515. ROWLINSON, J. S., 1951, *Trans. Faraday Soc.*, **47**, 120. BEN-NAIM, A., and STILLINGER, F. H., 1972, *Water and Aqueous Solutions*, edited by R. A. Horne (Wiley-Interscience), Chap. 8.
- [7] LEMBERG, H. L., and STILLINGER, F. H., 1975, *J. chem. Phys.*, **62**, 1677.
- [8] VAN LEEUWEN, J. M. J., GROENVELD, J., and DEBOER, J., 1959, *Physica*, **25**, 792.
- [9] RAHMAN, A., STILLINGER, F. H., and LEMBERG, H. L., 1975, *J. chem. Phys.*, **63**, 5223.
- [10] PERCUS, J. K., and YEVICK, G. J., 1958, *Phys. Rev.*, **110**, 1.
- [11] BORN, M., and GREEN, H. S., 1949, *A General Kinetic Theory of Liquids* (Cambridge University Press).
- [12] FRIEDMAN, H. L., 1971, *Modern Aspects of Electrochemistry*, Vol. 6, edited by J. O'M. Bockris and B. E. Conway (Plenum Press).
- [13] HANSEN, J. P., and McDONALD, I. R., 1975, *Phys. Rev. A*, **11**, 2111.
- [14] RICE, S. A., and GRAY, P., 1965, *The Statistical Mechanics of Simple Liquids* (Wiley-Interscience).
- [15] STILLINGER, F. H., and LOVETT, R., 1968, *J. chem. Phys.*, **48**, 3858.
- [16] COOLEY, J. W., and TUKEY, J. W., 1965, *Math. Comput.*, **19**, 297.