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**NGUYEN THI PHUONG THUY**

**STUDY OF THE SMECTIC TO ISOTROPIC LIQUID  
PHASE TRANSITION IN LIQUID CRYSTALS**

Major: Theoretical and Mathematical Physics

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**SUMMARY OF MATERIAL SCIENCE DOTAL THESIS**

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Advisor 1: Assoc. Prof. Dr. Ngo Van Thanh

Advisor 2: Dr. Nguyen Thi Lam Hoai

Reviewer 1:

Reviewer 2:

Reviewer 3:

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## INTRODUCTION

### Motivation for the Thesis

Liquid crystal science and applications now permeate almost all segments of society from large industrial displays to individual homes and offices.

Liquid crystals can be classified into two main categories: thermotropic liquid crystals, and lyotropic liquid crystals. The most widely used liquid crystals, and extensively studied for their linear as well as nonlinear optical properties are thermotropic liquid crystals. They exhibit various liquid crystalline phases as a function of temperature. There are three main classes of thermotropic liquid crystals: nematic, smectic, and cholesteric.

Smectic phase is viscous and fluid. In smectic phase, the molecules are arranged side by side in a series of layers. In each layer, the molecules are positionally random but directionally ordered with their long axis.

Several subphases of smectic have been discovered, in accordance with the arrangement or ordering of the molecules and their structural symmetry properties. When changing temperature, the smectic phase may undergo some phase transitions. The smectic-isotropic phase transition phenomenon is a phase change from the liquid crystal to the liquid phase.

There exist experimental works and theoretical works on this phase transition. The field really started to develop with the work of Stoebe and co-workers in 1994. The smectic-isotropic transition occurs through a series of layer-thinning transitions, causing the films to thin in a stepwise manner as the temperature increases. The temperature dependence of the film thickness has been found to be well-fitted by a simple power law. Most of the theoretical studies have used Landau-de Gennes theory. The main idea of Landau-de Gennes theory is that in the vicinity of the phase transition, the order parameter of the system will change. However, the order parameter of the smectic phase is defined very differently in theoretical studies. In addition, theoretical studies also focus on verifying the relationship between the number of layers and phase transition temperature.

In the computing works, including Monte Carlo simulations, in 2020, Prof. Hung T. Diep considered a mobile Potts model to simu-

late smectic phase. Though their work obtained the structure of the smectic phase by cooling the molecules from the isotropic phase to low temperatures, the phase transition process at the vicinity of the phase transition has not been clearly described.

Research on smectic-isotropic phase transition still has some limitations. First, there are limitations in the research model for the smectic phase. Second, is the limitation of research results. There have not really been any simulation studies describing the dynamic nature of the smectic-isotropic phase transition. The thinning transition process observed experimentally has not been described in any simulation studies.

That is the driving force that motivated us to conduct research on phase and liquid crystal phase transition phenomena with the title: **Study of the smectic to isotropic liquid phase transition in liquid crystals.**

## Objectives

The objectives of this thesis are to:

- Develop theoretical models describing microscopic interactions between molecules in order to simulate the phase transition of liquid crystals.
- Investigate smectic-isotropic phase transition and the characteristics of the phase transition.
- Optimize the Monte Carlo simulation algorithm suitable for liquid crystals.

## Research Content

- Research on the smectic phase transition of liquid crystals using the Potts model.
- Research on the smectic phase transition phenomenon of liquid crystals using the extended Potts model with the contribution of Lennard-Jones potential energy.

# Chapter 1

## BACKGROUND

### 1.1 Liquid crystals

Liquid crystals recognized as mesophase, are a state of matter whose properties are between those of simple liquids and those of solid crystals. This characteristic leads to many unique and exciting phenomena not seen in ordinary liquid.

### 1.2 Classification of Liquid Crystals

#### a) Thermotropic Liquid crystals

Thermotropic liquid crystals exhibit various liquid crystalline phases as a function of temperature: nematic, smectic, and cholesteric. In the nematic phase, the molecules maintain a preferred orientational direction as they diffuse throughout and possess long-range orientational order along the direction. In the smectic phase, the molecules are arranged side by side in a series of layers and their movement is mainly limited inside the layers, which are free to slide over each other. In the cholesteric phase, the molecules are chiral and gradually rotate in the direction. This gradual direction change describes a helix structure.

#### b) Lyotropic Liquid crystals

Lyotropic phases are those that occur in certain concentration ranges. The recipe of a lyotropic liquid crystal molecule is amphiphilic molecules. The lyotropic phases frequently found are lamellar, hexagonal (normal and inverse), and cubic.

### 1.3 Applications of Liquid Crystals

Liquid crystal technology has had a major effect on many areas of science and engineering, as well as device technology. Liquid crystals, in particular, can be found in many instruments, including Liquid Crystal Displays, Liquid Crystal Thermometers, and Optical Switch.

### 1.4 Literature Review on Phase transitions in thermotropic liquid crystals

The nature of phase transitions of liquid crystals has attached considerable experimental and theoretical studies. Optical polarising microscopy, differential scanning calorimetry and X-ray analysis are

the most widely used technique of liquid crystal phase identification and phase transitions. The theory for the phase at and in the vicinity of their phase transitions of liquid crystals has been developing in several directions. Most theoretical research has relied on Landau-de Gennes theory, Frank's free energy, and molecular statistical theory.

Computer simulations have played a key role in developing the understanding of phase transitions in liquid crystals. Some of the molecular models used in liquid crystal simulation are Lebwohl-Lasher model, Gay-Bern model, and the molecular model.

We shall present a summary of the current experimental and theoretical understanding of the smectic to isotropic phase transition. In 1994, with the help of calorimetric and optical reflectivity Stoebe et al. observed a reproducible series of layer-thinning transition at higher temperature. The smectic - isotropic phase transition is described in detail, including structure and nature revealed by experiments, molecular models, and Landau-de Gennes theory. To determine the mechanism of the thinning transition of smectic phase, researchers conducted experimental studies and theoretical research. However, the mechanism of occurrence of the present phenomenon of thinning transition is still not really clear. In 2020, Prof. H. T. Diep and colleagues published research describing the process dynamic of smectic - isotropic phase transition by a mobile Potts model. Nevertheless, their results did not reveal the layer thinning transitions.

## 1.5 Summary

We introduced the history of the discovery new state of matter the liquid crystal state. According to the way in which the liquid mesomorphic phases can be obtained, liquid crystals are classified as lyotropic and thermotropic. Dielectric anisotropy and birefringence are fundamental principles for many applications of liquid crystals. Currently, our knowledge about the mechanism of the thinning transition of the smectic-isotropic phase transition is still limited. Besides, there isn't really a theoretical model that describes fully and accurately the characteristics of the smectic-isotropic phase transition. The motivation for this doctoral work is to establish a theoretical physical model to study the smectic-isotropic phase transition of liquid crystals.

## Chapter 2

### SPIN MODEL AND MONTE CARLO METHOD

#### 2.1 Spin models

A spin model consists of lattice geometries, a set of spin values, and the total energy.

The Hamiltonian of the Ising model is:

$$H = - \sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j, \quad (2.1)$$

where  $\sigma_i$  is the spin at lattice site  $i$  with two possible values. The summation runs only over nearest-neighbor pairs  $\langle ij \rangle$  on the lattice,  $J_{ij}$  is the spin-spin exchange interaction.

Ising model describes the ordered phase very well at low temperatures, the disordered phase appearance at high temperatures, and the phase transition from order to disordered phase.

In XY model, the variables are two-dimensional unit vectors  $\mathbf{S}_i$  on each site. The Hamiltonian is provided by:

$$H = - \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = \sum_{\langle i,j \rangle} J_{ij} (S_i^x S_j^x + S_i^y S_j^y). \quad (2.2)$$

The XY model plays an important role when studying systems in space two-dimensional space such as liquid crystals, thin helium films, films of superconductors.

The Hamiltonian of the Heisenberg model is given by:

$$H = - \sum_{\langle i,j \rangle} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j), \quad (2.3)$$

where  $\mathbf{S}_i$  is three-dimensional vectors at the lattice  $i$ ,  $\langle i, j \rangle$  indicates the sum over the nearest neighbour spin pairs  $\mathbf{S}_i$  and  $\mathbf{S}_j$ .

The classical Heisenberg model has been of interest since the 1960s as a model for studying magnetism. The Heisenberg model is also applied to some cases where magnetic materials are alloys of rare earth metals and transition metals.

The  $q$ -state Potts model consists of a lattice of spins  $\sigma_i$ , which can take  $q$  different values,  $\sigma_i = 1, 2, \dots, q$  and whose Hamiltonian is:

$$H = - \sum_{\langle i,j \rangle} J_{ij} \delta_{\sigma_i, \sigma_j}, \quad (2.4)$$

where  $\delta_{\sigma_i, \sigma_j}$  denotes the delta Kronecker. The sum is performed over pairs of nearest neighbors.

The main focus of the Potts model is to find the critical point and to observe the phenomenon that occurs during the phase transition between ordered and disordered states.

## 2.2 Mobile Potts model

A mobile Potts model is a Potts model in which the spins do not completely fill the lattice sites. With the number of lattice positions  $N_L$ , we have the number of spins  $N_s$  satisfying  $N_L < N_s$  to ensure the mobility of spins in the lattice. The Hamiltonian expression of the mobile Potts model is given by:

$$\mathcal{H} = - \sum_{\langle i, j \rangle} J_{ij} \delta_{\sigma_i, \sigma_j}, \quad (2.5)$$

where  $\langle i, j \rangle$  are pairs of neighboring molecules,  $\sigma_i = 1, 2, \dots, q$  are molecular states,  $J_{ij}$  represents the exchange interaction. The Kronecker delta function is given by:

$$\delta_{\sigma_i, \sigma_j} = \begin{cases} 1, & \sigma_i = \sigma_j, \\ 0, & \sigma_i \neq \sigma_j. \end{cases} \quad (2.6)$$

The mobile Potts model has been used to study the phase transition of liquid crystals by Monte Carlo simulation, in which the mobility of the particles of the Potts model is characteristic of the mobility of the particles. The mobility of elements is shown in the simulation algorithm, that is, during the simulation process, elements can move to neighboring vacancies.

## 2.3 Monte Carlo Simulation

### 2.3.1 Introduction

The Monte Carlo simulation is a method of statistical sampling through computer-generated random numbers.

In thermal equilibrium, a system in state  $\mu$  with energy  $E_\mu$  at temperature  $T$  is found with the probability according to the Boltzmann distribution:

$$p_\mu = \frac{1}{Z} e^{-E_\mu/k_B T}, \quad (2.7)$$

where  $k_B$  is Boltzmann's constant.  $Z$  is called the partition function and has value:

$$Z = \sum_{\mu} e^{-E_{\mu}/k_B T}, \quad (2.8)$$

Normally, the statistical average of physical quantities is determined by the formula:

$$\langle A \rangle = \sum A_{\mu} p_{\mu}, \quad (2.9)$$

where  $A_{\mu}$  is the value of the observable in state  $\mu$ .

The biggest difficulty in statistical mechanics is to determine the partition function of the system. One of the research methods to solve the above problem is the Monte Carlo simulation method. The idea of the Monte Carlo simulation method is to replace the sum over all possible states with a sum over a subset  $\{\mu_1, \mu_2, \mu_3, \dots, \mu_M\}$  of states to determine the statistical average.

We consider sets of states that contribute greatly to the partition function, or in other words, we select states that follow the Boltzmann distribution (importance sampling). Then the statistical average is determined as follows:

$$\langle A \rangle = \frac{1}{M} \sum_{i=1}^M A_{\mu_i}. \quad (2.10)$$

### 2.3.2 Metropolis algorithm

The idea of the Metropolis algorithm is as follows: To calculate the average value, we create a continuous Markov chain of states, new states are created from old states with equilibrium transition probability  $P(\mu \rightarrow \nu)$ , where each state occurs with a probability given by the equilibrium Boltzmann distribution.

The generated Markov chain must be ergodicity and obey detailed equilibrium conditions:

$$p_{\mu} P(\mu \rightarrow \nu) = p_{\nu} P(\nu \rightarrow \mu). \quad (2.11)$$

We separate the equilibrium transition probability to include the transition probability  $g(\nu \rightarrow \mu)$  and the acceptance probability  $A(\nu \rightarrow \mu)$ :

$$P(\nu \rightarrow \mu) = g(\nu \rightarrow \mu) A(\nu \rightarrow \mu). \quad (2.12)$$

Combining the equations 2.7 and 2.11 we get:

$$\frac{A(\mu \rightarrow \nu)}{A(\nu \rightarrow \mu)} = \frac{g(\nu \rightarrow \mu)}{g(\mu \rightarrow \nu)} e^{-\Delta E/k_B T}, \quad (2.13)$$

where  $\Delta E = E_\nu - E_\mu$ .

For the Metropolis algorithm, the probability of accepting a new state is selected as follows:

$$A(\mu \rightarrow \nu) = \min \left( 1, e^{-\Delta E/k_B T} \right). \quad (2.14)$$

### 2.3.3 Histogram method

In the Metropolis algorithm, we calculate the thermodynamic average at discrete temperature points. We extrapolate the results between those temperature points. However, near the transition temperature points, extrapolation is not possible because the thermodynamic values are going to infinity at an exact temperature point.

#### a) Single histogram method

To avoid this difficulty of the standard Metropolis, Ferrenberg, and Swendsen have proposed the histogram method to simulate the system at the temperature  $T_0$  closest to the temperature  $T_c$  and determine the energy  $E$  of the system as long as the graph  $H(E)$  can be established. Using this histogram, we can calculate the probability  $P(T, E)$  at temperatures  $T$  near  $T_0$ :

$$P(T, E) = \frac{H(E) \exp \{ -(\beta - \beta_0) E \}}{\sum_E H(E) \exp \{ -(\beta - \beta_0) E \}}, \quad (2.15)$$

Using the formula, we can determine the average values:

$$\langle A \rangle = \sum_E A P(T, E). \quad (2.16)$$

#### b) Multiple-Histogram method

We have to realize many histograms  $H(E, T_i)$  in independent simulation. We can calculate the thermal of any physical quantity at  $T$  by:

$$\langle A(T) \rangle = \frac{\sum_E A(E) \rho(E) \exp(-E/k_B T)}{Z(T)}. \quad (2.17)$$

where the density of state  $\rho(E)$  is given by

$$\rho(E) = \frac{\sum_{i=1}^n H(E, T_i)}{\sum_{i=1}^n N_i Z(T_i)^{-1} \exp(-E/(k_B T_i))}, \quad (2.18)$$

where  $Z(T_i)$  is the partition function at the temperature  $T_i$ :

$$Z(T_i) = \sum_E \rho(E) e^{-E/k_B T_i}. \quad (2.19)$$

### 2.3.4 Wang-Landau technique

#### a) Introduction

Wang and Landau have proposed this algorithm which uses a random walk in the energy space in order to obtain an accurate estimate of the density of state  $g(E)$ .

#### b) Wang-Landau algorithm

The focus of the Wang-Landau technique is to determine the density of states  $g(E)$ . With the Wang-Landau technique, the probability that the system exists in state  $\mu$  with energy  $E$  is given by:

$$p_\mu \propto \frac{1}{g(E_\mu)}. \quad (2.20)$$

Then, the energy distribution function  $E$  is:

$$P(E) \propto g(E) e^{-E/k_B T}. \quad (2.21)$$

A move from state  $E_i$  and  $E_j$  are the energies of the initial state and the following state is accepted with probability

$$p(E_i \rightarrow E_j) = \min \left[ 1, \frac{g(E_i)}{g(E_j)} \right]. \quad (2.22)$$

The histogram is considered flat if:

$$H(E) \geq x\% \cdot \langle H(E) \rangle. \quad (2.23)$$

The thermodynamic quantities can be evaluated using  $g(E)$ :

$$\langle A \rangle = \frac{1}{Z} \sum_E A g(E) \exp(-E/k_B T), \quad (2.24)$$

with the statistical sum function  $Z$  given by:

$$Z = \sum_E g(E) \exp(-E/k_B T). \quad (2.25)$$

The energy distribution function  $E$  at a temperature  $T$  is determined by the formula:

$$P(E, T) = \frac{1}{Z} g(E) \exp(-E/k_B T), \quad (2.26)$$

Studies have shown that the distribution function for the energy will be expressed as a Gaussian distribution function. For the first-order transition, the distribution function at the phase transition temperature has a double peak corresponding to the two-phase coexistence. With the second-order transition, the distribution function has the form normally.

## 2.4 Summary

In this chapter, we gave an overview of the spin models that is often used in statistical mechanics. The liquid crystal model that is used as the basis of this thesis is that proposed by a mobile Potts model. Then we presented the Monte Carlo simulation. In Metropolis algorithm, this standard method is inefficient near a first-order phase transition. That problem brings us to the discussion of histogram method and Wang-Landau technique.

## Chapter 3

# POTTS MODEL OF SMECTIC - ISOTROPIC LIQUID CRYSTALS TRANSITION

### 3.1 Introduction

The smectic-isotropic phase transition is the transition of the liquid crystal state to the normal liquid state. Numerous research has carried out for smectic-isotropic transition. However, the studies also still have some limitations regarding the research model for the smectic phase and the simulation results.

In this study, we use a mobile Potts model which is proposed by Prof. Hung T. Diep. Besides, to overcome the disadvantages of previous research results, in terms of the simulation method, we have improved the Metropolis algorithm and at the same time used the Wang-Landau flat histogram technique.

### 3.2 Model

The model used in this study is based on a 6-state mobile Potts model. We consider an empty lattice of  $N_L$  sites. We fill this empty lattice with  $N_s = L^3$  molecules. The Hamiltonian used to model the smectic is given by:

$$\mathcal{H} = - \sum_{\langle i,j \rangle} J_{ij} \delta_{\sigma_i, \sigma_j}, \quad (3.1)$$

where  $\langle i, j \rangle$  indicates the pair of nearest neighbors (NN).  $J_{ij}$  denotes the spin-spin exchange interaction such as

$$J_{ij} = \begin{cases} J_{\parallel} = J > 0, & \text{in-plane interactions between NN,} \\ J_{\perp} = -aJ < 0, & \text{inter-plane interactions between NN.} \end{cases}$$

where  $a > 0$ .  $J$  is a constant and will be taken equal to 1.

### 3.3 The physical quantities

#### The average energy

$$\langle U \rangle = \frac{1}{N_2} \sum_{t=N_1+1}^{N_1+N_2} U(t), \quad (3.2)$$

where  $t$  is Monte Carlo time,  $N_1$ ,  $N_2$  are Monte Carlo steps to equilibrate and to average physical quantities,  $U(t)$  is energy at  $t$ .

## Specific heat capacity

$$C_v = \frac{\langle U^2 \rangle - \langle U \rangle^2}{k_B T^2}. \quad (3.3)$$

## Order parameter

$$\langle M \rangle = \frac{1}{N_2} \sum_{t=N_1+1}^{N_1+N_2} M(t), \quad (3.4)$$

where  $M(t)$  is order parameter at the Monte Carlo time  $t$ . For the smectic ordering, the order parameter for layer  $m$  by

$$M_m = \frac{1}{q-1} \left[ \frac{q}{N_m} \max_{j \in \llbracket 1, q \rrbracket} \left( \sum_{i=1}^{N_m} \delta_{j, \sigma_i} \right) - 1 \right], \quad (3.5)$$

where  $N_m$  is the number of molecules presents on layer  $m$

## The fluctuation of order parameter

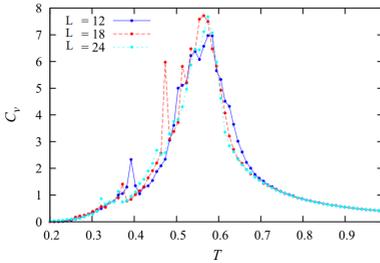
$$\chi = \frac{\langle M^2 \rangle - \langle M \rangle^2}{k_B T}. \quad (3.6)$$

## Diffusion coefficient

$$\langle D \rangle = \frac{1}{N_2} \sum_{t=N_1+1}^{N_1+N_2} D(t). \quad (3.7)$$

## 3.4 Size effect

We used Monte Carlo simulations for various  $N_s$  sizes of the system at each concentration. In this section, we will present the size effect for the concentration  $c = 50\%$  with an initial size of  $N_s = 12^3, 18^3, 24^3$ . The simulation results of the energy when the size changes are not significantly different as the system size increases. However, when investigating in detail the change of energy according to specific heat  $C_v(T)$  in Figure 3.6. The results reveal that  $C_v$  still has several temperature transitions, indicating that the layer transition phenomenon may be observed in all three survey sizes. We will use  $N_s = 12^3$  for the following investigations.



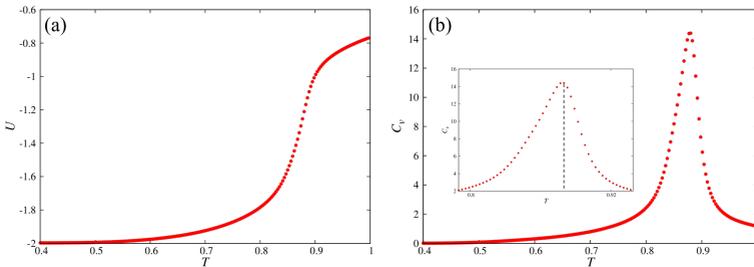
**Figure 3.6:** Specific heat vs. temperature at  $c = 50\%$  with  $L = 12, 18, 24$ .

### 3.5 Effect of concentration

In our simulations, we detect the change of the system behavior as a function of  $c$  where  $J_{\parallel} = 1.0$  and  $J_{\perp} = -0.5$ .

#### a) $c = 100\%$

We observe one peak corresponding to the second-order transition, which occurs at  $T = 0.8790$  (Figure 3.11). It is explained that this case is equivalent to the localized spin model.

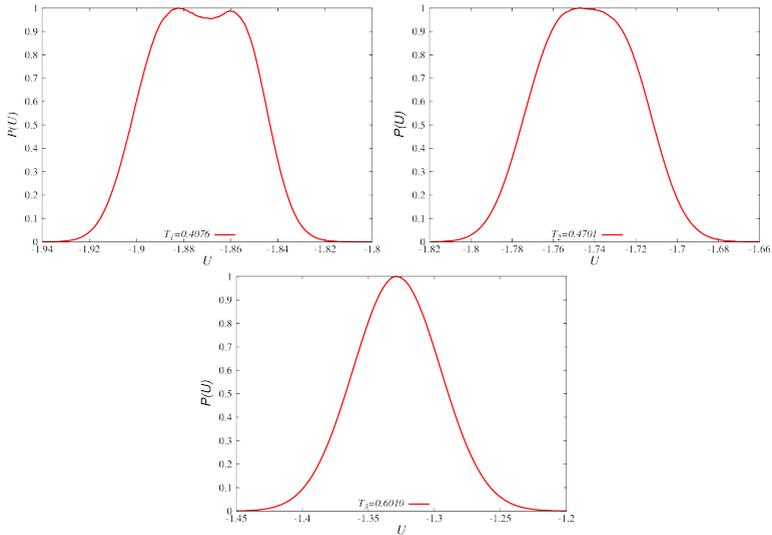


**Figure 3.11:**  $c = 100\%$ : Wang-Landau flat energy histogram results: (a) Energy  $U$ , (b) specific heat capacity  $C_v$  versus temperature  $T$ .

#### b) $c = 80\%$

We obtain the transition temperature are  $T_1 = 0.4684$  and  $T_2 = 0.8320$ . The model has a layer transition. However, vacancies may be too few. Only a small number of molecules move to empty positions and the molecules in the core layer remain in place. That is why we can only observe second-order transition.

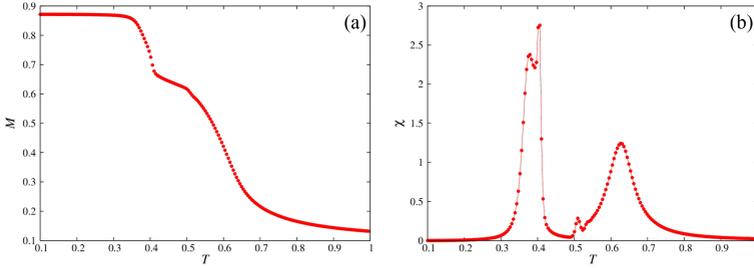
c)  $c = 60\%$



**Figure 3.21:**  $c = 60\%$ . Energy histograms by the Wang–Landau flat energy histogram method at the peak temperatures of  $C_v$ .

We observe that there are three peaks in the specific heat. The first two peaks correspond to the first-order transition. While the last peak represents the second-order transition (Figure 3.21). First-order transition appears to indicate the melting of layers, and second-order phase transitions represent disorder of some remaining layers before melting completely. However, the number of melting layers can not be determined clearly.

d)  $c = 50\%$

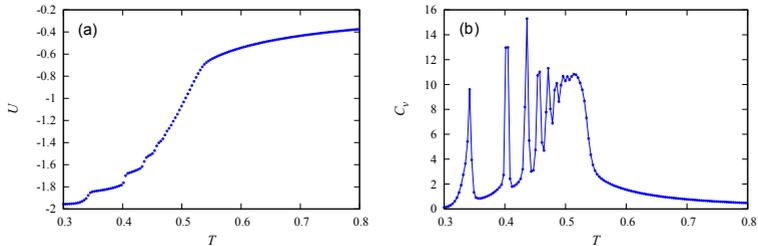


**Hình 3.25:**  $c = 50\%$ . Wang-Landau flat energy histogram results: (a) order parameter  $M$ , (b) variance of order parameter  $\chi$  versus temperature  $T$ .

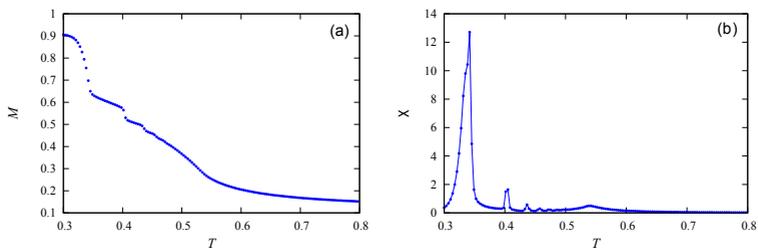
In this section, we reduce the concentration to increase the mobility of molecules. We hypothesize that the number of melting layers can be precisely determined. There are three transition temperatures. Note that in the case of  $c = 50\%$ , the free space to move is more than in the surveyed cases. As a result, we can imagine the surface molecules as more evaporation. Our simulation exhibits layer-thinning and shows the first peaks correspond to a first-order transition, and the following two peaks are a second-order transition. At the temperature  $T_1 = 0.40503$ , the order parameter  $M$  in Figure 3.25 rapidly decreases to 0.66, corresponding to the melting of 4 layers outside.

e)  $c = 30\%$

We expect to observe layer-by-layer transitions and their results are in agreement with the experimental observations. We can see that the energy curve  $U$  has 9 small changes corresponding to the 9 peaks of specific heat  $C_v$  (Figure 3.29). Our simulation exhibits layer-thinning and shows the eight first peaks correspond to a first-order transition, the ninth peak is a second-order transition. The observation at the temperature  $T_1 = 0.34182$  in Figure 3.30a, where  $M$  drops to 0.66, indicates a disorder of the four outer layers. We continue to observe as the temperature rises to  $T_2 = 0.40308$ : we see that  $M$  decreases to approximately 0.5, which shows the melting of the next 2 layers.



**Figure 3.29:**  $c = 30\%$ . Wang-Landau flat energy histogram results: (a) Energy  $U$ , (b) specific heat capacity  $C_v$  versus temperature  $T$ .

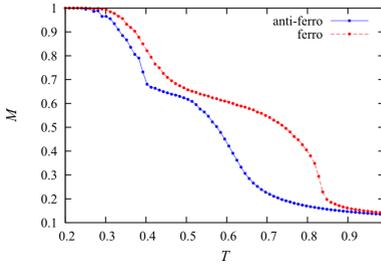


**Figure 3.30:**  $c = 30\%$ . Wang-Landau flat energy histogram results: (a) order parameter  $M$ , (b) variance of order parameter  $\chi$  versus temperature  $T$ .

### 3.6 Effect of inter-plane interaction

At this stage, let us investigate the influence of intermolecular interactions in two neighboring planes on the phase transition. We conduct Monte Carlo simulation in the following two cases:  $J_{\perp} = -0.5$  and  $J_{\perp} = +0.5$ .

Figure 3.33 shows the order parameter for both attractive (ferro) and repulsive (anti-ferro) interactions. We can observe that the order parameter of the system with attractive interactions (upper line) is larger than the order parameter of the system with repulsive interactions (bottom line). This is explained by the fact that in the case of attractive interactions, the thermal fluctuations have less effect on the orientation of molecules.



**Figure 3.33:**  $c = 50\%$ . The order parameter is shown in the two cases: ferromagnetic (red) and antiferromagnetic (blue) inter-layer couplings, for comparison.

### 3.7 Concluding Remarks

We studied the nature of smectic - isotropic phase transition by using the mobile Potts model. From Monte Carlo simulation results for various sizes, the system size  $N_s = 12^3$  molecules is chosen. In the next part of this chapter, we have shown the effect of molecular concentration on the phase transition of the smectic phase. At low molecular concentrations (30 %, 50 %, and 60 %) nature of these layer meltings at low  $T$  and found that they are of the first order in agreement with At high concentrations (80%, 100%), the smectic to isotropic transition is shown to be of second order. This transition is mostly due to the disordering of molecular orientations of the core layers because there is not enough empty space for molecule mobility. We also investigate the effect of inter-plane interaction. As seen, our results do not qualitatively change.

## Chapter 4

# EXTENDED MODEL FOR INVESTIGATING THE SMECTIC - ISOTROPIC TRANSITION

### 4.1 Model

For the model of this study, we consider a model, in addition to the microscopic interaction producing smectic ordering as in the standard model, Hamiltonian contains Lennard-Jones potential. Hamiltonian of the extended model is given by

$$\mathcal{H} = \sum_{\langle i,j \rangle} U(r_{ij}) - \sum_{\langle i,j \rangle} J_{ij} \delta_{\sigma_i, \sigma_j} \quad (4.1)$$

The first sum is a Lennard - Jones potential. Interaction is performed on pairs of NN  $\langle i, j \rangle$ .

$$U(r_{ij}) = U_0 \left[ \left( \frac{r_0}{r_{ij}} \right)^{12} - 2 \left( \frac{r_0}{r_{ij}} \right)^6 \right] \quad (4.2)$$

with  $r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\|$ ,  $r_0 \equiv a$  is the equilibrium distance between NN,  $U_0$  is a parameter of Lennard-Jones potential. The second one is described in the standard model. We consider here the effect of Lennard-Jones potential to phase transition of the smectic phase

### 4.2 Case $U_0 = 1.0$

In the case  $U_0 = 1.0$ , we observe the second-order transitions for both  $c = 50\%$  and  $30\%$ . This can be explained by the contribution of the large Lennard-Jones potential, which forces keep molecules in their place.

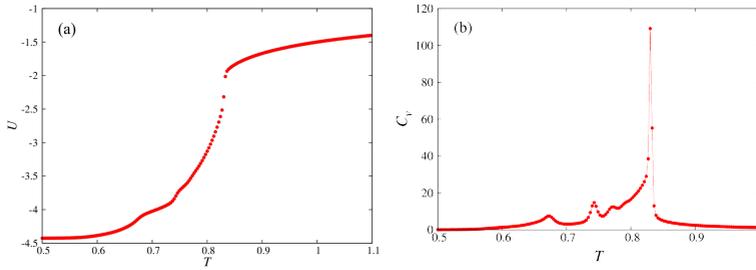
### 4.3 Case $U_0 = 0.85$

a)  $c = 50\%$

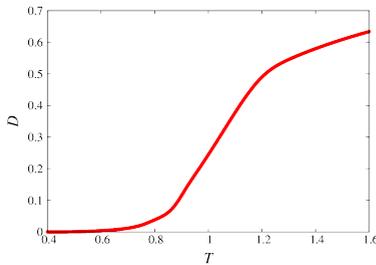
The transitions still are second-order transitions.

b)  $c = 30\%$

These findings show three transition temperatures in Figure 4.21.

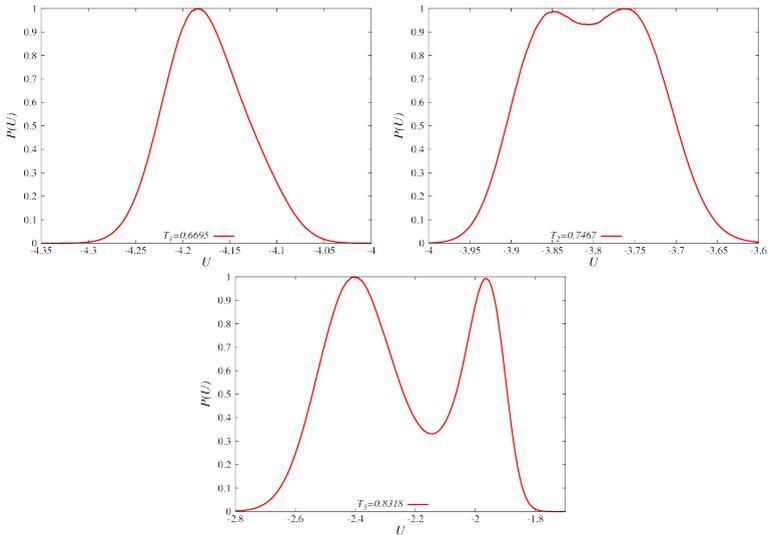


**Hình 4.21:**  $c = 30\%$ .  $U_0 = 0.85$ . Wang-Landau flat energy histogram results: (a) Energy  $U$ , (b) specific heat capacity  $C_v$  versus temperature  $T$ .



**Hình 4.20:**  $c = 30\%$ . Diffusion coefficient  $D$  versus  $T$ .

Specifically, one second-order transition in Figure 4.23a and two first-order transitions in Figure 4.23b and Figure 4.23c. At  $T_1$  (Figure 4.20), the molecules retain their positional order, and some of the molecular surface layers change in their orientation order. At  $T_2$  some of the outermost layers begin to melt, exhibiting disorder in both orientation and position ordering. At  $T_3$ , the molecules completely lose their orientation and position order. In this case, the system has a layer transition.



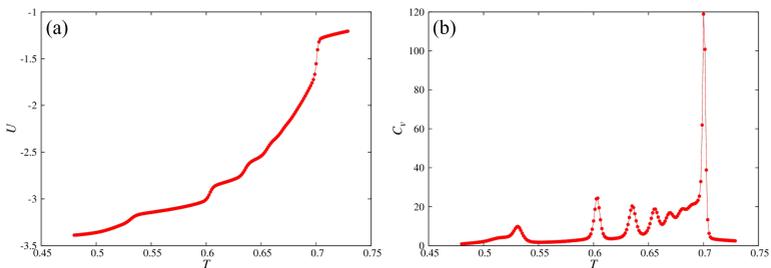
**Figure 4.23:**  $c = 30\%$ ,  $U_0 = 0.85$ : Energy histograms by the Wang–Landau flat energy histogram method.

## 4.4 Case $U_0 = 0.5$

### a) $c = 50\%$

In the case at  $c = 50\%$ , we only observe second-order transitions.

### b) $c = 30\%$



**Figure 4.31:**  $c = 30\%$ . (a) energy as a function of temperature  $T$ , (b) specific heat vs. temperature.

We see  $C_v(T)$  (Figure 4.31b) with six phase transitions. The energy histogram at all transition temperatures has a double peak structure. Therefore, the transitions are first-order transitions. This model does

not show the details of the smectic-isotropic phase transition.

## 4.5 Concluding Remarks

In the extended Potts model, we have extended the Hamiltonian expression to include exchange interactions and Lennard-Jones interactions. The Lennard-Jones interaction is an attractive interaction between the nearest neighboring molecules, which helps to establish the interaction in the third dimension of the smectic phase.

In the first part of this chapter, we have shown with  $U_0 = 1.0$ , the smectic - isotropic phase transition is the first-order transition for the molecular concentration  $c = 30\%$  and is the second-order phase for the case  $c = 50\%$ .

In the second part of this chapter, we have studied  $U_0 = 0.85$ , the system exists in both the first-order and the second-order phase transition. Our simulation results have presented the phase transition process or the behavior of atoms during the process in detail. Specifically, when the temperature of the system increases to  $T_1 = 0.6695$ , Molecules begin to lose orientation and then move up to these vacant positions. Meanwhile, the molecules in the core layers inside the liquid crystal structure retain the orientation order and liquid crystalline state. When the temperature of the system reaches the value large enough  $T_3 = 0.8318$ , the orientation order and position order are completely lost, and the smectic phase shifts to the isotropic phase. Besides, the research results have reduced the number of intermediate phase transitions compared to the previous study (only one phase transition left at  $T_2 = 0.7467$ ).

In the third part of this chapter, we have presented  $U_0 = 0.5$  the smectic - isotropic phase transition is the second-order phase transition for all molecular concentrations.

Comparing the two models for the smectic phase, we can see that the system has a first-order phase transition, but the detailed process differs slightly. We estimate that when adding the intermolecular interaction is the Lennard-Jones interaction, the system exhibits the phase transition in more detail. The obtained results also show the role of Lennard-Jones potential energy, which is a model control parameter.

## CONCLUSIONS

The smectic - isotropic phase transition of liquid crystals was investigated in this thesis using the Monte Carlo simulation. The smectic phase was established from the selection of appropriate microscopic interactions for the 6-state mobile Potts model. By improving simulation techniques compared to previous research, the simulation results have presented a general picture of the smectic-isotropic phase transition, indicating the layered melting of the smectic phase during the phase transition, which is consistent with experimental findings. Besides, the influence of molecular concentration and interaction type on the smectic - isotropic phase transition has also been analyzed in detail. Microscopic interactions in the Potts model are represented in the Hamiltonian, including exchange interactions between neighboring molecules in the same plane and molecules placed on two neighboring planes. Using the Monte Carlo simulation method with the Wang-Landau technique, we have studied the smectic - isotropic phase transition when the molecular concentration changes. Observe the graphs of thermodynamic quantities and energy distribution functions at the phase transition temperatures and types of phase transitions that have been determined. At high molecular concentrations (80 %, 100 %) the smectic - isotropic phase transition is a second-order phase transition. In the case of low molecular concentrations (30 %, 50 % and 60 %) we observe the melting layers and the system has a first-order phase transition. In addition, the exchange interaction energy between molecules located in neighboring layers is also considered and does not affect the layer melting of the smectic to the isotropic phase. The Hamiltonian of the Potts model is then modified to incorporate two forms of microscopic interactions, exchange interactions and Lennard-Jones interactions between nearest nearby molecules. The Lennard-Jones interaction component increases the intermolecular bonding of the smectic phase, especially the interplanar bonding. By investigating the value of the Lennard-Jones constant, we have obtained  $V_0 = 0.85$  as a suitable parameter for the smectic phase transition research model, demonstrating layered melting. At the same time, details about the orientation order and position order of the molecules are also shown in the simulation results.

## CONTRIBUTIONS OF THIS THESIS

1. The nature of the smectic–isotropic phase transition using Monte Carlo simulation was revealed in a previous scientific publication, but the simulation results are incomplete. We have improved the Metropolis algorithm at each Monte Carlo step. This is an extremely significant strategy for improving the accuracy of the simulation program. Our research findings define the characteristic properties of the smectic-isotropic phase transition in agreement with experimental data.
2. The use of advanced Monte Carlo techniques accurately determined the order of smectic - isotropic phase transition. The intermediate phase transition process is very complex, including both first-order and second-order phase transition.
3. A previously unexamined theoretical model for the smectic - isotropic phase transition was investigated. It is a 6-state mobile Potts model interacting by exchange interaction and Lennard-Jones interaction. The research also allows simulation of the smectic - isotropic phase transition, especially demonstrating the thinning transition of the smectic phase while simultaneously changing the orientation order and position order of liquid crystal molecules.

**LIST OF PUBLICATIONS**

1. Ngo, V. Thanh, **Phuong-Thuy Nguyen**, and Hung T. Diep. "Statistical Physics Approach to Liquid Crystals: Dynamics of Mobile Potts Model Leading to Smectic Phase, Phase Transition by Wang–Landau Method." *Entropy* 22.11 (2020): 1232.
2. **Phuong-Thuy Nguyen**, Van Anh T. Nguyen, V. Thanh Ngo. "Nghiên cứu chuyển pha smectic - đẳng hướng của tinh thể lỏng". *Tạp chí Khoa học và Công nghệ Việt Nam* 66.1 (2024): 01-07.