

One possible explanation for the α^* relation in non-crystalline materials

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The existence of natural occurring paracrystals, as an intermediate state of non-crystalline matter lying between crystals and gases, has been convincingly supported in recent years [1-3]. Paracrystalline materials can be detected by X-ray, neutron or electron diffraction and sometimes by electron microscopy [4]. One basic feature of real paracrystals is that they exhibit limited colloidal dimensions [2]. Paracrystalline materials cannot grow to macroscopic sizes mainly because of the gradual increase in the fluctuation of lattice points due to the presence of three dimensional statistically distributed motifs disturbing the lattice packing. When the lattice fluctuations reach values which are of the order of the average lattice spacing, \bar{d} , the paracrystal has essentially reached its limiting coherent lattice size, $\bar{D} = N\bar{d}$. The study of non-crystalline materials showing a paracrystalline behaviour has given rise to an empirical relation which states: the product of the square root of the number of N lattice planes within a paracrystal, $N^{1/2}$, times the value of the relative distance fluctuation (degree of distortion), $g = \Delta_1/\bar{d}$, (Δ_1 is the distance fluctuation between two neighbouring lattice planes) $g N^{1/2}$, is nearly a constant α^* . Fig. 1 illustrates the linear increase

$$N^{1/2} = \alpha^* (1/g) \tag{1}$$

for various materials [5-10], where $\alpha^* = 0.15 \pm 0.05$.

The purpose of the present note is to attempt to offer a possible simple explanation for this relationship. If we take the pair interaction energy of atoms (molecules or particles in general) at a distance r apart for a given system [11]:

$$U(r) \simeq Ar^{-p} - Br^{-q} \tag{2}$$

where A and B are positive constants and p and q are integers with $p > q$. In an ideal crystalline

(cubic) lattice all pairs of atoms are at their equilibrium separation, r_m , which is given by:

$$r_m = \left(\frac{pA}{qB} \right)^{1/p-q} \tag{3}$$

The system is, hence, in a state of minimum free energy with r_m defined by Equation 3 (Fig. 2). However, in the case of a paracrystalline arrangement r will take values which deviate from r_m .

If the paracrystalline lattice prevails, these values cannot, admittedly, exceed certain limiting boundaries r_0 and r_i , defined by the conditions $U(r_0) = 0$ and $\{\partial^2 U/\partial r^2\}_{r_i} = 0$, respectively. We assume that for distances $r > r_i$ (inflection point) each molecule is subjected to thermally stimulated dissociation. From the former conditions one obtains:

$$r_0 = \left(\frac{A}{B} \right)^{1/p-q} = r_m \left(\frac{q}{p} \right)^{1/p-q} \tag{4}$$

$$r_i = r_m \left(\frac{p+1}{q+1} \right)^{1/p-q} \tag{5}$$

The expected fluctuation range for the r distance if the paracrystal is to be preserved will be given by $(r_i - r_0)$. Therefore the relative fluctuation can be approximated by:

$$\Delta_r \sim \frac{1}{2} \frac{r_i - r_0}{r_m} \tag{6}$$

Since the lattice planes fluctuation cannot exceed the limiting value Δ_r the relative distance fluctuation will be:

$$g N^{1/2} < \frac{1}{2} \frac{r_i - r_0}{r_m} \tag{7}$$

expression which leads to the α^* law if

$$\alpha^* = \frac{1}{2} \frac{r_i - r_0}{r_m} \tag{8}$$

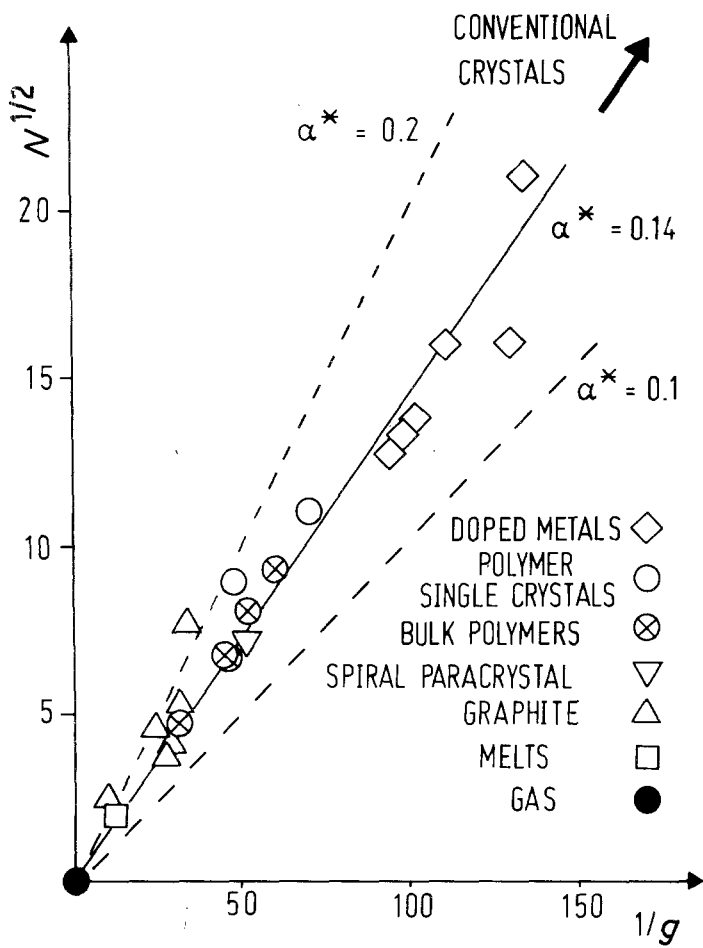
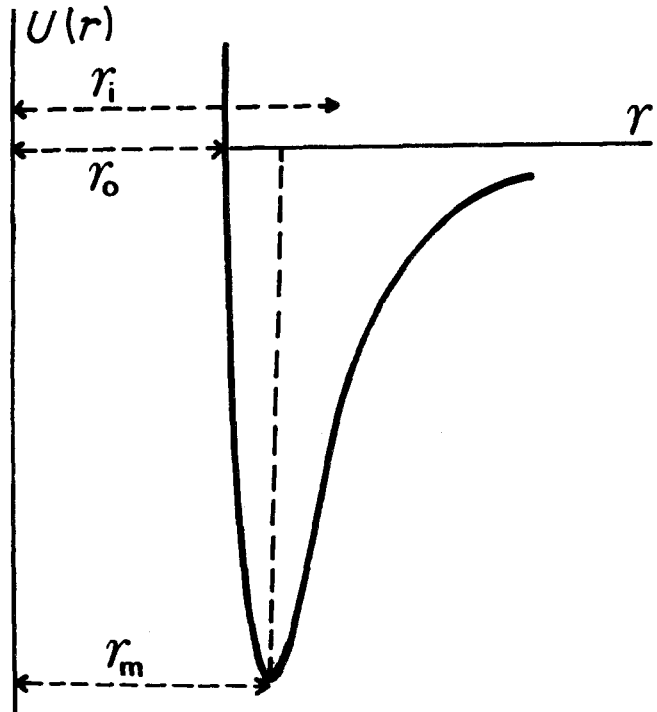


Figure 1 Plot of $N^{1/2}$ against $1/g$ for different natural paracrystals. The α^* -value is given by Equation 1 (see text). The number of lattice planes N , is calculated from D_{hkl}/\bar{d}_{hkl} where \bar{D}_{hkl} is the mean crystallite size derived from X-ray diffraction. For doped metals; α -iron ammonia catalyst [5]: $d_{110} = 0.203$ nm. For polymers; polyethylene [6]: $d_{110} = 0.41$ nm and polybutene-1 [7]: $d_{110} = 0.88$ nm. For graphite [8]: $d_{002} = 0.336$ nm. For metallic melts [9]; gold, copper, iron, aluminium, lead: $d_{111} \sim 0.28$ nm. The spiral paracrystal α^* -value was derived from a computer two-dimensionally simulated point lattice [10].

Figure 2 The relationship of the equilibrium separation r_m to the "closest distance of approach" r_0 .



If we now introduce the values of $p = 12$ and $g = 6$ for a Lennard-Jones potential in Equations 4 and 5 then:

$$r_0 \simeq 0.89 r_m, \quad r_i \simeq 1.11 r_m \quad \text{and} \quad \alpha^* = 0.11.$$

We are aware that this approach is rather crude because it considers a basic average potential without taking into account the anisotropy of the lattice distortions. However, despite this simplification the present development still offers an α^* value which undeniably is in excellent agreement with the experimental data.

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