THE LIMITING SIZE OF NATURAL PARACRYSTALS

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ABSTRACT

X-ray diffraction data for various materials reveal that natural 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 macro-lattices of natural proteins (Hosemann, 1951). Since then, knowledge on the structure and properties of natural occurring paracrystals has increased rapidly, due mainly to the use of X-ray diffraction (Hosemann and Bagchi, 1962; Lemm, 1970; Vogel, 1972; Loboda-Čačković and Čačković, 1972; Steffen, 1976) and these investigations lend support to the theoretical propositions. M.v. 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 distortions within the lattice. Before presenting these results and their implications we briefly summarize the basic assumptions of the theory.

The concept of 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 $\underline{a}_k$ of a paracrystalline lattice can be found with a certain statistical frequency $H_k(\underline{x})$ for a certain value $\underline{a}_k = \underline{x}$. The whole distance statistic $z(\underline{x})$ is defined by a three-dimensional convolution polynomial of $H_k(\underline{x})$:

$$z(\underline{x}) = \sum_{pqr} H_{pqr}(\underline{x}) ; \quad (1)$$

$$H_{pqr}(\underline{x}) = P(\underline{x}) \overbrace{H_{100}H_{100}\dots}^{p\text{-times}} \overbrace{H_{100}H_{010}H_{010}\dots}^{q\text{-times}} \overbrace{H_{010}H_{001}H_{001}\dots}^{r\text{-times}} H_{001}$$

where $P(\underline{x})$ is a point function at $x = 0$. If one averages $z(\underline{x})$ over all directions, like in a powder diagram, one obtains the "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 $H_k(\underline{x})$ contains a fluctuation tensor Δ_{ki} which describes the statistical variance of $\underline{a}_k$ in the direction $\underline{a}_i$. As a measure of the degree of lattice distortions the relative mean fluctuation of the distance between lattice planes,

$g_{ik} = \Delta_{ik}/\bar{a}_k$, is used. C. Hermann (1940) defined for the first time a lattice complex with such a kind of variances, the so called mesophases. In the light of the paracrystal theory these mesophases are simplified special cases of paracrystals. Smectic or nematic mesophases have g_{ik} -values which are all zero except for $g_{13} \sim g_{23} \sim 0,4$ or $g_{31} \sim g_{32} \sim 0,4$. Paracrystals such as polymers for instance, can present simultaneously smectic and nematic-like properties within the same lattice. Real paracrystals do not present such strong correlations between adjacent lattice cells as predicted by Eq. (1), and this leads to the existence of finite lattice boundaries. Hence, real paracrystals cannot grow unlimitedly, because with increasing number N of lattice planes the total fluctuation of lattice planes steadily increases (see the right hand side boundary in Fig. 1). If we denote by Δ_k the distance fluctuation between two neighbouring buckled netplanes, then according to the rules of statistics, the fluctuation between the netplanes of the boundaries of a paracrystal with $N + 1$ neplanes is given by $\sqrt{N} \Delta_k$. The domain size of the paracrystallite, $\bar{D} = \bar{N}\bar{d}$, refers to the extent of the structure over which the total fluctuation reaches the size of the mean separation of the netplanes. Thus if such a fluctuation reaches the order of magnitude of the average plane separation $\bar{d}$, then the crystallite size, $\bar{N}\bar{d}$, cannot increase any further. This occurs if $\sqrt{N} \Delta_k = \alpha^* \bar{d}$. The number N within a paracrystal is, therefore, inversely proportional to the square of the g -value :

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

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

Figure 2 illustrates the obtained linear increase of $\sqrt{N}$ as a function of $1/g$, according to Eq. (2), for various materials. The α^* -values obtained are comprised between 0,1 and 0,2. This empirically discovered α^* -law is of central interest in colloid science because it demonstrates that the larger are the lattice distortions, the smaller becomes the size of stable paracrystals and the larger turns out to be their inner surface. All metallic melts, such as Au (Hosemann and Lemm, 1964), Pb (Hosemann and Steffen, 1976), Cu, Fe and Al (Hosemann and Willmann, 1972) exhibit in Fig. 2 the largest lattice distortions ($g \sim 10\%$) and consequently the smallest paracrystalline domain size ($N \sim 4$). Carbon compounds, such as pyrolytic graphite (Vogel and Hosemann, 1979) and organic synthetic polymers, such as polyethylene (Hosemann, Čačković and Wilke, 1967), polybutene-1 (Haase, Köhler and Hosemann, 1978), and biopolymers, such as bone apatite (Wheeler and Lewis, 1977) show somewhat smaller distortions and limiting paracrystalline sizes between 10 and 120 lattice planes. Finally, doped metals, like the α -iron ammonia catalyst (Ludwiczek, Preisinger, Fischer, Hosemann, Schönfeld and Vogel, 1978) and the technical low pressure methanol-catalyst (Fischer, Hosemann, Vogel, Koutecky, Pohl and Ralek, 1980) present the smallest distortions ($g \sim 1\%$) and, as a result, the largest paracrystal size ($N = 170-450$). The value derived from a computer simulated (spiral) paracrystal (Janke and Hosemann, 1977) 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 Gauss-statistics

and a circle-construction. The mean fluctuations of this lattice model increase radially from the centre to the periphery upto 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 $g = 2,1 \%$. Herefrom follows that $\sqrt{N/g} = 0,15$ which is in best agreement with Q^* -values obtained for natural paracrystals. The plot of Fig. 2 clearly shows that the paracrystalline state is intermediate between the gaseous ($g \approx 0,3$) and crystalline ($g = 0$) states, having intermediate properties 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 not fit within the lattice of the environment. In the case of the α -iron ammonia catalyst doped with 3% Al_2O_3 the cause of paracrystalline distortions is the statistical incorporation of $Fe^{2+}Al_2^{3+}O_4^{2-}$ motifs within the iron lattice (Ludwiczek, Preisinger, Fischer, Hosemann, Schönfeld and 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 and Lewis, 1977). In long chain synthetic polymers, lattice distortions are produced by the occurrence of step chain defects,^{x)} such as kink isomers within the so called crystal lattice (Hosemann, Wilke and Baltá-Calleja, 1966). The increasing density of chain defects (branches) incorporated at interstitial crystal sites by means of a generation of 2g1 kink conformations

x) Step chain defects in PE defined by two gauche conformations $g\bar{g}$ of opposite sign incorporated into the paraffin-like chains with trans conformations t.

within the lattice provokes in meltcrystallized polyethylene (Martinez-Salazar and Baltá-Calleja, 1979) a substantial gradual increase of the lattice distortions, simultaneously reducing the size of the microparacrystals according to the α^* -law. In metallic melts, distortions within paracrystalline domains with mean life times of about 10^{-10} sec, 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 upto conventional crystals where lattices can reach macroscopic dimensions.

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Fig. 1

Figure 1

Schematics of paracrystalline lattice fluctuations increasing with the square root of the number N of netplanes. The left part of the paracrystal is omitted for convenience. The α^* -value of this model is $\alpha^* \sim 1$, which is much too large compared with natural paracrystals.

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