Phason Elasticity in Entropic Quasicrystals

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The equilibrium quasicrystal phase of a two-dimensional two-component Lennard-Jones atomic system and two different ensembles of random tilings (binary and unconstrained) are analyzed by means of Monte Carlo simulations. We find that the quasicrystal phase in the atomic system is well described by the random-tiling model. Despite the nonzero configurational entropy density, the phason fluctuations are found not to destroy the quasi-long-range translational order in this phase, in agreement with conjectured square-gradient phason elasticity. Nearly identical, temperature-independent, reduced, phason elastic constants are determined in all three cases.

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The recent experimental discovery[1-3] of stable quasicrystalline materials with resolution-limited Bragg peaks brings to the fore those equilibrium models with long-range translational order. One such model is the quasiperiodic crystal model (the prototype for which is the Penrose tiling).[4-6] In the quasiperiodic crystal model, the system is assumed to possess a quasiperiodic ground state; i.e., the quasicrystal is stabilized primarily by energetic considerations.

On the other hand, a simple atomic Lenndard-Jones (LJ) system in two dimensions suggests a different, entropically dominated mechanism for quasicrystal stabilization.[7] Two years ago, a simulation by Widom, Strandburg, and Swendsen of this atomic system showed that the system freezes into a phase possessing an apparent tenfold symmetry whose configurations are tilable with the Penrose rhombuses. However, the configurations displayed no apparent preference for a particular rhombus arrangement. Indeed, considerable tile rearrangement was observed even at very low temperatures in the quasicrystal phase.

These observations suggest a random-tiling picture of the quasicrystal phase.[8] In the random-tiling picture it is the large entropy available from many nearly degenerate tile rearrangements which stabilizes the quasicrystal phase. Such a quasicrystalline phase may easily be the equilibrium state over some temperature range for a system whose ground state is periodic. A random-tiling quasicrystalline phase requires only that the energetics of the system stabilize the appropriate local packing units and that the differences in energy between various packing arrangements be small relative to the melting temperature of the material.

In this paper we explore the random-tiling and atomic models. While the atomic model is not intended to be a good representation of a particular material, we do expect its properties to be quite general. Indeed, Lancon *et al.*[9,10] have shown that if the model is truncated to nearest-neighbor interactions, the random tiling is the ground state of the atomic model over a wide range of choices of the Lennard-Jones interaction strengths. In the truncated approximation, the energy of a tiling depends only on the concentration of fat and thin rhombuses and not on their arrangement. The long-range tails of the full Lennard-Jones interaction breaks this degeneracy between different tilings but, as we show here, the random-tiling picture remains appropriate over a broad temperature range.

In this paper we present the following results obtained by Monte Carlo (MC) simulation: (i) The atomic system is shown to possess quasi-long-range translational order and no average phason strain in the quasicrystal phase. (ii) The random-tiling model is also shown to possess quasi-long-range translational order in confirmation of the Henley[11] and Elser[12] conjecture of a square-gradient entropic phason free energy given in the absence of dislocations by $F/k_BT=\frac{1}{2}K\int[\nabla_i h_j(\mathbf{r})]^2 d^2r$, where K is a phason elastic constant. (iii) The reduced phason elastic constants are obtained for both the atomic system and the appropriate random-tiling model. They are in agreement, showing that the random-tiling model is an appropriate description of the atomic quasicrystalline phase. The reduced phason elastic constant for the atomic model is temperature independent in the quasicrystal phase as is to be expected for an entropy-dominated term in the free energy. (iv) Reduced phason elastic constants for two different random-tiling models are obtained and are found to be numerically indistinguishable.

Figure 1 shows an atomic quasicrystal configuration obtained by our Monte Carlo simulation. The atoms interact with Lennard-Jones potentials

$$V_{\alpha\beta}(r)=4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12}-2\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right], \tag{1}$$

where α and β refer to large (L) and small (S) atoms. The $\sigma_{\alpha\beta}$ are chosen according to the tile decoration

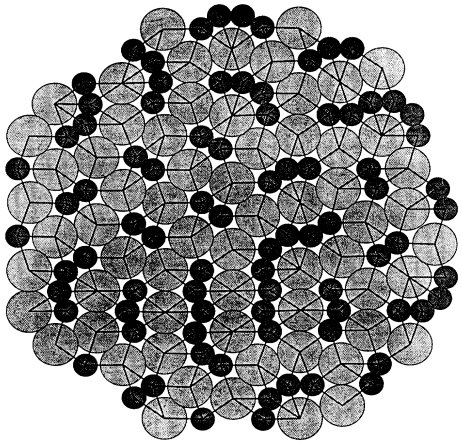

FIG. 1. Configuration of the two-component LJ atomic system at $T=0.05$. The corresponding binary tiling, defined in Ref. 10, is obtained by joining near-neighbor large-small pairs.

shown in Fig. 1 to be $\sigma_{LS}=1$, $\sigma_{LL}=2\sin\pi/5$, and $\sigma_{SS}=2\sin\pi/10$. The $\epsilon_{\alpha\beta}$ are chosen so as to discourage phase separation into single-atomic-species phases and set arbitrarily at $\epsilon_{LL}=\epsilon_{SS}=\frac{1}{2}\epsilon_{LS}$. The numbers of large and small atoms are chosen as appropriate for a quasiperiodic tiling.

In the absence of "untilable defects," the position of every atom in such a configuration can be described as

$$\mathbf{r}=a_{LS}\sum_{\alpha=0}^{4}n_\alpha\mathbf{e}_\alpha^{\parallel}+\mathbf{u}(\mathbf{R})\equiv\mathbf{R}+\mathbf{u}(\mathbf{R}), \tag{2}$$

where $\mathbf{e}_\alpha^{\parallel}=(\cos 2\pi\alpha/5,\sin 2\pi\alpha/5)$, a_{LS} is the average spacing between neighboring large and small atoms, $\{n_\alpha\}$ [13] are integers, and $\mathbf{u}(\mathbf{R})$ is a small displacement from the vertex $\mathbf{R}$ of a superimposed tiling. In the ideal tilings corresponding to these atomic configurations, the large atoms sit at vertices whose angles are all odd multiples of $\pi/5$ and the small atoms sit at vertices whose angles are all even multiples of $\pi/5$ (see Fig. 1). Thus, the ensemble of possible rhombus configurations corresponding to the low-temperature atomic configurations is the set of binary tilings.[10]

Any tilings by Penrose rhombuses can be represented by regarding the sets of integers $\{n_\alpha\}$ as sites on a 5D hypercubic lattice.[12,14] A decagonal tiling is obtained whenever the lattice points representing a particular tiling lie in a 2D strip of the appropriate average orientation. The displacement of the strip from a flat surface at the decagonal orientation is conveniently described by the phason or perpendicular-space coordinates[8,12,14]

$$\mathbf{h}(\mathbf{R})=\sum_{\alpha=0}^{4}n_\alpha\mathbf{e}_\alpha^{\perp},\quad h_z(\mathbf{R})=2^{-1/2}\sum_{\alpha=0}^{4}n_\alpha, \tag{3}$$

where $\mathbf{e}_\alpha^{\perp}=(\cos 4\pi\alpha/5,\sin 4\pi\alpha/5)$.

Depending on the severity of the fluctuations of this strip translational order may or may not be preserved. In a decagonal glass, for example, this strip will have "tears" and translational correlation lengths will be finite.[12] The fact that a tiling is, by definition, space filling requires that the strip be continuous although it may, in principle, still have large enough fluctuations to destroy the translational order.

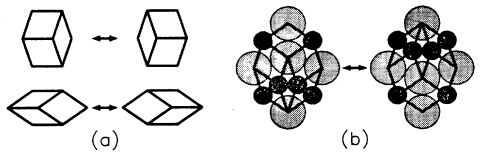

FIG. 2. Basic moves for the tiling simulations: (a) hexagonal flips, and (b) an octagon flip, corresponding to switching a large atom and two small atoms.

If a square-gradient form for the phason entropy turns out to be correct, the 2D random tilings, like 2D crystalline solids, will possess quasi-long-range translational order characterized by

$$\left\langle\frac{1}{N}\sum_{\mathbf{R}}\left|\mathbf{h}(\mathbf{R})-\frac{1}{N}\sum_{\mathbf{R}'}\mathbf{h}(\mathbf{R}')\right|^2\right\rangle=\frac{1}{2\pi K}\ln N+\text{const} \tag{4}$$

and power-law divergent diffraction peaks whose intensity goes as

$$I(\mathbf{Q}^{\parallel})\sim I_0(\mathbf{Q}^{\parallel})N^{2-\eta(\mathbf{Q}^{\perp},Q_z^{\perp})/2}, \tag{5}$$

where

$$\eta(\mathbf{Q}^{\perp},Q_z^{\perp})=\frac{1}{2\pi K}|\mathbf{Q}^{\perp}|^2+\eta_z(Q_z^{\perp}) \tag{6}$$

and a large number N of atoms or vertices and proper boundary conditions are assumed. Here K is a reduced phason elastic constant, and the scattering wave vector $\mathbf{Q}^{\parallel}$ and phason momentum $(\mathbf{Q}^{\perp},Q_z^{\perp})$ are complementary components of the reciprocal-lattice vector of the 5D hypercubic lattice.[15] The last term in Eq. (6) takes a nonvanishing value if the projection strip is rough in the h_z direction also.[16] The angular brackets in Eq. (4) denote an ensemble average.

Our basic MC moves for the unconstrained and binary random tilings are the hexagon and octagon flips shown in Fig. 2. It can be shown that these moves satisfy the detailed balance condition needed to generate equilibrium distributions with a fixed stoichiometry.[16] We studied tilings of 76, 199, 521, 1364, and 3571 rhombuses with rhombic periodic boundary conditions. These numbers are chosen to obtain best approximations to the zero phason strain rhombus ratios for a given system size. In the binary-tiling case, they correspond to systems of F_k large atoms and $2F_{k-1}$ small atoms, where F_k is the kth Fibonacci number. A typical simulation consisted of an equilibration stage, followed by a run of 10000–30000 MC steps per tile. A test run on a sixfold rhombus tiling[17] over eight different sizes ranging from 24 to 864 tiles yielded the exactly known elastic constant within the estimated error bars.

The MC simulations of the atomic quasicrystal were

carried out as described by Widom, Strandburg, and Swendsen.[7] Previously, they demonstrated that between a high-temperature liquid phase and an unknown low-temperature state lies a quasicrystal phase, possessing long-range decagonal order. The nature of the translational order and phason fluctuations in this phase were not analyzed.

Here we study systems ranging in size from 100 to 1000 atoms at $T=0.05$ (in units of ϵ_{LS}) and from 100 to 545 atoms at $T=0.1$, 0.125, and 0.2. Melting occurs between $T=0.2$ and 0.125. Phason-phason correlations complicate the analysis at $T=0.125$ but lead to results for the phason elastic constant consistent with those at $T=0.05$ 0.1. Therefore we discuss here the data for $T=0.05$ and 0.1.[18] Further details of these atomic simulations may be found in Ref. 18. About 16000 MC steps per atom were performed for each temperature and size. Free boundary conditions were used for the simulations and the atoms near the boundary were discarded for the analysis. These simulations were performed by beginning with a decorated tiling and running at low temperatures. Equilibration was checked by comparison with results of cooling runs for $T=0.05$ and $N=289$.

Equation (4) is observed to hold in all three models over the range of system sizes studied (see Fig. 3) within the accuracy of the data.[19] The elastic constant K is found to be 0.60 ± 0.02 for the unconstrained random tiling and 0.625 ± 0.025 for the binary random tiling. The latter is to be compared with the transfer-matrix result of 0.60 given by Widom, Deng, and Henley.[20] Apparently, the binary-tiling restriction does not change K appreciably.

For the atomic model, we find $K=0.63\pm0.03$ at $T=0.1$ and 0.60 ± 0.06 at $T=0.05$, giving us direct evidence for the validity of the random-tiling description of the atomic quasicrystal phase. The fact that K is the same to within statistical errors at both temperatures confirms the basically entropic nature of this phase. In contrast, two possibilities exist for a system with a Penrose-pattern ground state. Either the system will be pinned, i.e., nondivergent phason fluctuations, or the system will be unpinned with logarithmically diverging phason fluctuations. The unpinned case differs from the random-tiling case, however, in that the phason elastic constant K will be temperature dependent.[16,21]

In principle, the prefactor to the logarithm in Eq. (4) will have an additional term due to the coupling of phasons to phonons which could be temperature dependent. We measured the phason-phonon correlations in our atomic system and found them negligible at $T=0.05$ and 0.1, though large variations in their magnitude and sign hindered a precise determination.

The scaling relation (5) is also observed to hold for all the models at a number of peaks studied. The exponent η shows a nearly parabolic dependence on $\mathbf{Q}^{\perp}$ and no apparent systematic dependence on $|\mathbf{Q}^{\parallel}|$ [see Eq. (6) and Fig. 4]. For the atomic model, this dominance of phason fluctuations attests to the small effect of phonons in this temperature range, further validating the random-tiling approximation.

The third component of the phason coordinates $h_z(\mathbf{R})$ is restricted to one of three values in the atomic system and in the binary tilings but is unrestricted in the unconstrained random tilings. Although $h_z(\mathbf{R})$ is a discrete

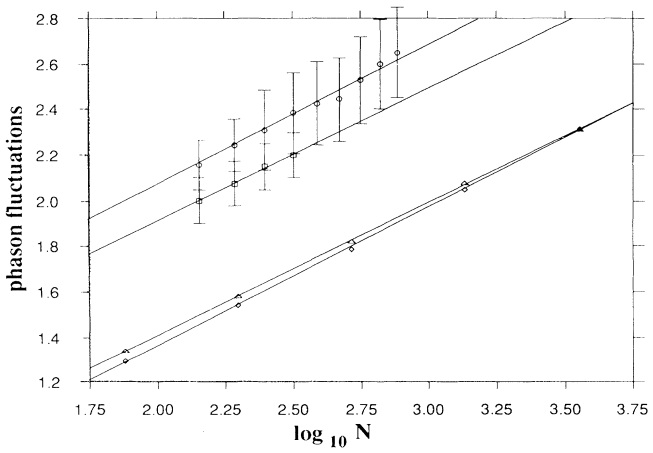

FIG. 3. Mean-square deviation of the perpendicular-space coordinates [see Eq. (4)] vs logarithm of system size N for the LJ system at $T=0.05$ (○) and 0.1 (□) and for the binary (△) and unconstrained (◇) random tilings. The lines through the data correspond to $K=0.60$ (○), 0.63 (□), 0.60 (◇), and 0.625 (△), respectively. Error bars for the random tilings were comparable to the size of the plotted symbols.

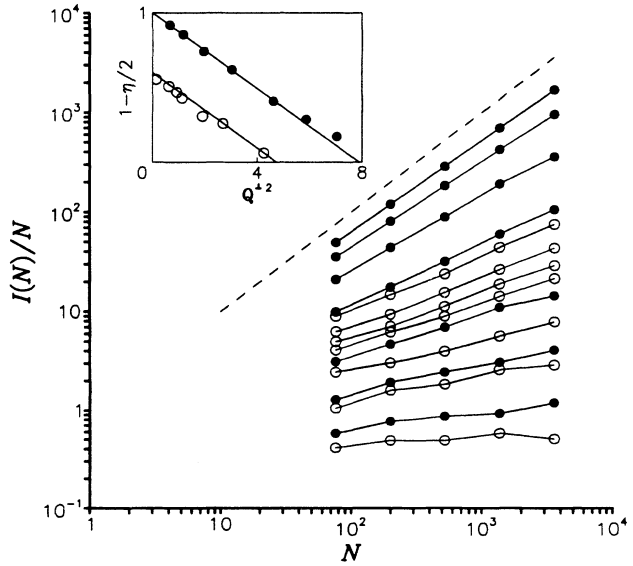

FIG. 4. Diffraction intensities vs logarithm of system size N for the unconstrained random tiling at a number of peaks studied. Inset: Slopes for each set of data at a given peak vs the square of the phason momentum $|\mathbf{Q}^{\perp}|$, with $Q_z=0$ (●) and $\pm 2\pi/5$ (○). The straight lines correspond to $K=0.61$.

variable, it also exhibits behavior consistent with a square-gradient free energy, with an elastic constant $K_z = 0.575 \pm 0.030$. (This behavior is analogous to that of a solid-on-solid model in the rough phase.[8,17,22]

In conclusion, we have demonstrated that in a 2D two-component LJ system, between the high-temperature binary liquid and a presumably ordered but unknown low-temperature state, there lies an entropic quasicrystal phase. This equilibrium quasicrystal is well described by a random-tiling model. The conjectured square-gradient form of entropy density is verified through the observation of logarithmically diverging phason fluctuations in the binary and unconstrained random tilings, and in the atomic system. Additional evidence for the quasi-long-range translational order is provided by the observation of power-law divergences of the diffraction peaks in these systems. The reduced phason elastic constant is determined for the three systems and is found to have a value of ~ 0.6 in all three cases. Future work should attempt to understand the apparent agreement of the reduced phason elastic constants for these distinct models. Questions concerning the nature of the $T=0$ phase and a possible low-temperature transition will also have to be answered.

Finally, we briefly address the question of experimentally distinguishing a quasiperiodic crystal phase from a random-tiling quasicrystal (since both models predict Bragg peaks in three dimensions). Studies of temperature dependence of Debye-Waller factors and diffuse scattering[15] will probe the phason elastic constants. If phason-phonon coupling is small, the random-tiling picture predicts, for example, temperature-independent Debye-Waller factors over a broad temperature range. Preliminary results from the study of the atomic model[18] indicate a reduction in peak intensity near melting due to phason-phonon coupling. Further exploration of this behavior, particularly in a three-dimensional model, would be helpful for more precise predictions of experimental observables.

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