

On Homometric Structures

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Structures which have the same squared transform but which are neither congruent nor enantiomorphic are defined as homometric structures.

Homometric structures can be expressed systematically by means of the convolution operation; their analysis starts out from the so-called Q -function. They may be conveniently classified as follows:

I. Pseudohomometric structures.—(a) Homometric structures which under suitable affine transformations degenerate to enantiomorphic or congruent structures. (b) Structures which are homometric only for infinitely large crystals.

II. Homomorphs.—Homometric structures which remain homometric under any arbitrary affine transformation.

A general expression of finite homometric structures which covers all the known examples is given by an integral equation of the folding type; its degenerate cases are discussed.

Introduction

From diffraction experiments only the intensity distribution is obtained directly. The scattered amplitude, $R(b)$, is proportional to the Fourier transform of $\varrho(x)$, the density distribution of the scattering material which obviously is always finite in size. The scattered amplitude, $R(b)$, is related to the so-called Q -function which is the 'convolution square' (symbol $\overset{2}{\varrho}$) of ϱ . Now this Q -function can be calculated from the experimentally obtained intensity data by inverse Fourier transformation (after correcting for polarization, Thomson, Lorentz and other relevant factors). Thus

$$\begin{aligned} I(b) &= \mathfrak{F}\{Q(x)\}, \\ R(b) &= \mathfrak{F}\{\varrho(x)\}, \\ RR^*(b) &= I(b), \\ Q(x) &= \overset{2}{\varrho} = \int \varrho(y)\varrho(y+x)dv_y. \end{aligned} \quad (1)$$

In the literature only the convolution product (symbol $\widehat{g_1 g_2}$) of two functions g_1 and g_2 is explicitly introduced as

$$\widehat{g_1 g_2} = \widehat{g_2 g_1} = \int g_1(y)g_2(x-y)dv_y. \quad (2)$$

Denoting by $\varrho^-(x)$ a function which is symmetrical to the function $\varrho(x)$ about the point $x = 0$, i.e.

$$\varrho^-(x) = \varrho(-x),$$

and substituting $g_1(x)$ by $\varrho(x)$, $g_2(x)$ by $\varrho^-(x)$ (or vice versa) in (2), it is seen that

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$$\overset{2}{\varrho} = \widehat{\varrho} \widehat{\varrho}^- = \int \varrho(y)\varrho(y-x)dv_y. \quad (3)$$

Substitution of $y-x$ by ψ shows immediately that this integral is identical with that of (1). Moreover, this proves that the function $Q(x)$ has always a centre of symmetry at $x = 0$ (cf. Friedel's rule), i.e.

$$Q(x) = Q(-x). \quad (4)$$

Structures which have the same squared transform cannot be distinguished by X-ray investigations alone. Convolution operations offer an elegant representation of such structures. They are related by

$$\overset{2}{\varrho_1} = \overset{2}{\varrho_2} = \overset{2}{\varrho_3} = \dots, \quad (5)$$

where $\varrho_1, \varrho_2, \dots$ denote the density distributions of the individual structures.

Now it is convenient to distinguish between special cases of (5).

$$\text{I. } \varrho_1(x) = \varrho_2(x): \text{congruence} \quad (6)$$

$\varrho_1(x)$ can differ from $\varrho_2(x)$ by a translation or a rotation or a combination of both.

$$\text{II. } \varrho_1(x) = \varrho_2(-x): \text{enantiomorphy} \quad (7)$$

From (1) it is immediately seen that

$$Q(x) = \overset{2}{\varrho_1} = \overset{2}{\varrho_2}.$$

Hence it is impossible to distinguish between ϱ_1 and ϱ_2 from the knowledge of the Q -function, i.e. of the intensity alone. The effect of specific absorption edges which allows Friedel's law to be violated and thus helps to distinguish between these cases will not be

considered here. Such structures ρ_1 and ρ_2 are called enantiomorphs and strictly do not belong to the conventional concept of homometric structures, since enantiomorphic forms in three-dimensional space, though not congruent, can be brought into coincidence by the combined operation of rotation, translation and inversion.

Patterson (1953) has pointed out a two-dimensional set consisting of six point atoms all having the same weight (see Fig. 1(a), (b)). They are enantiomorphic to

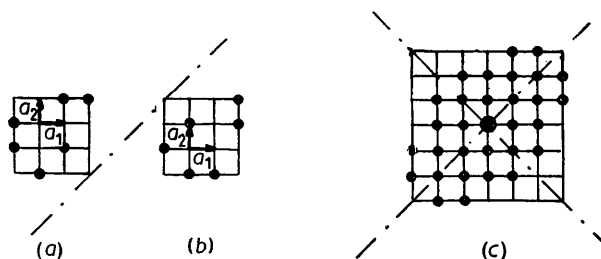


Fig. 1. Example of two two-dimensional functions (a) and (b) and their convolution square (c) which shows two planes of symmetry, though the functions themselves possess no such symmetry (after Patterson, 1953). In three-dimensional space the structures (a) and (b) are congruent but in two-dimensional space enantiomorphic. All the points in (a)-(c) have the same weight, namely 1. Only the centre (thickly marked) in (c) has weight 6.

one another in two-dimensional space but congruent in three-dimensional space since one can be transformed into the other by a simple rotation and parallel displacement. They are, however, very interesting in view of the fact that they give rise to homometric structures under suitable affine transformations (see Figs. 2 and 3).

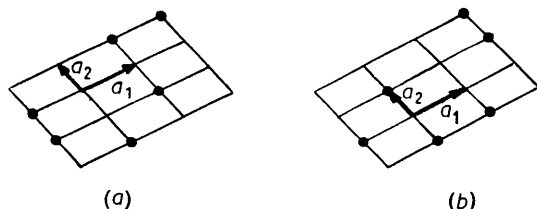


Fig. 2. The same structures as in Fig. 1 after affine transformation. Contrary to Fig. 1, they are now homometric and are classified as pseudohomometric (after Patterson, 1953).

Structures giving the same Q -function but still not belonging to I and II are defined as homometric structures. They can be broadly classified into pseudohomo-

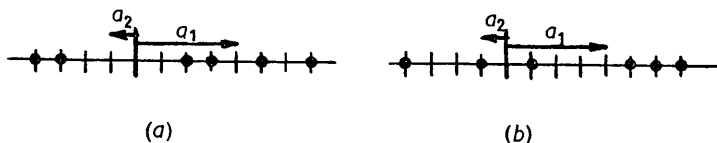


Fig. 3. Another example of pseudohomometric structure obtained from Figs. 1 or 2 by a singular affine transformation (a_1 parallel to a_2). It is the simplest possible example of one-dimensional homometric structures, in which all the points have the same weight (after Patterson, 1953).

metric structures and real homometric structures or homomorphs, as Patterson calls them. Homomorphs are characterized by the fact that they remain homomorph under any affine transformation whatsoever in contradiction to some homometric structures which degenerate to enantiomorphic or congruent structures under suitable affine transformations.

III. Pseudohomometry.

(a) *Homometric structures which under a suitable affine transformation degenerate to enantiomorphic or congruent structures.*—Figs. 2 and 3 obtained from Fig. 1 illustrate the case. Patterson (1953) has shown that the structures of Figs. 2 and 3 are the only possible 'six point pairs'. Other such homometric structures exist only for more than six equivalent point atoms. Structures containing fewer than six equivalent point atoms do not possess homometric mates.

(b) *Structures which are homometric only when the sets are infinitely extended.*—Let ρ_0 be the density distribution of a lattice cell and Q_0 its convolution square and let $z^1(x)$ be the lattice peak function. The convolution square of the infinitely large crystal is then proportional to its Patterson function $Pa(x)$, thus

$$Pa(x) = Q_0 \widehat{z^1}, \quad Q_0 = \frac{2}{Q_0}. \quad (8)$$

Fig. 4(a) and (b) shows respectively lattice cells of two structures (after Hermann, 1953) which are homometric only when the crystals are infinitely large. In the examples given here both of them are two-dimensional and each of them possesses a centre of symmetry. It is also interesting to note that they are complementary to each other. Their Q_0 -functions (Fig. 4(c) and (d)) differ from each other but their Patterson functions are identical (Fig. 4(e)). Hosemann & Bagchi (1952, 1953a, b) have shown that such structures of finite size can be uniquely analysed by taking into consideration, in addition to integral intensities, the displacements of the reflexion maxima from their ideal positions at the points of the ideal reciprocal lattice.

The cyclotomic and other related structures (Patterson, 1943) belong to this group, whether they possess a centre of symmetry or not. The authors have shown (Hosemann & Bagchi, 1953a, b) that all such structures, if finite in size, have different Q -functions and that their Q_0 -functions, which also differ from one another, can be separated.

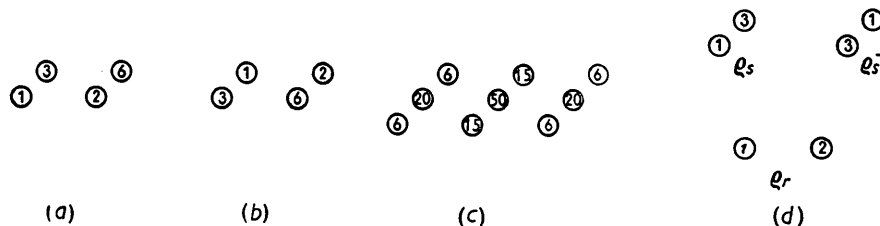


Fig. 6. Example of homomorphs without centres of symmetry, illustrating equation (10).

is a function with 2^{n-1} homometric mates and 2^{n-1} enantiomorphic forms when all the ρ_k are asymmetric.*

A simple two-dimensional example of point atoms is shown in Fig. 6. Here ρ_r consists of two point atoms with weights a and b at distance u , and ρ_s of two point atoms with weights c and d at distance v . Fig. 6(d) shows the arbitrarily chosen values of the weights, namely $a = 1, b = 2, c = 1, d = 3$. Fig. 6(c) shows their common convolution square.

Fig. 7 shows a complicated example corresponding to (12) of two-dimensional homometric point structures where all the three ρ_k are without centres of symmetry.

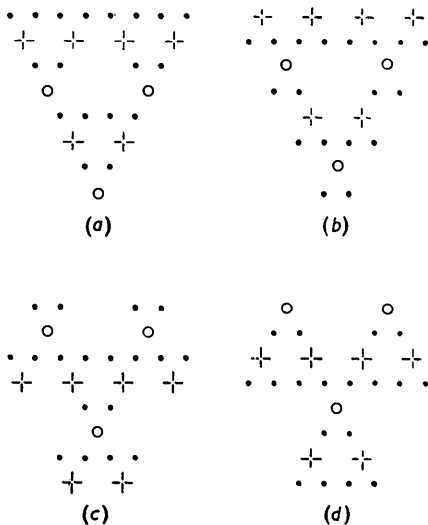


Fig. 7. Example of homomorphs without centres of symmetry, illustrating equation (12) (after Patterson, 1953). The circles, crosses and points denote the different weights of the point atoms.

* Patterson (1953) had communicated to us two theorems on homometric structures which are special degenerate cases of the general formulation given by (10) and (12). Patterson's theorems are:

Theorem A.—The set $a_i + b_j$ has as homometric mate the set $a_i - b_j$ provided that neither the set a_i nor the set b_j is centrosymmetric and provided that $a_0 = b_0 = 0$ ($0 \leq i \leq I, 0 \leq j \leq J$).

Theorem B.—Any two of the sets $a_i \pm b_j \pm c_k \dots$ form a pair provided that (i) at least one sign remains unchanged and at least one sign is changed, and (ii) that the set of vectors whose signs are not changed and the set of vectors whose signs are changed are both acentric.

In contrast to (10) and (12), here all the partial structures $\rho_r, \rho_s, \rho_t \dots$ consist of point atoms all of which have the same weight. The subsidiary condition $a_0 = b_0 = 0$ is not necessary.

Further, examples given in Figs. 1–3 are interesting special cases of (10). Let

$$\begin{aligned}\rho_s &= P(0, \bar{1}) + P(0, 0) + P(1, 0), \\ \rho_r &= P(\bar{1}, 0) + P(0, \bar{1}) + P(1, 1) - P(0, 0),\end{aligned}$$

where $P(p_1, p_2)$ denotes a point atom at the coordinate point $x = p_1 a_1 + p_2 a_2$. a_1, a_2 are two arbitrarily chosen vectors which in certain cases lead to enantiomorphic structures (cf. Fig. 1) and in the other cases to homometric pairs (cf. Figs. 2 and 3).

$$\text{Since } P(a_1, a_2) \widehat{P}(b_1, b_2) = P(a_1 + b_1, a_2 + b_2)$$

it follows that

$$\widehat{\rho_r \rho_s} = P(\bar{1}\bar{1}) + P(\bar{1}0) + P(0\bar{2}) + P(\bar{1}\bar{1}) + P(11) + P(21)$$

and

$$\rho_r \widehat{\rho_s} = P(\bar{2}0) + P(\bar{1}\bar{1}) + P(\bar{1}\bar{1}) + P(0\bar{1}) + P(11) + P(12)$$

correspond completely to the sets shown in Figs. 1–3. In contrast to the examples given in Figs. 5–7, it is not at first sight evident here that these structures also may be constructed by convolution operations from more elementary functions $\rho_r, \rho_s \dots$

Lastly we come to the case where *at the most one and only one* member of the homometric set is symmetric (or antisymmetric).

Substituting ρ_s by ρ_r in (10), we get

$$\rho_1 = \widehat{\rho_r \rho_r}, \quad \rho_2 = \widehat{\rho_r \rho_r} = \widetilde{\rho_r}^2. \quad (13)$$

Here also ρ_1 is the homometric mate of ρ_2 , but ρ_2 evidently always possesses a centre of symmetry which is lacking in ρ_1 provided ρ_r is asymmetric. In the cases of ρ_r possessing a centre of symmetry, ρ_1 becomes identical with ρ_2 .

Fig. 8 shows a simple example where ρ_r consists of two point atoms of weights a and b (e.g. $a = 1, b = 2$).

If ρ_r consists of three point atoms (of weight 1) not lying in a straight line, we get the homometric sets of Fig. 9(a), (b) and their common Q_0 -function (Fig. 9(c)). If these three points lie on the same straight line without possessing a centre of symmetry (see Fig. 10(d)) then we get the structures of Fig. 10(a), (b) which have the common convolution square. In the case of a centrosymmetric ρ_r , all the homometric structures of Figs. 6–10 become identical.

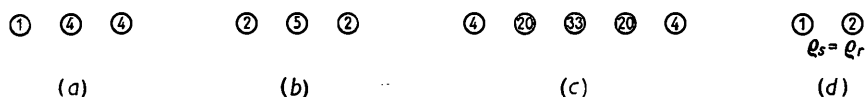


Fig. 8. A simple example of homomorphs, one of which has a centre of symmetry, illustrating equation (13).

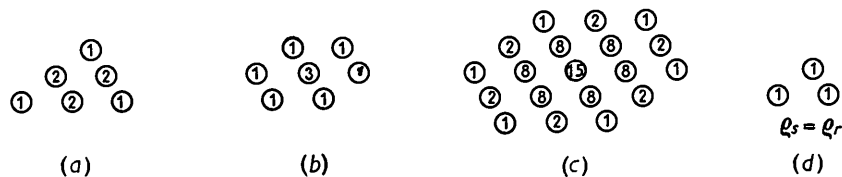


Fig. 9. Further example of homomorphs illustrating equation (13). (This figure was communicated to us independently by Hermann and Patterson.)

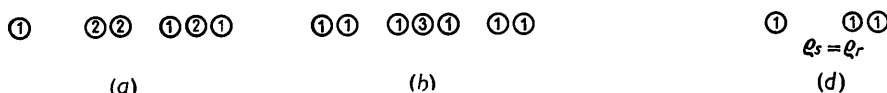


Fig. 10. Further example of homomorphs illustrating equation (13).

The considerations put forward above show clearly the task of an X-ray crystallographer confronting the problem of homometric structures.

First, it is very important to separate the Q_0 -function from the Q -function obtained from intensity data. The structures which are homometric only for infinitely large crystals are clearly distinguished.

Secondly, from the Q_0 -function it is possible to find the symmetrical (or antisymmetrical) ϱ function, if any such solution exists, by a recursion process. It can then be definitely concluded that this is *the only member* of the homometric set which possesses a centre of symmetry (or antisymmetry).

The expression (12), namely

$$\varrho = \widehat{\varrho_1} \widehat{\varrho_2} \widehat{\varrho_3} \cdots \widehat{\varrho_n}, \quad (12)$$

shows clearly that the problem of finding other members of the homometric set, all of which of necessity are asymmetric, depends on being able to resolve the obtained ϱ into the elementary factors ϱ_n , i.e. to solve the integral equation (12). It can be safely

concluded that in general there is an infinity of solutions. In some cases, however, it may be possible to resolve a previously determined ϱ into its folding factors ϱ_n ; this would then directly give all the members of the homometric set.

We would like here to express our thanks to Dr A. L. Patterson for private communications drawing our attention to many interesting examples of homometric functions which led to the present formulation of homometric functions.

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