Monte Carlo Simulation of Thermally Induced SmCP Phases of Bent-core Liquid Crystals

A Dissertation Submitted to the University of Hyderabad
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in
Computational Techniques
By

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UNIVERSITY OF HYDERABAD
सा विद्या या विमुक्तये

To

My Parents and Family

DECLARATION

I, GUMMULA SHWETHA, hereby declare that this Dissertation entitled "**Monte Carlo Simulation Of Thermally Induced SmCP Phases Of Bent-core Liquid Crystals**" submitted by me under the guidance and supervision of Prof. V. S. S. Sastry is a bonafide research work. I also declare that it has not been submitted previously in part or in full to this University or any other University or Institution for the award of any degree or diploma.

(GUMMULA SHWETHA)
Reg. No. 09PCMT10.

Date:
Place: Hyderabad

CERTIFICATE

This is to certify that the Dissertation entitled "**Monte Carlo Simulation Of Thermally Induced SmCP Phases of Bent-Core Liquid Crystals**" submitted by **GUMMULA SHWETHA** bearing Reg. No. 09PCMT10 in partial fulfillment of the requirements for the award of Master of Technology in Computational Techniquesis a bonafide work carried out by her under my supervision and guidance.

The Dissertation has has not been submitted previously in part or in full to this or any other University or Institution for the award of any degree or diploma.

Prof. V. S. S. Sastry
Thesis Supervisor.

Dean,
School of Physics,
University of Hyderabad.

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GUMMULA SHWETHA

Preface

In most of the ferroelectric liquid crystal displays, chirality at the molecular level develops usually a ferroelectric order in the system. In recent experiments a different mechanism was developed to realize the macroscopic chirality in a system of achiral bent-core molecules. In such cases the combination of polar order and tilt breaks the symmetry of the layer giving rise to chiral structure though they are formed by achiral molecules. This unique feature of bent-core structure has attracted more researchers into experimental and theoretical studies. It has been observed in the experiments that one could induce phase transitions between chiral and antichiral structure with an electric field. A microscopic theoretical model has recently been developed to explain the chiral switching induced by an electric field. Motivation of our present work is to investigate this Hamiltonian model to observe possible thermally induced phase transitions spanning a subspace of the parameters of this Hamiltonian.

In this disertation we report on such results based on Monte Carlo We simulation. This model involves three interacting variables P, χ, and θ with external field coupling to P. This model assumes ferro-magnetic coupling of the three variables within the layers. Inter-layer couplings of the chirality is ferro-magnetic nature, while it is antiferro-magentic in nature for polar and tilt, with coupling strengths C_χ, C_P, and C_θ, respectively. We examined the thermal behavior of this model in the presence of a strong field and strong coupling among the three variables, by performing Monte Carlo simulations on a 10x10x10 system. In this work, we focus on the subspace of C_χ and C_θ, looking for changes in the chiral state of an anticlinic system on cooling, in the presence of significant polarization due to the applied field. We present the result of our simulations carried out as a function of temperature, examining the role of the interlayer couplings of the different order parameters in favouring the ground state.

Contents

1

Introduction to liquid crystals

The three most common states of matter are solids, liquids, and gases. For example, water is a solid below 0^o C, liquid between 0^o C and 100^o C, and a gas above 100^o C. The difference between solids and liquid is that the molecules in the solids are ordered where as in liquid they are not ordered. The order in the crystal is both positional and orientational. In other words, the molecules are constrained to point only certain directions and to be only in certain positions with respect to each other. In liquids, the molecules do not have any positional or orientational order. The direction the molecules point and their positions are random. A transition between the different states of matter is generally induced by a change in temperature. Certain organic materials do not show a single transition from solid to liquid, but rather a cascade of transitions involving new phases. The mechanical and symmetry properties of these phases are intermediate between those of liquids and crystals. One type of such phases are grouped together, and are called liquid crystals.

In 1888, an intermediate state of matter between the liquid and solid was discovered by Austrian botanist Friedrich Reinitzer. He observed two melting points while heating cholesteryl benzoate. The cloudy liquid he observed between two melting points was first recorded observation of liquid crystalline phase. These phases are also called mesophases [1-5]. Liquid crystals are more ordered than liquids and less ordered than crystals. They share the properties between those of a conventional liquid and those of a solid crystal. For instance, liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way. An essential requirement for the liquid crystal phases to occur is that the molecules must be highly geometrically anisotropic like rodlike, disclike or banana shaped molecules. Depending on the detailed molecular geometry, the system may pass through the one or more mesophases before it is transformed into an isotropic liquid. The presence of anisotropic molecules in liquid crystalline material amounts to their having anisotropic physical properties, which depend on the direction of measurement. Refractive index, dielectric constant, diamagnetic susceptibilities and viscosity are examples of physical properties that can be anisotropic.

In the crystalline solid state, the arrangement of molecules has a regularly repeating pattern in all directions. The molecules are held in fixed positions discounting thermal motions by intermolecular forces. With the increase in the temperature of a substance molecules vibrate. Eventually, these vibrations overcome the intermolecular forces that hold the molecules in place, and the molecules start to move away from their mean values. In the liquid state, this motion overcomes the intermolecular forces which maintain a crystalline state, and the molecules move into random positions. In materials that form liquid crystals, the intermolecular forces in the crystalline solid are not the same in all directions. In some directions the forces are weaker than in other directions. As such a material is heated, the increased molecular motion overcomes the weaker forces first, but its molecules remain bound by the stronger forces. This produces a molecular arrangement that is random in some directions and regular in others. The molecules are in layers structure, but within each layer, they are arranged in random positions.The arrangement of molecules in solid, liquid and liquid crystal are shown in figure1.

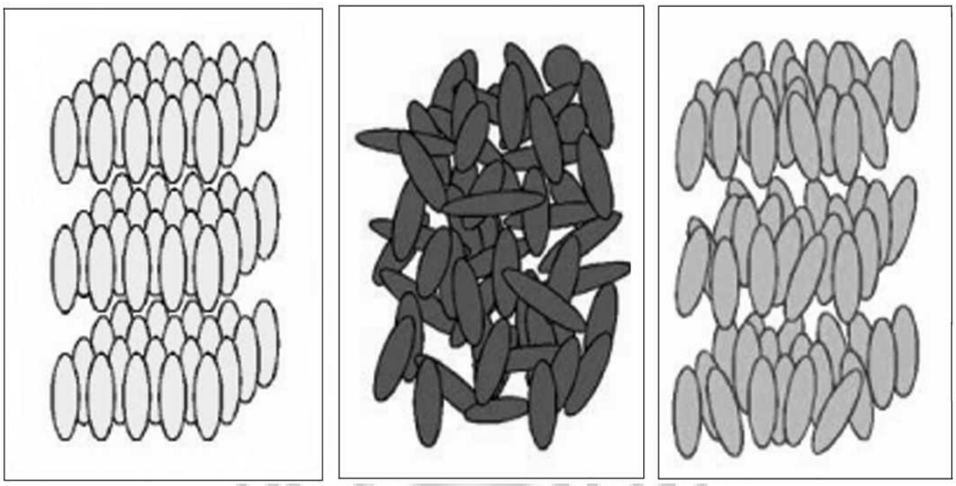

Figure 1.1: Schematic representation of molecular arrange of solid, isotropic liquid and liquid crystal

1.1 Types of liquid crystals

Liquid crystals can be divided into thermotropic, lyotropic and metallotropic phases. Thermotropic and lyotropic liquid crystals consist of organic molecules. Thermotropic liquid crystals exhibit phase transitions on varying the temperature. Lyotropic liquid crystals exhibit phase transitions as a function of both temperature and concentration of molecules in a solvent (typically water). Metallotropic liquid crystals are composed of both organic and inorganic molecules; their liquid crystal transition depends not only on temperature and concentration, but also on the inorganic-organic composition ratio. The present work deals with thermotropic liquid crystals.

The fundamental requirement of any substance to exhibit a liquid crystalline phase is shape anisotropy of the constituent molecules. On the basis this property, three types of thermotropic liquid crystals are typically realized.

1. Calamitic liquid crystals: formed by rod like molecules.
2. Discotic liquid crystals: formed by disk like molecules.
3. Banana liquid crystals: formed by banana shaped or bent core molecules.

Friedel classified the thermotropic liquid crystals made of rod-like molecules three classes based on the symmetry of the medium into nematics, cholesterics and smectic phases.

1.1.1 Nematic phase

The simplest thermotropic liquid crystalline phase is the nematic phase. The nematic liquid crystal has a high degree of long range orientational order, but no long range positional order. Usually, nematic liquid crystals made of rod-like molecules exhibit uniaxial cylindrical symmetry. In nematic phase the molecules are free to move in all directions, but on the average they keep their long axes locally parallel. In these mesophases, the average direction of molecular orientation is called director denoted by a headless vector $\hat{\mathbf{n}}$. As there is no long-range correlation in the centres of mass of molecules, nematic liquid crystals are fluid and flow like ordinary liquids. For the nematic phase formed by apolar molecules, the phase is indistinguished with the transformation $\hat{\mathbf{n}} \rightarrow -\hat{\mathbf{n}}$ i.e., molecules are equally pointing up and down. Nematics can be easily aligned by an external magnetic or electric field. This makes them extremely useful in liquid crystal display applications.

To specify the amount of orientational order a in nematic liquid crystal phase an order parameter is defined. It measures to what degree the molecules are aligned with the director. This is formulated as the average of the second Legendre polynomial.

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$$

Here the brackets denote a thermal average and θ is the angle between each molecule in the sample and the director. If the molecules are well aligned with the director then $S = 1$ and if the molecules are randomly oriented about $\hat{\mathbf{n}}$ then $S = 0$ i.e. isotropic phase. Higher the order parameter more

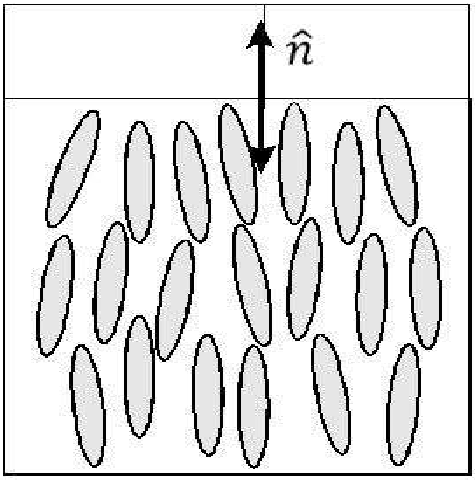

Figure 1.2: Schematic representation of molecular arrangement in a nematic liquid crystal, where $\hat{\mathbf{n}}$ represents the director.

ordered is the nematic phase.

1.1.2 Cholestric phase

Chirality

Chiral molecules are the molecules which are not super imposable on their own mirror images. The most illustration object having both the hands. Achiral molecules are the molecules that are identical to their mirror image. Chiral molecules lack an internal plane of symmetry. Achiral molecules show C_{2h} symmetry whereas chiral molecules show C_2 symmetry.

The chiral nematic phase exhibits chirality (handedness). This phase is often called the cholesteric phase because it was first observed for cholesterol derivatives. Only chiral molecules (i.e., those that lack inversion symmetry) can give rise to such a phase. In cholesteric phase the director rotates in helical fashion about an axis perpendicular to the director shown in figure 3.

The important characteristic of the cholesteric mesophase is the pitch. The pitch of the chiral nematic phase is the distance along the helix over which the director rotates by 360^o. However the structure repeats itself every half pitch due to equivalence $\hat{\mathbf{n}}$ and - $\hat{\mathbf{n}}$. The pitch of the chiral nematic phase can be as short as 100 nm. The pitch can be increased with the mixing of two optical isomers in different proportions. In racemic mixtures (equal parts of each optical isomer) pitch is infinite i.e. nematic phase.

Chiral nematic phase selectively reflects light of wavelengths equal to the pitch length, so that a specific colour will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum. This effect could be temperature sensitive, resulting in thermally induced changes in the reflected light. Pitch length of the mesophase can increased or decreesased with temperature.

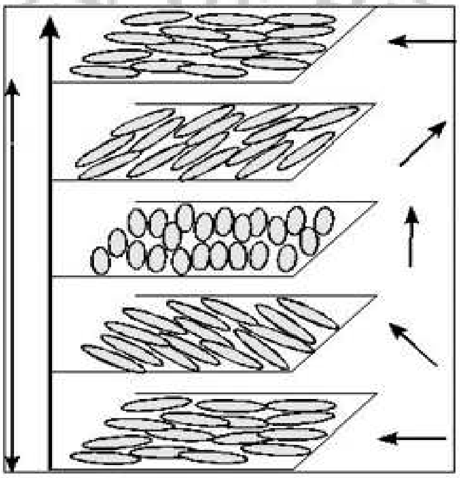

Figure 1.3: Schematic representation of molecular arrangement in cholesteric liquid crystal phase. The short arrows indicate continuous rotation of director along long axes

1.1.3 Smectic phase

In smectic A phases, in addition to the orientational order, there is a positional order and centres of mass are arranged in layers. Within the layers, the centres of gravity of the molecules are random i.e. no positional order within the layers. Despite this partial ordering of the molecular positions, the substance still flows, and is therefore a liquid. In these phases director is perpendicular to the layers. In smectic C phases, the molecules are arranged in layers and director is tilted with respect to layer normal. The arrangements of molecules in smectic A and smectic C phases are shown in figure 4.

The chiral smectic C phase (SmC*) exhibits a helical structure. In contrast to the cholesteric phase, the subsequent layers with the tilted molecules are slightly rotated with respect to each other. In a typical SmC* material the director rotates on the tilt cone about 1^o from one layer to the next. In these materials, the orientation of the tilt can be influenced by an electric field, and therefore this phase can be used in displays that in principle can be switched much faster than conventional nematic displays. When compared to a SmC phase which has C_{2h} symmetry, the symmetry of the SmC* phase is further reduced to C_2 and the phase is therefore necessarily polar. Depending on the

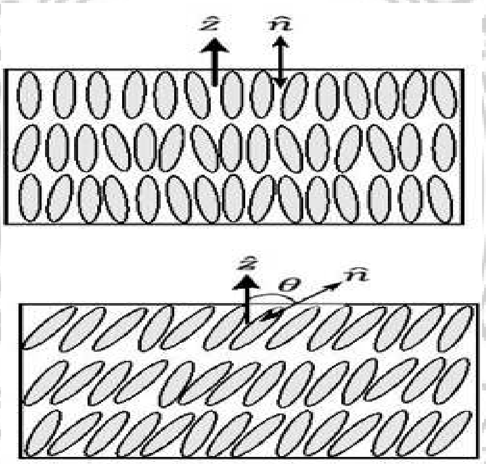

Figure 1.4: Schematic representation of molecular arrangement in Smectic A and Smectic C phases

chirality of the molecule the helix can be left-handed or right-handed. The symmetry of the smectic C* phase allows them to be polarized and hence this phase is also referred to be a ferroelectric liquid crystal.

A series of transitions among different mesophases could be observed as the temperature is increased. The equilibrium structure is determined by two competing factors. The energy part which favours the ordered phase and the entropic part that favours the randomness. The ordered phase is stable at very low temperatures. On increasing the temperature it gradually loses order until an isotropic phase is obtained. In most of the liquid crystals the different phases exist in fixed sequence with increasing the temperature. The general sequence is as follows:
Crystalline solid - smectic H - smectic K - smectic E - smectic G - smectic J - smectic F - smectic B -smectic I - smectic B - smectic C - smectic A Nematic - isotropic liquid.

There is no single compound in which the complete sequence is observed. In most of the compounds one or more intermediate phases may absent. The sequence of the transition could then be obtained simply by omitting the phases that are absent.

One of the major areas of interest is the ferroelectric liquid crystals because of their potential applications in liquid crystal displays (LCDs). In most of the ferroelectric LCDs, chirality at the molecular level is exploited to develop a ferroelectric order. In this contest the present work is based on the possibility of formation of ferroelectric liquid crystals by achiral bent core molecules. With the discovery of bent-core molecules, also called banana shaped molecules, this field has received fresh impetu.We now present a brief introduction to this type of systems.

1.2 Banana shaped molecules

Banana shaped compounds become new subfield in the liquid crystal area because of their extraordinary properties. These banana shaped liquid crystals are also known as bent core molecules [6-7]. The bent core molecules are interesting particularly from the viewpoint of polarity and chirality. Usually, these compounds are composed of a bent central aromatic part and two flexible tails shown in figure 5.

Even though bent liquid crystals are known much earlier, they did not attract much interest until a new mesogenic compounds with banana shaped molecular structure was synthesized by Matsunaga [8] more recently. One of the molecules, 1, 3-phenylene bis[4-(4- n-octyloxyphenyliminomethyl) benzoate], opened a new era of liquid crystal science. Before the discovery of polar switching in this molecule they did not realize the physical importance of this molecule. Niori [9] first observed ferroelectricity in smectic phases which were formed from achiral bent core molecules. Several other groups have reported banana shaped molecules which exhibit ferroelectric properties.

Most banana phases that have been characterized until now do not show many similarities with the liquid crystalline mesophases formed by calamatic (rodlike) molecules. These new mesophases are now known as B_n phases, with subscript n indicating the sequence of discovery of different phases.
Interesting aspect of this class of bent-core molecules is that these exhibit polar and chiral properties such as antiferro and ferroelectricity, although they are composed of achiral molecules. For many years the general perception was that such properties could arise only from tilted smectic phase composed of chiral molecules, this is not because of breaking of mirror symmetry but result from steric effect.

At an early stage of the discovery of the bent-core liquid crystals, seven

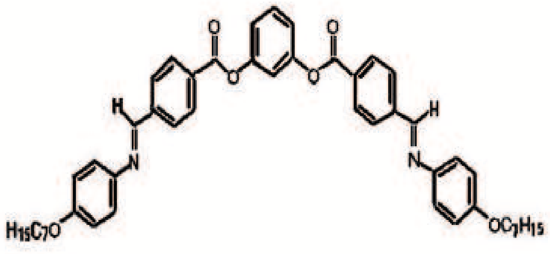

Figure 1.5: Schematic of bent-core molecules

mesogenic phases were identified and simply designated as B1-B7, where "B" stands for bent, banana, bow, or boomerang. All these phases together with another phase discovered later (B8) are called "banana phases". Two of the most well studied, B2 and B7, are smectic phases consisting of stacks of fluid layers with some internal tilt order, and are special because they can be switched with an electric field. These phases, different from conventional phases, are found are in calamatic liquid crystals.

1.3 Ferroelectric liquid crystals formed by achiral bent-core molecules

1.3.1 Ferroelectricity

Liquid crystal is said to be ferroelectric if it has permanent polarization in the absence of an electric field i.e. molecules have to exhibit spontaneous polarization. In ordinary liquid crystal phases like nematic ($D_{\infty h}$), smectic A ($D_{\infty h}$), smectic C (C_{2h}) symmetry is so high, and the mirror plane prevents the occurrence of polarization. If we introduce chiral molecule in the medium its presence removes the mirror symmetry and we are left with the two fold rotation axis only C_2. The C_2 axis is now a possible polar axis. Mayer [10-11] concluded that smectic C* is spontaneously polarized along C_2

direction which is parallel to the layers and perpendicular to the tilt plane.

In the chiral smectic C phase, due to helical arrangement the director rotates from layer to layer. The polarization vector will also precess resulting in complete cancellation of the polarization on a macroscopic scale. With the applied field all the molecules orient in the same direction so smectic C* phase switches to ferroelectric state. The main advantage of these smectic materials is they have fast switching behavior compared to conventional nematic phase. In addition to the polar order we also have tilt order in the case of smectic C*. If the direction of polarization vector and tilt are the same in the layers then we have ferroelectric state. If direction of polarization vector is the same and tilt varies in opposite direction from layer to layer then the resultant phases give rise to a possible antiferroelectric structure.

In the above case we have seen symmetry breaking through combination of chiral and tilt (chiral + tilt = polar). Apart from this, symmetry of the phase can also be broken by the combination of tilt and polar order (tilt + polar = chiral); e.g., it was found in banana shaped molecules. In other words, chirality can be observed though they are formed by achiral molecules, and this concept is elaborated below. With the introduction of banana shapes, the molecules can also rotate along their along axes (bow). In a system of banana shaped molecules one can order the system into ferroelectric and anti ferroelectric state based on the direction of polarization. Polar switching not only takes place due to rotation of the director around the tilt cone, but also by collective rotation of the molecules around their along axes. The direction of polar order $\hat{b}$ can arrange in two ways (±180), and tilt can be in either of the two directions (say, +ve x-direction or ve x-direction). If tilt is the same in all layers and polar axis alternates from layer to layer then it would be aniferroelectric and achiral. A second possible alternation of both polar and tilt directions within the layer gives rise to antiferroelectric but chiral medium. By the application of an electric field the two antiferroelectric ground states transformed to ferroelectric structure.

1.3.2 Achiral to chiral order bent core molecules

From many years it was believed that macroscopic chiral order is a direct consequence of molecular chirality, standard example being the cholesteric liquid crystal. However the relationship between molecular chirality and macroscopic chirality is more complex. Some materials may exhibit chiral order through symmetry breaking of transitions though they are composed of achiral molecules [12].

Bent-core molecules have two axes: they are bow axes along the molecular long axes and arrow axes along the bent direction. Steric factor of bent core molecules favours all the molecules to point in the same direction. Because of the packing constraint (steric factor), the organization of these molecules in smectic layer develops a polar order in the layer. If the molecules are tilted with respect to the layer normal, the combination of tilt and polar order breaks the symmetry of the layer giving rise to a chiral structure. Such a symmetry-breaking arises because of two events :
1. Bow directions of all points in the same direction within a layer.
2. The long axis of the molecules is tilted from the layer normal.
i.e. tilt + polar order=chirality.

It is important to realize that the chirality in this phase does not arise from a superhelical organization like smectic C* phase although symmetry in both cases is C_2. The unique feature of bent cores has attracted more researchers for experiment and theoretical studies. Let molecular long axes $\mathbf{\hat{n}}$ tilt with respect to layer normal $\hat{z}$ and θ is the tilt angle as shown in figure 6. Depends on the tilt angle (say, +ve x-direction or ve x-direction) polar vector changs. Polar vector $\hat{b}$ changes with tilt as given by the below equation.

$$\frac{\hat{z} \times \hat{\mathbf{n}}}{\sin\theta} = \pm\hat{b}$$

Within each smectic layer we have two types of orientation order : tilt order and polar order. Tilt order because of tilt of the molecular director $\hat{\mathbf{n}}$ with respect to layer normal and polar order because of ordering of the polarization vector $\hat{b}$. The combination of tilt order and polar order gives the chiral structure.

Magnitude and sign of the chiral order represented by the order parameter

$$\xi = \langle 2[(\hat{z} \times \hat{n})\,.\hat{b}]\,(\hat{z}.\hat{n})\rangle$$

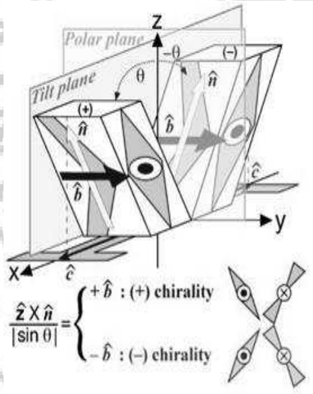

Figure 1.6: Geometry of smectic layers[7]

According to inter layer correlation of polarization, which is here assumed to be parallel to $\hat{b}$ and tilt direction, four states are possible, and they are shown in figure 7. Out of these four phases two of them are chiral and two of them are achiral. The phases with tilt and polar order are denoted by SmCP. Sm denotes smectic phase, and the letters C and P refer to the states of tilt and polarization respectively. If the tilt of the successive layers point in the same direction structure is said to be synclinic, if they are of opposite direction structure is anticlinic. If Molecular dipoles in successive layers are in same direction, then it is called ferroelectric liquid crystal; if in opposite direction then it is called antiferroelectric liquid crystal. As the tilt and polar order define the handedness of a layer, the macroscopic phases could be chiral or antichiral. A structure is said to be chiral if the neighboring layers have the same handedness. The macroscopic phase can have alternating layer chirality and is called racemic or antichiral [13].

The possible phases with different combinations of tilt and polarization are:
SmC_S P_F, SmC_A P_A , SmC_S P_A and SmC_A P_F. These are specified by
SmC_S P_F : Tilt and polar order of the successive layers are in same direction.
SmC_A P_A: Tilt and polar order of successive layers are of opposite direction.
SmC_S P_A: Tilt order of successive layers are same direction but polar order is of opposite direction.
SmC_A P_F: Tilt order of successive layers are of opposite direction but polar order same direction.
The first two are the chiral states, and the other two are antichiral states. Molecular arrangements and order of these phases are shown in figure 7.

The layer chirality alternates from layer to layer in SmC_S P_A and SmC_A P_F, and is recemic. In contract, the layer is homochiral in SmC_S P_F and SmC_A P_A. One important difference from the polar order in SmC^* and SmC^*_A phase is that the tilt and polarization sences are not correlated.

With the application of an electric field antiferroelectric state switches to ferroelectric state either by a change in chirality of phase, or not.

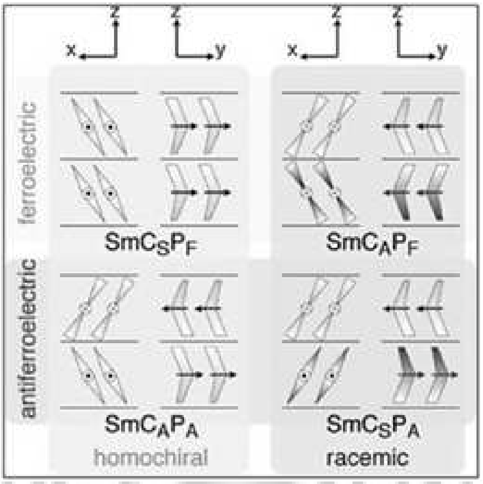

Figure 1.7: Geometry for layer stacking in liquid crystalline phase of bent core molecules these layers can organize into four possible states

Scope of present work

The present interest to study such phase transitions, as a function of temperature by applying Monte Carol simulation methods. For this purpose we considered a Hamiltonian which was studied very recently to understated field- induced phase transitions and chirality switching in SmCP phase of bent core molecules. Our interest is to study thermally induced phase transition predicted by this Hamiltonian model. The Hamiltonian is given as [12]

$$\begin{aligned} H &= -A\sum_{x,y}\chi_i\chi_j - B\sum_{x,y}P_iP_j - C\sum_{x,y}\theta_i\theta_j - C_\chi\sum_{z}\chi_i\chi_j \\ &+ C_p\sum_{z}P_iP_j + C_\theta\sum_{z}\theta_i\theta_j - g_1\sum_{i}\chi_iP_i\theta_i - E\sum_{i}P_i. \end{aligned} \tag{1.1}$$

This is a lattice Hamiltonian involving only nearest neighbour interactions. Here χ, P and θ represent chiral, polar and tilt orders, respectively; they can take only two values ±1, like in Ising model. The lattice sites are represented by i and j. These variables have different intra- and inter layer couplings: A, B, and C indicates the intra layer coupling among each of these variables, while C_χ, C_P and C_θ represent the inter-layer coupling (say, in the z-direction). It may be noted that the interlayer coupling in the case of polar and tilt variables are designed to promote anti-ferromagnetic coupling (in the notation of the Ising model), while the chiral inter-layer coupling is designed to encourage overall macroscopic chiral order (-ve sign in front of C_χ in the above equation). The polar variables is further coupled to an external field through the parameter E. the three Ising-like variables are finally coupled through a product term with strength g, with negative sign.

A detailed analysis of the consequence of this Hamiltonian (at low enough temperature) under the action of switching by an external electric field was a subject matter of a recent doctoral thesis [12]. We focus here the thermal behaviour of this system for different couplings, as a function of C_χ, C_θ and g. thus the objective of this work is to examine possible interesting thermally driven phase transitions in a small parameter phase of the Hamiltonian.

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2

Monte Carlo simulation of thermally induced SmCP phases of bent-core liquid crystals

To study thermally induced SmCP phases of bent core molecules predicted by the Hamiltonian model discussed in the earlier chapter, we construct the equilibrium canonical ensemble based on the Monte Carlo simulations. For convenience, we report the Hamiltonian below.

$$\begin{aligned} H &= -A\sum_{x,y}\chi_i\chi_j - B\sum_{x,y}P_iP_j - C\sum_{x,y}\theta_i\theta_j - C_\chi\sum_{z}\chi_i\chi_j \\ &+ C_p\sum_{z}P_iP_j + C_\theta\sum_{z}\theta_i\theta_j - g_1\sum_{i}\chi_iP_i\theta_i - E\sum_{i}P_i. \end{aligned} \tag{2.1}$$

This Hamiltonian [1] represents Smcp phase of bent core molecules which is having layer structure at low enough temperatures. Combination of the tilt and polar order breaks the symmetry of the layer giving chiral structure of liquid crystal from achiral molecules [2-6]. Here we considered the layers are along the x, y plane and layer planes in the z direction. The three order parameters χ, p and θ represent chirality, polarity and tilt orders, respectively. A, B and C are intra-layer coupling coefficient. C_χ, C_θ and C_P are

inter layer coupling constants of these respective variables. i, j are position of the lattice sites. g is parameter which couples the three order parameters. For zero values of g the three order parameters behave like three independent Ising spins. E is the strength of the applied field.
The coupling term $\chi P\theta$ is symmetric under reflection i.e. changing the sign of either P or θ (not both) change the chirality of the system. Seventh term is field interaction term with polar order. The other two order parameters i.e. chirality and tilt do not interact with the field directly. The positive values of A, B and C parameter favor ferro magnetic nature of the orders within the layer. In between the layers, inter-layer coupling favors chiral order, antiferro state for the polar order and anticlinic state for the tilt order. This state is the ground state for the system. Increases in the values of C_χ, C_θ and C_P enhances the probability of the system to be in the ground state. As already mentioned this model was earlier studied [1] for its switching properties. The salient features of that study can be summarized as:

1. With the application of large enough electric field antiferroelectric ground state switches to ferroelectric state.
2. During this transition, chirality may or may not be affected. It depends on the relatively inter-layer coupling of chirality and tilt variables.
3. In the case of weak inter layer chiral coupling (fourth term), anticlinic order could remain the same, while chirality may change through the transition.
4. In the case of strong inter layer coupling, anticlinic state changes to synclinic state and chirality is preserved through transition.

We present the result of an simulation carried out as a function of temperature, taken up to examine the role of the different interlayer couplings in favoring the ground state at various temperature. To appreciate these results, we first present the methodologies of Monte Carlo simulation that we carried out based on Markov chain dynamics.

2.1 Monte Carlo simulations

Condensed matter systems are composed of many parts, typically atoms or molecules. These parts are usually all the same or of a small number of different types and they obey quite simple equations of motion. So the behavior of the system can be expressed by mathematical equations. But the sheer number of equations makes it impossible to solve the equation. Allowing the system to interact with the surroundings so as to be in thermodynamic equilibrium makes calculations even conceptually difficult to formulate. Since the problem of statistical thermodynamics, namely explaining the macroscopic properties of matter resulting from the interplay of a large number of atoms, is very complex, computer simulations play a particularly important role there. Monte Carlo methods aim at a probabilistic description from the outset, relying on the use of random numbers to minimize the ab *inito* bias on the part of the algorithm. An efficient Monte Carlo technique is required to overcome the problems like critical slowing down at or close to critical temperature and energy barriers at first order phase transition. In our work, we follow metropolis algorithm to generate a Markov chain of microstates through suitable Monte Carlo sampling procedure

2.1.1 Periodic boundary condition

Simulation models typically involve a few thousands of particles i.e. we do simulations on finite size of the lattice, this is not realistic though. No matter how large system is, its number of atoms N would be negligible compare with the number of atoms contained macroscopic piece of matter of order of 10^{23}. A solution to minimize the finite size effect is to use periodic boundary conditions (PBC). When using PBC, particles are enclosed in a box, and we can

imagine that this box is repeated by rigid translation in all three Cartesian directions, completely filling the space.
Every particle at position of (x, y, z) in a box of side length k will have images at (x ± k, y, z), (x, y ± k, n) and (x, y, z ± k) etc. the key point is that now each particle *i* in the box should be thought as interacting not only with other particles *j* in the box, but also with their images nearby boxes. That is, interactions can go through box boundaries. By these PBC we can observe

1. We have virtually eliminated surface effects from the system.
2. The position of the box boundaries has no effect i.e. translation of the box with respective to the particles leave the force unchanged.
3. The number of interacting pairs increases.

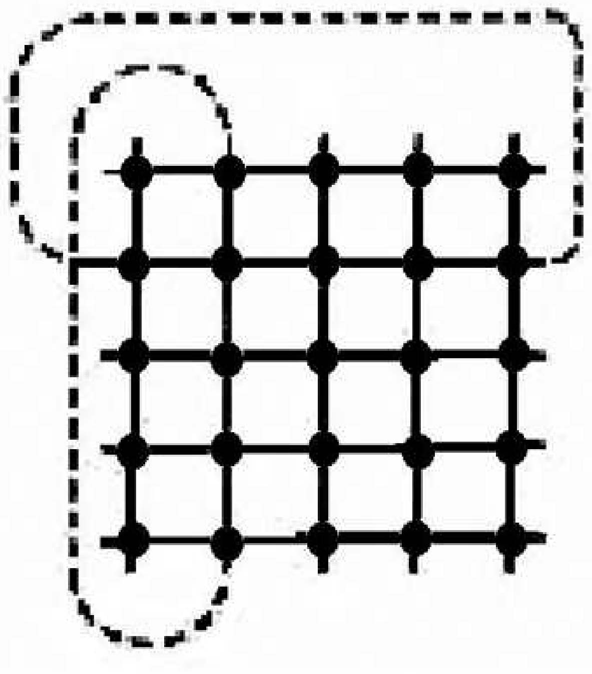


Figure 2.1: Periodic boundary conditions

2.1.2 Metropolis algorithm

This algorithm was introduced by Nicolas Metropolis [7] and his co-workers in a paper on simulations of hard-sphere gases in 1953 and is an algorithm based on a long sequence of random numbers. Metropolis algorithm [8] is the most simple example for canonical sampling methods. This algorithm has been very successful in simulating a wide range of problems connected with statistical mechanics in condensed matter physics. Consider a closed system, having set of microstates. We look for an algorithm which takes the chosen system through a Markov chain of microstates starting with an initial microstate, C_0 as shown:
$C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow$ ....
Metropolis algorithm produces this sequence [9-10]. Initially we choose random configuration C_0.
Considering lattice of spins with two possible configurations for each site, we randomly select the spin and flip it: this is new configuration call it as C_t (trial configuration). We can accept or reject the trail state based on their energy values. If the energy of the trial state is less than the initial configuration we accept the trial state. If the energy of the trial state more than the initial configuration we accept it with the probability (is independent of the partition function) is given by
P = exp(-$\beta \triangle E$)
Where $\beta = 1/k_BT$, T is temperature, k_B is Boltzmann constant,
$\triangle E = E(C_t) - E(C_0)$
Now we call for a random r number: if the probability is greater than the random number r we accept the trial state. If it is less than the trail state is reflected and the system remain in C_0. Each trial step is called Monte Carlo step. Such N number lattice size steps are called one Monte Carlo sweep. The algorithm is as follows.

1. Start with a random configuration and evolve it.
2. Select randomly one of the spins with equal probability and flip it and

call it as trial configuration.

3. if $\triangle E \leq 0$, we accept the trial state

   (a) if $\triangle E > 0$, we call for a random number r

   (b) If $r \leq \exp(-\beta\triangle \text{ E})$, we accept the trial state;

   (c) If $r > exp(-\beta\triangle E)$, we reject the trial state, and include the current microstate in the ensemble

4. Iterate this procedure for very large number of times

We perform this for large number times asymptotically till the system reaches equilibrium. Thus get the distribution of microstates representing an equilibrium ensemble. Properties of the system can be calculated by taking average over this distribution at each temperature or field.

2.2 Monte Carlo Simulation work

We considered lattice model(simple cubic) in order to study chiral switching phases of bent-core liquid crystals. Here we assume that the molecule at each lattice i is represented by three ising spins. They are chirality (χ_i), polarity (P_i) and tilt (θ_i). We start with completely random orientation of the molecules (random values for the three variables) and the molecules are positionally fixed at the lattice site. It has period boundaries in all directions. The three Ising spins associated with molecule take values χ_i=±1, P_i=±1 and θ_i=±1. The energy of this configuration is calculated using equation 1. This is the reference energy E_i before the Metropolis algorithm is applied.

We use dimensionless temperature defined as T^{*}=(k_BT)/ϵ, called reduced temperature.ϵ is the interaction constant and depends on the particular system and k_B is the Boltzmann constant. We randomly choose Ising spin set (χ, P,θ) and we flip the state which is a trial configuration. Trial energy is calculated E_t and compared with its original configuration. If $E_t \leq E_i$ then the trial configuration is accepted.

If $E_t \geq E_i$ then the trial configuration is accepted with the probability given by

P $= \exp((E_t - E_i)/k_B T^{*})$ where T^{*} is the reduced temperature and $k_B$is Boltzmann factor.

If the energy of trial configuration is accepted, we store this configuration and redefine the reference energy. In case the trail configuration is rejected we retain the reference energy as it is. But calculating the total energy for every trial configuration increases the computational time. There is an efficient way to decrease this time. We need not calculate all particle interaction energies with their nearest neighbors each time. We simply calculate the updated particle interaction energy with its nearest neighbors in the new (trial configuration) and old (reference configuration) configurations. i.e. Instead of calculating total energy by visiting each lattice site for every new configuration we can calculate the site energies where we flipped the spins. Here we have to calculate the energy before and after the flip at that particular lattice site. The difference in their energies is added to the initial configuration which will give the energy of the new state. This procedure is repeated for each molecule of the lattice. One complete sweep of lattice with this procedure is called Monte Carlo step (MCS). Repeating this procedure for a few thousands MCS lead to equilibration from any initial condition. We then generate microstates based on this algorithm after equilibration, and restore only the equilibrium configurations, leaving out the initial fluctuations, for calculating the thermodynamic quantities. The end configurations become the starting configuration for new nearby temperature or field. This procedure is repeated for various values of field or temperature.

With the above Hamiltonian we studied field and temperature dependences of phase transitions. For the sake of convenience we divided the work into

four cases. They are
Case A: Field induced phase transitions as a function of temperature and coupling coefficient of three order parameters viz g.
Case B: Thermally driven transitions for zero field values as a function of coupling coefficient of three order parameter g.
Case C: Thermally driven transitions for non-zero values of field as a function of coupling parameter g.
Case D: Thermally driven transitions for non-zero values of field as a function of the inter-layer coupling coefficients: (C_χ, C_p, C_θ)

CASE A: Field induced phase transition as a function of temperature and coupling coefficients of three order parameters

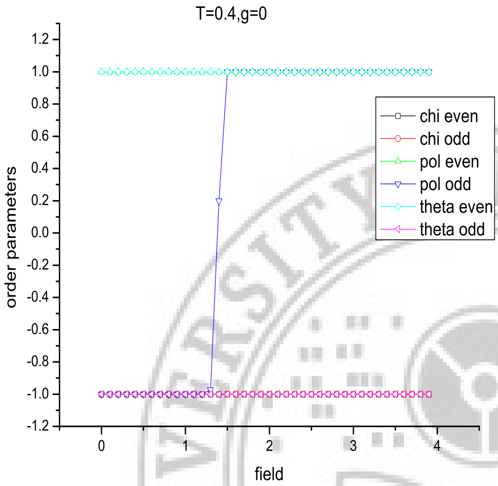
To study the field induced phase transitions of the system at different temperatures initially we construct an equilibrium ensemble of microstates at that particular temperature for zero values of the field. Then we choose a microstate from this ensemble and use it as the initial configuration of the system to study the field effect.

Step 1:collecting the appropriate

We have taken random configuration at the lattice site with the three order variables χ_i=±1, P_i=±1 and θ_i=±1 calculated the energy. Periodic boundary conditions are applied in all directions. Randomly chosen Ising spin is flipped, and the change in energy is calculated based on Metropolis algorithm. We can accept or reject the trial state. After a large such steps, the system is equilibrated. Starting from a higher temperature, the system is subjected to gradually decreasing temperature in steps of 0.1 until we reach the temperature where we want the system to equilibrate. The configuration at each temperature is taken as the initial configuration for the next temperature. At the end of temperature loop we collect a representating the microstate, which is then used to initiate the field effect at that particular temperature. We did simulations on lattice of size (10x10x10) for 10^5 MC sweep as of equilibrium runs and 10^5 for production run. We collected the states for temperatures T=0.4, 1.

Step 2: Field induced phase transition

Here the same procedure is repeated as above but instead of taking random configuration we take the collected microstate as the initial configuration at that temperature. Randomly flip the state we accept or reject based on Metropolis algorithm. Starting from zero field, the system is subjected to gradually increasing external electric field in steps of 0.1 units. The final equilibrated configuration (a representative microstate) at each field is taken as the initial configuration for the next higher field. We carried out 10^5 for equilibrated and other 10^5 for production. We calculated the averages of the three order parameters within the layers for even and odd layers during the production cycle.
Let χ_1, P_1 and θ_1 be the chirality, polarity and tilt order for even layers and χ_2, P_2 and θ_2 be the corresponding values for odd layers. We have taken the values of the coefficient in the coefficient in the Hamiltonian as follows:
A = B = C = 0.6, $C_\chi = 0.2$, $C_p = 0.4$, $C_\theta = 0.5$
Hamiltonian favors antiferroelectric, anticlinic and chiral ground state, as was indicated earlier. We studied the system for different values of g at different temperatures with field as a control parameter. The corresponding results are shown in figures as below. In the figure chieven, polareven and thetaeven stand for chirality, polarity and tilt of the even layers. Similarly chiodd, polarodd and thetaodd stand for chirality, polarity and tilt of odd the layers.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order parameters
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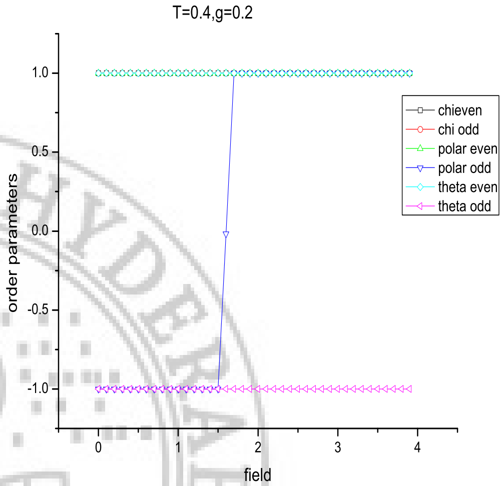
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
1
2
3
4
field
chi even
chi odd
pol even
pol odd
theta even
theta odd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order parameters
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0.5
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2
3
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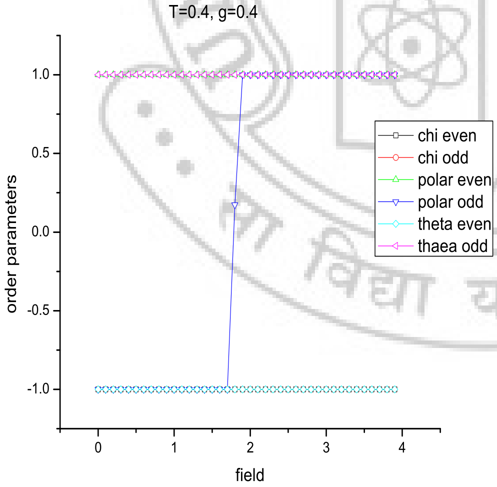
field
chieven
chi odd
polar even
polar odd
theta even
theta odd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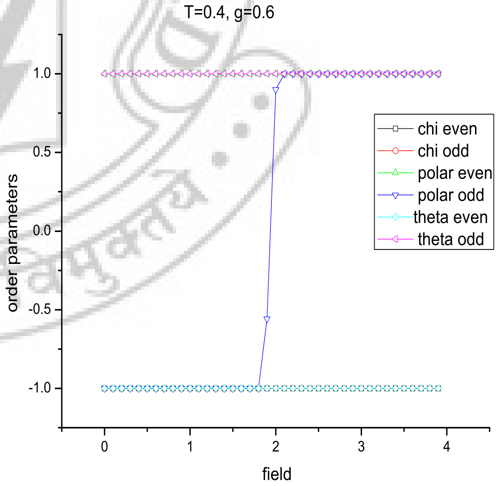
polar even
polar odd
theta even
thaea odd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3
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chi odd
polar even
polar odd
theta even
theta odd

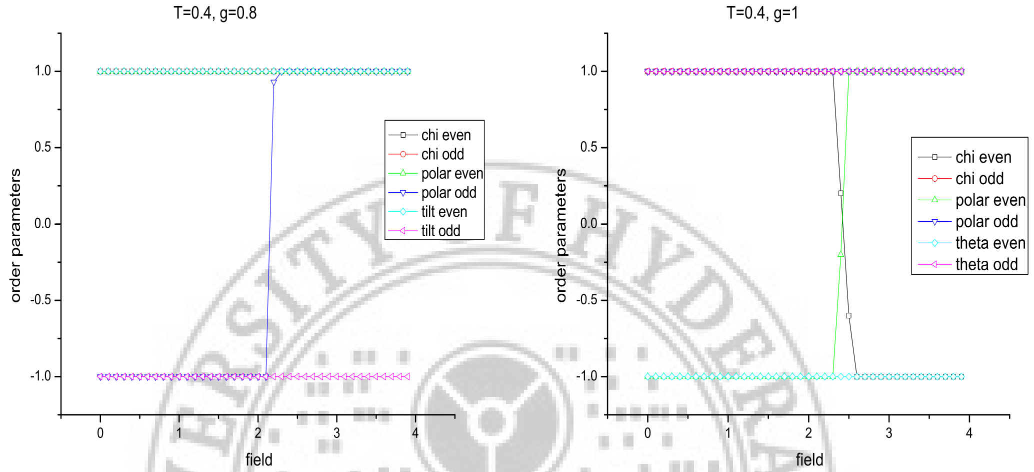
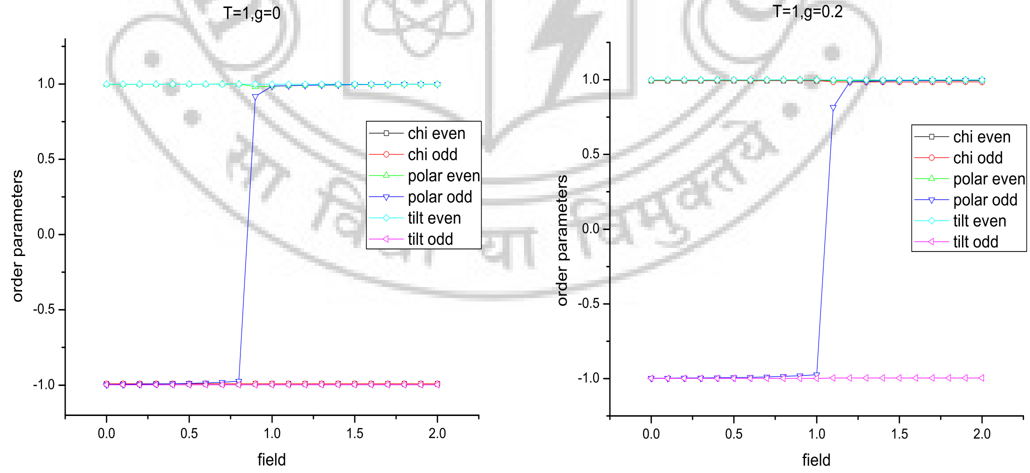


Figure 2.2: Monte carlo simulation results showing electric field dependence of order parameter For different g values at temperature T=0.4



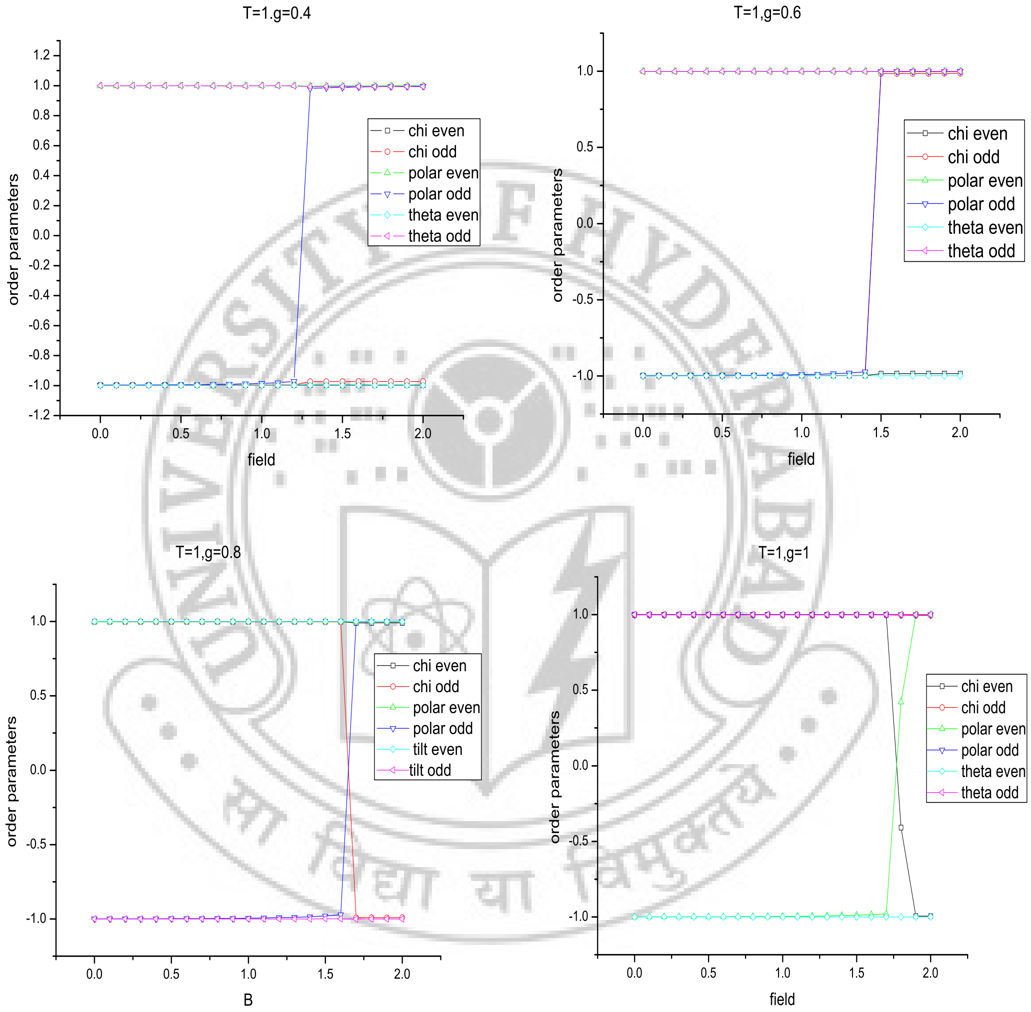
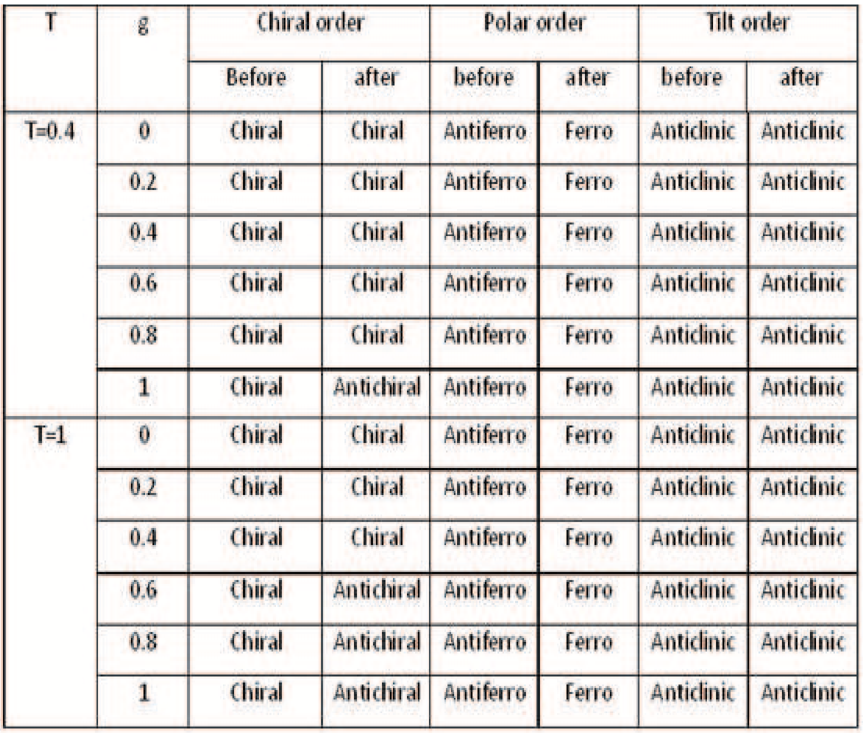


Figure 2.3: Monte carlo simulation results showing electric field dependence of order parameter For different g values at temperature T=1



T	g	Chiral order		Polar order		Tilt order	
		Before	after	before	after	before	after
T=0.4	0	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.2	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.4	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.6	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.8	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	1	Chiral	Antichiral	Antiferro	Ferro	Anticlinic	Anticlinic
T=1	0	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.2	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.4	Chiral	Chiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.6	Chiral	Antichiral	Antiferro	Ferro	Anticlinic	Anticlinic
	0.8	Chiral	Antichiral	Antiferro	Ferro	Anticlinic	Anticlinic
	1	Chiral	Antichiral	Antiferro	Ferro	Anticlinic	Anticlinic

Table 1: Results of field induced chiral switching at two temperature

1. T= 0.4, A = B = C = 0.6, C_χ = 0.2, C_p =0.4, C_θ=0.5
2. T = 1, A = B = C = 0.6, C_χ = 0.2, C_p = 0.4,C_θ=0.5

In this situation we varied the value of g from 0 to 1 in steps of 0.2. figure 2.2 and 2.3 show the result of field switching at the two chosen temperatures, for different values of the coupling constants g of the three order variables.

Preliminary temperature sweeps in the absence of an external field show that the three order parameters average to zero at the reduced temperature of about z, and hence all the field-induced experiments are to be investigated much below this value. We chose representatively two values: 0.4 and 1.0. The fixed points with regard to the sequence in which the various orders are set in the system as it is cooled are the subject matter of subsequent section. For g=0 polar order transits from antiferro to ferro state on application of field, because it is coupled with the field. Other order parameters behave as independent Ising order variables because there is no coupling between these three parameters. With increase in the value of g, the coupling among three order parameters increases. Once the g reaches to unity coupling become strong enough for the polar order to pull one of the order parameter to transit to maintain minimum free energy. Either chiral order or tilt order could take this transition. This issue is further decided by the strength of the inter-layer coupling of tilt and chiral variables. In the present case, tilt is coupled relatively strongly with other layers antiferroelectically, therefore the chiral parameter under goes the transition to make alternative layer to have different chirality.
The results are as follows

1. We observed field induced transitions with increase in the value of g at certain threshold field value.

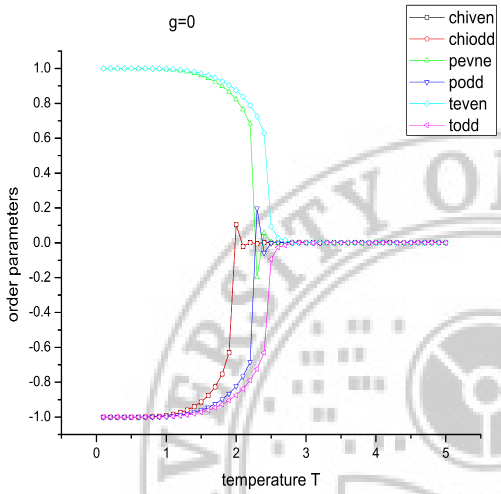
2. With the application of field antiferroelecric ground state switches to ferroelectric by changing chiral to achiral while tilt remains the same for higher values of g (for given values of coupling coefficient of intra and inter layer coupling).

3. For the low values of coupling coefficient g initially only polar order transits from antiferro to ferro state but with further increase in the value of g chirality also switches from chiral to achiral state. This is because with increase in g chirality couples stronger with the other two parameters, and this contribution has to be reduced by its switching.

4. The threshold field value decreases with increase in temperature, as to be expected.
5. The value of g where chirality switches from chiral to achiral state decreases with increase in temperature

CASE B: Thermally driven transitions for zero field values as a function of coupling *g* of three order parameters.

In this study we present result on the effect of temperature on the system as we vary the coupling parameter g among the three variables. we fix the other six parameters as given below. g is varied from 0 to 1 in steps of 0.2 for each such temperature sweep.
A = B = C= 0.6; $C_\chi = 0.2$; $C_p = 0.4$; $C_\theta = 0.5$.
The intra-layer coupling for three variables is identical qualitatively and quantitatively. Inter-layer coupling is antiferroelectric for polar and tilt, while it is ferroelectric type for chirality. The magnitude of constants chosen differently so as to possibly disperse these transitions with respect to temperature. We randomly choose values of spins for the three order variables and the initial energy is calculated. Periodic boundary conditions are applied in all directions. We randomly chose Ising spin and flipped it. The change in the energy is calculated, and based on Metropolis algorithm we as usual can accept or reject the trial state. After sufficient Monte Carlo steps system is equilibrated. Starting from higher temperature, the system is subjected to gradual decrease in temperature with step size of 0.1. The configuration at each temperature is taken as the initial configuration for the next temperature. We did simulations on a lattice of size (10x10x10) for 10^5 of equilibrium runs and 10^5 of production runs. After the system is equilibrated, we calculated the average order parameters for even and odd layers seperately.


g=0
chiven
chiodd
pevne
podd
teven
todd
order parameters
1.0
0.8
0.6
0.4
0.2
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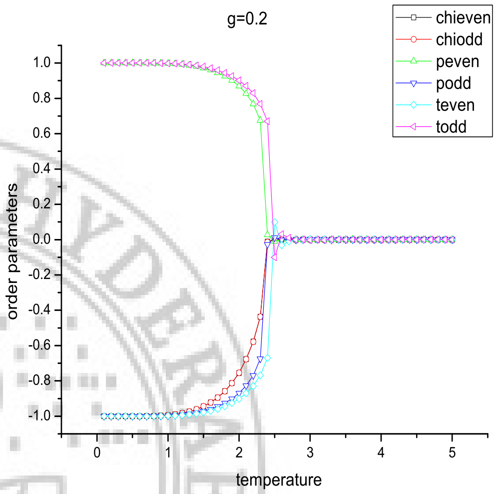
-0.4
-0.6
-0.8
-1.0
0
1
2
3
4
5
temperature T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teven
todd
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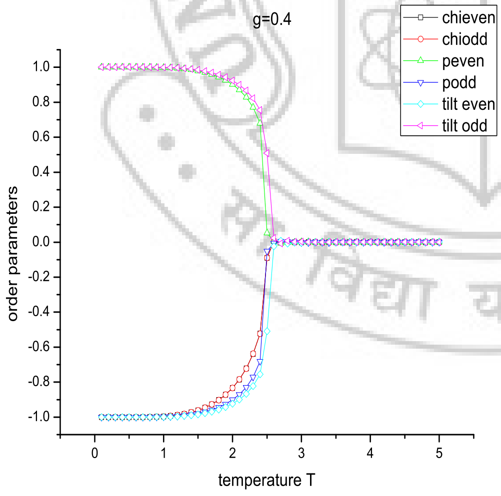
1
2
3
4
5
temperature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peven
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tilt even
tilt odd
order parameters
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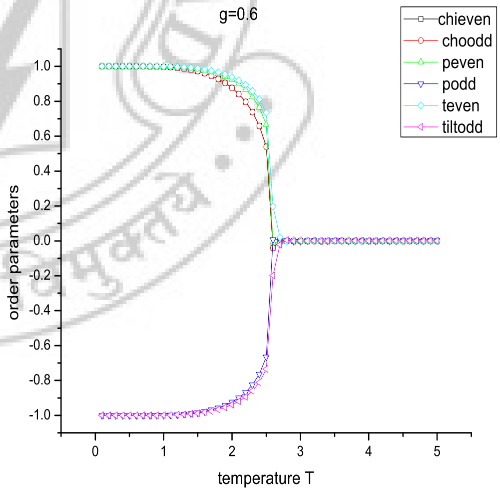
2
3
4
5
temperature T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podd
teven
tiltodd
order parameters
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2
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4
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temperature T

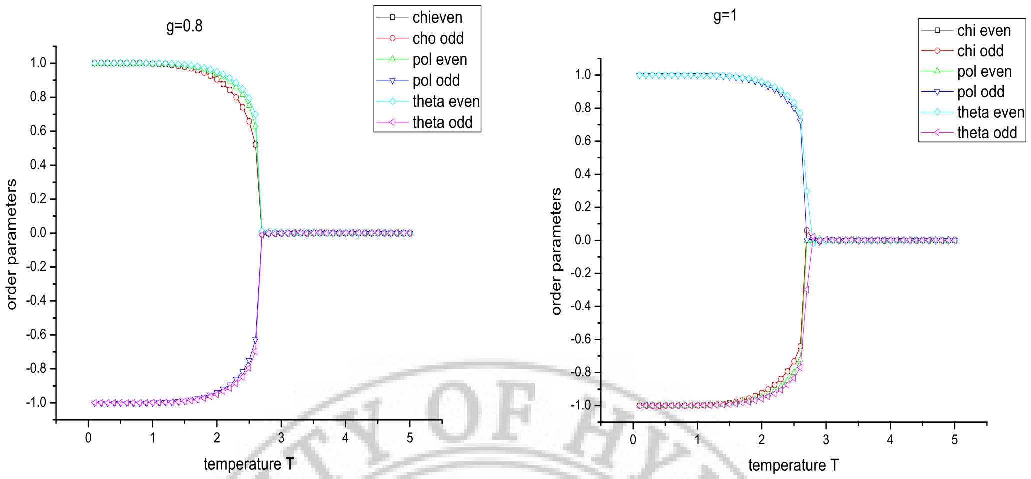
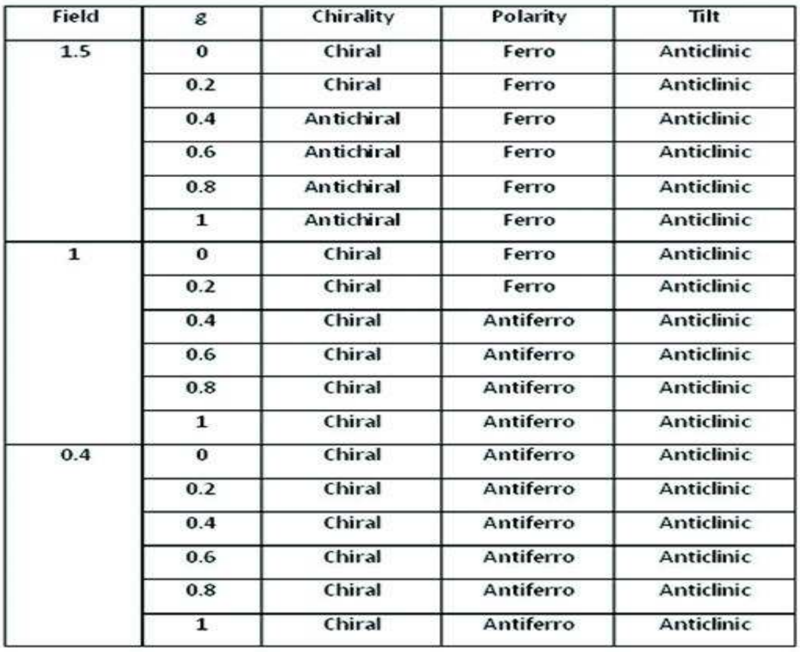


Figure 2.4: Monte Carlo simulation results showing temperature dependence of order parameter for different g values.



Field	g	Chirality	Polarity	Tilt
1.5	0	Chiral	Ferro	Anticlinic
	0.2	Chiral	Ferro	Anticlinic
	0.4	Antichiral	Ferro	Anticlinic
	0.6	Antichiral	Ferro	Anticlinic
	0.8	Antichiral	Ferro	Anticlinic
	1	Antichiral	Ferro	Anticlinic
1	0	Chiral	Ferro	Anticlinic
	0.2	Chiral	Ferro	Anticlinic
	0.4	Chiral	Antiferro	Anticlinic
	0.6	Chiral	Antiferro	Anticlinic
	0.8	Chiral	Antiferro	Anticlinic
	1	Chiral	Antiferro	Anticlinic
0.4	0	Chiral	Antiferro	Anticlinic
	0.2	Chiral	Antiferro	Anticlinic
	0.4	Chiral	Antiferro	Anticlinic
	0.6	Chiral	Antiferro	Anticlinic
	0.8	Chiral	Antiferro	Anticlinic
	1	Chiral	Antiferro	Anticlinic

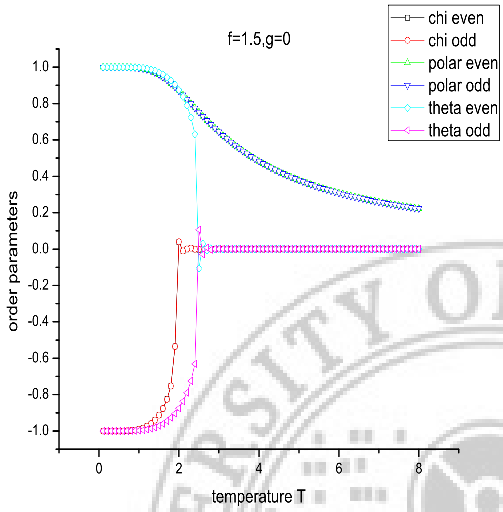
Table 2: Results of thermally driven transitions at different field values

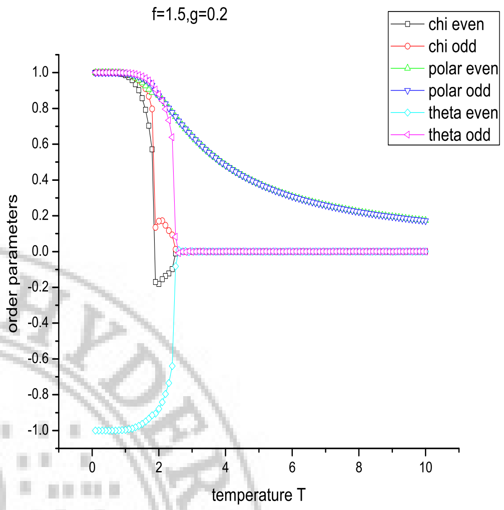
The results of these simulations are shown in figure 2.4.The observations are as follows:

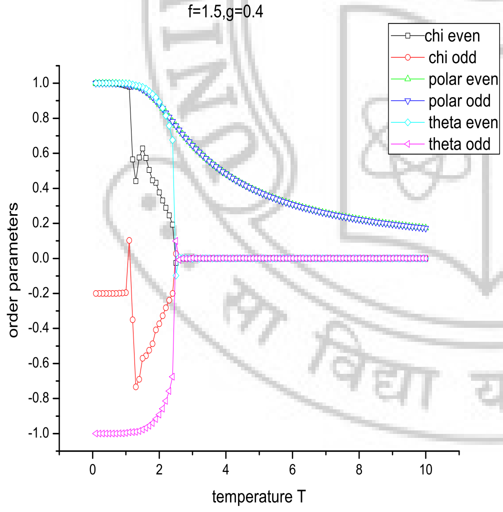
1. We find the range of low temperature where we can SmCP states with this model. Above this temperature, all the three order parameters i.e. chirality, polarity and tilt become zero.
2. The sequence in which each of the orders set in on cooling is determined by the inter-layer coupling is strengths of the respective order variables.
3. When the coupling parameter g is weak, these transitions are dispersed enough to observe the progressive onset of of each the orders, starting with tilt its C_θ is higher than C_χ and C_P.
4. With increase in the value of g the three order parameters couple each other tightly, so as to make the transitions occur almost at the same temperature, corresponding to the tilt.

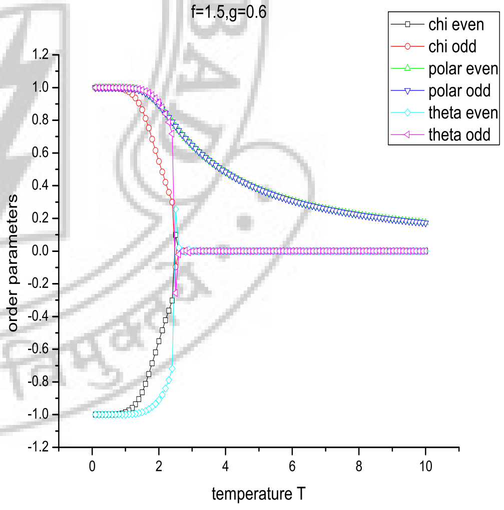
Case C: Thermally driven transitions for non-zero values of field as a function of coupling parameter *g*.

We now extended our study to examine the thermal behavior of the system for different coupling values of g (from 0 to 1 in steps of 0.2) but in the presence of variable field. For these simulations we retain the same values of A, B, C, C_χ, C_P and C_θ for purpose of comparison, and apply three distinct fields: F = 1.5, 1.0 and 0.4. For each of these field values we vary g and observe the thermal behavior in each such case. As before we consider a lattice system of 10x10x10 under periodic boundary conditions, and apply the field in the z-direction coincident with normal to the layers. In these studies we perform 2x10^5 MC lattice sweeps for equilibration, and 3x10^5 subsequent MC lattice sweeps for collecting the canonical ensemble. The temperature is varied from 0.1 to 8 (or 10) in steps of 0.1. The equilibrium values are computed as usual, as averages over the corresponding ensemble.


f=1.5,g=0
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
temperature T


f=1.5,g=0.2
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T


f=1.5,g=0.4
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T


f=1.5,g=0.6
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
2
4
6
8
10
temperature T

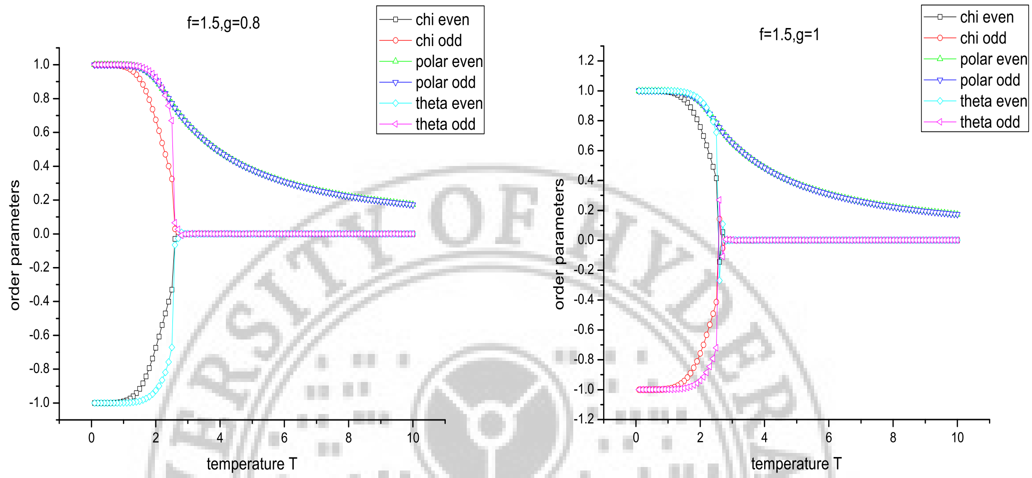
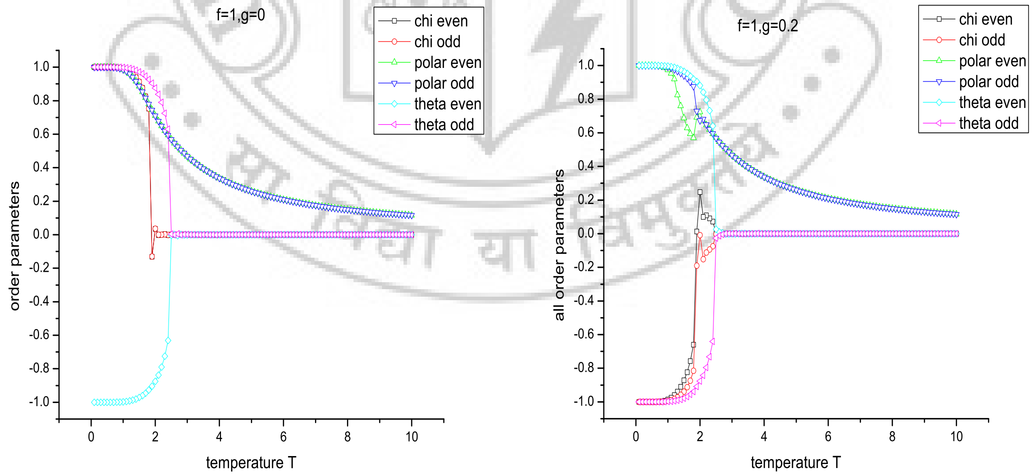


Figure 2.5: Monte Carlo simulation results showing temperature dependence of order parameter for different g values at field=1.5



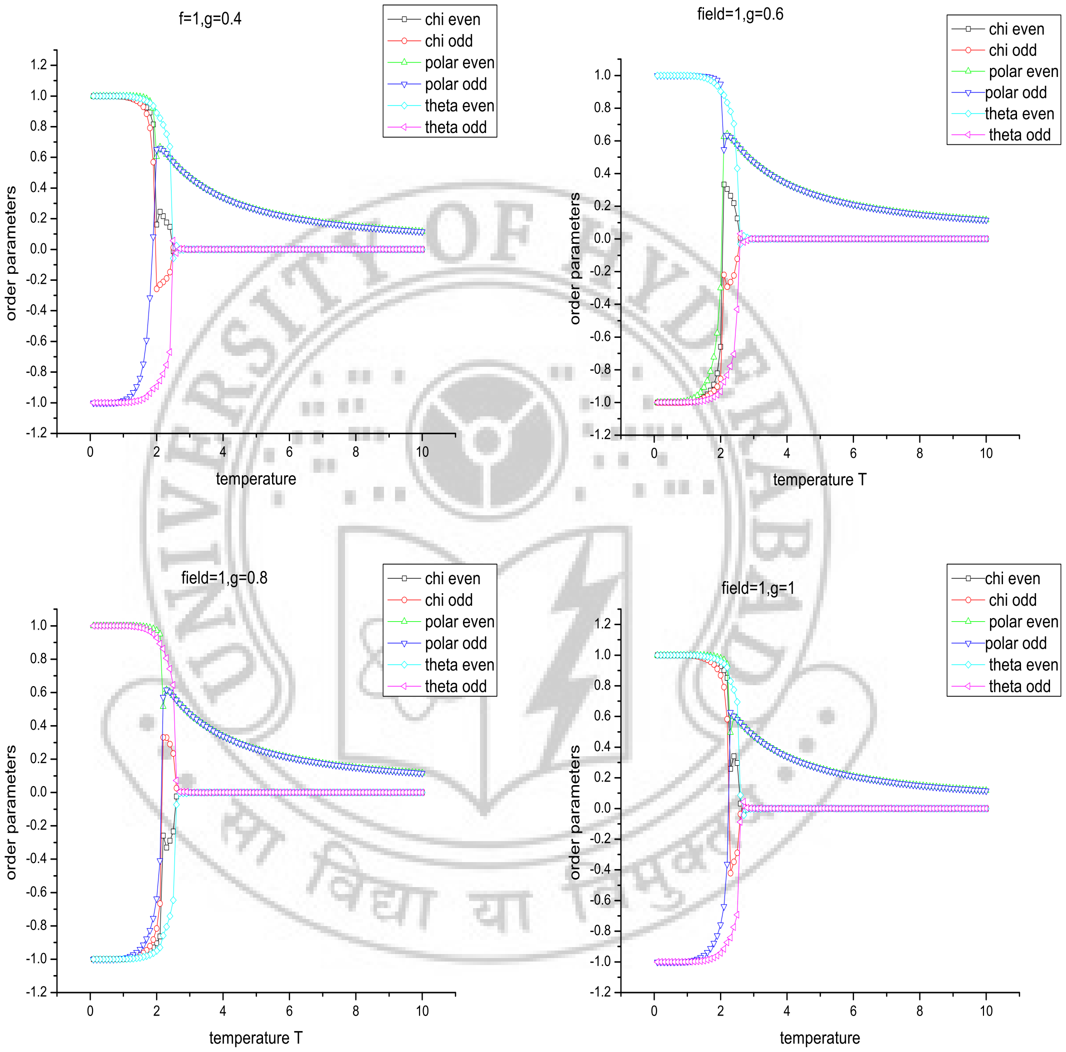
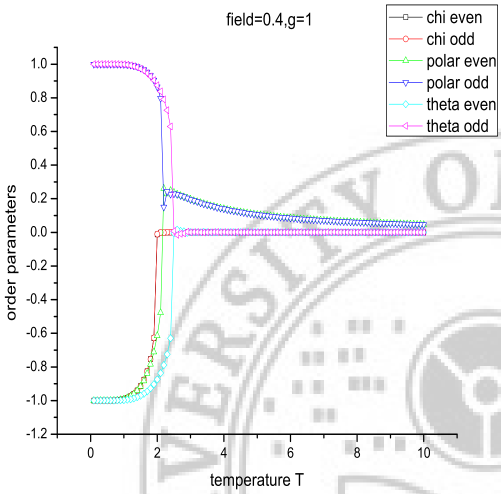
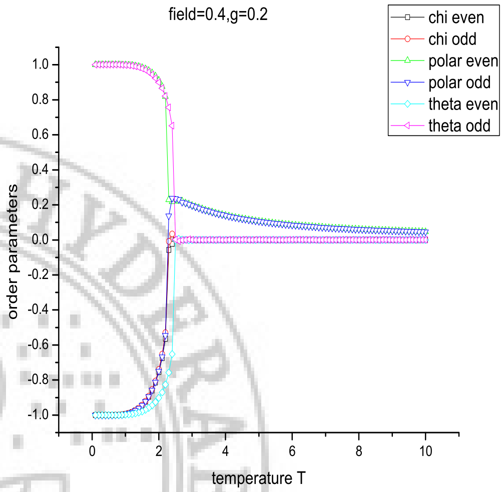
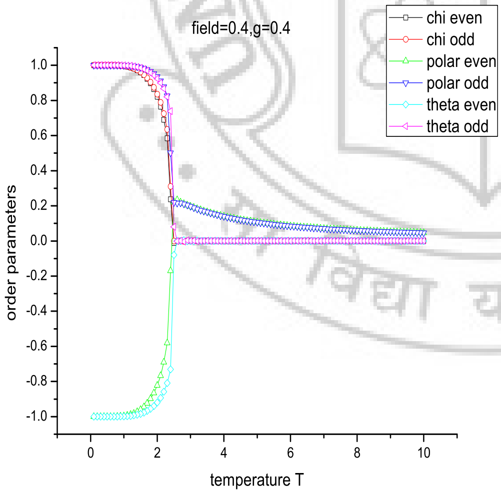
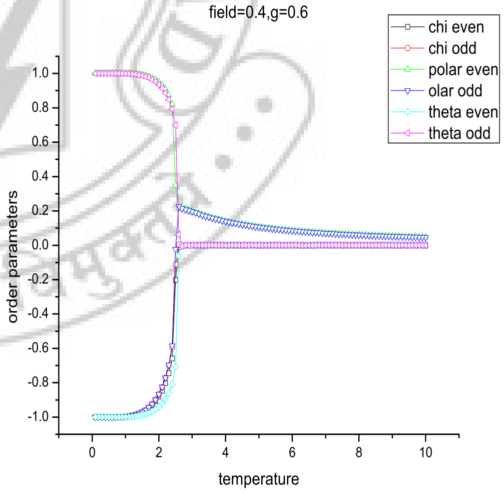


Figure 2.6: Monte Carlo simulation results showing temperature dependence of order parameter for different g values at field=1


field=0.4,g=1
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
2
4
6
8
10
temperature T


field=0.4,g=0.2
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T


field=0.4,g=0.4
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T


field=0.4,g=0.6
chi even
chi odd
polar even
olar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature

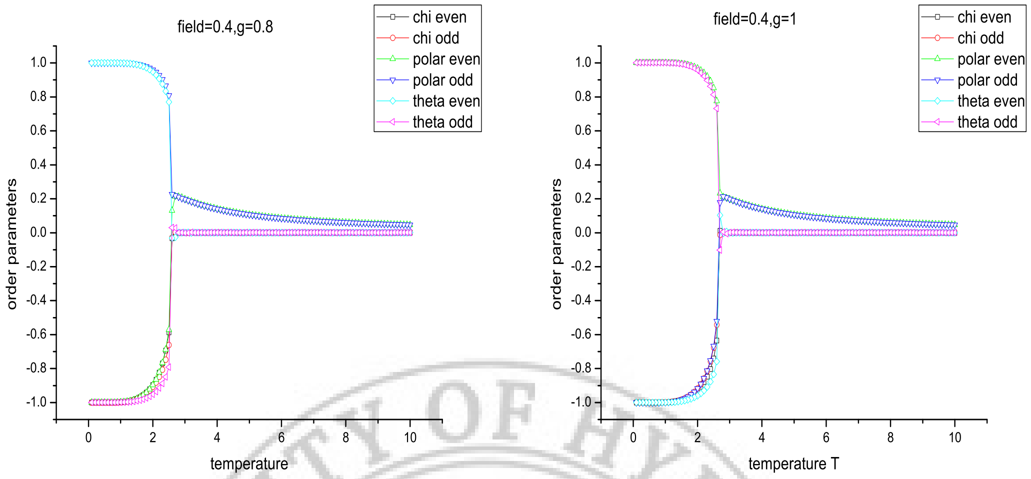


Figure 2.7: Monte Carlo simulation results showing temperature dependence of order parameter for different g values at field=0.4

1. F=1.5, A = B = C = 0.6, $C_\chi = 0.2, C_p = 0.4, C_\theta = 0.5$; g varies from 0 to 1 with step size 0.2

2. F=1, A = B = C = 0.6, $C_\chi = 0.2, C_p = 0.4, C_\theta = 0.5$; g varies from 0 to 1 with step size 0.2

3. F=0.4, A = B = C = 0.6, $C_\chi = 0.2, C_p = 0.4, C_\theta = 0.5$; g varies from 0 to 1 with step size 0.2

In this set of simulation we need to distinguish between two different scenarios. One is when g=0, thereby decoupling the three Ising spins. In this case application of strong field will lead to smearing out of the polar transition; instead there will be a steady increase of P with decrease of temperature, eventually leading to a saturated value (see figure 2.5 g=0, F=1.5 curve). Counting with g = 0, a decrease in F value makes this effect weaker, and below a threshold value, low temperature antiferroelectric order should result (see figure g=0, F=0.4 curve) with an application of these two limiting cases, one can now examine the case when the coupling g is varied progressively from zero to unity. We find some very interesting consequences. For example, focusing on the family of phase diagram corresponding to F=1.5, g=0.2 to 1.0, we find that this coupling among the three order variables (with the present choice of C_χ, C_p and C_θ) leads to an initial tendency of the system to develop antichiral nature, once the anticlinic structure has been established. This is further evidenced as g is set to 0.4 (F=1.5). However in both the cases the low temperature phase is different. With g=0.2, the system quickly recovers to totally chiral structure, despite the tendency initially to develop antichirality. With g=0.4, the system settles down at low temperature to a curious phase where alternate layers have very different chiral symmetry. One set of layers have an average chiral value of unity, and the other set settles to a value close to zero (-0.02). This being an MC average over such sets of layers, one can conclude the correlation between the tilt and polarization direction in these specific layer is not strong, and perhaps fairly random, so much so the average tends towards zero. On further increase of g to 0.6 and higher, the mutual coupling of three variables plays a very dominant role. Within the polarization having essentially decide by the high field value. The effect of such strong coupling is now to make chiral order to decisively become antichiral so that the product $\chi P \theta$ remain positive. Thus we see in the high field case a very curious interplay of the field, via polarization, on the chiral nature of the low temperature phase.

This set of observations should to contrasted with the plots for F=1.0. Here the effect on polarization is weak and hence the behavior of even P variable with temperature is sensitive to the choice of g value (unlike the case of F=1.5). As may be seen, even at g =0.2 (F=1.0), there is a tendency for alternate layers to differ in their polarization characteristic briefly, and after a transient temperature region, ferroelectric and chiral order set in respective ferroelectric mode. However this behavior qualitatively changes on further increase in g (see figure corresponding to g=0.6, 0.8, 1.0 F=1.0). One notice that at these coupling values, the applied field is not strong enough to retain the ferroelectric nature of the polarization at low temperatures, and hence an antiferroelectric order sets in. This facilitates the system to remain chiral, while $\chi P\theta$ is still positive since the states is also antiferroelectric and anticlinic.

These interesting changes become more accurate when the field is further reduced to 0.4, thereby making the effect of resultant polarization on the transition phenomenon comparatively much less effective. The interesting aspect of these simulation is to bring out the interplay of mutually coupling term (through g) in relation to the effect of the external field, with temperature playing curiously as a variable weightage factor making the system influenced by one interaction or other to a variable degree.

F=1.5: Polar order couples with the applied field. So with field application polar order smeared out the transition and coupling coefficient values are scaled. Polar order settles down as ferro electric. For the lower values of g (coupling coefficient) they are like independent spins. So chiral order takes transition to chiral and tilts order to anticlinic. With increase in the value of g coupling between the three order parameter increases. Inter layer coupling coefficient of tilt is more compare to chirality so tilt take first jump to anticlinic. Chirality is having lower values of interlayer coupling value is fluctuate because g favors anti ferro nature and inter layer coupling value favors chiral nature. For higher values of g coupling dominates the inter layer coupling as a result chiral take transition to achiral. Here we observed thermally driven transition from chiral to achiral with increase in the values of g.

F=1: This field is not sufficient to smear out the transition of polar order for all the values of g. For the lower values of g, they are like independent spins. chiral take transition to chiral, tilt to anticlinic and polar order to ferroelectric. With the increase in the values of g they couple strong. Field is not sufficient to dominate the inter layer coupling of polar order as a result it take transition to antiferro state. To maintain minimum energy chirality becomes chiral, tilt become anticlinic.

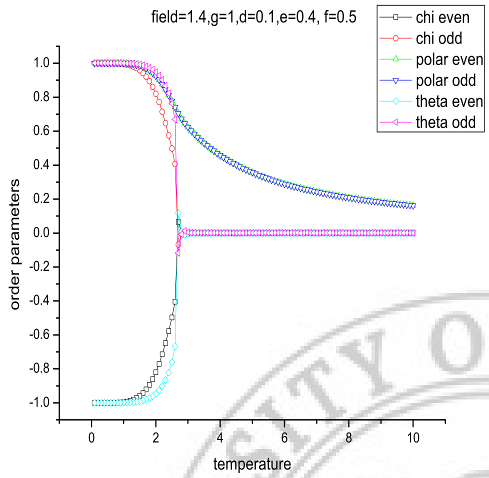
F=0.4: For still lower values of F inter layer coupling coefficient dominated by field so it take transition to antiferro. To minimum energy chirality to achiral and tilt to anticlinic. Results are as follows:

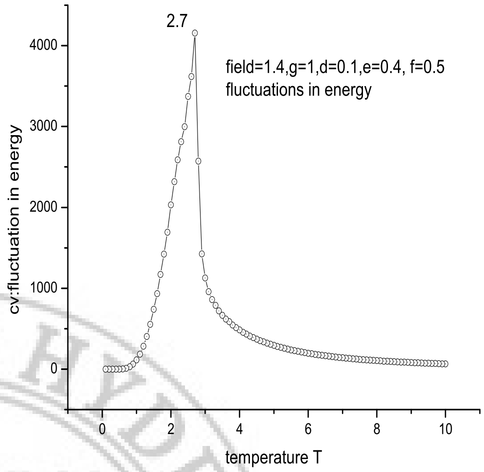
1. With the application of the field coupling coefficients are renormalized.

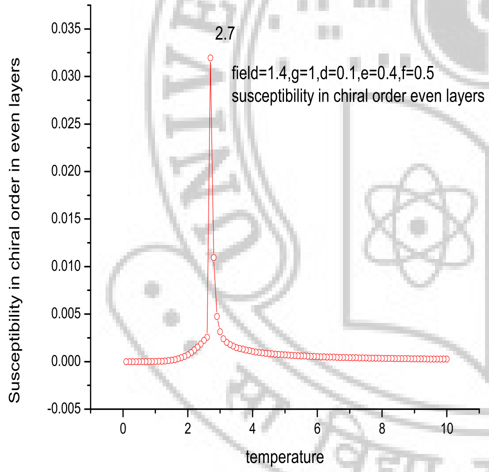
2. Depending on the value of the applied field order parameters take transition. If the field is strong enough to smear out the transition of polar order chiral order take transition to achiral and tilt as anticlinic. If the field is not sufficient polar order takes transition to antiferro, chirality to chiral and tilts to anticlinic.

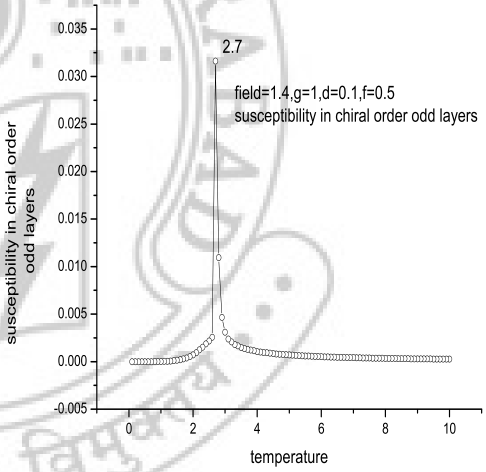
Case D: Thermally driven transitions for non-zero values of field as a function of the inter layer coupling coefficients. C_χ**,** C_P, C_θ)

We now explore the consequence of spanning the subspace of the Hamiltonian parameters determining the inter layer coupling of the three order variables. We simulate the thermal behavior at a constant field F=1.4, and strong coupling parameter g=1. As before the equilibration is achieved by 2x10^5 Mc lattice sweeps on a 10x10x10 system followed by 3x10^5 such sweeps to construct canonical ensemble at each temperature. The temperature is varied from 0.1 to 10 in steps 0.1. In this case (Case D), we augment the data by also computing the variances of different parameters to quantify the degree of fluctuations in each of the variables, as a function of temperature. Thus the set of computed quantities comprises of: ensemble averages of the three order parameter, specific heat at constant volume C_V (representing an energy fluctuations), layerwise (even and odd) susceptibilities of the three order parameters (say ${\sigma_\chi}^e, {\sigma_\chi}^o, {\sigma_P}^e {\sigma_P}^o, {\sigma_\theta}^e$, and ${\sigma_\theta}^o$), the subscript representing the specific order involved and the superscript indicating the nature of the layer, even or odd).
The first set of result reported here correspond to fixed value of the following: A = B = C = 0.6, C_p = 0.4, F=1.4 and g=1. We are thus left with variable parameters C_χ representing the (ferroelectric type) interlayer coupling strength of chiral order variable and C_θ specifying the (antiferroelectric type) inter-layer coupling strengths of the tilt variable. We present and discuss results for the following choice of values: C_θ = 0.5; and C_χ = 0.1, 0.2, 0.3, 0.4, 0.5. the five sets of data pertaining to this case are presented in figures 2.8 to 2.12. Out of them we see three sets are distinct and interesting in their thermal evaluation. We discuss briefly each case below:


field=1.4,g=1,d=0.1,e=0.4, f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature


2.7
field=1.4,g=1,d=0.1,e=0.4, f=0.5
fluctuations in energy
cv:fluctuation in energy
4000
3000
2000
1000
0
0
2
4
6
8
10
temperature T


2.7
field=1.4,g=1,d=0.1,e=0.4,f=0.5
susceptibility in chiral order even layers
Susceptibility in chiral order in even layers
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
0
2
4
6
8
10
temperature


2.7
field=1.4,g=1,d=0.1,f=0.5
susceptibility in chiral order odd layers
susceptibility in chiral order odd layers
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
0
2
4
6
8
10
temperature

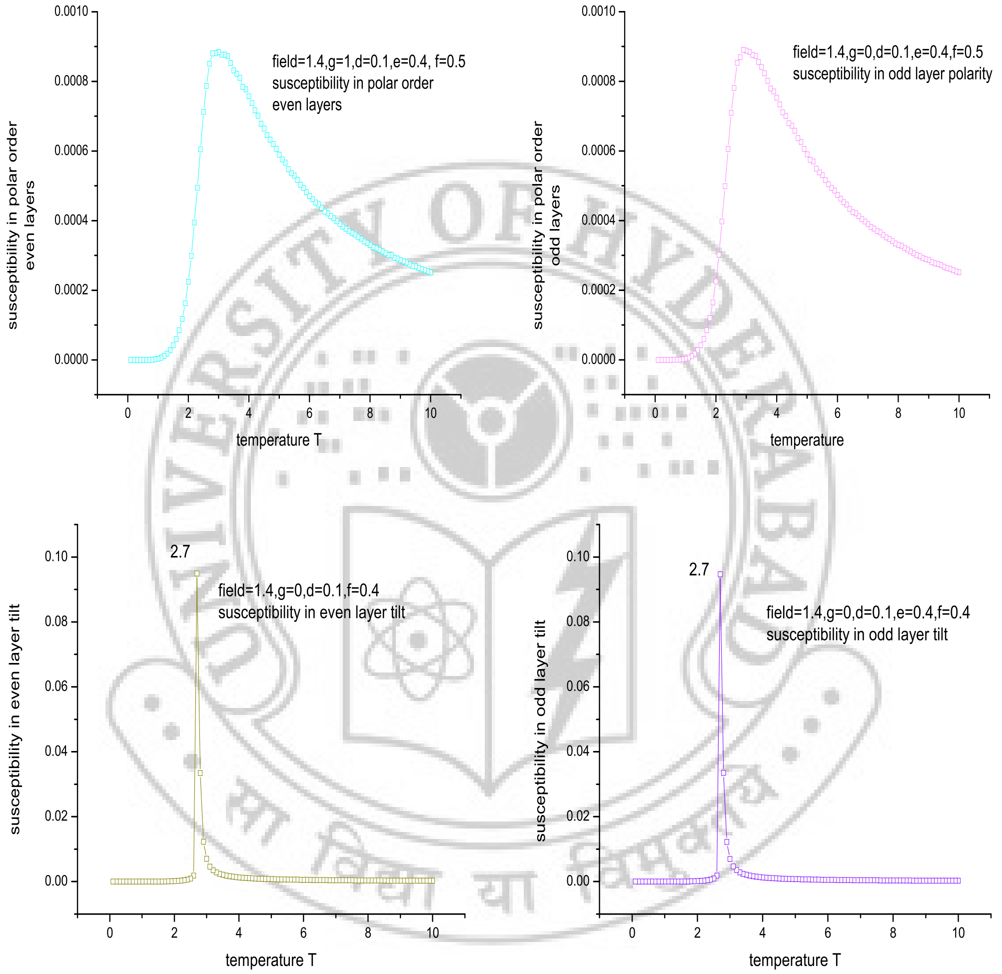
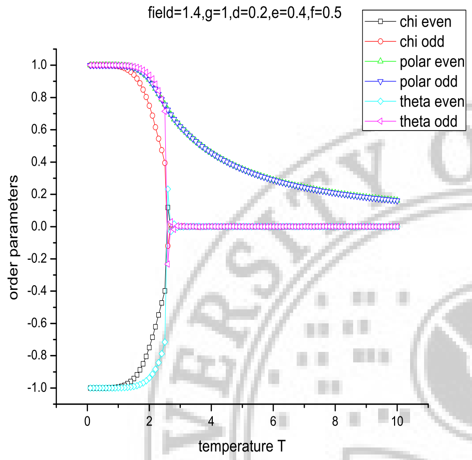
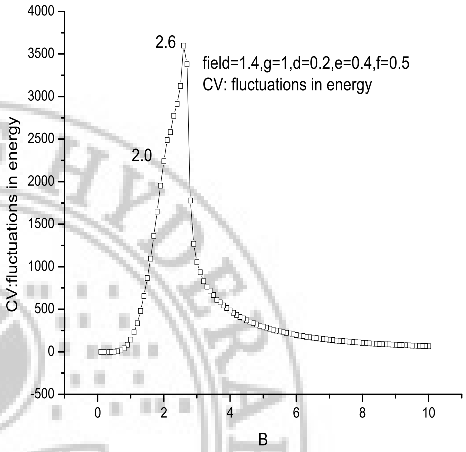
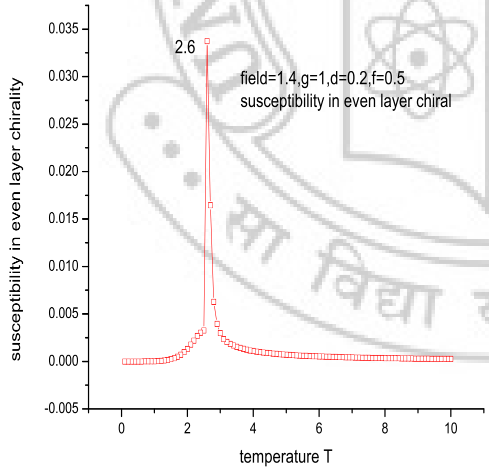
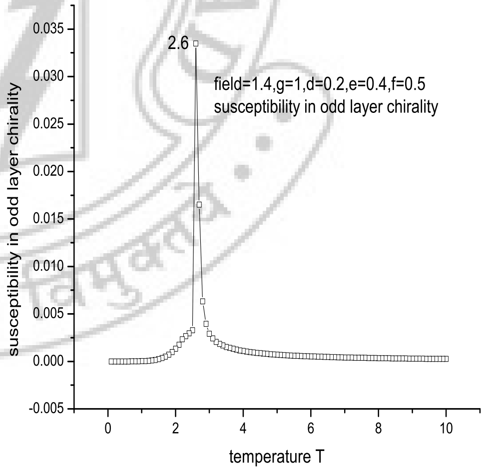


Figure 2.8: Monte Carlo simulation results showing temperature dependence of order parameter for different inter layer coupling coefficients, $C_\chi = 0.1$, $C_P = 0.4$, C_θ =0.5 and their susceptibility graphs.


field=1.4,g=1,d=0.2,e=0.4,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T


2.6
2.0
field=1.4,g=1,d=0.2,e=0.4,f=0.5
CV: fluctuations in energy
CV:fluctuations in energy
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
2
4
6
8
10
B


2.6
field=1.4,g=1,d=0.2,f=0.5
susceptibility in even layer chiral
susceptibility in even layer chirality
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
0
2
4
6
8
10
temperature T


2.6
field=1.4,g=1,d=0.2,e=0.4,f=0.5
susceptibility in odd layer chirality
susceptibility in odd layer chirality
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
0
2
4
6
8
10
temperature T

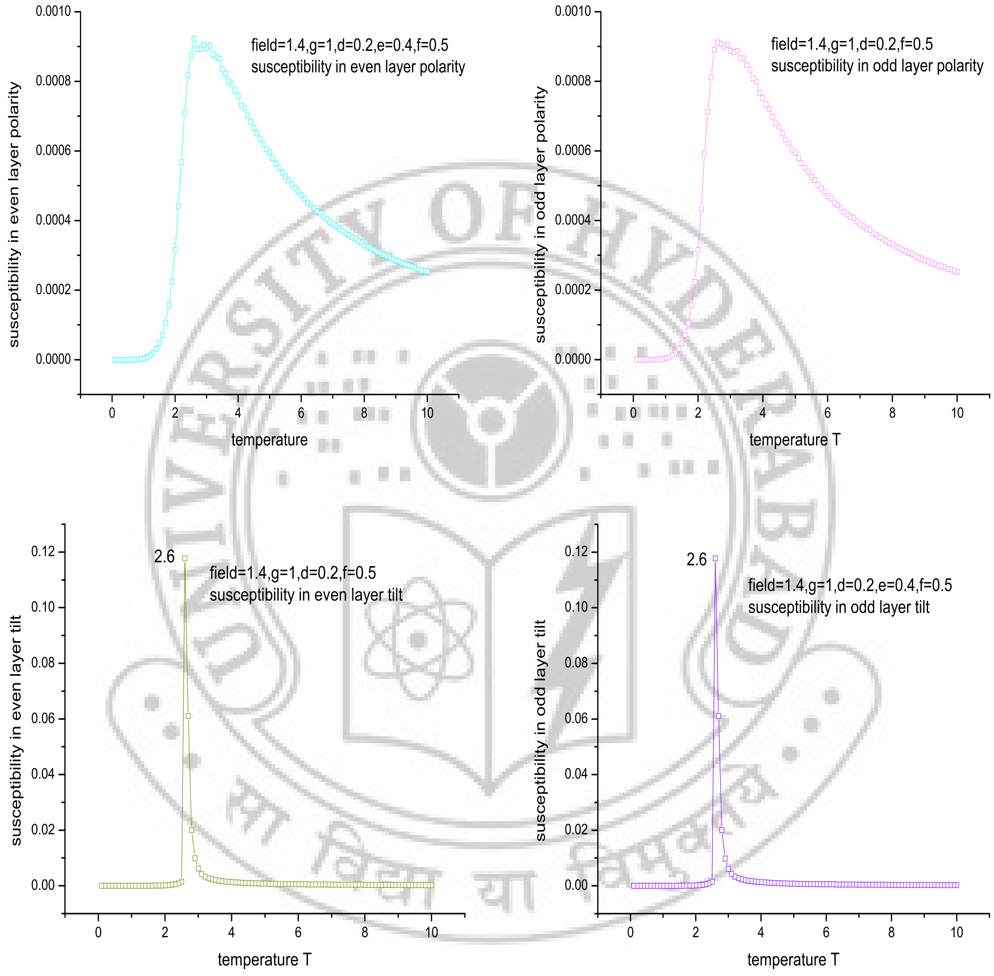
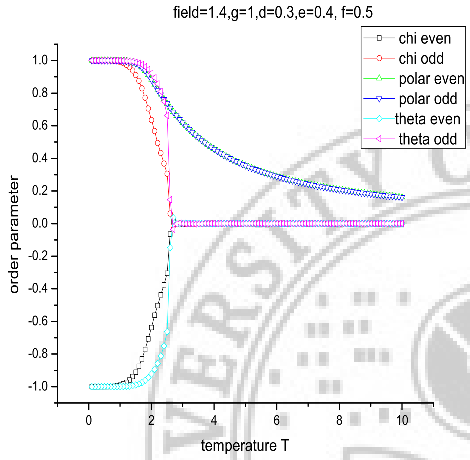
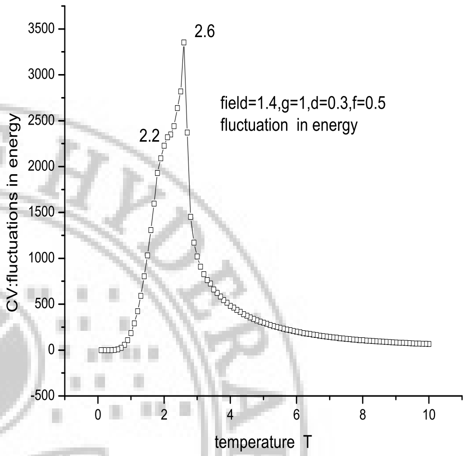
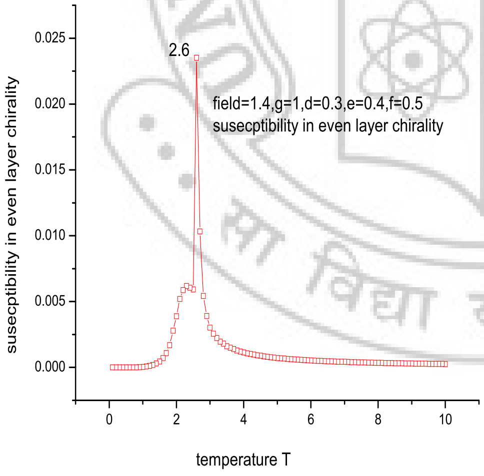
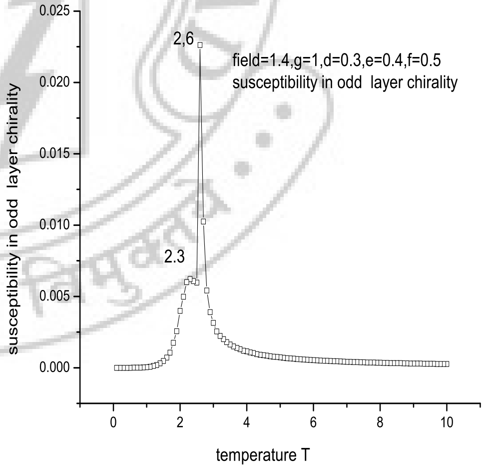


Figure 2.9: Monte Carlo simulation results showing temperature dependence of order parameter for different inter layer coupling coefficients, $C_\chi = 0.2$, $C_P = 0.4$, C_θ =0.5 and their susceptibility graphs.


field=1.4,g=1,d=0.3,e=0.4, f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameter
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T


2.6
2.2
field=1.4,g=1,d=0.3,f=0.5
fluctuation in energy
CV:fluctuations in energy
3500
3000
2500
2000
1500
1000
500
0
-500
0
2
4
6
8
10
temperature T


2.6
field=1.4,g=1,d=0.3,e=0.4,f=0.5
susecptibility in even layer chirality
susecptibility in even layer chirality
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
temperature T


2.6
2.3
field=1.4,g=1,d=0.3,e=0.4,f=0.5
susceptibility in odd layer chirality
susceptibility in odd layer chirality
0.025
0.020
0.015
0.010
0.005
0.000
0
2
4
6
8
10
temperature T

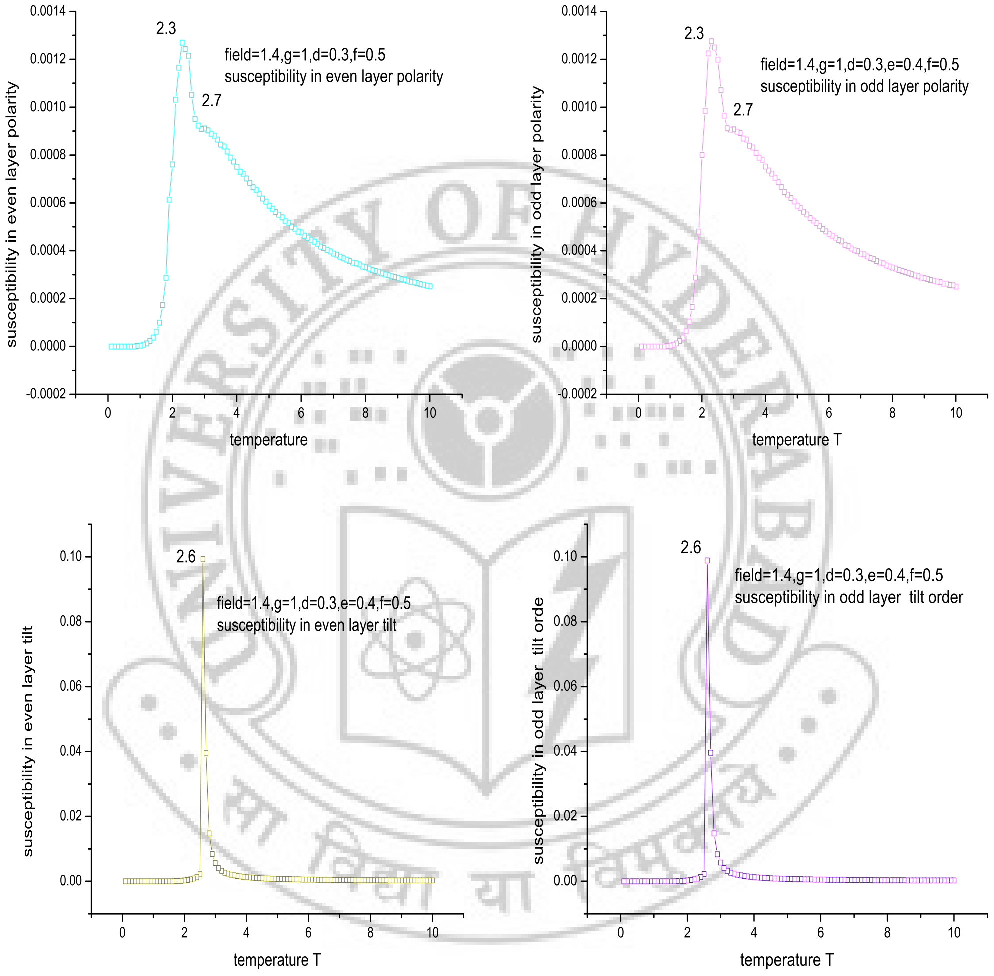
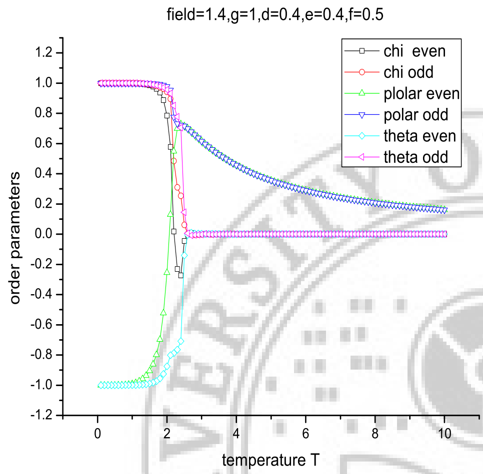
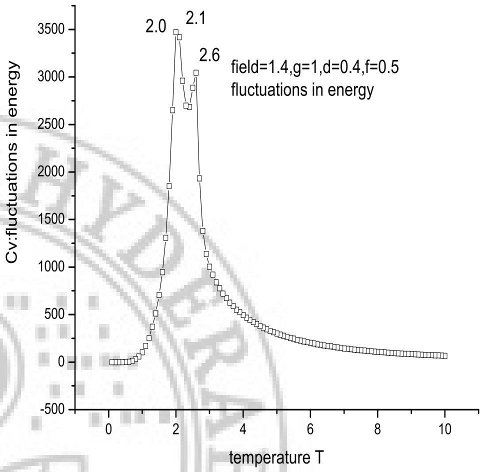
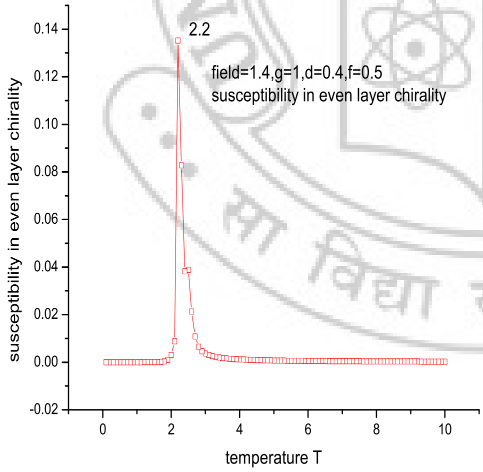
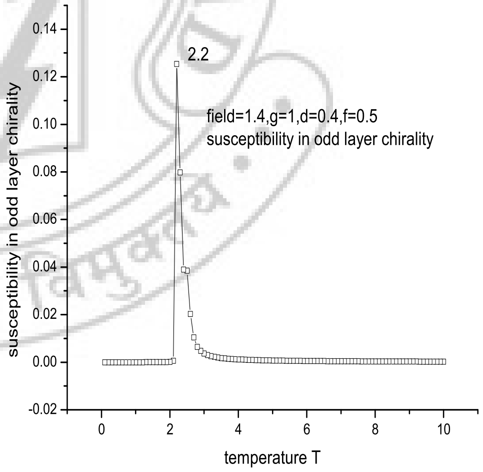


Figure 2.10: Monte Carlo simulation results showing temperature dependence of order parameter for different inter layer coupling coefficients, $C_\chi = 0.3$, $C_P = 0.4$, $C_\theta = 0.5$ and their susceptibility graphs.


field=1.4,g=1,d=0.4,e=0.4,f=0.5
chi even
chi odd
plolar even
polar odd
theta even
theta odd
order parameters
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
2
4
6
8
10
temperature T


2.0
2.1
2.6
field=1.4,g=1,d=0.4,f=0.5
fluctuations in energy
Cv:fluctuations in energy
3500
3000
2500
2000
1500
1000
500
0
-500
0
2
4
6
8
10
temperature T


2.2
field=1.4,g=1,d=0.4,f=0.5
susceptibility in even layer chirality
susceptibility in even layer chirality
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
0
2
4
6
8
10
temperature T


2.2
field=1.4,g=1,d=0.4,f=0.5
susceptibility in odd layer chirality
susceptibility in odd layer chirality
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
0
2
4
6
8
10
temperature T

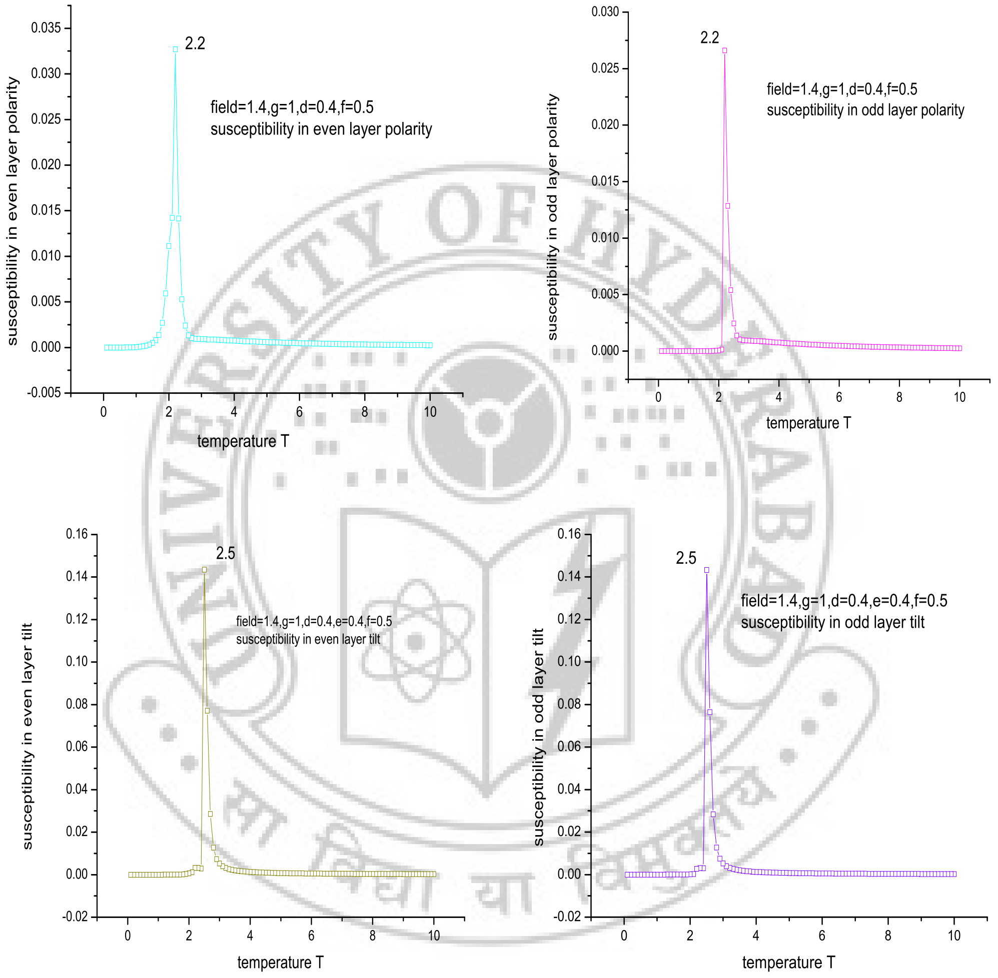
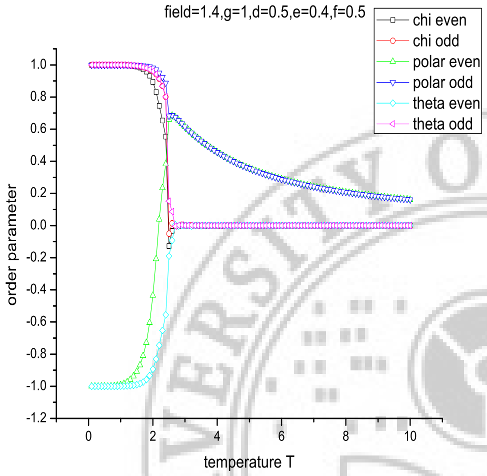
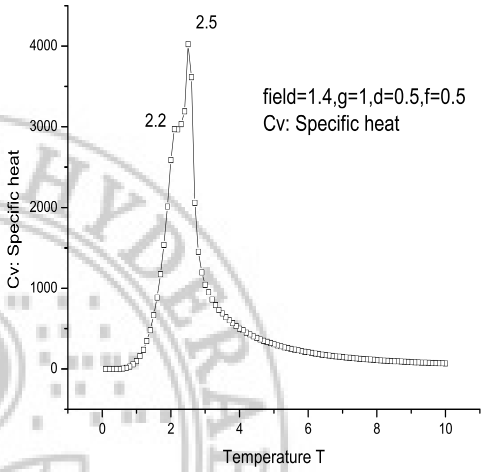
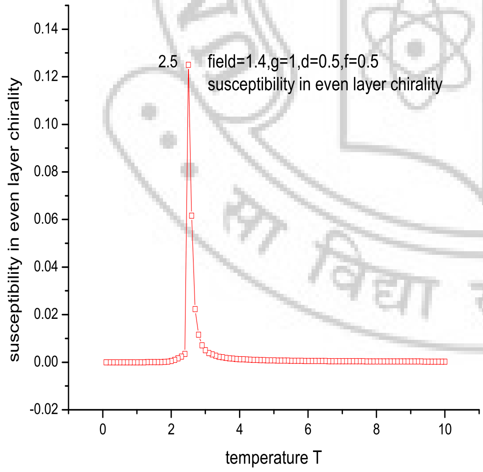
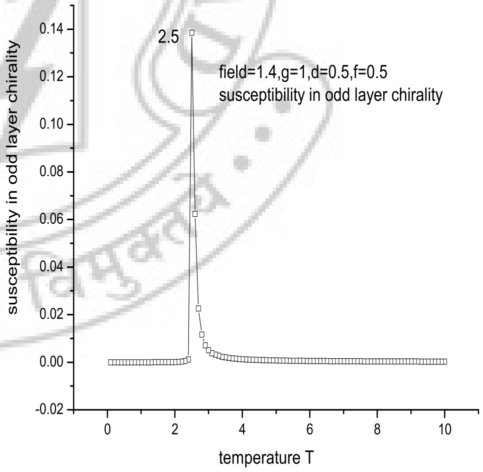


Figure 2.11: Monte Carlo simulation results showing temperature dependence of order parameter for different inter layer coupling coefficients, $C_\chi = 0.4$, $C_P = 0.4$, $C_\theta = 0.5$ and their susceptibility graphs.


field=1.4,g=1,d=0.5,e=0.4,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameter
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
2
4
6
8
10
temperature T


2.5
2.2
field=1.4,g=1,d=0.5,f=0.5
Cv: Specific heat
Cv: Specific heat
4000
3000
2000
1000
0
0
2
4
6
8
10
Temperature T


2.5
field=1.4,g=1,d=0.5,f=0.5
susceptibility in even layer chirality
susceptibility in even layer chirality
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
0
2
4
6
8
10
temperature T


2.5
field=1.4,g=1,d=0.5,f=0.5
susceptibility in odd layer chirality
susceptibility in odd layer chirality
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
0
2
4
6
8
10
temperature T

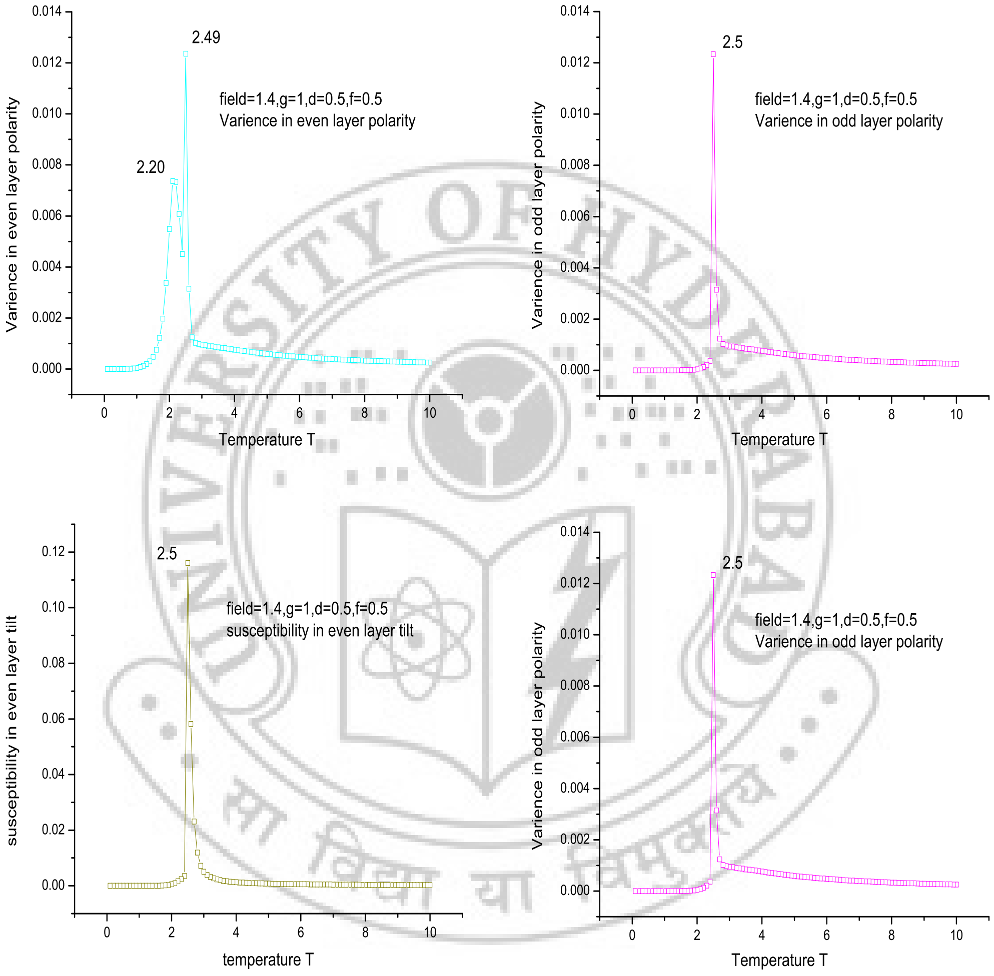
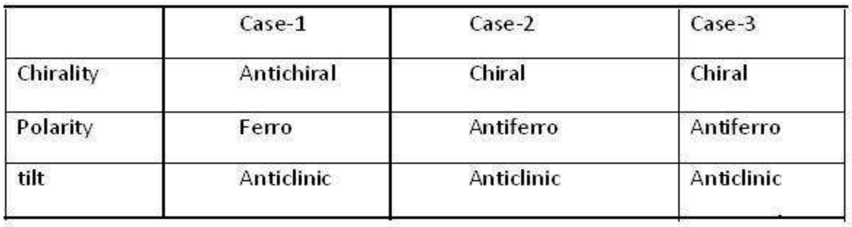
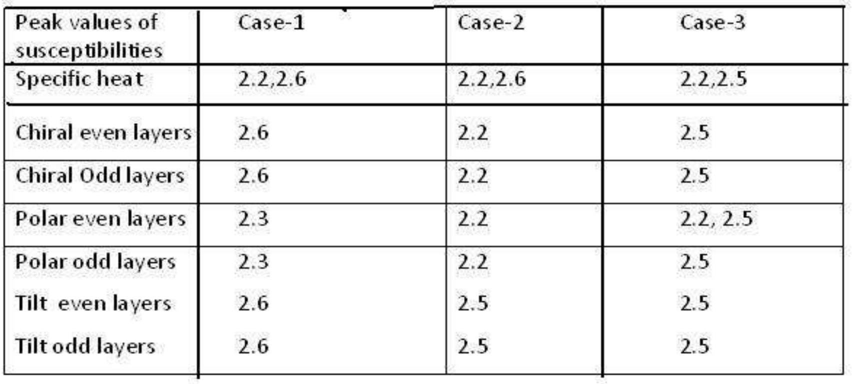


Figure 2.12: Monte Carlo simulation results showing temperature dependence of order parameter for different inter layer coupling coefficients, $C_\chi = 0.5$, $C_P = 0.4$, $C_\theta = 0.5$ and their susceptibility graphs.



	Case-1	Case-2	Case-3
Chirality	Antichiral	Chiral	Chiral
Polarity	Ferro	Antiferro	Antiferro
tilt	Anticlinic	Anticlinic	Anticlinic



Peak values of susceptibilities	Case-1	Case-2	Case-3
Specific heat	2.2,2.6	2.2,2.6	2.2,2.5
Chiral even layers	2.6	2.2	2.5
Chiral Odd layers	2.6	2.2	2.5
Polar even layers	2.3	2.2	2.2, 2.5
Polar odd layers	2.3	2.2	2.5
Tilt even layers	2.6	2.5	2.5
Tilt odd layers	2.6	2.5	2.5

Table 3:Show thermally driven transition and their susceptibility valuess

Case 1 $C_\chi = 0.3$, $C_P = 0.4$, $C_\theta = 0.5$

Due to large value of C_θ, the first transition on cooling results in an anticlinic state (even and odd layers have different tilt). Polar order in the presence of strong field is smeared and there is a gradual build up of polarization. The specific heat develops a shoulder (at T=2.2), and the susceptibility of layerwise chirality indicates a mirror peak corresponding to this value. More interesting the C_P corresponding to polarity fluctuations show a sharp peak at this value, distinguishing it from the broad hump developing at higher temperature. Fluctuations in tilt do not evidence this second transition. We conclude that at this choice of C_χ and C_P there are two transitions, one trigged by the onset of anticlinic state, and the other by the antichiral state. While the presence of two distinguishable peaks in σ_χ indicate this, the higher sensitivity of polar fluctuations in the antichiral transition is interesting, and will be discussed further later.

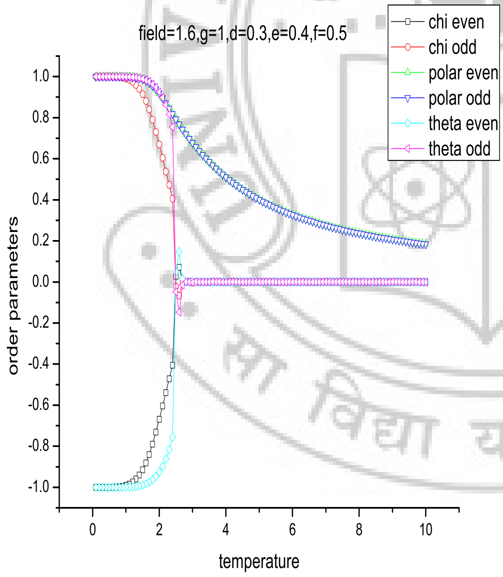
Case 2 $C_\chi = 0.4$, $C_P = 0.4$, $C_\theta = 0.5$

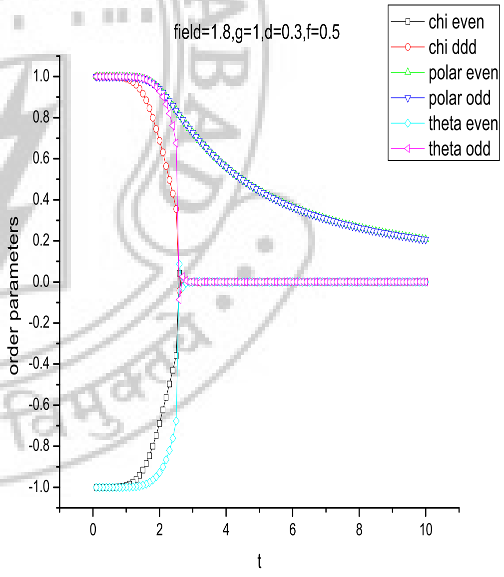
Referring to figure 2.11 corresponding to this case, one note that there is a qualitative difference in the set of transitions triggered in this case. As the sample is cooled, the anticlinic transition is followed by antiferroelectric transition with even and odd layers having opposite polarizations. The state remains chiral (not antichiral, with alternating layer chirality). While trying to preserve the overall minimization from the product term (-$g\chi P\theta$), it appears that in this case the onset of antichiral structure induces similar structure for polarization leaving the chirality in tact. The location of the susceptibilities peaks of the different variables in this case supports this scenario.

Case 3 $C_\chi = 0.5$, $C_P = 0.4$, $C_\theta = 0.5$

Figure 2.12 summarizes the data corresponding to this choice. The C_V profile indicates the presence of two transitions (approximately located at T=2.5

and 2.2). Interestingly the fluctuations in tilt (σ_θ) and chirality (σ_χ) show peak values at $T \sim 2.5$. the polar order in the two layers have on the other hand contrasting behavior. The value of $\sigma_P{}^o$ (polar order variance in odd layers) show a simple peak at T=2.5, and the polarization in these layers are in the direction of the applied field. Very interestingly $\sigma_P{}^o$ develops two peaks, at T=2.5 and 2.2, meaning that the polar variable associated with even layers (whose direction is eventually giving to oppose the field, to make the sample antiferroelectric) undergo yet another transition at a lower temperature, and it is duly reflected in the C_V peak as phase transition. Another interesting way of looking at the result of these the three cases is to suggest that in the process of variation of the relative strengths of chiral and tilt anisotropic couplings (at the fixed $C_P = 0.4$), the system might have evolved in a way that the threshold applied field needed to force the system from antiferro state to ferro state (Case A studied earlier) has effectively been changed. Or, in other words, the reason for the onset of antiferroelectric order in case-3, relative to case-1 (all within Case-D), is that the threshold field for switching this system from its inherent preference to form an antiferroelectric state itself has changed due to reassignment of the parameters in the Hamiltonian . This can easily be verified by repeating these simulations for all these three cases at higher fields. We take up this exercise by considering Case-1 to Case-3, and apply a variable field from 1.4 to 2.6 in steps of 0.2. For these studies, we present the variation of only average values of different order parameters, suppressing the graph of their variance to avoid cluttering of data. Figures 2.13 to 2.15 provide the field dependence of Case-1, Case-2 and Case-3, respectively. A perusal of this data shows that the enhancement of field has a significant and quantitatively different effect on Case-3 [$C_\chi = 0.5$, $C_P = 0.4$, $C_\theta = 0.5$]. Referring to figure 2.15 one notes that the phase diagram of the order parameters for field value F=1.6 is very similar to the case with F=1.4 (figure 2.12) with an antiferroelectric polar order at low temperature the only difference have that the C_V peaks are more separated. However for values of F=1.8 and above, the system does not transit at all to an antiferroelectic state. The field is too large to allow this state, though the two types of layers show small difference in the polarization for a very short temperature range. The effect of high field is to induce a low temperature phase which is anticlinic (opposite tilts for alternate layers), a chiral structure (same type of chirality for all layers) and eventually a ferroelectric state. Thus the effect of the coupling term (-$g\chi P\theta$) seems to have been overcome once the field crossed a threshold value which seem to some value between F=1.6 and 1.8. The simulation for higher fields (F=2 to 2.6) show that the system develops many instabilities because of the very many competing interactions introduced, fuelled by a strongly held polar order. What is observed hence in an interplay between the coupling term to keep the product $\sigma P\theta$ positive and its strength progressively increasing as the polarization builds up on cooling. At this stage of discussion, one should view them more as curiousities that could be induced in the toy model.





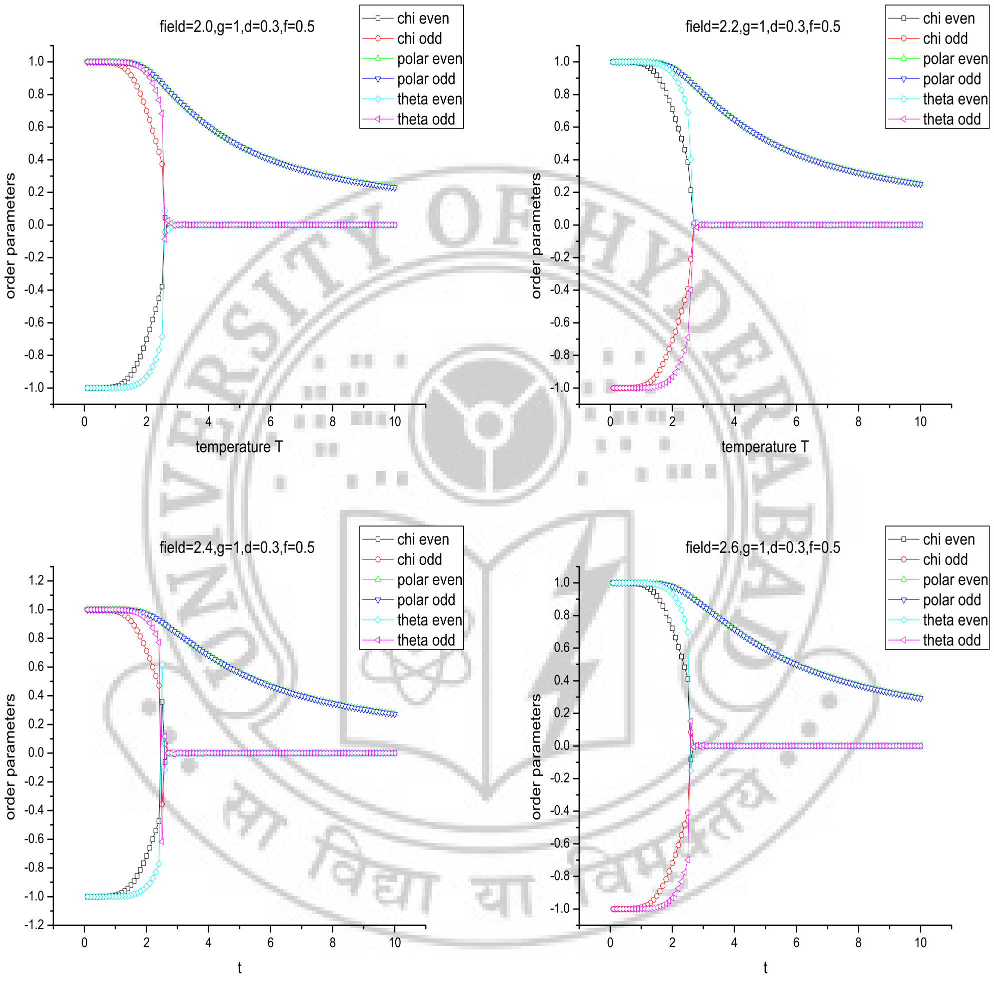
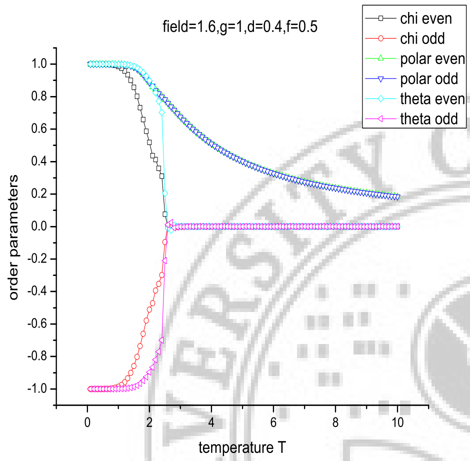
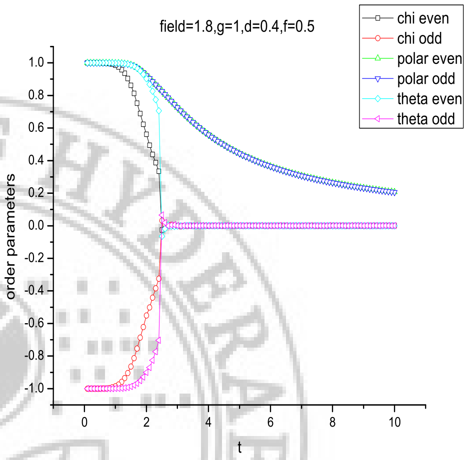
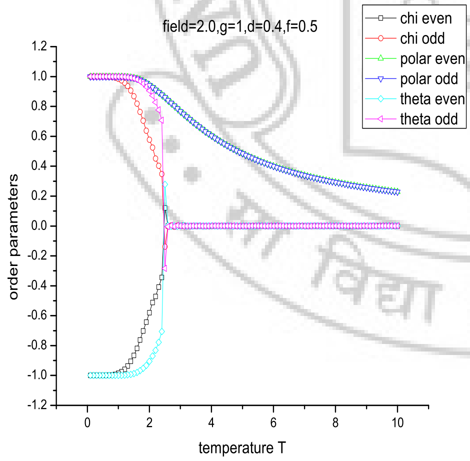
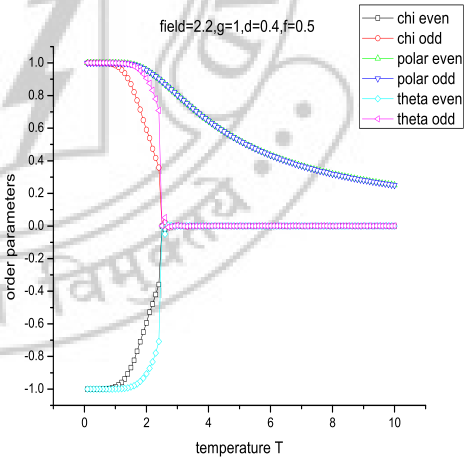


Figure 2.13: Monte Carlo simulation results showing temperature dependence of order parameter $C_\chi = 0.3$, $C_P = 0.4$, $C_\theta = 0.5$ and for different field values.


field=1.6,g=1,d=0.4,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T


field=1.8,g=1,d=0.4,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
t


field=2.0,g=1,d=0.4,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
2
4
6
8
10
temperature T


field=2.2,g=1,d=0.4,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
temperature T

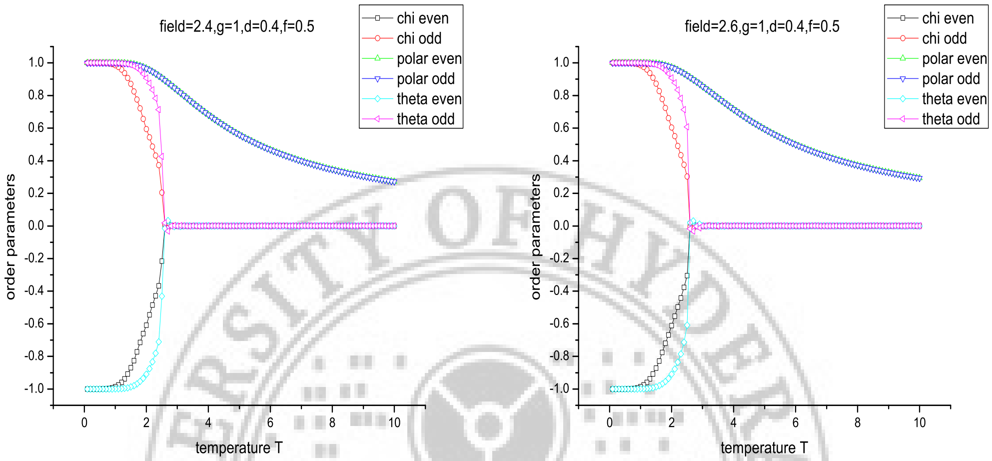
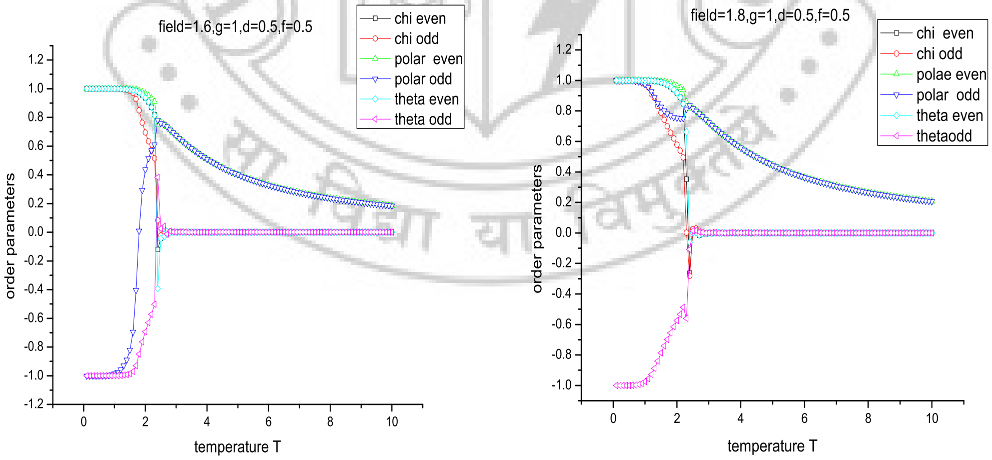


Figure 2.14: Monte Carlo simulation results showing temperature dependence of order parameter $C_\chi = 0.4$, $C_P = 0.4$, $C_\theta = 0.5$ and for different field values.



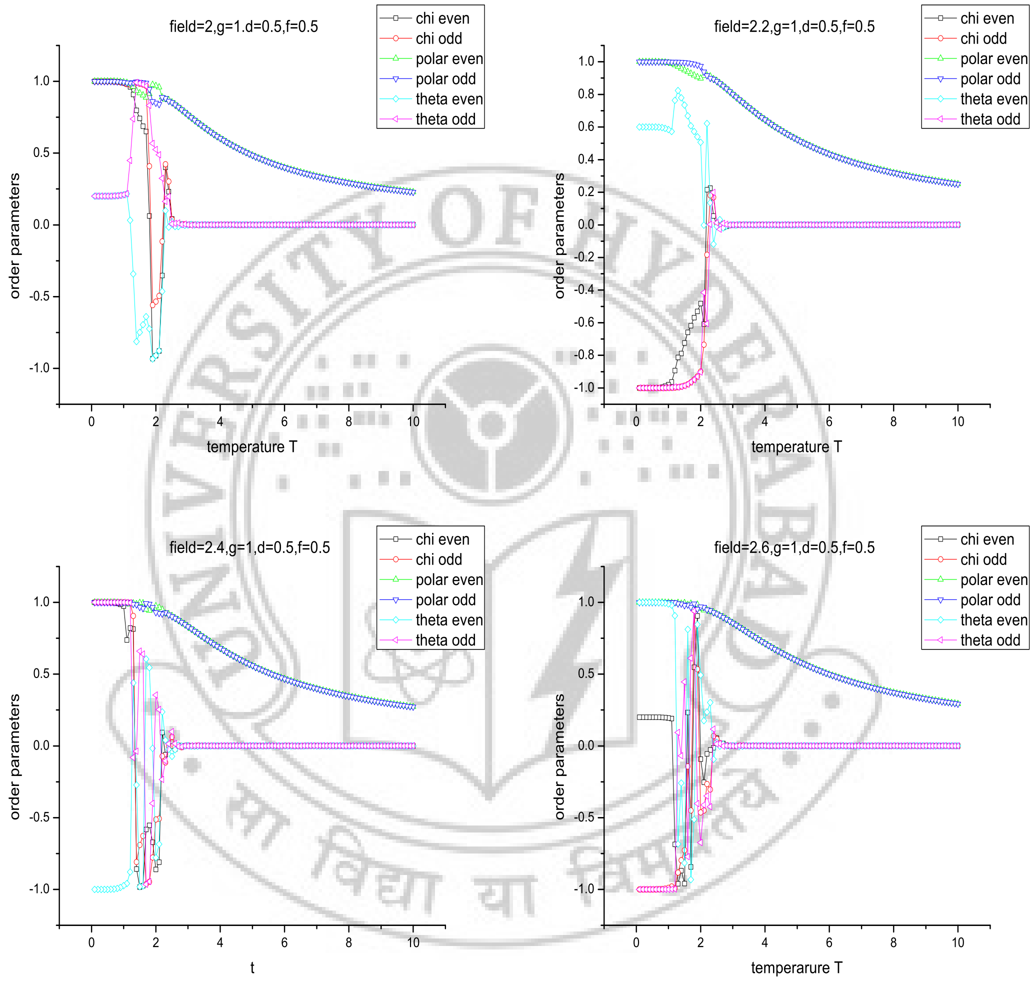
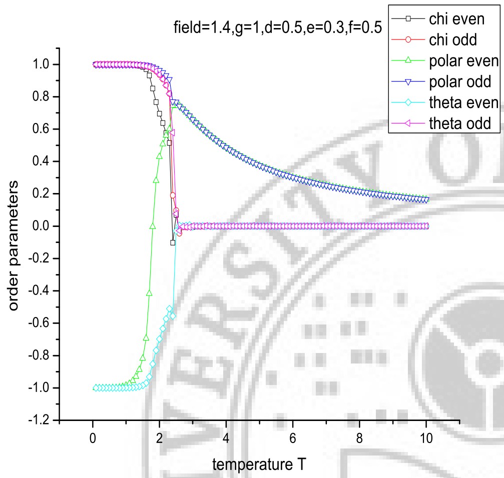
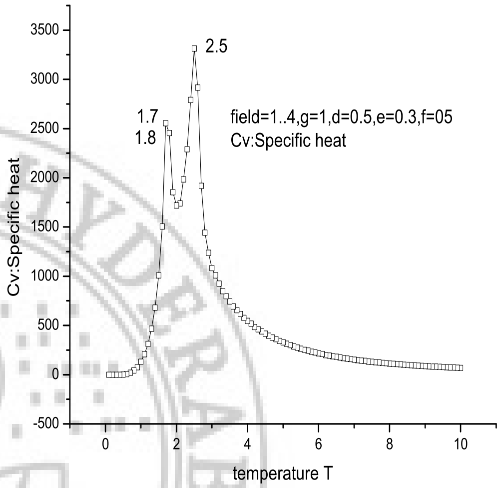


Figure 2.15: Monte Carlo simulation results showing temperature dependence of order parameter $C_\chi = 0.5$, $C_P = 0.4$, $C_\theta = 0.5$ and for different field values.

Case E: Thermally driven transitions for non-zero values of field as a function of the inter layer coupling coefficient C_P.
We present final set of results based on the curious behavior of the system in the field range 1.4 to 1.6. We consider this case of $C_\chi = 0.5$ and $C_\theta = 0.5$ (the extrema values for these parameters in case D), and now change C_P (which was held at 0.4 in case D) to 0.3 and o.5. To keep the discussion simple and more illustrative we present the result only for one interesting field strength F = 1.4. Figures 2.16 and 2.17 present the phase diagram and corresponding layerwise susceptibilities for $C_P = 0.3$ and 0.5 respectively.


field=1.4,g=1,d=0.5,e=0.3,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
2
4
6
8
10
temperature T


2.5
1.7
1.8
field=1..4,g=1,d=0.5,e=0.3,f=05
Cv:Specific heat
Cv:Specific heat
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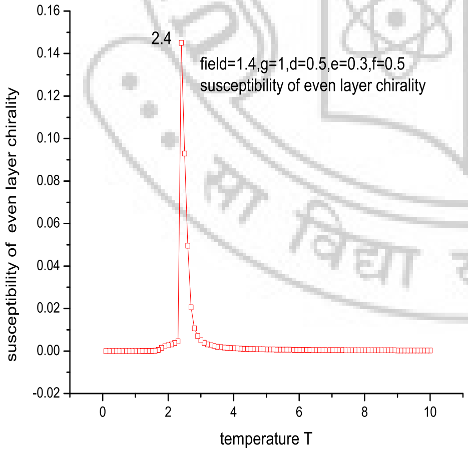
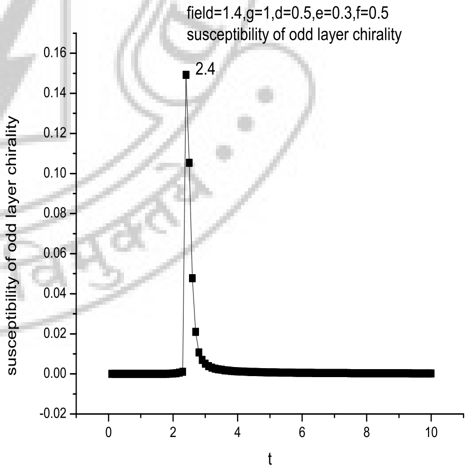
3000
2500
2000
1500
1000
500
0
-500
0
2
4
6
8
10
temperature T


2.4
field=1.4,g=1,d=0.5,e=0.3,f=0.5
susceptibility of even layer chirality
susceptibility of even layer chirality
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
0
2
4
6
8
10
temperature T


field=1.4,g=1,d=0.5,e=0.3,f=0.5
susceptibility of odd layer chirality
2.4
susceptibility of odd layer chirality
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
0
2
4
6
8
10
t

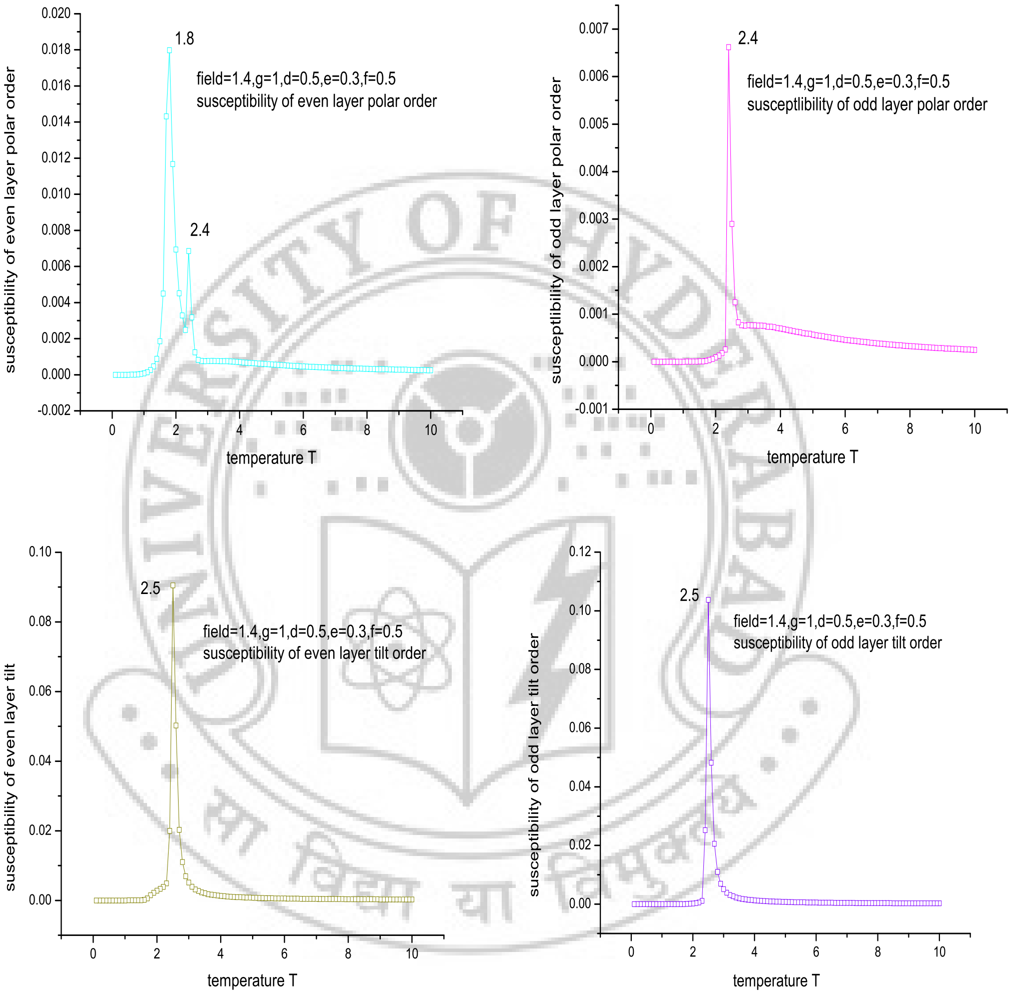
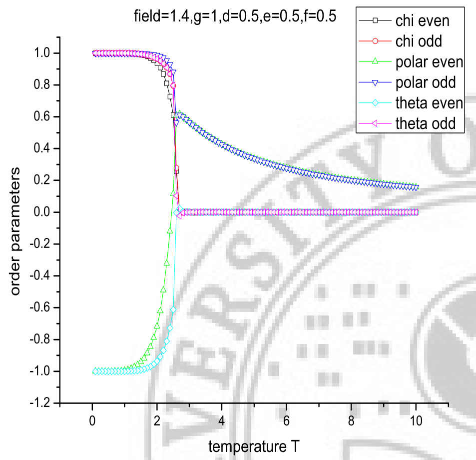
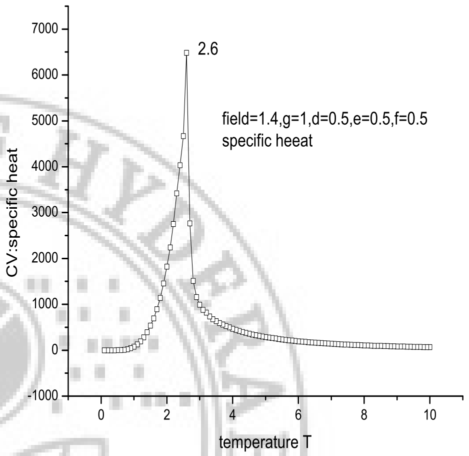
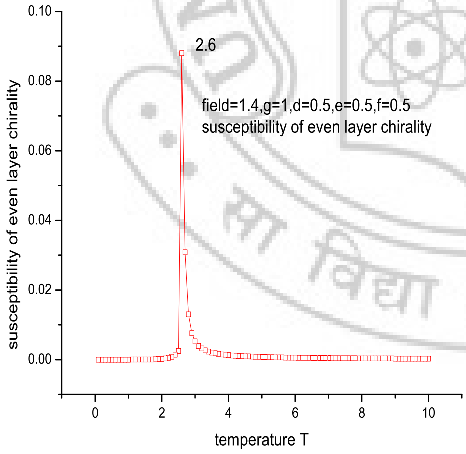
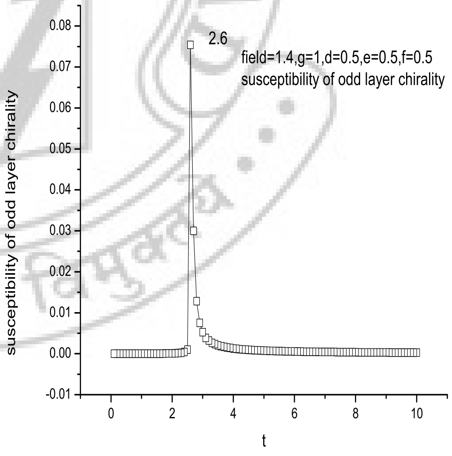


Figure 2.16: Monte Carlo simulation results showing temperature dependence of order parameter $C_\chi = 0.5$, $C_P = 0.3$, C_θ=0.5 and for different field values and their susceptibility plots


field=1.4,g=1,d=0.5,e=0.5,f=0.5
chi even
chi odd
polar even
polar odd
theta even
theta odd
order parameters
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
2
4
6
8
10
temperature T


2.6
field=1.4,g=1,d=0.5,e=0.5,f=0.5
specific heeat
CV:specific heat
7000
6000
5000
4000
3000
2000
1000
0
-1000
0
2
4
6
8
10
temperature T


2.6
field=1.4,g=1,d=0.5,e=0.5,f=0.5
susceptibility of even layer chirality
susceptibility of even layer chirality
0.10
0.08
0.06
0.04
0.02
0.00
0
2
4
6
8
10
temperature T


2.6
field=1.4,g=1,d=0.5,e=0.5,f=0.5
susceptibility of odd layer chirality
susceptibility of odd layer chirality
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
0
2
4
6
8
10
t

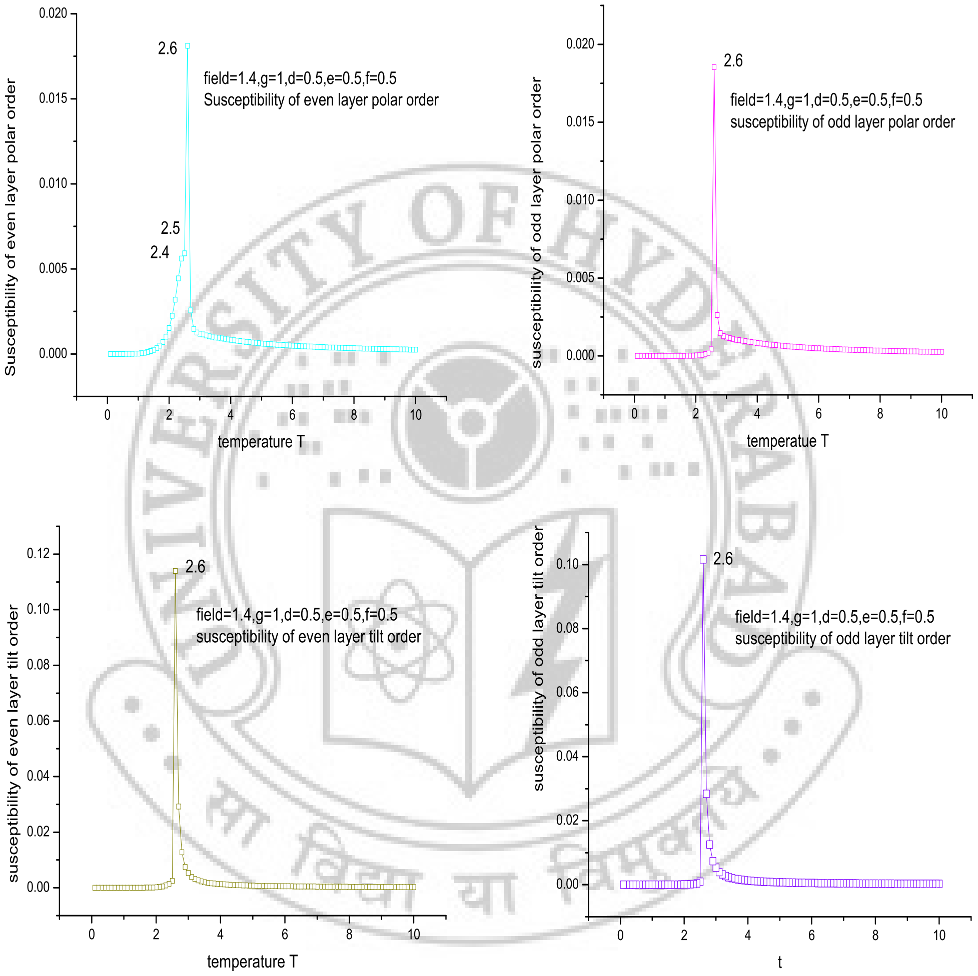


Figure 2.17: Monte Carlo simulation results showing temperature dependence of order parameter C_χ = 0.5, C_P = 0.5, C_θ=0.5 and for different field values and their susceptibility plots

Referring to figure 2.16, we see that the C_V peak splits showing approximate transition temperatures as $\sim$ 2.5 and $\sim$1.7. This may be compared with figure 2.12, where the only difference is the value of C_P: its value was 0.4 in figure 2.12, and 0.3 in figure 2.16. The transitions are well separated in the present case. The plots of $\sigma_\chi{}^{o,e}$ and $\sigma_\theta{}^{o,e}$ show that these order parameters show divergence of their fluctuations coincident with T $\cong$ 2.5 on the other hand the plots depecting $\sigma_P{}^e$ and $\sigma_P{}^o$are very illustrative. $\sigma_P{}^e$ representing fluctuations in the polar order of the odd layer (whose polarization direction coincides with the field direction) shows a peak at T $\sim$ 2.4, like the other two parameters. On the other hand, $\sigma_P{}^e$ shows a small peak at T=2.4, but significantly large peak at T$\sim$1.8. Even keeping the reduction of the temperature in these simulations ($\triangle T = 0.1$), the implication is clearly seen. There is a well separated several transition wherein the even layers develop antiferroelectric order. This is also seen by Inspecting the average polar order of this set of layers in the phase diagram depicting average values.
A contrasting limit is observed when C_P is increased from 0.4 (Case D) to 0.5, see figure 2.17. In this case, the two C_V peaks essentially coalesce compared to figure 2.12 ($C_P = 0.4$), and in the even layer fluctuations, $\sigma_P{}^e$, there only a limit of the existence of two transitions. From this case study we conclude that the inter-layer coupling parameter C_P plays a very curious role in this subspace region of the order parameter space, and a fine tuning of the field variable provides another interesting direction to investigate the interplay between effective threshold values for field induced switching versus thermally driven onset of different phases.

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3

Conclusions

The close packing of achiral bent core molecules exhibit polar order in the smectic phases. Polar order in combination with molecular tilt with respect to the layer normal induces chiral structures. The interplay of polar and tilt order gives SmCP structures with same or different layer chirality. Recent experiments observed that one can induce phase transitions between chiral and achiral structures with an electric field.

Lattice Hamiltonian considered involves neighboring interactions of the order parameter (polar (P), tilt (θ) and chiral (χ) orders) both intra-as well as inter-layer couplings, coupling between these three order parameters (with coupling coefficient g) and field interaction term. Intra-layer couplings favor ferromagnetic nature to these three order parameters within the layers. Inter-layer couplings of the chirality (coupling coefficient (C_χ), polarity (C_P) and tilt (C_θ) orders favor chiral, antiferro and anticlinic structures to the ground state. Recently field-induced chiral switching was studied with this Hamiltonian. We examine thermally driven transitions for different couplings as a function of C_χ, C_θ and g. we observed certain interesting thermally driven phase transitions in the small chosen parameter subspace of Hamiltonian.

We made an attempt to study field induced transition as a function of coupling coefficient of the three order parameters (g) at different temperatures by performing Monte Carlo simulations. With the application of an electric field antiferroelectric state switches to ferroelectric state by either change in chirality of phase or not, depending on the inter layer chiral coupling coefficient (C_χ) and coupling coefficient of three order parameters. For lower values of coupling coefficient of three order parameters (g) only polar order transits from antiferro to ferroelectric state. With increase in g coupling between three order parameters becomes strong so polar order pulls the chiral order, and as a result chirality switches from chiral to achiral state. This threshold field value (where chirality switches to antichiral from chiral state) seem to moves to lower values with increase in temperature, as seen by the change in the requisite g values to exhibit the transition. Considering the coupling among three variables through parameter g. in the presence of field the polarization initially increase with decrease of temperature. This effectively makes this coupling among these variables makes temperature dependence (increase on decrease of temperature). We can say chirality switching in the presence of temperature as a whole as a function of temperature.

Thermally driven transitions are observed with the zero and nonzero values of the field as a function of coupling coefficient (g). For zero values of the field transitions of three order parameters are observed at three different temperatures for low values of g and for its higher values the transition take place at the same temperature because of strong coupling. Transitions are obviously influenced by the value of applied value. If the field is strong enough to smear out the transition of polar order chiral order transits to an achiral state and tilt result in an anticlinic state. If the field is not sufficient polar order transits antiferro, chirality transforms to chiral, and tilts transform to anticlinic states.

We then moved on to the subspace of chirality (C_χ) and tilt (C_θ) in the presence of a strong field and strong coupling among three order parameters (g) to observe thermal behavior of this model. Strong field favors the system to be in ferroelectric state but inter-layer coupling constant (C_χ) essentially decides this state. Depending on the value of C_χ, system could remain ferroelectric (weak inter-layer coupling coefficient) by changing the chiraliy of the system to achiral or it may transform to ferroelectric state (strong inter-layer coupling coefficient) by preserving the chirality of the phase. In these cases tilt remains in anticlinic state. One more interesting result observed while system transforming to antiferoelectric state is that transition to antiferroelectric state is observed at two different temperatures. This indicates that two types of layers i.e. even and odd layers, are having opposite polarization. Odd layer which is the field direction take transition very sharply at one temperature while the even layers (having polar order opposite to field direction) transit at different temperature, to complete the antiferroelectric transition.