

1 Extraction of the 2D Tubule Lattice

The typical manner in which a nanotube is thought of is as a small section cut from a 2D graphite lattice. The two chirality parameters, n and m , inherently describe the angle at which this “cut” is made and are proportional to the diameter of the resulting tube. In the first section I define the nanotube lattice vectors with respect to the chirality parameters, as well as several other key quantities (tubule diameter and chiral angle).

1.1 Defining the Tubule Lattice Vectors

The nanotube lattice vectors are defined in terms of a chirality vector, \vec{C}_h which is defined as

$$\vec{C}_h \equiv n\vec{a}_1 + m\vec{a}_2 \quad (1)$$

where the basis vectors \vec{a}_1 and \vec{a}_2 can be defined in terms of the nearest-neighbor carbon distance, a_{cc} :

$$\vec{a}_1 \equiv \left\langle \frac{3}{2}a_{cc}, \frac{\sqrt{3}}{2}a_{cc} \right\rangle \quad (2)$$

$$\vec{a}_2 \equiv \left\langle \frac{3}{2}a_{cc}, -\frac{\sqrt{3}}{2}a_{cc} \right\rangle \quad (3)$$

If we equate the length of the chirality vector to the circumference of the tubule, we can find the resulting diameter of the tubule:

$$\begin{aligned} \|\vec{C}_h\| &= 2\pi r = \pi d_t \\ d_t &= \frac{\|\vec{C}_h\|}{\pi} \end{aligned} \quad (4)$$

The magnitude of the chirality vector can be determined in terms of the two lattice parameters, n and m , and the nearest-neighbor carbon distance:

$$\begin{aligned} \|\vec{C}_h\|^2 &= \vec{C}_h \cdot \vec{C}_h = (n\vec{a}_1 + m\vec{a}_2) \cdot (n\vec{a}_1 + m\vec{a}_2) \\ &= n^2\vec{a}_1 \cdot \vec{a}_1 + m^2\vec{a}_2 \cdot \vec{a}_2 + 2nm\vec{a}_1 \cdot \vec{a}_2 \\ &= n^2 \left(\sqrt{3}a_{cc} \right)^2 + m^2 \left(\sqrt{3}a_{cc} \right)^2 + 2nm \left(\frac{3}{2}a_{cc}^2 \right) \\ &= \left(\sqrt{3}a_{cc} \right)^2 (n^2 + nm + m^2) \end{aligned} \quad (5)$$

Thus the diameter of the tubule associated with an arbitrary chirality vector \vec{C}_h as defined in Eq. (1) is:

$$\begin{aligned} d_t &= \frac{\|\vec{C}_h\|}{\pi} \\ &= \frac{\sqrt{(\sqrt{3}a_{cc})^2 (n^2 + nm + m^2)}}{\pi} \\ &= \frac{\sqrt{3}a_{cc}\sqrt{n^2 + nm + m^2}}{\pi} \end{aligned} \quad (6)$$

The chiral angle, θ , is a basic symmetry operation for the lattice. The vector \vec{r} shown in Figure 19.2a on pp. 759 of Dresselhaus defines the translational operation which moves the two-atom basis to an equivalent position. The chiral angle determines the degree of helicity to the lattice, with a zig-zag $(n, 0)$ lattice defined as $\theta = 0$. This value can also be determined in terms of the lattice parameters. We start with the definition of the tangent in terms of two vectors, \vec{a} and \vec{b} :

$$\tan \theta \equiv \frac{|\sin \theta|}{\cos \theta} = \frac{\|\vec{a} \times \vec{b}\|}{\vec{a} \cdot \vec{b}} \quad (7)$$

The inner product in the denominator of Eq. (7) is easily determined (the vector $\vec{\tau}$ is exactly equivalent to \vec{a}_1 in the coordinate system presented on pp. 759):

$$\begin{aligned}
\vec{C}_h \cdot \vec{\tau} &= (n\vec{a}_1 + m\vec{a}_2) \cdot \vec{a}_1 \\
&= n\vec{a}_1 \cdot \vec{a}_1 + m\vec{a}_1 \cdot \vec{a}_2 \\
&= n(3a_{cc}^2) + m\left(\frac{3}{2}a_{cc}^2\right) \\
&= \frac{3}{2}a_{cc}^2(2n + m)
\end{aligned} \tag{8}$$

Next we need to find the cross product of the two vectors \vec{C}_h and $\vec{\tau}$:

$$\vec{C}_h \times \vec{\tau} = \begin{pmatrix} x & y & z \\ C_{hx} & C_{hy} & C_{hz} \\ \tau_x & \tau_y & \tau_z \end{pmatrix} \equiv \begin{pmatrix} x & y & z \\ C_{hx} & C_{hy} & 0 \\ a_{1x} & a_{1y} & 0 \end{pmatrix}$$

The x- and y-components of the cross product will both be zero, and the z-component will be:

$$\begin{aligned}
(\vec{C}_h \times \vec{\tau})_z &= \det \begin{pmatrix} C_{hx} & C_{hy} \\ a_{1x} & a_{1y} \end{pmatrix} \\
&= C_{hx}a_{1y} - C_{hy}a_{1x} \\
&= \frac{3\sqrt{3}}{2} m a_{cc}^2
\end{aligned}$$

This makes the magnitude of the cross product

$$\|\vec{C}_h \times \vec{\tau}\| = \frac{3\sqrt{3}}{2} m a_{cc}^2 \tag{9}$$

Using Eq. (8) and Eq. (9), the tangent of the chiral angle is

$$\begin{aligned}
\tan \theta &= \frac{\frac{3\sqrt{3}}{2} m a_{cc}^2}{\frac{3}{2}a_{cc}^2(2n + m)} \\
&= \frac{\sqrt{3}m}{(2n + m)} \\
\Rightarrow \theta &= \arctan \frac{\sqrt{3}m}{(2n + m)}
\end{aligned} \tag{10}$$

Orthogonal to the chiral vector and extending along the tubule axis to the next equivalent cell position is the tubule translation vector, \vec{T} . This vector is also defined in terms of the chirality parameters:

$$\vec{T} = [(2m + n)\vec{a}_1 - (2n + m)\vec{a}_2] / d_R \tag{11}$$

The value of d_R is defined using the greatest common divisor of n and m :

$$\begin{aligned}
d &= \text{gcd}(n, m) \\
d_R &= \begin{cases} d & (n - m) \bmod 3d \neq 0 \\ 3d & (n - m) \bmod 3d = 0 \end{cases}
\end{aligned} \tag{12}$$

Several trivial bits of information for the lattice can subsequently be calculated. For instance, the number N of hexagonal carbon rings contained in the cell defined by \vec{C}_h and \vec{T} :

$$N = \frac{2(m^2 + n^2 + nm)}{d_R} \tag{13}$$

There are additional symmetry properties which can be calculated for the lattice; however, these properties will not be discussed here as they do not play a role in the generation of a nanotube lattice in the *TubeGen* program.

1.2 Generating Unique Atomic Positions

Given the chirality vector (\vec{C}_h) and tubule translation vector (\vec{T}) there are two ways to define the nanotube unit cell. The first method generates the lattice as a flat sheet of carbon atoms, exactly as they would appear when snipped from a graphite sheet. The second method uses the first as a starting point but wraps the "sheet" around a cylinder, actually forming a 3D tubular structure.

1.2.1 2D Sheet Generation

Once we've calculated \vec{C}_h and \vec{T} for a given set of chirality parameters, the magnitude of the two vectors describe the length of the unit cell in two directions. In *TubeGen*, the chiral vector is taken as the x-axis of the cell and the tubule translation vector is taken as the y-axis; the z-axis is set to a large enough displacement such that the contents of neighboring cells will not interact. The cell itself is an orthorhombic rectangular prism. We previously defined two basis vectors which are translational operations from one position to another. An arbitrary integral linear combination of these two vectors will generate an equivalent position within the infinite lattice; picking all interior positions generated in this manner leads to the generation of the chemical basis for the crystal cell. So essentially using the chirality parameters to define a range for the linear combination coefficients, recognizing that the positions have two atoms attached to them, and testing for inclusion of all generated positions within the cell will allow us to generate the fractional coordinates needed. The fractional coordinates are in terms of displacement along the chiral and tubule translation axes, so simple vector algebra can be used for the inclusion testing:

$$\begin{aligned} \text{Given : } \quad \vec{\alpha} &= s\vec{a}_1 + t\vec{a}_2 \quad \text{for } s \in [-2n, +2n] \text{ and } t \in [-2m, +2m] \\ x &= \frac{\vec{C}_h \cdot \vec{\alpha}}{\|\vec{C}_h\| \|\vec{\alpha}\|} \\ y &= \frac{\vec{T} \cdot \vec{\alpha}}{\|\vec{T}\| \|\vec{\alpha}\|} \end{aligned}$$

if ($0 \leq x < 1$ and $0 \leq y < 1$) Point is interior to cell.

The values x and y are actually the fractional coordinates of the given point along the chiral and tubule axes, respectively. The ranges specified for the integral coefficients s and t are not chosen to be computationally optimal but to assure inclusion of all points in the cell.

1.2.2 Rolled Tube Generation

Rolling the lattice generated in the previous section into a cylindrical structure is straightforward. In Eq. (4) we related the chiral vector magnitude to the diameter of the nanotube; in that equation, it is assumed that the chiral vector represents the circumferential path of the rolled nanotube. This implies that the fractional coordinate along the chiral vector (x in the prior section) is actually a fractional distance along the circumference of the nanotube. Knowing the distance travelled along the circumference of a circle, the angle ϕ subtended is calculated as

$$\begin{aligned} \|\vec{C}_h\| &= 2\pi r \\ s &= \|\vec{C}_h\| x = 2\pi r x \\ s &= r\phi \\ r\phi &= 2\pi r x \Rightarrow \phi = 2\pi x \end{aligned} \tag{14}$$

Essentially, the unit cell is set up to be a rectangular prism with a square base. The tube extends orthogonal to this square base (along the z-axis of the cell). Taking the fractional coordinates specified in the previous section, y becomes the fractional coordinate along this z-axis and the coordinates along the x- and y-axes of the rolled cell are taken relative to the center of the square base (fractionally speaking, (0.5, 0.5)!):

$$\vec{q} = \langle 0.5(1 + \cos(\phi)), 0.5(1 + \sin(\phi)), y \rangle \tag{15}$$

The cylinder generated in this manner actually touches the edge of the cell, and would mimic a fused bundle of nanotubes. To eliminate such an interaction, empty space is added around each side of the cylinder. So adding a buffer region of length δ_b around the coordinates generated in Eq. (15), the new fractional coordinates are

$$q'_x = \frac{q_x \|\vec{C}_h\| + \delta_b}{\|\vec{C}_h\| + 2\delta_b} \quad (16)$$

$$q'_y = \frac{q_y \|\vec{C}_h\| + \delta_b}{\|\vec{C}_h\| + 2\delta_b} \quad (17)$$

The fractional coordinates along the tubule axis are not modified.