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Paracrystalline Structure of Molten Metals

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When discussing matter on an atomic level it is often useful to employ the notion of a three-dimensional lattice even if the x-ray diffraction pattern is diffuse and, hence, the long-range order characteristic of a crystalline lattice is absent. Phases in which this notion is particularly helpful are called paracrystalline phases. The theory of paracrystals has been applied to various solids and has recently been employed for analyzing the diffraction pattern from liquid metals. In this paper the theory is used for analyzing the diffraction pattern from liquid Cu at 1100 °C, as measured by Ruppersberg. The radial density function out to distances of 25 Å is synthesized extremely well by means of the paracrystalline convolution polynomial made up only of first-neighbor or "coordination" statistics. These statistics are inhomogeneous in the sense that two different first-neighbor distances are employed. Forty percent of the first-neighbor distances are 10% larger than the others and arise from intercrystalline distances measured across the paracrystalline grain boundaries. Since, it is well known from inelastic neutron scattering that the lifetime of the paracrystalline domains is about 10^{-11} sec, the intercrystalline distances include diffusive motion. The melt is described in terms of a fcc lattice and consists of microparacrystallites with a mean diameter (for copper of about 5 Å and for alkaline metals up to 100 Å) of about 5 Å. The results of the paracrystalline theory are compared with the model of Kaplow and Averbach which is based on the known structure of the solid. The two approaches agree in the assignment of the same lattice type above and below the melting point.

I. INTRODUCTION

The concept of a three-dimensional lattice is not employed in the common theories[1-5] of liquids and of amorphous materials since reflections of crystalline character are not observed in their x-ray diffraction patterns. In the theory of paracrystals,[6] on the other hand, well-defined three-dimensional lattices exist which give several different types of pattern varying from quasicrystalline to a more diffuse type with partially crystalline features and, finally, to totally diffuse amorphouslike scattering. In the paracrystalline theory the lattice planes are statistically bent and displaced so that there is no long-range order.[7] If one specifies the atomic arrangement by giving the pair probability function $z(\vec{x})$, i.e., the probability of finding a structural unit at a given distance from any other, it has been found that this pair probability function is well defined in terms of first-neighbor or "coordination" statistics, $H_1(\vec{x})$.[8,9] That is, if one knows the pair probability function only out to a distance corresponding approximately to the first-nearest-neighbor distance (the coordination statistics), the entire pair probability for distances greater than this are then well described in terms of the coordination statistics. Moreover, this description yields an x-ray scattering pattern that agrees with that observed experimentally.

The theory of paracrystals has been applied to inorganic "crystals" such as manganese-rich ferrites[10] and promoted ammonia crystals,[11] to polyethylene single crystals,[12] and to other synthetic and biological polymers.[13,14] In all these cases the paracrystalline description in terms of a three-dimensional lattice having no long-range order was found to be appropriate. The distortions in the paracrystalline structure are produced when the structural units—"bricks" or "motifs"—having different volumes or irregular shapes are distributed randomly on the lattice points.

The theory has also been used to calculate the radial density function (RDF) for monatomic liquids out to distances of 10 Å.[15] The calculations have recently been extended out to distances of 25 Å, and it has been shown that additional new information is accessible by this approach.[16] In this paper a brief account of these results is given.

II. CONVOLUTION POLYNOMIAL

In Refs. 1–6 it was proven that three-coordination or first-neighbor statistics $H_1(\vec{x})$, $H_2(\vec{x})$, and $H_3(\vec{x})$ can be determined by line profile analysis of the x-ray diffraction pattern. These functions give the probability of finding the center of a structural unit or brick as a first neighbor at the point $\vec{x}$ along a direction $\vec{a}_1$, $\vec{a}_2$, or $\vec{a}_3$, where $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ define the edges of the mean paracrystalline lattice cell. The pair distribution is defined by the convolution polynomial[6,7] $z(\vec{x})$ as

$$z(\vec{x}) = \sum_{pqr} H_{pqr}(\vec{x}) \ , \tag{1}$$

where $H_{pqr}(\vec{x})$ gives the *a priori* distance statistics between the centers of gravity of the structural units or bricks at the lattice point (k, l, m) and at the lattice point $(k+p, l+q, m+r)$. Now, it is an essential feature of the theory that

$$H_{pqr}(\vec{x}) = \underbrace{(P(\vec{x}) * H_1 * H_1 * \cdots)}_{\text{convolution} \quad p \text{ times}} \underbrace{(* H_2 * H_2 * \cdots)}_{q \text{ times}} \underbrace{(* H_3 * H_3 \cdots)}_{r \text{ times}} \ . \tag{2}$$

The symbol $*$ stands for the convolution product

$$g * h = \int g(\vec{y}) h(\vec{x} - \vec{y})\, d\vec{y}$$

and $P(\vec{x})$ is a Dirac δ function. In Eq. (2) thermal vibrations are not yet included. Contrary to conventional crystallography the lattice cell is unambiguously defined by the directions whose distance statistics are the sharpest, that is, have the smallest statistical fluctuation.[17]

For example, in the spinel $Fe_{3-x}Mn_xO_4$ with $x = 1.88$ the conventional lattice cell is fcc and contains 32 O^{-2} ions. In the theory of paracrystals the structure is described in terms of the eight edge vectors with components $(\pm\frac{1}{4}, \pm\frac{1}{4}, \pm\frac{1}{4})$ along the four-body diagonals of the conventional lattice cell. A bcc lattice is thus built up of alternating bricks of $Me^{+2}O_4^{-1/2}$ tetrahedra and $Me_4^{+3/2}O_4^{-3/2}$ cubes,[18] connected along the body diagonal. This arrangement shows that the structure consists of chains of these structural bricks which correspond directly to the "periodic bond chains" (PBC) of the PBC theory of Hartmann.[19]

III. SIMPLIFIED THEORY FOR LIQUIDS

The x-ray diffraction pattern from a liquid usually consists of only one relatively sharp peak which is fairly well separated from the other, more diffusely distributed intensity. The RDF is obtained from this pattern by a one-dimensional Fourier transform. The RDF is connected with Eq. (1) by[7]

$$4\pi r^2 \rho(r) = \int_{\vec{x} = |\vec{r}|} z(\vec{x})\, df_x \ . \tag{3}$$

The integration is carried out over the surface of a sphere with radius r and center at $x = 0$; df_x is a surface element.

For simplicity we interchange the order of the two integrations and build up a one-dimensional convolution polynomial of the RDF[14]:

$$4\pi r^2 \rho(r) = \sum_n K_n B_k * H_{f(n)}(r, r_n) \ , \tag{4}$$

where K_n is the number of atoms in a shell at the mean distance r_n, $H_{f(n)}$ is the $[f(n) - 1]$-fold convolution product of H_1, and $f(n)$ is the number of direct steps in the paracrystalline lattice from $r = 0$ to the nth shell. K_n, r_n, and $f(n)$ are unambiguously defined by the lattice type and the shape of the normalized coordination statistics H_1. B_k is the vibrational statistic[7,15,20] and k is an index that enumerates the maxima of the RDF. H_1 and B_k must be varied until the best fit with the experimentally observed RDF is found. In Fig. 1 the RDF of molten Cu at 1100 °C, as measured by Ruppersberg,[21] is shown together with a synthesis according to Eq. (4).[22] For H_1 a five-parameter Gaussian function was used:

$$H_1(r) = \frac{f}{(2\pi)^{1/2} a_1} \exp\left[-\left(\frac{r - r_1}{\sqrt{2}\, a_1}\right)^2\right] + \frac{1 - f}{(2\pi)^{1/2} a_2} \exp\left[-\left(\frac{r - r_2}{\sqrt{2}\, a_2}\right)^2\right] . \tag{5}$$

Taking $f = 0.6$, $r_1 = 2.5$ Å, $r_2 = 2.8$ Å, $a_1 = 0.1$ Å, and $a_2 = 0.2$ Å and employing a fcc lattice containing 20% stacking faults, one obtains an excellent fit to the experimental data.[22] The standard deviation from the Debye function B_k was taken as 0.3 Å for all B_k with $k \geqq 3$. Cooperative oscillations were taken into account by setting $B_1 = 0.15$ Å and B_2

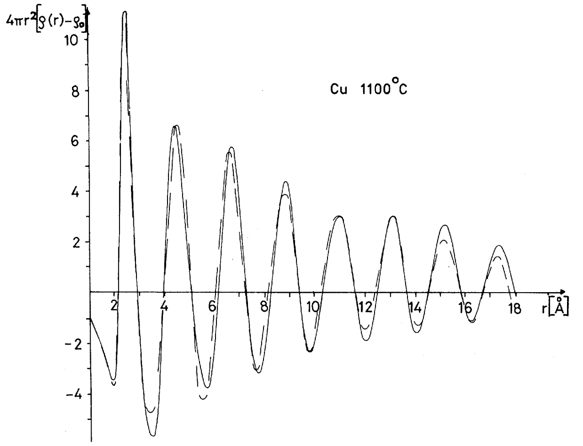

FIG. 1. Radial density difference function (RDDF) of molten Cu at 1100 °C as measured by Ruppersberg (Ref. 21) (dashed line) and the synthesized function (solid line) calculated from Eq. (4). ρ_0 is the mean density.

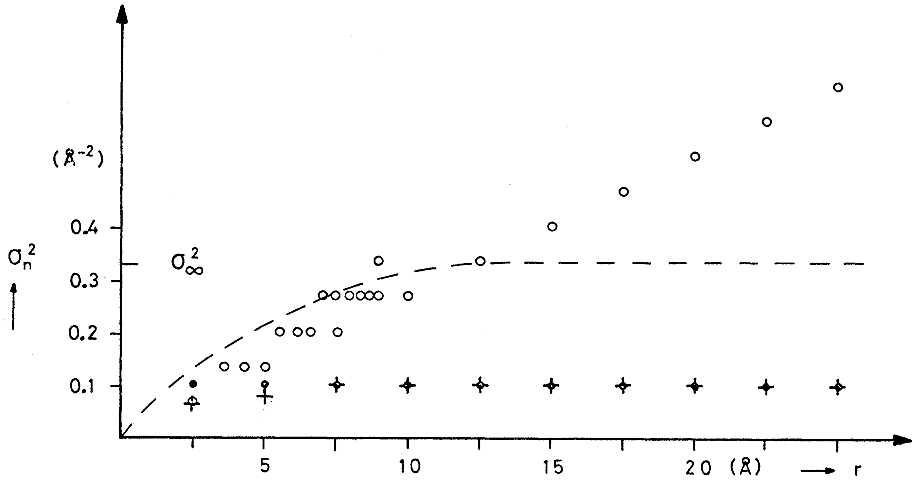

FIG. 2. Mean-square atomic displacements σ_k^2 of the shells k of Cu. Dashed line, Averbach's approach; open circles, pure paracrystalline distortions; closed circles, thermal vibrations without (and crosses with) coupling effects. (The latter values have been used in the synthesized function shown in Fig. 1.

= 0.25 Å. As indicated in Eq. (5), H_1 consists of two kinds of distances, intraparticular with average value r_1 and interparticular with average value r_2. Thus 40% of the distances are interparticular arising from first-neighbor atoms of adjacent paracrystallites. The mean number of atoms in one direction within a domain is given by $1/(1-f)$ and hence, the mean diameter of the paracrystallites is very small and of the order of 5 Å.[23]

For other molten metals much larger paracrystallites, up to mean diameters of 200 Å and more[16] were found. It is also of interest that for all liquids investigated so far the lattice type does not change at the melting point. In particular, Li, Na, K, Rb, and Cs remain bcc and Cu, Ag, Fe, Co, Ni, Pb, Ne, Ar, and Xe remain fcc usually with 20% stacking faults or more. Mg remains hexagonal close packed and also contains stacking faults.

IV. COMPARISON WITH THE MODEL OF KAPLOW–AVERBACH

Kaplow *et al.*[24] also studied the RDF out to large distances and found that the liquid pattern was strikingly similar to that of the lattice below the melting point. In addition they found a significant increase in the broadening of the functions used to describe the shells of the RDF. They attributed this to a diffusive motion superimposed upon the vibrational motion owing to thermal oscillations in a "quasicrystalline" lattice. If we let σ_1 be the broadening owing to diffusive and σ_2 that owing to thermal oscillations, then the statistical fluctuation of the shell k for Gaussian distribution functions is given by

$$\sigma_k^2 = \sigma_{1k}^2 + \sigma_{2k}^2 . \tag{6}$$

The σ_k^2 values of Kaplow *et al.*[24] used for Pb are adapted to the Cu diagram of Fig. 1 and are shown by the dashed line in Fig. 2. This adaption can easily be performed, since Pb and Cu have identical RDF's in reduced coordinates.[22] As a consequence of introducing coupling factors into their model, σ_k^2 increases with increasing k and is assigned a constant value σ_∞^2 for distances larger than their "correlation length" d. At these larger distances, they argue, a coupling of the motions by means of elastic waves no longer exists in the time-averaged distance statistics.

Kaplow *et al.* found, that the RDF calculated in this way fits very well at smaller distances but is not sufficiently damped at larger distances. Consequently they introduced a so-called "damping factor" into the radial density difference function (RDDF), $\rho - \rho_0$ which has the value of 1 for r smaller than d, and decreases for larger values of r to 0. The correlation length d is a distance of the order of 20 Å and is a measure of the loss of correlation with increasing r and thus corresponds to the diameter of quasicrystalline domains. This result is quite similar to the results of our analysis. Our interpretation, based upon the theory of paracrystals, however, is somewhat different. In contrast tothe interpretation of Kaplow *et al.*, in the paracrystalline theory the σ_k^2 values do not become constant at these larger distances, but increase monotonically. The paracrystalline theory when applied to lattices with no long-range order gives an excellent fit to the experimental measurements and, hence, automatically provides the required damping of the RDDF. In Fig. 2 the σ_{1k}^2 values for Cu, calculated from Eqs. (1) and (5), are plotted together with the σ_{2k}^2 values from the Debye function after introducing the coupling effects for B_1 and B_2 [Eq. (4)]. It is these parameters which have been used in synthesizing the curve shown in Fig. 1. If, on the other hand the paracrystalline σ^2 values are made constant for

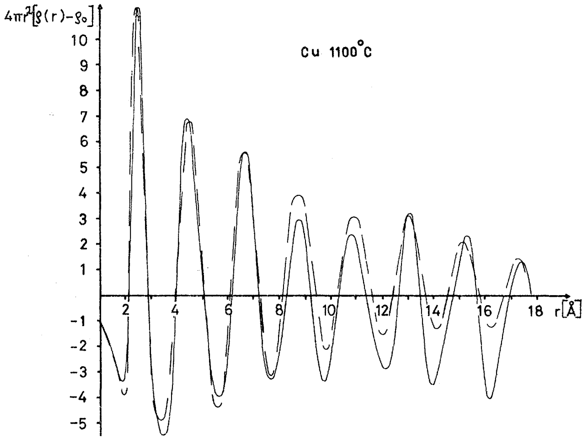

FIG. 3. RDDF of Cu at 1100 °C based on the theory of paracrystals, using a convolution polynomial, Eq. (4), where $f(n)$ has been set equal to 4 for all values of n for which $f(n)$ is larger than 4 (solid line), compared again with Ruppersberg's results (dashed line).

$n \geq 14$, which means that $f(n)$ has the constant value 4, the RDDF is no longer damped enough for $r \geq 10$ Å (Fig. 3).

The analysis of Kaplow *et al.* and the approach of the paracrystalline theory are both capable of reproducing the experimental results. The parameters employed in the paracrystalline theory, however, lead to a substantially different physical interpretation. In particular, the coordination statistics H_1 always contain two different kinds of distances [see Eq. (5)]. The one with average distance r_1 arises from the intraparticular distances within the paracrystalline domains, the other, with the longer mean distance r_2, arises from interparticular distances and, hence, includes what Kaplow *et al.* have called diffusive motion. The size of paracrystalline domains can be calculated directly from these "inhomogeneous" coordination statistics H_1 and gives, for copper, much smaller values than the correlation lengths d introduced by Kaplow *et al.* In addition, the paracrystalline theory shows that a statistical description of the first-nearest-neighbor distances based upon an appropriate lattice suffices to determine the RDF.

V. DISCUSSION

Bernal[25, 26] has proposed that the atoms in a simple liquid are arranged as randomly as possible. Unfortunately the differences between the experimental and randomly packed structures were deemphasized by plotting the RDF instead of RDDF, where the deviations of Bernal's theory are very large (cf. Fig. 10 of Fessler *et al.*[27]). It is also interesting to note that Bernal always found low packing densities for irregular arrangements and that there is an absolute impossibility of forming a homogeneous assembly of points of volume intermediate between those of long-range order and close packed disorder.[25]

In the theory of paracrystals one has a homogeneous assembly with some well-defined *a priori* distance statistics by which the long-range order is partially destroyed and partially still exists. This very general theory, well established for polymers and some other low molecular systems, can be applied to simple liquids too and yields quite easily the correct observed density and the experimentally obtained RDDF with high accuracy by means of a convolution polynomial.

An essential idea in the theory of paracrystals is that the bricks, or units from which the structure is built up, have different sizes or shapes. These units are then distributed randomly on the lattice points. Accordingly, one must understand how, in a monatomic liquid such variations in size or shape occur. In the paracrystalline description of such a monatomic liquid, each brick consists of the atom itself plus the additional volume required by the thermal oscillations that the atom experiences. Based on the results of inelastic neutron scattering, Rahman[28] points out that the lifetime of a given phonon in the liquid is extremely short; that is, each elastic wave is so strongly damped that the wave essentially consists of only one peak.[23] In the solid the elastic waves propagate coherently through the entire crystalline domain and the amplitudes of the oscillations in the ξ average are the same,[7] whereas above the melting point practically no correlation exists between the amplitudes of the atomic oscillations.

Since the volume occupied by a brick increases with increasing amplitude of the phonon wave, the volume of the different paracrystalline lattice cells or bricks varies statistically. Thus the bricks do, indeed, have different sizes. Since the theory of paracrystals accounts for the experimental intensity of monatomic liquids in a very satisfactory way, and since the question of the source of paracrystalline distortions has been adequately explained, it is of interest to demonstrate the validity for liquids of the relation[29]

$$N_{\max} \sim (\alpha/g)^2 , \qquad (7)$$

obeyed by all paracrystalline solids, where $N_{\max}$ is the maximum possible number of net planes in a paracrystalline domain with the relative paracrystalline distance fluctuations g. The dimensionless quantity α is of the order of 0.1 to 0.25 depending on the nature of the chemical forces between the bricks. In the solid structures mentioned in Secs. I and II one finds g values of the order of 0.5 to 3% and paracrystalline domains of the order of 1000 down to 50 Å. For molten Cu the g value, according to Eq. (5), is of the order of 10% and, hence, the diameter only a few Å. Moreover, it can be shown from inelastic neutron scattering, that the paracrystalline domains have a lifetime of the order of 10^{-11} sec.[30] This implies that distances r_2, which are momentarily regarded as interparticular, must, in a very short time, be regarded as intraparticular r_1 (that is, after the domain boundary has moved). The x-rays, which do not differentiate between elastic and inelastic scattering, only yield the information that at any moment the liquid structure consists of paracrystalline clusters.

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Source-Field Approach to the Two-Level Atom in a Closed Cavity[*]

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The problem of the time evolution of a closed system, consisting of a two-level atom and its field in a cavity, is investigated by a quantum formalism in which the field is assumed to be a part of the atomic source and is expressible directly in terms of source variables. The source and its field form an irreducible quantum system, that is completely representable within the two-dimensional Hilbert space of the atom. The behavior of the system has features that are similar to those predicted by conventional quantum electrodynamics.

I. INTRODUCTION

In recent years there has been renewed interest in the subject of the interaction of electromagnetic radiation with atoms and electrons. The question has been raised whether quantum electrodynamics is necessary in order to account for the observed effects,[1-7] or whether the effects are adequately