The Minimum Image Convention in Non-Cubic MD Cells

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Introduction

In molecular dynamics simulations of liquids the most common (but not the only [1, 2]) periodic boundary conditions employed are those of the simple cube. However in simulations of crystalline ionic systems, these periodic boundary conditions are not generally suitable and an alternative is required which matches the natural periodicity of the crystal. The most obvious choice under these circumstances is a parallelepiped MD cell, which may be defined simply as a multiple of the unit cell for the crystal lattice (Figure 1). Thus if the unit cell has vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$, the MD cell is defined analogously by vectors $\underline{A}=\mathrm{l}\times\underline{a}$, $\underline{B}=\mathrm{m}\times\underline{b}$ and $\underline{C}=\mathrm{n}\times\underline{c}$ respectively (l,m and n being integers). The volume of the MD cell is then l×m×n times the unit cell volume. The advantages of this approach, particularly when constructing the initial lattice or analysing the simulated structural properties, are obvious.

Two questions that immediately arise from this are: (a) how does one go about formulating such a scheme? and (b) is it an efficient way to proceed? The purpose of this note is to discuss some aspects of these questions.

Formulating the Scheme

Since the problem arises most commonly in simulations of crystalline systems, it is natural to resort to the methods of crystallographers. In crystallography, the crystal structure is defined by the unit cell vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$ and the so-called fractional coordinates $\underline{s}_i$ of the ions within the unit cell [3]. The components s_{xi}, s_{yi} and s_{zi}, of the vectors $\underline{s}_i$ range in value from 0 to 1, hence their name. The positions $\underline{r}_i$ of the ions in the crystal are given by:

$$\underline{r}_i = s_{xi}\underline{a} + s_{yi}\underline{b} + s_{zi}\underline{c}$$

or in matrix notation:

$$\underline{r}_i = \underline{\underline{h}}\ \underline{s}_i$$

Where the columns of the matrix $\underline{\underline{h}}$ are composed of the vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$. It therefore appears that we have two ways of defining the location of an ion in the cell; the location in *real* space defined by $\underline{r}_i$ and the location in *dimensionless* space defined by $\underline{s}_i$. It turns out that we need to use both of these coodinate systems to formulate a periodic boundary condition for MD simulations. In what follows, to reduce verbiage, I refer to $\underline{r}_i$ as vectors in $\mathcal{R}$ space and $\underline{s}_i$ as vectors in $\mathcal{S}$ space.

Figure 1

The relationship between the unit cell and the MD cell (in 2D).

Figure 2

A problematic arrangement of ions in the proposed periodic boundary scheme (a 2D analogy). Ion A is near the centre line of the cell. The scheme will select the image B' in preference to B", which is actually the nearer of the two images. The use of an appropriate spherical cutoff removes this difficulty (see text).

In this formulation we therefore think of the MD cell as being a kind of "unit cell" defined by the vectors $\underline{A}$, $\underline{B}$ and $\underline{C}$ described above. The locations of the ions within the cells are therefore defined in matrix notation by:

$$\underline{r}_i = \underline{\underline{H}}\ \underline{s}_i$$

Where matrix $\underline{\underline{H}}$ is composed of the vectors $\underline{A}$, $\underline{B}$ and $\underline{C}$ analogous to the unit cell case. We may perform the simulation in either $\mathcal{R}$ or $\mathcal{S}$ space, though if we use the latter we will have to use the Lagrangian formulation of mechanics in place of the more common Newtonian [4]. Despite this apparent additional complexity I have found this option advantageous in dealing with ionic systems, since then the Ewald sum is more easily dealt with [5]. However to avoid a lengthy digression I will assume that we are to work in $\mathcal{S}$ space, but note that the alternative is equally acceptable. I will use the relationship between the $\underline{r}_i$ and $\underline{s}_i$ coordinates to refer back to the *real* world where necessary.

It is a characteristic of $\mathcal{S}$ space coordinates that the location of the periodic images in the infinite crystal of an ion labeled i is accomplished by the simple addition of an integer to each of the components of $\underline{s}_i$. If we are concerned only to find those image ions in the immediately adjacent cells, they can all be found by adding or subtracting unity. This is all we need to know to formulate the periodic boundary scheme in the MD simulation!.

In MD the periodic boundary is employed in two circumstances. Firstly, it is used to relocate ions, that have moved out of the MD cell in the course of the simulation, back into the cell at its image point, to maintain the total number of ions in the cell. Secondly, for a given ion, it is used to find the nearest image of each other ion in the MD cell, in order to calculate the pair forces and energies.

The first case is easy to describe and, if we are working in $\mathcal{S}$ space, easy to apply; we simply replace each $\underline{s}_i$ by its corrected vector $\underline{s}_i^c$:

$$\underline{s}_i^c = \underline{s}_i - INT(2\underline{s}_i - \underline{1})$$

Where $\underline{1}$ is a vector with unit components. (Note that the MD cell has faces at $s_x = 0$ and $s_x = 1$ in this case, and not at $s_x = -1$ and $s_x = +1$ as is commonly used in MD. The same comment applies in the y and z directions also.) The second case is more complicated, because we do not wish merely to locate an image ion, but we must be sure it is the *nearest* image and this necessitates working in both $\mathcal{S}$ and $\mathcal{R}$ spaces. To be specific, we have an ion pair labelled i and j and we wish to calculate their separation in both $\mathcal{S}$ and $\mathcal{R}$ spaces (i.e. $\underline{s}_{ij}$ and $\underline{r}_{ij}$), such that the $\underline{r}_{ij}$ *is the smallest possible*. It turns out to be simpler than may be anticipated. Working in $\mathcal{S}$ space we calculate

$$\underline{s}_{ij} = (\underline{s}_i - \underline{s}_j) - INT(2(\underline{s}_i - \underline{s}_j) - \underline{1})$$

Which is essentially the same as the above equation for relocating wayward ions. Our next step is even simpler:

$$\underline{r}_{ij} = \underline{\underline{H}}\ \underline{s}_{ij}$$

Where $\underline{\underline{H}}$ is the matrix defining the MD cell. This is all we need!

An argument I have heard opposing this scheme is that it may not pick out the correct nearest image for ions separated by distances close to half the width of the MD cell. That such a suggestion is made is understandable when one realises that the selection of the nearest image is made in $\mathcal{S}$ space, where the anisotropy of the real MD cell has been removed. (The kind of circumstances where problems are most easily seen are shown in Figure 2.) However, the procedure is safe if one is using a spherical cutoff in $\mathcal{R}$ space, the radius of which *is not greater than half the smallest perpendicular width of the MD cell.* In mathematical terms: If we define the perpendicular widths of the cell as:

$$W_A = |\underline{A} \bullet \underline{B} \times \underline{C}|/|\underline{B} \times \underline{C}|$$

$$W_B = |\underline{B} \bullet \underline{C} \times \underline{A}|/|\underline{C} \times \underline{A}|$$

$$W_C = |\underline{C} \bullet \underline{A} \times \underline{B}|/|\underline{A} \times \underline{B}|$$

(This is, of course, merely the shortest distance between opposing faces of the MD cell). Then the condition for non-violation of the minimum image convention is:

$$R_c < 0.5 * MIN(W_A, W_B, W_C)$$

The proof of this simple. In the appendix I show that an ion at the centre of a sphere of radius R_c defined as above, can only interact with one of the images of the other ions in the MD cell and that this image must necessarily be the nearest.

Efficiency

The algorithm described above has the merit of simplicity, but something should be said about its efficiency. The main point I should raise is that the requirement of a spherical cutoff to guarantee the minimum image can result in lower efficency than for simple cubic boundary conditions. There is not only the matter of the additional computation associated with the matrix operations described above and which may or may not matter much if the forces being calculated are relatively expensive. There is also the fact that volume of the sphere enscribed by the cutoff *at best* can only contain approximately half the ions that the cell contains. Therefore if one choses to use a parallelepiped MD cell that is far removed from a cube, one should recall that much effort will go into calculating the distance between ions which subsequently will be deemed to be non-inteacting. In such circumstances the use of a 'Neighbour List' method [6] may be essential. Alternatively, one could consider an alternative unit cell for the system, which is more like a cube. Fortunately this is often easier than it sounds.

Readers who have their own methods for dealing with the problem outlined in this note are invited to contribute their solutions!

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Appendix

Proof of Validity of Minimum Image

The proof given here is not rigorous in the mathematical sense, but I hope the argument is sufficiently clear to warrant its acceptance. Basically, it goes as follows:

1. Each ion has a fractional coordinate $\underline{s}_i$ in $\mathcal{S}$ space that is related to its coordinate in $\mathcal{R}$ space by the relation:
$$\underline{r}_i = \underline{\underline{H}}\ \underline{s}_i$$
where $\underline{\underline{H}}$ is the matrix defining the MD cell.
2. Since the system is infinitely periodic the location of the cell origin is immaterial. Suppose we chose the origin to be at the location of one of the ions. I call this the shifted cell, to distinguish it from the original cell.
3. The shifted cell will, by definition, contain *unique* images of all the ions. i.e. within this cell no two ions will be periodic images of each other. The shifting procedure is best carried out in $\mathcal{S}$ space, using the integer arithmetic described above.
4. Even though the shift of the cell origin is performed in $\mathcal{S}$ space, the same ion will be at the origin of the corresponding cell in $\mathcal{R}$ space. Furthermore, there will be a one-to-one correspondence between all the ions in the $\mathcal{S}$ space cell and those in the $\mathcal{R}$ space cell. Hence the ions in the $\mathcal{R}$ space cell also form a unique set - none is the periodic image of another in the same cell.
5. A sphere drawn in $\mathcal{R}$ space around the central ion of radius less than the minimum width of the cell *cannot include ions that are periodic images of each other.* This must follow because the sphere is contained within the cell and the cell has no internal periodic images.

6. *Therefore all pair interactions between the central ion and the other ions within the same sphere are unique and necessarily represent the nearest image interactions of the central ion.*
7. Clearly, we may now consider any other ion as being at the centre of the cell and repeat the argument. This proves that all the interactions calculated in this scheme satisfy the minimum image convention.

References

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