

Quasicrystal Equilibrium State

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We obtain quasicrystalline structures in Monte Carlo simulations of a simple two-component Lennard-Jones system in two dimensions. The quasicrystal, which shows tenfold symmetry, appears to be an equilibrium state of the system. Although the structure corresponds to tiling of the plane with rhombuses, it is not a Penrose pattern.

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Shechtman *et al.*¹ found that the diffraction patterns of some rapidly quenched metal alloys consist of sharp spots arranged with icosahedral symmetry. Their discovery has forced physicists to reevaluate their traditional abhorrence² of the icosahedral symmetry group. Although the mathematical prohibition against the combination of icosahedral symmetry with translational periodicity remains, it proves possible to replace periodicity with other types of translational order which allow both sharp diffraction peaks and icosahedral symmetry.³ Abandoning spatial periodicity in well-ordered solids questions a second assumption that all solid equilibrium states must be periodic.⁴

The discovery of long-range icosahedral order in alloys raises the possibility that the local energetic preference for noncrystallographic symmetry could lead to a non-periodic state with lower free energy than any crystalline structure. If we could fill space with atoms in such a manner that each atom were surrounded by an icosahedron of other atoms, this structure would form the ground state for a wide range of elements. However, icosahedral frustration^{5,6} prohibits such a structure. We can achieve this packing locally, but must include energetically costly defects over larger length scales. An interplay of energetic preferences, geometric constraints, and entropy determines the true equilibrium states which may or may not be periodic.

Experimental studies of quasicrystal formation have not settled this issue. Initially, quasicrystals were formed by rapid quenching of a liquid alloy of aluminum and manganese.¹ Slow cooling resulted in conventional crystal formation, suggesting that quasicrystals are metastable, or even unstable states. More recent studies of annealing show that the quasicrystal phase of UPdSi is more stable than the amorphous phase, but less stable than conventional crystals.⁷ In general, certain quasicrystal phases of ternary alloys containing small concentrations of silicon appear more stable than the corresponding phases of binary alloys. Perhaps these alloys are chemically "close" to an equilibrium quasicrystal phase which has not yet been discovered. Finally, large, stable, single quasicrystals of AlLiCu have been reported.⁸

Landau theories show that quasicrystals may form

equilibrium phases in two and three dimensions.⁹ Unfortunately, these theories provide no microscopic picture of atoms arranged in space, and no direct connection between the phenomenological parameters of the Landau free energy and microscopic forces. Numerical simulations¹⁰ have confirmed the mechanical stability of decorated Penrose patterns but have not been able to obtain these configurations by cooling from the melt.

In this paper, we demonstrate that a simple, realistic, two-component Lennard-Jones system in two dimensions spontaneously forms a quasicrystal (Fig. 1). The quasicrystal is apparently an equilibrium state of the system. We choose the parameters of our Lennard-Jones system to encourage local decagonal order. At low temperatures, this local order induces long-range decagonal bond-orientational order without creating spatial periodicity. We also present a related, analytically tractable, model which actually possesses quasicrystal equilibrium and ground states.

These simulations also provide insight into the structure of quasicrystals. Our configurations show a more general type of ordering than a Penrose pattern. The

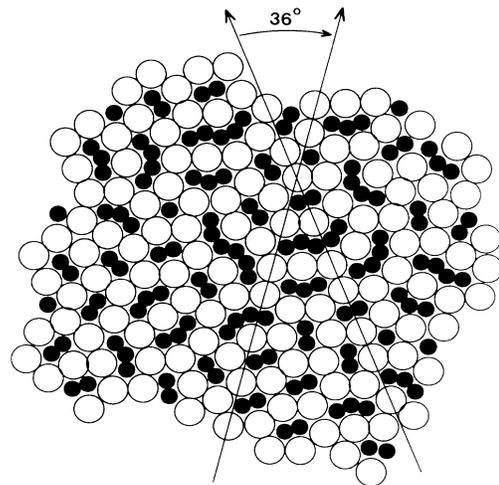


FIG. 1. Low-temperature configuration of pure Lennard-Jones system showing quasicrystal equilibrium state.

Penrose-pattern inflation and deflation symmetries are absent, but sharp diffraction peaks (possibly delta functions) remain.¹¹ Our equilibrium states are intermediate in structure between a Penrose pattern and an orientationally ordered glass.¹² We will follow the experimentalists' terminology and call such structures quasicrystals because they combine a high degree of spatial order with noncrystallographic symmetry.

The form of the potential is

$$V_{\alpha\beta}(r) = E_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - 2(\sigma_{\alpha\beta}/r)^6], \quad (1)$$

where $\alpha = L$ or S denotes large or small atoms, $\sigma_{\alpha\beta}$ is the bond length, and $E_{\alpha\beta}$ the bond strength. We choose bond lengths to promote local decagonal order:

$$\begin{aligned} \sigma_{LS} &= 1.0, & \sigma_{LL} &= 2\sin 36^\circ = 1.176\dots, \\ \sigma_{SS} &= 2\sin 18^\circ = 0.618\dots \end{aligned} \quad (2)$$

Note that our atoms are not well described by hard disks because $\sigma_{LS} > (\sigma_{LL} + \sigma_{SS})/2$. Figure 2 shows a Penrose pattern decorated with these atoms.

Our Monte Carlo simulations find quasicrystal equilibrium states over a range of bond strengths. In order to prevent phase separation into single-species triangular lattices, we choose the interaction E_{LS} between unlike species to dominate the interactions E_{LL} and E_{SS} between like species. Figure 1 shows the result of a Monte Carlo simulation in which we chose

$$E_{LS} = 1, \quad E_{LL} = E_{SS} = \frac{1}{2}, \quad (3)$$

and cooled slowly from high to low temperatures. The particles were initially placed at random in a large circular container with hard walls.

Our simulation employs three types of Monte Carlo moves. In addition to traditional local, single-particle moves, we allow moves to any position in the system, and

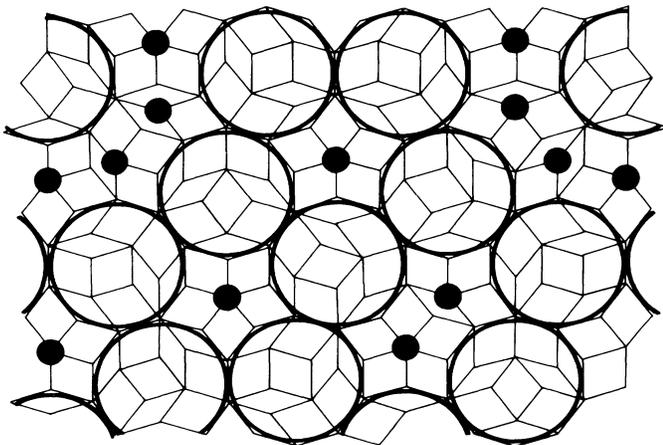


FIG. 2. Decorated Penrose pattern. Large atoms inscribed in decagonal regions, small atoms distributed among remaining vertices.

three-particle "flips" which interchange the position of a large atom with two adjoining small atoms. While the acceptance ratios for the latter two types of moves are small (generally less than 1% below the transition), they are an extremely effective aid to equilibration. In particular, the flips efficiently break up metastable configurations containing close-packed triangles of like particles.

We studied a range of system sizes, from seven atoms up to 132 small atoms and 140 large atoms (Fig. 1). All of the systems showed quasicrystalline states at low temperatures. The most defect-free configurations were obtained for concentration ratios near 1.06 large atoms per small atom (the value expected from decoration of a Penrose pattern). When the proportion of large disks was higher, the extra large disks tended to be rejected from the bulk, accumulating at the surface.

The configuration shown in Fig. 1 is the result of cooling from $\beta = 3.3$ by factors of 1.025 for twenty temperatures with 8000 Monte Carlo steps per particle at each temperature. Flips were attempted after every five attempts to move each particle individually. The system was then quenched to a β of 20.0. The ordering transition occurs at a β of approximately 4.4. Several separate cooling runs were performed. The results for internal energy and for bond-angular order parameters from these separate runs were in good agreement in the ordered phase, although some discrepancies were observed near the transition. Hysteresis was observed upon heating of the system through the transition.

The reproducibility of our results leads us to believe that the quasicrystalline state in this system is, in fact, the equilibrium phase of these temperatures.

Notice the nearly perfect short-range order in the interior of Fig. 1. Each bond is close to its optimum length. All local configurations may be found in a Penrose pattern, with one exception which will be discussed shortly. All pairs of bonds form angles which are close to integer multiples of 36° . In two dimensions, perfect local bond-orientational order guarantees perfect long-range bond-orientational order.¹³ Calculating the bond-orientational order parameters¹⁴

$$Q_n = |\langle \exp(2\pi i n \theta) \rangle|, \quad (4)$$

we find sharp maxima when n is an integral multiple of 10.

Figure 3 shows all local environments which are likely to occur in the equilibrium phase at low temperatures. Note that there are just three distinct ways to pack atoms around a small atom, and six ways to pack atoms around a large atom. What about those equilibrium configurations which are not found in Penrose patterns? These are the rows of three colinear adjacent large atoms which may be seen in Figs. 1, 3, and 4. Penrose matching rules prohibit linear chains of three or more large atoms. Our system consists of Lennard-Jones atoms with two-body central forces only, and so there is no ob-

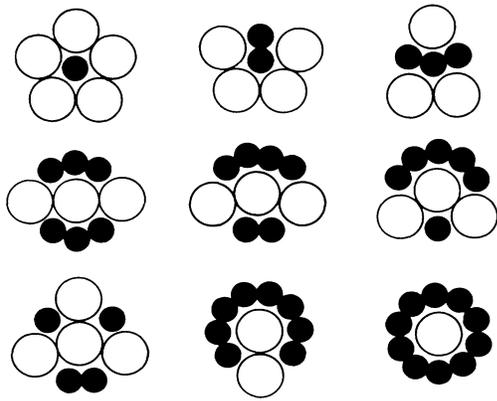


FIG. 3. Complete set of low-energy local environments.

vious mechanism for creating Penrose matching rules. We believe that our quasicrystals exploit the configurational entropy available by violating the matching rules.

Figure 4 shows a configuration which contains a metastable defect in the interior of the sample. Defects of this sort are likely to occur with great frequency in rapidly quenched quasicrystals. Indeed, it is almost impossible to eliminate this defect by annealing of our system below the freezing temperature. The reason is that although the atoms in the defect-free region of the sample display perfect short-range order, there is an inconsistency in the positions of atoms near the defect which prevents the region in between from filling with atoms in the low-energy configuration of Fig. 3. Because we must disturb a large number of atoms which sit in low-energy configurations in order to remove the defect, it is relatively stable.

Although no numerical simulation can provide a rigorous proof that the quasicrystalline states are equilibrium states, a related model can be analyzed simply and proven to have quasicrystalline equilibrium and ground states. This model utilizes the same decoration of a Penrose pattern (Fig. 2) as our Lennard-Jones system. However, instead of the bond strengths of Eq. (3) we take

$$E_{LS} = E_{SS} = 1, \quad E_{LL} = 2. \quad (5)$$

Recognizing that the interactions (5) encourage phase separation, we exclude from consideration configurations containing close-packed triangles of identical atoms. For convenience, we truncate the Lennard-Jones potential at nearest neighbors. Finally, we ignore vibrational contributions to the entropy (explicit calculations in 1D suggest that they are unimportant anyway).

The choice of interactions (5) plus the truncation of the potential creates an interesting degeneracy among configurations. Setting $E_{SS} = E_{LS}$ ensures that all three environments of a small atom are degenerate. Similarly, for each large atom the number of LS bonds plus twice

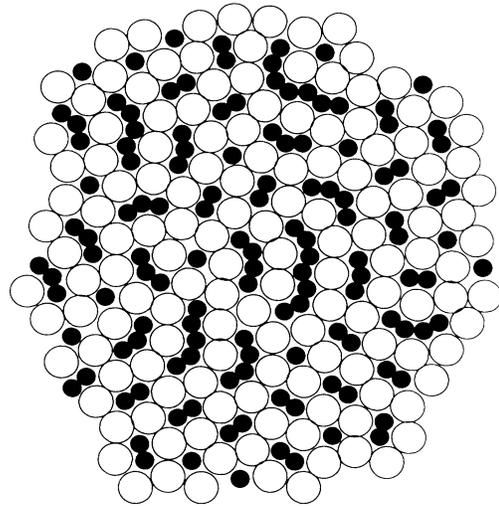


FIG. 4. Metastable quasicrystal configuration containing defect.

the number of LL bonds always totals ten. Thus the condition $E_{LL} = 2E_{LS}$ ensures that all six environments of a large atom are degenerate.

As a result of this degeneracy among local environments, all candidates for ground-state structures have equal energy. Thus crystals with large unit cells, Penrose patterns with matching rules, and quasicrystals without matching rules are degenerate at zero temperature. The true ground state must then be determined by entropy differences in the limit as $T \rightarrow 0$. The configurational entropy available from violations of Penrose matching rules makes the quasicrystal the equilibrium and ground state of this model.

This model of a quasicrystalline ground state is reminiscent of Pauling's ice model.¹⁵ The third law of thermodynamics is apparently violated because of the high degeneracy of the ground state. Of course, in both Pauling's ice model and our quasicrystal model, long-range interactions are likely to lift the degeneracy of the ground state. The quasicrystal should still be the equilibrium state down to very low temperatures. The determination of the complete phase diagram of this model including long-range interactions and atomic vibrations will be a great challenge.

In summary, we present Monte Carlo simulations of a two-component Lennard-Jones system which spontaneously forms a quasicrystalline state. This state appears to be in thermodynamic equilibrium. The quasicrystalline configurations belong to a general class of structures which include Penrose patterns as a small subset. Finally, we present a simplified model which has quasicrystalline equilibrium and ground states.

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