The Limiting Size of Natural Paracrystals

BY F. J. BALTA-CALLEJA

Instituto de Estructura de la Materia, Serrano 119, Madrid-6, Spain

AND R. HOSEMANN

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Teilinstitut für Strukturforschung, Faradayweg 4-6, 1 Berlin 33, Federal Republic of Germany

(Received 7 November 1979; accepted 9 June 1980)

Abstract

X-ray diffraction data for various materials reveal that naturally occurring microparacrystals cannot exceed a certain limiting size. The empirically obtained linear relationship between the square root of the limiting number of lattice planes within a paracrystal and the reciprocal value of the relative distance fluctuation between planes (degree of distortion) is discussed in the light of the paracrystal approach.

The paracrystal theory (Hosemann, 1950) was proposed to bridge the existing gap between crystals and amorphous materials and gases. The first paracrystals in nature were found in 1951 in the macrolattices of natural proteins (Hosemann, 1951). Since then, knowledge of the structure and properties of naturally occurring paracrystals has increased rapidly, owing mainly to the use of X-ray diffraction (Hosemann & Bagchi, 1962; Lemm, 1970; Vogel, 1972; Loboda-Čačković & Čačković, 1972; Steffen, 1976) and these investigations lend support to the theoretical propositions. M. von Laue (1960) had in fact foreseen a development of crystallography as a generalized discipline lying between the crystalline and amorphous states. The aim of this note is to show that real paracrystals cannot exceed a certain limiting size which is related to the degree of distortion within the lattice. Before presenting these results and their implications we briefly summarize the basic assumptions of the theory.

The concept of a paracrystal can be regarded as a new lattice complex which, contrary to conventional crystallography, contains at least nine new parameters. Each of the three edge vectors \( a_k \) of a paracrystalline lattice can be found with a certain statistical frequency \( H_a(x) \) for a certain value \( a_k = x \). The whole distance

\[
H_{pq}(x) = P(x)H_{100}H_{100} \ldots H_{100}H_{010}H_{010} \ldots H_{010}H_{001}H_{001} \ldots H_{001},
\]

where \( P(x) \) is a point function at \( x = 0 \). If one averages \( z(x) \) over all directions, as in a powder diagram, one obtains the \textit{a priori} distance probability function \( W(x) \) familiar in the theory of liquids after Debye (1927). Most of the modern theories of liquids do not take into account this important fact. Each \( H_a(x) \) contains a fluctuation tensor \( A_{sk} \) which describes the statistical variance of \( a_k \) in the direction \( a_i \). As a measure of the degree of lattice distortion, the relative mean fluctu-
The limiting size of natural paracrystals

The existence of finite lattice boundaries. Hence, real mesophases. In the light of the paracrystal theory is used. Hermann (1940) defined for the first time a paracrystallite, the domain size of the paracrystallite, the distance fluctuation between two neighbouring lattice planes steadily increases (see the right-hand-side boundary in Fig. 1). If we denote by \( \Delta_k \) the distance fluctuation between two neighbouring buckled net-planes, then, according to the rules of statistics, the fluctuation between the net-planes at the boundaries of a paracrystal with \( N+1 \) net-planes is given by \( \sqrt{N} \Delta_k \). The domain size of the paracrystallite, \( D = N d \), refers to the extent of the structure over which the total fluctuation reaches the size of the mean separation of the net-planes. Thus, if such a fluctuation reaches the order of magnitude of the average plane separation \( d \), then the crystallite size, \( Nd \), cannot increase any further. This occurs if \( \sqrt{N} \Delta_k = \alpha d \). The number \( N \) within a paracrystal is, therefore, inversely proportional to the square of the \( g \) value:

\[
N = (\alpha^*/g_{kk})^2; \quad g_{kk} = \Delta_k/\bar{a}_k.
\]

The numerical values of \( N \) and \( g \) can be directly derived from the profile analysis of X-ray diffraction data (Hosemann & Bagchi, 1962).

Fig. 2 illustrates the obtained linear increase of \( \sqrt{N} \) as a function of \( 1/g \), according to (2), for various materials. The \( \alpha \) values obtained are between 0.1 and 0.2. This empirically discovered \( \alpha \) law is of central interest in colloid science because it demonstrates that the larger the lattice distortions, the smaller the size of stable paracrystals becomes and the larger their inner surface turns out to be. All metallic melts, such as Au (Hosemann & Lemm, 1964), Pb (Steffen & Hosemann, 1976), Cu, Fe and Al (Hosemann & Willmann, 1972), exhibit in Fig. 2 the largest lattice distortions (\( g \approx 10\% \)) and consequently the smallest paracrystalline domain size (\( N \approx 4 \)). Carbon compounds, such as pyrolytic graphite (Vogel & Hosemann, 1979) and organic synthetic polymers, such as polyethylene (Hosemann, Čačković & Wilke, 1967), poly(1-butene) (Haase, Köhler & Hosemann, 1978), and biopolymers, such as bone apatite (Wheeler & Lewis, 1977) show somewhat smaller distortions and limiting paracrystalline sizes between 10 and 120 lattice planes. Finally, doped metals, like the \( \alpha \)-iron ammonia catalyst (Ludwiczek, Preisinger, Fischer, Hosemann, Schönfeld & Vogel, 1978) and the technical low-pressure methanol catalyst Fischer, Hosemann, Vogel, Koutecky, Pohl & Ralek, 1980) present the smallest distortions (\( g \approx 1\% \)) and, as a result, the largest paracrystal size (\( N = 170-450 \)). The value derived from a computer simulated (spiral) paracrystal (Janke & Hosemann, 1978) is also included in Fig. 2. A two-dimensional paracrystal was drawn, stepwise, from the origin along a spiral of lattice points using a Monte-Carlo method with Gaussian statistics and a circle construction. The mean fluctuations of this lattice model increase radially from the centre to the periphery up to a limiting \( N \) value of 50 where the two circles of the lattice cell construction could not intersect any further. The model was constructed with Monte-Carlo statistics with \( g = 2.1\% \). From this it follows that \( \sqrt{N} \approx 0.15 \), which is in good agreement with \( \alpha^* \) values obtained for natural paracrystals. The plot of Fig. 2 clearly shows that the paracrystalline state is intermediate between the gaseous (\( g > 0.3 \)) and crystalline (\( g = 0 \)) states, having properties intermediate between those of these two states.

The origin of paracrystalline distortions has to be sought in the three-dimensional statistically distributed incorporation of motifs which disturb the crystalline regularity or in conformational singularities which do

![Fig. 2. Plot of \( \sqrt{N} \) versus \( 1/g \) for different natural paracrystals. The \( \alpha^* \) value is given by (2). The number of lattice planes, \( N \), is derived from \( D_{\text{avr}}/d_{\text{av}} \) where \( D_{\text{avr}} \) is the mean crystallite size derived from X-ray diffraction data. For doped metals, \( \alpha \)-iron ammonia catalyst, \( d_{\text{av}} = 2.03 \AA \). For polymers, polyethylene crystals and bulk materials, \( d_{110} = 4.1 \AA \) and bulk poly(1-butene), \( d_{110} = 8.8 \AA \). For graphite, \( d_{002} = 3.36 \AA \). For metallic melts, Au, Cu, Fe, Al, Pb, \( d_{111} \approx 2.8 \AA \). The spiral paracrystal \( \alpha^* \) values was derived from a computer two-dimensionally simulated point lattice (see text).](image-url)
not fit within the lattice of the environment. In the case of the $\alpha$-iron ammonia catalyst doped with 3% Al$_2$O$_3$, the cause of paracrystalline distortions is the statistical incorporation of Fe$^{2+}$Al$^{3+}$O$_4^-$ motifs within the iron lattice (Ludwiczek, Preisinger, Fischer, Hosemann, Schönfeld & Vogel, 1978). In bone apatite, ions, such as hydroxyl carbonate and other species, having size and shape differences from the phosphate and calcium ions, are incorporated into the lattice (Wheeler & Lewis, 1977). In long-chain synthetic polymers, lattice distortions are produced by the occurrence of step chain defects,* such as kink isomers within the so-called crystal lattice (Hosemann, Wilke & Baltá-Calleja, 1966). The increasing density of chain defects (branches) incorporated at interstitial crystal sites by means of a generation of 2g1 kink conformations within the lattice provokes in melt-crystallized polyethylene (Martínez-Salazar & Baltá-Calleja, 1980) a substantial gradual increase of the lattice distortions, simultaneously reducing the size of the microparacrystals according to the $\alpha^*$ law. In metallic melts, distortions within paracrystalline domains with mean life-times of about $10^{-10}$ s are produced by largely damped phonon waves. In conclusion, the paracrystal approach provides a valuable approximation for the understanding of the structure and properties of non-crystalline substances having lattice sizes within colloidal dimensions and offers, in addition, a gradual transition from the disordered gaseous state of matter to conventional crystals where lattices can reach macroscopic dimensions.

One of us (FJBC) is greatly indebted to the Alexander von Humboldt-Stiftung for the generous support of this work.

* Step chain defects in polyethylene are defined by two gauche conformations $gg$ of opposite sign incorporated into the paraffin-like chains with $trans$ conformations $t$.

References