Quasi crystals—an overview

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Abstract. This paper gives a broad overview of recent developments concerning quasi crystals. After briefly recapitulating various experimental facts, the architecture of quasi periodic systems in various dimensions is discussed. The various density-wave models are then reviewed. This is followed by a discussion of the extra long wavelength models which appear in such systems. Some comments are then made about possible relationship to recent theories of glass which stress local icosahedral order. The paper concludes with an outlook for the future.

Keywords. Quasi crystals; icosahedral order; incommensurate structures.

2. The facts

Not too many facts are available as yet in the published literature, but enough is known about the basic features of quasi crystals to appreciate why they are exciting.

Shechtman et al (1984) investigated alloys of Al with 10–14 at. % Mn, Fe and Cr. Alloy buttons were first prepared by arc melting. Small pieces cut from these were then induction heated and melt spun to the desired, rapidly-quenched specimens. Electron diffraction showed sharp spots (see figure 1) such as one observes with single crystals, except that the observed pattern corresponded to icosahedral point group symmetry which is inconsistent with translational periodicity. Twinning was ruled out, and the liquid → quasi crystal transition was found to be of first order. The quasi crystalline phase was quite resistant to crystallization, and would convert only when heated to at least 400 C.

1. Introduction

The recent discovery of quasi crystals by Shechtman et al (1984) has severely jolted our notions about the architecture of solids. Under the influence of crystallography, we had come to associate extended structural order with translational periodicity, thereby excluding long-range order with a non-crystallographic rotational symmetry, e.g. five fold. No doubt a few toyed with such ideas (Mackay 1981, 1982; Kramer 1982; Kramer and Neri 1984), but the latter did not receive much notice. As for the occasional electron diffraction pattern exhibiting five-fold symmetry, it was dismissed as being due to twinning (which it was e.g. in gold, Ino 1966).

Late last year, while experimenting with Al-Mn alloys, Shechtman et al discovered that a new state of matter with forbidden rotational symmetry was indeed possible. Apparently, Nature does tolerate non-crystallographic rotational symmetry by large and this discovery of a new phase (promptly christened quasi crystal) has created much excitement. The present article gives a broad overview of these stimulating developments.

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Figure 1. Electron diffraction patterns observed by Shechtman et al. (1984).
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Figure 2. Grains of quasi crystals (after Chattopadhyay et al 1985a).

Around the same time, Field and Fraser (1984) also reported icosahedral symmetry in rapidly-quenched Al-15 at. % Mn alloy, but attributed the observed diffraction pattern to twinning in the sample—fluence of the central dogma (Ramaseshan 1985) no doubt! In a subsequent work, Chattopadhyay et al (1985a) discounted the possibility of twinning via high resolution electron microscopy. They also noted that the individual grains were highly faceted (see figure 2), suggesting that each one of them was a single quasi crystal.

Bancel et al (1985) have performed high resolution x-ray diffraction measurements using synchrotron radiation and confirmed that the single-domain icosahedral point symmetry does obtain in the rapidly quenched Al-14 % Mn alloy.

Parthasarathy et al (1985) have investigated the effect of pressure, and they find that the metastable icosahedral phase irreversibly transforms (via first order) into a crystalline phase (figure 3).

There is thus enough evidence not only to assert that an icosahedral phase exists, but also that it is metastable, and can be transformed into a crystalline phase. Several questions automatically follow, some of which we deal with in the following sections.

3. The architecture of quasi crystals

The first thing one would like to know is how exactly the atoms are arranged in a quasi crystal, in contrast to the arrangement, say, in an ordinary crystal.

3.1 One-dimensional quasi crystal

It is convenient to start with a one-dimensional quasi crystal, although there is no such thing as a non-crystallographic rotational symmetry in 1D. What is distinctive is the
replacement of periodicity by quasi periodicity, a feature that is present in higher dimensions also.

Figure 4a shows a periodic chain. There is only one length scale, and the pattern repeats after every one step. Figures 4b, c show extensions obtained by the replacement rules: $A \rightarrow AB, B \rightarrow A$. We observe that with every replacement, the step length for repetition increases. The ratio of the number of $A$ tiles to the number of $B$ tiles (stoichiometry) evolves as below:

<table>
<thead>
<tr>
<th>Period</th>
<th>5</th>
<th>8</th>
<th>13</th>
<th>21</th>
<th>34</th>
<th>55</th>
<th>\ldots</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of $B$ tiles</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>8</td>
<td>13</td>
<td>21</td>
<td>\ldots</td>
</tr>
<tr>
<td>No. of $A$ tiles</td>
<td>3</td>
<td>5</td>
<td>8</td>
<td>13</td>
<td>21</td>
<td>34</td>
<td>\ldots</td>
</tr>
</tbody>
</table>

The series 1, 1, 2, 3, 5, 8, 13, 21, \ldots is the famous Fibonacci sequence determined by the recursion formula

$$f_0 = 0, f_1 = 1, \quad f_k + f_{k+1} = f_{k+2}.$$ 

Observe that

$$\left(\frac{f_k}{f_{k+1}}\right) \to 1.61803 = (\sqrt{5} + 1)/2 \equiv \tau \quad \text{(golden ratio)}.$$ 

Closely related to $\tau$ is the quantity

$$\sigma \equiv (\sqrt{5} - 1)/2 = 0.618.$$ 

Note also $\tau \sigma = 1$.

From a geometric structure point of view, the case where the ratio of step lengths
Figure 4. This figure illustrates how a period infinity $ABAAB \ldots$ 1D Penrose sequence can be built up from a periodic chain by replacing $A$ by $AB$ and $B$ by $A$. That is, every chain is derived from the preceding chain of the hierarchy (or chains) by this scheme. When the chains are iterated an infinite number of times, one obtains a Penrose sequence.

equals $\tau$ is particularly interesting. We shall refer to a period $\infty ABAAB \ldots$ sequence with step length ratio of $\tau$ as a Penrose chain. Taking for convenience the length of step $B$ to be unity, the density function for the Penrose chain is

$$\rho (x) = \sum \delta (x - x_n)$$ (1)

where $x_n$ is the position of the $n$th site, and is given by

$$x_n = n_1 \tau + n_2$$ (2)

where $n_1$ and $n_2$ are integers. Note, however, that not all integer values are allowed.

The above $\delta$-function sequence can be obtained by superposing the waves $\cos qx$ and $\cos Qx$ (with $Q/q = \tau$), their harmonics and various combinations thereof, as illustrated in figure 5. Now since $\tau$ is irrational, the sum ($\cos qx + \cos Qx$) never repeats. A function of this type is said to be quasi periodic (-this terminology is quite common in the study of turbulence). In general, $f(x)$ is quasi periodic on $(-\infty, \infty)$ if it is a superposition of plane waves $\exp (2\pi i \omega_k x)$ with the frequencies $\omega_k$ being irrational i.e.
for rational \( r_k, \sum_r r_k^2 \omega_k = 0 \) if and only if all \( r_k = 0 \). Since the Penrose chain is built up this way, it may be deemed to be quasi periodic.

3.2 Penrose tiles

Moving to 2D, we will see why the name of Penrose was associated with the quasi periodic chain.

Roger Penrose is a distinguished mathematician, relativist and all that, who often indulges in mathematics also for recreation! Wondering about covering floors with nonperiodic tiles, he proved that a set of two tiles can be found such that neither a single shape nor the entire set tile 2D space periodically but the set as a whole generates a nonperiodic tiling. While the shape of a pair of Penrose tiles can vary, the most interesting pair is the kite and the dart (figure 6). In a fascinating article, Martin Gardner (1977) illustrates the extraordinary richness of Penrose tiles.

de Bruijn (1981) has given a detailed mathematical prescription for constructing
Penrose tilings. Essentially it involves a superposition of five grids as in figure 7, leading to what is called a *pentagrid*. The dual of this grid is an arrowed rhombus (AR) pattern, which is one version of the Penrose tiling. A prescription exists to convert the AR pattern into a kite-and-dart one. Arising out of the flexibility in superposing the five grids, a variety of Penrose patterns can be generated. More technically, with each pentagrid one associates five real numbers $\gamma_j (j = 0, 1, 2, 3, 4)$ such that $\Sigma_j \gamma_j = 0$. Different sets $\gamma \equiv \{\gamma_j\}$ lead to different patterns. In passing we note that the golden ratio occurs not only in the ratio of the number of kites to darts or the number of thick rhombuses to the number of thin rhombs (stoichiometry) but also in the geometry of the shapes. The reason for terming the 1D chain $ABAAB \ldots$ with step length ratio $\tau$ as a Penrose chain should now be clear.

It is interesting to replace the AR and the kite-and-dart patterns with patterns of circles (located at vertices, inscribed etc). Such exercises are suggestive in looking for real-life 2D quasi periodic structures. It would seem (Levine and Steinhardt 1984) that structures with atoms of two or more different species are likely to be stable. One wonders whether such structures can be realized with colloids for example, the way Pieranski (1983) has produced 2D colloid crystals. If one can experiment with colloids, one would be able to directly photograph the structure and this would be particularly helpful in elucidating the defect structure (see also §5).

### 3.3 Symmetry of Penrose tiles

Penrose tilings obviously lack translational periodicity, but do they have any group symmetry at all? There is no explicit answer to this question in the literature but de Bruijn does identify transformations of the type $\gamma \rightarrow \gamma^*$ which leave the pentagrid invariant. Presumably from this one could construct a *group* of transformations. One suspects that as in the case of nonsymmorphic crystallographic space groups (e.g. that of the hexagonally closed packed lattice) one can talk of an *underlying point group*
which has a five-fold rotational symmetry. Certainly, various arbitrary Penrose tilings constructed as described by de Bruijn all appear to have the same rotational symmetry as far as the diffraction pattern is concerned (G Athithan, private communication).

Self similarity is another interesting feature of Penrose tilings. Suppose in the 1D Penrose chain one systematically omits a particular set of points. The resulting (depleted) chain is a copy of the original one, though inflated. This is self similarity, and obtains with higher-dimensional Penrose structures also. One must however be cautious and remember that self similarity applies only to tiles as such. When tiles are replaced with atoms and potentials are switched on, the resulting atomic structure may not be self similar (Sachdev and Nelson 1985). Elser (1985) also has drawn attention to the possibility that 3D Penrose structures could be configurationally disordered. He notes, however, that the symmetry and sharpness of the diffraction pattern is unaffected by this kind of disorder.

Operationally, one can visualize the build up of a Penrose-type system by starting with a seed quasi crystal and going through a sequence of successive generations (as one does in the rabbit breeding problem often used to illustrate the Fibonacci numbers). In 1D this is readily illustrated. Let the seed be $A, B$. The next generation is then given by

\[
\begin{pmatrix}
1 & 1 \\
1 & 0
\end{pmatrix}
\begin{pmatrix}
A \\
B
\end{pmatrix}
\]

(3)
where the $2 \times 2$ matrix is the transfer matrix. Repeated application of the transfer matrix leads to higher generations and finally to the Penrose sequence.

3.4 The Levine-Steinhardt scheme

Levine and Steinhardt (1984) generate quasi periodic structures by a scheme which is an extension of de Bruijn's. Instead of using five equally-spaced fringe patterns as in figure 7, they use fringe patterns each of which is a quasi periodic string (figure 8). The intersection points of these five quasi periodic fringe systems define a quasi periodic 2D network.

The individual fringe systems could be more general quasiperiodic strings based on a $(k \times k)$ transfer matrix whereupon one obtains a $k$-quasi crystal. These ideas have been extended to $3D$ also.

3.5 Penrose structures in 3D

Three-dimensional Penrose-type structures have been considered by Mackay (1981), Kramer (1982) and Kramer and Neri (1984), and it emerges that analogous to the thick and the thin rhombuses, one has two types of quasi unit cells namely, the acute and the obtuse rhombohedra. Kramer and Neri offer a systematic scheme for generating such 3D icosahedral structures. In a sense, their method is an extension of de Bruijn's, and involves first projecting a (hyper) cubic lattice from 12-dimensional space onto 3D space (defined by the representation space of an appropriate 3D irreducible representation of the icosahedral point group); this leads to a hexagrid. The dual structure then defines a tiling of 3D Euclidean space with the two types of rhombohedra mentioned above. In practical terms, the hexagrid is defined by six sets of equally-spaced parallel planes, each set being perpendicular to one of the six (distinctive) faces of a regular dodecahedron (—compare with figure 7). In a quest for amorphous structures "which

![Figure 8](image-url)
propagate an icosahedral symmetry", Levy (1985) has indicated a similar mapping of simple cubic structure in 6D onto 3D space.

Nelson and Sachdev (1985) have employed a different approach based on an earlier work by Mosseri and Sadoc (1984) concerning amorphous structures. The latter authors sought to build a model for glass by starting with a regular polytope, the analogue of a Platonic solid in 4D, and introducing disclinations. The quintessence of their construction is described by the recursion relation

$$
\begin{pmatrix}
Z'_{12} \\
Z'_{14} \\
Z'_{16}
\end{pmatrix}
= 
\begin{pmatrix}
13 & 12 & 12 \\
0 & 3 & 4 \\
5 & 6 & 8
\end{pmatrix}
\begin{pmatrix}
Z_{12} \\
Z_{14} \\
Z_{16}
\end{pmatrix}.
$$

Here $Z_{12}$, $Z_{14}$ and $Z_{16}$ denote the number of atoms in a given generation with coordination numbers 12, 14 and 16 respectively, while the primed quantities indicate the numbers in the succeeding generation. The $(3 \times 3)$ matrix is the transfer matrix of the problem. Mosseri and Sadoc found that the end product of their effort was not an amorphous structure (which they had hoped for), but a Penrose-type structure. Taking a cue from this, Nelson and Sachdev tried a similar iteration, but starting with a regular

![Diagram](attachment:image.png)

**Figure 9.** (a) Iterative procedure for splitting a tetrahedron into more tetrahedra. Basically it involves introducing new vertices on each face as shown in (b). In all, 20 small tetrahedra are generated for each large one [see (c)].
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icosahedron as the seed. Operationally, their iteration is equivalent to dividing every tetrahedron into smaller tetrahedra as shown in figure 9. This automatically generates the desired icosahedral symmetry. In the process, atoms with \( Z = 14 \) and 16 also appear.

Structures with coordination numbers \( Z = 12, 14, 16 \) were first considered by Frank and Kasper (1958, 1959) in the context of complex alloys. They noted that atoms with \( Z \neq 12 \) (i.e. with anomalous coordination) form endless chains, now known as Frank–Kasper chains. The Nelson-Sachdev structure has such chains. We return to this point again later.

Nelson and Sachdev have confirmed the emergence of icosahedral order in their model structure by computing the diffraction pattern. While the five-fold symmetry and self similarity are no doubt reproduced, some features not found in experiment were also noted. It would seem that their model structure has some 'collineations' of regularly-spaced particles along the symmetry axes which are absent in real-life structures.

3.6 Incommensurate structures

Quasi crystals are not the only condensed matter systems exhibiting the presence of two or more waves incommensurate with each other. Even before their discovery, structures referred to as modulated crystals were known in which also incommensurate waves were present.

The notion of a modulated crystal may be understood by referring to figure 10a, where a perfect lattice with spacing \( a \) is illustrated. In figure 10b is shown a system where the \( B \) atom positions are displaced by a static wave of wavelength \( \lambda \). The resulting structure is a modulated crystal. If \( (\lambda/a) \) is rational, then the modulated crystal is a commensurate structure with period several times \( a \). If on the other hand \( (\lambda/a) \) is irrational, one has an incommensurate structure, and the structure never repeats no matter how far one goes down the chain. The atomic positions can be represented as

\[
X_A(n) = na \\
X_B(n) = \frac{1}{2} na + g(na),
\]

where \( g(x) \) is a periodic function of period \( \lambda \), describing the modulation. If \( (\lambda/a) \) is irrational, the chain forms a quasi periodic sequence.

One can visualise incommensurate structures in 2D and 3D also. Real-life examples include the helical structures in magnetic materials like Tm, displaceable modulations in ionic crystals like \( \text{Na}_2\text{CO}_3 \), charge-density waves in layered compounds like TaSe\(_2\) etc.

Levine et al (1985) make a distinction between quasi periodicity occurring in modulated crystals and that occurring in crystals with five-fold symmetry etc. The reason for making such a distinction can be understood as follows: Consider a 2D system with five-fold symmetry. The incommensuration present is unique and directly related to the rotational symmetry. On the other hand, one can visualize a structure as in figure 10c, where there is nothing unique about the two waves which are incommensurate. There is no constraint on the rotational symmetry, and in fact it is one allowed crystallographically. Levine et al therefore use the term quasi crystal whenever the rotational symmetry is one disallowed by crystal symmetry. Otherwise, quasi periodic structures are referred to as incommensurate crystals (as they were even earlier).
Recall that space groups were constructed by forming semi direct products of rotation groups with (periodic) translational groups. Perhaps incommensurate and quasi crystals can be built up in a somewhat similar manner (by combining rotations with "quasi translations")? It remains to be seen whether there are formal entities like quasi space groups.

It is also appropriate here to call attention to an interesting suggestion by Ruelle (1982, 1983) who feels that quasi periodic structures could possibly become turbulent when confronted with additional, incommensurate modulations.

4. Density wave approach

In the preceding section we described various attempts at visualizing directly a quasi crystalline structure. There is, however, no guarantee that Nature would actually choose such a structure. To study Nature's preferences, one must necessarily consider energetics.

Landau's theory of phase transitions provides one route, and in the process also shifts the focus from direct to reciprocal space.
4.1 Pre-discovery work

In Landau’s theory, the density is expressed as

$$\rho(r) = \sum_k \rho(k) \exp i \mathbf{k} \cdot \mathbf{r}$$

and it is argued that out of the set of all possible wave vectors \( \{ \mathbf{k} \} \) present in a liquid, a subset \( \{ \mathbf{G} \} \) of plane waves take over to form a crystal. Given this viewpoint about symmetry breaking, the transition itself is analyzed via the free-energy expansion

$$F = F_0 + \frac{1}{2} \sum \alpha(G) \rho(G) \rho^*(G) + \omega \sum_{G_1, G_2, G_3} \rho(G_1) \rho(G_2) \rho(G_3) \times \delta(G_1 + G_2 + G_3)$$

$$+ u \sum_{G_1, G_2, G_3, G_4} \rho(G_1) \rho(G_2) \rho(G_3) \rho(G_4) \times \delta(G_1 + G_2 + G_3 + G_4),$$

where the various terms have their usual meanings. Density waves with \( \mathbf{k} \) not in the subset \( \{ \mathbf{G} \} \) are lumped into \( F_0 \), along with other, non pertinent contributions. The discrete set \( \{ \mathbf{G} \} \) generates the reciprocal lattice.

Most of the density wave theories follow the above approach, with the subset(s) of \( \{ \mathbf{k} \} \) suitably chosen as to produce a quasi crystal instead of a regular crystal. In 1D, one would choose, for example,

$$\rho(x) = \rho(q) \cos qx + \rho(Q) \cos Qx,$$

with \( (Q/q) = \tau \) (recall figure 5). The quasiperiodic structure is thus basically the result of “competing cosines”. Of course one obtains an improved representation for \( \rho(x) \) by adding the harmonics and combination frequencies.

The same idea can be extended to higher dimensions. In fact, much before Shechtman et al, Alexander and McTague (1978) in their studies on bcc structures noted that if the star \( \{ q \} \) is such that its members are parallel to the edges of an icosahedron, then icosahedral symmetry could be favored. But they did not seriously pursue the idea since “the regular icosahedron with its five-fold axis cannot form a periodic structure”. However, in the post-discovery era, these ideas have been resurrected.

4.2 Bak’s viewpoint

Bak (1985) takes off where Alexander and McTague leave. His Landau expansion includes a fifth-order term

$$\sim \text{const} \sum_{i,j,k,l,m} \rho_i \rho_j \rho_k \rho_l \rho_m \delta(q_i + q_j + q_k + q_l + q_m)$$

where we have written \( \rho_i \) for \( \rho(q_i) \) etc. The reason for including such a term may be appreciated by considering figure 11. For a 2D structure with five-fold symmetry, the candidate star is obviously that in figure 11a. However, the participating wavevectors cannot form an equilateral triangle. The third-order term therefore does not contribute and stability becomes a problem; but with a fifth-order term, the structure is stabilized.

In 3D, Bak favors the star in figure 11b (which is the one earlier considered by Alexander and McTague). The third-order term can now contribute, and the fifth-order one acts as a bonus, stabilizing the icosahedral phase against competing crystalline
ones. Bak feels that since a single $|q|$ is involved, the structure should not be regarded as a fundamentally new state of matter but rather as just an incommensurate structure.

4.3 Mermin and Trojan model

Mermin and Trojan (1985) also appeal to the Landau theory but prefer to keep more than one length scale instead of having a fifth-order term. They thus provide room for several clusters $\{q\}$, $\{Q\}$, $\ldots$. However, these clusters are all not unrelated, and the ratios $(Q/q)$ $\ldots$ play a delicate role.

Assuming there are only two length scales, and taking into account their inter-relationship, the Landau expansion reads (after rescaling suitably to absorb some of the coefficients),

$$ F = F_2 + F_3 + F_4 + F_4 $$

$$ = -\frac{1}{t} \sum_i \rho_i \rho_i^* - \sum_{ijm} \rho_i \rho_j \rho_m \rho_n \delta(q_i + q_j + q_m) + \sum_{ijmn} \rho_i \rho_j \rho_m \rho_n \delta(q_i + q_j + q_m + q_n) - \frac{1}{4\tau} \sum_{mn} \rho_m \rho_n \rho_m^* \rho_n^* $$

Here $t \sim (T - T_c)$ as usual, and $\tau$ is a positive constant. The sum in the last term is over all $m$ and $n$ with $|q_m + q_n| = |Q|$.

With an expansion as above, the icosahedral structure is found favoured in certain range of values for the parameter $\tau$. For $(Q/q)$ Mermin and Trojan suggest the value $\{2[1 - (1/\sqrt{5})]\}^{1/2} = 1.0515$, the ratio of the nearest neighbour distance in the icosahedron to the distance of the centre from a vertex.
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No doubt Mermin and Troian succeed in producing a stable, free-energy minimum for the quasi crystal, but it is not clear how with the third-order term not contributing, the transition is of first order. Indeed, one may wonder whether a Landau-type theory is at all meaningful for discussing a kinetic transition which is what the liquid → quasi crystal transition appears to be. The Landau theory is however adequate to identify the stationary states of the free energy.

4.4 Role of diffraction studies

The number of independent wavelength scales prevailing in the icosahedral structure is not yet a settled issue. One way this question can be resolved is via diffraction.

Consider the Penrose chain, and let a, b denote the lengths of steps A and B. Define now two reciprocals by 
\[ a^{*} = (2\pi/a) \text{ and } b^{*} = (2\pi/b) \]

The Fourier transform of \( \rho(x) \) [see (1)] is given by
\[
\rho(q) = f(q) \delta(q-k)
\]

where
\[
k = ma^{*} + m'b^{*}, \quad m, m' \text{ being integers.}
\]

The above result is to be compared with
\[
\rho(q) = F(q) \delta(q-G), \quad G = 2\pi m/(a+b)
\]

for the ABABAB ... (antiferromagnetic) chain. We note that in (12), any integer combination of \( a^{*} \) and \( b^{*} \) is allowed. As a result, one can come arbitrarily close to any specified point in q-space. Thus, in principle, the diffraction pattern is a continuous string of \( \delta \)-functions densely filling reciprocal space. However if one confines attention to “lower-order reflections”, then they lead to a set of spots which form a Penrose-type sequence. Note that since the diffracted intensity is proportional to \( |\rho(q)|^2 \), the diffraction pattern has inversion symmetry although the direct space structure lacks it. Parenthetically we also remark that observed diffraction patterns (e.g. in figure 1) show sharp spots presumably because only lower-order reflections have been captured.

Diffraction patterns in 2D can similarly be built up using the star in figure 11c, and spots of various orders generated in this fashion are shown in figure 11d. As noted by Mackay, Bak and several others, these spots can be indexed by five Miller indices (one of which is redundant as in the case when one uses four indices for hexagonal lattices). Observe that on account of the angle of 72° between adjacent vectors in the star, the golden mean automatically enters in the description of spots like C.

Thanks to the five-index labelling scheme, one can formally construct a lattice of points in a five-dimensional space such that these points are also indexed the same way. A correspondence is thus established between the observed diffraction spots in 2D (which, observe, lack periodicity) with a lattice of points in a higher dimensional space. Taking note of the redundancy, one could restrict the dimensionality \( N_{r} \) of the reciprocal lattice space to four (Levine et al 1985).

Similar ideas apply to 3D icosahedral order. According to all views, the basic star involves an icosahedron. Depending on whether the star corresponds to vectors radiating to the vertices or to the face centres or are parallel to the edges, one has respectively the vertex model, the face model and the edge model. However, whatever be the model, a minimum of six Miller indices are required implying that \( N_{r} = 6 \).
In general, \( N_R \) depends on the minimal set \( \{ q \} \) from which the reciprocal lattice can be constructed. In periodic crystals \( N_R = d \) the dimensionality of the crystal. For quasi crystals, \( N_R = n_1 \) where \( n_1 \) is the number of relatively incommensurate lengths (Levine et al, 1985). In 2D Penrose structures, although the star itself has only one length scale, there is a combination (see figure 11d) whose length is incommensurate with \( q \). Therefore \( n_1 = 2 \). Such irrational multiples are forbidden in periodic structures, whence \( n_1 = 1 \). Using this reasoning, we see that for Penrose tiles, \( N_R = 2 \times 2 = 4 \) as already noted while for icosahedral crystals, \( N_R = 2 \times 3 = 6 \).

Intensity is one important means of distinguishing between various models. In some cases, the geometry of the diffraction spots can itself provide a clue. Figure 12 shows the pattern of spots expected in a plane perpendicular to the two-fold axis in various icosahedral models (Nelson and Sachdev, 1985). While all these models respect the basic symmetry, there are nevertheless variations in the diffraction patterns. Nelson and Sachdev indicate that comparison with experiment shows that the vertex model provides the best fit. See also Chattopadhyay et al (1985b).

4.5 Density functional approach

It is known (Baym et al, 1971) that the Landau theory is inadequate when the transition is strongly first order, as it is in the case of Al-Mn icosahedral system. An alternate approach is via the density functional method used by Ramakrishnan and Yussouff (1979, abbreviated ry) in their studies on crystallization.

\[ \text{ry} \] start by noting that in a classical system, the density \( \rho (r) \) of the system relative to the fluid density \( \rho_0 \) is given by

\[
\rho (r) / \rho_0 = \exp \left[ - \beta v (r) \right], \quad \beta = 1 / k_B T
\]  

where \( v (r) \) is the total potential at \( r \) (as in the Weiss molecular field theory of magnetism). The potential \( v \) is the sum of a (possible) external potential \( v_{\text{ext}} (r) \) and a contribution due to internal density fluctuations. To first order,

\[
\rho (r) / \rho_0 = \exp \left[ - \beta v_{\text{ext}} (r) + \int c (r - r') (\rho (r') - \rho_0) \, dr' \right]
\]

\[ \text{(15)} \]

\[ \text{Figure 12. Diffraction patterns predicted for the icosahedral structure normal to the two-fold symmetry axis. The patterns are for three different models discussed in the text. Four generation of spots are shown; larger spots correspond to "low-order reflections" (after Nelson and Sachdev, 1985).} \]
where \( c(r) \) is the fluid direct correlation function, and is related to the structure factor \( S(q) \) by

\[
S(q) = \frac{1}{[1 - c(q)]}
\]  

(16)

where \( c(q) \) is the Fourier transform of \( c(r) \).

The free energy is a functional of the density distribution given by

\[
\beta F[\rho] = \int \! dr \, \rho(r) \left[ \ln \left( \frac{\rho(r)}{\rho_0} \right) - 1 \right] - \frac{1}{2} \int \! dr_1 \, dr_2 \, c(r_1 - r_2) \left( \rho(r_1) - \rho_0 \right) \left( \rho(r_2) - \rho_0 \right).
\]  

(17)

Here the first term comes from the entropy associated with dividing up the particles into various cells while the second term is the first non-zero quantity in an expansion in terms of density fluctuations.

One now minimizes the free energy keeping in mind (15). The problem is where to hunt for the minimum in \( q \)-space. Here \( \rho \) give a valuable hint. They observe that if one expands \( \rho(r) \) in terms of density waves as

\[
\rho(r) = \rho_0 \left[ 1 + \sum_G \mu(G) \exp i \mathbf{G} \cdot \mathbf{r} \right]
\]  

(18)

where the vectors \( \mathbf{G} \) belong to the reciprocal lattice of some Bravais lattice, then one could confine one's search to the region where \( |\mathbf{G}| = q_m \), the wave vector corresponding to the first maximum in the liquid diffraction pattern \( S(q) \). In other words, that lattice will be favoured, for which the smallest \( \mathbf{G} \) is such that \( |\mathbf{G}| = q_m \). The genes of the crystalline state are thus already encoded in the parent state.

Sachdev and Nelson (1985) follow \( \rho \) and try a similar approach vis-a-vis the quasi crystalline state. There are, however, practical problems since the latter lacks unit cells. Sachdev and Nelson get over this difficulty by exploiting the fact that the quasi crystal may be regarded as the projection of a hyper cubic lattice in six dimensions (—recall § 3.5). All the manipulations of \( \rho \) are thus carried out in 6-dimensional space! The input structure factors are those for relaxed dense-random-packed structures (Ichikawa 1983) and for amorphous cobalt (Leung and Wright 1974).

Among the principal findings are: (i) Undercooled liquids are metastable with respect to the icosahedral crystal; (ii) Tendency for formation of the icosahedral structure is significant when the liquid structure factor \( S(q) \) is high at the wavevector corresponding to that for the icosahedral structure; (iii) Conventional bcc and fcc have even lower free energies; (iv) There is a rapid fall off of intensities in reciprocal space at small wavevectors; (v) Vis-a-vis the sites of a geometrically generated Penrose structure (see § 3), one can assign mean occupation numbers to the sites. It turns out that this number varies considerably across the structure. When it is > 1, it is speculated that the sites are occasionally filled with split interstitials. On the other hand, clusters of sites with small occupation probability correspond to atoms which hop among various vacancy sites.

The above analysis is no doubt for a monatomic system whereas the (only) known example of a quasi crystal is a binary. Sachdev and Nelson however indicate how their analysis can be extended to multicomponent systems.
5. Hydrodynamic modes

The long-wavelength behaviour of a quasi crystal has the interesting feature of extra hydrodynamical modes. Extra modes always arise whenever a continuous symmetry is broken (e.g. in superfluidity); only in this case, they are related to the specific way in which translational symmetry is broken.

To understand the origin of the extra modes, consider first an incommensurate crystal. As already noted, the atomic positions are dictated by two waves. The phase difference between these can be anything, and in fact the Hamiltonian is insensitive to changes in the relative phase. However, a given incommensurate crystal will have a particular value for the phase; the continuous phase symmetry of the Hamiltonian is thus broken. The low-lying excited states will involve not only positional fluctuations, but also fluctuations of the relative phase from its equilibrium value. Thus, apart from the usual acoustic mode, there exists also a phason mode whose frequency $\omega \to 0$ as the wavevector $k \to 0$ (see, for example, Axe and Bak 1982).

Bak (1985) and Levine et al (1985) have noted that such modes occur in quasi crystals also. Consider a 2D example. As already remarked, there are effectively four degrees of freedom. If two of these are mapped onto the conventional displacement degrees of freedom, we still have two extra. Excitations associated with these would be the analogue of the phason modes. As is to be expected, hydrodynamical modes arise when, due to thermal energy, the condition $\Sigma_j \gamma_j = 0$ on the pentagrid is instantaneously violated. Frozen defects are also described by the deviation of $\Sigma_j \gamma_j$ from zero. In particular, defects like dislocations occur when this deviation equals the Burger's vector (Levine et al 1985).

By similar arguments, one expects 6 hydrodynamical modes in an icosahedral medium.

6. Relationship to gauge theories for glass

Recently, there has been much speculation regarding a possible gauge theory for glass (—for a review and pertinent references, see Venkataraman and Sahoo 1985a). It is reasonable to wonder whether quasi crystals fit into such theories. A clear cut answer is not available as yet but some speculations are possible.

Gauge theories for glass center around the fact that amorphous materials contain line defects of topological origin. Such defects, referred to as disclinations, were originally considered by Frank and Kasper (1958, 1959) in the context of complex alloy structures. They surmised that such structures are normally built with atoms having icosahedral coordination i.e. $Z = 12$, but since space filling with $Z = 12$ atoms alone is not possible, atoms with $Z = 14, 15, 16$ are also required. Such atoms with anomalous coordination numbers form endless chains known as Frank-Kasper (FK) chains. Analysis in the context of amorphous structures has revealed that such chains are in fact topological defects, and have been labelled disclinations. It is further believed that FK chains actually occur in sphere-packed amorphous structures (e.g. metallic glass). The only difference between a crystal and an amorphous structure is in the disposition of the FK chains. While they are ordered in a crystal, they are a tangled mess in an amorphous structure.

In contemplating a gauge theory for quasi crystals, the crucial question is whether
there are Frank-Kasper lines in them. As yet there is no firm evidence for topological defects of this nature in the model structures but this is mainly due to lack of sufficient studies. Efforts are in progress in our Centre (G Athithan, private communication) to construct a model \textit{a la} Kramer and Neri and to examine it for disclinations. If they are present, the gauge theory of Nelson and Widom (1984) for glass could conceivably be extended. Meanwhile we note that Frank-Kasper lines do occur in the model of Nelson and Sachdev (see §3.5).

One should not be too surprised if one is able to give a unified description of amorphous, quasi crystalline and crystalline structures. Let us remember that Bernal (1964) noted the existence of five-fold symmetry even in liquids, though only on a local scale. In the quasi crystal, one has this symmetry in the large also. In the crystal, translational symmetry prevents a manifestation of five-fold symmetry in the large but local icosahedral clustering is still to be found (at least in the complex alloy structures). The connecting concept is the Frank-Kasper chain. These chains are present in all the three phases mentioned above; only their geometric disposition seems to be such that \textit{global} five-fold symmetry is suppressed in two of the three phases. If topological defects are the key thing, then gauge theory is an attractive possibility for dealing with their various possible arrangements.

7. Concluding remarks

Quasi crystals represent a new phase of condensed matter, the distinctive feature of which is the replacement of periodicity by quasiperiodicity on the one hand, and the presence of long-range orientational order on the other. Phases with orientational order have been proposed in the past \textit{e.g.} the hextatic phase in 2D (Nelson and Halperin 1979; for a review see Venkataraman and Sahoo 1985b), but the Al-Mn quasi crystal represents the first, real-life example with \textit{non crystallographic} rotational symmetry.

As of now, not much is known about quasi crystals. For example, we do not know which elements favour quasi crystal formability (—one would not be surprised if boron features prominently in the list)*. Full details of the structure of even Al-14\% Mn are still elusive. And about defects we know even less. Then there are the elementary excitations, band structure and so on. Last, but not the least, there is the question of the relationship of the quasicrystalline phase to the crystalline one as well as the glassy phase.

In a nutshell, the questions confronting us are numerous. A lively future for the subject is therefore guaranteed!

\textbf{Dedication and acknowledgements}

With much sadness, I dedicate this article to the memory of my good friend, the late Dr N S Satya Murthy, especially for his many efforts in the cause of Indian Physics. My understanding of quasi crystals has benefitted much from discussions with

* I understand a BHU-DMRL collaboration has uncovered some trends and systematics (Arunachalam, private communication).
several friends, particularly G Athithan, V Balakrishnan, K Neelakantan, N Kumar, V C Sahni, A K Sood and R Subramanian. The support of the Jawaharlal Nehru Memorial Fund is acknowledged.

Post-script

After this manuscript was completed, I became aware of the following papers:
1. Two bell Lab preprints by V Elser who discusses a simple means of visualizing quasi crystalline structures as projections of higher-dimensional periodic structures, and also the diffraction pattern of such structures,
2. A paper by Duneau and Katz (1985 Phys. Rev. Lett. 54 2688) who generalize de Bruijn’s work to produce quasi periodic tiling in arbitrary dimension, and
3. A letter by Zia and Dallas (1985 J. Phys. A18 L341) who not only describe an elegant means of obtaining the Fourier transform of quasi periodic structures, but also call attention to several useful mathematical references, besides speculating on novel applications like coding!

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