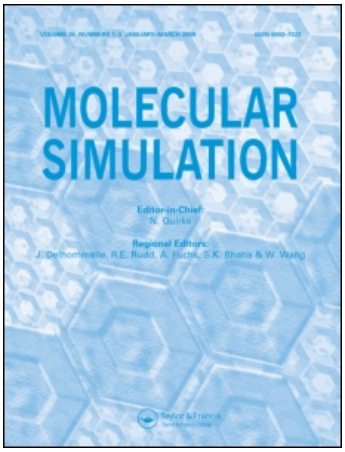

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Note

THE EWALD SUM IN TRUNCATED OCTAHEDRAL AND RHOMBIC DODECAHEDRAL BOUNDARY CONDITIONS

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1 INTRODUCTION

The truncated octahedron (TO) and the rhombic dodecahedron (RD) are two space filling shapes, which have special advantages as simulation cells for molecular dynamics [1, 2]. This article addresses the particular problem of how to incorporate the Ewald sum [3, 4] in simulations employing these unusual boundary conditions.

2 GENERATING THE TO AND RD

Both the truncated octahedron and the rhombic dodecahedron can be thought of as the Wigner-Seitz cells of a particular orthorhombic body centred lattice [1]. Thus starting with a body centred orthorhombic cell the TO or RD can be generated by locating the planes that perpendicularly bisect the vectors drawn from the centre of the cell to its eight vertices. The combined set of these planes, plus whatever is left of the faces of the original cell, form the faces of the TO or RD. In principle other cells can be generated this way, but the TO and RD are of primary interest because they possess a particular symmetry, such that every face is equivalent by reflection symmetry to one on the opposite side of the cell. This makes these cells highly suitable as simulation cells [1]. Which of the cells results, (TO, RD, or something else) depends on the relative lengths of the sides of the original orthorhombic cell. In fact if $a = b = c$, TO results, and if $a = b$ *with* $c = \sqrt{2}$a, RD results.

Thus, assuming the orthorhombic 'parent' cell has sides a, b, c, the corresponding Wigner-Seitz cell has the following characteristics.

1. The final volume of the cell is exactly half that of the parent cell.

2. The eight vertices of the parent cell now represent the centres of the neighbouring Wigner-Seitz cells in the periodic lattice. (It follows therefore that each of these eight neighbours has taken 1/16th of the volume of the parent cell.)
3. Since the lattice sites are equivalent by definition, the volume of the parent cell removed by each vertex is exactly equivalent to an 'octant' of the surviving cell, to which it is related through translation by a vector $T = \frac{1}{2}(\pm a, \pm b, \pm c)$. (There are of course eight such vectors.)

3 ADAPTING THE EWALD SUM

It is well known that coding up the Ewald sum for an orthorhombic simulation cell is simple to do [3, 4], and the same basic methodology applies here. In effect the TO or RD is replaced by the corresponding 'parent' orthorhombic cell. The parent cell contains twice as many ions, but the 'missing' ions can be generated by translation of the contents of each octant of the TO or RD by one of the **T** vectors. However it is not actually necessary to double the contents of the cell in real applications, as a more elegant procedure is available, which substantially reduces the computational and memory requirement.

Firstly it should be noted that the reciprocal lattice vectors of the parent orthorhombic cell are given by

$$\mathbf{k} = 2\pi(l/a, m/b, n/c)^{\dagger}$$

where l, m, n are integers. (The † indicates a transpose.)

The central term in the reciprocal space part of the Ewald sum is the summation

$$Q_{\text{sum}} = \sum_{j}^{2N} q_j \exp(i\mathbf{k} \cdot \mathbf{r}_j),$$

from which the structure factor is calculated. (Note that the sum now runs over all the $2N$ ions in the bigger cell.) Using the properties of the Wigner-Seitz cell outlined above, this sum can be written as:

$$Q_{\text{sum}} = \sum_{j}^{N} q_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) + \sum_{j}^{N} q_j \exp(i\mathbf{k} \cdot (\mathbf{r}_j + \mathbf{T})).$$

Where the first sum refers to ions within the TO/RD and second sum to ions outside the TO/RD but in the parent cell. (Which of the eight **T** vectors is added to each $\mathbf{r}_j$ is not specified at this stage, and in fact need not be, as shall be seen below). This second sum can be factorised into:

$$\sum_{j}^{N} q_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) \exp(i\mathbf{k} \cdot \mathbf{T}).$$

The second exponential in this expression is simply a phase factor, which from the definition of the vectors **k** and **T** can easily be shown to be

$$\exp(i\pi(\pm l \pm m \pm n))$$

None of the signs in this exponent matter, what matters is whether the sum of l, m and n is even or odd. In fact:

$$\exp(i\pi(\pm l \pm m \pm n)) = -1 \quad \text{if} \quad l + m + n \quad \text{odd},$$

$$\exp(i\pi(\pm l \pm m \pm n)) = +1 \quad \text{if} \quad l + m + n \quad \text{even}.$$

From this it is easy to see that:

$$Q_{\text{sum}} = 2 \times \sum_{j}^{N} q_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) \quad \text{if} \quad l + m + n \text{ even},$$

$$Q_{\text{sum}} = 0 \quad \text{if} \quad l + m + n \text{ odd}.$$

So that it is not necessary to double the number of ions in the simulation. Nor is it necessary to handle all the **k** vectors in the Ewald sum, only those that can be considered 'even' by the above criterion.

There are no adaptations of the real space terms necessary, except to note that the appropriate TO or RD boundary conditions are applied in the usual way [1, 2].

4 IMPLEMENTATION

The implementation of this procedure is trivial and differs very little from the prescription given elsewhere [3, 4]. The procedure is as follows:

Real Space Part

1. Apply a spherical cutoff to the real space (erfc) terms, of radius no greater than $\sqrt{3}\, d/4$ in the TO and $d/2$ in the RD, where d is the smallest of the cell parameters (a, b, c).
2. Use the TO/RD periodic boundary conditions when obtaining the minimum image of each ion [1, 2].

Reciprocal Space Part

1. Assume the reciprocal lattice vectors are of the form $2\pi(l/a, m/b, n/c)^{\dagger}$, where a, b, c are the widths of the parent cell.
2. Calculate the reciprocal space contributions as normal, but make use of the above rules regarding the even-ness or odd-ness of the sum of l, m and n, as above. i.e. double the contributions for 'even' **k** vectors and disregard them for 'odd' **k** vectors.

It should be remembered that this procedure effectively doubles the number of ions in the reciprocal space sum. Hence the reciprocal space contribution to the configuration energy (of the simulation cell) must divided by 2 to yield the correct value.

5 EXAMPLE

To test the method we simulated molten sodium chloride with both simple cubic (SC) and TO periodic boundary conditions, and compared the results. The state point was $T = 1427\,\text{K}$, $V = 39.006\,\text{cm}^3\,\text{mol}^{-1}$, and the rigid-ion potentials of Tosi and Fumi [5] were used. The SC simulation had 216 ions in the unit cell, whereas the the TO simulation had 166 ions. The latter number was chosen to ensure that the maximum cut-off, the radius of the inscribed sphere, had the same value of

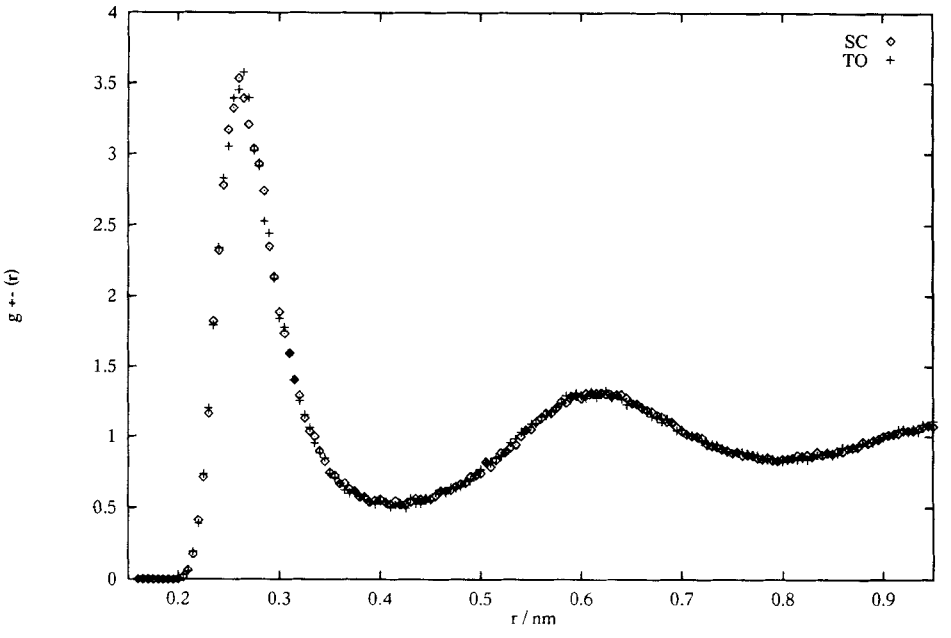

Figure 1 The unlike-ion radial distribution function in molten sodium chloride, comparing simulations in simple cubic periodic boundaries (diamonds) and in truncated-octahedral boundaries (crosses).

0.956 nm in each case. We used this cut-off with a convergence parameter of $\alpha = 3.53\,\text{nm}^{-1}$ and a reciprocal space cut-off at $22.8\,\text{nm}^{-1}$ to give an accurate Ewald sum. In the usual dimensionless units [6] the Ewald sum parameters were: for the SC case, $R_c/L = 0.5$, $\alpha L = 6.75$, $(l^2 + m^2 + n^2)_{max} = 49$; and for the TO case, $R_c/L = \sqrt{3}/4, \alpha L = 7.8$, $(l^2 + m^2 + n^2)_{max} = 64$. The reciprocal space sum included 1418 vectors in the SC case, and 1054 vectors in the TO case. The two simulations were run for 24 ps after equilibration, using a time step of 8 fs. A heat bath was applied to ensure that both simulations had identical temperatures.

The average Coulombic energy was $-795.22 \pm 0.30\,\text{kJ mol}^{-1}$ in the SC case, and $-795.62 \pm 0.33\,\text{kJ mol}^{-1}$ in the TO case. The uncertainties shown here are the true standard errors obtained by the method of Friedberg and Cameron [7]. The agreement between the two simulations is therefore very satisfactory. This is also the case for the pressure, with values of 493 ± 13 MPa in the SC simulation and 513 ± 16 MPa in the TO case. Radial distribution functions were also found, and the (+ -) distribution is shown in Figure 1. Agreement is excellent, with perhaps a very slight difference at the tip of the first peak. Diffusion coefficients were also found, from linear fits to mean-square-displacements over the time interval 1 to 4 ps. The SC simulation gave values of $D_+ = 12.2$, $D_- = 11.0$, whereas the TO simulation gave $D_+ = 11.7$, and $D_- = 10.6$, all in units of $10^{-9}\,\text{m}^2\text{s}^{-1}$. We regard these values, with discrepancies of no more than 4%, as being in satisfactory agreement.

The mean execution time per step of the SC simulation was 1.73 s (on an i860 processor) whereas that of the TO simulation was 1.15 s.

6 CONCLUSION

We have shown how TO or RD boundaries may be used in conjunction with the Ewald method in the the simulation of ionic systems. The example showed that the use of TO boundaries, rather than the usual simple cubic boundaries, gives good results with a smaller number of ions and a useful saving of computer time.

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