COMPETITIVE INTERACTIONS AND 2–D STRUCTURES AT FINITE TEMPERATURES

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Abstract

The phase diagram of a triangular lattice with competitive interactions is obtained at finite temperatures. At high temperatures the existence of an incomplete Devil's staircase points to the existence of incommensurate states near the disorder line. 1–d domain walls and large periodicity 2–d domains are discussed.

1. Introduction

Polytypes [1] is a class of solids, which have the common characteristic to appear in various phases, under small changes in temperature, pressure or other physical parameters. The ground state of such a system may be a periodic structure with a short wavelength (most commonly observed), a long commensurate periodicity, or even incommensurate formations. As examples one can mention the classical structural polytype silicon carbide that presents a large sequence of short period phases, the rare–gas monolayers adsorbed in graphite (2–d systems) that show commensurate and incommensurate phases [2] and the magnetic substance $CeSb$ with an experimentaly observed succesion of long period phases [3].

Although growth kinetics around screw dislocations could contribute to modulated structures, it is commonly accepted that they can exist as stable states in thermodynamic equilibrium with some form of "competition"[4]. This may arise either by antagonistic effective interactions between constituent units , or by competing periodicities. In many cases short range competing interactions give a rather consistent explanation of the multiplicity of phases encountered in polytypes or other structures [1]. Two main categories of models have been proposed to explain the behavior of systems developing modulated structures. These are the discrete variable models, such as the ANNNI type [5] or the clock type models [6] and the continuous variable models of the type of the Frenkel–Kontorova [7,8]. In both the above microscopic class of models the lattice is considered discrete.

In the present work we shall be dealing with a continuous variable model, which can be of one or two degrees of freedom. In the first case, it can represent on one hand a displacement perpendicular to the plane as in the surface reconstruction of the Si (111) surface [9]. On the other hand the variable can be an angle representing rotations,

as in an N_2 molecule adsorbed on graphite [10,11] which by lowering the temperature changes to $\sqrt{3}\times\sqrt{3}$ and 2×1 phases. For two degrees of freedom a 2–d model has been proposed [12,13] to explain the three phases of $LiIO_3$.

Very often the competition does not come from the substrate and the interplanar forces, but can be a result of interactions among the atoms as was done in a model used to describe 1–d ferroelectrics [14,15]. In this case for the ground state to be incommensurate one needs at least up to 3rd neighbour interactions. By considering the nearest neighbour strains in the 1–d chain problem, one can transfer to one with a substrate and up to 2nd neighbour interactions.

In the following we shall be presenting a nonlinear model on a triangular lattice, at finite temperature, whose phase diagram exhibits short and long period commensurate phases. In addition, incommensurate phases leave their signature in the form of a "devil's staircase". Also, domain walls are studied, either in 1– or 2–dimensions.

2. Model and Methods

Consider atoms or molecules (of mass M) forming a triangular lattice, having one degree of freedom (displacement or rotation) denoted by $u_{n,m}$. Each particle interacts harmonically with its first and second neighbours with a force constant f_1 and f_2 respectively. An on–site nonlinear double well potential, of the form of ϕ^4 acts on each site ($g_0, g_4 > 0$). The Hamiltonian of the system is the following:

$$\mathcal{H} = \sum_{n,m}\left\{\frac{1}{2}M\dot{u}_{n,m}^2 + \frac{1}{4}g_4\left(u_{n,m}^2 - \frac{g_0}{g_4}\right)^2 + \sum_{NN}\frac{1}{2}f_1(u_{NN}-u_{n,m})^2 + \sum_{NNN}\frac{1}{2}f_2(u_{NNN}-u_{n,m})^2\right\}. \tag{1}$$

The last two terms denote summation over nearest neighbours (NN) and next–nearest neighbours (NNN), respectively. The fact that the on–site potential is double well and that $f_1, f_2 \gtrless 0$ arises a conflict between the respective terms in $\mathcal{H}$, and as a result commensurate, incommensurate and even chaotic phases may appear.

Our aim is to construct a phase diagram in the space of the reduced force constants $c_1 = f_1/2g_0$, $c_2 = f_2/2g_0$ (normalized to the frequency of the well minimum) and the temperature. In order to do that one should in principle calculate the full quantum mechanical free energy of the system for every periodicity, as a function of temperature. Since this is an almost impossible task, we confine ourselves to a semi–quantum approximation, based on the Gibbs–Bogoliubov inequality [16]. It gives an upper bound to the free energy in question $\mathcal{F}$, by the use of an auxiliary Hamiltonian $\mathcal{H}_0$.

$$\mathcal{F} \leq \tilde{\mathcal{F}} = \mathcal{F}_0 + < \mathcal{H} - \mathcal{H}_0 >_0 . \tag{2}$$

The upper bound to $\mathcal{F}$ is approximated by $\mathcal{F}_0$ (the free energy corresponding to $\mathcal{H}_0$) plus a correction term. The above expectation value is calculated with the known quantum density matrix ρ_0 of $\mathcal{H}_0$.

The trial Hamiltonian $\mathcal{H}_0$ is chosen in the frame of the independent–site approximation, to be a set of displaced harmonic oscillators, with different frequency at each site.

$$\mathcal{H}_0 = \frac{1}{2}\sum_{n,m}\left[-\frac{\hbar^2}{M}\frac{\partial^2}{\partial u_{n,m}^2} + M\omega_{n,m}^2(u_{n,m}-\alpha_{n,m})^2\right]. \tag{3}$$

The density matrix ρ_0 and the free energy $\mathcal{F}_0$ of such a system are known exactly, and therefore the r.h.s of Eq.(2) can be explicitely calculated. The $\alpha_{n,m}$ and $\omega_{n,m}$ are considered as variational parameters and can be obtained by minimizing the free energy.

An optimisation method for the free energy that has proven to be very succesfull is the Monte Carlo Simulated Annealing (MCSA). It has been introduced by Kirkpartick *et al* [17] using the Metropolis Monte Carlo algorithm [18]. It provides an efficient method to determine a global minimum, while with the possibility of climbing over barriers, it avoids being trapped into local minima. The algorithm consists of a basic step, which is used repeatedly in order to simulate a collection of atoms at a given "fictitious" temperature. In each step, an atom is given a small random displacement and the resulting change in energy of the system is computed. The change is accepted unless the energy is higher, in which case the new configuration is accepted, if the probability factor $\exp(-\Delta E/kT)$ is larger than a random number. Here ΔE is the increase in energy from the previous configuration. Thus the system can get out of a local minimum well, and by lowering the "fictitious" temperature, to find the global minimum well.

There are certain parameters involved in this algorithm, as the sequence of lowering the "fictitious" temperature, the number of steps at each temperature, the displacement step, and others, which in practice for finite computer time, must be determined empirically [19], since they strongly depend on the particular form of the function to be minimized. Following the Monte Carlo Simulated Annealing method one proceeds with the Steepest Descent method to locate the exact position of the minimum.

3. Phase Diagram of Periodic Structures and Domain Walls

For the construction of the phase diagram of our model system in the (c_1, c_2, τ) phase space, (τ being the temperature in some convienient units), we have to search at each phase space point for the ground state. For this purpose we compare for each temperature and force constants, the free energies of quasi–one–dimensional periodic structures from 1×1 up to 15×1 and of 2–dimensional ones up to 3×3. The higher 2–dimensional periodic structures were examined by calculating the number of opposite sign first and second neighbours. Depending on the sign of the neighbouring interactions, the vast majority of the 2-d structures have been excluded, and only the ambiguous cases were treated numerically, due to the computing time required. For clarity, we present in

Figure 1 a cross–section of the full phase diagram at constant second neighbour interaction parameter $c_2 = -0.5$. (For other values of c_2 refer to [20]). The notation used to describe one particular configuration is to note the number of consecutive atoms that have the same sign displacement, e.g. a 7×1 structure with signs of displacements as $(+ + - - + + -)$ is indicated as $2^3 1$.

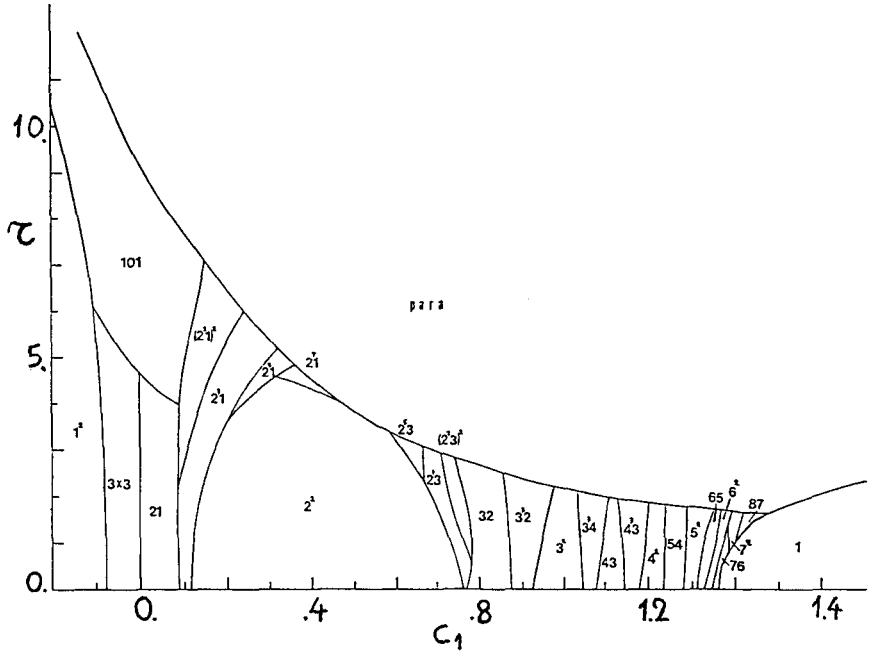

Figure 1 Phase diagram in the τ, c_1 plane for $c_2 = 0.5$.

The great variety of structures observed in this diagram must be attributed to the great competition between the two ordering mechanisms, the on–site potential and the harmonic interactions of opposite sign. At high temperatures and positive first neighbour interactions the ground state is the para–phase, in which the average displacement of all atoms is zero, i.e. they lie above the potential wells of the ϕ^4 potential. It is important to note that an analogous situation in a classical calculation at zero temperature would be unstable.

For both the first and second neighbour interactions being negative, the structures that persist at high temperatures are those that have the highest number of large relative displacements between first and second neighbours. These are the 2×1 and the symmetric 3×1 $(+0-)$.

At lower temperatures let us concentrate on the part of the diagram between the 4×1 and the 1×1 phase. A close look reveals that between two configurations, a third appears with a periodicity the sum of the two. A more quantitative picture of this fact can be obtained by plotting the wavevector $q = 2\pi s/N$ of each state against one of the systems parameters. The number $2s$ accounts for the number of sign changes within one period consisting of N atoms. In the following Figure 2, we are presenting a plot of

s/N versus c_1 for a high temperature. The maximum number of atoms within a period is $N = 30$.

At low temperatures [20], low periodicities occupy large regions of the diagram, but the higher periodicities form a characteristic curve described as a complete devil's staircase. This implies that if there was an infinitely fine grid in c_1 and an infinitely large period searched, then all the rational fractions s/N could be found in the plot. This means that the character of this devil's staircase is complete. At higher temperatures though, and just below the border to the para–phase, the devil's staircase of Fig. 2 appears to have complete and incomplete parts. This is a strong indication of the existence of an incommensurate phase, near the transition to the para–phase. For a more quantitative description of such an incommensurate phase one has to perform discrete mapping techniques [21], which however, are plagued by numerical difficulties since the physically stable states of minimum free energy correspond to unstable orbits of the map.

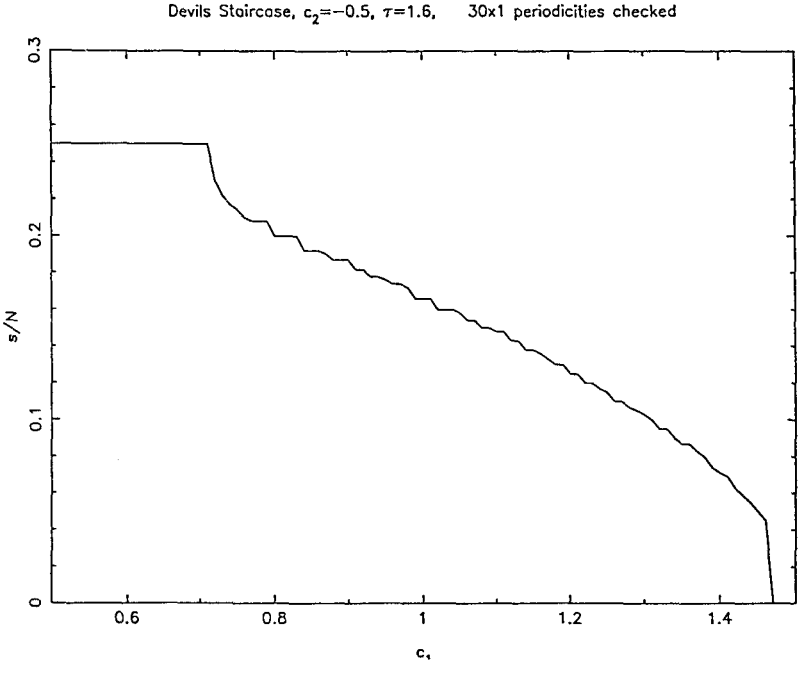

Figure 2 Devil's staircases for fixed $c_2 = -0.5$ and $\tau = 1.6$.

It has been proposed that there is a close relation between the existence of domain wall structures and the incommensurate to commensurate phase transition. Also, it is important to know when and if they can become ground state, in particular on a discrete lattice. On the triangular lattice one can have either 2–d or quasi–one–dimensional walls. The simplest one is the so–called ferro domain wall, of the later kind, that separates two regions with periodicity 1×1, but opposite sign. The method we have studied such formations is the Steepest Descent method, and thus calculated the arrangement of atoms with the lowest free energy.

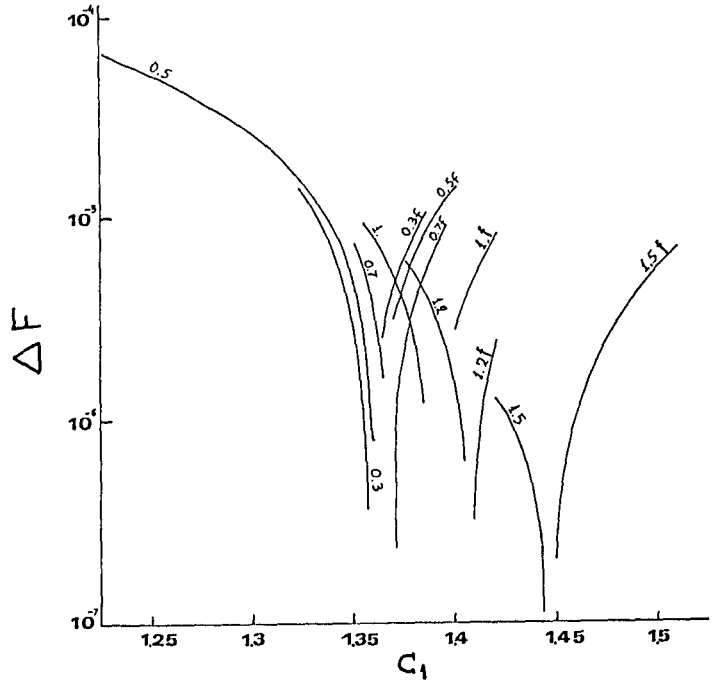

Figure 3 Plot of $\Delta F = (\mathcal{F}_{1\times1}/\mathcal{F}_{wall})-1$ for the ferro wall vs c_1 at $c_2 = -0.5$ and varying $\tau = 0.3, 0.5, 0.7, 1., 1.2, 1.5$. Negative curves are reflected and denoted as "folded" (f).

Let us consider the ferro domain wall free energy in relation to the ferroelectric 1×1 state. It is clear that if the wall free energy becomes lower than the respective 1×1 then the later is no longer the ground state. We shall concentrate in the region between the period 1 and the modulated phases in the phase diagram of Fig. 1. In Figure 3 we make a log–plot of the quantity $(\mathcal{F}_{1\times1}/\mathcal{F}_{wall}) - 1$ as a function of c_1 for various temperatures and fixed c_2. For each temperature there are two curves corresponding to positive and negative (folded) values of the quantity plotted. Moving from higher to lower c_1 values, for the same temperature, the wall free energy becomes lower than 1×1, when the above quantity is positive. This c_1, τ value is near the border line between 1×1 and modulated phases in the diagram. Conversely, when a domain wall becomes energetically favorable it usually means that a modulated phase is the ground state. It was never found, although searched thoroughly a wall being a ground state.

The 2–dimensional walls seem to be better candidates for the ground state due to entropy gain. The pattern shown in Figure 4 is a triangular wall formation, with a 9×9 unit cell, whose short diagonal is a domain wall between two 3×3 structures. Similar to this structure was found to be ground state in an Ising spin system [22]. We have found that such a formation is stable at high temperatures but its free energy is always slightly lower that the 3×3. This leads us to the conclusion that it is a metastable state which could become gound state if additional interactions were important.

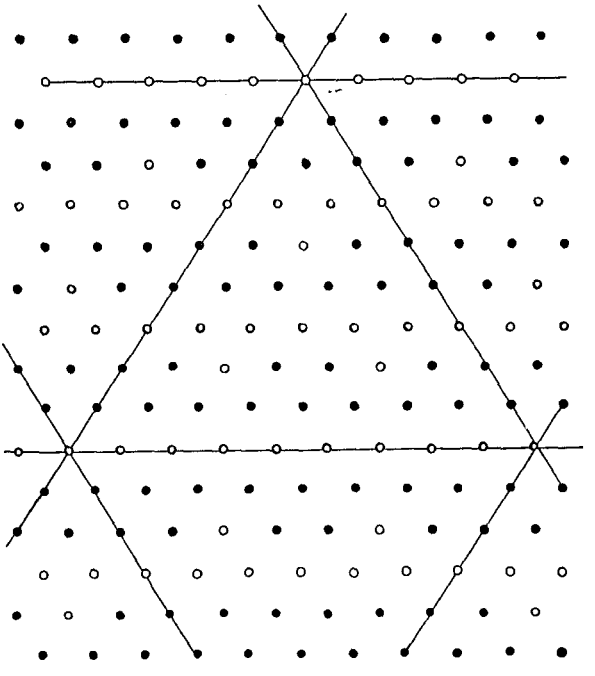

Figure 4 Triangular domain structure (9×9) consisted by the 3×3 asymmetric phase and 2×1.

We have extended the calculations to a two degrees of freedom system and applied it to $LiIO_3$. The phase diagram is in good agreement with the experimentally observed $\alpha \rightarrow \gamma$ transition and previous numerical classical equilibrium calculations. Of course the zero point energy introduces even at $T = 0$ a region in the phase digram, where the para–phase is the ground state [13].

4. Concluding Remarks

In summary, using a semi–quantum variational principle based on the Gibbs–Bogoliubov inequality and the MCSA optimization method, we can obtain the phase diagram for a 2–d model with competitive interactions at finite temperatures. The phase diagram shows some similarities with 1–d ANNNI models except that a number of 2–d structures appear. Sequences of ground states given in the phase diagram have also been observed in $CeSb$ [1] by varying a physical parameter like temperature.

The inclusion of weak longer range interactions does not change the phase diagram, while for strong we can expect significant changes. The degree of changes depends on n_i, i.e. the number of i*th* neighbours with large relative displacements and of course the surface symmetry. This is evident also from lattice gas models of surface reconstruction, where as a function of overlayer coverage, different range interactions come into play and

the corresponding ground state can be very different. Assymetries in the interactions can also influence the ground state. These effects are under investigation along with non convex interplanar nonlinear interactions and interactions that include strain gradient terms.

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