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Some Remarks on Quasi-Crystal Structure

BY BARRY W. NINHAM* AND SVEN LIDIN

Department of Inorganic Chemistry 2, *Chemical Centre, University of Lund, POB* 124, *S*221 00 *Lund, Sweden*

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Abstract

The Fourier transform of a skeletal delta function that characterizes the most striking features of experimental quasi-crystal diffraction patterns is evaluated. The result plays a role analogous to the Poisson summation formula for periodic delta functions that underlie classical crystallography. The real-space distribution can be interpreted in terms of a backbone comprising a system of intersecting equiangular spirals into which are inscribed (self-similar) gnomons of isosceles triangles with length-to-base ratio the golden mean τ. In addition to the vertices of these triangles, there is an infinite number of other points that may tile space in two or three dimensions. Other mathematical formulae of relevance are briefly discussed.

1. Introduction

This paper attempts to draw together some observations that may have a bearing on the problem of structure in quasi-crystals. So far the mathematical tools that have been brought to bear, be they geometric packing (Kowalewski, 1938; Penrose, 1974), group theory or use of projections from hyper-Euclidean spaces to three dimensions (Gratias & Mechel, 1986; Jaric, 1988, 1989), are unquestionably deep, and some real progress has been made in understanding. Some real-space models that must capture at least the main features of particular systems have been constructed (Lidin, Andersson, Bovin, Malm & Terasaki, 1989).

Despite these advances, the real problem is to relate observed diffraction patterns with nonstandard crystallographic symmetries to the atomic distributions that give rise to them. This problem remains. This can be seen if we recall that the interpretation of diffraction experiments on translationally invariant crystals depends ultimately on the existence of the Poisson-summation formula. This relation asserts that the Fourier transform of a periodic delta function is itself a periodic delta function, whence the use of reciprocal space. Explicitly, we have the identity

$$f(x) \equiv \sum_{m=-\infty}^{\infty} \delta(x-m) = \sum_{-\infty}^{\infty} \exp(2\pi i m x) = 1 + 2\sum_{m=1}^{\infty} \cos(2\pi m x) \quad (1)$$

so that the Fourier transform of a translationally invariant array of atoms represented by the periodic delta function (1) is

$$\tilde{f}(k) = \int_{-\infty}^{\infty} \mathrm{d}x \exp(-2\pi i k x) \sum_{-\infty}^{\infty} \delta(x-m) = \sum_{-\infty}^{\infty} \exp(-2\pi i k m) = \sum_{-\infty}^{\infty} \delta(k-m). \quad (2)$$

The determination of the crystal structure is then immediate, since any diffraction pattern will be related to the product of an appropriate combination of three such delta functions with atomic form factors. Inversion is then possible *via* the convolution theorem for Fourier transforms if the problem of the undetermined phase can be solved. No such analogous identity on which to base experiments appears to have been written down for quasi-crystalline diffraction, where successive values exhibit geometric ratios instead of properties characteristic of translational invariance. It is our purpose to give such a relation and to quote others that relate to the general problem.

2. Quasi-crystal spectra and self-similarity

The classical observed quasi-crystal spectrum is shown in Fig. 1. This illustrates schematically a two-dimensional section in reciprocal space of a diffraction pattern. The fivefold symmetry is exact and typically six indices instead of three are required to index each point, with the choice of origin arbitrary and, for assignment of indices, ambiguous. The

* Permanent address: Department of Applied Mathematics, RSPhysE ANU, Canberra ACT, Australia 2601.

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features on which we wish to focus are as follows.

(i) Along a given fivefold axis the spacing of the main peaks is in the ratio $k_n/k_{n+1}=1/\tau$ where τ is the golden mean, $(5^{1/2}+1)/2$.

(ii) Between each two such peaks are a sequence of further peaks of lower intensity that all lie on an infinite set of coincident interpenetrating Fibonacci sequences of arbitrary origin [they may be described through a projection from Euclidean two-space onto a strip bounded by two lines at an angle of $\pi/5$ to the x axis].

(iii) Surrounding each fivefold axis are other sequences of lesser intensity that can be connected to their neighbours to form regular self-similar pentagonal figures (icosahedra in three dimensions).

(iv) Along the fivefold axes the density of points as one approaches any chosen origin becomes infinite.

(v) Increasing time of exposure results in the appearance of more and more points throughout reciprocal space in an eventually dense space-filling array. All points satisfy the same symmetry and self-similarity properties.

(vi) Through a set of initial points on adjoining fivefold axes can be drawn a set of 20 intersecting equiangular spirals emanating from any chosen origin as illustrated.

The distinction between features (i) and (ii) above can be disputed: sometimes what we have identified (through their intensity) as 'main' peaks can be out of the main sequence and belong to the subsequences (ii). Nonetheless, we can still ask the questions: What would the Fourier transform of such a system be? Does it even exist, and if so how can it be interpreted? Is it unique? To that end we focus first on property (i) of the spectrum and take as a representation of

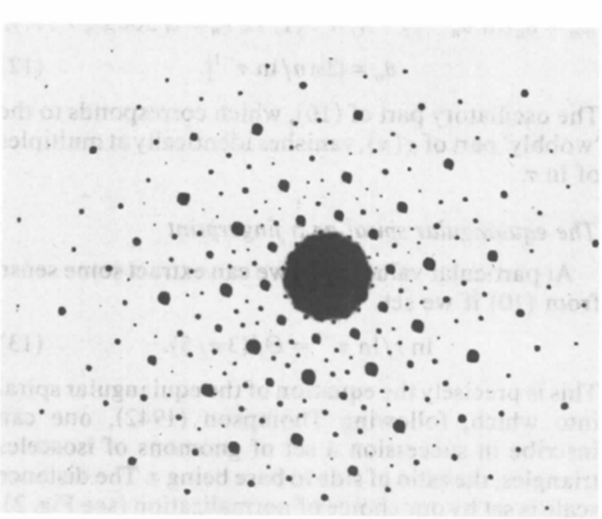

Fig. 1. Experimental electron diffractogram of an icosahedral quasi-crystal. (Picture courtesy J.-O. Malm.)

the main structure of the distribution the expression

$$\tilde{f}(k)=|k|^{-j}\sum\delta(|k|-\tau^{-m}),$$

$$j=0,1,2 \text{ in } 1,2,3 \text{ dimensions.} \quad (3)$$

The postulated phase-space factor $|k|^{-j}$ will be seen later to be necessary for reasons that will become clear, and this 'skeletal' delta function exhibits spacing of the main points along a given fivefold axis. We ask [analogously to (1) and (2)]: Is the Fourier transform of such a function a meaningful object and, if so, what would it look like? We postulate that the relation between the diffraction pattern of a quasi-crystal and its atomic structure is basically the same as that for an ordinary crystal and, further, that this generalization of the Fourier transform be performed by summation analogous to that of a periodic function. The two-dimensional transform along a particular axis, say $\theta=\pi/5$, along the same axis in real ($\mathbf{r}$) space will then be

$$f(|r|,\theta=\pi/5)=\int_{-\infty}^{\infty}\exp(-2\pi ikr)(k/|k|)\,\mathrm{d}k \times\sum_{-\infty}^{\infty}\delta(|k|-\tau^{-m})$$

$$=\sum_{m=\infty}^{\infty}\cos[2\pi r\exp(m\ln\tau^{-1})]. \quad (4)$$

This formal expression is what we have to deal with. It exists, if at all, only in the sense of generalized function theory, but so too do (1) and (2). It is not a Fourier series but, as we shall see, carries a good deal of information.

To show this, we consider a related function defined by

$$g(x)=\sum_{m=-\infty}^{\infty}[\exp(-x\exp m)-\exp(-\exp m)]. \quad (5)$$

Now, $g(x)$ so defined is a uniformly convergent sum, so that $g(x)$ is everywhere continuous in $(0,\infty)$. It satisfies the functional equation

$$g(ex)=g(x)+g(e), \quad (6)$$

where e is the transcendental number. This is the same functional equation as that for $\ln x$, and both $g(1)$ and $\ln(1)$ are equal to zero. It is natural to ask if $g(x)$ is in fact identical to $\ln x$, at least up to a constant factor. The derivations in Appendices A and B show that this is not the case. Explicitly, $g(x)$ can be cast in the form

$$g(x)=-\ln x+\sum_{n=-\infty}^{\infty}\Gamma(2\pi in)(x^{-2\pi in}-1), \qquad n\neq 0. \quad (7)$$

Here $\Gamma(z)$ is the gamma function. We see that $g(x)$ does coincide with $-\ln x$ at isolated points (where $x^{-2\pi in}-1=0$, *i.e.* for all integers n) at $x=\exp m$, where $m = 0, 1, 2, 3, \ldots$. In between these points $g(x)$ wobbles about the value of the function $-\ln x$ in an apparently chaotic manner. A similar problem led Ramanujan to his famous fallacious proof (Hardy, 1940) of the prime-number theorem. He forgot the wobbles. So the behaviour of the function $g(x)$, related to our skeletal delta function is much deeper than it might appear at first sight. The wobbly part $[g(x)+\ln x]$ is self-similar, *i.e.* it scales at every level, but it is *not* fractal in the sense of Mandelbrot because it is everywhere differentiable infinitely many times. A fractal is nowhere differentiable, but everywhere continuous.

An analogous but more complicated problem than this one has been encountered in the context of Fourier analysis of random walks with self-similar clusters (Hughes, Montroll & Shlesinger, 1981, 1982, 1983). Analogies between this random-walk Fourier-analysis problem and real-space renormalization have also been explored (Shlesinger & Hughes, 1981). We remark in passing that computation shows that, in addition to the points $x = \exp m$, there exists another infinite set of real zeros of $g(x)+\ln x$. Further, if we write $x = \exp t$ and $g(x) = -1/N(t)$, we can convert the nonlinear functional equation (6) into the nonlinear functional equation

$$N(t+1) = N(t)/[1-g(e)N(t)]. \qquad (8)$$

Our analysis has therefore produced a solution to the nonlinear difference equation (6), which, although simple for integer of t, behaves in a somewhat irregular way for intermediate values.

3. The skeletal Fourier transform and equiangular spirals

The self-similar oscillations within oscillations exhibited by $g(x)$ are computationally extremely small in magnitude and appear to be of at most academic interest. However, this is not the case for our pseudo-quasi-crystal spectrum (4). Keeping the behaviour of $g(x)$ in mind we will consider the modified form

$$f(|r|, \theta = \pi/5) = \sum_{m=-\infty}^{\infty} \{\cos[2\pi r \exp(m \ln \tau^{-1})] - \cos[2\pi \exp(m \ln \tau^{-1})]\}. \qquad (9)$$

At first sight the choice of this normalization by subtracting the constant sum seems nothing more than a mathematical trick to guarantee self-similarity. But through this choice we are operating on the skeletal delta function with the difference of two operators

$$\int d^2k\, [\exp(2\pi ikr) - \exp(2\pi ilr)].$$

We can then interpret the resulting expression (9) as the difference or excess in density distribution over that existing for any point specified for a particular k vector and taken to have unit magnitude. Any multiple of τ will do just as well. If these arguments are accepted, then (5) is nothing more than a variant of $g(x)$, except that the argument is now purely imaginary and the scaling parameter is τ not e.

The sum involved in (9) is not formally convergent, but neither is a periodic delta function, and we will persist on the assumption that it will emerge by a formal analysis through, for example, convolution with an atomic form factor that will yield convergence in practice.

Granted these assumptions, the analysis can proceed exactly as for $g(x)$ [see Appendix A]. The result, corresponding to (4), is

$$f(|r|, \theta = \pi/5) = (1/\ln \tau^{-1}) \times \left\{ \ln r - \sum_{n=-\infty}^{\infty} \cosh(2\pi^2 n/\ln \tau^{-1}) \times \Gamma(2n\pi i/\ln \tau^{-1})[(2\pi r)^{-2\pi i n/\ln \tau^{-1}} - (2\pi)^{-2\pi i n/\ln \tau^{-1}}] \right\}. \qquad (10)$$

The differences from previously are that (i) $f(|r|)$ scales with τ instead of e; $f(\tau x) = f(x) + f(\tau)$ and (ii) the self-similar wobbles are vastly enhanced because of the cosh function in the infinite sum.

The sum converges conditionally and is real, as can be seen if the nth term T_n is written asymptotically. Thus

$$T_n \simeq n^{-1/2}\{\sin[(2\pi n/\ln \tau^{-1})(\ln 2\pi x - \ln 2\pi)/2] \times \sin[\varphi_n - (2\pi n/\ln \tau^{-1})(\ln 2\pi x + \ln 2\pi)/2]\} \qquad (11)$$

where

$$\varphi_n = \theta_n(\ln \theta_n - 1) - \pi/4 - (1/12\,\theta_n + 1/360\,\theta_n^3 + \ldots);$$
$$\theta_n = |2\pi n/\ln \tau^{-1}|. \qquad (12)$$

The oscillatory part of (10), which corresponds to the 'wobbly' part of $g(x)$, vanishes identically at multiples of $\ln \tau$.

The equiangular spiral as a fingerprint

At particular values of $|r|$ we can extract some sense from (10) if we set

$$\ln r/\ln \tau^{-1} = \Theta/(3\pi/5). \qquad (13)$$

This is precisely the equation of the equiangular spiral into which, following Thompson (1942), one can inscribe in succession a set of gnomons of isosceles triangles, the ratio of side to base being τ. The distance scale is set by our choice of normalization (see Fig. 2). The appearance of the equiangular spiral is called the trace, the shape, the ghost or signature of our skeletal delta function.

One can speculate that, if indeed the phase-space factor is a requirement of the distribution that reflects the self-similarity characteristic of quasi-crystals, all such spectra will be dominated in their intensities by such a term and all appear very similar. That seems to be the case. Those analyses attempted so far do produce R values that imply astonishingly good fits (Elswijk, De Hosson, van Smaalen & de Boer, 1988). This makes sense if the atomic-form-factor contributions are less important than ordinarily, as they would be if masked by those from the phase-space factor. Without this factor, the self-similarity is lost (see Appendix A).

However we seem to have recovered much more positional information. In addition, we now generally set

$$f(|r|, \theta=\pi/5)=\Theta/(3\pi/5)=0 \qquad (14)$$

and recall that according to prescription the zeros of this equation are to be interpreted as points in real space. Because of the oscillations in (10) there will be in addition to the apexes of the ever-expanding triangles set by (13) an infinity of real-space points that also satisfy self-similarity and fill up unoccupied regions between the isolated triangular apexes. The degree to which they will do so presumably depends on the minimum distance scale one is prepared to accommodate.

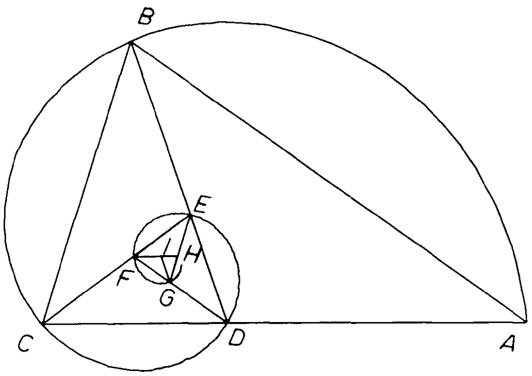

Fig. 2. Succession of gnomons of isoceles triangles with side-to-base ratio τ:1 (after Thompson, 1942). The apices or other corresponding points of all these triangles are self-similar and have their locis on an equiangular spiral at the trivial zeros of the excess-density function (13). If the centre of the spiral is taken as the origin, O, and OA as the x axis, the coordinates of successive apices are $[Y_0=(\tau^2+1)^{1/2}]$ $A=(1, Y_0\times 0)$; $B=\frac{1}{2}\tau^{-1}(-1/\tau, Y_0)$; $C=\frac{1}{2}\tau^{-2}[-\tau, Y_0/(-\tau)]$; $D=\frac{1}{2}\tau^{-3}[\tau, Y_0/(-\tau)]$; $E=\frac{1}{2}\tau^{-4}(1/\tau, Y_0)$ *etc.* The ratio of the sides of successive triangles is $AB/BC=BC/CD=CD/DE=\ldots=\tau$. The equation of the spiral is $\ln r=\ln \tau^{-1}\Theta/(3\pi/5)$. The successive angles $\widehat{AOB}$, $\widehat{BOC}$, $\widehat{COD}$, $\widehat{DOA}$ are $3\pi/5, 3\pi/5, 3\pi/5, \pi/5$ and the lengths AO, BO, CO, DO are in the ratio $1:\tau^{-1}:\tau^2:\tau^3\ldots$. The equiangular spiral coincides with the inverse Fourier transform, rather than the free apices of the triangles inscribed, if the point A is chosen to coincide with the vector $\mathbf{l}$ of (9) and P is chosen to be the origin for the skeletal delta function along a particular observed fivefold axis. However, the points $A, B, C, D, E, \ldots$ determine only the basic shape of the inverse position space transform. The complete expression (9) has an infinite number of other zeros at intermediate points that satisfy the condition $f(r, \pi/5)=\Theta/(3\pi/5)$ and that are also positions in the skeletal quasi-crystal lattice.

4. Angular dependence and three-dimensional skeleton spectra

Our discussion so far has focused on a particular angle in space. In general, for the full fivefold two-dimensional skeleton spectrum of Fig. 1 we should write

$$\tilde{f}(k)=(1/|k|)\sum_{j=1}^{10}\delta(\theta-j\pi/5)\sum_{m=-\infty}^{\infty}\delta(|k|-\tau^{-m}). \qquad (15)$$

This would lead to a sum of intersecting equiangular spirals as the trace of the quasi-crystal distribution. Thus we can take

$$\begin{aligned} f(r) &= \textstyle\int \exp(-2\pi i k r)\, \mathrm{d}^2k \tilde{f}(k) \\ &= \sum_{j=1}^{10}\sum_{m=-\infty}^{\infty}\{\exp[-2\pi i r\cos(\theta-j\pi/5) \\ &\quad \times \exp(m\ln\tau)]-\exp[-2\pi i\cos(\theta-j\pi/5) \\ &\quad \times \exp(m\ln\tau)]\}. \qquad (16)\end{aligned}$$

The leading term in $f(r)$, *i.e.* omitting the oscillations, is similar to (13),

$$f(r)=\sum_{j=1}^{10}[\ln|r\cos(\theta-j\pi/5)|]/\ln\tau^{-1}, \qquad (17)$$

which produces ten intersecting spirals as the basic skeleton. The independence of origin and self-similarity and rotational invariance seems to be guaranteed as can be seen in § 7.

In three dimensions the phase-space factor to preserve self-similarity would be $1/|k|^2$ instead of $1/|k|$ and in both two and three dimensions additional points of the structure that fill in the pattern beyond the intersecting triangular gnomons are provided by the oscillatory part of the whole function. In three dimensions, we can expect that the overall structure predicted will be made up of intersecting equiangular helices of geometrically increasing pitch.

5. Decorations of the skeleton

In our argument so far we have ignored a most important feature of real spectra, namely point (ii) of § 2. Between each two successive values of the argument of our skeletal delta function in, say, the interval of k space $[\tau^{-m}, \tau^{-(m+1)}]$, *cf.* (3), lie a further sequence of points. Along any given line these points form a whole additional interpenetrating and interlocking set of Fibonacci sequences. We have supposed these to be less important in arriving at a picture of the real-space Fourier transform than the usually more intense peaks of the skeletal k space representation. It is possible to build an approximate representation of this reality. However, we do not intend to pursue this development further until the distribution of (14) is explored further computationally or experimentally. Another kind of decoration that is amenable to treatment is one in which the gaps between the skeleton spirals are decorated with a random sequence of points in the spectrum in each interval $(\tau^{-m}, \tau^{-(m+1)})$ and assigned statistical or equal weights. The analysis required needs to invoke only the known properties of Pearson's random walk, but will not be pursued further here, although clearly such an analysis can be used to construct a theory of liquids.

6. Extensions of Poisson's formula

There exists another class of relations analogous to the Poisson formula, which may provide some insights into other incommensurate phases. This class of formulae has been derived elsewhere (Ninham, Hughes, Frankel & Glasser, 1992; Ninham, 1991). Here we omit the derivations and simply quote the result:

$$\sum_{m=1}^{\infty} |\mu(m)| \cos mx = \tfrac{1}{2} \sum_{m=1}^{\infty} \mu(m) \left[\sum_{n=-\infty}^{\infty} (2\pi/m^2)\delta(x - 2\pi n/m^2) - 1 \right]. \tag{18}$$

In this equation $\mu(m)$ is the Möbius function defined by

$$\mu(m) = \begin{cases} 1 & \text{if } m = 1 \\ 1 & \text{if } m \text{ is a product of } r \text{ distinct primes} \\ 0 & \text{otherwise.} \end{cases} \tag{19}$$

This formula relates a sum of cosines, *i.e.* the Fourier transform of a set of delta functions, to a sum of delta functions requiring two indices. The distribution that gives rise to this array is one in which some of the integers are missing - those for which $|\mu(m)| = 0$ - in an apparently random but completely deterministic manner. Thus on a one-dimensional array of atoms labelled by the integers, the missing lattice points from 1 to 50 are 4, 8, 9, 16, 18, 20, 24, 25, 27, 28, 32, 36, 40, 44, 45, 48, 49 and 50. (The frequency of missing points diminishes with increasing number.) The Fourier transform of this distribution requires two indices for its specification and thus there is no arbitrariness therein. The product of three such pseudo-periodic or aperiodic delta functions, in (x, y, z) directions, is a completely determined array in three dimensions that requires six indices to label its also completely determined Fourier transform. We hope to explore such distributions in a later publication.

7. Relation to Penrose tilings

The Penrose tiling problem seems first to have been touched upon by Kepler (see Kowalewski, 1938). It is clear that our approach must in some ways parallel that of the Penrose tiling, and it is indeed not surprising to find that the Penrose tiling can be generated from Thompson's triangular tiling of the equiangular spiral. We start with the observation that the gnomonic isoceles triangles of Thompson (see Fig. 2) are identical to those used by Robinson (1975; see Grünbaum & Shephard, 1987) to analyse the Penrose tiles. Since any one of the aperiodic pentagonal Penrose tilings can be decomposed into these triangles, it is evident that the Thompson construction can be used to generate a Penrose-type tiling. The single equiangular spiral

$$\ln r/\ln \tau = \Theta/(3\pi/5)$$

is related to the set of spirals

$$\ln r/\ln \tau = (\Theta + \alpha)/(\pi/5)\alpha \in \{0, 2\pi/5, 4\pi/5, 6\pi/5, 8\pi/5\},$$

as is shown in Fig. 3. The intersections of the latter set (together with the set of points obtained from the intersections by an inversion in the origin) form the base for a Penrose-type tiling. Note how the original gnomons stand out in the tiling (see Fig. 4).

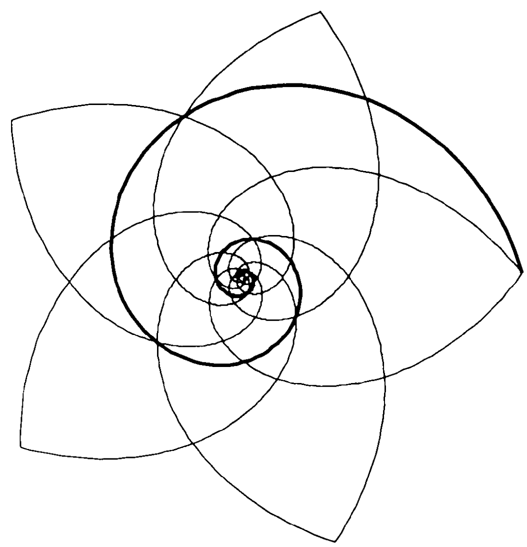

Fig. 3. The apices of the gnomons of the equiangular spiral $\ln r/\ln \tau = \Theta/(3\pi/5)$ can be seen as a subset of the intersections between the equiangular spirals $\ln r/\ln \tau = (\Theta + \alpha)/(\pi/5)$; $\alpha \in \{0, 2\pi/5, 4\pi/5, 6\pi/5, 8\pi/5\}$. These intersections are the set of peaks in the skeletal delta function and from them a Penrose-type tiling is easily constructed.

8. Concluding and miscellaneous remarks

In this note we have posed ourselves the question: how can one write down a relation that could play the role of the Poisson summation formula that underlies translationally invariant crystallography and that might be used to glean some insight into quasi-crystal structure? The approach we have taken is neither entirely rigorous nor conventional. We have simply taken an experimental diffraction, selected and subsumed what stand out as its salient features in a skeletal sum of delta functions and written down the Fourier transform. The constraints of self-similarity, scaling, fivefold symmetry and independence of origin are automatic.

The emergence of the logarithmic spiral as the signature of the Fourier transform is not surprising, and Thompson would have taken this as self-evident. In his words: 'In the growth of the shell, we can conceive of no simpler law than this, namely, that it shall widen and lengthen in the same unvarying proportions; and this simplest of laws is that which Nature tends to follow. The shell, like the creature within it, grows in size, but it *does not change its shape*; and the existence of this constant relativity of growth, or constant similarity of form, is the essence of the equiangular spiral.' The maintenance of shape or the constant change of curvature is indeed of the essence.

What is new, however, is not the emergence of spirals in two dimensions or helices in three dimensions from the analysis, but the existence of additional self-similar oscillations, which, at fixed prescribed curvature dictated by the spiral, fill in 'atomic' positions between the spirals. That seems to be as it should be.

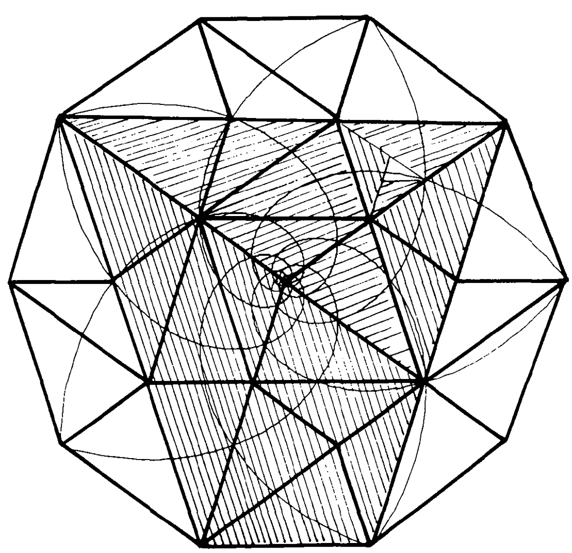

Fig. 4. A Penrose-type tiling constructed from the skeletal delta function.

The infinite sum of (10) has some most interesting features. It is not a Fourier series, and it is conditionally convergent. As an experiment, for several values $|r|$ of the argument we have computed a million terms of the sum and it has still not settled down, the two sine functions of (11) beating together over very long intervals. This is no cause for dismay. It would, after all, be impossible to compute a periodic delta function numerically. Applications would require the convolution of our skeletal delta function with a form factor that would result in rapid convergence exactly as for conventional crystallography.

Perhaps the most interesting feature is that our Fourier-transform sum seems to have much in common with the distribution of the zeros of the Riemann zeta function (Dyson, 1984), the greatest unsolved problem in pure mathematics! That indicates something of the depth of the problem. That the zeta function ought to come into the scheme of things somehow is not surprising - the Poisson and related summation formulae are special cases of the Jacobi theta function. [Indeed the Bravais lattices can be enumerated systematically through an integral over all possible products and sums of products of any three of the four theta functions in different combinations that automatically preserve translational and rotational symmetries (Barnes, Hyde & Ninham, 1990).] The theta-function transformations are themselves just another way of writing the Riemann relation connecting $\zeta(s)$ with $\zeta(1-s)$. Additionally, the properties of the zeta function are automatically connected to the theory of prime numbers. So one expects that the Rogers-Ramanujan relations [see Hardy (1940) and Appendix A] must eventually play a central role in the scheme of things for quasi-crystals. Indeed, the golden mean itself is the limit of the continued fraction $F(1)/F(y)$,

$$\lim_{y\to 1}[F(1)/F(y)] \equiv 1+\cfrac{y}{1+\cfrac{y^2}{1+\cfrac{y^3}{1+\dots}}} = \frac{5^{1/2}+1}{2} = \tau \tag{20}$$

[the function $F(y)$ is defined in Appendix B], where the continued fraction is the ratio of two theta functions,

$$\begin{aligned}\frac{F(1)}{F(y)} &= \exp(-x/5)(\cos \pi/10)\\ &\quad\times \prod_{m=1}^{\infty}[1+2(\cos \pi/5)\exp(-4\pi^2 m/5x)\\ &\quad+\exp(-8\pi^2 m/5x)]/(\cos 3\pi/10)\\ &\quad\times \prod_{m=1}^{\infty}[1+2(\cos 3\pi/5)\exp(-4\pi^2 m/5x)\\ &\quad+\exp(-8\pi^2 m/5x)], \qquad y=\exp(-x), \end{aligned} \tag{21}$$

themselves the ratio of generating functions (Hardy, 1940) that enumerate the ratio of the sums over all partitionings of the integers n into parts $5m+1$ and $5m+4$, to that which partitions the integers into parts $5m+2$ and $5m+3$. We note the further identities of Ramanujan (Hardy, 1940)

$$F(1)/F(\exp[-2\pi/5])$$
$$=\exp(-2\pi/5)\{(5+5^{1/2})/2-(5^{1/2}+1)/2\}$$
$$\times\frac{F(1)}{F(\exp[-2\pi/5^{1/2}])}$$
$$=\exp(2\pi/5)$$
$$\times\left[\frac{5^{1/2}}{1+\{5^{3/4}[(5^{1/2}-1)/2]^{5/2}\}^{1/5}}-\frac{5^{1/2}+1}{2}\right]$$

since they seem not to be widely known in crystallographic literature. There are already 130 new versions of the Rogers-Ramanujan relations that exist due to the work of Andrews and Askey (Andrews, 1984; Andrews, Askey, Berndt, Ramanathan, & Rankin, 1988) that suggest a host of possible new symmetries. In fact, the prediction of fivefold and other symmetries had already been made by Askey more than a decade earlier on the basis of his work on q series.

That the inverse of an equiangular spiral is identical to the original curve in some sense has long been known. As Thompson says, it was this that led Jacob Bernoulli, in imitation of Archimedes, to have the logarithmic spiral inscribed on his tomb. The equation of the equiangular spiral that occurs in our analysis quite naturally is $r=\exp[(\ln\tau^{-1})\Theta\pi/5]$, and its multiplicative and additive properties are reminiscent of complex algebra with $z=|z|\exp(i\Theta\pi)$ and $(\ln\tau^{-1})/5$ taking the role of the imaginary quantity i in some sense. It is here that the Rogers-Ramanujan relations provide some clues to the matter. For example, most partitions of the form $(5m+1)$ and $(5m+4)$ can be written as products of the form $(m-n5^{1/2})(m+n5^{1/2})$, m and n integers, and other decompositions exist for the other partitions that occur. There is similarity with the complex numbers, with $5^{1/2}$ or $\ln\tau=\ln[(5^{1/2}+1)/2]$ playing the role of i. The geometry of quasi-crystal structure and arithmetic must thereby be linked. (This is suggestive of the possibility that the connections between areas, lengths and volumes are hidden in the identities. One can even speculate that the multidimensional representation groups of physics that underlie modern theories of particles, presently facing fundamental difficulties, are defective in omitting the space-filling characteristic infinite groups responsible for the quasi-crystal packing of space. Indeed it would not be surprising if the translational symmetries are degenerate cases. We have risked over-elaboration because number theory has much to offer that is not widely recognized.)

Several additional observations may be made.

(i) Whether or not our skeletal delta function, with geometric ratios for its spacing, underlies the real structure, wave and transport phenomena in such a medium must exhibit some extraordinary properties.

(ii) In water, the maintenance of constant density is an easy matter, as is the accommodation of a cavity such as a hydrophobic molecule because of the large enthalpy-entropy compensation that accrues to its peculiar molecular structure allowing the breaking and rearrangement and sharing of bonds with ease. In quasi-crystals, since regular figures that satisfy the tetrahedral bonding requirements of constituent molecules cannot fill space, the large van der Waals self-energy associated with a defect or cavity must be accommodated by the imposition of a constant curvature of bonds, so that nucleation and growth proceed in a space-filling manner with the characteristics of spirals.

(iii) Quasi-crystal structures have been known for a long time to occur in surfactant-water mesophases and rejected as inexplicable curiosities. Their existence, which will probably turn out to be ubiquitous, is not surprising. In the ternary or binary phase diagram of such solutions, they would be expected to occur between the lamellar and cubic phases. The closed topology of the lamellar phase must be disrupted to form the open bicontinuous network of the cubic phase, a matter easy to visualize through the formation of real equiangular helices that can then reform and lay down in a surfactant bilayer arrangement with cubic symmetry.

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APPENDIX A

We give here a derivation of (7) and, to avoid unnecessary symbolism, use a particular form of $g(x)$ [(5)],

$$g(x)=\sum_{m=-\infty}^{\infty}[\exp(-x\exp m)-\exp(-\exp m)]. \qquad (A\text{-}1)$$

{In fact the analysis holds for

$$g(x)=\sum_{m=-\infty}^{\infty}[h(x\exp m)-h(\exp m)]$$

with only mild restrictions on the function h.} To exhibit the structure of $g(x)$ we use the Mellin inversion formula

$$\exp(-ax)=(1/2\pi i)\int_{c-i\infty}^{c+i\infty}\Gamma(s)/(ax)^s\,ds,$$
$$0<c=\operatorname{Re}(s), \qquad (A\text{-}2)$$

where the contour of integration in the complex s plane is the line specified parallel to the imaginary axis. If we use this representation we have from (A-1)

$$g(x) = (1/2\pi i) \sum_{m=-\infty}^{\infty} \int_{c-i\infty}^{c+i\infty} \Gamma(s) \times \exp(-ms)(x^{-s}-1)\,ds, \qquad c = \mathrm{Re}\,(s) > 0. \qquad (A\text{-}3)$$

The summation may be divided into two parts: summations σ_1 and σ_2 over non-negative and negative values of m respectively. For σ_1 the sum converges uniformly and we can interchange orders of integration and summation to get

$$\sigma_1(x) = (1/2\pi i) \int_{c-i\infty}^{c+i\infty} \Gamma(s)(x^{-s}-1)\,ds, \qquad c>0. \qquad (A\text{-}4)$$

For σ_2 we cannot interchange orders of integration and summation because the sum diverges on the contour. However, since the pole of $\Gamma(s)$ at $s=0$ is cancelled by the zero of $x^{-s}-1$ at $s=0$, we can translate the contour to the left of the origin in the s plane. On the new contour $c'-1 = \mathrm{Re}\,(s) < 0$, the sum now converges and interchanging the order of integration and summation is possible. This yields

$$\sigma_2(x) = -(1/2\pi i) \int_{c'-i\infty}^{c'+i\infty} \Gamma(s)(x^{-s}-1)/[1-\exp(-s)], \qquad -1 < c' < 0. \qquad (A\text{-}5)$$

Hence,

$$\sigma \equiv \sigma_1 + \sigma_2 = (1/2\pi i) \oint (x^{-s}-1)\Gamma(s)[1-\exp(-s)]^{-1}\,ds,$$

where the contour encircles the imaginary axis in the positive (anticlockwise) direction. The integrand has poles at $s = 2n\pi i$, $n = 0, 1, 2, 3 \ldots$ and evaluation of their residues gives (7). For the summation (5) we can use the relation

$$\cos \alpha y = (1/2\pi i) \int_{c-i\infty}^{c+i\infty} \Gamma(s)(\cos \pi s/2)/(\alpha y)^s\,ds, \qquad 0 < c = \mathrm{Re}\,(s) < 1. \qquad (A\text{-}6)$$

The result, (4) and (10), for the nth term of the series follows from the observation that, if $z = i\xi$, then

$$|\Gamma(z)| = [\pi/(\xi \sinh \pi\xi)]^{1/2} \qquad (A\text{-}7)$$

and also, from the known result that, as $\theta_n \to \infty$, $\arg(\theta_n) < \pi$,

$$\Gamma(i\theta_n) = |\Gamma| \exp(i\varphi_n),$$

where

$$\varphi_n \simeq \theta_n(\ln \theta_n - 1) - \pi/4 - [(1/12\theta_n) + \ldots] \qquad (A\text{-}8)$$

and the analysis proceeds exactly as above.

APPENDIX B
Rogers–Ramanujan relations, partitions and generating functions

These relations, which are probably central to an eventual solution to the quasi-crystal pattern, are discussed best by Hardy (1940). They occur in Baxter's (1982) famous solution to the statistical mechanics of hard hexagons. We shall need a few definitions and shall borrow some from Hardy.

A partition of any number, n, is a division of n into any number of possible integral parts. Thus, $4 = 3+1 = 2+2 = 2+1+1 = 1+1+1+1$. The number of partitions of n is designated $p(n)$. Thus $p(1) = 1$, $p(4) = 5$ and $p(0)$ is defined as 1. The function $F(x)$

$$F(x) = [(1-x)(1-x^2)(1-x^3)\ldots]^{-1} \qquad (B\text{-}1)$$

can be expanded in powers of x as

$$F(x) = \sum_{n=0}^{\infty} p(n)x^n. \qquad (B\text{-}2)$$

$F(x)$ is said to generate $p(n)$ or enumerate it.

Other products can be written down that enumerate partitions of n into parts restricted in various ways. For example, it can be shown that

$$F_1(x) = x^{m^2}/[(1-x)(1-x^2)\ldots(1-x^m)]$$

enumerates partitions of n into at most m parts without repetitions or sequences (sequences meaning parts differing by 1) or parts with minimal difference two. If $F_1(x)$ is expanded as a power series, the coefficient, say $p_1(n)$, is the number of ways of writing down such partitions of n. Thus, for $n = 9$, there are five partitions of this type: 9, 8+1, 7+2, 6+3 and 5+3+1. Also, the product

$$[(1-x)(1-x^6)(1-x^{11})\ldots]^{-1} \times [(1-x^4)(1-x^9)(1-x^{14})\ldots]^{-1},$$

where the exponents in the products inside the square brackets differ by five, enumerates partitions of n into parts of the form $(5m+1)$ and $(5m+4)$. For $n = 9$ [$(5m+1) = (1, 6)$; $(5m+4) = (4, 9)$], these partitions are 9, 6+1+1+1, 4+4+1, 4+1+1+1+1+1, 1+1+1+1+1+1+1+1+1. There are five, the same number of partitions as of the above type.

The first of the Rogers–Ramanujan identities is

$$1 + \frac{x}{(1-x)} + \frac{x^4}{(1-x)(1-x^2)} + \ldots + \frac{x^{m^2}}{(1-x)(1-x^2)\ldots(1-x^m)} + \ldots = \frac{1}{[(1-x)(1-x^6)(1-x^{11})\ldots]} \times \frac{1}{[(1-x^4)(1-x^9)(1-x^{14})\ldots]}. \qquad (B\text{-}3)$$

The combinatoric statement of (B-3) is: the number of partitions of n into parts of minimal difference two is equal to the number of partitions of n into parts of the form $(5m+1)$ and $(5m+4)$. The second Rogers–Ramanujan relation is

$$1+\frac{x^2}{(1-x)}+\frac{x^6}{(1-x)(1-x^2)}+\dots+\frac{x^{m(m+1)}}{(1-x)(1-x^2)\dots(1-x^m)}+\dots$$
$$=\frac{1}{[(1-x^2)(1-x^7)(1-x^{12})\dots]}\times\frac{1}{[(1-x^3)(1-x^8)(1-x^{13})\dots]}. \quad (B\text{-}4)$$

Again, the exponents in the products inside the square brackets form arithmetic progressions with difference five. Its combinatoric statement is: the number of partitions of n into parts of minimal difference two, the least member of which is two, is equal to the number of partitions of n into the form $(5m+2)$ and $(5m+3)$. Thus, for $n=10$, partitions of the first kind are 10, 8+2, 6+4+2, 7+3 while those of the second kind are 7+3, 8+2, 3+3+2+2, 2+2+2+2+2. There are four of each type. It can be shown that the continued fraction

$$\frac{F(1)}{F(y)}=1+\cfrac{y}{1+\cfrac{y^2}{1+\cfrac{y^3}{1+\dots}}}$$
$$=\frac{(1-y^2)(1-y^7)\dots(1-y^3)(1-y^8)\dots}{(1-y)(1-y^6)\dots(1-y^4)(1-y^9)\dots}, \quad (B\text{-}5)$$

where the ratio on the right-hand side is the ratio of (B-3) and (B-4). In the limit $y\to 1$, $F(y)\to\tau$, successive approximations to which are ratios of the successive terms in the Fibonacci sequence. What is implied by (B-5) is the assertion that the ubiquitous occurrence of τ in quasi-crystals is a global property, the packing rules for construction implied by the combinatoric identities for every n necessarily having to be satisfied and satisfied uniquely. This is because in the limit $y\to 1$ all terms in the ratio of the two generating functions (B-3) and (B-4) have to be included, and that

$$\tau=\frac{\text{the sum of all partitions of all numbers } n \text{ of the form } (5m+1) \text{ and } (5m+4)}{\text{the sum of all partitions of all numbers } n \text{ of the form } (5m+2) \text{ and } (5m+3)}$$

or the equivalent statement in terms of the other kinds of partitions. It seems likely that also implicit in these combinatoric identities are rules for construction of tilings. The infinite-product forms of the generating functions also indicate that a violation of such a packing rule will repeat in successively higher hierarchies as the packing proceeds.

If the continued fraction in the product form is expanded out, one has

$$F(1)/F(y)=\sum_{n=0}^{\infty}p_\alpha(n)y^n\Big/\sum_{n=0}^{\infty}p_\beta(n)y^n, \quad (B\text{-}6)$$

where $p_\alpha(n)$ and $p_\beta(n)$ represent partitions of the two kinds, and necessarily

$$\lim_{n\to\infty}p_\alpha(n)/p_\beta(n)=\tau,$$

an apparently new result. The result (B-4) of the main text follows by recognizing that the infinite product form is the ratio of two theta functions,

$$\frac{F(1)}{F(y)}=\sum_{n=-\infty}^{\infty}(-1)^n\exp[-(5n^2+n)x/2]\times\left\{\sum_{n=-\infty}^{\infty}(-1)^n\exp[-(5n^2+3n)x/2]\right\}^{-1};$$
$$y\equiv\exp(-x),$$

then using the Jacobi-theta-function transformations.

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SHORT COMMUNICATIONS

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Largest likely *R* factors for normal distributions.

By R. P. MILLANE, *Whistler Center for Carbohydrate Research, Purdue University, West Lafayette, Indiana* 47907-1160, *USA*

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Abstract

An expression is obtained for the largest likely R factor for data that are normally distributed. For zero-mean data, the largest likely R factor is $2^{1/2}$ and, for positive data ($\mu \gg \sigma$), it is equal to $2\sigma/(\mu\pi^{1/2})$. These results are applied to fiber diffraction and other possible applications in crystallography are discussed.

R factors are used in a variety of areas in crystallography as a measure of the similarity between two sets of parameters or data. Some applications are in assessing accuracies of structures, errors in scaling, effectiveness of derivatization and lack of phase closure in isomorphous replacement. Evaluating the significance of a particular-valued R factor is aided by comparison with the largest likely R factor; that which would be obtained if the two sets of parameters or data were unrelated or uncorrelated. The largest likely R factor depends on the statistical distribution of the data. Largest likely R factors have been derived for structures determined by crystallography (Wilson, 1950) and by fiber diffraction (Stubbs, 1989; Millane 1989*a*, *b*, 1990*a*, 1992). Largest likely R factors are derived here for data that are normally distributed. Applications to fiber diffraction are described and other possible applications are discussed.

Consider two sets of data x and y (not necessarily positive) that are compared by calculating the R factor

$$R = \sum_i |x_i - y_i| \Big/ \sum_i |x_i| = \langle \delta \rangle / \langle |x| \rangle, \qquad (1)$$

where $\delta = |x - y|$ and $\langle\,\rangle$ denotes the average. From Wilson (1950), the probability density for δ, $Q(\delta)$, is given by

$$Q(\delta) = \int_{-\infty}^{\infty} P(x)P(x+\delta)\,\mathrm{d}x \qquad (2)$$

and $G(x)$ is defined by

$$G(x) = \int_{-\infty}^{x} x'P(x')\,\mathrm{d}x'. \qquad (3)$$

Using these equations shows that

$$\langle \delta \rangle = 2[\langle x \rangle - 2\langle G(x) \rangle] \qquad (4)$$

so that the largest likely R factor is given by

$$R = [2\langle x \rangle - 4\langle G(x) \rangle]/\langle |x| \rangle. \qquad (5)$$

Equation (5) is a general result for any distribution of x, and reduces to equation (6) of Wilson (1950) if $x \geq 0$.

If the random variables x and y are identically normally distributed with mean μ and variance σ^2, *i.e.*

$$P(x) = (2\pi)^{-1/2}\sigma^{-1} \exp[-(x-\mu)^2/2\sigma^2], \qquad (6)$$

then $\langle x \rangle = \mu$ and $\langle |x| \rangle$ is given by

$$\langle |x| \rangle = \int_0^{\infty} x[P(x) + P(-x)]\,\mathrm{d}x \qquad (7)$$

so that

$$\langle |x| \rangle = (2/\pi)^{1/2}\sigma \exp(-\mu^2/2\sigma^2) + \mu \operatorname{erf}(\mu/2^{1/2}\sigma), \qquad (8)$$

where $\operatorname{erf}(\cdot)$ denotes the error function. Note that, for $\mu/\sigma \to \infty$, $\langle |x| \rangle \to \mu$ (as it must, since when $\mu \gg \sigma$ most values of x will be positive) and that, for $\mu = 0$, $\langle |x| \rangle = (2/\pi)^{1/2}\sigma$. Substituting (6) into (3) shows that

$$G(x) = -(2\pi)^{-1/2}\sigma \exp[-(x-\mu)^2/2\sigma^2] + (\mu/2)\{1 + \operatorname{erf}[(x-\mu)/2^{1/2}\sigma]\} \qquad (9)$$

and evaluating the mean gives

$$\langle G(x) \rangle = \mu/2 - \sigma/(2\pi^{1/2}). \qquad (10)$$

Substituting (10) into (5) gives

$$R = 2\sigma/(\pi^{1/2}\langle |x| \rangle), \qquad (11)$$

where $\langle |x| \rangle$ is given by (8), which is the desired result. Note that, for zero-mean data, the largest likely R factor is

$$R = 2^{1/2}, \qquad \text{for } \mu = 0. \qquad (12)$$

It is instructive to examine the dependence of $\langle |x| \rangle$ on μ, shown as the solid line in Fig. 1. The approximation

$$\langle |x| \rangle \simeq \mu \qquad (13)$$

is the first term in the asymptotic expansion for $\langle |x| \rangle$ as $\mu/\sigma \to \infty$, and is quite accurate for $\mu/\sigma \gtrsim 1.5$ (broken line in Fig. 1). For small μ, the power-series expansions for the

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