

## Alternatives to the Periodic Cube in Computer Simulation

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In two dimensions, if you want periodic boundary conditions, there is a choice of a periodic cell with either four sides or six, the square or the hexagon. Any parallelogram is just a distorted square and fills space with the same packing as squares. Periodic cells have to fill space merely by translation, so triangles are no use:

In three dimensions there are five shapes which fill space in the required way, the five parallelohedra of the crystallographer E.S. Fedorov. They are:

1. The good old cube or parallelepiped which packs as simple cubic.
2. The hexagonal prism. I have never heard of this being used in computer simulation, but there is no great reason why it should not be. However, as even hexagonal close packing can be accommodated in the periodic cube<sup>1</sup> there has never been any need for it.
3. The "elongated" dodecahedron with 28 edges, 18 vertices, and 12 faces, eight of them with four and four with six edges. I have never heard of this being used in computer simulation and I can't think of any sound, scientific reason why it should be used.
4. The rhombic dodecahedron, with 24 edges, 14 vertices and 12 faces, each with four edges. It packs as face centred cubic. It can be produced by taking a cube and cutting off the edges, while preserving the full symmetry of the cube, until exactly one quarter of the cubes' volume is left. This periodic cell has been used<sup>2</sup>, though hardly extensively. It has the advantage in that of all the five shapes it has the largest inscribed sphere, much larger than that of the cube, which has a very unspherical shape. So if you want the maximum possible range for a radial distribution function for a given number of particles in the periodic cell, this is the periodic shape to use. Of all possible shapes this will give you the maximum distance between a particle and its own periodic images. Its disadvantage is obvious, it isn't too easy to program, and is likely to be sufficiently slow that its

advantages are outweighed: it is probably better to use a periodic cube with a larger number of particles. However, I think some research into this could be useful.

5. The 14-hedron or cubo-octahedron or orthic tetrakai-decahedron or truncated octahedron, with 36 edges, 24 vertices and 14 faces. It packs as body centred cubic. It can be produced by taking a cube and cutting off the corners, while preserving the full symmetry of the cube, until exactly one half of the cubes' volume is left. This periodic cell is being used<sup>3,4</sup> and deserves serious consideration. Of the five shapes it has the smallest circumsphere and so may fairly be described as the most nearly spherical of the periodic cell-shapes available. It is compared with the cube and the rhombic dodecahedron in table 1. It has only a slightly smaller inscribed sphere than the rhombic dodecahedron. Its advantage over the rhombic dodecahedron is that truncated octahedral boundary conditions are relatively simple to program. Figure 1 is a drawing of a truncated octahedron inside a cube and figure 2 shows the FORTRAN code used in the inner, force calculating loop of a molecular dynamics program. The code assumes that the truncated octahedron is cut from a cube of unit length. The first part is identical to the code required for simple cubic periodic boundary conditions<sup>5</sup>. This either brings the vector (DX, DY, DZ) into the nearest-neighbour truncated octahedron or leaves it in one of eight surrounding truncated octahedra which share one of its six sided faces. The equation of the plane containing this shared surface in the positive octant is:

$$x + y + z = 3/4$$

Given this, the code to find the true nearest-neighbour (DX, DY, DZ) is fairly obvious. The code can be vectorized for the CRAY by replacing the IF statement with the CVMGM function. Both Steve Thompson and myself have experimented with various vectorized versions and we found it to be always much slower than when simple cubic periodic boundary conditions are used. However, that was only for the CRAY and the extra overhead of the truncated octahedron should not be large on other machines, or when the force calculation itself is substantial. So although these boundary conditions would be unfavourable with a simple Lennard-Jones potential on the CRAY, they might be attractive with an Ewald potential. The k-space part of the Ewald

summation is then slightly different as the reciprocal lattice of body centred cubic is face centred cubic. The attraction of the truncated octahedron with the Ewald summation is that the anisotropic parts of the potential, and in particular the interactions between charges out into the corners of the cell, should be smaller and the extra time required to find the nearest images easily outweighed by a reduction in the number of reciprocal lattice vectors required. The truncated octahedron becomes doubly attractive if one is simulating a single ion in a dipolar solvent, for then the distance between periodic images of the ion is considerably increased without increasing the quantity of solvent.

Truncated octahedral periodic boundary conditions may be used with a number of crystal structures, the list of numbers available with the most common is shown in Table 2.

There is a way round having to use one of the five shapes: use a non-Euclidean space. At a liquid-state conference at the University of Canterbury in 1973 Isenberg read a paper called "Optimum Boundary Conditions in Molecular Dynamics Calculations." The final two paragraphs of the abstract of that paper say:

"The solution to the anisotropy problem in 2-D is to calculate the motions of the particles on the surface of a sphere, with particles interacting along great circles only. In 3-D the volume is the surface of a 4-D, in which interactions lie along the great circles of the 4-D sphere. This model gives complete, statistical, isotropy of directional properties and isotropy of 'image' distances. However, the coordinate system is no longer cartesian but will approach a cartesian system with short-range forces as the size of the sphere is increased.

"This 'spherical' box has the additional advantage that the total potential energy between any two particles, summed over all images, can be calculated analytically. Thus no 'cut off' in the potential energy function has to be introduced."

This method has not received much attention, though it does crop-up occasionally. There are two minor variants. The interaction between two particles may be taken along the shorter area of the great circle or both long and short routes may be included. As far as I can determine the first publication in which spherical

boundary conditions were used was for the 2D one component plasma by Hansen et al<sup>6</sup>. Schreiner<sup>7</sup> presented some results for the 3D Lennard-Jones fluid at the CCP5 Manchester meeting; they struck me as more number dependant than one would expect with normal boundary conditions. However, Kratky<sup>8</sup> has shown that a rigorous correction for the number dependence might be possible.

An obvious disadvantage of the non-Euclidean space is that one does not get ordinary crystalline solid packing<sup>9</sup>. Quite possibly the packing of a high density fluid phase will also be distorted. The advantage of spherical boundary conditions, as seen by Isenberg, is that they avoid the considerable anisotropy of periodic cube boundary conditions. My own feeling is that periodic truncated octahedron boundary conditions offer a better compromise. The anisotropy is much smaller than with a cube and the distortions of a non-Euclidean geometry is avoided. However, there is scope for more work in this area, little is known about the effects of the shape of the periodic cell on the results obtained.

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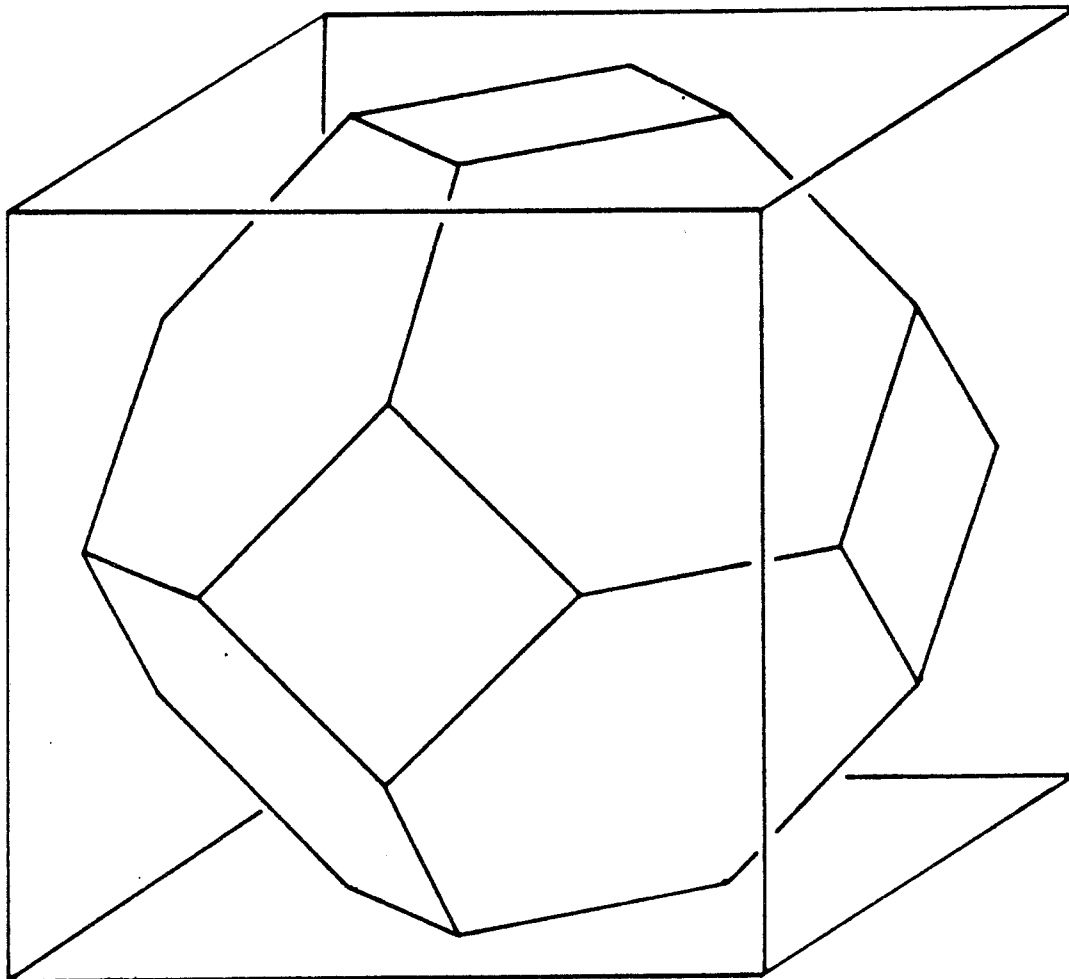


Fig. 1 The Truncated Octahedron

Table 1

Comparison of cube, truncated octahedron (TO), and rhombic dodecahedron (RD)

Shape	$\frac{\text{Circumsphere radius}}{\text{Inscribed sphere radius}}$	$\frac{\text{Inscribed sphere volume}}{\text{volume}}$	$\frac{\text{Circumsphere volume}}{\text{volume}}$
Cube	$\sqrt{3} \approx 1.73$	$\pi/6 \approx 0.52$	$\sqrt{3}\pi/2 \approx 2.72$
TO	$\sqrt{5/3} \approx 1.29$	$\sqrt{3}\pi/8 \approx 0.68$	$5\sqrt{5}\pi/24 \approx 1.46$
RD	$\sqrt{2} \approx 1.41$	$\sqrt{2}\pi/6 \approx 0.74$	$2\pi/3 \approx 2.09$

Table 2

Numbers of primitive cells that can be used with periodic truncated-octahedral boundary conditions.

Lattice type	General Formula	1st few terms
simple cubic	$\frac{1}{2}(2n)^3$	4, 32, 108, 256, 500, 864 ...
body-centred cubic	$(2n)^3$	8, 64, 216, 512, 1000 ...
face-centred cubic	$1/4(4n)^3$	16, 128, 432, 1024 ...

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DX = X(I) - X(J)
DX = DX - AINT (2 * DX)
DY = Y(I) - Y(J)
DY = DY - AINT (2 * DY)
DZ = Z(I) - Z(J)
DZ = DZ - AINT (2 * DZ)
IF (ABS(DX) + ABS(DY) + ABS(DZ).LT. 0.75) GOTO 1
DX = DX - SIGN (0.5, DX)
DY = DY - SIGN (0.5, DY)
DZ = DZ - SIGN (0.5, DZ)
1 CONTINUE

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Fig. 2 Calculation of the vector (DX, DY, DZ) between the nearest-neighbour images of particles I & J as it might appear in the inner loop of a m.d. force calculation. The containing cube of the truncated octahedron is of unit length.