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Monte-Carlo simulation of water

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The convergence properties of long-range interactions in a periodic polar system are considered and an efficient method for their evaluation proposed. This method is applied to a Monte-Carlo simulation of water at 1 g cm^{-3} and a nominal temperature of 300 K, using the ST2 potential of Rahman and Stillinger.

1. INTRODUCTION

There have been several attempts over the past few years to simulate the properties of water by Monte-Carlo [1–7] and molecular dynamics [8–11] techniques, the most extensive being the molecular dynamics work of Rahman and Stillinger [8–11]. The major problems are the accurate specification of an effective pair potential between the water molecules and a practical treatment of the long-range dipolar interactions.

It is only recently that accurate potential surfaces for the water dimer have become available [6, 7], and most workers have used empirical pair potentials. Despite the fact that atom–atom potentials may be more realistic than point-charge rigid molecule models, the atom–atom potentials proposed to date yield notably poorer radial distribution functions than the most recently developed point-charge models, e.g. the ST2 potential of Rahman and Stillinger [10] and the Hartree–Fock + C.I. parameterized potential of Lie *et al.* [7]. The latter is a true (isolated) pair potential and would not be expected to simulate accurately the properties of condensed phases, such as energy and pressure, which depend strongly on many-body interactions, though the radial distribution functions are closer to experiment than those obtained from any other potential. The ST2 potential is thought to be a useful pair potential for a wide range of properties and was therefore chosen for the calculations reported here.

The problem of the long-range dipolar interactions has only been considered relatively recently. The original procedure [1, 5–10] was to neglect all interactions between molecules whose oxygen–oxygen separation was greater than some fixed value. The neglect of long-range interactions was subsequently questioned by Barker and Watts [2, 3], who included a reaction field correction, assuming that the molecules outside the cut-off radius of a particular molecule could be represented by a uniform dielectric. However, this assumption neglects the periodicity of the system and is thus not consistent with the model chosen, and perhaps more importantly, assumes that water molecules at relatively short distances (typically about 10 Å) interact as a macroscopic dielectric.

An alternative approach, and one which is followed in this work, is to evaluate the properties of the periodic system. The advantage of this approach is that the system can be accurately studied, and artifacts introduced by periodicity isolated by considering the dependence of the properties on the size of the system. Theoretical expressions for the long-range dipolar interactions have been derived by Jansoone [12] and Smith and Perram [13]. Unfortunately, these methods require repeated evaluation of involved, though rapidly converging, lattice sums, and use far more computer time than the straightforward spherical truncation scheme. The aim of this work is to consider an expansion of the interactions outside the cell of nearest neighbours in a periodic system, and to demonstrate that these interactions can be included in a simple computation if required, but can sometimes be ignored without significant loss of accuracy.

Friedman [14] has attempted to remove the artifacts induced by periodic boundaries by enclosing the system in a spherical container, outside which is a uniform dielectric. The system must be large enough, however, for wall effects to be negligible and for the reaction field due to the uniform dielectric to be an accurate representation of the long-range interactions. Only numerical comparison can decide whether systems with these boundary conditions converge more rapidly to the infinite system limit than those with periodic boundary conditions.

2. LONG-RANGE INTERACTIONS IN A PERIODIC SYSTEM

Consider an infinite, periodic lattice of cells, each containing an identical configuration of N molecules. The periodicity implies that the system is completely determined by the configuration of any set of N molecules contained in a cell. This result is invariant under a translation of the lattice of cells, as the periodicity is maintained under these conditions, and as a consequence simple expressions for the long-range interactions can be derived.

Consider a particular molecule, molecule i, which has been brought to the exact centre of its cell by an appropriate translation of the lattice of cells. If the cell is large enough, the interactions between molecule i and those outside the cell are dominated by electrostatic interactions, which are identically pairwise additive [15]. The interactions between molecule i and those inside the cell of nearest images can be decomposed into pair, triplet, quadruplet and higher-order contributions. Taking, at present, only the contributions from pairs of molecules, the potential energy of molecule i due to all the other molecules can be written as

$$U_i = \sum_j u_{ij}{}^{(\text{elec})} + \sum_k u_{ik} \tag{1}$$

where the first term contains all the contributions from molecules outside the cell of nearest images and the second term the $N-1$ pair contributions from molecules inside the cell. In a similar fashion, the potential energy of each of the other $N-1$ molecules can be evaluated and the total potential energy per molecule, U, can be written as

$$U = (2N)^{-1} \left(\sum_{i=1}^{N} \sum_j u_{ij}{}^{(\text{elec})} + \sum_{i=1}^{N} \sum_{\neq k=1}^{N} u_{ik} \right). \tag{2}$$

The sum over j extends over all the molecules outside the cell of nearest images of molecule i and the sum over k extends over all the molecules inside the cell of nearest images. The second term can immediately be simplified to a sum over pairs of molecules whose cartesian coordinates differ by less than half the cell length, and so, for pairwise interactions,

$$U = N^{-1}\left(\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j} u_{ij}{}^{(\mathrm{elec})} + \sum_{i>k=1}^{N}\sum u_{ik}\right). \tag{3}$$

Many-body contributions can be included in a sum over groups of molecules which are inside the nearest image cell of every molecule in the group. This implies a summation over molecules whose cartesian coordinate differences are all less than half the cell length. In this case,

$$U = N^{-1}\left(\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j} u_{ij}{}^{(\mathrm{elec})} + \sum_{i>k=1}^{N}\sum u_{ik} + \sum_{i>k>l=1}^{N}\sum\sum u_{ikl} + \dots\right). \tag{4}$$

The restriction that all interactions between molecules at separations greater than half cell length are pairwise additive is not serious, since even in small simulations (200–300 molecules) the cell length is typically 20 Å and at 10 Å electrostatic interactions are predominant in polar system. The interactions between molecules inside the nearest neighbour cells of each molecule are evaluated explicitly and we now seek a simple expression for the interactions between a molecule at the centre of the cell and the molecules outside the cell. It has been shown [13] that the pair potential between two point dipoles in an infinite periodic system consists of the finite difference between two divergent sums. However, it will be shown that the dipole and higher multipole potentials due to all the molecules in neighbouring cells taken at once is, by contrast, rapidly convergent. The electrostatic energy of molecule i due to the molecules in the neighbouring cells can be written as a sum over the interactions between the multipoles of molecule i and the total multipoles of all the molecules in each of the neighbouring cells. The origin of these total multipoles is taken to be the centre of the cell.

Since all the cells are identical, their multipole moments are equal and, so using cartesian tensor notation, the electrostatic energy of molecule i due to the surrounding cells can be written as [15]

$$\begin{aligned} U_i{}^{(\mathrm{elec})} = {} & -\mu_\alpha{}^{(i)}\mu_\beta{}^{(\mathrm{c})}T_{\alpha\beta} - \tfrac{1}{3}(\mu_\alpha{}^{(i)}\Theta_{\beta\gamma}{}^{(\mathrm{c})} - \mu_\alpha{}^{(\mathrm{c})}\Theta_{\beta\gamma}{}^{(i)})T_{\alpha\beta\gamma} \\ & + (\tfrac{1}{9}\Theta_{\alpha\beta}{}^{(i)}\Theta_{\gamma\delta}{}^{(\mathrm{c})} - \tfrac{1}{15}\mu_\alpha{}^{(i)}\Omega_{\beta\gamma\delta}{}^{(\mathrm{c})} - \tfrac{1}{15}\mu_\alpha{}^{(\mathrm{c})}\Omega_{\beta\gamma\delta}{}^{(i)})T_{\alpha\beta\gamma\delta} + \dots, \end{aligned} \tag{5}$$

where $\boldsymbol{\mu}^{(i)}$ is the dipole moment of molecule i and $\boldsymbol{\mu}^{(\mathrm{c})}$ is the total dipole moment of the cell. $\boldsymbol{\Theta}$ and $\boldsymbol{\Omega}$ are quadrupole and octopole moments respectively. The gradient tensors, $\mathbf{T}$, represent lattice sums over all cells of the gradient tensors between the central cell and the surrounding cells, e.g.

$$T_{\alpha\beta} = \sum_{\mathbf{n}}{}' T_{\alpha\beta}{}^{\mathbf{n}}, \quad T_{\alpha\beta}{}^{\mathbf{n}} = (4\pi\epsilon_0)^{-1}\nabla_\alpha\nabla_\beta(1/\mathbf{R}^{(\mathbf{n})}). \tag{6}$$

$\mathbf{R}^{(\mathbf{n})}$ is the vector from the central cell (i.e. molecule i) to the centre of the cell defined by the Miller indices $\mathbf{n}$.

The prime indicates that the term with $n_x = n_y = n_z = 0$ in the summation is excluded.

Using the results of Buckingham [15],

$$T_{\alpha\beta}=(a^3\,4\pi\epsilon_0)^{-1}\sum_{n_x=-\infty}^{\infty}\sum_{n_y=-\infty}^{\infty}{\sum_{n_z=-\infty}^{\infty}}'(3n_\alpha n_\beta-n^2\,\delta_{\alpha\beta})n^{-5}, \tag{7}$$

$$T_{\alpha\beta\gamma}=(a^4\,4\pi\epsilon_0)^{-1}\sum_{n_x=-\infty}^{\infty}\sum_{n_y=-\infty}^{\infty}{\sum_{n_z=-\infty}^{\infty}}'-3[5n_\alpha n_\beta n_\gamma - n^2(n_\alpha\delta_{\beta\gamma}+n_\beta\delta_{\gamma\alpha}+n_\gamma\delta_{\alpha\beta})]n^{-7}, \tag{8}$$

$$T_{\alpha\beta\gamma\delta}=(a^5\,4\pi\epsilon_0)^{-1}\sum_{n_x=-\infty}^{\infty}\sum_{n_y=-\infty}^{\infty}{\sum_{n_z=-\infty}^{\infty}}'3[35n_\alpha n_\beta n_\gamma n_\delta - 5n^2(n_\alpha n_\beta\delta_{\gamma\delta}+n_\alpha n_\gamma\delta_{\beta\delta}+n_\alpha n_\delta\delta_{\beta\gamma}+n_\beta n_\gamma\delta_{\alpha\delta}+n_\beta n_\delta\delta_{\alpha\gamma}+n_\gamma n_\delta\delta_{\alpha\beta}) + n^4(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})]n^{-9}, \tag{9}$$

where a is the cell length.

It can be seen that if the **T** tensor has an odd number of subscripts, it will be an odd function of at least one subscript and since the summations extend from $-\infty$ to $+\infty$, all its components will be zero. Furthermore, even for those **T** tensors with an even number of subscripts, each coordinate must appear in pairs for the component to be non-vanishing, and therefore

$$T_{xy}=T_{yz}=T_{zx}=0. \tag{10}$$

Finally, since all directions in the lattice sums are equivalent and the gradient tensors are traceless.

$$T_{xx}=T_{yy}=T_{zz}=\tfrac{1}{3}T_{\alpha\alpha}=0. \tag{11}$$

Thus the dipole–dipole and dipole–quadrupole terms vanish identically, and the leading terms in the expansion are the quadrupole–quadrupole and dipole–octopole contributions. The non-zero components of the corresponding gradient tensor, $T_{\alpha\beta\gamma\delta}$, are either of the form T_{xxxx} or T_{xxyy}. Since $T_{xx\alpha\alpha}$ is zero,

$$T_{xxxx}=-2T_{xxyy}, \tag{12}$$

and so $T_{\alpha\beta\gamma\delta}$ has only one independent component, T_{xxxx}. The lattice sums contributing to T_{xxxx} from a rapidly converging series with the sums from $-1\leqslant n_x, n_y, n_z\leqslant 1$ contributing over 95 per cent of the total. The convergence of T_{xxxx} with successive cubic shells of cells is illustrated in table 1. Since T_{xxxx} is the most slowly convergent of all the non-zero lattice sums, it follows that the first cubic shell of cells contributes at least 95 per cent of the total potential energy due to molecules outside the nearest neighbour cell.

Table 1. Convergence of T_{xxxx} ; $-n\leqslant n_x, n_y, n_z\leqslant n$.

n	$(4\pi\epsilon_0 a^5)\ T_{xxxx}$	n	$(4\pi\epsilon_0 a^5)\ T_{xxxx}$
1	71·786	6	74·452
2	73·613	7	74·488
3	74·095	8	74·512
4	74·293	9	74·529
5	74·394	10	74·542

The dipole moment of the cell is origin independent, and so

$$\mu_\alpha{}^{(c)} = \sum_{i=1}^{N} \mu_\alpha{}^{(i)}. \tag{13}$$

The quadrupole and octopole moments are origin dependent [15], and neglecting terms arising from the requirement that the quadrupole and octopole moments are traceless, which do not contribute to the potential energy,

$$\Theta_{\alpha\beta}{}^{(c)} = \sum_{i=1}^{N} [\Theta_{\alpha\beta}{}^{(i)} + \tfrac{3}{2}(r_\alpha{}^{(i)}\mu_\beta{}^{(i)} + r_\beta{}^{(i)}\mu_\alpha{}^{(i)})], \tag{14}$$

$$\begin{aligned}\Omega_{\alpha\beta\gamma}{}^{(c)} = \sum_{i=1}^{N} [\Omega_{\alpha\beta\gamma}{}^{(i)} &+ \tfrac{5}{3}(r_\alpha{}^{(i)}\Theta_{\beta\gamma}{}^{(i)} + r_\beta{}^{(i)}\Theta_{\alpha\gamma}{}^{(i)} + r_\gamma{}^{(i)}\Theta_{\alpha\beta}{}^{(i)}) \\ &+ \tfrac{5}{2}(r_\alpha{}^{(i)}r_\beta{}^{(i)}\mu_\gamma{}^{(i)} + r_\alpha{}^{(i)}r_\gamma{}^{(i)}\mu_\beta{}^{(i)} + r_\beta{}^{(i)}r_\gamma{}^{(i)}\mu_\alpha{}^{(i)})],\end{aligned} \tag{15}$$

where $r_\alpha{}^{(i)}$ is the vector from the centre of the cell to molecule i. The cell quadrupole and octopole moments, $\Theta_{\alpha\beta}{}^{(c)}$, $\Omega_{\alpha\beta\gamma}{}^{(c)}$, are different for each molecule, since the origin of the cell is different. They must therefore be re-evaluated for each molecule before determining the long-range contribution to its potential energy, $U_i{}^{(\mathrm{elec})}$. Since all the distances involved in the computation of the cell moments for a particular molecule are required in the calculation of its nearest image interactions, the evaluation of the long-range contributions to the potential energy, at least for the quadrupole–quadrupole and dipole–octopole terms, is not a particularly lengthy computation. In the case of systems involving only dipolar forces, or in systems where these forces are predominant at distances of half-cell-length or greater, the expressions are considerably simplified,

$$U_i{}^{(\mathrm{elec})} = -\tfrac{1}{15}\mu_\alpha{}^{(i)}\Omega_{\beta\gamma\delta}{}^{(c)}T_{\alpha\beta\gamma\delta} + \dots \tag{16}$$

$$\begin{aligned} &= -\tfrac{1}{15}(\mu_x{}^{(i)}(\Omega_{xxx}{}^{(c)} - \tfrac{3}{2}\Omega_{xyy}{}^{(c)} - \tfrac{3}{2}\Omega_{xzz}{}^{(c)}) \\ &\quad + \mu_y{}^{(i)}(-\tfrac{3}{2}\Omega_{yxx}{}^{(c)} + \Omega_{yyy}{}^{(c)} - \tfrac{3}{2}\Omega_{yzz}{}^{(c)}) \\ &\quad + \mu_z{}^{(i)}(-\tfrac{3}{2}\Omega_{zxx}{}^{(c)} - \tfrac{3}{2}\Omega_{zyy}{}^{(c)} + \Omega_{zzz}{}^{(c)}))T_{xxxx}, \end{aligned} \tag{17}$$

all other terms being zero. The cell octopole moment is given in this case by

$$\Omega_{\alpha\beta\gamma}{}^{(c)} = \tfrac{5}{2} \sum_{j=1}^{N} (r_\alpha{}^{(j)}r_\beta{}^{(j)}\mu_\gamma{}^{(j)} + r_\alpha{}^{(j)}r_\gamma{}^{(j)}\mu_\beta{}^{(j)} + r_\beta{}^{(j)}r_\gamma{}^{(j)}\mu_\alpha{}^{(j)}), \tag{18}$$

where $r_\alpha{}^{(j)}$ is the vector from the centre of the appropriate cell (i.e. molecule i) to molecule j.

However, it would seem likely that the quadrupole–quadrupole and dipole–octopole contributions are often small compared with the nearest image interactions, and in the present calculations interactions outside the nearest neighbour cells were neglected. The approximation was tested on an equilibriated configuration of 256 molecules by explicitly evaluating the interactions between a molecule and those in the 26 cells surrounding its nearest neighbour cell. As was shown earlier, this contributes more than 95 per cent of the total potential energy due to molecules outside the nearest-neighbour cell. These interactions produced a potential energy of approximately 0·05 kJ mole^{-1} (0·02 kT) which, even allowing for fluctuations due to different configurations, is negligible. (It should be noted that this is a different procedure to that employed by Sarkisov *et al.* [4] who summed round the 26 cells surrounding the base cell rather than the nearest-neighbour cell of each molecule.) The error involved in the 256 molecule system is so small that the approximation is probably valid (i.e. the errors in the energy $< 0{\cdot}1\ kT$) for all the systems used in these calculations.

3. RESULTS

Monte-Carlo calculations have been carried out on systems of 32, 129 and 256 molecules, at a density of 1 g cm^{-3} and a nominal temperature of 300 K. The specifications of the ST2 effective pair potential used in the calculations are given in reference [10]. Successive trial configurations were generated by small, random rotational or translational displacements of a randomly selected molecule, and the algorithm of Metropolis *et al.* [16] was used to accept configurations with the correct canonical distribution of energies. It is possible to vary the ratio of rotational and translational trial displacements, without disturbing the Boltzmann weighting, in the hope of exploring phase space more efficiently, but this was not tested in this work, a 1 : 1 ratio being used throughout.

The nearest-image truncation scheme used in this work would involve approximately twice as much computer time as the spherical truncation scheme, since there are nearly twice as many interparticle interactions in the cubic cell of nearest images as in a sphere inside this cell. This disadvantage can be remedied by defining a sphere around each molecule, outside of which, but still inside the cell of nearest images, the intermolecular interactions are represented by point dipoles of the same magnitude as those of ST2 water molecules. The sphere of explicitly calculated interactions was always chosen to be sufficiently large so that the errors involved in the point dipole approximation were negligible, i.e. less than $0{\cdot}01\ kT$ when compared to energies of configurations where all the interactions in the cell of nearest images were evaluated explicitly. This involved cut-offs of 4·5 Å, 6·0 Å and 8·5 Å for the 32, 129 and 256 molecule systems respectively. Since the point-dipole interactions involve a negligible amount of computation the present scheme should be no slower computationally than one with spherical truncation. The programme written for this work generates approximately 40 000 configurations per hour for the 256 molecule system on an IBM 370/165. It was tested with a run of 216 molecules at 1 g cm^{-3} and 391 K, starting from a random configuration, and only considering those interactions between molecules whose oxygen–oxygen separation was less than 8·46 Å. This is an identical system to one used by Rahman and Stillinger [10], and after 240 000 configurations, the potential energy was within 1 per cent of their reported value.

Table 2. Thermodynamic properties.

System	kJ mole^{-1}	$PV/N_A kT$	C_v J mole^{-1} K^{-1}
32	$-45{\cdot}8 \pm 0{\cdot}5$	$-0{\cdot}8 \pm 0{\cdot}8$	≈ 80
129	$-42{\cdot}1 \pm 0{\cdot}3$	$-0{\cdot}2 \pm 0{\cdot}5$	≈ 70
256	$-39{\cdot}9 \pm 0{\cdot}3$	$0{\cdot}6 \pm 0{\cdot}3$	≈ 70
R.S. [10]	$-43{\cdot}1$	0·05	100
Expt [24]	$-41{\cdot}4$	0·05	75

The calculation on the 32 particle system was started from a face-centred cubic lattice, with all molecules aligned in an identical orientation. The initial configuration of the 256 molecule system was generated by duplicating an equilibriated 32 molecule configuration in each of the cartesian directions. The 129 molecule system was started by taking a cube of molecules from an equilibriated 256 molecule configuration. Under these conditions, 100 000, 100 000 and 250 000 configurations respectively were required to equilibriate the 32, 129 and 256 molecule systems, and 350 000, 400 000 and 400 000 configurations were used to compute the ensemble averages of the properties of these systems.

3.1. *Thermodynamic properties*

The configurational energy per molecule, Φ, the constant-volume heat capacity and the equation of state have been computed for each of the three systems. The results and statistical errors are summarized in table 2. The

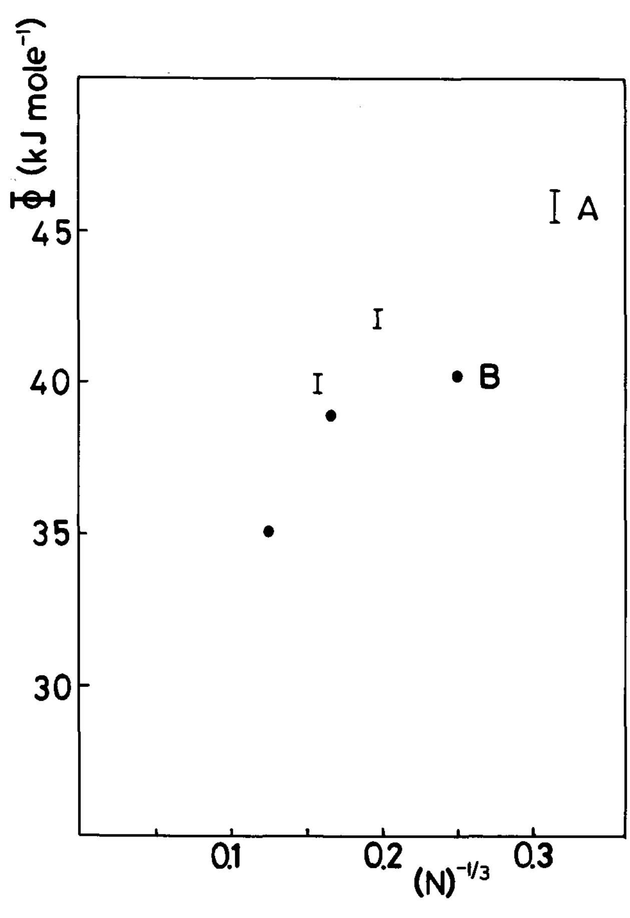

Figure 1. Convergence of the configurational energy. A : Present calculations using the ST2 potential and nearest image truncation. B : Watts' calculations (reference [3]) using the BNS potential and spherical truncation.

equation of state was obtained from the mean virial per molecule, Ψ, but because of the large statistical fluctuations, the results are not very precise :

$$PV/N_{A}kT = 1 - \Psi/3kT, \tag{19}$$

$$\Psi = (N)^{-1}\left\langle \sum_{i>}^{N} \sum_{j=1} \mathbf{r}_{ij} \cdot \frac{\partial u_{ij}}{\partial \mathbf{r}_{ij}} \right\rangle. \tag{20}$$

The constant-volume heat capacity was calculated from fluctuations in the potential energy [17]

$$C_v = \left(\frac{\partial \Phi}{\partial T}\right)_v = \frac{N}{N_{A}kT}(\langle \Phi^2 \rangle - \langle \Phi \rangle^2) + 3N_{A}kT. \tag{21}$$

The results are compared with those estimated from Rahman and Stillinger's results for the 216 molecules system using a linear interpolation at 300 K between the reported temperatures of 283 K and 314 K.

The magnitudes of the potential energy and virial deduced from Rahman and Stillinger's results are much greater than those reported here for the 256 molecule system, and in fact are quite similar to those of the 129 molecule system. This indicates that a considerable perturbation is introduced into the system by the spherical truncation used in their calculations which is confirmed by the results of Watts [3] for the older but similar BNS potential. These results show poorer convergence of the potential energy with increasing system size than the results reported here for the more polar ST2 potential (see figure 1).

The heat capacity of the 256 molecule system was found to be approximately 70 J mole^{-1} K^{-1} compared with an experimental result of 75 J mole^{-1} K^{-1}. The large heat capacity found by Rahman and Stillinger ($\approx$100 J mole^{-1} K^{-1}), attributed by them to neglect of quantum effects, is probably due to energy fluctuations induced by molecules crossing the spherical truncation boundaries surrounding each molecule.

The configurational energy has been found to be strongly dependent on the number of molecules in the system because of the large orientational correlation introduced by the periodic boundaries. It is therefore important to investigate fully the N-dependence of the properties of polar systems and to determine the values of these properties in the thermodynamic limit. Only then can the results of molecular dynamics or Monte-Carlo simulations be meaningfully compared with experiment, and the accuracy of intermolecular potentials assessed.

3.2. *Dielectric properties*

The orientational correlation in a polar liquid is a sensitive test of both the potential and the boundary conditions. As a consequence, there has been considerable interest in the ability of molecular dynamics and Monte-Carlo simulations to predict accurate values of the orientational correlation parameter, g_k, first introduced by Oster and Kirkwood [20], and defined by

$$g_k = \sum_{j}^{\text{sphere}} \langle \cos \theta_{1j} \rangle, \tag{22}$$

where θ_{1j} is the angle between the permanent dipole moments of molecules 1 and j and where the sum is taken over all molecules j inside a sphere of large, but arbitrary, radius centred on molecule 1. However, Kirkwood's theory of dielectric polarization [22] is not strictly applicable to polarizable molecules [21] and so estimates of g_k derived from experimental dielectric contents are only approximate.

The values of g_k obtained from small simulations are affected by both the orientational correlation induced by the periodic boundaries, and by errors in $\sum_j \cos\theta_{1j}$ caused by the smallness of the sphere of molecules used to evaluate it. These effects can be separated by computing g_k for different sized spheres of molecules as well as different sized systems. Results were obtained for the 129 and 256 molecule systems and are summarized in table 3 (The 32 molecule system was too small for useful results to be obtained.)

Table 3. Kirkwood g_k-factor ; R is the radius of the sphere used to compute g_k.

System	$R=4{\cdot}65$ Å	$R=6{\cdot}2$ Å	$R=7{\cdot}75$ Å	$R=9{\cdot}3$ Å
129	3·7	3·7	0·5	
256		4·6	4·1	1·9

The sharp decrease of g_k for the largest sphere in each system is probably due to including molecules that are strongly correlated across the periodic boundary. This effect decreases with increasing system size, as would be expected.

The values for g_k obtained in these calculations do not exhibit a strong dependence on either system size or the size of the sphere of molecules used to compute it (except for the effect noted previously), and the results indicate a value of g_k in the range 4–5 for the infinite system. This compares with the estimate of 2·6 obtained from the experimental dielectric constant [23], and represents a dramatic improvement over that obtained by Rahman and Stillinger [10] of approximately 0·16 (before an empirical correction was applied for the effect of the spherical truncation). Watts [3] has found that inclusion of the reaction field suggested by Barker and Watts [2] gave a value of g_k of about 2 for a 64 molecule system using the BNS potential, a considerable improvement over the results obtained using spherical truncation.

3.3. *Structural properties*

The oxygen–oxygen, oxygen–hydrogen and hydrogen–hydrogen radial distribution functions shown in figures 2, 3, 4 were computed by sampling the pair distributions in the 256 molecule system every 250 configurations for 100 000 configurations. A comparison of these results with those of Rahman and Stillinger [10], Lie *et al.* [7] and the experimental results of Narten and Levy [18, 19], taken from reference [7] is summarized in table 4.

The results indicate a general reduction in the pair correlation when compared with those of Rahman and Stillinger [10]. The most notable is the second maximum in $g_{00}(r)$ which is broader and centred at much larger r than the peak in Rahman and Stillinger's calculations. These results compare less well in general with the experimental results and indicate that some of the correlation found in Rahman and Stillinger's calculation was an artifact of the spherical truncation rather than a consequence of the intermolecular forces.

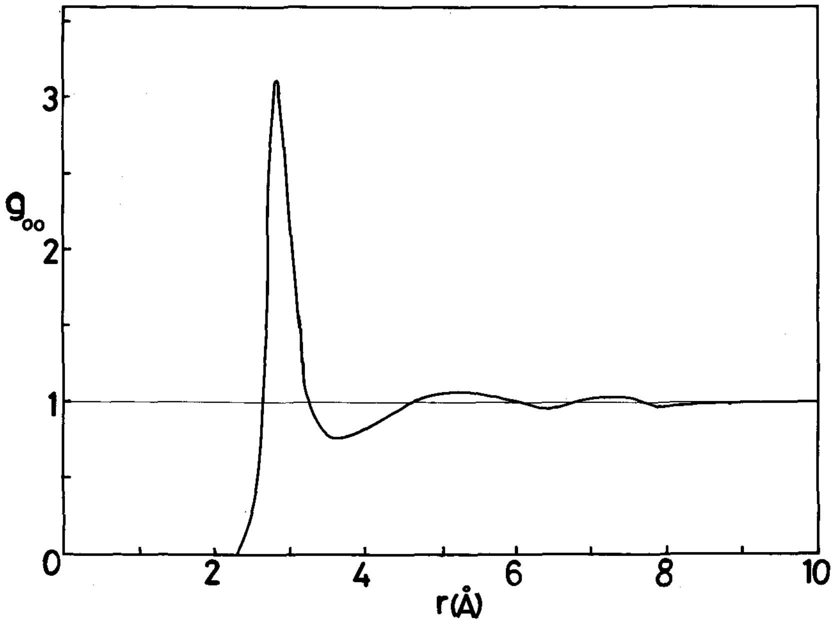

Figure 2. Oxygen–oxygen pair distribution function.

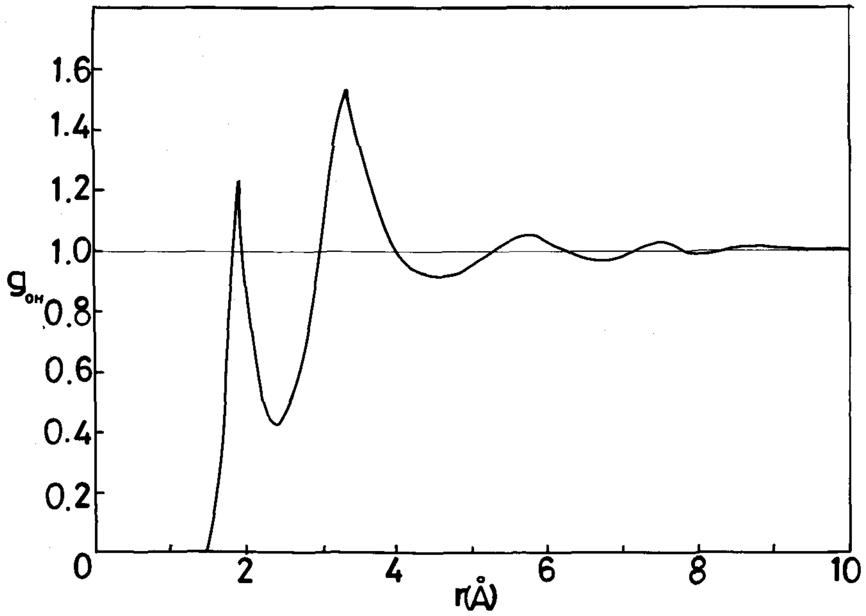

Figure 3. Oxygen–hydrogen pair distribution function.

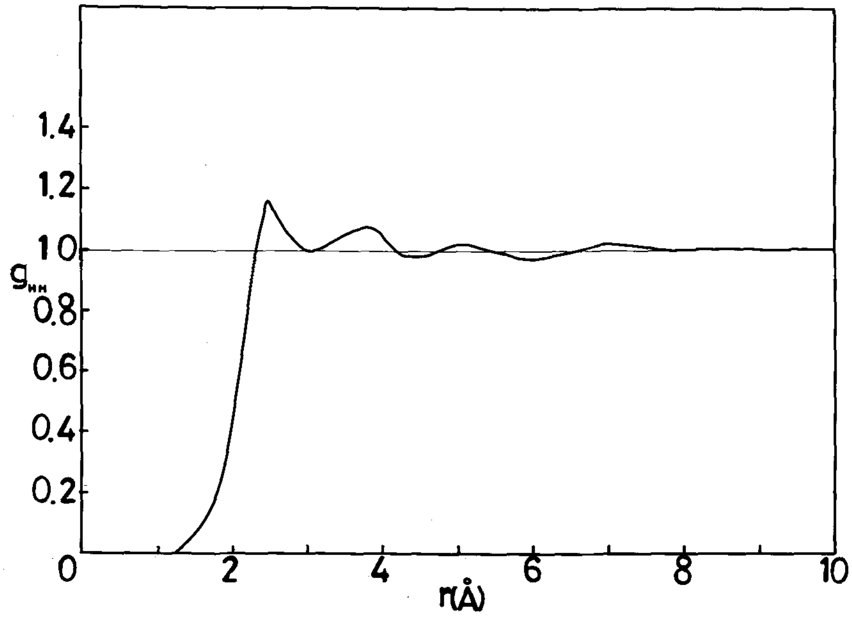

Figure 4. Hydrogen–hydrogen pair distribution function.

Table 4. Comparison of radial distribution functions. R_i, M_i, r_i, m_i are the positions and values of maxima and minima respectively of the radial distribution functions.

		R_1	M_1	r_1	m_1	R_2	M_2	r_2	m_2
g_{OO}	256	2·85	3·11	3·63	0·75	5·30	1·06	6·4	0·96
	R.S. [10]	2·85	3·09	3·53	0·72	4·70	1·13	5·8	0·80
	L.C.Y. [7]	2·83	2·46	3·53	0·94	4·25	1·08	5·6	0·89
	Expt [18]	2·83	2·31	3·45	0·85	4·53	1·12	5·6	0·86
g_{OH}	256	1·91	1·24	2·43	0·42	3·32	1·53	4·30	0·92
	R.S. [10]	1·90	1·38	2·50	0·31	3·40	1·60	4·60	0·92
	L.C.Y. [7]	1·90	1·08	2·55	0·28	3·35	1·68	4·85	0·90
	Expt [19]	1·90	0·80	2·45	0·50	3·35	1·70	—	—
g_{HH}	256	2·50	1·15	3·05	0·99	3·75	1·07	4·4	0·98
	R.S. [10]	2·50	1·50	3·10	0·78	4·00	1·15	5·40	0·96
	L.C.Y. [7]	2·50	1·40	3·10	0·86	3·90	1·20	5·50	0·93
	Expt [19]	2·35	1·04	3·00	0·47	4·00	1·08	—	—

4. CONCLUSIONS

It has been found that long-range interactions play a significant role in determining the properties of polar liquids but this work has shown that their inclusion is not a formidable task. Unfortunately, we have found that the periodic boundaries considerably perturb these systems and further research on the N-dependence of the properties to determine their values in the thermodynamic limit is needed, before meaningful comparisons with experiment can be made.

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