Q: How can we describe these lattice vectors (there are an infinite number of them)?
A: Using primitive lattice vectors (there are only d of them in a d-dimensional space).

For a 3D lattice, we can find three primitive lattice vectors (primitive translation vectors), such that any translation vector can be written as

\[ \vec{t} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \]

where \( n_1, n_2 \) and \( n_3 \) are three integers.

For a 2D lattice, we can find two primitive lattice vectors (primitive translation vectors), such that any translation vector can be written as

\[ \vec{t} = n_1 \vec{a}_1 + n_2 \vec{a}_2 \]

where \( n_1 \) and \( n_2 \) are two integers.

For a 1D lattice, we can find one primitive lattice vector (primitive translation vector), such that any translation vector can be written as

\[ \vec{t} = n_1 \vec{a}_1 \]

where \( n_1 \) is an integer.
**Primitive lattice vectors**

Red (shorter) vectors: \( \vec{a}_1 \) and \( \vec{a}_2 \)

Blue (longer) vectors: \( \vec{b}_1 \) and \( \vec{b}_2 \)

\( \vec{a}_1 \) and \( \vec{a}_2 \) are primitive lattice vectors

\( \vec{b}_1 \) and \( \vec{b}_2 \) are NOT primitive lattice vectors

\[
\vec{b}_1 = 2\vec{a}_1 + 0\vec{a}_2
\]

Integer coefficients

\[
\vec{a}_1 = \frac{1}{2}\vec{b}_1 + 0\vec{b}_2
\]

Noninteger coefficients
The choices of primitive lattice vectors are NOT unique.
The parallelogram defined by two primitive lattice vectors form a primitive cell.

- The area of a primitive cell: \( A = |\vec{a}_1 \times \vec{a}_2| \)
- Each primitive cell contains 1 site.
The **parallelepiped** defined by the three primitive lattice vectors are called a **primitive cell**.

The volume of a primitive cell: \( V = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)| \)

- each primitive cell contains 1 site.
The volume of a Wigner-Seitz cell is the same as a primitive cell.

Each Wigner-Seitz cell contains 1 site (same as a primitive cell).
Rotational symmetries:
If a system goes back to itself when we rotate it along certain axes by some angle $\theta$, we say that this system has a rotational symmetry.

- For the smallest $\theta$, $2\pi / \theta$ is an integer, which we will call $n$.
- We say that the system has a $n$-fold rotational symmetry along this axis.

For Bravais lattices,
- It can be proved that $n$ can only take the following values: 1, 2, 3, 4 or 6.
Mirror Planes:
2D Bravais lattices

1. $|a_1| \neq |a_2|, \varphi \neq 90^\circ$
2. $|a_1| \neq |a_2|, \varphi = 90^\circ$
3. $|a_1| \neq |a_2|, \varphi \neq 90^\circ$
4. $|a_1| = |a_2|, \varphi = 120^\circ$
5. $|a_1| = |a_2|, \varphi = 90^\circ$

http://en.wikipedia.org/wiki/Bravais_lattice
3D Bravais lattices

http://en.wikipedia.org/wiki/Bravais_lattice
Cubic system

Conventional cells

- For a simple cubic lattice, a conventional cell = a primitive cell
- NOT true for body-centered or face-centered cubic lattices

How can we see it?
- sc: one conventional cell has one site (same as a primitive cell)
- bcc: one conventional cell has two sites (twice as large as a primitive cell)
- fcc: one conventional cell has four cites (1 conventional cell=4 primitive cells)
Simple cubic

Lattice sites: $a(l \hat{x} + m \hat{y} + n \hat{z})$

Lattice point per conventional cell: $1 = 8 \times \frac{1}{8}$

Volume (conventional cell): $a^3$

Volume (primitive cell): $a^3$

Number of nearest neighbors: 6

Nearest neighbor distance: $a$

Number of second neighbors: 12

Second neighbor distance: $\sqrt{2}a$

Packing fraction: $\frac{\pi}{6} \approx 0.524$

Coordinates of the sites: $(l, n, m)$

For the site $(0,0,0)$,
6 nearest neighbors: $(\pm 1,0,0), (0, \pm 1,0)$ and $(0,0, \pm 1)$
12 nest nearest neighbors: $(\pm 1, \pm 1,0), (0, \pm 1, \pm 1)$ and $(\pm 1,0, \pm 1)$
Packing fraction:
We try to pack $N$ spheres (hard, cannot deform).

The total volume of the spheres is $N4 \pi \frac{R^3}{3}$

The volume these spheres occupy $V > N4 \pi \frac{R^3}{3}$ (there are spacing)

Packing fraction = total volume of the spheres/total volume these spheres occupy

\[
Packing\ fraction = \frac{N4 \pi \frac{R^3}{3}}{V} = \frac{4 \pi \frac{R^3}{3}}{V/N} = \frac{4 \pi \frac{R^3}{3}}{Volume\ per\ site}
\]

\[= \frac{4 \pi \frac{R^3}{3}}{Volume\ of\ a\ primitive\ cell}\]

High packing fraction means the space is used more efficiently
Lattice sites: \(a(l \hat{x} + m \hat{y} + n \hat{z})\)

Lattice point per conventional cell: \(1 = 8 \times \frac{1}{8}\)

Volume (conventional cell): \(a^3\)

Volume (primitive cell): \(a^3\)

Number of nearest neighbors: 6

Nearest neighbor distance: \(a\)

Number of second neighbors: 12

Second neighbor distance: \(\sqrt{2}a\)

Packing fraction: \(\frac{\pi}{6} \approx 0.524\)

\[
Packing\ fraction = \frac{4\pi\frac{R^3}{3}}{Volume\ of\ a\ primitive\ cell} = \frac{4\pi\frac{R^3}{3}}{\frac{4\pi}{3} \left(\frac{R}{a}\right)^3} = \frac{4\pi}{3} \left(\frac{a/2}{a}\right)^3 = \frac{\pi}{6} \approx 0.524
\]

- About half (0.524=52.4%) of the space is really used by the sphere.
- The other half (0.476=47.6%) is empty.
Lattice sites
\[ a(l \hat{x} + m \hat{y} + n \hat{z}) \text{ and } a[(l + \frac{1}{2}) \hat{x} + (m + \frac{1}{2}) \hat{y} + (n + \frac{1}{2}) \hat{z}] \]

Lattice point per conventional cell: \[ 2 = 8 \times \frac{1}{8} + 1 \]
Volume (conventional cell): \( a^3 \)
Volume (primitive cell): \( a^3 / 2 \)
Number of nearest neighbors: 8
Nearest neighbor distance: \[ \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{\sqrt{3}}{2} a \approx 0.866 a \]
Number of second neighbors: 6
Second neighbor distance: \( a \)

Packing fraction: \[ \frac{\sqrt{3}}{8} \pi \approx 0.680 \]
Coordinates of the sites: \((l, n, m)\)
For the site \((0,0,0)\),
8 nearest neighbors: \( \left(\pm \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2}\right) \)
6 nest nearest neighbors: \((\pm 1,0,0), (0, \pm 1,0) \text{ and } (0,0, \pm 1)\)
Volume (primitive cell): \( a^3 / 2 \)

Nearest neighbor distance: \( \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{\sqrt{3}}{2} a \approx 0.866 a \)

Packing fraction: \( \frac{\sqrt{3}}{8} \pi \approx 0.680 \)

Packing fraction = \( \frac{4 \pi \frac{R^3}{3}}{\text{Volume of a primitive cell}} \)

\[
= \frac{4 \pi \frac{R^3}{3}}{\frac{a^3}{2}} = \frac{8\pi}{3} \left(\frac{R}{a}\right)^3 = \frac{8\pi}{3} \left(\frac{\sqrt{3}}{4} a\right)^3 = \frac{\sqrt{3}\pi}{8} \approx 0.680
\]

- About 68.0% of the space is really used by the sphere.
- About 32.0% of the space is empty.
Lattice sites
\[ a(l \hat{x} + m \hat{y} + n \hat{z}) \quad a\left[(l + \frac{1}{2}) \hat{x} + (m + \frac{1}{2}) \hat{y} + n \hat{z}\right]\]
\[ a\left[(l + \frac{1}{2}) \hat{x} + m \hat{y} + (n + \frac{1}{2}) \hat{z}\right]\]
\[ a[l \hat{x} + (m + \frac{1}{2}) \hat{y} + (n + \frac{1}{2}) \hat{z}]\]

Lattice point per conventional cell: \(4 = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3\)
Volume (conventional cell): \(a^3\)
Volume (primitive cell): \(a^3 / 4\)
Number of nearest neighbors: 12

Nearest neighbor distance: \(\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + (0)^2} = \frac{\sqrt{2}}{2} a \approx 0.707a\)

Number of second neighbors: 6
Second neighbor distance: \(a\)

For the site \((0,0,0)\),
12 nearest neighbors: \((\pm \frac{1}{2}, \pm \frac{1}{2}, 0), (\pm \frac{1}{2}, 0, \pm \frac{1}{2})\) and \((0, \pm \frac{1}{2}, \pm \frac{1}{2})\,
6 nest nearest neighbors: \((\pm 1, 0, 0), (0, \pm 1, 0)\) and \((0,0, \pm 1)\)
Packing fraction = \( \frac{4 \pi \frac{R^3}{3}}{\text{Volume of a primitive cell}} \)

\[
\begin{align*}
\text{Volume (primitive cell)} & : \frac{a^3}{4} \\
\text{Nearest neighbor distance:} & = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + (0)^2} = \frac{\sqrt{2}}{2} a \approx 0.707 a \\
\text{Nearest distance} & = 2R \\
R & = \text{Nearest distance}/2 = \frac{\sqrt{2}}{4} a \\
\end{align*}
\]

- About 74.0% of the space is really used by the sphere.
- About 26.0% of the space is empty.

0.740 is the highest packing fraction one can ever reach.
This structure is called “close packing”
There are other close packing structures (same packing fraction)
### Cubic System

#### Table 2: Characteristics of cubic lattices

<table>
<thead>
<tr>
<th></th>
<th>Simple</th>
<th>Body-centered</th>
<th>Face-centered</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume, conventional cell</strong></td>
<td>$a^3$</td>
<td>$a^3$</td>
<td>$a^3$</td>
</tr>
<tr>
<td><strong>Lattice points per cell</strong></td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>Volume, primitive cell</strong></td>
<td>$a^3$</td>
<td>$rac{1}{2}a^3$</td>
<td>$\frac{1}{4}a^3$</td>
</tr>
<tr>
<td><strong>Lattice points per unit volume</strong></td>
<td>$1/a^3$</td>
<td>$2/a^3$</td>
<td>$4/a^3$</td>
</tr>
<tr>
<td><strong>Number of nearest neighbors</strong></td>
<td>6</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td><strong>Nearest-neighbor distance</strong></td>
<td>$a$</td>
<td>$3^{1/2}a/2 = 0.866a$</td>
<td>$a/2^{1/2} = 0.707a$</td>
</tr>
<tr>
<td><strong>Number of second neighbors</strong></td>
<td>12</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td><strong>Second neighbor distance</strong></td>
<td>$2^{1/2}a$</td>
<td>$a$</td>
<td>$a$</td>
</tr>
<tr>
<td><strong>Packing fraction</strong></td>
<td>$\frac{1}{6}\pi$</td>
<td>$\frac{1}{8}\pi \sqrt{3}$</td>
<td>$\frac{1}{6}\pi \sqrt{2}$</td>
</tr>
<tr>
<td></td>
<td>0.524</td>
<td>0.680</td>
<td>0.740</td>
</tr>
</tbody>
</table>
hexagonal

2D planes formed by equilateral triangles
Stack these planes on top of each other

Primitive cell: a right prism based on a rhombus with an included angle of 120 degree.

Volume (primitive cell):

\[ Vol = \text{Area} \times \text{height} \]
\[ = 2 \left( \frac{1}{2} \times \frac{\sqrt{3}}{2} a_1^2 \right) a_3 = \frac{\sqrt{3}}{2} a^2 c \]
Let’s start from 2D (packing disks, instead of spheres).
Q: What is the close-pack structure in 2D?
A: The hexagonal lattice (these disks form equilateral triangles)

Now 3D:
Q: How to get 3D close packing?
A: Stack 2D close packing structures on top of each other.
Hexagonal Close-Packed Structure (hcp)

hcp: ABABAB...

fcc: ABCABCABC...

<table>
<thead>
<tr>
<th>Crystal</th>
<th>c/a</th>
<th>Crystal</th>
<th>c/a</th>
<th>Crystal</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.633</td>
<td>Zn</td>
<td>1.861</td>
<td>Zr</td>
<td>1.594</td>
</tr>
<tr>
<td>Be</td>
<td>1.581</td>
<td>Cd</td>
<td>1.886</td>
<td>Gd</td>
<td>1.592</td>
</tr>
<tr>
<td>Mg</td>
<td>1.623</td>
<td>Co</td>
<td>1.622</td>
<td>Lu</td>
<td>1.586</td>
</tr>
<tr>
<td>Ti</td>
<td>1.586</td>
<td>Y</td>
<td>1.570</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
We choose three lattice vectors
Three lattice vectors form a primitive or a conventional unit cell
Length of these vectors are called: the lattice constants

We can mark any unit cell by three integers: \( lmn \)
\[
\vec{t} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3
\]

Coordinates of an atom:
We can mark any atom in a unit cell by three real numbers: \( xyz \).
The location of this atom: \( x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3 \)
Notice that \( 0 \leq x < 1 \) and \( 0 \leq y < 1 \) and \( 0 \leq z < 1 \)

Q: Why \( x \) cannot be 1?
A: Due to the periodic structure. 1 is just 0 in the next unit cell
Sodium Chloride structure

Face-centered cubic lattice
Na⁺ ions form a face-centered cubic lattice
Cl⁻ ions are located between each two neighboring Na⁺ ions

Equivalently, we can say that
Cl⁻ ions form a face-centered cubic lattice
Na⁺ ions are located between each two neighboring Na⁺ ions
Sodium Chloride structure

Primitive cells
### Cesium Chloride structure

<table>
<thead>
<tr>
<th>Period</th>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 3</th>
<th>Group 4</th>
<th>Group 5</th>
<th>Group 6</th>
<th>Group 7</th>
<th>Group 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>He</td>
<td>Na</td>
<td>Li</td>
<td>Be</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
</tr>
<tr>
<td>2</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
</tr>
<tr>
<td>4</td>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
</tr>
<tr>
<td>5</td>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
</tr>
<tr>
<td>6</td>
<td>Fr</td>
<td>Ra</td>
<td>Ac</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
</tr>
</tbody>
</table>

### Lanthanides

| 57  | La  | 58  | Ce  | 59  | Pr  |
| 60  | Nd  | 61  | Pm  | 62  | Sm  |
| 63  | Eu  | 64  | Gd  | 65  | Tb  |
| 66  | Dy  | 67  | Ho  | 68  | Er  |
| 69  | Tm  | 70  | Yb  | 71  | Lu  |

### Actinides

| 89  | Ac  | 90  | Th  | 91  | Pa  |
| 92  | U   | 93  | Np  | 94  | Pu  |
| 95  | Am  | 96  | Cm  | 97  | Bk  |
| 98  | Cf  | 99  | Es  | 100 | Fm  |
| 101 | Md  | 102 | No  | 103 | Lr  |
Cesium chloride structure

Simple cubic lattice
Cs+ ions form a cubic lattice
Cl- ions are located at the center of each cube

Equivalently, we can say that
Cl- ions form a cubic lattice
Cs+ ions are located at the center of each cube

Coordinates:
Cs: 000
Cl: $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

Notice that this is a simple cubic lattice
NOT a body centered cubic lattice
➢ For a bcc lattice, the center site is the same as the corner sites
➢ Here, center sites and corner sites are different
# Diamond structure

![Diamond structure diagram]

## Periodic Table

<table>
<thead>
<tr>
<th>Group</th>
<th>Period</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Li, Be</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Na, Mg</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>Cs, Ba, Lanthanides, Actinides</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>Fr, Ra, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr</td>
</tr>
</tbody>
</table>

Lanthanides: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Actinides: Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr
Carbon atoms can form 4 different crystals

- Graphene (Nobel Prize carbon)
- Diamond (money carbon/love carbon)
- Graphite (Pencil carbon)
- Nano tubes
Not all lattices are Bravais lattices: examples the honeycomb lattice (graphene)
Diamond lattice is **NOT a Bravais Lattice** either

Same story as in graphene:
We can distinguish two different type of carbon sites (marked by different color)
We need to combine two carbon sites (one black and one white) together as a (primitive) unit cell
If we only look at the black (or white) sites, we found the Bravais lattice: fcc
Cubic Zinc Sulfide Structure

Very similar to Diamond lattice
Now, black and white sites are two different atoms
fcc with two atoms in each primitive cell

Good choices for junctions

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$a$ (Å)</th>
<th>Crystal</th>
<th>$a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>4.35</td>
<td>ZnSe</td>
<td>5.65</td>
</tr>
<tr>
<td>ZnS</td>
<td>5.41</td>
<td>GaAs</td>
<td>5.65</td>
</tr>
<tr>
<td>AlP</td>
<td>5.45</td>
<td>AlAs</td>
<td>5.66</td>
</tr>
<tr>
<td>GaP</td>
<td>5.45</td>
<td>InSb</td>
<td>6.46</td>
</tr>
</tbody>
</table>

Diode
Matter

gas/liquid:
Atoms/molecules can move around

solids:
Atoms/molecules cannot move

Crystals:
Atoms/molecules form a periodic structure

Random solids:
Atoms/molecules form a random structure