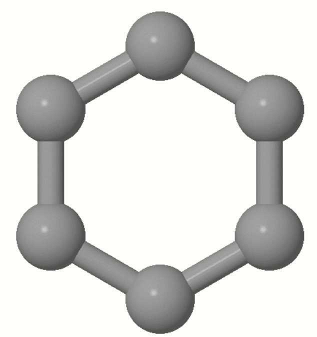
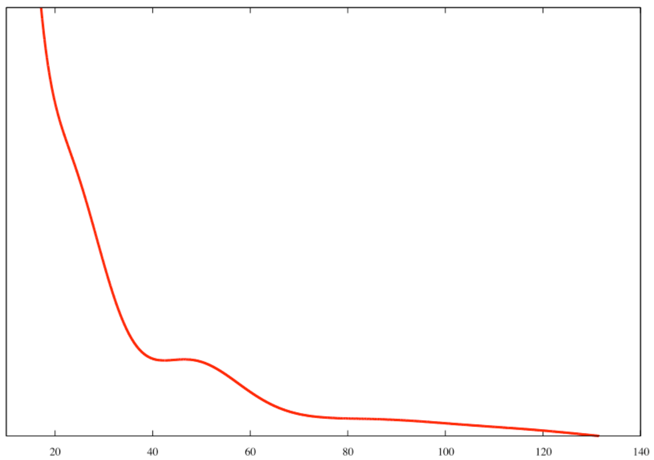
EXAMPLE - Benzene Ring

From the atomic positions...

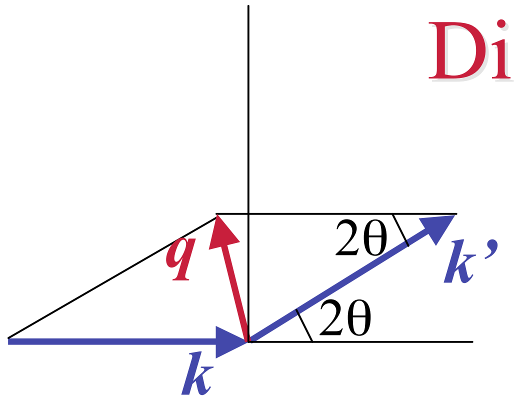
$$\{\boldsymbol{r}_j, \qquad j = 1, \ldots, N\}$$

...we can easily evaluate the interatomic distances and from them we can calculate the powder diffraction response.





Diffraction …



$$\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'; \qquad k = k' = \frac{1}{\lambda}; \qquad q = \frac{2\sin(\theta)}{\lambda}$$

elastic scattering

d_{ij}

$$\frac{\partial \sigma}{\partial \Omega} = \left| \sum_{j=1}^{N} b_j \mathrm{e}^{-2\pi \mathrm{i} \boldsymbol{q}\cdot\boldsymbol{r}_j} \right|^2 = \sum_{j=1}^{N} b_j^2 + 2 \sum_{j>i=1}^{N} b_j b_i \cos\left(2\pi \boldsymbol{q} \cdot (\boldsymbol{r}_j - \boldsymbol{r}_i)\right)$$

Powder diffraction:

many identical particles, in all possible 3D orientations, isotropically distributed!

We need the **spherical average** of the differential cross section.

$$\left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{orient.} = \frac{1}{4\pi} \int_0^{2\pi} \mathrm{d}\beta \int_0^{\pi} \sin(\phi) \mathrm{d}\phi \, \frac{\partial \sigma}{\partial \Omega}$$

Now, for each cosine, we take the polar axis along $\boldsymbol{q}$:

$$\frac{1}{4\pi} \int_0^{2\pi} \mathrm{d}\beta \int_0^{\pi} \sin(\phi) \mathrm{d}\phi \;\; \cos(2\pi d_{ij} q \cos(\phi)) = \frac{\sin(2\pi d_{ij} q)}{2\pi d_{ij} q}$$

and

$$\left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{orient.} = \sum_{j=1}^{N} b_j^2 + 2 \sum_{j>i=1}^{N} b_j b_i \frac{\sin(2\pi d_{ij} q)}{2\pi d_{ij} q}$$

Debye's formula

Peter Debye,
Ann. Phys. 1915, **46**,809.

The PDF

$I_0(q)$ - "constant term"

$I(q)$

$$\left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{orient.} = \sum_{j=1}^{N} f_j(q)^2 + 2 \sum_{j>i=1}^{N} f_j(q) f_i(q) T_j(q) T_i(q) \frac{\sin(2\pi d_{ij} q)}{2\pi d_{ij} q}$$

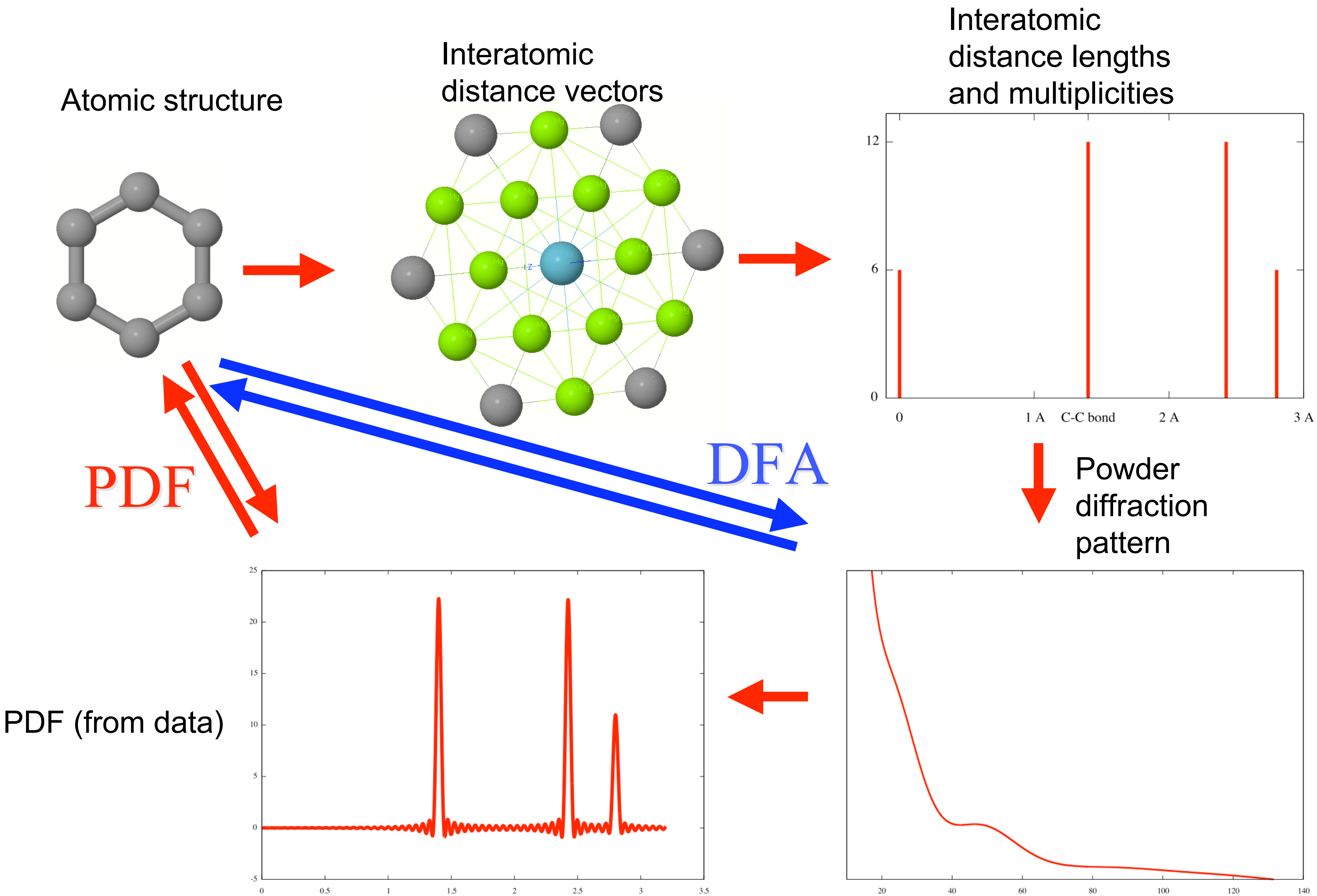
Case of fixed scattering lengths (or if you factor the *f*'s and *T*'s out):

$$I(q) = 2 \sum_{j>i=1}^{N} b_j b_i \frac{\sin(2\pi q d_{ij})}{2\pi q d_{ij}}$$

PDF

$$\int_0^{+\infty} 4\pi q^2 I(q) \frac{\sin(2\pi q r)}{2\pi q r} \mathrm{d}q = 2 \sum_{j>i=1}^{N} b_j b_i \frac{\delta(r - d_{ij})}{4\pi r d_{ij}}$$

Sinc Fourier transform



Atomic structure
Interatomic distance vectors
Interatomic distance lengths and multiplicities
12
6
0
0
1 A
C-C bond
2 A
3 A
Powder diffraction pattern
DFA
PDF
PDF (from data)

PDF advantages:

- clearly <u>see some interatomic distances</u>, modeling can be strongly constrained

DFA advantages:

- simpler experiments, no need for high q and very clean data, very sensitive to <u>size/shape distributions</u>, <u>complex mixtures are OK</u>