

# Phase transitions in liquid crystals

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Liquid crystals can be classified into 5 phases; Liquid, Nematic, Smetic, Columnar and Crystalline according to their position order and orientational order. To explain these phases, many models have been employed; Landau-de Gennes theory, Onsager-type theory, Maier-Saupe theory and the van der waals type theory. In this paper, I'll explain these theories and their computer simulations. At the end, experiment will be introduced for comparison.

## I. INTRODUCTION

It is fairly easy to define a crystal and a liquid separately or come up with their simple properties. In crystals, molecules are well ordered and constrained to each site. In liquids, they can move randomly pointing any directions. Liquid crystal, which sounds quite paradoxical, is a state in the middle of those two states and we can classify it according to degrees of order. Most disordered type is a nematic phase. It has an orientational order which is called a director, but no positional order. Next type is a smectic phase. In this phase, molecules are arranged in sheets with well-defined interlayer spacing in addition to orientational order. Next type is a columnar phase. In this phase, molecules are aligned in disk-like way and the columns that molecules form make two dimensional array. As expected, when isotropic liquid is cooled down, it goes through nematic, smectic and columnar phase. (There are more sub-phases under each nematic, smectic and columnar phase but I will not discuss them in this paper.) Also depending on the structures, it can skip one phase such as jumping from nematic to columnar phase or more disordered phase can appear such as nematic phase after smectic phase. (re-entrant phase transition.) As seen in phase transition of various systems, phase transition in liquid crystal also exhibits spontaneous symmetry breaking, strong fluctuation, diverging susceptibility and discontinuity, which come from cooperative interactions at microscopic level. In this essay, I will focus on relatively well-discovered isotropic-nematic(NI) transition.

## II. THEORY

### A. Landau-de Gennes(LD) Theory

First, we need to define an order parameter for orientational order, which take 0 for complete disorder, and 1 for complete order. There can be a different definition for the order parameter with this property but we are going to use the definition:  $P = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \int \frac{1}{2} (3 \cos^2 \theta - 1) f(\theta) d\theta$  where  $\theta$  is an angle to the director and  $f(\theta)$  is an orientation function. Experimentally, the order parameter's abrupt drop from 0.25-0.5 to zero at transition temperature has been observed, which is manifestation of first order transition. In LD theory[1], to explain this first order transition, following Landau free energy was employed.

$$F = \frac{1}{3}a(T - T_{NI}^*)P^2 - \frac{2}{27}BP^3 + \frac{1}{9}CP^4 \quad (2.1)$$

where a,B,C is a positive constant and  $T_{NI}^*$  is a temperature close to transition temperature  $T_{NI}$ . Differentiating (2.1) by  $P$ , we get equilibrium value of  $P$ , which satisfies

$$a(T - T_{NI}^*)P - \frac{1}{3}BP^2 + \frac{2}{3}CP^3 = 0 \quad (2.2)$$

The solutions of (2.2) are

$$\begin{aligned} P_i &= 0 && \text{isotropic case} \\ P_{\pm} &= \frac{B}{4C} \left[ 1 \pm \left( 1 - \frac{24aC(T - T_{NI}^*)}{B^2} \right)^{1/2} \right] && \text{nematic case} \end{aligned} \quad (2.3)$$

At  $T < T_{NI}$ , the value of  $P$  which gives us minimum free energy is  $P_{\pm}$ . Also at  $T = T_{NI}$  the equation (2.1) should satisfy

$$a(T_{NI} - T_{NI}^*)P^2 - \frac{2}{9}BP^3 + \frac{1}{3}CP^4 = 0 \quad (2.4)$$

With two equations (2.2) and (2.4), we can get two solutions.

$$\begin{aligned} P_{NI} &= 0, & T_{NI} &= T_{NI}^* \\ P_{NI} &= \frac{B}{3C}, & T_{NI} &= T_{NI}^* + \frac{B^2}{27aC} \end{aligned} \quad (2.5)$$

In conclusion, we can distinguish three different temperature regions.

1.  $T > T_{NI}^*$ : the free energy minimum corresponds to  $P = 0$ .
2.  $T_{NI} < T < T_{NI}^*$ : Relative minimum of free energy exists at  $P = P_+$ , but the free energy minimum still corresponds to  $P = 0$
3.  $T < T_{NI}$ : The minimum corresponds to nematic phase,  $P_{\pm}$ .

We can also include fluctuation of order parameter in Landau free energy, but I will not describe it because it's the same derivation as we did in class.

## B. Onsagar-type theory (Hard rod theory)

This is an important idealization that attributes the orientational ordering to the anisotropic shape of molecules[2]. In this theory, NI transition originated from effective repulsion of molecules, which affect entropy with excluded volume.

If  $U_N$  is a potential energy of interaction,

$$U_N = \sum_{1 < i < j < N}^N u_{ij} \quad (2.6)$$

In a hard rod theory, this can be approximated to

$$u_{ij} = u_{ij}(r_{ij}, \theta_i, \theta_j) = \begin{cases} \infty & \text{if } i \text{ and } j \text{ overlap} \\ 0 & \text{otherwise} \end{cases} \quad (2.7)$$

In a perfect gas, entropy can be written as

$$S_{ideal} = k_B \ln\left(a \frac{V}{N}\right) \quad (2.8)$$

$$S = k_B \ln\left(a \frac{V - Nb}{N}\right) \quad (2.9)$$

$$= S_{ideal} + k_B \ln\left(1 - \frac{Nb}{V}\right) \approx S_{ideal} - k_B \left(\frac{N}{V}b\right) \quad (2.10)$$

where  $b$  is a finite volume of a molecule. Then  $F = F_0 + k_B T \ln(n) + k_B T n b$ . Here, we will take two factors into consideration.

1. orientational entropy :  $\Delta S = -k_B \int f(\theta) \ln(4\pi f(\theta)) d\Omega$
2. excluded volume from the potential.

For 2nd factor, consider two rods whose lengths are  $L$ , diameter is  $D$  and angle is  $\gamma$ . Then the excluded volume will be  $2L^2 D \sin(\gamma)$  and its average volume will be  $2L^2 D \int \int f(\theta) f(\theta') \sin(\gamma) d\Omega d\Omega'$ . Thus final free energy will be

$$F = F_0 + k_B T (\ln(n) + \int f(\theta) \ln(4\pi f(\theta)) d\Omega + L^2 D n \int \int f(\theta) f(\theta') \sin(\gamma) d\Omega d\Omega') \quad (2.11)$$

This is a functional and it's hard to get an exact function which minimizes it. We will approximate a trial function with a parameter and get a parameter to minimize it. With a trial function[3],  $f(\theta) = (\text{const}) \cosh(\alpha \cos(\theta))$ , we could see abrupt first order phase transition from isotropic ( $\alpha = 0$ ) to nematic ( $\alpha > 18$ ) with an order parameter  $P \cong 0.84$ . This model doesn't predict a right solution in high density but it gives a correct qualitative picture of NI transition from the anisotropic shape of the molecules.

### C. Maier-Saupe(MS) type theory

In this theory, it was assumed that there should be anisotropic interaction to cause an orientational ordering. The interaction can originate from several mechanism and one of the strong candidates is van der Waals forces. For the simple and phenomenological interaction, the following potential was assumed

$$U_{ij} = -u \frac{P^2}{2} \quad (2.12)$$

where  $u$  is a parameter that expresses the strength of interaction. Then the free energy will be

$$F = -u \frac{P^2}{2} + k_B T \int f(\theta) \ln[4\pi f(\theta)] d\Omega \quad (2.13)$$

To minimize this free energy, we need to know  $f(\theta)$  which maximizes the entropy for different order parameter  $P$ . We use Euler-Lagrange equation to find a stationary value of  $\int f(\theta) \ln[4\pi f(\theta)] d\Omega$  with a constrain that  $\int \frac{1}{2}(3 \cos^2 \theta - 1) f(\theta) \sin \theta d\theta = P$  is a constant. Using a calculus of variation, we can get

$$\ln f + \frac{3\lambda}{2} \cos^2 \theta + 1 - \frac{\lambda}{2} = 0 \quad (2.14)$$

which has the solution

$$f(\theta) = \exp(3\lambda \cos^2 \theta) \quad (2.15)$$

where  $\lambda$  is the Lagrange multiplier which is the value of the order parameter  $P$ . With these, we can plot the free energy as a function of  $P$  for different value of  $u/k_B T$ .(FIG1)

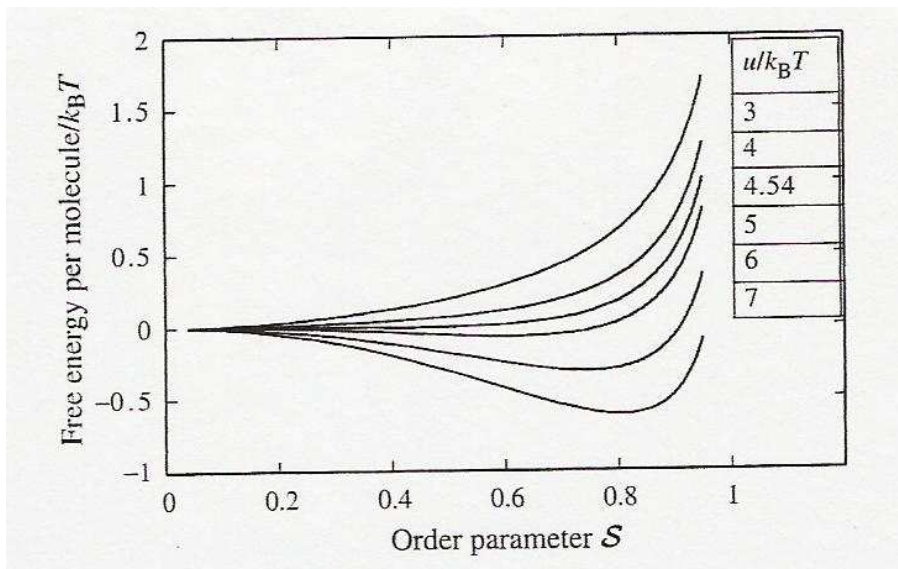


FIG. 1: Free energies for different values of  $u/k_B T$

As the value of  $u/k_B T$  increases from zero,  $P$  also starts from zero, which corresponds to isotropic phase. When  $u/k_B T$  is 4.55, we can observe discontinuous change of  $P$  from  $P=0$  to  $P=0.44$ , which corresponds to nematic phase(FIG2). Also this discontinuous change of  $P$  indicates the first order transition. In order to compare this with experiment, we need to assume the value of  $u$  first. If we set the value  $u$  which reproduces the experimentally observed transition temperature, the prediction of order parameter from the theory agrees with the value from experiment well.

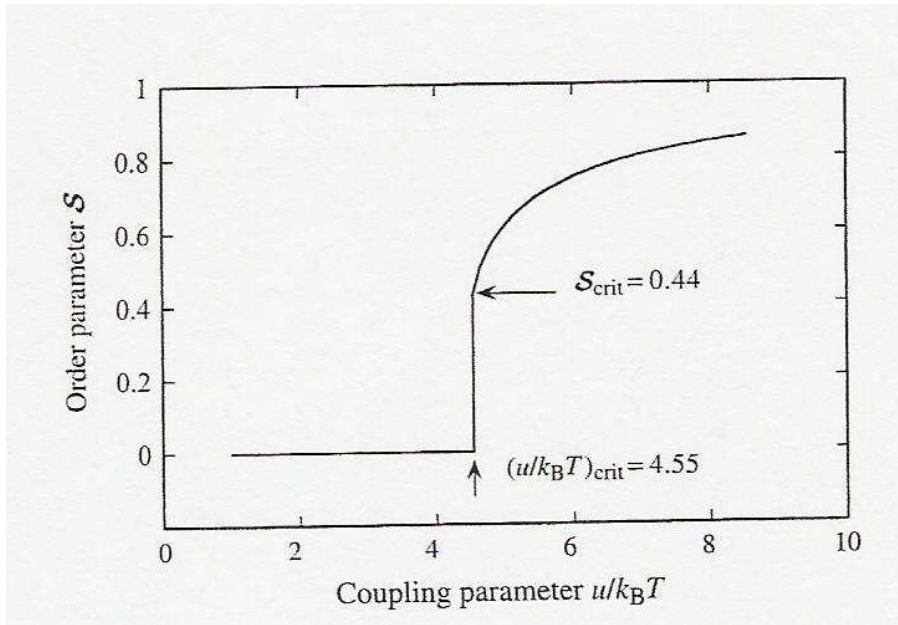


FIG. 2: The value of order parameter which minimizes free energy as a function of coupling parameter  $u/k_B T$

#### D. The van der Waals(vdW) type theory

In Onsagar-type theory and MS theory, we realized that short-range repulsive potential and long range attractive potential contribute to the NI phase transition. Also in the construction of molecular theory, the spatial and angular variables of molecules should be taken into account. Many models, known as vdW type theory, have been developed considering these conditions. In these theories, geometry of molecules is recognized as a predominant factor. Long range attraction is taken as a negative and spatially uniform mean field to the first order. Here, I'll develop a perturbation theory in the mean field approximation.

First, interaction potential between two molecules can be written as

$$u(x_i, x_j) = u^{(0)}(x_i, x_j) + \lambda u^{(p)}(x_i, x_j) \quad (2.16)$$

where  $u^{(0)}(x_i, x_j)$  is a rapidly varying short range repulsive interaction,  $u^{(p)}(x_i, x_j)$  is a smoothly varying long range attraction and  $\lambda$  is a perturbation parameter. Then the configurational integral is

$$Q_N = \frac{1}{N!(4\pi)^N} \int dr^N \int d\Omega^N \exp[-\beta U_N(x_1, x_2, \dots, x_N)] \quad (2.17)$$

If we divide unit sphere into arbitrary small angles  $\Delta\Omega$  ( $n = 4\pi/\Delta\Omega$ ) and define  $N_p$  as the number of molecules whose orientation is in the  $p$ th solid angle,

$$Q_N = \frac{1}{N!(4\pi)^N} \sum_{N_1} \dots \sum_{N_n} \frac{N!(\Delta\Omega)^N}{N_1! \dots N_n!} \int dr^N \exp[-\beta U_N(r^N, N_1 \dots N_n)] \quad (2.18)$$

For a simpler form, if we consider the maximum values of  $N$ ,

$$Q_N \simeq \left(\frac{\Delta\Omega}{4\pi}\right)^N \left[\prod_{p=1}^n \hat{N}_p!\right]^{-1} \int dr^N \exp[-\beta U_N(r^N, N_1 \dots N_n)] \quad (2.19)$$

Considering (2.16), if we take a derivative w.r.t.  $\lambda$

$$\frac{\partial \ln Q_N}{\partial \lambda} = -\frac{1}{2V}\beta \sum_{p=1}^n \sum_{p'=1}^n \hat{N}_p \hat{N}_{p'} \int dr u^{(p)}(r, \Omega_p, \Omega_{p'}) g(r, \Omega_p, \Omega_{p'}) \quad (2.20)$$

where

$$g(r, \Omega_p, \Omega_{p'}) = \frac{V^2}{Q_N} \left(\frac{\Delta\Omega}{4\pi}\right)^N \left[\prod_{p=1}^n N_p!\right]^{-1} \int dr^N \exp[-\beta U_N(r^N, \hat{N}_1 \dots \hat{N}_n), \lambda] \quad (2.21)$$

Integrating (2.20), we can get Helmholtz free energy

$$F = F^0 + \frac{1}{2} N \rho \int_0^1 d\lambda \int f(\Omega_p) d\Omega_p \int f(\Omega_{p'}) d\Omega_{p'} \int dr u^p(r, \Omega_p \Omega_{p'}) g(r, \Omega_p, \Omega_{p'}) \quad (2.22)$$

where  $f(\Omega)$ , continuous orientational distribution, means

$$\hat{N} = N f(\Omega_p) d\Omega_p \quad (2.23)$$

If we expand  $g(r, \Omega_p, \Omega_{p'})$  and free energy w.r.t.  $\lambda$

$$g(r, \Omega_p, \Omega_{p'}) = g^{(0)}(r, \Omega_p, \Omega_{p'}) + \lambda g^{(1)}(r, \Omega_p, \Omega_{p'}) + \dots \quad (2.24)$$

$$A = A^{(0)} + \lambda A^{(1)} + \lambda^2 A^{(2)} + \dots \quad (2.25)$$

With these and (2.22), we can get

$$F = F^0 + \frac{1}{2} N \int f(\Omega_p) d\Omega_p \left[ \sum_{r=1}^{\infty} \Psi^{(r)}(\Omega) \right] \quad (2.26)$$

where  $\Psi^{(r)}$  is defined as the effective one-body potential:

$$\Psi^{(r)}(\Omega) = \frac{1}{2r} \rho \int f(\Omega_{p'}) d\Omega_{p'} \int dr u^p(r, \Omega_p \Omega_{p'}) g^{(r-1)}(r, \Omega_p, \Omega_{p'}) \quad (2.27)$$

The vdW-type theory considers only the first order perturbation[4], which is :

$$\Psi^{(1)}(\Omega_1) = \rho \int f(\Omega_2) d\Omega_2 \int dr u^p(r, \Omega_1 \Omega_2) g^{(0)}(r, \Omega_1, \Omega_2) \quad (2.28)$$

Then,

$$F = F^0 + \frac{1}{2} N \int d\Omega_1 f(\Omega_1) [\Psi^{(1)}(\Omega_1)] \quad (2.29)$$

where

$$\Psi^{(1)}(\Omega_1) = \rho \int f(\Omega_2) d\Omega_2 \int dr u^{(p)}(r, \Omega_1 \Omega_2) \exp[-\beta u^{(0)}(r, \Omega_1, \Omega_2)] \quad (2.30)$$

Because the potential  $u^0(r, \Omega_1 \Omega_2)$  is same as (2.7),  $\exp(-\beta u^0(r, \Omega_1 \Omega_2))$  is 0 within rods and 1 outside rods. For  $u^{(p)}(r, \Omega_1 \Omega_2)$ , assume

$$u^{(p)}(r, \Omega_1 \Omega_2) = -\frac{1}{r^6} [C_{iso} + C_{aniso} \cos^2 \Omega_{12}] \quad (2.31)$$

Then we use a calculus of variation as in MS theory assuming the orientational function,

$$f(\Omega) = \frac{\lambda \cosh(\lambda \cos \theta)}{4\pi \sinh \lambda} \quad (2.32)$$

Computer simulation[5] of vdW does not quantitatively agree with experiment, but it shows that the anisotropy of short-range repulsion is important in NI transition.

### III. COMPUTER SIMULATIONS

Because of complexity of liquid crystals, computer simulation is a very important method to understand a system. In reality, molecules consist of rigid cores and flexible side chains and their interactions become very complicated to describe. Thus molecules and their interactions should be simplified for a computer simulation.

#### A. Lebwohl-Lasher models

This is a computer simulation of MS model. First, simple cubic lattice of molecules with no translational motion is assumed. The Hamiltonian is

$$H = -J \sum \frac{1}{2} (3\cos^2\theta_{ij} - 1) \quad (3.1)$$

where the sum is over nearest-neighbor pairs of lattice. Lebwohl and Lasher carried out Monte Carlo(MC) simulation on the system[6] and observed strong first order NI transition with a jump of order parameter from 0 to 0.33 near  $J/k_B T = 0.89$ . Zhang and co-workers[7] simulated the same model including more lattices,  $28^3$  and showed good agreement with the experimental data.

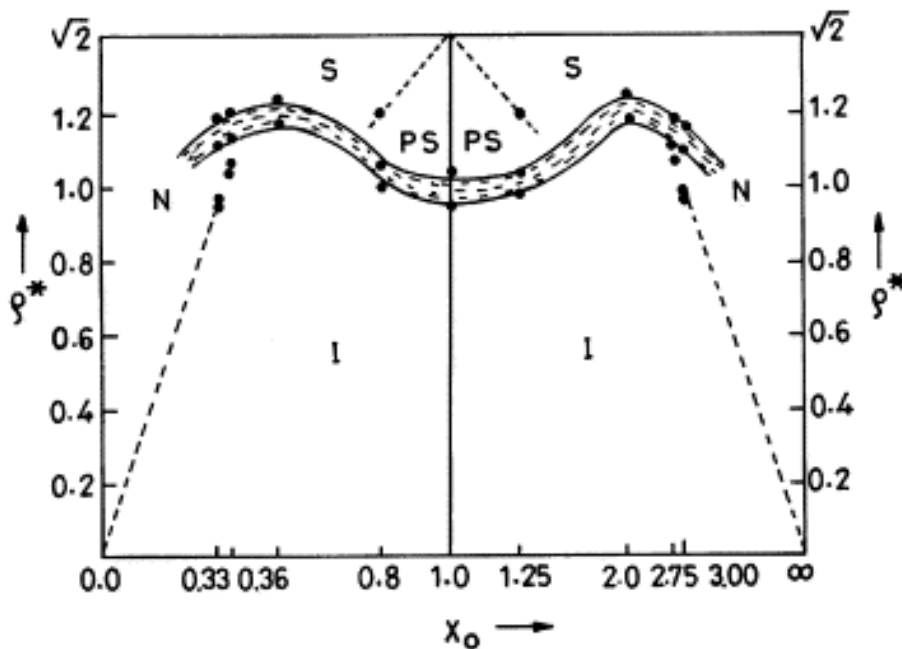


FIG. 3: Phase diagram in the hard ellipsoid model. I: Isotropic, S: Orientationally ordered crystal, PS: Plastic crystal and N: Nematic

#### B. Hard-core Models

Frenkel and Mulder[12] performed a simulation of three dimensional hard ellipsoid using MC simulation. They defined length to width ratio as  $x$  and varying  $x$ , they found that first transition occurs in the range  $x > 2.5$  or  $x < 0.4$ (FIG3). Also Cuesta and Frenkel[13] carried out a simulation with two dimensional ellipses with aspect ratios 2, 4 and 6. For aspect ratios 4 and 6, stable nematic phase with

power-law decay of orientational correlation is observed. For aspect ratio 4, the first order transition was found.

### C. Gay-Berne model

This is a computer simulation with a more elaborate potential, called Gay-Berne(GB) potential, which is

$$u(r, \Omega_1, \Omega_2) = 4\varepsilon(\hat{r}, \Omega_1, \Omega_2) \left[ \left( \frac{\sigma_0}{r - \sigma(\hat{r}, \Omega_1, \Omega_2) + \sigma_0} \right)^{12} - \left( \frac{\sigma_0}{r - \sigma(\hat{r}, \Omega_1, \Omega_2) + \sigma_0} \right)^6 \right] \quad (3.2)$$

where

$$\varepsilon(\hat{r}, \Omega_1, \Omega_2) = \varepsilon_0 (1 - \chi^2 [\hat{e}_1 \cdot \hat{e}_2]^2)^{(-1/2)} x (1 - \chi' \frac{(\hat{r} \cdot \hat{e}_1)^2 + (\hat{r} \cdot \hat{e}_2)^2 - 2\chi'(\hat{r} \cdot \hat{e}_1)(\hat{r} \cdot \hat{e}_2)(\hat{e}_1 \cdot \hat{e}_2)}{1 - \chi'(\hat{e}_1 \cdot \hat{e}_2)^2}) \quad (3.3)$$

$$\sigma(\hat{r}, \Omega_1, \Omega_2) = \sigma_0 \left[ 1 - \chi' \frac{(\hat{r} \cdot \hat{e}_1)^2 + (\hat{r} \cdot \hat{e}_2)^2 - 2\chi'(\hat{r} \cdot \hat{e}_1)(\hat{r} \cdot \hat{e}_2)(\hat{e}_1 \cdot \hat{e}_2)}{1 - \chi'(\hat{e}_1 \cdot \hat{e}_2)^2} \right]^{(-1/2)} \quad (3.4)$$

where  $\chi' = (\sqrt{k'} - 1)/(\sqrt{k'} + 1)$ ;  $k'$  is the ratio of the potential well depths for side by side and end to end configurations. DeMiguel and coworkers[8] performed a simulation with 256 molecules in GB potential and obtained the phase diagram, FIG4.

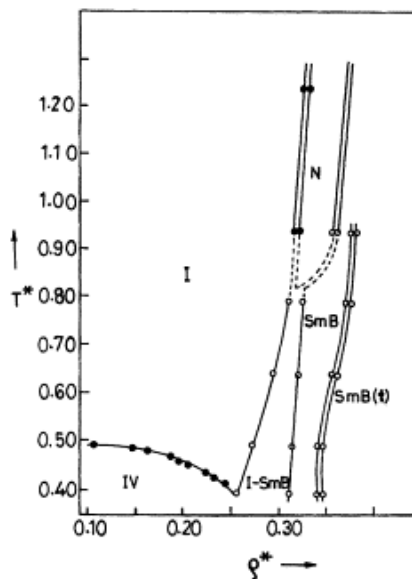


FIG. 4: Phase diagram obtained using GB potential. SmB: Smectic B,  $T^* = k_B T / \varepsilon_0$  and  $\rho^* = \rho / \sigma_0^3$

In the simulation, the first order is observed in NI transition. Also in their study of GB fluid, molecules diffusing with cylindrical axis parallel to the director in nematic phase were observed. There are similar types of simulations such as Luckhurst et al[10]'s and Emerson[11]'s work. Their results were comparable to DeMiguel's and all of these show that NI transition is mainly achieved by the excluded volume effects.



#### IV. EXPERIMENT

Among many experimental techniques, mottler oven and differential scanning calorimetry(DSC) are widely used. Mottler oven is a method to obtain phases of a liquid crystal by detecting transmission as a function of temperature. The transmission of a liquid crystal increases with decreasing order parameter. Thus shining a light and placing photodiode in the other side, we can measure the change of transparency of the sample. DSC is the method to observe the phase transition by detecting the enthalpy change associated with. Also by measuring the level of enthalpy change, we can learn the type of the phase transition[14].

For the NI transition, the abrupt jump of order parameter from zero to 0.25-0.5 is observed at NI transition temperature over a stretches of 0.6-0.8K. Enthalpy change measured is small(1-2kJ/mol) comparing the enthalpy change, 30-50kJ/mol of the solid to isotropic liquid phase transition[15].

#### V. CONCLUSION

Since the first order type NI transition was observed, many attempts have been made to explain it theoretically. Phenomenological description of the system, Landau-De Gennes theory could show important features of the NI transition. For molecular level description, Onsager's hard rod theory, which maintained that molecules's anisotropic shape and their excluded volume lead to orientational ordering, and Maier-Saupe type theory, which proposed that anisotropic interaction of molecules cause the ordering, were introduced. Computer simulations followed by them showed their good agreement with experimental data.

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