# Equilibrium Crystal Shapes of Ideal and Random Quasicrystals

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(Received 24 December 1987)

The scaling behavior of interfaces is studied for ideal and random quasicrystals in two and three dimensions, and its consequences for the equilibrium crystal shape are discussed. For a 3D decagonal phase, a facet with a fivefold symmetry axis is found to undergo a roughening transition. For a 3D icosahedral phase, such a facet is likely to stay smooth at *all* temperatures, $T$, in the ideal case, but is predicted to be rough on sufficiently large scales for $T>0$ in the random case. The singular behavior of the equilibrium crystal shape near the edge of a facet is also determined.

PACS numbers: 68.35.Bs, 61.50.Jr, 64.60.Cn

In thermal equilibrium, an interface separating a crystal from a disordered phase can be smooth or rough. A smooth interface is essentially flat and leads to a facet of the equilibrium crystal shape (ECS); a rough interface makes arbitrarily large excursions from its average position and leads to a rounded part of the ECS. In the latter case, the interface has nontrivial scaling properties characterized by critical exponents. As the temperature is changed, the interface may undergo a roughening transition from a smooth to a rough state.

In this paper, we study the interfacial roughness and the ECS for quaiscrystals. This theoretical study is motivated by the recent observation of the icosahedral phases of Al-Cu-Li, Ga-Mg-Zn, and Al-Cu-Fe,[1] which are believed to be equilibrium structures. Two simple models will be considered[2]: (i) *ideal* tilings of space which are characterized by long-ranged orientational and quasiperiodic translational order (in this case, the tiles have to fulfill certain matching rules) and (ii) equilibrium ensembles of *random* tilings which can be obtained by a random rearrangement of the tiles in the ideal tiling thereby abandoning the matching rules.[3]

With each tiling, we associate a cell model[4,5] in which we place lattice-gas atoms or spins on the tiles. Spins on nearest-neighbor tiles are taken to interact with a coupling constant $J/2$. Then, we enforce an interface which runs through the tiling by imposing appropriate boundary conditions.[6] The effective Hamiltonian $\mathcal{H}$ for this interface is $JN_s$, where $N_s$ is the total number of bonds broken by the interface, and the probability to find a certain interface configuration is given by the Boltzmann factor $\simeq\exp(-\mathcal{H}/T)$.

As a result, we find that the interfacial behavior is, in general, very different for *ideal* and for *random* quasicrystals. Compared with a periodic system, the interfacial roughness is found to be *reduced* for the ideal tilings but to be *enhanced* for the random tilings both in 2D and in 3D systems. For the 3D icosahedral phase at $T>0$, a facet with a fivefold axis is predicted to stay smooth in the ideal case but to be rough on sufficiently large scales in the random case. In the latter case, a sharp crossover is found which could mimic a roughening transition. The interfacial free energy is discussed for $T=0$ and for $T>0$, and its scaling properties are used to determine the ECS. The details of this study will be presented elsewhere.[7]

*Interfacial roughness*: $d=1+1$.—First, let us review the interfacial behavior in an *ideal* Penrose tiling[4,5]; see Fig. 1(a). Within the cell model, the interface runs along the tile edges and has minimal energy when its normal points along one of the five possible edge orientations. We take the $x$ and $z$ axes to be perpendicular and parallel to such an orientation. Now, the tiling can be decomposed into lanes and rows; see Fig. 1(a). At $T=0$, the interface is confined to one of the lanes and is, therefore, *smooth*. However, its ground state within a lane is degenerate. There are essentially two types of lanes, narrow and wide ones [see Fig. 1(a)], with interfacial

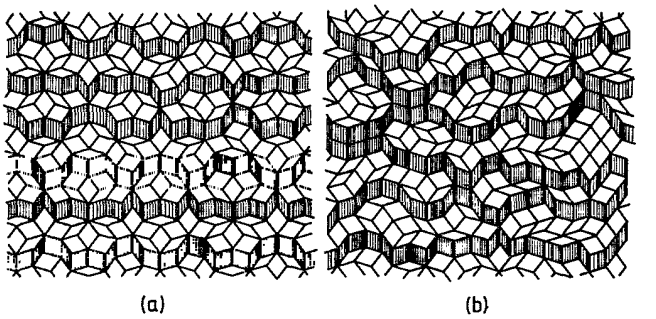


FIG. 1. Decomposition of (a) ideal and (b) random Penrose tiling into lanes and shaded rows. The rows contain all tiles with two edges parallel to the $z$ axis.

 

ground-state *entropies* per step, $S_N \simeq 0.45$ and $S_W \simeq 0.54$, which form a Fibonacci sequence. Thus, the interface feels a quasiperiodic potential of entropic origin which has been studied within a lattice model.[4,5] As a result, the difference correlation function, $\Delta C(x) \equiv \langle [z(x)-z(0)]^2 \rangle/2$, was found to behave as

$$\Delta C(x) \sim x^{2\zeta} \text{ with } \zeta = \zeta(T) < \tfrac{1}{2}, \quad (1)$$

i.e., the interface is *less rough* than in a periodic system with $\zeta = \frac{1}{2}$.

Next, consider a *random* Penrose tiling as shown in Fig. 1(b) which is obtained by "reshuffling" the tiles of the ideal tiling until one reaches a steady state.[8,2] Such a tiling can again be decomposed into rows and lanes. However, the sharp division into two categories of wide and narrow lanes is now lost: The rows go up and down in an erratic fashion and frequently collide. On large scales, these behave like random walks with short-ranged repulsive interactions. The difference correlation function of such a walk diverges logarithmically.[9] Thus, the difference correlation function, $\Delta C_R(x)$, of a row in the random Penrose tiling behaves in the same way. This can be derived more systematically if one represents the random tiling by an undulating 2D hypersurface with coordinate $\mathbf{h}_\perp(x,z)$ embedded in 5D space. It can be shown that, when the hypersurface is projected to make a tiling, $\Delta C_R(x) \sim \langle [\mathbf{h}_\perp(x,0) - \mathbf{h}_\perp(0,0)]^2 \rangle$. It has been argued[2,8] that the hypersurface undulations are governed by a gradient-squared free energy of entropic origin. This leads again to $\Delta C_R(x) \sim \ln(x)$. Now, consider the cell model for the random tiling and an interface running along the tile edges. At $T=0$, the interface is confined to a lane, and

$$\Delta C(x) \sim \ln(x) \text{ for } T=0. \quad (2)$$

For $T>0$, the interface makes excursions from one lane to another. Within each lane, the interface samples a random sequence of contact zones where the two rows bounding the lane touch each other. Between two contact zones, the lane has a finite and highly variable width. An interface within such a lane has a unique ground state along the contact zones but a degenerate one between the zones. Now, consider a partition of the lane into segments $m$ consisting of the same number $b$ of steps within the lane. Then, the degeneracy $g_b(m)$ of the possible ground states within segment $m$ gives rise to an effective random potential $V(m) = T \ln[g_b(m)]/b$ acting on the interface. Such a potential belongs to the same universality class as the 2D random-bond Ising model for which[10] $\zeta = \frac{2}{3}$. Therefore,

$$\Delta C(x) \sim x^{2\zeta} \text{ with } \zeta = \tfrac{2}{3} \text{ for } T>0. \quad (3)$$

At low $T$, one has a crossover from (3) to the logarithm in (2). An interface, which samples $\sim L$ entropically induced random bonds of strength $\sim T$, has free energy fluctuations of size $\sim T L^{1/2}$. This also represents the free energy which the interface of length $L$ can gain in one lane compared with a neighboring lane. It will then stay within a lane for $L_0 \sim (J/T)^2$ steps in order to overcome the energy loss, $J$, from hopping across a row. Thus, (3) and (2) hold for $x \gg L_0$ and $x \ll L_0$, respectively.

*Interfacial roughness*: $d = 2+1$.—First, consider a 3D *decagonal* phase[11] which is modeled by a periodic stack of an *ideal* or a *random* 2D Penrose tiling such that the tiles are parallelepipeds with four faces parallel to the fivefold axis. Within the cell model, an interface with a fivefold axis is parallel to the 2D tilings and feels a *periodic* potential, $V(z) = B\cos(2\pi z)$, where $z = z(x_1, x_2)$ is the interfacial height parallel to the fivefold axis. Such a potential leads to a roughening transition at $T = T_R > 0$ as can be shown, e.g.,[12] by renormalization up to $V^2$.

On the other hand, an interface within the ideal decagonal phase, which is perpendicular to the 2D Penrose tilings but parallel to the rows within this tiling, feels a *quasiperiodic* potential of entropic origin as in $d = 1+1$. At $T=0$, such an interface is smooth. At $T>0$, the quasiperiodic potential tends to reduce the interfacial roughness and, thus, to increase $T_R$. In fact, $T_R$ may even become infinite. Indeed, renormalization up to $V^2$, when applied to $V(z) = B\cos(2\pi z) + B_\sigma \cos(2\pi z/\sigma)$ with $B, B_\sigma < 0$ and irrational $\sigma$, leads to an infinite stiffness, $\tilde{\Sigma} = \infty$, for all $T > 0$.[12] As argued below, $\tilde{\Sigma} = \infty$ implies a smooth interface in $d = 2+1$.

An ideal *icosahedral* tiling can be constructed, e.g., by the dual-grid method.[13] Then the tiling is built up from parallelepipeds (rhombohedra) and can be decomposed, for each of the six edge orientations, into parallel sheets and slabs. The sheets contain all tiles with four faces parallel to the chosen orientation, and the slabs are composed of the remaining tiles. At $T=0$, an interface parallel to the sheets is confined to a slab and, thus, is smooth. Furthermore, it has a finite ground-state entropy per unit area which should vary quasiperiodically from slab to slab. This should lead to $T_R = \infty$ as mentioned.

Now, let us define a *random* icosahedral tiling in $d = 3$ just as in $d = 2$. The random rearrangement of the tiles in the ideal structure leads to undulations and frequent collisions of the sheets. On large scales, these sheets can be described by a displacement field $u(z, x_1, x_2)$, and an effective Hamiltonian for $u$ which is harmonic in all three derivatives of $u$. It then follows that the sheets are *smooth*, and this also applies to an interface in the random tiling at $T=0$. At $T>0$, the random fluctuations in the width of the slab act on the interface like random bonds with strength $\sim T$. Now, consider a step across a sheet which connects two interfacial segments within two neighboring slabs. A step segment of length $L$, which makes a transverse fluctuation $\sim L_\perp$, sweeps $\sim L_\perp L$ new random bonds. It can then gain a free energy $\sim T(L_\perp L)^{1/2}$ since the scale of the random bonds is

again set by $T$. Thus, it behaves like a 1D interface in a 2D random-*field* Ising model for which the random field is $\sim T$.[7] This implies that the *step free energy becomes scale dependent* and vanishes on scales $L \gg L_0$, where $L_0$ is expected to be $\sim \exp(J/T)^{4/3}$.[14] Thus, it costs no free energy to create steps of length $L \gg L_0$, and the 2D interface is rough with $0 < \zeta < \frac{2}{3}$ as in the 3D random-bond Ising model.[15]

*Interfacial free energy.*—At $T=0$, the step free energy per tile, $\Sigma_s$, is equal to the step energy per tile, $J$. Now, consider a macroscopic interface and let $\theta$ denote the tilt of the interface normal from its easy axis. Then, the interfacial free energy per unit area, $\Sigma$, behaves as

$$\Sigma(\theta) \approx \Sigma_0 + \Sigma_1 |\theta| \quad \text{for small } \theta. \tag{4}$$

At $T>0$, (4) remains valid provided that $\Sigma_s$ is still finite. For $\Sigma_s = 0$, the $\theta$ dependence of $\Sigma$ can be obtained as follows. Consider an interfacial segment of size $L$ and area $\sim L^{d-1}$. Its fluctuations have a typical amplitude, $L_\perp \sim L^\zeta$. These fluctuations make two contributions to the free energy[16]: (i) an overall increase in the bending energy per unit area, $\Delta e \sim (L_\perp/L)^2$, and (ii) an overall loss of entropy per unit area, $\Delta s \sim -1/L^{d-1}$. Therefore, the total free-energy increase per unit area scales as

$$\Delta\Sigma(L_\perp) \sim \Delta e - T\Delta s \sim 1/L_\perp^\tau, \tag{5}$$

with

$$\tau = \begin{cases} 2(1-\zeta)/\zeta & \text{for } \zeta \geq \zeta_0 \equiv (3-d)/2, \quad (6) \\ (d-1)/\zeta & \text{for } \zeta \leq \zeta_0. \quad (7) \end{cases}$$

The exponent (6) agrees with various results for random systems.[16] The exponent (7) represents a new prediction which has been confirmed for $d=2$ in the context of wetting.[17]

The scaling behavior as given by (5)–(7) implies, via $\theta \approx L_\perp/L$, that

$$\Sigma(\theta) \approx \Sigma_0 + \Sigma_k |\theta|^k \quad \text{for small } \theta \tag{8}$$

with

$$k = \begin{cases} 2 & \text{for } \zeta \geq \zeta_0, \quad (9) \\ (d-1)/(1-\zeta) & \text{for } \zeta \leq \zeta_0. \quad (10) \end{cases}$$

Usually, one has $k=2$ for a rough interface implying a finite stiffness, $\tilde{\Sigma} \equiv \Sigma_0 + (\partial^2\Sigma/\partial\theta^2)_0$. However, it follows from (10) that $\tilde{\Sigma}$ is *infinite* in the ideal 2D Penrose tiling even though the interface is rough. On the other hand, this *cannot* happen in $d=3$ since, in this case, the overall entropy loss $\sim 1/L^2$ cannot dominate the overall energy increase $\sim (L_\perp/L)^2$. Therefore $\tilde{\Sigma} - \infty$ implies a smooth interface in $d=3$.

*Equilibrium crystal shape (ECS).*—For the ideal and random 2D Penrose tilings, the interfacial free energy behaves as in (4) at $T=0$. Then the ECS is a regular decagon.[4,5] At $T>0$, the decagon becomes rounded but the ECS is *anomalously flat* for the ideal tiling. Indeed, the Wulff construction together with (8) and (10) leads to an ECS which is given by $z(x) \approx z_0[1 - c(x/z_0)^{1/\zeta}]$ for small $x \sim \sin(\theta)$ with $\zeta < \frac{1}{2}$ and $c \equiv \zeta(\Sigma_0/\Sigma_k)^{(1-\zeta)/\zeta}$.[7]

For the ideal and random 3D *decagonal* tiling defined above, the Wulff construction leads to a $T=0$ ECS composed of two decagons and ten rectangles which form a column with decagonal cross section.[7] Such columns have been observed in the growth morphology of Al-Mn.[11] For $T>0$, the two decagonal facets undergo a roughening transition with $0 < T_R^{(d)} < \infty$ while, in the ideal tiling, the ten rectangular facets are likely to have $T_R^{(r)} = \infty$ as a result of the quasiperiodic potential. Furthermore, for $T>0$, the facets will often be separated by rounded parts composed of terraces and steps. Let $z(x)$ describe the ECS near an edge of a facet [at $z(x=0) = 0$]. Then the excess free energy of the steps is $[\Delta\Sigma(l) - H]/l$ where $l$ is the mean step separation with $1/l \sim dz/dx$, $\Delta\Sigma(l)$ is given by (5), and[18] $H \sim x$ acts as an effective thermodynamic field.[19] Minimization of this free energy with respect to $l$ leads to

$$z(x) \sim x^\lambda \quad \text{with } \lambda = 1 + 1/\tau \tag{11}$$

as $x \to 0$. It then follows from (6), (1), (7), and (3) that the edge of a decagonal facet has $\lambda = 1 + \zeta(T) < \frac{3}{2}$ and $\lambda = 2$ for the ideal and random case, respectively (while $\lambda = \frac{3}{2}$ near the edge of a rectangular facet as for periodic crystals).

For the 3D *icosahedral* tiling at $T=0$, the ECS is composed of decagonal, hexagonal, and square facets.[5,3] The decagonal facets are parallel to the sheets and slabs of the icosahedral tiling. Then, the above results on the interfacial roughness imply that these facets should stay smooth for all $T>0$ in the ideal quasicrystal. The edge of such a facet again has $\lambda = 1 + \zeta(T) < \frac{3}{2}$. For the random tiling, two $T$ regimes must be distinguished: For $T \ll J$, the scale $L_0$ will exceed the size of the quasicrystal which implies that the ECS has decagonal pseudofacets; for $T > J$, $L_0$ is microscopic and these facets have disappeared. Since $L_0$ depends exponentially on $J/T$, this crossover will be sharp and thus could mimic a roughening transition. The steps near the edge of a decagonal pseudofacet feel an effective random field which implies $\zeta = 1$, $\tau = 0$, and $\lambda = \infty$ indicating an essential singularity of $z(x)$.

In summary, we have determined the interfacial roughness for several models of 2D and 3D quasicrystals and its consequences for the ECS. Two aspects of our study should be accessible to experiments: (i) the thermal evolution of facets with a fivefold axis, and (ii) the singular behavior of the ECS near the edge of such facets. The shape of real crystals will often reflect the *nonequilibrium* growth conditions. However, for small crystals with a size of a few micrometers, equilibration via surface diffusion could be rapid enough to obtain the ECS as has been observed, e.g.,[18] for lead. Thus, we suggest systematic experiments on sufficiently small crystals

of Al-Cu-Li, Ga-Mg-Zn, and Al-Cu-Fe.

We thank David A. Huse, Daniel Kroll, Thomas Nattermann, and Jacques Villain for helpful discussions and Heiner Müller-Krumbhaar for a critical reading of the manuscript. One of us (C.L.H.) was supported by U.S. Department of Energy Grant No. DE-FG02-87ER-45323.

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