THE UNSTABLE CHEMICAL STRUCTURE OF QUASICRYSTALLINE ALLOYS ☆

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We show that a typical toy model of an ordered quasicrystalline alloy has a range of stoichiometries.

We consider the low temperature ordered phases of general classical statistical mechanical models, allowing several species of structureless particles interacting through translation invariant, short range forces and with positions in $\mathbb{R}^n$ ("continuous models") or $\mathbb{Z}^n$ ("discrete models"). We do not consider incommensurate models.

Until recently every such known model fell into one of two classes: either the model had a unique periodic ground state, as in the lattice gas on $\mathbb{Z}^2$ with nearest neighbor repulsion [1], or else it had a degenerate ground state, as in the lattice gas on $\mathbb{Z}^2$ with nearest neighbor attraction and critical value of the chemical potential [1]. By ground state we mean the translation invariant zero temperature limit of the (grand canonical) equilibrium ensemble, and the ground state is degenerate if this limit is not unique. Also, one determines the periodicity of a ground state by its many body correlation functions in the usual way [2,3]. Since ground states are nondegenerate for generic interactions [4] we will only consider such models in the following.

Consider a continuous model with two species of opposite electric charge and with crystalline ground state as in a toy model of NaCl. The addition of a small uniform external electric field would deform (polarize) the crystal continuously as the field amplitude is varied. In particular the ground state would change continuously with the perturbation and it is important to note that this change is local – it occurs uniformly over the state. Now consider some discrete model with nondegenerate periodic ground state. A small change in the external conditions could not produce such a local effect in the ground state; as long as the period remains bounded with the perturbation, there is a finite gap in energy density above the original ground state which cannot be bridged by a short range perturbation of sufficiently small amplitude.

In this letter we note a new mode of behavior exhibited by a relatively new class of models [5–7]. Using a discrete model with unique quasicrystalline ground state we show that certain arbitrarily small, short range perturbations change the ground state (necessarily) nonlocally. Intuitively, in common models (as in the toy model of NaCl) which have nondegenerate periodic ground states a small perturbation can only cause a local change in the ground state, and therefore none at all in a discrete model, whereas in quasicrystalline models where the ground state has in some sense periodic components of arbitrarily large period, a (short range) perturbation can couple to these long periods, entering at "infinite period" so to say, and thereby change the ground state nonlocally.

The (toy) model we use is a nearest neighbor lattice gas model on the square lattice, with many (56) particle species allowed at each site. The general form of the model is thus familiar, but to completely specify it we must list the energy of interaction for each possible pair of nearest neighbor occupation states. As there is no simple formula for these energies this is rather involved. In our model all chemical potentials are initially taken to be zero, and there is one

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particle species for each class of tiles in the tiling example in ref. [9] (or alternatively, refs. [8,10]), with interaction energy -1 if two titles match and energy $+1$ if they do not match. Our argument is based on one step in the middle of the proof that this tiling example forces nonperiodicity. Therefore those who wish to follow the details of our proof in the next paragraph are referred to the argument in ref. [9] (or ref. [10]); our conclusions are presented in our last paragraph.

We know that our model has a nondegenerate quasicrystalline ground state [4] and consider a perturbation of the model. The tiles, or corresponding particle species, fall into five classes: "crosses", up-arms, down-arms, left-arms and right-arms. Consider the perturbation which raises the chemical potential of the left-arms by the amount $\epsilon > 0$. We will show that in the ground state for the perturbed model the percentage of left-arms is lower than in the unperturbed model. To see this note that if, in building up the "(2^n-1)-squares" of an allowed tiling (corresponding to the unperturbed model) we change the tiles in the horizontal corridors between (2^n-1)-squares (for some fixed n) by replacing each left-arm by the right-arm with reversed horizontal arrows but unchanged vertical arrows, the energy density is increased by an amount proportional to 2^{-2n}. However if the perturbed chemical potential is used, the energy density is also decreased by an amount proportional to 2^{-n}, which proves that the ground states of the perturbed and unperturbed models are different for any $\epsilon > 0$.

So in our quasicrystalline model arbitrarily small changes in chemical potentials lead to changes in stoichiometries, even at zero temperature, in distinction with all previously known models and real alloys. Now even though ours is only a toy model, the effect we computed seems likely to hold in any low temperature quasicrystalline model, and we therefore suggest that it may well be true for real quasicrystalline alloys such as $Al_{86}Mn_{14}$ [11,12].

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