Topics in x-ray diffraction

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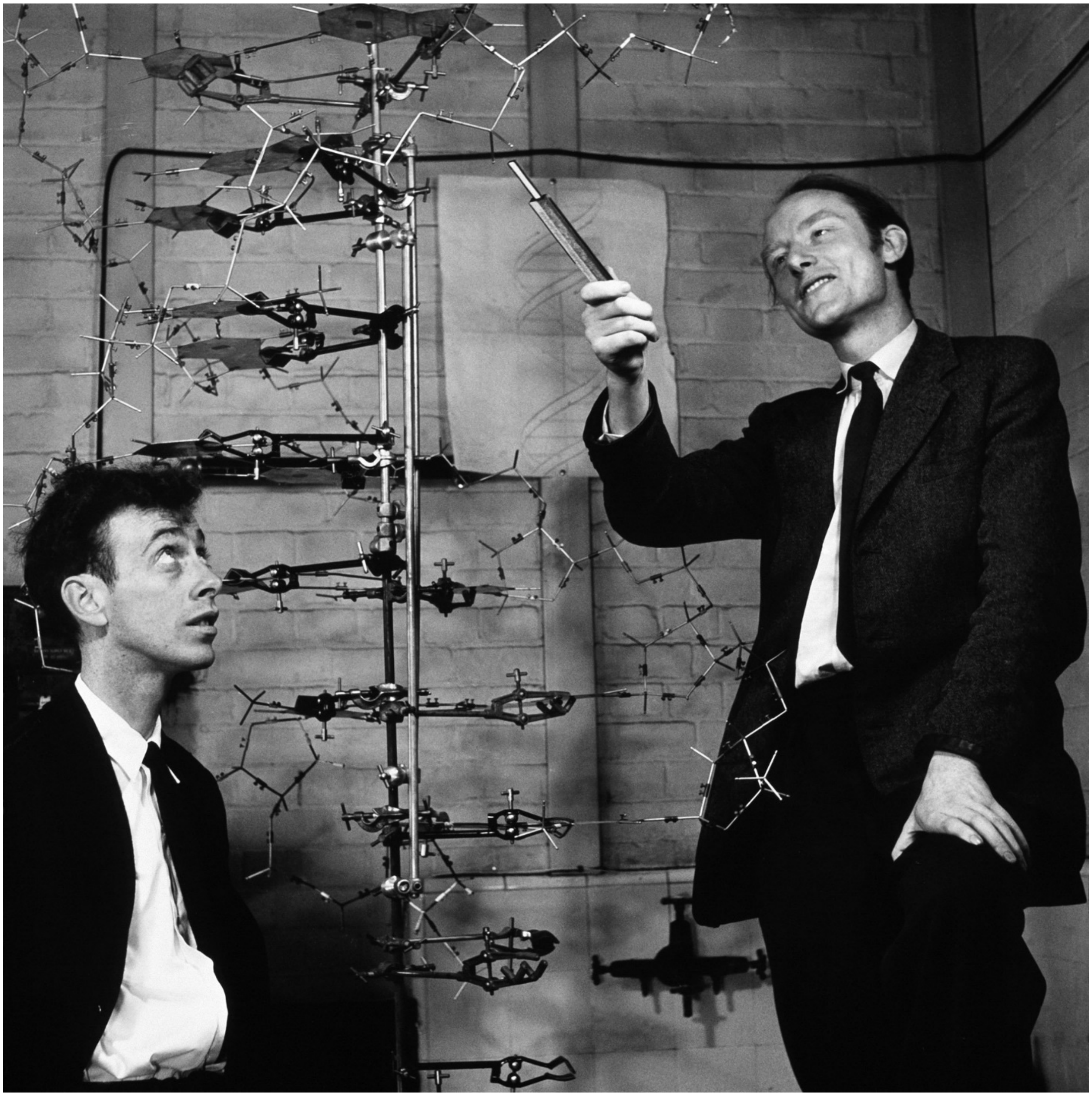
(Date: February 06, 2019)

((**James Watson and Francis Crick**))

Watson and Crick shared the Nobel Prize in 1962 for their discovery, along with Maurice Wilkins (1916 - 2004), who had produced a large body of crystallographic data supporting the mode. Working in the same lab, Rosalind Franklin (1920 - 1958) had earlier produced the first clear crystallographic evidence for a helical structure. Crick went on to do fundamental work in molecular biology and neurobiology. Watson become Director of the Cold Spring Harbor Laboratory, and headed up the Human Genome Project in the 1990s.



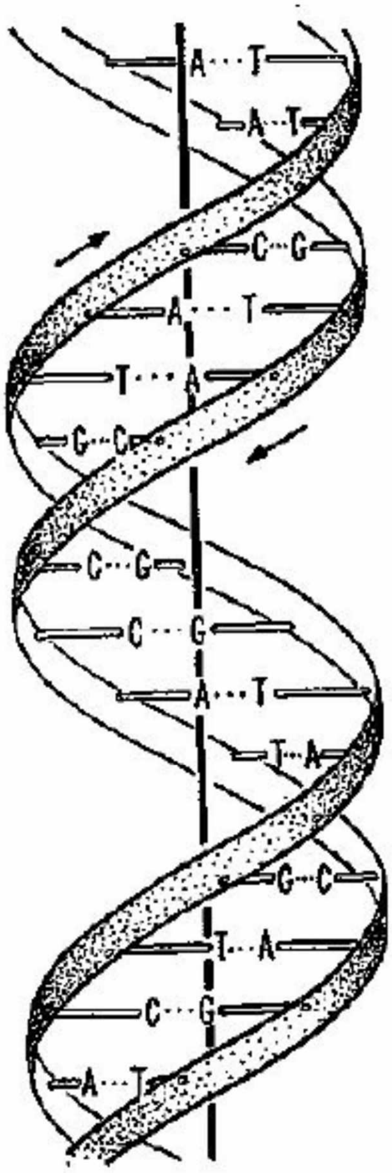
http://dataphys.org/list/wp-content/uploads/2014/12/Watson-Crick-DNA-model.jpg

Fig. 1953 Watson and Crick with their DNA model

Lames D. Watson, The Double Helix (Touchstone, 2001).

1. X-ray diffraction of DNA (double helix)

J. Als-Nielsen and D. McMorrow, Elements of Modern X-ray Physics, second edition (Wiley, 2011)



Inspired by Pauling's ideas, Cochran et al. calculated the generic diffraction pattern from a helix [Cochran et al., 1952]. As the scattering from helices has assumed such significance in structural biology an outline of this calculation is given here. The starting point is to imagine that a uniform and continuous distribution of material lies on an infinitely long helical string of period *P*. The problem in calculating the diffraction pattern is to add up the phase factor for each differential element along the helix. As the material is uniformly distributed the scattering amplitude is found by evaluating the integral,

$$S_{\boldsymbol{G}} \propto \delta(G_z - \frac{2\pi}{P}m)\int_0^P dz \exp(-i\boldsymbol{G}\cdot\boldsymbol{r})$$

where $\boldsymbol{Q} = \boldsymbol{G}$ (Bragg condition), z is taken to be along the axis of the helix. For a helix with a period of P and a radius of R, any point $\boldsymbol{r}_\perp$ on the helix for $0 \le z \le P$
is given by

$$\boldsymbol{r} = \{R\cos\left(\frac{2\pi z}{P}\right), R\sin\left(\frac{2\pi z}{P}\right), z\}$$

As the helix is periodic, the integral decomposes into a sum over all periods (or lattice sites) multiplied by the structure factor of a single period. The scattering amplitude then becomes

$$S(G_z = \frac{2\pi}{P}n) \propto \int_0^P dz \exp(-i\boldsymbol{G}\cdot\boldsymbol{r})$$

where n is an integer. To evaluate the phase $\boldsymbol{G}\cdot\boldsymbol{r}$, it is convenient to use cylindrical coordinates and express the scattering vector as

$$\boldsymbol{G} = (G_\perp \cos\phi, G_\perp \sin\phi, \frac{2\pi}{P}n)$$

where $G_\perp$ is the radial component and ϕ is the azimuthal angle. We note that

$$\begin{aligned}\boldsymbol{G}\cdot\boldsymbol{r} &= G_\perp R\cos\phi\cos(\frac{2\pi z}{P}) + G_\perp R\sin\phi\sin(\frac{2\pi z}{P}) + \frac{2\pi n}{P}z \\ &= G_\perp R\cos(\frac{2\pi z}{P} - \phi) + \frac{2\pi n}{P}z\end{aligned}$$

It is convenient to rewrite this as

$$\boldsymbol{G}\cdot\boldsymbol{r} = \xi\cos\theta + n(\theta + \phi)$$

where

$$G_\perp R = \xi, \qquad \theta = \frac{2\pi z}{P} - \phi$$

Then we get

$$S(G_z = \frac{2\pi}{P} n) = e^{-in\phi} \int_0^{2\pi} d\theta e^{-i(\xi \cos\theta + n\theta)} = e^{-in\phi} J_n(\xi)$$

where

$$J_n(x) = \frac{1}{2\pi i^n} \int_0^{2\pi} d\theta e^{i(x\cos\theta + n\theta)}$$

or

$$J_{-n}(-x) = J_n(x) = \frac{1}{2\pi i^{-n}} \int_0^{2\pi} d\theta e^{-i(x\cos\theta + n\theta)}$$

since

$$J_{-n}(-x) = J_n(x)$$

The scattered intensity given by the above equation is plotted in Fig. The scattering intensity is given by the form as

$$f(n, x, y, \sigma) = [J_n(x)]^2 [g(y, n, \sigma)]^2$$

with the Gaussian distribution function

$$g(y, n, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp[-\frac{1}{2\sigma^2}(y-n)^2].$$

((**Mathematica**))

```
Clear["Global`*"];
g1[y_, n_, σ_] := 1/(Sqrt[2 π] σ) Exp[-1/(2 σ^2) (y - n)^2];
f[n_, x_, y_, σ_] := BesselJ[n, x]^2 g1[y, n, σ]^2;
h1 = ContourPlot[Evaluate[f[1, x, y, 0.1]] == 2, {x, -10, 10},
  {y, 0, 10}, ContourStyle → {Red, Thick}, PlotPoints → 60] ;
h2 = ContourPlot[Evaluate[f[2, x, y, 0.1]] == 2, {x, -10, 10},
  {y, 0, 10}, ContourStyle → {Red, Thick}, PlotPoints → 60] ;
h3 = ContourPlot[Evaluate[f[3, x, y, 0.1]] == 2, {x, -10, 10},
  {y, 0, 10}, ContourStyle → {Red, Thick}, PlotPoints → 60] ;
h4 = ContourPlot[Evaluate[f[4, x, y, 0.1]] == 2, {x, -10, 10},
  {y, 0, 10},  ContourStyle → {Red, Thick}, PlotPoints → 60] ;
h5 = ContourPlot[Evaluate[f[5, x, y, 0.1]] == 2, {x, -10, 10},
  {y, 0, 10},  ContourStyle → {Red, Thick}, PlotPoints → 60];
h6 = ContourPlot[Evaluate[f[6, x, y, 0.1]] == 2, {x, -10, 10},
  {y, 0, 10}, ContourStyle → {Red, Thick}, PlotPoints → 60];
h7 = ContourPlot[Evaluate[f[7, x, y, 0.1]] == 2, {x, -10, 10},
  {y, 0, 10}, ContourStyle → {Red, Thick}, PlotPoints → 60];
f1 = Show[h1, h2, h3, h4, h5, h6, h7, PlotRange → All];
g1 = Graphics[{Blue, Thick, Line[{{-7, 0}, {7, 0}}],
   Line[{{0, -7}, {0, 7}}]}]; s1 = Show[f1, g1];
Graphics[{Translate[s1[[1]], {0, 0}], Rotate[s1[[1]], π, {0, 0}],
  Text[Style["Gz P/(2 π)", Black, 12, Italic], {1, 6.5}],
  Text[Style["GxyR", Black, 12, Italic], {6.6, 0.4}]}]
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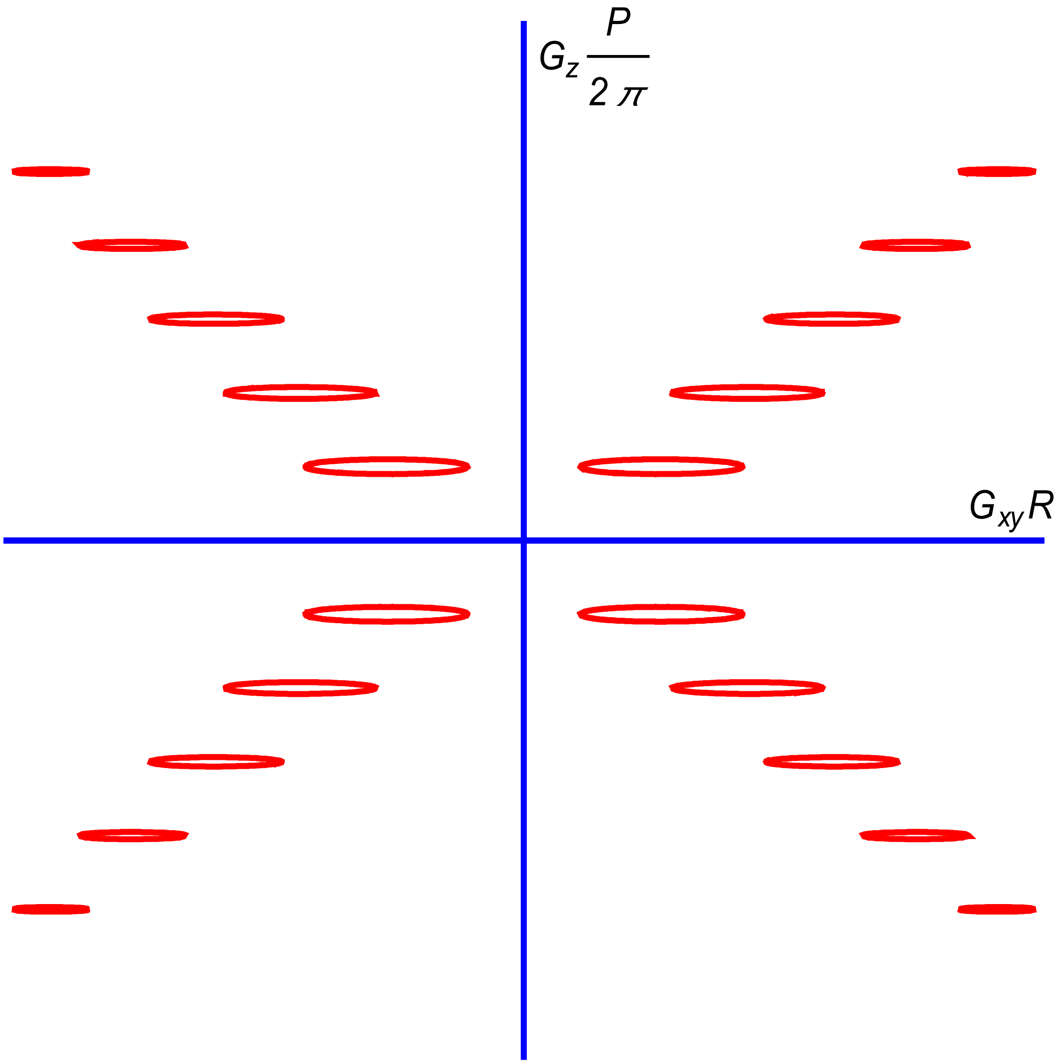
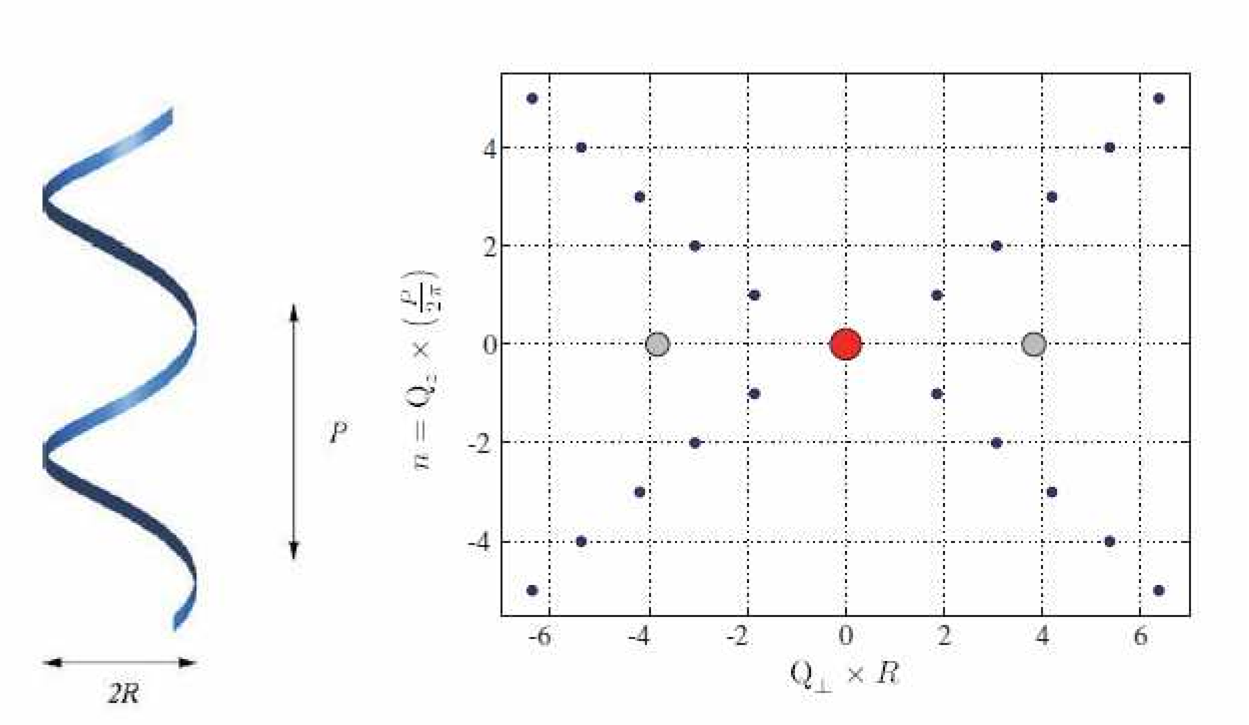
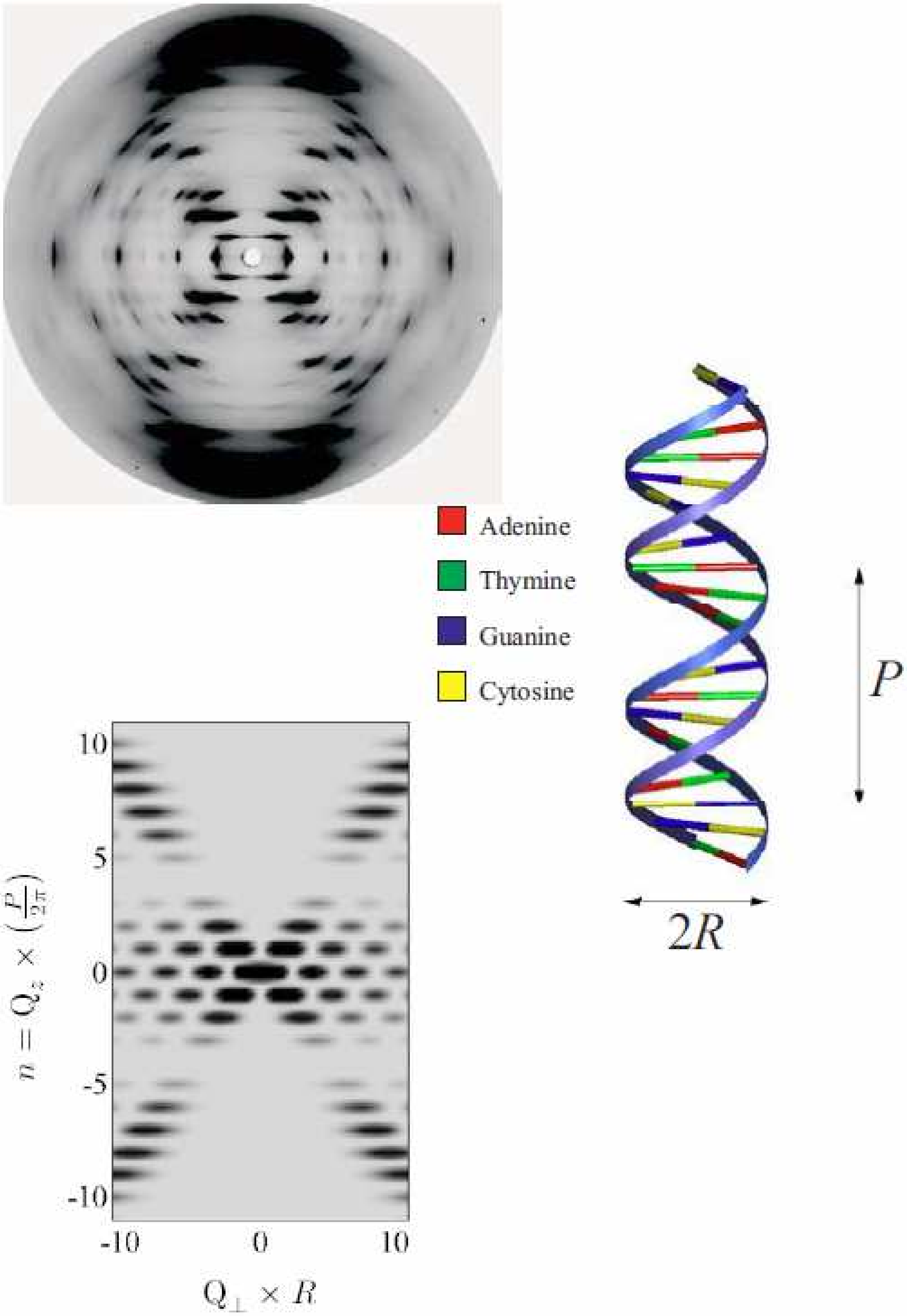


Fig. Reciprocal lattice plane of double helix (Mathematica).

Perhaps the most celebrated helical structure in biology is the double helix of DNA (deoxyribose nucleic acid). The structure of DNA was first solved by James Watson and Francis Crick [Watson and Crick, 1953], who mainly used stereo-chemical arguments to build a model which helped them deduce the correct structure. They were assisted greatly in their work by the x-ray diffraction experiments performed around the same time by Wilkins et al. [Wilkins et al., 1953] and Franklin and Gosling [Franklin and Gosling, 1953]. These experiments established the helical nature of the DNA molecule, and provided decisive structural parameters, such as its period and radius. The discovery of the double helix probably ranks as one of the most important scientific advances of the twentieth century.



((Experimental results))


🟥 Adenine
🟩 Thymine
🟦 Guanine
🟨 Cytosine
P
$2R$
$n = Q_z \times \left(\frac{P}{2\pi}\right)$
10
5
0
-5
-10
-10
0
10
$Q_\perp \times R$

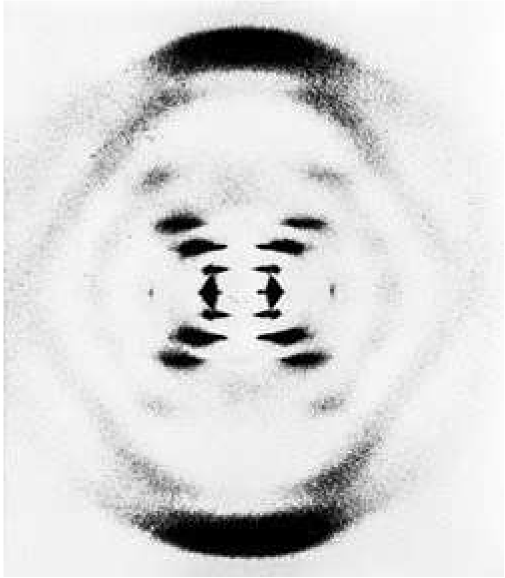


Fig. From the book of Als-Nielsen

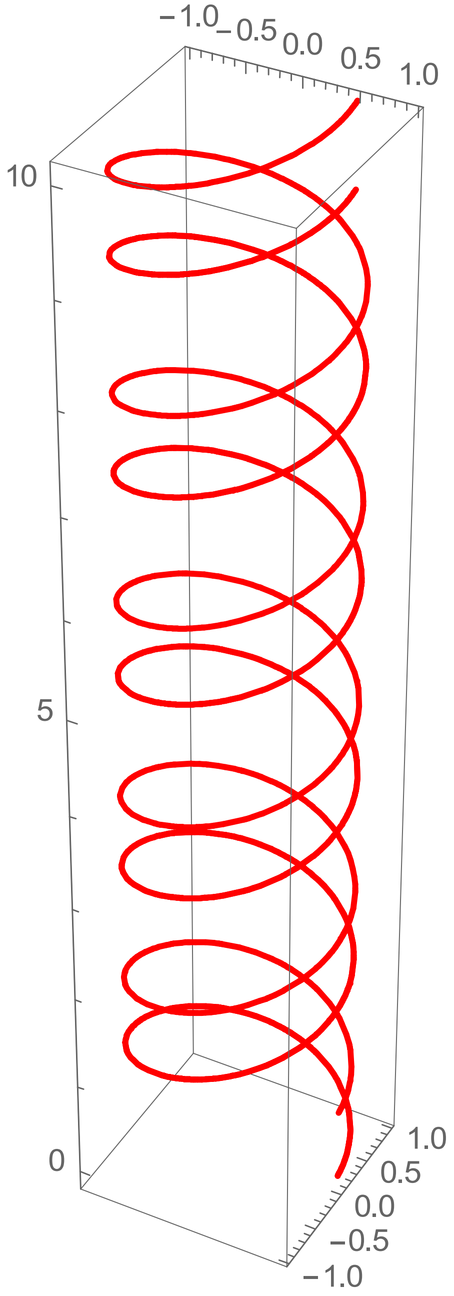
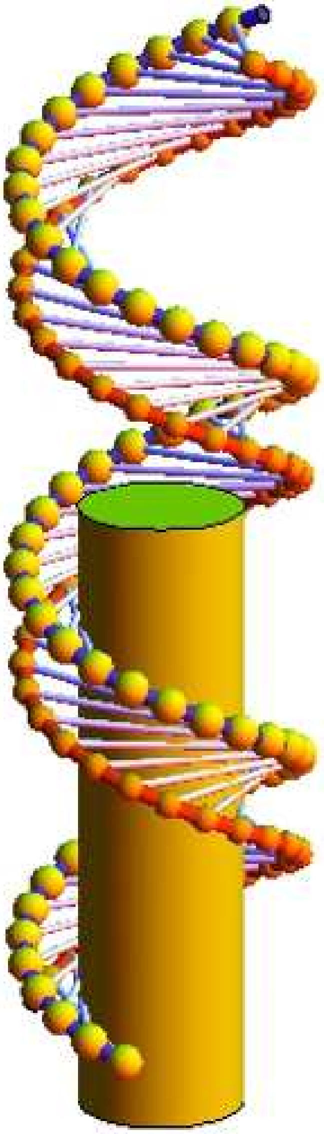


Fig. Model of double helix DNA. We use the parameters $P = 2. R = 1$, and $\Delta = \frac{3}{8}P = 0.75$



It is evident that the diffraction pattern from DNA possesses some of the features predicted by Cochran et al. for the scattering from a helix. In particular there is a characteristic cross of Bragg peaks. From the position of these peaks along the meridional (vertical) axis the period of the helix is found to be 34 Å, while from the angle of the cross it can be deduced that the radius of the helix is 10 Å. The double nature of the helix is only apparent from a detailed analysis of the pattern. Most tellingly the reflections from the 4-th order layer are missing on the film, although the 3-rd and 5-th order are clearly apparent. Indeed Rosalind Franklin herself was aware that this feature of the diffraction pattern could be explained naturally by assuming that DNA is formed from two intertwined helices. If the two helices are displaced along the common z axis by an amount Δ, the scattering amplitude becomes

$$A_2(Q_\perp, \phi, Q_z) \propto [1 + e^{in\frac{2\pi\Delta}{P}}] J_n(Q_\perp R)$$

with $Q_z = \frac{2\pi n}{P}$. The waves scattered by the two helices interfere in such a way that the intensity of the 4-th layer reflections becomes vanishingly small when Δ/P=1/8, 3/8, 5/8, etc. It can be seen that it accounts for most of the qualitative features of the central part of the diffraction pattern. To obtain better agreement it would obviously be necessary to specify the position of all the molecules in the structure and their scattering factors. One feature not accounted for by the simple model described here is the existence of strong, but diffuse reflections on the meridional axis close to the 10-th layer. These reflections arise from the fact that the double helix has 10 pairs of bases per period.

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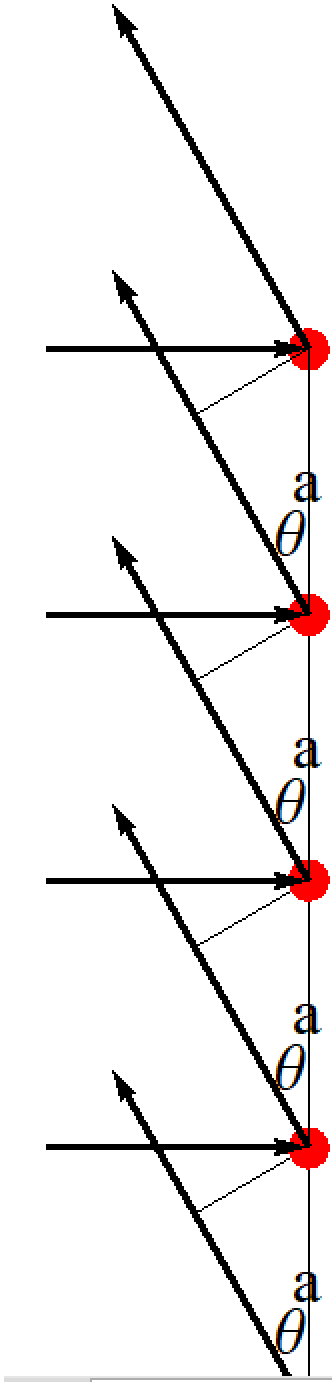
2. x-ray diffraction of 1D system (fiber)

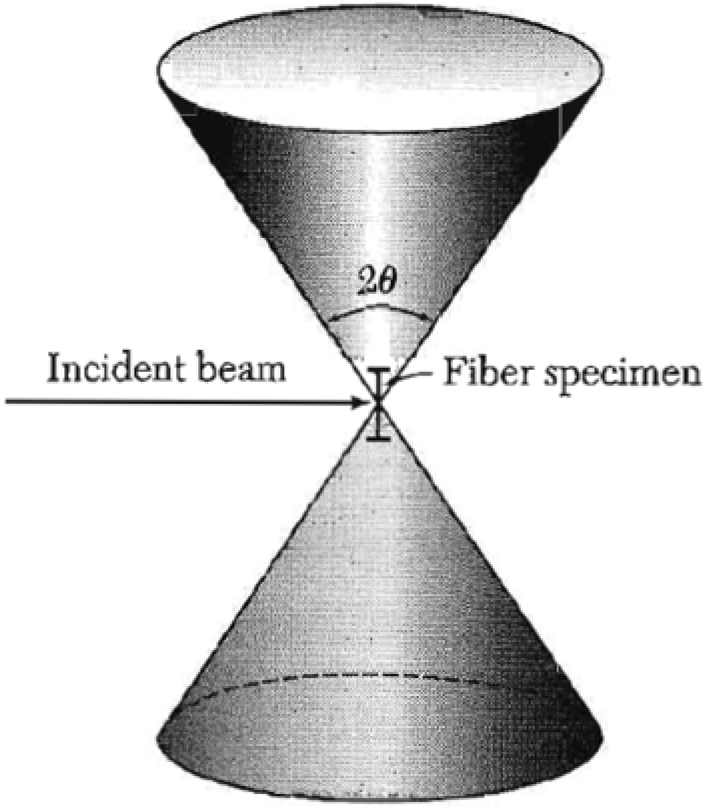
Part-1

(a) Consider a line of atoms ABAB…AB, with an A-B bond length of *a*/2. The form factors are f_A, f_B for atoms A, B, respectively. Show that the intensity of the diffracted beam is proportional to $|f_A - f_B|^2$ for *n* odd and to $|f_A + f_B|^2$ for *n* even. Explain what happens if $f_A = f_B$.

Part-II

(b) The incident beam of x-rays is perpendicular to the line of atoms with the lattice constant *a*. Show that the Bragg condition is $n\lambda = a\cos\theta$, where θ is the angle between the diffracted beam and the line of atoms. Note that this Bragg condition can be derived by using the Ewald sphere, where the 2D Bragg plane is formed for the one-dimensional system.


a
θ
a
θ
a
θ
a
θ



((**Solution**))

(a) The structure factor is given by

$$S_G = \sum_j f_j \exp(-i\boldsymbol{G}\cdot\boldsymbol{r}_j)$$

where $\boldsymbol{r}_j = 0$, and $\boldsymbol{r}_j = \frac{1}{2}a\boldsymbol{e}_z$

$$\boldsymbol{G}\cdot\frac{1}{2}a\boldsymbol{e}_z = \frac{2\pi}{a}n\frac{a}{2} = n\pi$$

Then we have

$$S_n = f_A + f_B \exp(-in\pi)$$

The intensity is

$$\begin{aligned} I_n &= |S_n|^2 \\ &= [f_A + f_B \exp(-in\pi)][f_A^* + f_B^* \exp(in\pi)] \\ &= |f_A|^2 + |f_B|^2 + f_A^* f_B \exp(-in\pi) + f_A f_B^* \exp(in\pi) \end{aligned}$$

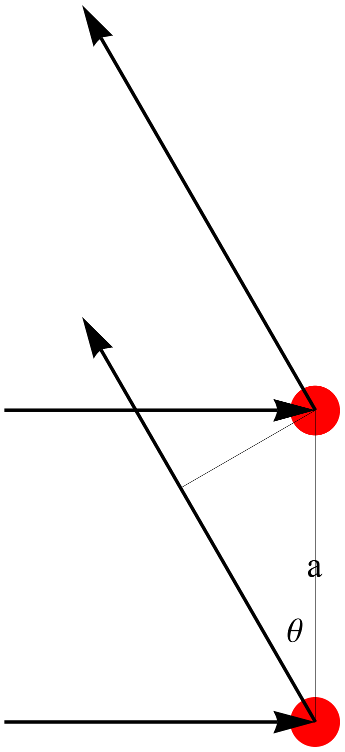
For odd *n*,

$$I_n = |f_A - f_B|^2$$

For even *n*,

$$I_n = |f_A + f_B|^2$$

(b)
((**Method-1**))



The path difference between two adjacent x-rays is given by

$$\Delta L = a\cos\theta\,.$$

The Bragg reflections occur when $\Delta L = n\lambda$, where λ is the wavelength and n is an integer. Then we get the Bragg condition;

$$a\cos\theta = n\lambda \,.$$

((Method-2))

For the one dimensional system with the lattice constant d (=a) there exist Bragg planes with $k_z = (2\pi/d)n$. The Bragg reflections occur on the surface of Ewald sphere where the Bragg planes intersect with the sphere. The incident beam of x-ray is perpendicular to the line of atoms.

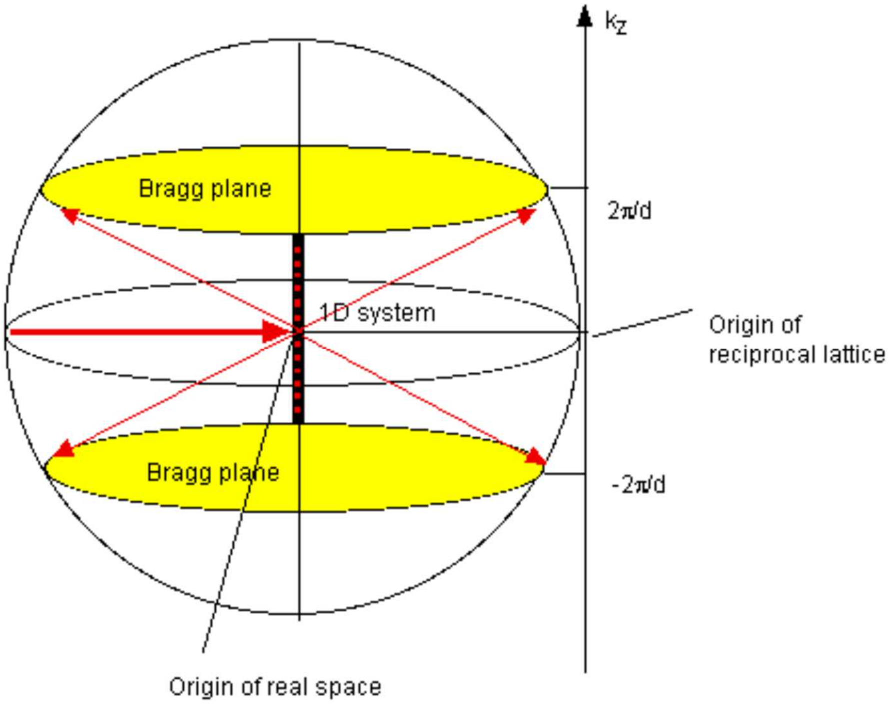


Fig. Schematic diagram of the Ewald construction. Because of the 1D chain, there are Bragg planes in the reciprocal lattice plane. The direction of 1D chain is the same as the direction of incident beam.

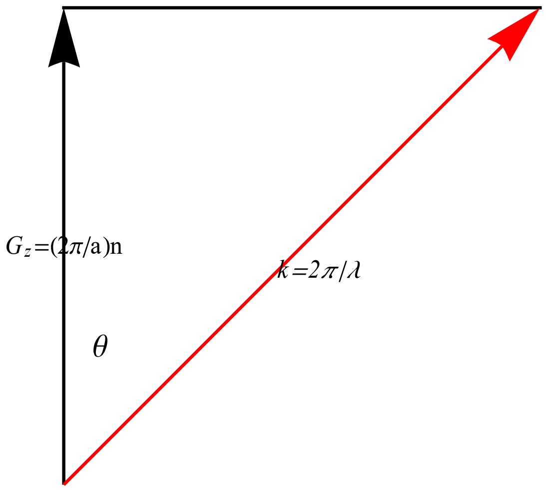


Fig. Reciprocal space.

The interference condition is

$$k\cos\theta = (2\pi/d)n.$$

Since $k = 2\pi/\lambda$, this is rewritten as $(2\pi/\lambda)\cos\theta = (2\pi/d)n$. or $d\cos\theta = n\lambda$, where d is the lattice constant of the 1D system.

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3. Debye-Scherrer diffractogram

In a Debye-Scherrer diffractogram, we obtain a measure of the Bragg angles θ. In a particular experiment with Al (Aluminium) powder, the following θ data were obtained when CuKα radiation (the wavelength λ = 1.54184 Å) was used:

19.48°, 22.64°, 33.00°, 39.68°, 41.83°, 50.35°, 57.05°, 59.42°.

Aluminium has atomic weight 27 g/mol and density 2.7 g/cm^3. (c) Show that Al has a fcc (face centered cubic) structure, where $h^2+k^2+l^2$ = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, 35, 40, 36, 43, 44, 48. (d) What is the lattice parameter of Al of the conventional cubic unit cell? (e) Calculate the Avogadro's number.
Hint: The basis consists of four lattice points if the cell is taken as the conventional cube for fcc.

$$\frac{4\pi}{\lambda}\sin\theta = \frac{2\pi}{a}\sqrt{h^2+k^2+l^2}\ .$$

((**Solution**))

We use the Bragg condition given by

$$\frac{4\pi}{\lambda}\sin\theta = \frac{2\pi}{a}\sqrt{h^2 + k^2 + l^2}$$

where h, k, l are the integers, a is the lattice constant of the conventional cubic lattice. λ = 1.54184 Å for CuKα. This formula can be rewritten as

$$a\frac{2}{\lambda}\sin\theta = \sqrt{h^2 + k^2 + l^2}$$

Suppose that Al has a fcc structure. In this case, it is expected that

$h^2 + k^2 + l^2$ = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32,.....

We make a plot of the date of $\frac{2}{\lambda}\sin\theta$ as a function of $\sqrt{h^2 + k^2 + l^2}$.

θ= 19.48°, $\sqrt{h^2 + k^2 + l^2} = \sqrt{3}$

θ= 22.64°, $\sqrt{h^2 + k^2 + l^2} = \sqrt{4}$

θ= 33.00°, $\sqrt{h^2 + k^2 + l^2} = \sqrt{8}$

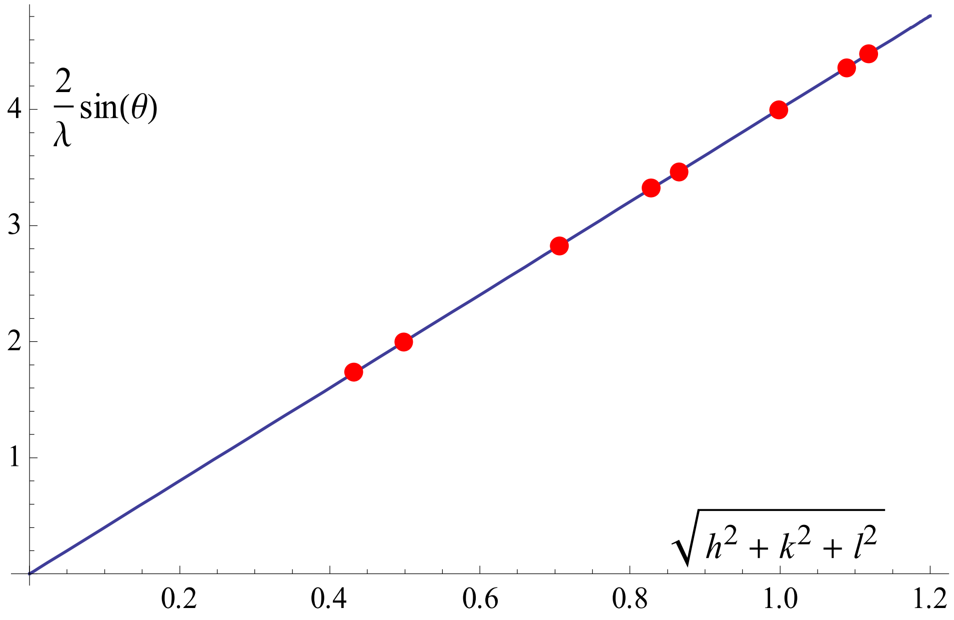
θ= 39.68°, $\sqrt{h^2 + k^2 + l^2} = \sqrt{11}$

θ= 41.83 $\sqrt{h^2 + k^2 + l^2} = \sqrt{12}$

θ= 50.35°, $\sqrt{h^2 + k^2 + l^2} = \sqrt{16}$

θ= 57.05°, $\sqrt{h^2 + k^2 + l^2} = \sqrt{19}$

θ= 59.42°. $\sqrt{h^2 + k^2 + l^2} = \sqrt{20}$



The least-squares fit of the data yield the lattice constant a as $a = 4.0045$ Å.
The Avogadro number can be evaluates as follows, based on the lattice constant a. In Al (fcc), there are 4 Al toms in the conventional cubic lattice.

The volume for Al 1mol is

$$V_A = \frac{M}{\rho} = \frac{27}{2.7} = 10$$

where $M = 27$ g/mol and $\rho = 2.7$ g/cm^3. There are N_A (Al atoms) in this volume V_A. Then we have

$$\frac{V_A}{N_A} = \frac{a^3}{4}$$

The Avogadro number is evaluated as

$$N_A = \frac{4V_A}{a^3} = 6.229 \text{ x } 10^{23}$$

Note that the correct value is 6.023 x 10^{23}.

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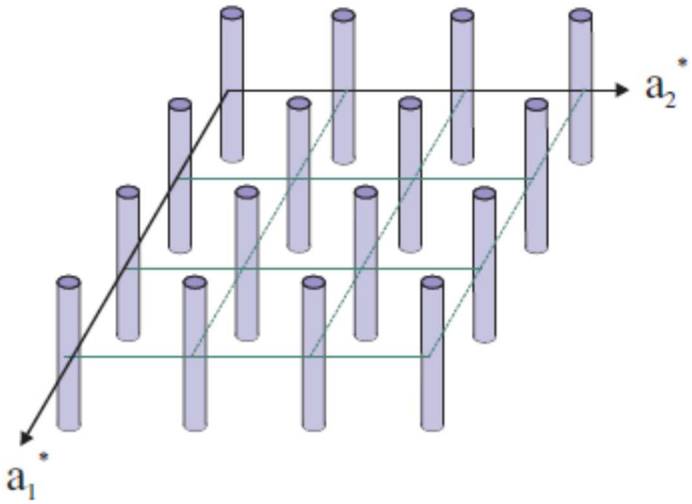
4. 2D Bragg rods


a_2^*
a_1^*

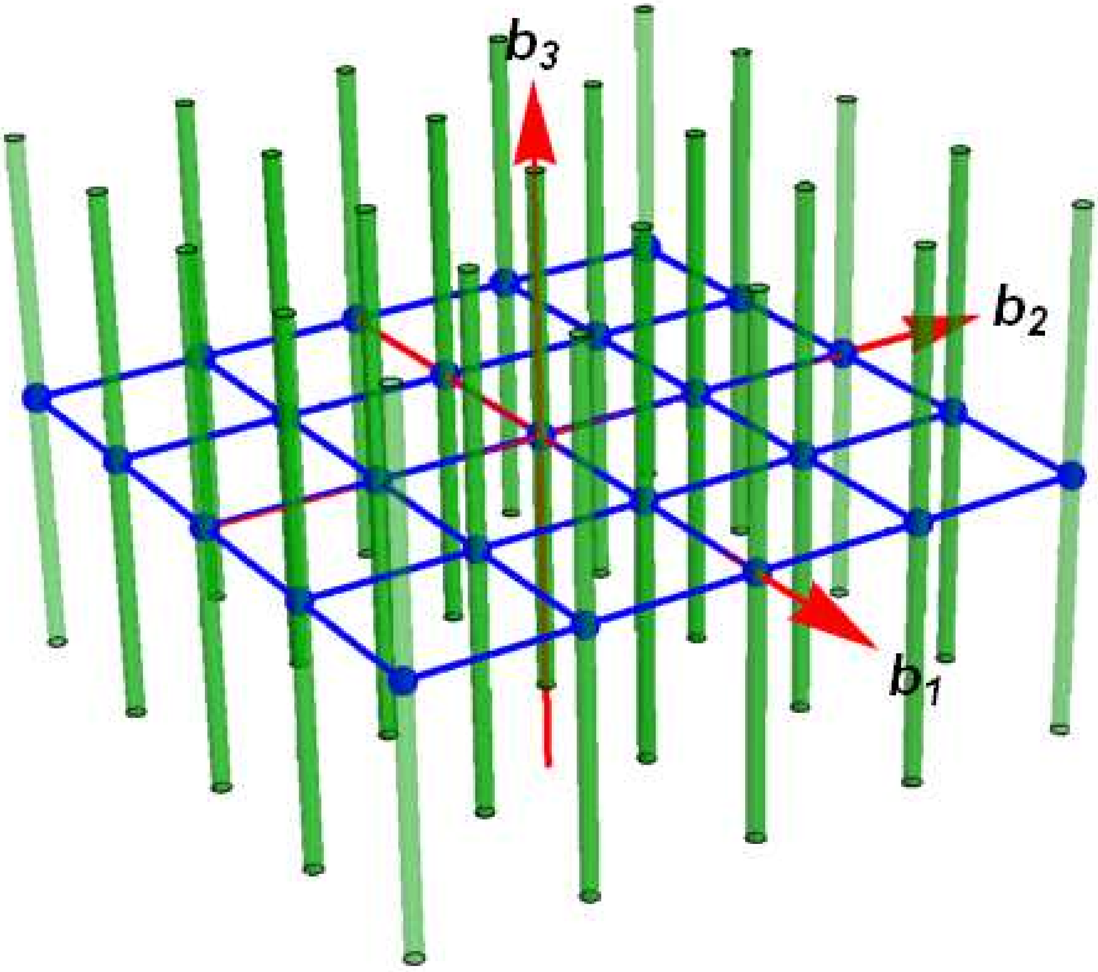
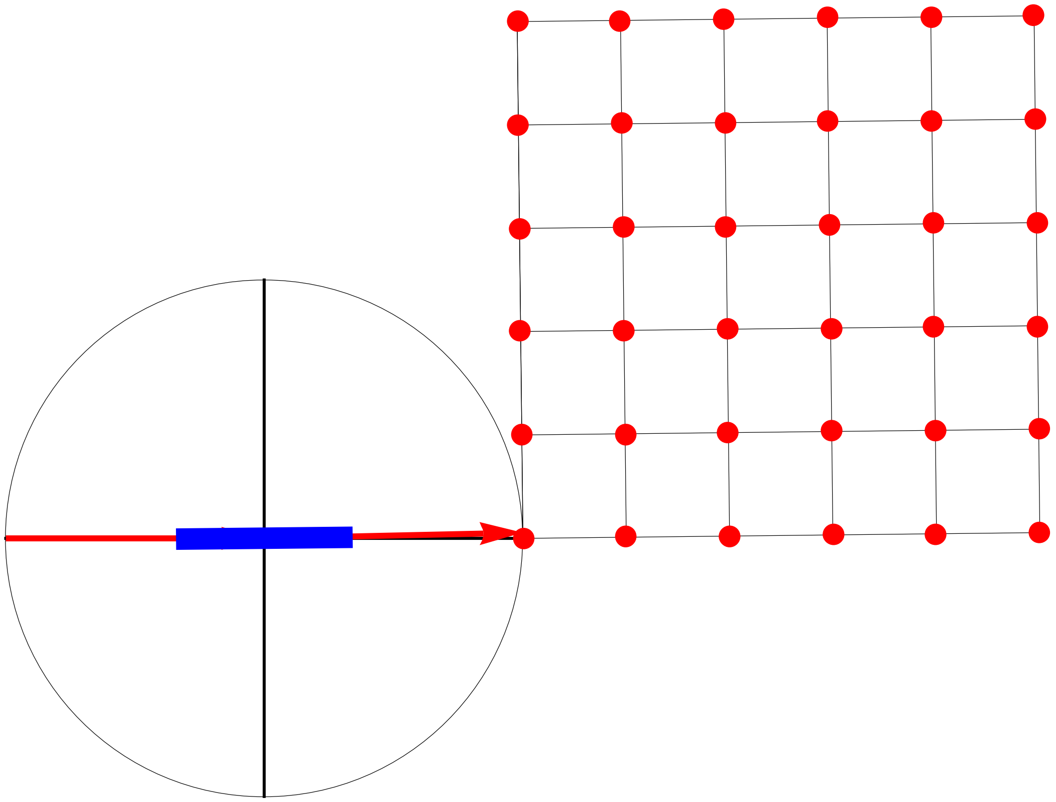
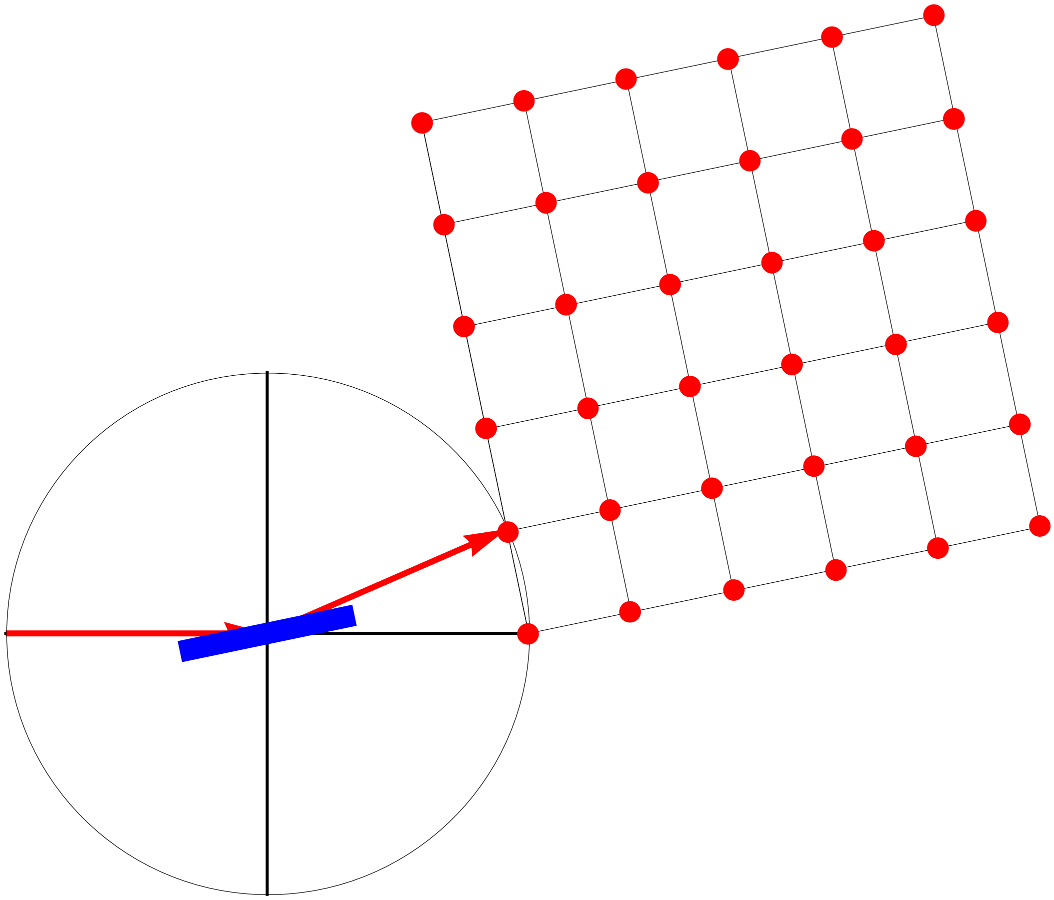
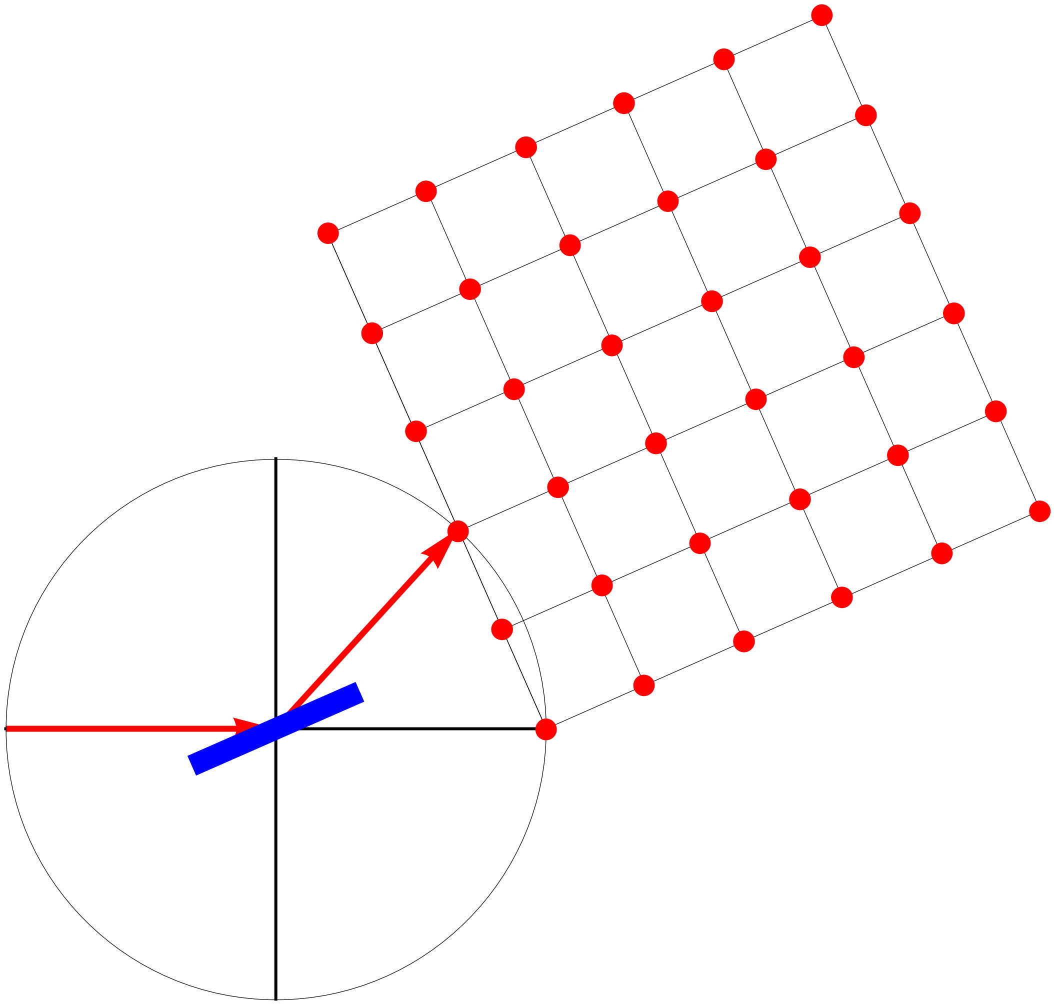

b_3
b_2
b_1

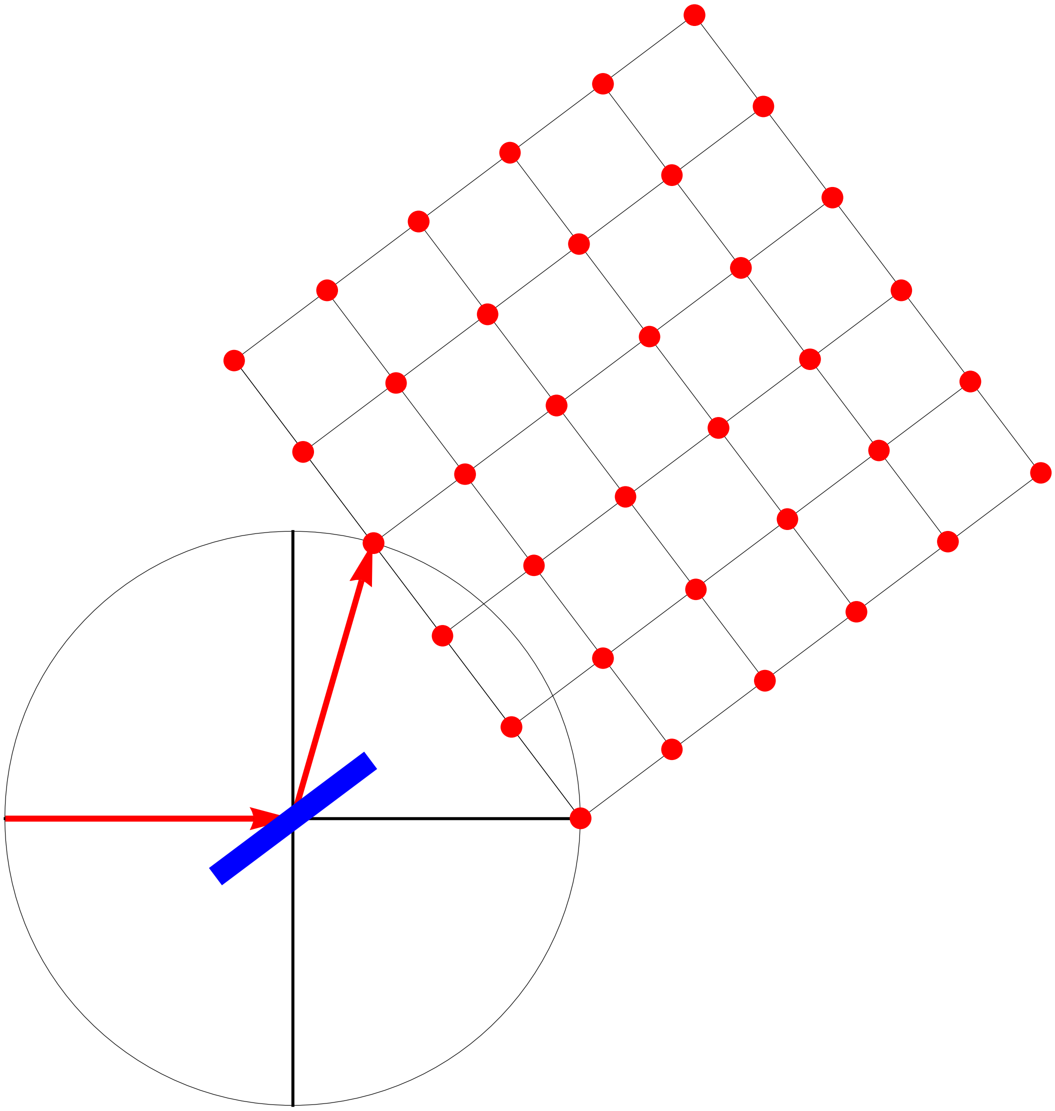
Fig. Bragg rod (ridge) for the 2D system

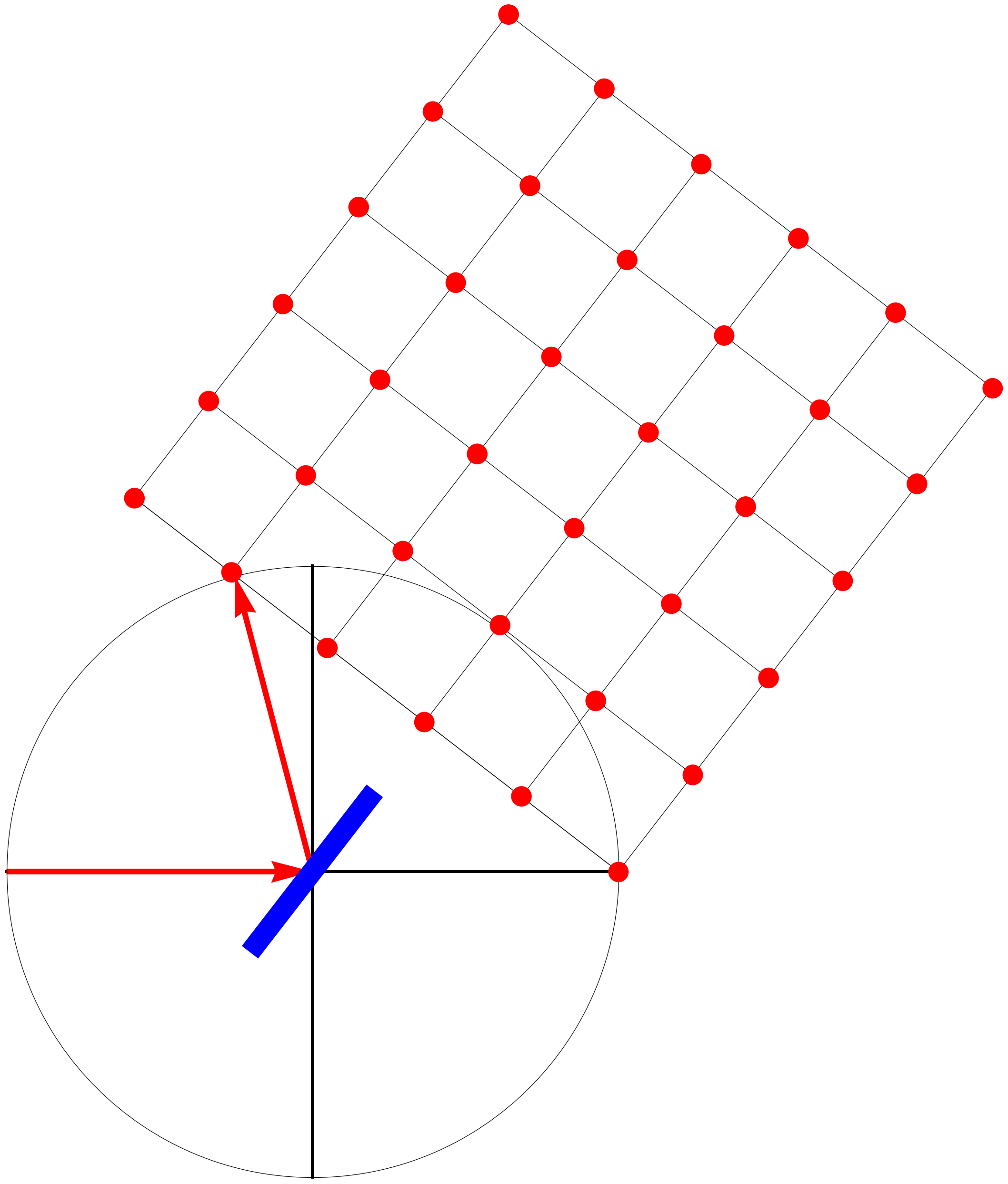
5. Ewald sphere; theta-two theta scattering

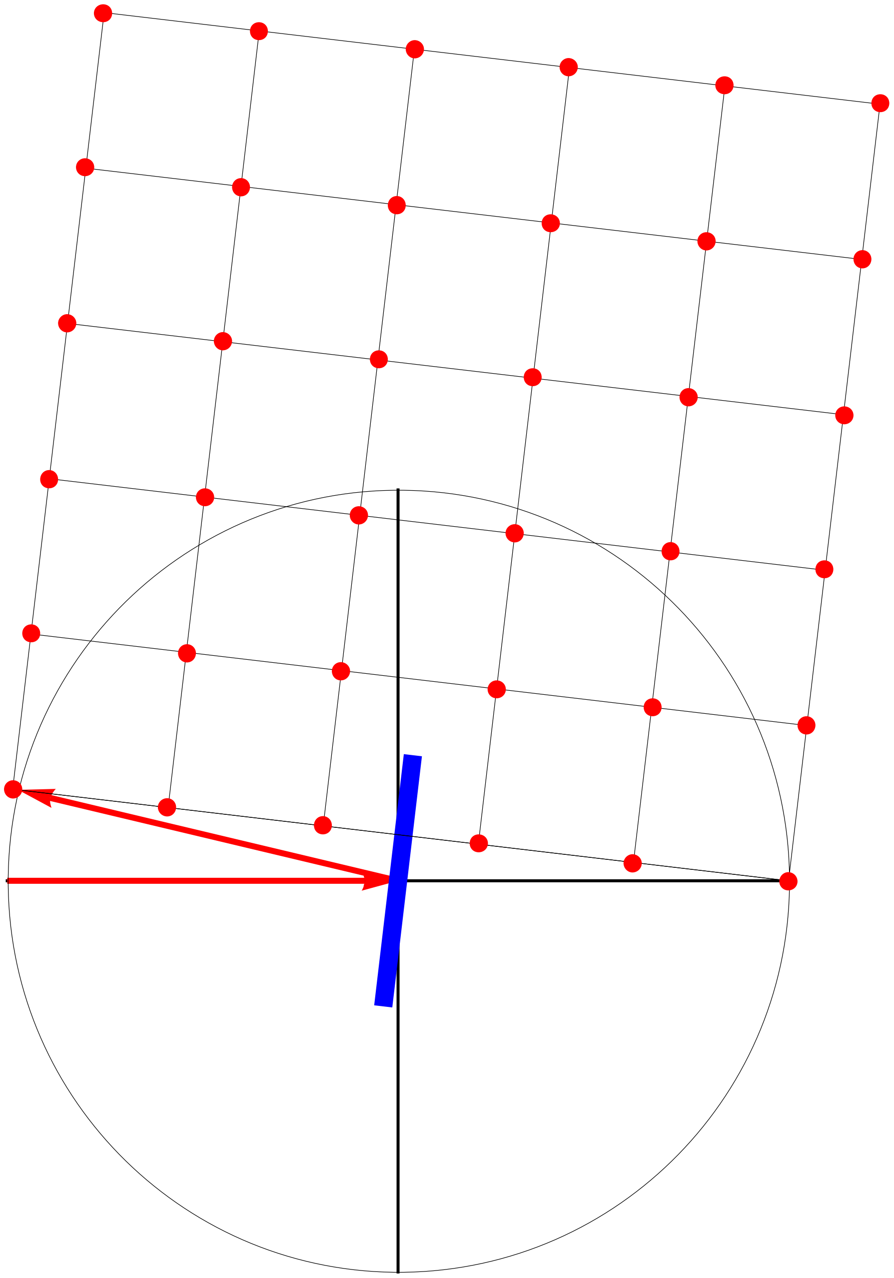












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