Icosahedral Quasiperiodic Ground States?

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An icosahedral quasiperiodic zero-temperature phase with lower enthalpy than in Bravais and close-packed crystal structures has been found for a system of particles interacting via a square-well potential. This remains true after small changes in the potential, pressure, and even after small changes within a class of icosahedral structures. Above a certain critical pressure, the icosahedral phase transforms into the bcc Bravais crystal structure.

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The discovery of icosahedral quasicrystals four years ago[1] opened a Pandora's box of solid-state physics, exposing a carefully guarded secret that solid-state physics does not even have an explanation of its very basis: why, or whether the ground state of a solid should be crystalline, periodic. For example, it is still not known what the densest packing of hard spheres in three dimensions is. If a solid-state physicist would be asked what the densest packing of hard spheres is, the answer would undoubtedly be hcp or fcc packing. It is probably the right answer, but nobody was ever able to either prove or disprove it. More generally, for almost three quarters of a century no precedent to the periodic ground-state myth has been established, either experimentally or theoretically.

Are icosahedral quasicrystals stable or metastable, ordered or glassy, quasiperiodic or periodic?

A picture which emerges from a phenomenological Landau-Ginzburg theory suggests that an "icosahedratic," orientationally ordered phase may play a major role in the formation of icosahedral quasicrystals.[2] If the coupling between the orientational and the positional order parameters is sufficiently strong, then the icosahedratic order can stabilize an equilibrium icosahedral quasiperiodic phase. If, on the other hand, this coupling is not sufficiently strong, the quasicrystal could be viewed as a glassy but orientationally ordered metastable state[3] resulting from a sufficiently rapid quench of the icosahedratic phase.

Despite this appealing phenomenological picture, a deeper physical understanding of quasicrystals at a microscopic level is still lacking. For example, it is desirable to determine and compare competing crystal, icosahedratic glass, and quasiperiodic model structures. Before this ambitious goal can be met, it will be important to establish a precedent by finding a simple physical model with an icosahedral quasiperiodic ground-state structure. Although it is typically not possible to predict the zero-temperature structure of an interacting system, its enthalpy, or cohesive energy, can often be optimized within a relatively broad class of structures. Alternatively, one may ask what the main features of the interactions which would favor formation of a given structure should be.

Since the observed icosahedral quasicrystals are metallic, the electronic contribution to the cohesive energy is probably substantial. While insights about the effects of electronic degrees of freedom on the stability of quasicrystals can be gained, for example, by means of quantum structural diagrams[4] or within a self-consistent effective medium theory,[5] the required optimization of the total energy over a large class of aperiodic structures is well beyond today's computational power. Comparatively simpler are the calculations of the classical cohesive energy of systems of particles interacting via an effective short-ranged interatomic pair potential. In this case, optimization within a reasonably large class of structures is possible. At the same time, insights about those aspects of the interaction which favor quasicrystal ordering will also hold true when electronic degrees of freedom are explicitly included.

This Letter reports results of a symmetric calculation of pair distribution functions and cohesive energies for a large class of single-component icosahedral quasiperiodic structures. A more detailed exposition will be published elsewhere.[6] Our method, which relies on the six-dimensional hypercrystal description of icosahedral quasicrystals,[7] enables us to evaluate the pair distribution function exactly, avoiding the slow convergence problem of the direct summation approach. We will present our results for the square-well (SW) potential,

$$U(x)=\begin{cases}\infty, & 0\le x\le\sigma,\\ -\epsilon, & x\le\sigma+w,\\ 0, & \sigma+w\le x,\end{cases}\tag{1}$$

and for the 6-12 Lennard-Jones (LJ) potential,

$$U(x)=4\epsilon\left[\left(\frac{\sigma}{x}\right)^{12}-\left(\frac{\sigma}{x}\right)^{6}\right].\tag{2}$$

For SW interaction we establish a precedent: A portion of the zero-temperature phase diagram is occupied by icosahedral quasiperiodic structures with higher cohesive energy than in primitive and close-packed (cp)

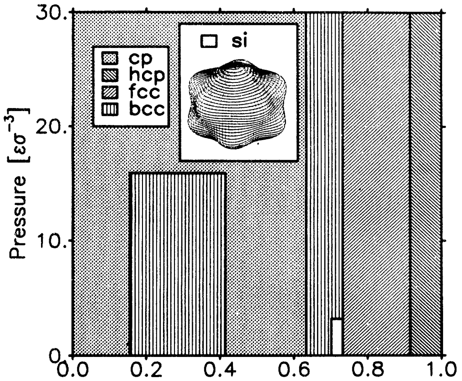

FIG. 1. Zero-temperature pressure vs well-width phase diagram for the square-well potential of depth ϵ and hard-sphere diameter σ. The simple icosahedral (si) quasiperiodic structure which wins over the Bravais and cp crystal structures is obtained as a cut through a six-dimensional crystal whose unit cell contains a single flat atomic surface. Inset: The domain of the structure.

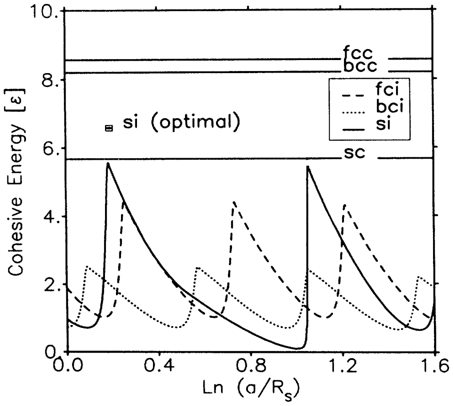

FIG. 2. Lennard-Jones cohesive energy for si, bci (body-centered-icosahedral) and fci (face-centered-icosahedral) quasiperiodic structures with a single flat atomic surface per six-dimensional unit cell vs the radius R_s of the spherical domain of the surface (a is the hypercubic lattice constant and ϵ is the LJ bond strength). The apparent periodicity is a consequence of the inflation symmetry. The energy is optimized (⊟ in the figure) for the si structure and the nonspherical domain of Fig. 1. The energies of sc (simple-cubic), bcc, and fcc Bravais structures are shown for comparison.

crystalline structures (see Fig. 1). This result is robust in that it remains valid for slightly altered icosahedral structures and a range of pressure and interaction potentials. We also determine icosahedral quasiperiodic structures with the high packing fraction and LJ cohesive energy within only 17% and 24%, respectively, of the assumed optimal values found in close-packed structures (see Fig. 2).

Since icosahedral quasicrystals were not monatomic, it became a matter of folklore after their discovery that icosahedral ground states, if at all possible, can only be found in multicomponent systems. In light of this, the fact that we found an icosahedral phase in a simple monatomic system seems particularly surprising. However, this fact suggests that there are also multicomponent systems with icosahedral quasiperiodic ground states. Namely, for a range of the added parameters, such as interspecie bond lengths and bond strengths which might favor local icosahedral clustering, stable icosahedral quasiperiodic structures can be expected.

The SW potential is certainly not the only potential which can produce icosahedral ground states. More realistic effective pair potentials for metals are quite different from the unfavorable LJ potential. They have a much slower decay and often show large Friedel oscillations which could stabilize the icosahedral phase. For example, a slowly decaying potential with oscillations giving rise to relatively sharp minima at around 1, 1.45–1.49, and 1.7, separated by broader maxima, could also give a stable icosahedral phase. Such an effective pair potential could also be viewed as resulting from integrating out all but one component of a multicomponent system.

A stable zero-temperature structure of an interacting system can be determined by minimizing the enthalpy per particle,

$$H=\min(E+Pv)\,, \tag{3}$$

where E is the energy per particle, P is pressure, v is the volume per particle, and the minimization is over all possible structures. Both the energy and the specific volume depend on the structure. For a given structure and a given central pair potential $U(x)$, the energy is simply given by

$$E=\tfrac{1}{2}\int_0^\infty g(x)U(x)\,dx=\tfrac{1}{2}\sum_R f(R)U(R)\,, \tag{4}$$

where $g(x)$ is the radial pair distribution function, which is often discrete, $g(x)=\sum_R f(R)\delta(x-R)$, yielding the second equality. The radial distribution function and the bond frequency $f(R)$ are purely geometrical properties of a structure. Therefore, after first establishing a suitable parametrization of a large class of icosahedral structures, it is necessary to calculate the bond frequencies as a function of these parameters. Then, these features of interparticle interactions which favor icosahedral structures should be identified and the zero-temperature free enthalpy minimized.

As is well known, any icosahedral quasiperiodic crystal can be represented as a cut through a six-dimensional hypercubic crystal whose unit cell is decorated by three-dimensional atomic *surfaces*.[7] We shall consider all three icosahedral Bravais classes (si, fci, and bci), but only the case where the space group of the hypercrystal is symmorphic and there is a single atomic surface per unit hypercell.

The atomic surface can be specified as a three-component vector field $\mathbf{S}(\mathbf{x}^\perp)$ defined on a volume $v^\perp$ in the perpendicular space and valued in the physical space,

$$\mathbf{x}=\mathbf{S}(\mathbf{x}^\perp),\quad \mathbf{x}^\perp \in v^\perp . \tag{5}$$

The volume $v^\perp$ directly determines the specific volume of the quasiperiodic structure, $v=v_c/v^\perp$, where v_c is volume of the unit hypercell. The boundary of the domain $v^\perp$ can be defined by a function on the sphere, $x^\perp=r(\hat{\mathbf{x}}^\perp)$. The domain must be invariant under the full symmetry group of the icosahedron, while $\mathbf{S}$ must transform as a covariant. That is, for all $y \in Y_h$, $r(y^\perp \cdot \hat{\mathbf{x}}^\perp)=r(\hat{\mathbf{x}}^\perp)$, while $\mathbf{S}(y^\perp \cdot \mathbf{x}^\perp)=y\cdot\mathbf{S}(\mathbf{x}^\perp)$, where $y^\perp$ is the three-dimensional irreducible representation of Y_h, irrational conjugate to y. With use of group theory, $r(\hat{\mathbf{x}}^\perp)$ can be expanded in invariant polynomials, or icosahedral harmonics, and the expansion coefficients can be used to parametrize the atomic surfaces. For example,

$$r(\hat{\mathbf{x}}^\perp)=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty} r_{n_1,n_2} I_1^{n_1}(\hat{\mathbf{x}}^\perp) I_2^{n_2}(\hat{\mathbf{x}}^\perp) , \tag{6}$$

where I_1 and I_2, the basic invariants, can be chosen as the products of the planes perpendicular to the six fivefold and the ten threefold icosahedral rotation axes, respectively.[8]

To the lowest order $v^\perp$ is a sphere, and the only free parameter is its radius $r_{0,0}=R_s$. In the next order $r_{1,0}\neq 0$ and $v^\perp$ acquires an icosahedrally symmetric modulation. We also considered the case $r_{0,1}\neq 0$, and the cases where $v^\perp$ is an icosahedron or a dodecahedron, which would require the entire expansion in Eq. (6).

The vector field $\mathbf{S}(\mathbf{x}^\perp)$ can be expanded in covariant polynomials (icosahedral vector harmonics), similarly to Eq. (6). To the lowest order, the surface is flat, that is, $\mathbf{S}=\mathbf{0}$. We have also considered the first-order term which produces rippling of the surface.[6] However, as we shall see, already the flat surface, and the parameters R_s, $r_{1,0}$, and $r_{0,1}$ are sufficient to obtain structures with very good cohesive energy.

For periodic crystals with q atoms per unit cell nonzero bond frequencies are rationals p/q, thus bounded from below by $1/q$. For quasiperiodic crystals, where each particle has a different environment, they are irrational (and split into a continuous distribution when the atomic surfaces are not flat). Therefore, bonds with arbitrarily low frequencies will appear. Since low-frequency bonds may occur at the short distances, which dominate the cohesive energy, it is not possible to use a brute-force method—summation over a large cluster. Evaluation of arbitrarily small bond frequencies would require summation over arbitrarily large clusters.

However, by using the six-dimensional description of quasicrystals we can give an explicit closed expression for the radial distribution function. The key observation is that the domain $v^\perp$ will be cut by the physical space with uniform density. That is, the physical space will cut the atomic surface arbitrarily close to any point in some unit cell of the hypercrystal. Therefore, if an atomic surface is attached to the hyperlattice point at the origin, and another one to a hyperlattice point at $\bar{\mathbf{R}}=(\mathbf{R},\mathbf{R}^\perp)$ then the contribution of $\bar{\mathbf{R}}$ to the pair distribution function is

$$\frac{1}{v^\perp}\int_{v^\perp \cap v^\perp(\bar{\mathbf{R}})} \delta(\mathbf{x}-\mathbf{R}-\mathbf{S}(\mathbf{x}^\perp-\mathbf{R}^\perp)+\mathbf{S}(\mathbf{x}^\perp))\,d^3x^\perp , \tag{7}$$

where $v^\perp(\mathbf{R})$ is the domain $v^\perp$ translated to $\bar{\mathbf{R}}$. For a flat surface, frequency of a bond between these two surfaces is simply proportional to the overlap volume.

For interactions with a sharply repulsive core, such as the LJ or SW interactions, the cohesive energy and the enthalpy, are dominated by the shortest bonds. Therefore, such interactions favor structures with a large number of short bonds. The bond frequency for the shortest bond is bounded from above by twelve. This bound is saturated in cp structures such as hcp and fcc but apparently cannot be saturated in icosahedral structures. Therefore, for central interactions with a sharp minimum, that is, a well-defined bond length such as the LJ interaction, icosahedral structures will be less favorable. Indeed, as shown in Fig. 2, we found the optimal icosahedral LJ cohesive energy of 6.57ϵ for $R_s=1.22\bar{a}$, $r_{1,0}=-12.0\bar{a}$, $r_{0,1}=-7.8\bar{a}$, and $\mathbf{S}=\mathbf{0}$. This is about 24% lower than 8.58ϵ for fcc structure.[9] Because of the short range of the LJ interaction, we found that the lowest $\mathbf{S}\neq\mathbf{0}$ term does not improve the cohesive energy.

If the total number of neighbors up to some (not necessarily shortest) distance can be increased in icosahedral structures more than in periodic structures, a wider potential well could take advantage of this increase. Therefore, it is interesting to consider the SW potential and to determine its zero-temperature pressure-well width phase diagram. In the limit of a narrow well, we are in the situation discussed above, and the equilibrium structure is degenerate: all close-packed structures, including fcc and hcp structures, have the same energy, -6ϵ. In the limit of a very wide well, $H\approx -2\pi\epsilon w^3/3v+Pv$, as in the limit of very large pressure, the structures with the highest density, presumably the close-packed structures, win.[9] Nevertheless, as shown in Fig. 1, we find that there is an intermediate region of the phase diagram where an icosahedral structure has lower enthalpy than either close-packed or Bravais crystal structures. Using the same icosahedral structure which optimized the LJ cohesive energy, we found this phase between $w/\sigma=0.701$ and 0.732 and for pressures below $P_c=3.2\epsilon/\sigma^3$. The enthalpy of this structure is -13.5ϵ at $P=0$ and -10.9ϵ at $P=P_c$.

The robustness of the icosahedral phase is important.

First, it occupies a finite volume of the phase diagram. Second, this phase persists as one makes small changes in the interaction potential. Finally, the icosahedral quasiperiodic structures which are near the optimal structure also have larger cohesive energy than the crystalline structures.

In summary, we have found a quasiperiodic icosahedral phase, a precedent to a commonly accepted belief. This zero-temperature result is robust. Future work is necessary to explore this phase at nonzero temperatures. Recently, the role of low-temperature fluctuations has been investigated in two-dimensional model quasicrystals.[10] A large number of "random" structures were found almost degenerate with a quasiperiodic ground-state structure, giving rise to a finite entropy per particle at low temperatures. Nevertheless, the large entropy does not destroy quasi-long-range order, and algebraic diffraction peaks remain. This indicates that also in three dimensions, a quasiperiodic state might persist and even be entropically stabilized at nonvanishing temperatures.

General symmetry arguments can be used to prove that the space of icosahedral structures is extremal. That is, if left unperturbed, an icosahedral structure may distort only within this space. However, this structure could still be unstable, for example, a local maximum rather than a minimum. Therefore, further work will have to examine structural stability with respect to small nonsymmetric perturbations. It is, in principle, possible that a periodic structure with a large unit cell would be more stable. This can best be examined by the examination of crystal approximants of the icosahedral structure. The same calculation could be also used to evaluate the phason elastic moduli.[11]

Finally, we have considered here the case of a single atomic surface. An alternative parametrization would be to consider a set of N small flat surfaces whose positions are optimized within the unit hypercell. This could be termed a minimization with quasiperiodic boundary conditions, in analogy with the periodic boundary conditions with N particles per unit cell.

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