Transfer-matrix analysis of the canonical-cell model of a quasicrystal

M. E. J. Newman and C. L. Henley

Laboratory of Atomic and Solid-State Physics,

Cornell University,

Ithaca, NY 14853–2501.

Abstract

Using a computational algorithm, we have calculated transfer matrices for the $\frac{2}{1}$, $\frac{3}{2}$ and $\frac{5}{3}$ approximants to the quasi-periodic canonical-cell tiling. In the last case this algorithm leads directly to a new set of large cubic approximants. The transfer matrices also give us information about the entropy of ensembles of random tilings with periodic boundary conditions along two out of the three real-space axes. By introducing chemical potentials coupling to various properties of the members of this ensemble, we have calculated the variation of the entropy with the mean phason strain and volume of the tilings. The maximum of the entropy gives us the preferred values of the strain and volume, and the coefficients of its quadratic variation about this maximum give us the phason elasticity tensor, which is measurable in diffraction experiments.

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I. INTRODUCTION

In the canonical-cell model of a quasicrystal [1] icosahedral clusters of atoms or 'nodes' are linked by 'bonds' of two types. The 'b-type' bonds run parallel to the two-fold symmetric axes of the icosahedron, and the c-type ones, a factor $\sqrt{3}/2$ shorter, run along the three-fold axes. The rules of the model allow the volumes framed by the bonds in the lattice to take only four distinct shapes—the so-called canonical-cells—and this in turn constrains the arrangement of bonds about each node to be one of 32 possible 'node environments'. Decorations of canonical-cell tilings have been suggested to turn them into possible structures for AlMn, AlCuFe and AlCuLi alloys.

As well as providing a promising structural model for icosahedral quasicrystals, the canonical-cell model can be regarded as a random tiling, and used to assess the entropic contribution to the free energy for the alloys that it models. We are particularly interested to investigate the variation of the entropy per unit volume S_V with the 'phason strain', $\mathbf{E}$, on the lattice. The idea of phason strain is most easily understood by representing the canonical-cell tiling as a projection onto the three dimensions of real space of a slice though a six-dimensional hypercubic lattice. There exists a variety of essentially equivalent projection operators which accomplish this task. We use that of Shaw *et al.* [2] The projection leaves us with three remaining degrees of freedom forming a three-dimensional 'perpendicular' or 'perp' space. If we write positions in real and perp space as $\mathbf{r}$ and $\mathbf{h}$, then the ratios of the two, averaged across a tiling, form the phason strain tensor for that tiling:

$$E_{ij} = \frac{\Delta h_j}{\Delta r_i}. \tag{1}$$

In this paper we measure lengths in both real and perp space in multiples of the length of the longer (b-type) bond which connects nodes along the two-fold symmetry axes.

In general the entropy density, S_V, will depend on the value of the phason strain tensor. It is conjectured that its maximum should fall at $\mathbf{E} = 0$, and in all cases investigated so far this conjecture has been borne out. The coefficients of the quadratic expansion of the entropy about this maximum form the 81-element phason elasticity tensor $\mathbf{K}$:

$$S_V = S_V^{(0)} - \frac{1}{2} K_{ijkl} E_{ij} E_{kl} + \ldots \tag{2}$$

(Not all the elements of the elasticity tensor are independent. In fact, for an infinite quasi-crystal, it can be shown using group-theoretical arguments [3,4] that all the elements may be specified in terms of just two scalar parameters K_1 and K_2.) The elasticity affects the Debye-Waller factors for the model and is therefore experimentally measurable.

In this paper, we present a method which involves enumerating surfaces of nodes within partially constructed approximants, and finding moves which take us from one surface to another. We tabulate all such moves in the form of a transfer matrix, which can then be used to calculate S_V for an ensemble of random tilings whose dimensions in two directions are those of the corresponding approximant, but whose size in the third, z-direction is arbitrarily large [5,6]. By introducing 'chemical potentials' [7,8] coupling to the components of the phason-strain tensor for the members of this ensemble, and to the total volume V, we can study the variation of S_V with $\mathbf{E}$ and V, maximizing it to find its equilibrium value, and extracting the coefficients of its quadratic variation about this maximum to find the phason elasticity tensor. In this paper, we present the results of such analyses for the largest known cubic approximant.

At present, the main problem with the canonical-cell model is that there is no known set of inflation rules or projection method that allows us to generate a hierarchy of successively larger and better approximants to the infinite quasi-periodic tiling, in the way that one can for example generate arbitrarily large tilings of rhombohedra. A number of moderate-sized approximants, both cubic and of other shapes, have been produced [1], the largest of which, the '$\frac{3}{2}$' cubic approximant contains 32 nodes. But without inflation rules for the tiling, there is no obvious way of improving on these. It turns out that our transfer matrix is useful in this context too; if we can calculate the transfer matrix for a given size of approximant, it immediately gives us all possible arrangements of nodes that fit in the unit cell of that approximant. We have done this for the '$\frac{5}{3}$' cubic approximant whose base is a factor $\tau \equiv \frac{1}{2}(1+\sqrt{5})$ larger than that of the $\frac{3}{2}$, and thus we have found a set of new approximants containing between 134 and 138 nodes. [*]

II. TRANSFER MATRICES

The definition of the transfer matrix for a tiling of canonical cells centers on the idea of a 'dead surface'. Consider a construction such as that described above in which square periodic boundary conditions are enforced in the x- and y-directions, but not in the z-direction. We have an open surface on top of the tiling in which there lie incomplete nodes, with bonds yet to be added to them before they conform to one of the 32 allowed environments. We build up the tiling by adding bonds to these nodes, creating new nodes on the ends of those bonds. For most surfaces it is found that at least one move is forced—there is at least one node which can be completed in only one way to form an allowed node environment. Making such a forced move will normally bring us to a new surface which also has at least one move forced. When, finally, we arrive at a surface for which no moves are forced, a surface for which there are at least two lawful ways to complete each of the incomplete nodes in the surface, we call that surface 'dead'. We label every dead surface we find with an integer, starting from 1. Then for each surface we choose the node which has the fewest possibilities for completion (or, if there are several nodes which tie for the honor, choose one of them at random) and make each of the possible moves, plus any other moves which are forced as a consequence, until we reach a new dead surface or, as occasionally happens, until we are forced into creating an unlawful node environment, in which case we abandon that particular line of investigation altogether. In this way we can construct a table showing which dead surfaces can be reached from which others.

As a simple example, let us consider the small $\frac{2}{1}$ approximant, which is cubic with a base of length τb on each side, where b is the length of a b-type bond. For such a small system, the dead surfaces are easily constructed, and there turn out to be three of them, each of which is accessible from each of the others in only one move. We represent this information in the form of a transfer matrix, having one row and one column for every dead surface. We make a non-zero entry in the transfer matrix at each position whose row and column indices are, respectively, the labels of the initial and final surfaces for one of these moves. In the simplest case these entries are 1, though we will later find it useful to give them other values. All other elements of the matrix are zero. For the $\frac{2}{1}$ approximant, the transfer matrix is

$$\mathbf{T} = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}. \tag{3}$$

In this case the transfer matrix is symmetric, but in general it need not be so; just because we can get to surface i from surface j in one move does not imply that we can get back again.

Powers of the transfer matrix tell us which surfaces we can reach in more than one move. For the matrix in which the non-zero entries are 1, the element $[\mathbf{T}^n]_{ij}$ is the number of ways in which we can get from surface j to surface i forming n new dead surfaces *en route.* Thus the trace $\mathrm{Tr}[\mathbf{T}^n]$ is the number of arrangements of canonical cells with the given periodic boundary conditions that start and finish with the same surface and have n surfaces in total. In other words they are approximants. For the matrix above, for example, we have $\mathrm{Tr}\,\mathbf{T}^3 = 6$, which tells us that there are six approximants with three dead layers. In fact these are the known $\frac{2}{1}$ cubic approximants. (It could be argued that this is an over-estimate of the number of approximants, since the method counts the cyclic permutations of surfaces $1 \to 2 \to 3 \to 1$ and $2 \to 3 \to 1 \to 2$ and so forth as different, when in fact they correspond to the same arrangements of nodes. For the calculation of the entropy of an ensemble of tilings however, this is exactly how we want to count the configurations.)

To investigate the entropy of the model, we take the logarithm of $\mathrm{Tr}\,\mathbf{T}^n$, and then the limit as $n \to \infty$, which gives us the entropy *per surface* for the ensemble of all possible tilings with the given boundary conditions in two directions:

$$S_S = \lim_{n\to\infty} \frac{1}{n} \log \mathrm{Tr}\,\mathbf{T}^n = \log \lambda_0, \tag{4}$$

where λ_0 is the largest eigenvalue of $\mathbf{T}$. The quantity we are really interested in however, is the entropy per unit volume S_V. To find this, we need to know the average volume per dead surface. It is straightforward, though a little tedious, to calculate the volume added between a dead surface and each of its possible successors, and the frequency with each surface occurs on average in the ensemble can be calculated from the left- and right-eigenvectors corresponding to the largest eigenvalue of the transfer matrix. Thus we can find S_V.

In a similar way we can calculate the averages of other quantities over the surfaces in the ensemble. For example, we can calculate the average real- and perp-space displacements in going from one layer to the next. The ratios of the various components of these quantities give us the nine components of the phason strain tensor. Six of these components have values fixed by the periodic boundary conditions, but three—E_{xz}, E_{yz}, and E_{zz}—are free, and can be 'measured' in this calculation.

III. CHEMICAL POTENTIALS

By choosing the non-zero elements of our transfer matrix to be unity, we have forced some assumptions on the ensemble of tilings that we have been considering. We have said, in effect, that if a surface 1 can go to surfaces 2 or 3, then the tilings in which these two moves occur will have equal weight in our ensemble. The probability of making each of these transitions will be the same. By changing the values of the non-zero matrix elements we can arrange things so that some moves are more favorable than others. If we are clever, we can arrange them to favor specific outcomes. For example, if we make the elements larger for those moves which add a larger volume to the tiling we are constructing, then larger tilings will in general be favored in the ensemble. The simplest way to do this is to generalize the non-zero elements to the form $\mathrm{e}^{-\mu_V \Delta V_{ij}}$, where ΔV_{ij} is the volume added in going from surface j to surface i, and μ_V is a 'chemical potential' whose value we are free to choose. When we now calculate the trace of a large power of the transfer matrix, we are calculating the partition function for an ensemble in which the total volume makes a contribution to the Hamiltonian proportional to the chemical potential μ_V. The largest eigenvalue of the transfer matrix then gives us the free energy per dead surface for this ensemble: $F = -\log \lambda_0 = -S_S + \mu_V \overline{\Delta V}$. (There is no parameter corresponding to temperature in this ensemble, since there are no physical energies to set the energy scale.) The mean volume added between layers, $\overline{\Delta V}$, can be calculated for this new ensemble as it was for the old, using the eigenvectors corresponding to the largest eigenvalue, and hence we can again find the entropy.

Similar chemical potentials μ_x, μ_y, μ_z can be introduced coupling to the components of the perp-space displacement between layers, and thus favoring ensembles with a particular average phason strain. In this way the variation of the entropy with volume and phason strain can be explored, to find the maximum of entropy and the elasticity coefficients which describe its variation about this maximum.

In passing, we should emphasize that it *is* possible to vary the mean volume $\overline{\Delta V}$ per layer independently of the phason strain. The possibility of the existence of such a degree of freedom even when the phason strain is fixed was noted by Henley [1], who quantified it according to a parameter ζ which controls the ratio of the numbers of the largest and smallest of the canonical cells appearing in the tiling.

IV. RESULTS

We have employed these techniques in the study of the $\frac{2}{1}$, $\frac{3}{2}$, and $\frac{5}{3}$ approximants. Our results are summarized in Table I. For the $\frac{5}{3}$ approximant the number of dead surfaces is far too large to permit their construction by hand, and we were forced to use a computational method. In essence our algorithm involves generating all possible orientations of the 32 allowed node environments under the icosahedral group (giving a total of 2780 allowed arrangements of bonds), and constructing dead surfaces by comparing each incomplete node in a surface to each arrangement of bonds in turn, to find nodes with only one possible completion. It was found however, that, although this method ensures that all node environments in the final tiling are lawful ones, some of the cells formed between the bonds are not in the set of four allowed shapes. A non-local forcing rule is necessary to remedy this shortcoming, which we implement by creating another set of bonds, of type d, which have length $b\sqrt{7}/2$—the next largest node separation after the b-type bond—and including these in the allowed node environments. If we now stipulate that as well as the b- and c-type bonds in an incomplete node, the d-type bonds also must match an allowed environment if that environment is to be considered a possible completion of that node, then we can prove that a true canonical-cell tiling is always generated.

As a check on the algorithm, the transfer matrix for the $\frac{3}{2}$ approximant has also been generated manually, using hand-built models.

V. CONCLUSIONS

Using a computational algorithm, we have found the transfer matrices for the $\frac{3}{2}$ and $\frac{5}{3}$ approximants to the quasi-periodic canonical-cell tiling. This procedure leads to a set of new $\frac{5}{3}$ cubic approximants to the tiling, and to values for the entropy density and phason elasticity for the random tiling of canonical cells.

It is probably not possible to extend this method to larger approximants. We estimate that the next approximant up, the $\frac{8}{5}$ approximant, will have around one million dead surfaces. The calculation of the transfer matrix for such a system would be far beyond our present resources. However, it may be feasible to study an approximant of base $2\tau^2 b \times 2\tau^2 b$, i.e., the size of four $\frac{3}{2}$ approximants side by side, which we would expect to have about ten thousand distinct dead surfaces. Such a calculation might be profitable in helping separate the effects on the entropy of the finite system size from those of the fixed finite phason strain in the horizontal directions.

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TABLES

	base side	τb	$\tau^2 b$	$\tau^3 b$
	approximant	$\frac{2}{1}$	$\frac{3}{2}$	$\frac{5}{3}$
	dead surfaces	3	17	5327
approximants:	number of nodes	8	32	134–138
	approximants found	2	5	317
	packing fraction	0.642	0.606	0.600–0.617
random tilings:	maximum of S_V	0.610	0.215	0.125
	(E_{xz}, E_{yz}, E_{zz})	(0, 0, 0.0824)	(0, 0, 0.250)	(0, 0, 0.0328)
	packing fraction	0.60105	0.60513	0.60639
	elasticity K_1	–	–	69.5
	elasticity K_2	–	–	210.1

TABLE I. Results of the transfer matrix analysis of the ensembles of base τb, $\tau^2 b$ and $\tau^3 b$.

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* In a recent private communication, M. Mihalkovič and P. Mrafko have informed us that they have found a single cubic $\frac{5}{3}$ approximant for the canonical-cell tiling containing 136 nodes, using a Monte Carlo method in which hard spheres move about with their centers constrained to lie on the vertices of a fine rhombohedral Penrose tiling. By the same method they have also found examples of $\frac{8}{5}$ and $\frac{13}{8}$ cubic approximants.

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