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DEFINITION OF A PARAMETER WHICH MEASURES THE HOMOGENEITY OF A MATERIAL

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Abstract. — The fluctuations of the quantity of matter contained in a test volume are calculated, in relation to the diffraction data. Under some conditions, they can be approximated by the sum of two terms, proportional respectively to the test volume, and to the surface which limits it. The volume term is already known, and the surface term is proportional to an integral of the diffracted intensity, taken over the whole reciprocal space, with a weight which dominates near the origin. This integral partly characterizes the homogeneity of the material. Its values in some simple periodic structures, are given.

1. Introduction. — The results of diffraction experiments made on liquid or amorphous samples are often interpreted through the radial distribution function \( P(r) \); the calculation of this one implies a Fourier integral of \( s \mathcal{J}(s) \) (where \( \mathcal{J}(s) \) is the interference function, versus the radial reciprocal variable). One gives, in this operation, a small weight to \( \mathcal{J}(s) \) for \( s \approx 0 \). The present work is an attempt to define a parameter which could express, better than \( P(r) \), the information collected near the origin of the diffraction diagram.

It is known that the limiting value of \( \mathcal{J}(s) \) for \( s \to 0 \) (we call it \( \mathcal{J}(0) \)) is a measurement of the fluctuations of the amount of matter contained in an infinitely large volume [1]. Since we are concerned here, with small but non zero values of \( s \), we have to estimate these fluctuations in a large but finite volume.

2. Calculation of the fluctuations. — In the following discussion, we use the atom as the unit of amount of matter, and we suppose that there is only one type of atom; but any other unit could be used, for example the electron. We consider a (fictitious) test volume \( V_r \) whose shape, dimensions, and orientation are fixed, and we move it, by translations, through the material; for each position, we count how many atoms are included in \( V_r \).

The notations are:

- \( V_r; \mathcal{S}_r \) the test volume; the area of its limiting surface;
- \( N_r(r); < N_t > \) the number of atoms contained in \( V_r \) when it is centred on \( r \); its mean value, when \( r \) moves through the whole material;
- \( V; N \) the total volume of the material \( (V \gg V_r) \); the total number of atoms;
- \( \nu = V/N \) the mean atomic volume;
- \( \rho(r); \rho_0 = 1/\nu \) the atomic density; its mean value;
- \( U_t(r) \) the function equal to 1 inside \( V_r \), and 0 outside, if \( V_r \) is centred at the origin;
- \( F(s); U_t(s) \) the Fourier transforms of \( \rho(r) \) and \( U_t(r) \);
- \( \mathcal{J}(s) = \int F(s) - \rho_0 \delta(s) \mid^2/N \) the interference function, after subtraction of the peak at the origin.
- \( s = |s| = 2 \sin \theta/\lambda \).
The mean value of the fluctuations of the number of atoms contained into $V_i$ is
\[
< (N_i(r_i) - < N_i >)^2 > = \frac{1}{V} \int_V d^3r_i \left( \int_V d^3r (\rho(r) - \rho_0) U_i(r-r_i) \right)^2.
\] (1)

This expression can be calculated in reciprocal space (Bessel-Parseval theorem)
\[
< (N_i(r_i) - < N_i >)^2 > = \frac{1}{V} \int d^3k \left| X(s) - \rho_0 \delta(s) \right| U_i(s) \right|^2. \quad (2)
\]

Whence
\[
< (N_i(r_i) - < N_i >)^2 > = \frac{1}{V} \left( \frac{1}{V} \right) + \int d^3k \left| X(s) \right|^2. \quad (3)
\]

This calculation is known, eventually under different formulations, but the integral in (3) is usually neglected, since $U_i(s)$ has appreciable values only near the origin, where $K(s)$ is negligible; the mean value of the fluctuations is then $\langle V_i^{-1} \rangle \delta(0)$. Here the volume $V_i$ is finite, and this involves a spreading of the function $U_i(s)$; therefore the integral in (3) is not exactly zero.

It is possible to calculate this integral for two special shapes of $V_i$: a sphere, and a parallelepiped. In these two cases, one obtains the following results:

a) The shape of $\left| U_i(s) \right|^2$ is that of a central peak, with wings oscillating around a mean value represented by $s^{-n}$.

b) Let $s_0$ be a rough estimation of the width of this peak. Provided that $K(s)$ is negligible for $s < s_0$, one can ignore the contribution of the peak, retaining only the one of the wings. If the oscillations of $U_i(s)$ have a short period, compared to those of $K(s)$, one can furthermore neglect these oscillations, and put in the integral the mean asymptotic value $s^{-n}$ in place of $U_i(s)$.

c) In the case where $V_i$ is a parallelepiped whose faces are parallel to axes of real space, one can neglect the integral everywhere in reciprocal space, except in the vicinity of reciprocal axes.

d) If $K(s)$ has the spherical symmetry, the integral has the same value in both cases, which is
\[
\frac{s_0}{2 \pi^2} \int_0^s \frac{K(s)}{s^2} ds. \quad (4)
\]
e) The interval $(0 - s_0)$ must give no contribution to this last result, from consideration of the first conclusion in b; this implies that $K(s)$ is not more than proportional to $s^2$ near $s = 0$; if not, the expression (4) is wrong.

Since the above discussion applies to the cases where $V_i$ has the shape of a sphere, or of a parallelepiped, and since in both cases the expression (4) is the same it can reasonably be inferred that it applies too, when $V_i$ is limited by any surface, provided it has not too much singularities.

One can now define for a given material, two parameters (one is already known), $V_h$ and $S_h$, such that
\[
\begin{align*}
\frac{1}{V_h} &= \frac{\delta(0)}{v} \\
\frac{1}{S_h} &= \frac{1}{2 \pi^2 v} \int_0^\infty \frac{K(s)}{s^2} ds.
\end{align*}
\] (5)

and the fluctuations are given by
\[
< (N_i(r_i) - < N_i >)^2 > = \frac{V_i}{V_h} + \frac{S_i}{S_h} \quad (6)
\]

$V_h$ and $S_h$ can be called homogeneity volume and area, but they cannot be identified to a particular volume or surface found in the material.

One must remind that this applies only if $K(s)$ has the spherical symmetry and $K(s) \propto s^2$ or less near the origin (from e), and if $V_i$ is large compared to distances where correlations in the material are noticeable (from b). These conditions are not all satisfied for the crystalline state; in that case, one can nevertheless calculate $S_h$ formally, by taking $K(s)$ equal to the spherical mean of $K(s)$.

3. Discussion. — The meaning of the parameter $S_h$ has to be cleared up. For an ideal gas $S_h = \infty$ (or $S_i/S_h = 0$) and the density fluctuations are represented by $1/V_h$ only; for a crystal the situation is reversed. One can say that $1/V_h$ represents uncorrelated fluctuations, which do not compensate one another in an infinite volume, and $1/S_h$ represents correlated fluctuations. It should be noticed that $S_h$ can be negative in some cases; this means that the correlations tend to make the fluctuations smaller in the short range than in the long range. For example, if in the description of a gas, we take into account the size of the molecules, one sees that the density is less inhomogeneous than when they are point shaped; and in that case $S_h$ is negative; $V_h$ does not depend on the molecular size. In the case of liquid or amorphous materials, one finds highly correlated fluctuations, which nearly compensate in an infinite volume; $V_h$ is very high, and $S_h$ is expected to be lower than in a crystal, but of the same order of magnitude.

One may have an idea on the behaviour of $S_h$ by calculating it for some simple periodic structures. If the unit of length is such that $v = 1$, one finds the values given in table I. This table contains an indication on the homogeneity, given by the dimension of holes (the distance between a hole and the nearest atoms) and the number of holes which can be simultaneously filled up. The main trend which can be seen in this result is the variation of the sensitivity of $S_h$; the lower it is, the more sensitive to a change in homogeneity it seems to be.
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Table

Homogeneity and value of $S_n$ for some types of structure

<table>
<thead>
<tr>
<th>Type</th>
<th>$\bar{d}_{\text{hole-atom}}$</th>
<th>$N_{\text{holes}}$</th>
<th>$N_{\text{atom-atom}}$</th>
<th>$N_{\text{atoms}}$</th>
<th>$S_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face centred cubic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexagonal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Close packed</td>
<td>0.707</td>
<td>1</td>
<td>15.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centred cubic</td>
<td>0.646</td>
<td>1.5</td>
<td>15.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simple cubic</td>
<td>0.866</td>
<td>1</td>
<td>15.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td>1</td>
<td>1</td>
<td>13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sites 16d of Fd3m (*)</td>
<td>{1.173}</td>
<td>0.25</td>
<td></td>
<td></td>
<td>11.6</td>
</tr>
</tbody>
</table>

(*) Sites occupied by cations in octahedral coordination in spinel structure (space group Fd3m).

4. Practical considerations and conclusions. — The difficulties which may be encountered in the experimental determination of these homogeneity parameters arise from, eventually, the measurement of the density $\rho_0$, and from the measurement of $\bar{J}(s)$ at low $s$. A good technique for the last seems to be the one used by A.-M. Levelut and A. Guinier [2], who measure $\bar{J}(s)$ for $s$ between 0.3 and $0.7 \times 10^{-2}$ Å$^{-1}$. Their results indicate that these values of $s$ are probably low enough for the calculation of $S_n$. The small angle measurements must be associated to conventional medium angle ones; it is not necessary to do them at angles higher than the ones of the first or second peak of $\bar{J}(s)$ (for a liquid or amorphous sample), provided that an extrapolation is made by taking $\bar{J}(s) = 1$ between this limit and infinity.

Another difficulty arises from the ambiguity of the definition of $\rho(r)$, and therefore of $V_h$ and $S_h$, when several atomic species are present.

The measurement of $V_h$ and $S_h$ could help one to characterize the materials, as far as homogeneity is concerned; the differences observed by the cited authors [2], between several liquids is an encouragement to take such a characterization into consideration. This measurement would also give a supplementary test for comparisons between real samples and models; but $V_h$ and $S_h$ can be calculated in large enough models only.

5. Acknowledgments. — I became conscious of this problem through numerous discussions with Dr M. Brunel.

References