

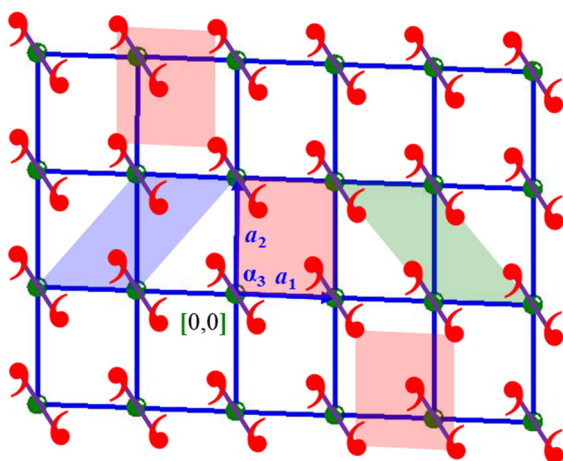
TRANSLATIONAL SYMMETRY

Crystals consist of molecules or atoms that repeat regularly throughout real space. Regular repetition is *translational periodicity*. Therefore, translational periodicity in a crystal means that the electron density $\rho(\mathbf{r})$ at any point \mathbf{r} follows the two equations:

$$\rho(\mathbf{r} + \mathbf{T}) = \rho(\mathbf{r}) \text{ and } \nabla\rho(\mathbf{r} + \mathbf{T}) = \nabla\rho(\mathbf{r})$$

in which \mathbf{T} represents a member of a *lattice*. Not only does the value of electron density repeat periodically but so also does its directional derivatives. In other words, for any specified point \mathbf{r} in a crystal, a lattice locates all points $\mathbf{r} + \mathbf{T}$ that have identical and identically oriented environments as point \mathbf{r} .

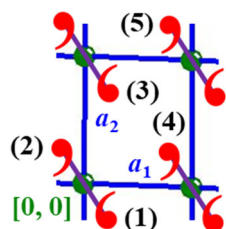
- (5) Lattices: In two-dimensional (2-d) real space, a lattice can be described in one of three ways:
- an infinite, discrete set of points $\{[n_1, n_2]\}$;
 - an infinite, discrete set of vectors $\{\mathbf{T}_{n_1 n_2}\}$; and
 - an infinite set of space-filling (non-overlapping) identical unit cells.



2-d crystalline structure showing its lattice (blue) and some unit cells. Lattice points are noted in green. The standard choice of unit cell is shaded in red.

For 2-d space, there are two linearly independent basis vectors \mathbf{a}_1 and \mathbf{a}_2 between adjacent lattice points, so that every lattice vector $\mathbf{T}_{n_1 n_2} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$ for any pair of integers n_1 and n_2 . The basis vectors form a parallelogram with sides a_1 and a_2 and interior angle α_3 . Although selection of the origin point $[0, 0]$ is arbitrary, it is chosen to be a site of either highest point symmetry or inversion of the overall crystalline structure. Often, these two characteristics coincide, but sometimes these two positions differ. In the illustration, the lattice points $[n_1, n_2]$ are at the corners of the unit cells and are shared by 4 adjacent unit cells. As a result of the space-filling nature of these shapes, each lattice point belongs to one unit cell, the so-called *primitive cell*. In other words, the area of one primitive unit cell contains one and only one lattice point of the crystalline lattice. As the figure indicates, basis vectors are not unique because there are different shapes that have the same area. However, the standard choice of unit cell is to use the smallest independent distances and an angle falling between 90° and 120° inclusive.

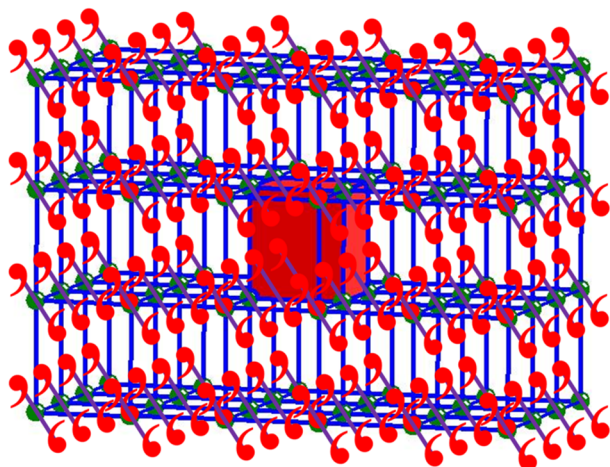
Once the unit cell (basis) vectors are chosen, then every point \mathbf{r} in 2-d space can be identified by *fractional coordinates* $[x, y]$ relative to the origin $[0, 0]$: $\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2$. Points within the unit cell assigned to the origin have fractional coordinates $0 \leq x < 1$ and $0 \leq y < 1$. Therefore, $\mathbf{r} + \mathbf{T}_{n_1 n_2} = (x + n_1)\mathbf{a}_1 + (y + n_2)\mathbf{a}_2$. The figure below illustrates the application of fractional coordinates to locate five different points of the structure with respect to the origin point:



- (1) A visual estimate is $[+0.20, -0.25]$: $0.20\mathbf{a}_1 - 0.25\mathbf{a}_2$.
 (2) Related to (1) via inversion $[-0.20, +0.25]$: $-0.20\mathbf{a}_1 + 0.25\mathbf{a}_2$.
 (3) Related to (1) by translation along \mathbf{a}_2 $[+0.20, +0.75]$: $0.20\mathbf{a}_1 + 0.25\mathbf{a}_2$.
 (4) Related to (2) by translation along \mathbf{a}_1 $[+0.80, +0.25]$: $0.80\mathbf{a}_1 + 0.25\mathbf{a}_2$.
 (5) Related to (2) by translation $\mathbf{a}_1 + \mathbf{a}_2$ $[+0.80, +1.25]$: $0.80\mathbf{a}_1 + 1.25\mathbf{a}_2$.

2-d Lattices are useful for identifying translational periodicity of surfaces, 2-d structures like graphene, and 2-d projections of 3-d crystals.

- (6) In three-dimensional (3-d) real space, a lattice can also be described in one of three ways:
 (a) an infinite, discrete set of points $\{[n_1, n_2, n_3]\}$;
 (b) an infinite, discrete set of vectors $\{\mathbf{T}_{n_1n_2n_3}\}$; and
 (c) an infinite set of space-filling (non-overlapping) identical unit cells.



3-d crystalline structure showing its lattice (blue) and unit cell. Lattice points are noted in green.

Now, there are three linearly independent basis vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 between adjacent lattice points, so that every lattice vector $\mathbf{T}_{n_1n_2n_3} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ for any triplet of integers n_1 , n_2 , and n_3 . The basis vectors form a parallelepiped with sides a_1 , a_2 , and a_3 and interior angles α_1 (between \mathbf{a}_2 and \mathbf{a}_3), α_2 (between \mathbf{a}_1 and \mathbf{a}_3), and α_3 (between \mathbf{a}_1 and \mathbf{a}_2). This region is a primitive unit cell because it belongs to one lattice point and its origin, albeit arbitrary, falls at the site of either highest point symmetry or inversion. In the figure, the lattice points are at the 8 unit cell corners, which are each shared with 8 adjacent cells. Therefore, the volume of one primitive unit cell contains one and only one lattice point. Like 2-d lattices, the basis vectors of 3-d lattices are not unique, but the standard choice is to use the smallest independent distances and angles ranging between 90° and 120° inclusive. Conventional crystallographic descriptions of unit cell vectors use the symbols \mathbf{a} , \mathbf{b} , and \mathbf{c} : lengths a , b , c , and angles α , β , γ .

(7) The Lattice as a Group: Each description of a lattice is a set that forms a mathematical group. Using the vector description for 2-d space $\{\mathbf{T}_{n_1n_2}\}$, the members of the lattice set combine under vector addition. This set obeys the four characteristics of every group:

- (i) the set is *closed*: $\mathbf{T}_{m_1m_2} + \mathbf{T}_{n_1n_2} = \mathbf{T}_{m_1+n_1, m_2+n_2}$, which is a member of the same set because addition of integers gives integers;
 (ii) vector addition is *associative*: $(\mathbf{T}_{m_1m_2} + \mathbf{T}_{n_1n_2}) + \mathbf{T}_{p_1p_2} = \mathbf{T}_{m_1m_2} + (\mathbf{T}_{n_1n_2} + \mathbf{T}_{p_1p_2})$;

- (iii) the *identity* exists $\mathbf{T}_{00}: \mathbf{T}_{n_1 n_2} + \mathbf{T}_{00} = \mathbf{T}_{n_1 n_2} = \mathbf{T}_{00} + \mathbf{T}_{n_1 n_2}$; and
- (iv) an *inverse* exists for every member $\mathbf{T}_{n_1 n_2}: \mathbf{T}_{-n_1 -n_2} = -\mathbf{T}_{n_1 n_2}$,
 $\mathbf{T}_{n_1 n_2} + \mathbf{T}_{-n_1 -n_2} = \mathbf{T}_{-n_1 -n_2} + \mathbf{T}_{n_1 n_2} = \mathbf{T}_{00}$.

Since vector addition is also *commutative*, i.e., $\mathbf{T}_{m_1 m_2} + \mathbf{T}_{n_1 n_2} = \mathbf{T}_{n_1 n_2} + \mathbf{T}_{m_1 m_2}$, the set of lattice translations is an *abelian group*. As a result, each member $\mathbf{T}_{n_1 n_2}$ belongs to its own class, which has important implications for features of the electronic states of crystals.

(8) Identifying Lattices and Unit Cells in Periodic Structures: The Dutch graphic artist M.C. Escher, who lived 1898-1972, constructed diagrams that include periodic wallpaper patterns. These diagrams exhibit 2-d periodicity and were inspired by his visit to El Alhambra, a Spanish palace and fortress complex that contains numerous tilings. Here are two examples:



Source: <https://mcescher.com/gallery/symmetry/> (© The M.C. Escher Company B.V.)

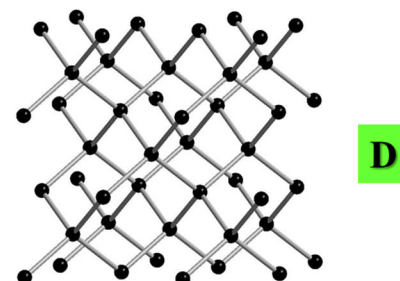
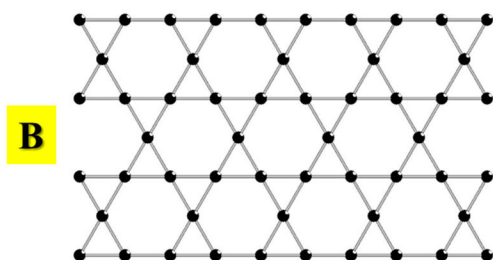
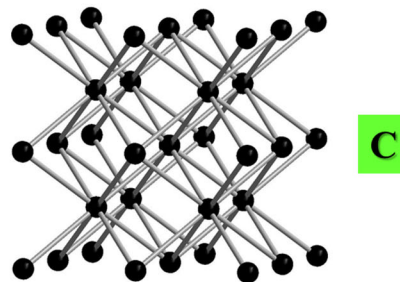
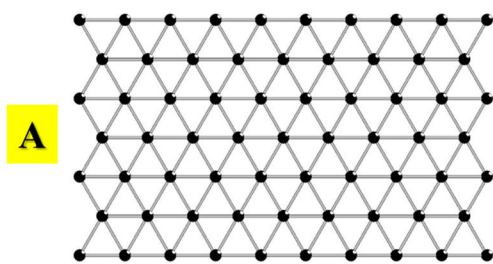
To identify the lattice and unit cells for each 2d pattern, follow these steps:

- Place a first lattice point at any site in the pattern. Although this is an arbitrary decision, we are probably drawn to positions of highest rotational symmetry in the diagram. For example, the left figure has points with 3-fold symmetry.
- Examine the pattern for all positions that have identical environments as the location of the “first lattice point”. These environments must also be identically oriented in the plane. Place points at these positions in the diagram. You have now successfully drawn the lattice.
- From one lattice point, draw connections to the nearest points in two different directions, which identify two sides of the unit cell. Complete the cycle of connections by drawing two parallel connections, and you have a unit cell for the lattice.



Using these two patterns, one can find different locations for sets of lattice points in a repeating pattern. Nevertheless, the shapes and sizes of the smallest unit cells are the same, regardless of where the lattice points are placed in a pattern.

(9) QUESTION: Four networks of atoms (points) and bonds (lines) are shown. Which ones are lattices; which ones are not?



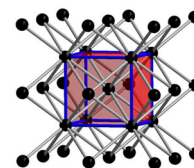
ANSWER: Synonyms of “lattice” include “frame”, “framework”, “grid”, “net”, “network”, and “trellis”, all of which are less strict than any mathematical definition, like the one described above. To establish whether or not a network of atoms is a *lattice*, then its surroundings must be completely identical in shape and orientation in space.

A: The 2-d triangular net. Every point is surrounded by 6 neighboring atoms in a regular hexagon. The Schläfli symbol of this 2-d network is 3^6 , which means that every point is surrounded by 6 triangles (“3”). The primitive unit cell is a rhombus. YES, the 2-d triangular net is a lattice.

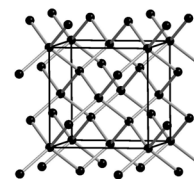
B: The 2-d Kagomé net. Every point is surrounded by 4 atoms, but they occur in three different orientations. Therefore, not all points in the network are *translationally equivalent*. The Schläfli symbol is 3636. The unit cell that describes the translational periodicity of this structure contains 3 points. NO, the 2-d Kagomé net is not a lattice.

Representations of 3-d structures are more challenging because they must be projections in 2-d. Learning how to visualize 3-d structures is an important skill for chemists that requires imagination and practice.

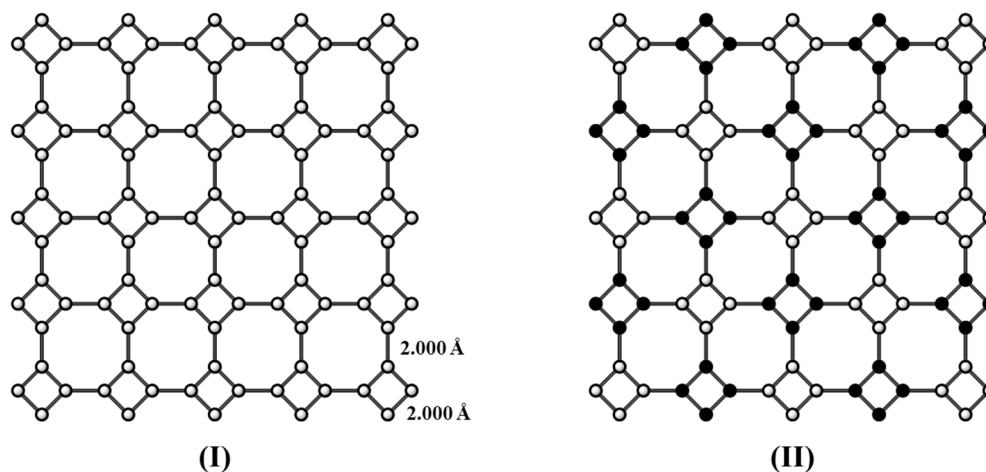
C: The 3-d body-centered cubic (BCC) network. Every point is surrounded by a cube with 8 neighbors. YES, the 3-d BCC net is a lattice.



D: The 3-d diamond network. Every point is surrounded by 4 others in a local tetrahedral arrangement, but with two different orientations. Therefore, like the 2-d Kagomé net, not all points in the diamond net are *translationally equivalent*. A unit cell that represents 3-d translational periodicity, i.e., one that connects a set of points with identically oriented environments, is a face-centered cubic (FCC) lattice. NO, the diamond net is not a lattice. (NOTE: given the broader definition of “lattice” mentioned above, you may find the term “diamond lattice” in the literature.)

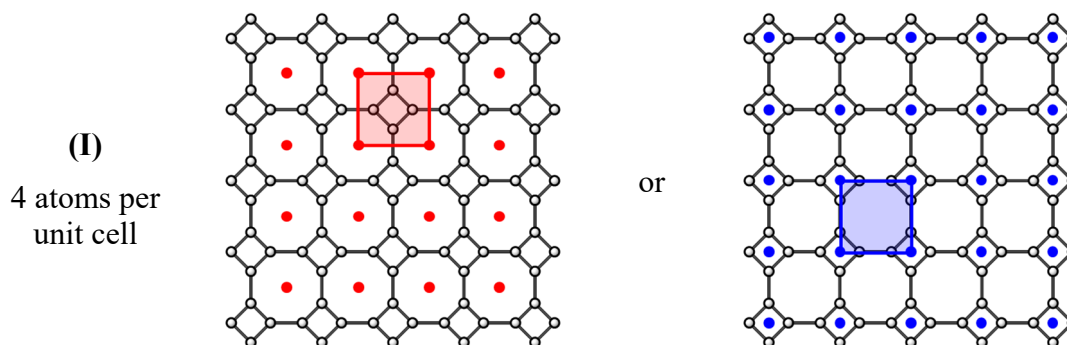


(10) PROBLEM: (a) For each structure illustrated, draw a lattice and one unit cell. How many atoms fall within one unit cell? (b) For your choice of unit cell in structure (I), evaluate the lattice constants and determine the fractional coordinates of the atoms in one unit cell using the interatomic distances shown.

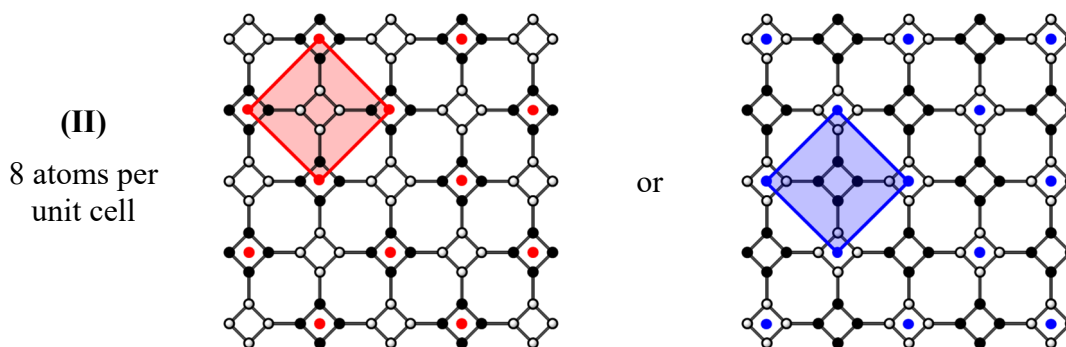


ANSWER: There are multiple satisfactory choices for assigning the location of lattice points in each structure, but there are symmetry-based guidelines to select the *best choice* for the lattice and its unit cells. Lattice points should have the highest-order rotational symmetry or should coincide with inversion centers of the structure. For many cases, the locations with highest order point symmetry include inversion centers, but this is not always the case. When these two specifications yield different positions in the crystal, then the lattice will have *two settings*.

(a) Using these guidelines, the sites of highest rotational symmetry coincide with inversion centers in both structures I and II. Nevertheless, there are two possible solutions for each structure:

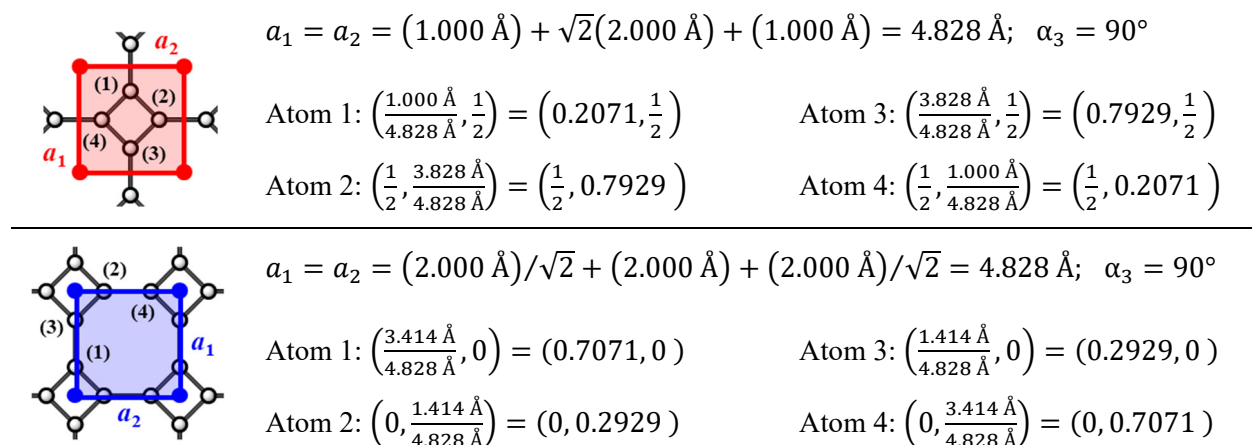


There is just one kind of atom in structure (I) and four-fold symmetry occurs at the centers of the squares and octagons, characteristics that give two acceptable solutions for setting the lattice. In both cases, the unit cells are identical in size and shape. When the lattice points are placed at the centers of octagons, it is straightforward to count 4 atoms in one unit cell. For the other choice, the atoms fall on unit cell edges, which are shared between two adjacent cells. Since there are 8 atoms on the edges, then there are $8/2$ or 4 atoms per unit cell.



There are two kinds of atoms forming two different squares in structure (II). As a result, four-fold symmetry occurs only at the centers of the squares; the centers of octagons have two-fold symmetry. Again, there are two acceptable solutions, with lattice points located at the centers of one type of square. In each case, there are 8 atoms per unit cell: 4 open circles and 4 closed circles.

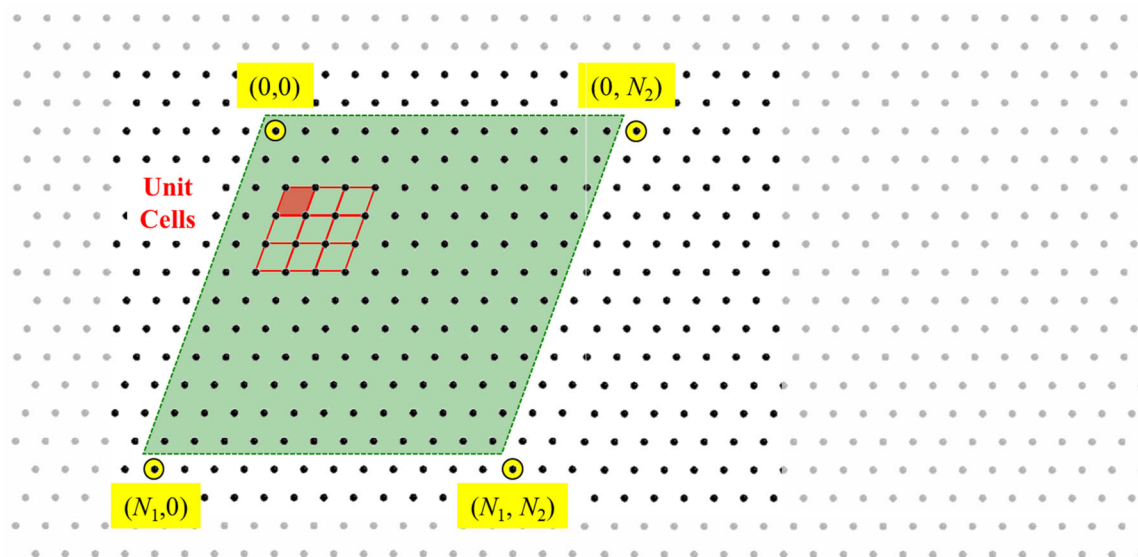
(b) For structure (I), all interatomic distances are 2.000 \AA and the interior angles of the four-membered rings are 90° . Then, apply straightforward geometry as follows:



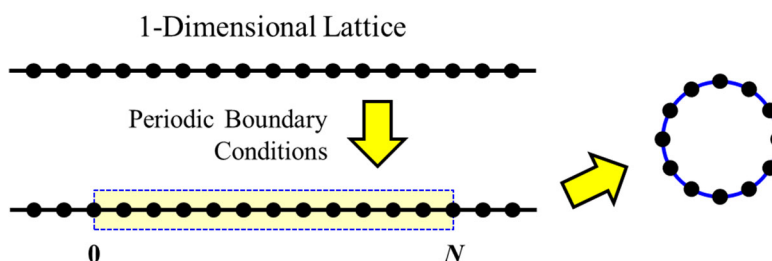
As expected, geometry gives the identical sizes and shapes for the two unit cells, but the fractional coordinates of the atoms depend on their exact locations in each cell. Nevertheless, the numbers assigned in each diagram are for the same atoms in the structure.

(11) Periodic Boundary Conditions: The definition of a crystalline lattice is an infinite set of points, vectors, or unit cells, but all real crystals are finite in size. The best quality single crystals consist of grains that contain 10^{19} - 10^{21} unit cells, so the lattice is, at best, a quasi-infinite set. Such dimensions, however, make computations of electronic structures and other properties intractable, so an approximation is needed to lower the order of the lattice set while keeping important characteristics of the crystal. *Periodic (Born-von Karman) boundary conditions* are designed to make physical problems for crystalline structures reasonably solvable and involve selecting a large, finite subset of lattice points for any crystalline lattice.

Consider the following 2-d lattice in which any lattice vector is $\mathbf{T}_{mn} = m\mathbf{a}_1 + n\mathbf{a}_2$ for all integers m and n . The lattice vectors \mathbf{a}_1 and \mathbf{a}_2 outline the basic primitive cell for this lattice, outlined in red. The finite region for which periodic boundary conditions apply is designated by the set $\{\mathbf{T}_{n_1 n_2} : 0 \leq n_1 < N_1; 0 \leq n_2 < N_2\}$ for large integers N_1 and N_2 and is emphasized by green:



Then, for all functions $f(\mathbf{r})$ of the crystalline structure, application of periodic boundary conditions means that $f(\mathbf{r} + \mathbf{T}_{N_1N_2}) = f(\mathbf{r})$. In other words, the lattice vector $\mathbf{T}_{N_1N_2}$ behaves like the identity \mathbf{T}_{00} . As a result, the subset of the quasi-infinite lattice remains an abelian group. Applied to a 1-d lattice, the periodic boundary condition converts a quasi-infinite chain of lattice points into a ring of N points:



Likewise, the 2-d plane is mathematically transformed into a torus, and so on. Now, the electron density $\rho(\mathbf{r})$ of a crystal has the full periodicity of the lattice, $\rho(\mathbf{r} + \mathbf{T}_{n_1n_2}) = \rho(\mathbf{r})$ for all integers n_1 and n_2 . On the other hand, the electronic wavefunctions (crystal orbitals) do not, but *they must obey the periodic boundary conditions*, i.e.,

$$\psi(\mathbf{r} + \mathbf{T}_{n_1n_2}) = e^{i\omega T_{n_1n_2}} \psi(\mathbf{r}) \text{ but } \psi(\mathbf{r} + \mathbf{T}_{N_1N_2}) = e^{i\omega T_{N_1N_2}} \psi(\mathbf{r}) = \psi(\mathbf{r}).$$

The resulting finite lattice set allows for effective computations of electronic states.

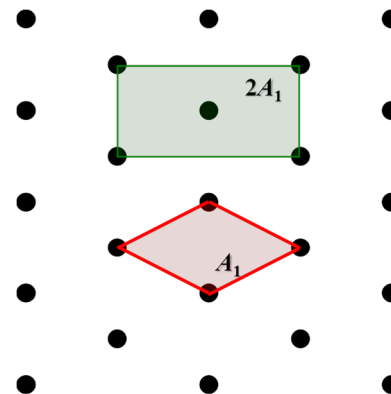
(12) Unit Cells with Rotational Symmetry: Unit cells are non-overlapping regions of crystalline structures that completely fill real space by repeating periodically. For any crystalline lattice, the smallest fundamental region is a primitive unit cell with edges that connect adjacent lattice points in the independent directions. For 2-d lattices, these regions are parallelograms with 4 edges and 4 corners with area A_1 ; for 3-d lattices, they are parallelehedra with 6 faces, 12 edges, and 8 corners with volume V_1 . Therefore, the primitive unit cell of any lattice contains one and only one lattice point. Using the standard nomenclature for primitive cell edge lengths and angles, A_1 and V_1 are:

$$\text{2-d: } A_1 = a_1 a_2 \sin \alpha_3;$$

$$\text{3-d: } V_1 = a_1 a_2 a_3 [1 - \cos^2 \alpha_1 - \cos^2 \alpha_2 - \cos^2 \alpha_3 + 2 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3]^{1/2}.$$

Although any primitive unit cell of a crystalline structure contains all atoms needed to generate the entire structure by translational periodicity, the cell's shape may not display the full rotational symmetry of the lattice. Since rotationally symmetric unit cells are useful for many applications, there are two important types of unit cells that account for both translational and rotational symmetry:

- (1) *Crystallographic unit cells* are rotationally symmetric primitive or non-primitive cells. If the primitive unit cell does not display the complete rotational symmetry of its lattice, then a non-primitive cell can be identified that does. Such cells are called *centered* because of the locations of additional lattice points. For the 2-d lattice shown here, the primitive cell is diamond-shaped, but a larger rectangular-shaped cell is also possible. The larger cell contains 2 lattice points, one at the corners and one at the center, so that this lattice is described as *centered-rectangular*. Although the primitive, diamond-shaped cell also satisfies the rotational constraints, the centered rectangular cell directly mimics the rectangular symmetry of this lattice.



Centered rectangular (crystallographic) unit cell and the diamond-shaped primitive cell for a 2-d lattice.

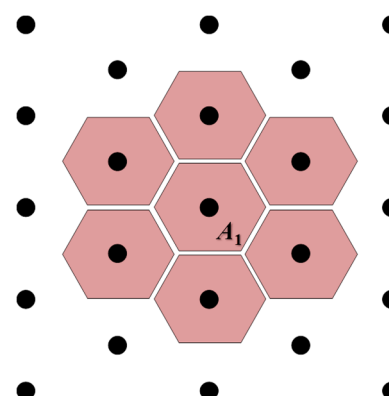
Crystallographic unit cells, whether primitive or centered, are used to describe the structures of crystalline solids. Their unit cell vectors are designated as \mathbf{a} , \mathbf{b} , and \mathbf{c} , so that the unit cell sides have lengths a , b , c and interior angles α (between \mathbf{b} and \mathbf{c}), β (between \mathbf{a} and \mathbf{c}), γ (between \mathbf{a} and \mathbf{b}). If a non-primitive crystallographic cell contains n lattice points, then its size is n times the size of the primitive cell. For 2-d and 3-d lattices, the corresponding area and volume of the crystallographic cells are:

$$2\text{-d: } A_n = ab \sin \gamma = nA_1;$$

$$3\text{-d: } V_n = abc[1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2 \cos \alpha \cos \beta \cos \gamma]^{1/2} = nV_1.$$

These unit cells are used by crystallographers, but the primitive unit cells are sufficient for computational scientists to use as structural input for most electronic structure calculations.

- (2) *Wigner-Seitz cells* are rotationally symmetric primitive unit cells that enclose the regions of space closest to one lattice point. To construct a Wigner-Seitz cell, choose one lattice point and identify all surrounding lattice points, which extend to nearest and possibly next-nearest neighbor points. Then, construct the perpendicular bisectors between the selected origin point and every neighbor. The region formed by these bisectors completely encloses the origin lattice point and is the Wigner-Seitz cell for the lattice. Like crystallographic cells, Wigner-Seitz cells completely fill the space of the lattice without overlapping or gaps. Being a primitive cell, its size is A_1 in 2-d or V_1 in 3-d. These cells are important for electronic structure calculations, but their generally complex shapes have limited their application in crystallography. In real space, these regions are called Voronoi polyhedra (polygons) and Dirichlet domains and can be useful to evaluate coordination numbers at atoms.



2-d Wigner-Seitz cells