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MONTE CARLO SIMULATION OF MODULATED PHASES

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INTRODUCTION

Modulated phases exist over a wide range of material classes. In general, the term 'modulated phases' refers to the existence of an ordered array of multiple constituent elements of the material. These elements are typically either atoms of different Z or blocks of different phases. A good example of the former are intermetallics, such as the $L1_2$ structure Ni_3Al which consists of four interpenetrating simple cubic lattices (one occupied by Al and the other three by Ni). If we ignore chemical type, this structure is simply face centered cubic. Materials such as SiC are also ordered, but unlike Ni_3Al it exhibits a wide range of phases, some with unit cells as large as 1200 nm on an edge¹. The existence of multiple ordered structures of the same material is known as polytypism and has been observed for such disparate materials as metal iodides, micas, chalcogenides, opal, and graphite¹. Different polytypes are often related to each other by the presence of periodic arrays of planar defects such as stacking faults or antiphase boundaries. Recent work² has suggested that spin models, such as the Axial Next Nearest Neighbor Ising (ANNNI) model provide a reasonable description of polytypism. In two dimensions, this model exhibits³ both ferromagnetic and ordered (alternating two spin wide stripes - |||||) phases at low temperatures. In addition to a low temperature ferromagnetic phase, the three dimensional ANNNI model has a large number of different ordered phases at different temperatures and magnitudes of the frustration parameter.

In addition to exhibiting a number of different ordered crystal structures, the Ni-Al system also shows modulation of the microstructure in the two phase regime. This modulation consists of a relatively regular array of cuboidal, $L1_2$ Ni_3Al particles, separated by regions of Ni with Al in solution. Application of a uniaxial external stress can convert these arrays of cuboidal particles to arrays of needle-like or plate-like particles⁴. This change in the morphology on application of an external stress is due to the elastic anisotropy of the particles versus the matrix

and occurs by the diffusional linking of the cuboidal particles. Since the modulation, in this case, is due to the presence of elastic interactions between precipitates, no spin model has yet been applied to this type of modulation.

In this paper, we present Monte Carlo simulation results for the formation of modulated phases in the framework of the two dimensional ANNNI model with a nonconserved order parameter⁵. This work complements the earlier studies of Kaski, et al.⁶ by examining a different, wider area of parameter space and temperature. Like Kaski, et al., we find⁵ that for certain temperatures and values of the frustration parameter, κ , ordered domains form quickly and the correlation length grows as the square root of time. However, there exists a range of κ for which a quench from high to low temperature results in the formation of a metastable glassy phase. In addition to the ANNNI model study, preliminary results are presented on a newly developed model which exhibits phase modulation due to the presence of elastic interactions between the different phases and with an externally applied stress.

2-d ANNNI MODEL

Simulation Procedure

In two dimensions, the ANNNI Hamiltonian may be written as:

$$H = -(1/2) \sum_{i,j} J_0 S_{i,j} S_{i\pm 1,j\pm 1} + J_1 S_{i,j} S_{i\pm 2,j} \quad (1)$$

where $S_{i,j}$ is the spin orientation (± 1) on site i,j , and J_0 and J_1 are constants. It is convenient to normalize the ANNNI Hamiltonian by the nearest neighbor coupling constant, J_0 , such that the site energy, $E_{i,j}$, is:

$$E_{i,j} = -S_{i,j} [S_{i\pm 1,j\pm 1} + \kappa S_{i\pm 2,j}] / 2 \quad (2)$$

where $\kappa = J_1/J_0$. The temperature, T , has been normalized by J_0/k_B , where k_B is Boltzmann's constant. The phase diagram for the 2-d ANNNI model is well established^{3,7} and is indicated in fig. 1. The ferromagnetic phase is denoted by F, the paramagnetic phase by P, the incommensurate phase by I, and the modulated phase by <2>, indicating that it corresponds to alternating stripes of two up and two down spins oriented perpendicular to the axial direction (i.e. the i direction).

In the present study, we perform⁵ Monte Carlo simulation of the evolution of the ANNNI model quenched from $T \gg T_c$ to a finite temperature, $0.02 \leq T \leq 0.4$, for $0.5 \leq \kappa \leq 20.0$. Simulations were also performed for $\kappa < 0.5$, however those results are presented elsewhere⁵. The simulations were performed with nonconserved dynamics with a random updating scheme. The transition probability employed was: $W = [1 + \tanh(\delta E/2T)]/2$, where δE is the change in energy of the system due to an attempted spin flip. All of the simulations were performed on $N = 200 \times 200 = 40,000$ site square lattices and the data was averaged over at least 5 simulations.

The simulations were analyzed by monitoring the magnitude of the structure factor in the axial (i) and perpendicular (j) directions. Since the excess energy of the system, ΔE , (i.e., the instantaneous energy minus the ground equilibrium energy) scales inversely with the correlation length⁸, the time dependence of the excess energy was also monitored. The equilibrium energy was determined as a function of κ from 2000 MCS (1 MCS is defined as N microtrials) simulations starting from the appropriate $T=0$

Fig. 1. The 2-d ANNNI phase diagram, after Beale, et al.⁷

Fig. 2. The temporal evolution of the ANNNI microstructure following a quench from $T > T_c$ to $T = 0.02$ for $\kappa = 20.0$. The dark and light regions correspond to spin up and down, respectively.

Fig. 3. The time dependence of the structure factor in the direction (a) parallel and (b) perpendicular to the axial direction for the microstructure of Fig. 2. The curves correspond to 400, 300, 200, 100, and 0 MCS, in order from top to bottom.

ground state.

Quenches With $\kappa > 1$

The temporal evolution of the ANNNI microstructure following a quench from $T > T_c$ to $T = 0.02$ for $\kappa = 20$ is shown in Fig. 2. The $\langle 2 \rangle$ phase, which consists of two spin wide stripes, forms rapidly and the resultant domain structure coarsens with time. Unlike in the 2-fold degenerate Ising model, the $\langle 2 \rangle$ phase in the ANNNI is 4-fold degenerate and hence has domain wall vertices. The orientation of the domain walls in the $\langle 2 \rangle$ phase region depends on the relative energies of the different types of domain walls and their relative orientation. For $\kappa > 1$, the energies of the domain walls are such that the domain walls lying in the axial direction are lower in energy than those in the perpendicular direction. This asymmetry is manifested in the microstructures of Fig. 2, where the domain walls are seen to lie preferentially in the low energy, axial direction.

Figure 2 shows that the model has both 3- and 4- fold vertices, like the 4-fold degenerate Potts and clock models, respectively. The 4-fold vertices are such that as one circumscribes the vertex, the 4-spin pattern of the $\langle 2 \rangle$ phase is phase shifted by one spin at each domain wall. This leads to two types of 4-fold vertices having either a clockwise or counter-clockwise vorticity. It is convenient to describe the properties of the vertex in the framework of dislocation theory in the sense that a Burger's circuit around the vertex yields a closure failure which is associated with an extra half-stripe either pointing up or down (depending on the sign of the vorticity). This extra half-stripe is akin to the extra half-plane of atoms associated with an edge dislocation. 3-fold vertices are equivalent to partial dislocations separated by stacking faults.

The asymmetry between the axial and perpendicular directions is seen clearly in Fig. 3 where we show the time dependence of the structure factor. In the axial direction, a peak at $q = 1/4$ forms at early times and then slowly sharpens. The width of the peak indicates the $\langle 2 \rangle$ phase domain size. On the other hand, one should expect a peak at $q = 0$ in the structure factor in the perpendicular direction. The lack of a pronounced peak at $q = 0$ is attributed to the preponderance of domain walls in the axial direction which tend to destroy long range order in the perpendicular direction.

The temporal evolution of the correlation length is indicated in Fig. 4a where we plot ΔE vs time for quenches to $T = 0.02$ at $1 \leq \kappa \leq 20$. The slopes of these curves indicate that the correlation length is increasing as $t^{1/2}$ for all κ in this range. This result is consistent with that observed in the 4 state Potts and clock models. However, as pointed out by Kaski, et al.⁶, the domain coarsening is anisotropic in that the growth in the axial and perpendicular directions occur at different rates. Varying the temperature to which the model is quenched (Fig. 4b) has relatively little effect on the domain growth kinetics.

Quenches With $\kappa \leq 1$

When the system is quenched from $T > T_c$ to $T = 0$ for $1/2 \leq \kappa \leq 1$, microstructures such as those shown in Fig. 5 typically result. Although the temperature and κ for the simulation shown in this figure are well within the ordered $\langle 2 \rangle$ phase region, the characteristic two spin wide strip pattern clearly does not form. Instead we observe a disordered phase which does not appear to be evolving toward the equilibrium $\langle 2 \rangle$ state. Comparison of the spin configurations at early and late times show little difference. There does, however, appear to be an extremely slow

Fig. 4. The time dependence of the excess energy, ΔE , following a quench from $T \gg T_c$. (a) Quench to $T=0.02$ with $\kappa = 1$ (squares), 1.2 (circles), 2.0 (triangles) and 20 (+s). (b) Quench to $T=0.02$ (squares), 0.1 (circles), 0.2 (triangles), 0.3 (+s), and 0.4 (x's) at $\kappa=1$.

Fig. 5. The temporal evolution of the ANNNI microstructure following a quench from $T \gg T_c$ to $T=0.02$ for $\kappa=0.8$.

Fig. 6. The time dependence of the structure factor in the (a) axial and (b) perpendicular direction for a quench to $T=0.02$ at $\kappa=0.6$. The curves in each figure correspond to 2000, 1500, 1000, and 500 MCS, in order from top to bottom.

increase in the correlation length with time. Although the equilibrium $\langle 2 \rangle$ phase does not appear, short range order clearly exists. The presence of short range order with no accompanying long range order is a common feature of glassy systems. The microstructures quenched into this region of the phase diagram are nearly indistinguishable from those quenched to low temperature for $0 \leq \kappa \leq 1/2$, where the equilibrium state is ferromagnetic.

The time dependence of the structure factor for a quench from $T > T_c$ to $T = 0.02$ at $\kappa = 0.6$ is shown in Fig. 6. The structure factor in the axial direction shows only a very small amplitude for $q > 1/4$ and a larger amplitude in the range $0 < q < 1/4$. While the amplitude is largest around $q = 1/4$ (as is expected for the $\langle ? \rangle$ state), it is interesting to note that an increased amplitude is also present near $q = 0$. This shows the remarkably strong competition between the F and the $\langle 2 \rangle$ phases, even when κ is well within the $\langle 2 \rangle$ state phase field. In the perpendicular direction, the model clearly exhibits ferromagnetic tendencies, as indicated by the peak near $q = 0$. The amplitude of this peak appears to increase slowly with time, although no clear $\langle 2 \rangle$ or F ordering is apparent in the microstructure. The temporal evolution of the correlation length is indicated in Fig. 7a for quenches with $0 \leq \kappa \leq 1$. In the range of κ between $1/2$ and 1 , the growth is sub-power law, indicative of a kinetically frozen system.

Increasing the temperature to which the quench was performed leads to the formation of the equilibrium phase for $1/2 < \kappa < 1$ (see Fig. 7b). For $T > 0.2$ at $\kappa = 0.6$ and $T > 0.1$ at $\kappa = 0.8$, the $\langle 2 \rangle$ state appears to form and exhibits power law kinetics within the 2000 MCS simulations. However, the $\langle 2 \rangle$ state does appear even at lower temperature given sufficient time (see Fig. 7c). As for all true glasses, the glass transition temperature is only defined once the time scale of observation is set. The existence of a transition temperature is also seen by consideration of the structure factor after a 2000 MCS aging of the system following quenches to different temperature at $\kappa = 0.6$ (Fig. 8). As with the kinetics (Fig. 7b), a transition is observed for $T > 0.2$.

The transition from defected $\langle 2 \rangle$ phase formation and growth to glass formation that occurs at $\kappa = 1$ can be understood in terms of the growth of a single stripe. For an individual stripe to grow in the perpendicular direction, its tip must be able to advance through all possible environments presented by the quench from high temperature. The most unfavorable configuration that the tip must be able to grow through occurs when, say, the up spin strip encounters a region of down spins at its tip. The energy required for such growth is proportional to $1 - \kappa$. Therefore only for $\kappa > 1$ can the $\langle 2 \rangle$ phase form following a quench to $T = 0$. For $1/2 < \kappa < 1$, the $\langle 2 \rangle$ phase can form only by thermally activated growth. The required thermal activation increases with decreasing κ . The glass transition temperature is, therefore, expected to scale linearly with $1 - \kappa$. The magnitude of the transition temperature also depends on the duration of the observation. Recognizing that the time required for the formation of the equilibrium phase scales as the exponential of the energy barrier over temperature, we expect the glass transition temperature to scale inversely with the logarithm of the observation time. This relative insensitivity of the transition temperature to the duration of the observation is another hallmark of a glass.

MODULATED PHASES - ELASTIC INTERACTIONS

Simulation Procedure

The model employed in simulating a two phase system with elastic

Fig. 7. The time dependence of the excess energy following a quench from $T > T_c$. (a) The curves correspond to a quench to $T=0.02$ at $\kappa=0$ (squares), 0.2 (circles), 0.4 (triangles), 0.6 (+s), 0.8 (x's), and 1.0 (diamonds). (b) Quenches at $\kappa=0.4$, and $T=0.02$ (squares), 0.1 (circles), 0.2 (triangles), 0.3 (+s), and 0.4 (x's). (c) Same as (a) but for 20,000 MCS for $k=0.4$ (upper) and 0.6 (lower).

Fig. 8. The time dependence of the structure factor in the (a) axial and (b) perpendicular directions for a quench to $T=0.02$ at $\kappa=0.6$. The different curves in each figure correspond to 2000, 1500, 1000, and 500 MCS, in order from top to bottom.

interactions is based upon an Ising phase description with a finite element elastic analysis. The Hamiltonian for the model may be written as:

$$H = \sum_{i,j} -(J_0/2) S_{i,j} S_{i\pm 1, j\pm 1} + E_{el}(S_{i,j}, S, \sigma_{ext}) \quad (3)$$

where J_0 is a positive constant, $S_{i,j} = \pm 1$ indicates the phase of site i,j , and $E_{el}(S_{i,j}, S, \sigma_{ext})$ is the elastic energy of the system associated with site i,j , which depends on all of the other spins in the system (S) and the externally applied stress σ_{ext} . The first term in Eq. 3 accounts for the energy of the phase 1/phase -1 interface. The simulations were performed on square lattices using spin-exchange (Kawasaki) dynamics with the same transition probability as employed in the ANNNI model simulations.

In performing the elastic analysis we allow one phase to have a misfit with respect to the other and the two phases may have different elastic constants (cubic symmetry is assumed). Since a finite element calculation must be performed for each spin exchange attempt, it is impractical to evaluate the elastic energy over the entire Monte Carlo grid. Instead, once the two nearest neighbor sites to be exchanged are identified, a small grid (between 6x6 and 18x18) centered on these sites is chosen on which a finite element analysis is performed before and after the attempted exchange. The nodes of the finite element grid are the same as the lattice sites of the Monte Carlo grid. The finite element calculations were performed using simplex grid elements and the finite element code adopted was that described in Ref. 9. Although the elastic energy depended sensitively on grid size, the change in energy due to a spin exchange showed less than a 1% variation on going from the 6x6 to 18x18 finite element grid size. Since each finite element calculation was performed on a sub-grid, the elastic effect of the material outside the sub-grid was included by applying stresses to the surface of the sub-grid equal to that obtained by averaging over the entire system. In effect, these stresses are simply the external stresses (i.e., $\langle \sigma \rangle = \sigma_{ext}$).

Stress Dependence of Particle Shape

Elastic theory predicts that the equilibrium shape of a particle depends on the relative modulus of the particle to the matrix, the misfit of the particle, and the nature of the applied stress¹⁰. Ignoring surface energy Pineau¹¹ has produced a map of stable particle shapes as a function of the appropriate elastic parameters. In order to provide a preliminary test of the simulation technique, we have performed a series of simulations to compare with these results¹¹. The spin configuration was initialized by assigning $S=-1$ to four sites arranged in a square in a uniform background of $S=1$. An external stress was then applied and the particle shape was monitored during the simulation. A direct comparison between the shapes of the particles determined in the present study and those predicted from elastic theory are shown in Fig. 9. Clearly, excellent correspondence is found across the whole of the map, thereby indicating that the approximate finite element elastic calculations are reproducing the exact (within linear elasticity) theoretical results.

The interaction between particles can modify the particle shapes determined in the single particle simulations. In order to investigate this effect we initialized the spin configuration to consist of two particles (4-spin, square particles; $E_p/E_m = 0.8$, where E is Young's modulus of the particle and matrix, respectively) in an otherwise uniform matrix. An external stress was then applied and the system was allowed to equilibrate at $T=0$ (again with zero surface tension). The resultant

Fig. 9. Equilibrium particle shapes in the absence of surface tension. S, P, and N correspond to spheres, plates and needles after Ref. 11. The open circles, filled squares, and filled circles correspond to spheres, plates, and needles determined by simulation. Note σ and δ correspond to the applied stress and particle misfit, respectively.

Fig. 10. Particle shape dependence on spacing and stress. The circle, open and closed squares correspond to spheres, plates and needles.

Fig. 11. The temporal evolution of the microstructure following a quench from $T > T_c$ to $T = 0$ with $E_p/E_m = 1.2$, $\delta = 0.0005$, and a negative stress.

Fig. 12. Stress dependence of the microstructure starting from a regular array of particles (center).

particle shapes as a function of applied stress and the interparticle separation, d , are indicated in Fig. 10. The influence of the second particle is clearly to bias the particle away from the equiaxed and towards elongated shapes. This effect becomes stronger as the particle separation decreases.

The evolution of the microstructure following a quench from $T > T_c$ to $T = 0$, with an applied stress is shown in Fig. 11. Although no kinetic data is currently available, the characteristic striped morphology is clearly developing and the order increases with time. However, only short range order is visible and no well defined domain structure is evident. This type of ordering appears to be similar to that seen in the evolution of the glass-like phase observed in the ANNNI model. In making a comparison, it is important to note that in this model the evolution is controlled by spin-exchange dynamics, instead of the spin-flip (conserved) dynamics employed in the ANNNI study.

Finally, we note that even when the structure is completely ordered at $T < T_c$, application of an external stress creates a rafted (elongated) structure (see Fig. 12). Such a change in order may be surprising in light of recent nonconserved order parameter studies where highly ordered metastable states are found to be relatively stable¹². However, in the present case interactions are relatively long ranged compared to the interactions assumed in those nonconserved order parameter studies.

FUTURE WORK

Additional work is currently underway to examine the kinetics of the ordering processes in the framework of the elastically modulated phase model. Since this model employs a finite element technique for the evaluation of the elastic energy, it is easily extendible to the case of elastic anisotropy and more than two elastically distinct phases.

Although the 2-d ANNNI model exhibits a modulated phase within the framework of a relatively simple Hamiltonian, the 3-d ANNNI model exhibits an extremely wide variety of modulated phases. Therefore, it may be expected that the glass forming tendency of the 2-d model may be even more pronounced in 3-d. Future work aimed at providing a clearer understanding of this metastable, glass-like phase and a search for similar phases in other simple spin models is currently planned.

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