

Diffraction Intensity by a Bounded Radial Distribution Function

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The convolution of $(\sin Rs/s)^n$ and the intensity diffracted by gaseous, liquid, and amorphous substances is proved to give a modified intensity function expected from the radial distribution function bounded by nR and modified by function M_n as follows,

$$\frac{1}{\pi} \int_{-\infty}^{\infty} t I(t) \left(\frac{\sin R(s-t)}{s-t} \right)^n dt = 4\pi R^{n-1} \int_0^{nR} r D(r) M_n(r/R) \sin sr dr,$$

where

$$M_n(r/R) = \frac{1}{\pi} \int_{-\infty}^{\infty} \left(\frac{\sin x}{x} \right)^n \cos \left(\frac{r}{R} x \right) dx.$$

The integration can be properly approximated by a summation, if the spacing is selected with due consideration for the non-zero range of the substance.

Since the modified intensity can be calculated from the observed intensity, from the modified intensity, atomic distances shorter than nR can be analyzed, regardless of the presence of the longer atomic distances than nR , by the correlation method.

The structure of gas molecules has been effectively analyzed by so-called correlation method consisting in the calculation of the diffraction intensity for various models and comparison with the observed intensity data. In the case of liquid and amorphous substances, however, the method may not be so effectively applied as in above case because of the vast number of structural parameters and models. It may be a problem that even bond distances cannot be definitely determined without the adequate information about all distances longer than the distances. But this can be solved and atomic distances shorter than a distance R can be determined independently of the longer distances beyond R by the correlation method, if from the observed intensity data one can obtain the diffraction intensity due to the atomic distances shorter than R (a modified diffraction intensity).

The convolution of the observed intensity function and the function $(\sin Rs/s)^n$ ($s=(4\pi/\lambda)\sin(\theta/2)$, n =positive integer) such that

$$\begin{aligned} s I_{n,R}(s) &= \frac{1}{\pi} \int_{-\infty}^{\infty} t I(t) \left(\frac{\sin R(s-t)}{s-t} \right)^n dt \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} (s-t) I(s-t) \left(\frac{\sin Rt}{t} \right)^n dt, \end{aligned}$$

can be expressed in terms of the radial distribution function $D(r)$ as follows:

$$s I_{n,R}(s) = 4\pi R^{n-1} \int_0^{\infty} r D(r) M_n(r/R) \sin sr dr,$$

where

$$r D(r) = (1/2\pi^2) \int_0^{\infty} s I(s) \sin sr dr,$$

and

$$\begin{aligned} M_n(\lambda) &= \frac{1}{\pi} \int_{-\infty}^{\infty} \left(\frac{\sin x}{x} \right)^n \cos \lambda x dx \\ &= 0 \quad \text{for } |\lambda| \geq n. \end{aligned}$$

(Dirichlet integral)

Thus $I_{n,R}(s)$ is the intensity function due to a bounded radial distribution function, which vanishes beyond $r=nR$ and is modified by $M_n(r/R)$; illustrated in Fig. 1. Consequently

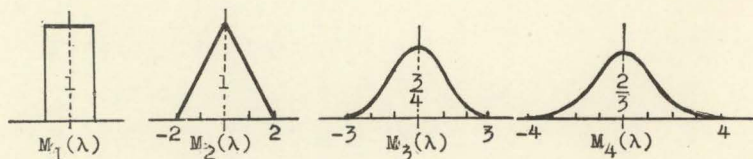
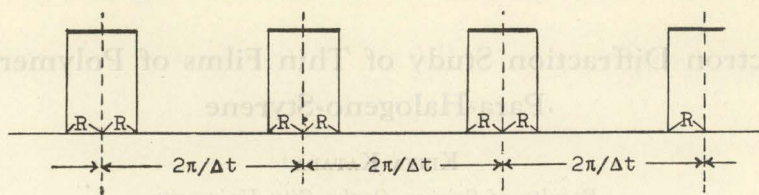


Fig. 1.


 Fig. 2. $M_1(r/R)$

the desired modified intensity can be obtained from the observed one by this procedure.

In the numerical calculation of the modified intensity, as usual, the integral should be approximated by a sum over evenly spaced t values as follows.

$sI_{n,R}(s)$

$$= (\Delta t/\pi) \sum_{i=-\infty}^{\infty} (s-i\Delta t) I(s-i\Delta t) \left(\frac{\sin Ri\Delta t}{i\Delta t} \right)^n$$

This can be transformed further:

$$sI_{n,R}(s) = 4\pi R^{n-1} \int_0^{\infty} rD(r) M_n(r/R) \sin sr \, dr,$$

where

$$M_n(\lambda) = (\Delta t/\lambda) \sum_{i=-\infty}^{\infty} \left(\frac{\sin i\Delta t}{i\Delta t} \right)^n \cos(\lambda i\Delta t).$$

The discrepancy between $I_{n,R}(s)$ and $I_{n,R}(s)$ can be estimated from that between $M_n(\lambda)$ and $M_n(\lambda)$. $M_n(\lambda)$ is an even periodic function with the period $2\pi/\Delta t$, and if $\pi/\Delta t > nR$ we have $M_n(\lambda) = M_n(\lambda)$ for $|\lambda| \leq \pi/\Delta t$, as illustrated in Fig 2. Consequently, if a spacing smaller than π/nR is taken for the summation and $rD(r)$ of the substance vanishes beyond $r = (2\pi/\Delta t) - nR$,

we have $I_{n,R}(s) = I_{n,R}(s)$. In order to compute adequately the modified intensity, an information is required about the non-zero range of the substance, beyond which the $rD(r)$ must vanish.

The information can be derived from the observed intensity data by the following treatment. In case $I_{1,R}(s)$ equals to $I(s)$, the Fourier inversion derives the relation

$$rD(r)(1 - M_1(r/R)) = 0, \text{ and } rD(r) = 0$$

for $((2m-1)\pi/\Delta t) - R < r < ((2m-1)\pi/\Delta t) + R$ (m =positive integer), since $M_1(\lambda)$ is a square wave function, as illustrated in Fig. 2. Therefore, the comparison of $I_{1,R}(s)$ with $I(s)$ can supply the information required for the calculation.

As the result, the modified intensity due to atomic distances shorter than a selected length can be calculated properly from the observed intensity with due consideration for the non-zero range of the substance, and the atomic distances shorter than the selected length can be analyzed by the correlation method as effectively as in the case of small gas molecules.

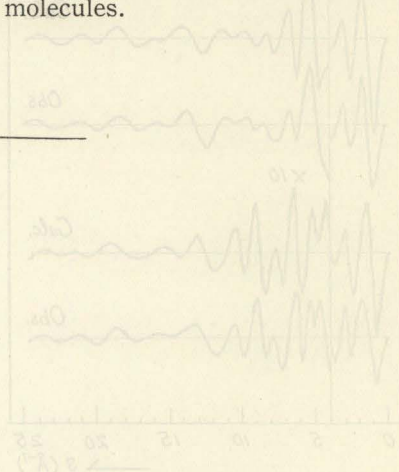


Fig. 3. Comparison between the intensity calculated from the best model and the observed intensity (see Table 1).