A6180/8180:
Modern Scattering Methods in Materials Science

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Scattering by non-crystalline materials

Debye-formula

Zernicke-Prins equation

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the scattered intensity in the most general form:

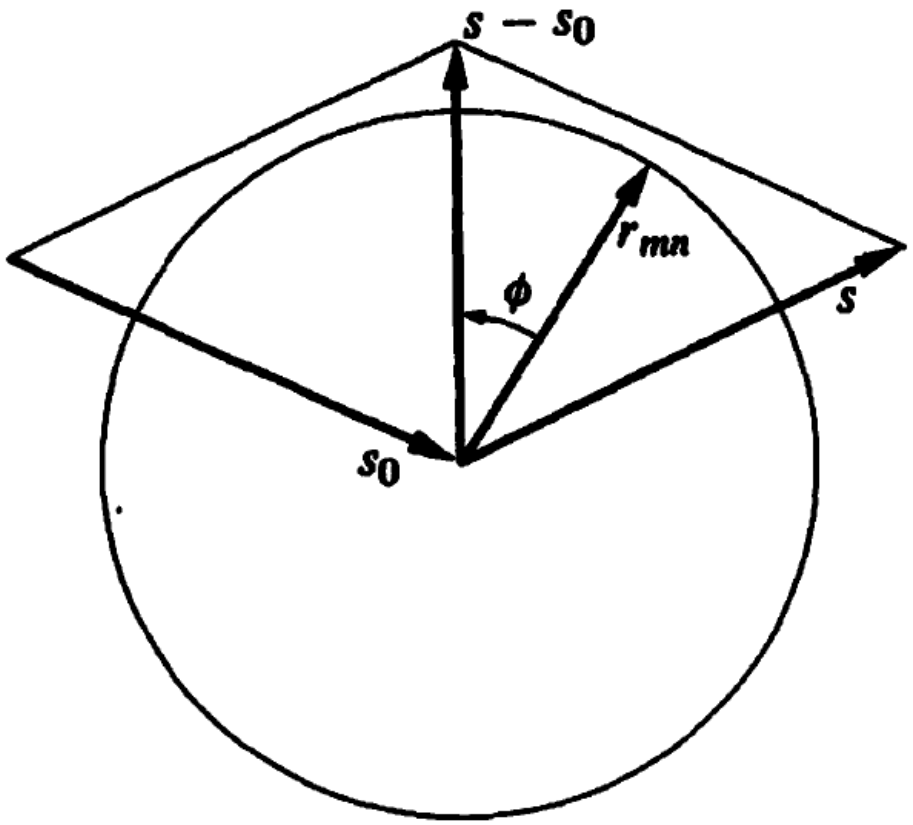
$$I_{eu} = \sum_m f_m e^{(2\pi i/\lambda)(s-s_0)\cdot r_m} \sum_n f_n e^{-(2\pi i/\lambda)(s-s_0)\cdot r_n}$$

where summation has to be done over all the atoms within the illuminated region,

with the difference vector $\mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n$:

$$I_{eu} = \sum_m \sum_n f_m f_n e^{(2\pi i/\lambda)(s-s_0)\cdot r_{mn}}$$

Fig. 10.1 Relations involved in letting the $\mathbf{r}_{mn}$ vector take all orientations in space.



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with $k = (4\pi \sin\theta)/\lambda$, the average for each exponential term:

$$\left\langle e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_{mn}} \right\rangle =$$

$$= \frac{1}{4\pi r_{mn}^2} \int_{\phi=0}^{\pi} e^{ikr_{mn}\cos\phi} 2\pi r_{mn}^2 \sin\phi \, d\phi$$

$$= \frac{\sin kr_{mn}}{kr_{mn}}$$

after summation

$$I_{eu} = \sum_m \sum_n f_m f_n \frac{\sin kr_{mn}}{kr_{mn}}$$

Debye-formula

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gas of polyatomic molecule:

$$I_{eu}/N = \sum_m \sum_n f_m f_n \frac{\sin kr_{mn}}{kr_{mn}} + R \sum_m i(M)_m$$

where the last term on the right-hand side if the *modified* Compton scattering and N is the number of molecules in the illuminated volume.

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carbon-tetrachloride CCl_4:

$$f_C\left\{f_C + 4f_{Cl}\,\frac{\sin kr(C-Cl)}{kr(C-Cl)}\right\} +$$

$$+ 4f_{Cl}\left\{f_{Cl} + f_C\,\frac{\sin kr(C-Cl)}{kr(C-Cl)} +\right.$$

$$\left. + 3f_{Cl}\,\frac{\sin kr(Cl-Cl)}{kr(Cl-Cl)}\right\}$$

For a tetrahedral molecule $r(Cl-Cl) = \sqrt{\frac{8}{3}}\, r(C-Cl)$

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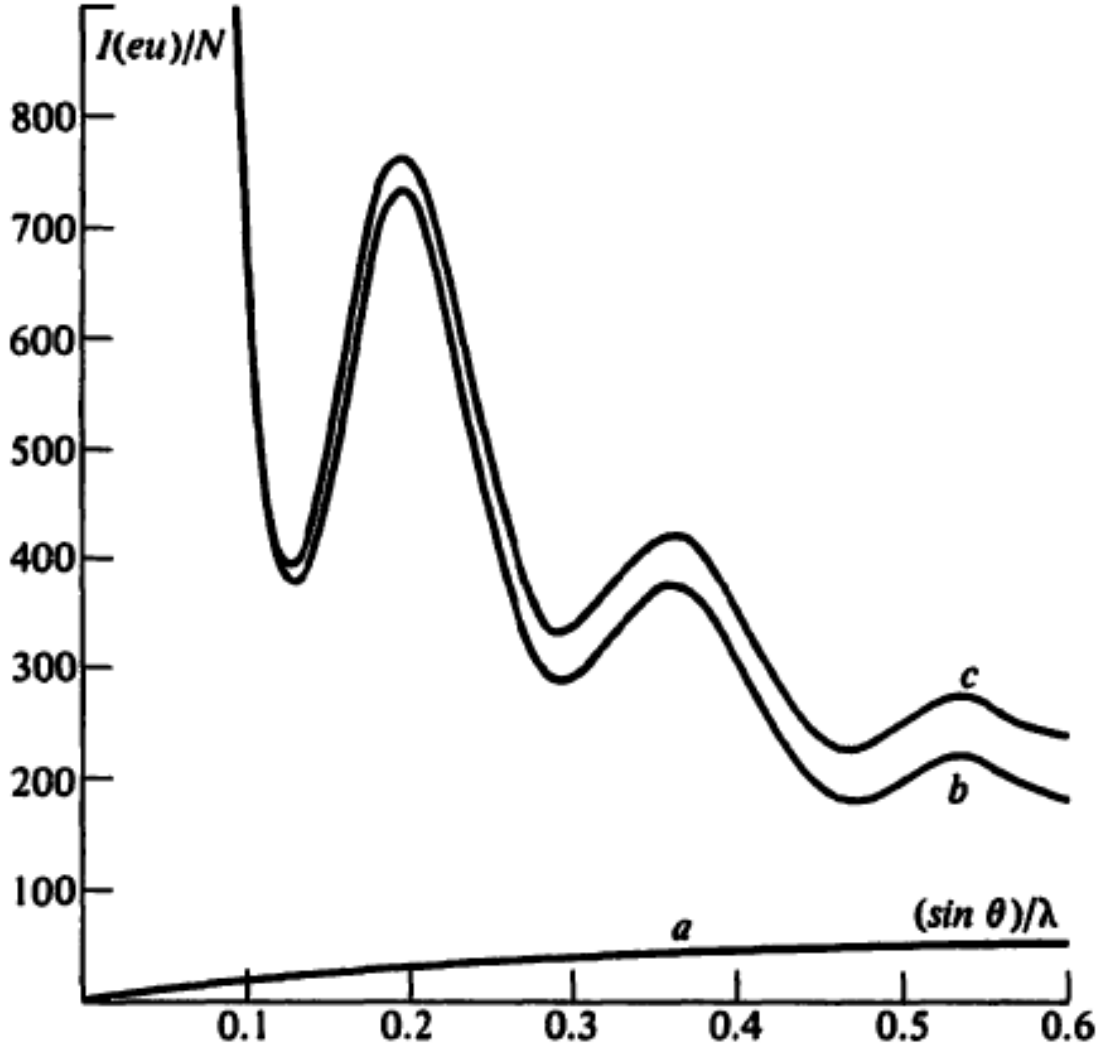

Fig. 10.2 The intensity in electron units per molecule for a CCl_4 gas in which the carbon-chlorine distance is taken as $r = 1.82$ A. (a) The modified intensity per molecule. (b) The unmodified intensity. (c) The total intensity per molecule, unmodified plus modified.

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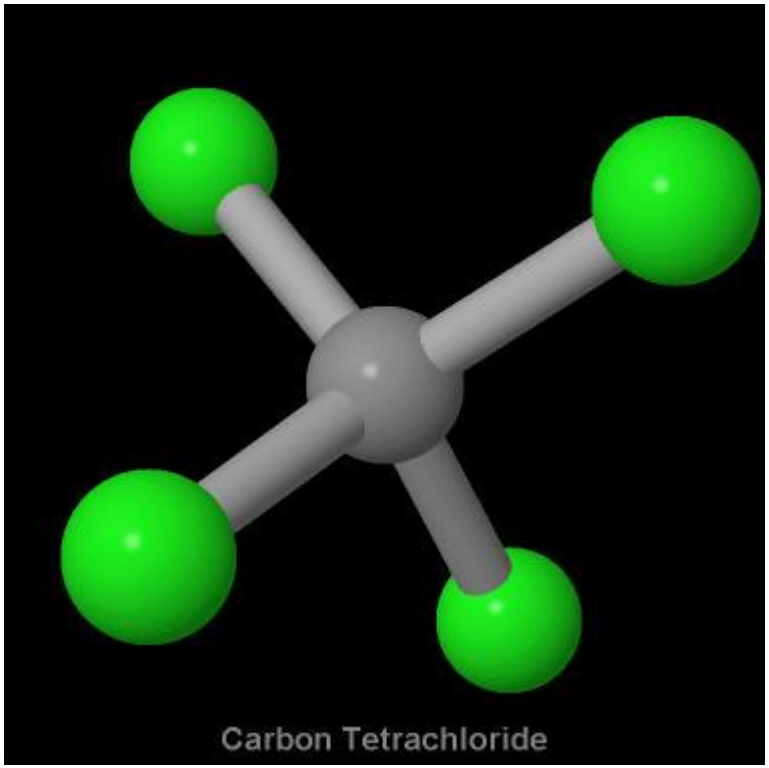

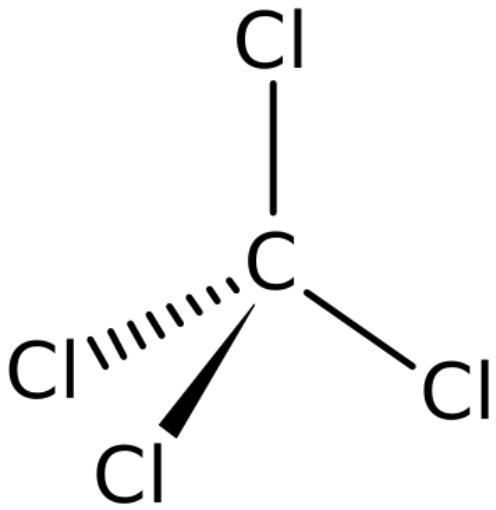

$r_{\text{C-Cl}} = 0.182$ nm

Scattering by liquid or non-crystalline materials

if there is only one kind of atom, the scattered intensity will be:

$$I_{eu} = \sum_m f^2 + \sum_m f^2 \sum_{n \neq m} e^{(2\pi i/\lambda)(s-s_0)\cdot r_{nm}}$$

we introduce a density function: $\rho_m(\mathbf{r}_{nm})$

where $\rho_m(\mathbf{r}_{nm})\, dV_n$ is the number of atoms in dV_n at $\mathbf{r}_{nm}$.

With this the summation can be replaced by the integral:

$$I_{eu} = \sum_m f^2 + \sum_m f^2 \int_S \rho_m(\mathbf{r}_{nm}) e^{(2\pi i/\lambda)(s-s_0)\cdot r_{nm}}\, dV_n$$

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Scattering by liquid or non-crystalline materials

with introducing the average density, ρ_a:

$$I_{eu} = \sum_m f^2 + \sum_m f^2 \int_S [\rho_m(\mathbf{r}_{nm}) - \rho_a] e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_{nm}} \, dV_n +$$

$$+ \sum_m f^2 \int_S \rho_a e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_{nm}} \, dV_n$$

for a fixed distance $\boldsymbol{r}_{mn}=\boldsymbol{r}$ let $\boldsymbol{\rho(\mathbf{r}) = \langle \rho_m(\mathbf{r}_{nm}) \rangle}$, where the average

is over all $\rho_m(\boldsymbol{r})$ within the sample at the distance $\boldsymbol{r}$ from any atom in the sample.

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for a fixed distance in the sample,

$$\mathbf{r}_{nm} = \mathbf{r}, \text{ let } \rho(\mathbf{r}) = \langle \rho_m(\mathbf{r}_{nm}) \rangle,$$

where the average is taken over all $\rho_m(r)$ within the sample at the distance r from any atom.

With this, $[\rho_m(\mathbf{r}_{nm}) - \rho_a]$ in the integral can be replaced by:

$$\rho(\mathbf{r}) - \rho_a$$

Scattering by liquid or non-crystalline materials

For a mon-atomic amorphous sample the term

$$\rho(\mathbf{r}) - \rho_a$$

goes to zero at distances of $\boldsymbol{r}$ larger than a few atomic distances.
Since the volume $\boldsymbol{S}$ is considerably larger than a few atomic distances
the summation over m can be replaced
by the number of atoms in $\boldsymbol{S}$, i.e., N.

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if there is no preferred orientation in the sample,

$$\rho(\mathbf{r}) - \rho_a$$

will have spherical symmetry and can be written as:

$$\rho(r) - \rho_a$$

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Scattering by liquid or non-crystalline materials

if there is no preferred orientation in the sample,

$$\rho(\mathbf{r}) - \rho_a$$

will have spherical symmetry and can be written as:

$$\rho(r) - \rho_a$$

Using the notations in Fig. 10.1 and the variable $k = 4\pi \sin\theta/\lambda$ we obtain:

$$Nf^2 \int_0^\infty \int_0^\pi [\rho(r) - \rho_a] e^{ikr\cos\phi} 2\pi r^2 \sin\phi \, d\phi \, dr =$$

$$= Nf^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho_a] \frac{\sin kr}{kr} \, dr$$

Scattering by liquid or non-crystalline materials

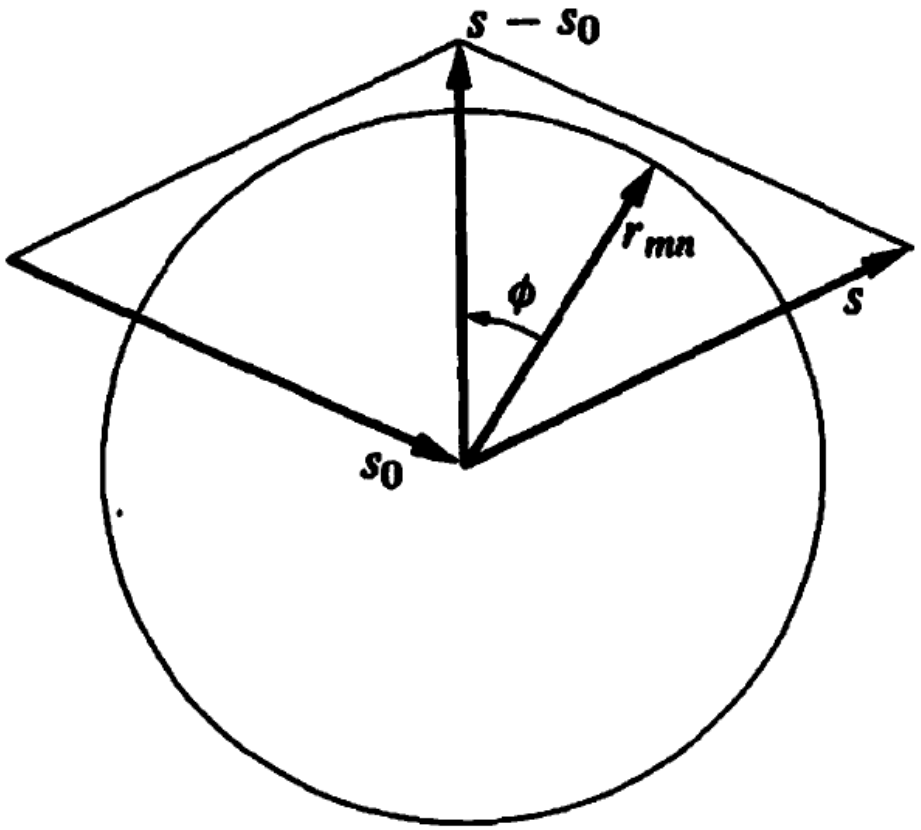

Fig. 10.1 Relations involved in letting the $\mathbf{r}_{mn}$ vector take all orientations in space.

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after some rearrangements:

$$I_{eu} = Nf^2 + Nf^2 \int_0^\infty 4\pi r^2[\rho(r) - \rho_a] \frac{\sin kr}{kr}\, dr \; +$$

$$+ f^2 \sum_m e^{-(2\pi i/\lambda)(s-s_0)\cdot r_m} \int_S \rho_a e^{(2\pi i/\lambda)(s-s_0)\cdot r_n}\, dV_n.$$

next we analyze the integral in the third term:

$$\int_S \rho_a e^{(2\pi i/\lambda)(s-s_0)\cdot r_n}\, dV_n.$$

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since ρ_a is a constant, the integral can be written as:

$$\rho_a \int_S e^{\left(2\pi\frac{i}{\lambda}\right)(\boldsymbol{s}-\boldsymbol{s}_0)\boldsymbol{r}_n} dV_n$$

the integral here is the Fourier transform of the form-factor of the volume of the sample within *S*. If S is macroscopic then the integral is close to a delta function around the direct-beam direction, and therefore has no effect on the diffraction experiment.

The third term on the right-hand site of I_{eu} can be omitted.

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the scattered intensity per atom will become:

$$I'_{eu}/N = f^2 + f^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho_a] \frac{\sin kr}{kr} dr.$$

We introduce the abbreviation:

$$i(k) = \frac{I'_{eu}/N - f^2}{f^2} \quad ,$$

and do some rearrangements:

$$ki(k) = 4\pi \int_{r=0}^\infty r[\rho(r) - \rho_a] \sin kr \, dr$$

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with taking into account the rules of Fourier transformation:

$$\phi(k) = 4\pi \int_0^\infty f(r) \sin kr \, dr,$$

$$f(r) = \frac{1}{2\pi^2} \int_0^\infty \phi(k) \sin rk \, dk.$$

the inverse Fourier transformation provides:

$$r[\rho(r) - \rho_a] = \frac{1}{2\pi^2} \int_0^\infty ki(k) \sin rk \, dk$$

and with some rearrangements:

Scattering by liquid or non-crystalline materials

we arrive at the Zernicke-Prins equation:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_a + \frac{2r}{\pi} \int_0^\infty k i(k) \sin rk \, dk.$$

$4\pi r^2 \rho(\boldsymbol{r})$ is the *radial-distribution-function (RDF)*

F. ZERNICKE and J. A. PRINS, *Zeit Physik*, **41**, 184 (1927).

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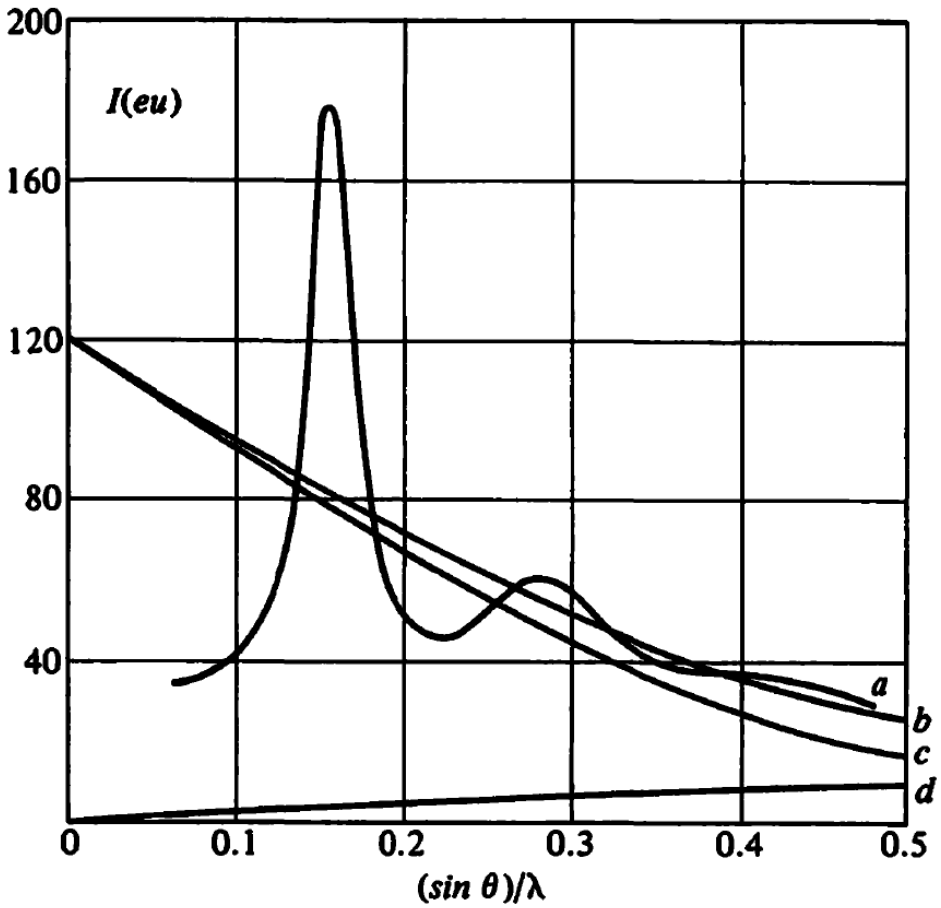

Fig. 10.4 (a) Total intensity curve for liquid sodium in electron units per atom, unmodified plus modified. (b) Total independent scattering per atom. (c) Independent unmodified scattering per atom f^2. (d) Modified scattering per atom $i(M)$.

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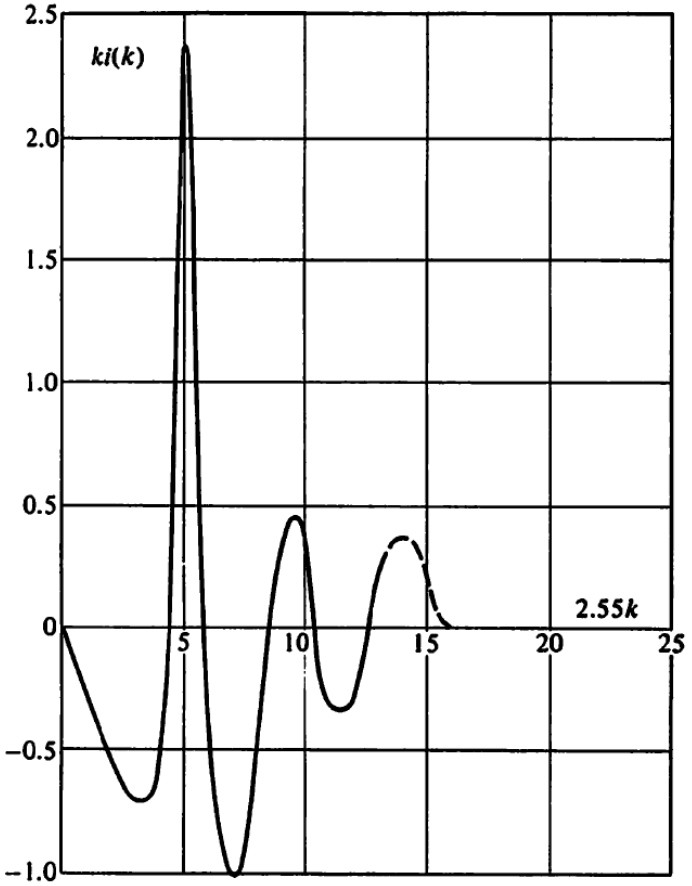

Fig. 10.5 The experimental curve $ki(k)$ for liquid sodium. The abscissa scale $2.55k$ was chosen for convenience in the use of a harmonic analyzer.

Scattering by liquid or non-crystalline materials

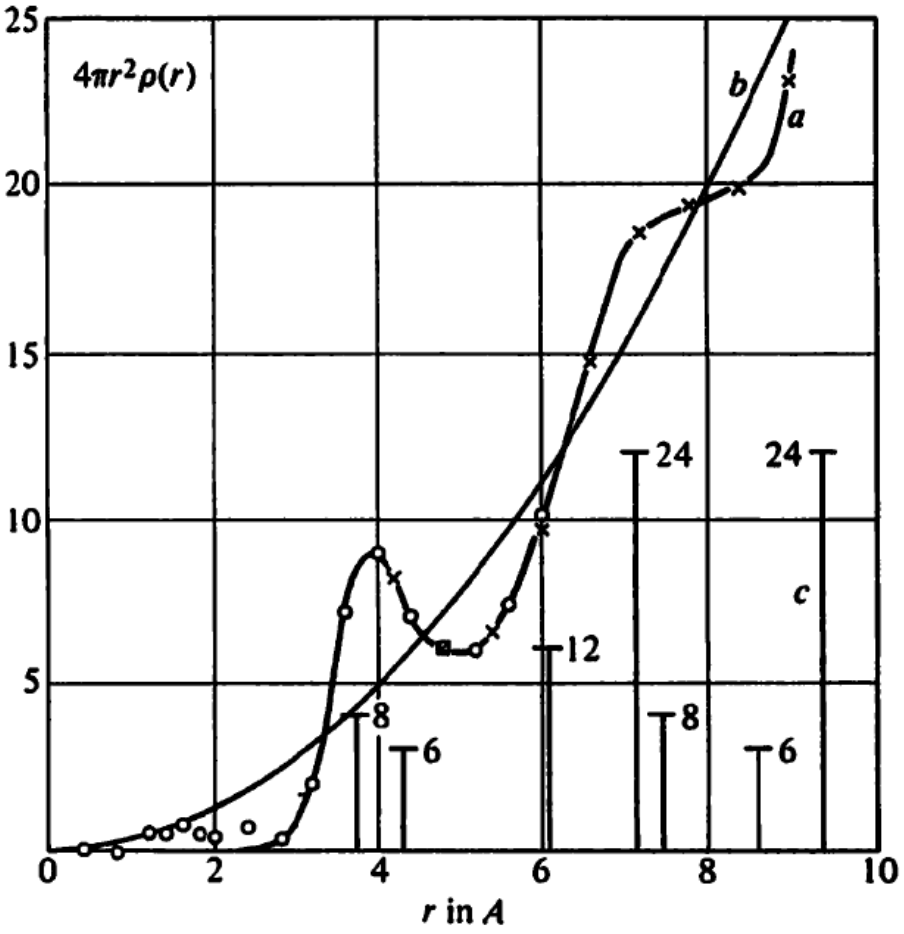

Fig. 10.6 (a) The radial distribution function $4\pi r^2\rho(r)$ for liquid sodium. (b) The average density curve $4\pi r^2\rho_a$. (c) The distribution of neighbors in crystalline sodium.

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Thank you