Transfer-Matrix Analysis of a Two-Dimensional Quasicrystal

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We investigate the quasicrystalline state of a two-dimensional binary alloy in a discrete tiling approximation. Through transfer-matrix calculations we determine the configurational entropy over a range of concentrations. We find that the entropy density is maximized by a state with tenfold symmetry at the quasicrystal concentration. Derivatives of the entropy density at its maximum yield values for the phason electric constants. Our results confirm the existence of quasi-long-range translational order in equilibrium quasicrystalline alloys and lend support to the random-tiling model of quasicrystals.

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Quasicrystals are solid metallic alloys whose diffraction pattern shows sharp peaks arranged with noncrystallographic symmetry.[1,2] Their structure and physical origin remain controversial five years after their discovery.[3] Recent experiments[4,5] on AlCuFe appear to rule out the icosahedral glass[6] model for thermodynamically stable quasicrystals. In this paper we investigate a random-tiling model. Random-tiling models describe thermodynamically stable quasicrystals with sharp diffraction peaks, without invoking special matching rules to force a particular structure such as a Penrose pattern.[2]

Our theory examines a simple model binary alloy which forms an equilibrium quasicrystal phase in two dimensions. Computer simulations[7-9] allow determination of atomic positions and explicit calculation of the diffraction pattern and correlation functions. We utilize the transfer matrix in this paper to determine the configurational entropy at low temperatures. We argue that the entropy explains thermodynamic stability, accounts for power-law peaks in the diffraction pattern, and determines the value of the "phason" elastic constants.

Figure 1 shows a low-temperature configuration obtained from a Monte Carlo simulation.[7] The length scales of the Lennard-Jones potential were chosen to encourage local decagonal order by allowing ten small (S) atoms to fit around one large (L) atom and five large atoms to fit around one small atom. At low temperatures the system freezes from a liquid into an equilibrium quasicrystal state. We emphasize that this result requires no "fine tuning" of parameters.

Careful analysis of the Monte Carlo results reveals that there is not a single quasicrystalline configuration, but rather a large family of nearly degenerate configurations. In fact, the Lennard-Jones system can be well approximated by truncating the potential beyond the first coordination shell. All nearest-neighbor bonds then assume their optimal length in the ground state.

Drawing the set of all LS bonds reveals that every atomic ground state corresponds to a unique decoration of the plane by rhombi as shown in Fig. 2. Of course, all rhombus vertices meeting at a point must share a single species of atom. All tilings of the plane obeying this constraint (we call these "binary tilings"[8]) are exactly degenerate in the thermodynamic limit at fixed concentration. Our transfer-matrix calculation is carried out in this random-binary-tiling approximation. The potential is truncated at nearest neighbors, and all bonds set to their optimal lengths. Our ensemble includes all binary tilings of the plane by these rhombi (various crystalline

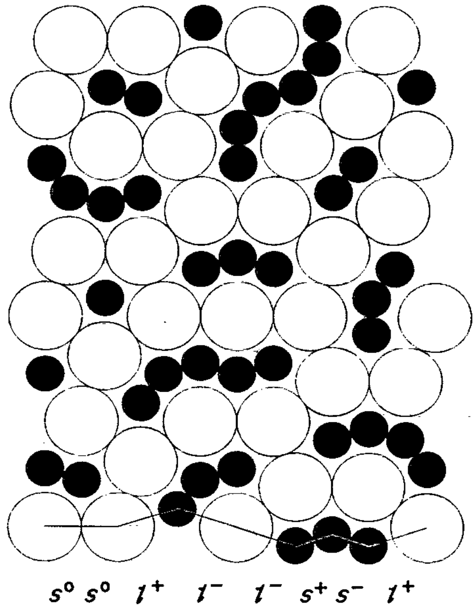

FIG. 1. Typical low-temperature configurations of a binary alloy for a Monte Carlo simulation. The line segments (labeled $l^{\pm}$ and $s^{\pm 0}$) on the bottom define a layer of atoms.

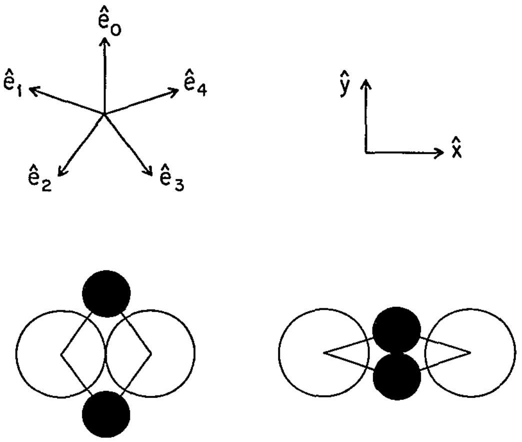

FIG. 2. Decorations of fat and thin rhombi and their relationship to $\hat{\mathbf{e}}_\alpha$. Note weak matching rules arising from atoms at rhombus vertices.

and quasiperiodic structures are subsets of measure zero).

The strict Penrose-tiling model of quasicrystals,[2] which has zero entropy, relies on energetically imposed matching rules to achieve quasicrystalline order. The icosahedral glass model,[5] on the other hand, produces energetically unfavorable, nonequilibrium quasicrystal structures. In the random-tiling model quasicrystalline order is favored at finite temperatures by virtue of combined low energy and high entropy. Even if we relax the approximations leading to the exact degeneracy, we expect the random structures to be favored above some low temperature.

These different models are best understood through the five-dimensional representation[10] of atomic configurations. Note that each large-small (LS) bond in Fig. 1 is parallel to one of the five vectors $\hat{\mathbf{e}}_\alpha^\parallel$ shown in Fig. 2. Choose an arbitrary atom in a configuration and define its coordinates as (0,0,0,0,0). All other atoms in the configuration can be reached by a sequence of LS bonds. Denote by R_α the number of bonds of type α taken to reach a given atom (R_α decreases on steps in the $-\hat{\mathbf{e}}_\alpha^\parallel$ direction). Then this atom has five-dimensional (5D) coordinates

$$\mathbf{R}=\sum_\alpha R_\alpha \mathbf{e}_\alpha , \tag{1}$$

where $\mathbf{e}_\alpha$ are the 5D basis vectors.[11,12] One can verify that the values R_α are independent of the path taken. In this manner we assign a five-dimensional position $\mathbf{R}\in\mathbb{R}^5$ to every atomic position $\mathbf{r}\in\mathbb{R}^2$.

After coarse graining the five-dimensional variable $\mathbf{R}$ over lengths much larger than the rhombus edge length we find for random-tilings models that $\mathbf{R}(\mathbf{r})$ is a smoothly varying function describing a 2D surface in 5D space. The different models of quasicrystals may be compared and contrasted in "perpendicular space." First, define a perpendicular space position,

$$\mathbf{h}^\perp=\sum_\alpha R_\alpha \hat{\mathbf{e}}_\alpha^\perp , \tag{2}$$

where

$$\hat{\mathbf{e}}_\alpha^\perp=\hat{\mathbf{e}}^\parallel_{(2\alpha \bmod 5)} , \tag{3}$$

and R_α now are the coarse-grained coordinates as a function of parallel space position $\mathbf{r}$. There is actually a third component of perpendicular space

$$h_z^\perp=\frac{1}{\sqrt{2}}\sum_\alpha R_\alpha . \tag{4}$$

Inspecting the rhombus decorations (Fig. 2), however, reveals that all large atoms have identical $h_z^\perp$ and the value for small atoms differs by ± 1, so binary tilings have no fluctuations in this direction. Alternative decorations of tiles leading to the same atomic system[7,8,11] have equivalent definitions of $\mathbf{h}^\perp$.

Perfectly quasiperiodic structures correspond to flat surfaces with essentially constant $\mathbf{h}^\perp$. The icosahedral glass model contains energetically costly tears in the surface.[11] For an arbitrary tiling $\mathbf{h}^\perp$ is a function of $\mathbf{r}$. Random-binary tilings gain entropy through fluctuations in h_x and h_y. Thus, the difference between a perfect Penrose tiling and arbitrary binary tiling is given by the phason strain

$$E_{ij}=\partial h_i^\perp/\partial r_j , \tag{5}$$

where i and j denote x and y components of $\mathbf{h}^\perp$ and $\mathbf{r}$.

Fluctuations of the surface create configurational entropy which, we now argue, is responsible for thermodynamic stability and translational order in the quasicrystal phase. Because nonzero average phason strain lowers the rotational symmetry, and because large phason strains lead to zero entropy crystalline structures, it is plausible that the entropy density per unit area, $\sigma(\tilde{E})$, has a global maximum when $\tilde{E}=0$. Elser[13] and Henley[12] postulated that the entropy density is quadratic in the phason strain. The most general form consistent with tenfold rotational symmetry is[14]

$$\begin{aligned}\sigma(\tilde{E}) = \sigma_0 &- \tfrac{1}{4}K_1[(E_{xx}+E_{yy})^2+(E_{xy}-E_{yx})^2]\\ &- \tfrac{1}{4}K_2[(E_{xx}-E_{yy})^2+(E_{xy}+E_{yx})^2] ,\end{aligned} \tag{6}$$

where K_1 and K_2 are independent phason elastic constants. Equation (6) governs the fluctuations of $h^\perp(\mathbf{r})$ about the perfect quasicrystalline value $h^\perp(\mathbf{r})=\text{const}$. The total entropy [spatial integral of Eq. (6)] is conveniently represented in Fourier space as

$$S=S_0-\frac{K}{2}\int\frac{d^2\mathbf{q}^\parallel}{(2\pi)^2}\,|\mathbf{q}^\parallel|^2\,|h^\perp(q^\parallel)|^2 , \tag{7}$$

where $K=(K_1+K_2)/2$. Note that K_1-K_2 does not appear in Eq. (7) in the absence of dislocations.[15] From Eq. (7) one can show that the correlation function of

$h^{\perp}(\mathbf{r})$ grows logarithmically,

$$\langle | \mathbf{h}^{\perp}(\mathbf{r}) - \mathbf{h}^{\perp}(0) |^2 \rangle \sim \frac{2}{\pi K} \ln |\mathbf{r}| \,. \tag{8}$$

The diffraction pattern therefore has power-law peaks and the density-density correlation function falls off with exponent

$$\eta(\mathbf{q}^{\perp}) = (q^{\perp})^2 / 2\pi K \,. \tag{9}$$

In this paper we employ transfer-matrix calculations[12] to verify that entropy density is maximized at zero phase strain, confirm the expression (6), and evaluate σ_0 and K. We show (Table I) that the entropy density is maximized providing the atomic concentration has the value $2/\tau = 1.23607$ of the phason-strain-free quasicrystal ($\tau = 1.618\ldots$ is the golden mean) and providing the band orientational order has tenfold symmetry. From the curvature of entropy density at its maximum we determine the phason elastic constant.

TABLE I. Transfer-matrix results for the entropy density, its second derivative with respect to E_{yy} (which converges to $-K$), and the concentration at which the entropy density is maximized.

Sequence	E_{xx}	σ	σ''	$\bar{N}_S/\bar{N}_L$
LS	$1/\tau$	0.4621	−1.051	1.4971
LSL	$-1/\tau^3$	0.3005	−0.770	1.2316
LSLLS	$1/\tau^5$	0.2791	−0.604	1.2488
LSLLSLSL	$-1/\tau^7$	0.2521	−0.610	1.2353
LSLLSLSLLSLLS	$1/\tau^9$	0.2435	−0.601	1.2363

We set up our transfer matrices in a cylindrical geometry so that we have periodic boundary conditions in the horizontal (x) direction, and we grow the lattice to infinity in the vertical (y) direction. We define a layer of atoms by a sequence of bonds which are horizontal or at ±18°. The long *LS* bonds are denoted $l^{\pm}$, the short *SS* bonds are denoted $s^{\pm}$, and the horizontal *LL* bonds are denoted $s^0 s^0$. Each atom belongs to a single layer. Layers are just one atom thick except at vertical *SS* bonds where they are two atoms thick. One such layer is shown at the bottom of Fig. 1.

For a given width we must determine the set of all allowed layers $\{\alpha\}$ and then form a matrix,

$$T_{\alpha\beta} = \begin{cases} \exp(\mu_L N^{\alpha}_{\text{large}} + \mu_S N^{\alpha}_{\text{small}}), & \text{if layer } \alpha \text{ is allowed on top of layer } \beta, \\ 0, & \text{otherwise.} \end{cases} \tag{10}$$

A layer is allowed if the s^0 bonds occur in pairs forming horizontal *LL* bonds, and if $N_{l^+} = N_{l^-}$ and $N_{s^+} = N_{s^-}$ so that the y coordinates are well defined as we circle the layer. Adjacent layers are allowed if the resulting atomic configuration is equivalent to a rhombus tiling by drawing all *LS* bonds. Other configurations have energy greater than the ground-state energy and thus do not contribute to the low-temperature state. The chemical potentials μ_S and μ_L which appear in (10) allow control of the phason strain.

In order to test the conjecture (6), and evaluate the parameters σ_0, and K, we must evaluate the entropy density and phason strain as we vary the chemical potentials μ_L and μ_S. Given a transfer matrix, the partition function for N layers is formed by the trace of the Nth power of the matrix. In the $N \to \infty$ limit we have simply,

$$Z \sim \Lambda_0^N \,, \tag{11}$$

where Λ_0 is the largest eigenvalue of T. By the Perron-Frobenius theorem Λ_0 is positive and nondegenerate. Energy and temperature enter the calculation only through the chemical potentials because we restrict our attention to the ground state. The entropy per row is, therefore,

$$\bar{S} = \ln\Lambda_0 - \mu_L \bar{N}_L - \mu_S \bar{N}_S \,, \tag{12}$$

where $\bar{N}_L$ and $\bar{N}_S$ are the average number of large and small atoms per row. (These averages are calculated from the left and right eigenvectors of the transfer matrix.) We calculate the area per row,

$$\bar{A} = (2\sin 72° - \sin 36°)\bar{N}_L + (\tfrac{3}{2}\sin 36° - \tfrac{1}{2}\sin 72°)\bar{N}_S \,, \tag{13}$$

then evaluate the entropy density

$$\sigma = \bar{S}/\bar{A} \,. \tag{14}$$

Our choice of boundary conditions forces the values of certain components of the phason strain. In particular, the equilibrium states have reflection symmetries in the x and y axes requiring the phason-strain components E_{xy} and E_{yx} to vanish. Furthermore, the change in $h_x^{\perp}$ across the strip is fixed for a given width strip so that E_{xx} is defined by the number of l and s bonds in any layer,

$$E_{xx} = \frac{N_l - \tau N_s}{\tau N_1 + N_s} \,. \tag{15}$$

Finally, the remaining component of phason strain E_{yy} can be controlled by the chemical potentials. For a given choice of μ_L and μ_S we calculate E_{yy} from

$$\det\tilde{E} = \tau^2 \frac{2 - \bar{N}_S \tau / \bar{N}_L}{2\tau + \bar{N}_S/\bar{N}_L} \,. \tag{16}$$

Our goal is to calculate the entropy density and derivatives at zero phason strain. For finite-length ($\Delta x^{\parallel}$) layers, Eq. (15) shows $E_{xx} \neq 0$ atom width so that each layer consists of either a single large atom, or two small atoms. The phason strain in this case is $E_{xx}^{(0)}=-\tau$ and the entropy vanishes. We thus consider a sequence of layer lengths $\Delta x^{\parallel}$ growing as τ^n (Table I) for which $E_{xx}^{(n)}$ vanishes as $(-\tau^2)^{-n}$. Because the dimensionality of the transfer matrix grows exponentially in the length $\Delta x^{\parallel}$, it is impractical to calculate beyond the largest size shown here (matrix dimensionality of 8438 after exploiting symmetries). Table I lists the entropy densities and their second derivatives with respect to E_{yy} (evaluated at $E_{yy}=0$) for $n=1$–5, and also the concentrations at which the entropy density is maximized.

In order to determine the bulk values of σ_0 and K we must extrapolate the values given here for small n. Numerical evidence regarding the ratio of largest to next-largest eigenvalues suggests an infinite correlation length in the $n\rightarrow\infty$ limit, consistent with the hypothesis of quasi-long-range order in the quasicrystal state. We postulate that the finite-size corrections will be of the form $1/(\Delta x^{\parallel})^2$, which is typical of many two-dimensional systems at their critical point. The data in Table I fit this form well with $\sigma_0=0.2374\pm0.0003$ and $K=0.600\pm0.006$. Finally, the concentration at which the entropy density is maximized converges rapidly to 1.2360 ± 0.002. Inspecting Eq. (16) we note that a concentration of $2/\tau=1.23607$ corresponds to $E_{yy}=0$. Further details of our numerical results and extrapolations will be published elsewhere.

Our value of K can be compared to the value 0.60 ± 0.06 obtained by Monte Carlo simulations[16] on the continuum Lennard-Jones system at $T=0.05$. The agreement of these values of K demonstrates that entropy provides the dominant contribution to the phason stiffness constant for this simple binary alloy. It is intriguing that this value coincides with the value $K=0.60\pm0.02$ obtained for a Penrose tiling without any matching rules.

The value of σ_0 yields a ground-state entropy of 0.193/atom which dominates the energy differences among configurations arising from the long-range tail of the Lennard-Jones potential down to temperatures of about 25% of the quasicrystalline melting temperature. Thus entropy may explain the thermodynamic stability of the quasicrystalline phase in addition to its elastic constants.

In conclusion, we have calculated the entropy density of a binary random tiling, shown that this is maximized by phason-strain-free tilings, and verified the conjecture in Eq. (6). Our results include the configurational entropy density of a quasicrystal, and a predicted value of the phason elastic constant. The magnitude of the entropy and agreement of the elastic constant with that found in the continuum Lennard-Jones alloy support the random-tiling model of this quasicrystalline alloy. Random-tiling models can be formulated for other symmetries and dimensionalities as well. It is even conceivable that such a model could apply to real quasicrystalline materials in thermal equilibrium.

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