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A Phase Diagram of the Nematic, Smectic A and Smectic C phases in Liquid Crystals

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Abstract

In this study we have obtained a phase diagram for the nematic, smectic A and smectic C phases in liquid crystals. For this phase diagram we have studied two different mean field models for a mixture of liquid crystalline system. In our first model we consider the NC and AC transitions as first order, and the NA transition as a second order. In our second model we consider the NC and NA transitions as first order, and the AC transition as a second order.

1. Introduction

Critical phenomena near the NAC point in liquid crystals have been studied extensively both experimentally [1]-[8] and theoretically [9]-[12]. An experimental review on the NAC point has been given by Anisimov [13]. A phase diagram around the NAC point has been calculated by Kallel and Mlik [14].

We consider the NAC point as a tricritial point. The NA and AC transitions can be first order or second order. The NC transitions is usally taken as first order. Therefore, to make the NAC point as a tricritical point we consider in this study two models. In the first model we take the NC and AC transitions as first order, and the NA transition as a second order. In the second model we take the NC and NA transitions as first order, and the AC transition as a second order. In order to make the transition as a first order we consider in the free energies a term which is proportional to the third power of the order parameters. There is a simple coupling between two order parameters in the free energies of these two models. The temperature dependences are included in the coefficients of the second power of the order parameters. The concentration dependences are included in the coefficients of the fourth power of the order parameters. This is the usual way of expressing the free energy according to the Landau theory.

Using these two models we calculate the equations for the phase lines of NA, NC and AC transitions.

In Section 2 we give our two models and we obtain the equations for the phase lines. In Section 3 we obtain the phase diagrams. In Section 4 conclusions are given.

2. Theory

2.1. Model I

In this model we take NC (nematic-smectic C) and AC (smectic A-smectic C) transitions as first order and NA (nematic-smectic A) transition as a second order.

The free energy of this model is

$$F = a_2\Psi^2 + a_4\Psi^4 + b_2\eta^2 + b_3\eta^3 + b_4\eta^4 + c\Psi^2\eta^2. \tag{1}$$

In Eq.(1) Ψ characterizes the smectic layering and η is the tilt angle. Here $c < 0$, $b_3 < 0$ and

$$\begin{aligned} a_2 = b_2 &= a(T - T_{NAC}) \\ a_4 = b_4 &= b(x - x_{NAC}), \end{aligned} \tag{2}$$

where x is the concentration of the mixture of liquid crystals.

From Eq.(1) we have the minimizing conditions

$$\frac{\partial F}{\partial \Psi} = 2\Psi(a_2 + 2a_4\Psi^2 + c\eta^2) = 0 \tag{3}$$

and

$$\frac{\partial F}{\partial \eta} = \eta(2b_2 + 3b_3\eta + 4b_4\eta^2 + 2c\Psi^2) = 0 \tag{4}$$

2.1a. NA phase line

The nematic phase is characterized by $\Psi = 0$, $\eta = 0$, and the smectic A phase is characterized by $\Psi \neq 0$, $\eta = 0$. Hence, the free energy for the second order NA transition is

$$F_{NA} = a_2\Psi^2 + a_4\Psi^4. \tag{5}$$

The minimizing condition gives

$$\frac{\partial F_{NA}}{\partial \Psi} = 2\Psi(a_2 + 2a_4\Psi^2) = 0. \tag{6}$$

Then, on the phase line, by putting $\Psi = 0$ we have the phase line equation for the NA transition

$$a_2 = b_2 = 0, \tag{7}$$

2.1b. AC phase line

The AC transition is taken as a first order transition. For the smectic A phase $\Psi \neq 0$, $\eta = 0$ and for the smectic C phase $\psi \neq 0$, $\eta \neq 0$. Hence, the free energy for the smectic A phase is

$$F_A = a_2\Psi^2 + a_4\Psi^4, \tag{8}$$

and the free energy for the smectic C phase is

$$F_C = a_2\Psi^2 + a_4\Psi^4 + b_2\eta^2 + b_3\eta^3 + b_4\eta^4 + c\Psi^2\eta^2. \tag{9}$$

The condition that $F_A = F_C$ on the phase line gives

$$b_2 + b_3\eta + b_4\eta^2 + c\Psi^2 = 0. \tag{10}$$

Solving Ψ^2 from Eq.(10) gives

$$\Psi^2 = -\frac{1}{c}(b_2 + b_3\eta + b_4\eta^2). \tag{11}$$

By inserting Eq.(11) into Eq.(3), we have

$$A\eta^2 - B\eta + C = 0 \tag{12}$$

where

$$\begin{aligned} A &= c - \frac{2a_4b_4}{c} \\ B &= \frac{2a_4b_3}{c} \\ C &= a_2 - \frac{2a_4b_2}{c} \end{aligned} \tag{13}$$

This equation has the solution

$$\eta = \frac{B + (B^2 - 4AC)^{1/2}}{2A} \tag{14}$$

$$b_3 + 2b_4\eta = 0. \tag{15}$$

By substituting Eq.(14) into Eq(15) and using $a_2 = b_2$, $a_4 = b_4$ we get

$$b_3^2c^2 + 2b_3^2b_4^2 - 8b_4^3b_2 + 4b_4^2b_2c = 0. \tag{16}$$

This equation is the AC phase line equation.

2.1c. NC phase line

We take the NC transition as first order. For the nematic phase we have $\Psi = 0$, $\eta = 0$ and for the smectic C phase $\Psi \neq 0$, $\eta \neq 0$. Hence, the free energy for the nematic phase is

$$F_N = 0 \tag{17}$$

and the free energy for the smectic C phase is

$$F_C = a_2\Psi^2 + a_4\Psi^4 + b_2\eta^2 + b_3\eta^3 + b_4\eta^4 + c\Psi^2\eta^2. \tag{18}$$

From the condition that $F_N = F_C$ on the phase line, we have

$$a_2\Psi^2 + a_4\Psi^4 + b_2\eta^2 + b_3\eta^3 + b_4\eta^4 + c\Psi^2\eta^2 = 0 \tag{19}$$

By solving Ψ^2 from the minimizing condition given by Eq.(4), we get

$$\Psi^2 = -\frac{1}{2c}(2b_2 + 3b_3\eta + 4b_4\eta^2). \tag{20}$$

Inserting Eq.(20) into Eq.(3) and taking $a_2 = b_2$, $a_4 = b_4$ gives

$$D\eta^2 - E\eta + F = 0, \tag{21}$$

where

$$\begin{aligned} D &= c^2 - 4b_4^2 \\ E &= 3b_3b_4 \\ F &= b_2c - 2b_2b_4. \end{aligned} \tag{22}$$

From Eq.(21) we have the solution

$$\eta = \frac{E + (E^2 - 4DF)^{1/2}}{2D}. \tag{23}$$

Substituting Eq, (20) into Eq. (18) gives

$$\begin{aligned} &(4b_4^3 - 2b_4c^2)\eta^4 + (6b_3b_4^2 + b_3c^2 - \frac{3}{2}b_3c^2)\eta^3 \\ &+(-2b_2b_4c + \frac{9}{4}b_3^2b_4 + 4b_2b_4^2)\eta^2 \\ &+(-\frac{3}{2}b_2b_3c + 3b_2b_3b_4)\eta + (-b_2^2c + b_2^2b_4) = 0. \end{aligned} \tag{24}$$

By putting Eq.(23) into Eq.(24) we get

$$\begin{aligned}
&2b_4(2b_4^2-c^2)[\frac{E+(E^2-4DF)^{1/2}}{2D}]^4\\
&+b_3(6b_4^2-\frac{c^2}{2})[\frac{E+(E^2-4DF)^{1/2}}{2D}]^3\\
&+b_4(-2b_2c+\frac{9}{4}b_3^2+4b_2b_4)[\frac{E+(E^2-4DF)^{1/2}}{2D}]^2\\
&+3b_2b_3(b_4-\frac{c}{2})[\frac{E+(E^2-4DF)^{1/2}}{2D}]\\
&+b_2^2(b_4-c)=0,
\end{aligned} \tag{25}$$

where D, E and F are given in Eq.(22). This equation is the NC phase line equation.

2.2. Model II

In this model we take the NA and NC transitions as first order, AC transition as a second order. The free energy of this model is given by

$$F=a_2\Psi^2+a_3\Psi^3+a_4\Psi^4+b_2\eta^2+b_4\eta^4+c\Psi^2\eta^2. \tag{26}$$

Here, $c<0$, $a_3<0$ and

$$\begin{aligned}
a_2=b_2=a(T-T_{NAC})\\
a_4=b_4=b(x-x_{NAC})
\end{aligned} \tag{27}$$

From Eq.(26) we have the minimizing conditions

$$\frac{\partial F}{\partial \Psi}=\Psi(2a_2+3a_3\Psi+4a_4\Psi^2+2c\eta^2)=0 \tag{28}$$

and

$$\frac{\partial F}{\partial \eta}=2\eta(b_2+2b_4\eta^2+c\Psi^2)=0. \tag{29}$$

2.2a. AC phase line

For the smectic A phase we have $\Psi\neq 0$, $\eta=0$. For the smectic C phase we have $\Psi\neq 0$, $\eta\neq 0$. Hence, the free energy for the second order AC transition is given by

$$F_{AC}=a_2\Psi^2+a_3\Psi^3+a_4\Psi^4+b_2\eta^2+b_4\eta^4+c\Psi^2\eta^2, \tag{30}$$

From the minimizing condition Eq.(29), we get

$$\Psi^2 = -\frac{1}{c}(b_2 + 2b_4\eta^2). \tag{31}$$

Inserting Eq.(31) into Eq.(28) gives

$$\begin{aligned} &[2a_2 + 3a_3(-\frac{1}{2})^{1/2} b_2^{1/2} - \frac{4}{c} a_4 b_2] \\ &+ [3a_3(-\frac{1}{c})^{1/2} \frac{b_4}{b_2^{1/2}} - \frac{8}{c} a_4 b_4 + 2c]\eta^2 \\ &+ [-\frac{3}{2}(-\frac{1}{2})^{1/2} a_3 \frac{b_4}{b_2^{1/2}}]\eta^4 = 0. \end{aligned} \tag{32}$$

When $\eta = 0$ on the phase line, we have $a_2 = b_2 = 0$ as a solution, hence we have

$$a_2 = 0 \tag{33}$$

as a phase line equation for the AC transition.

2.2b. NA phase line

The NA transition is taken as a first order transition. For the nematic phase we have $\Psi = 0$, $\eta = 0$. For the smectic A phase we have $\Psi \neq 0$, $\eta = 0$. Hence, we have

$$\begin{aligned} &F_N = 0 \\ &F_A = a_2\Psi^2 + a_3\Psi^3 + a_4\Psi^4. \end{aligned} \tag{34}$$

The condition that $F_N = F_A$ gives

$$a_2 + a_3\Psi + a_4\Psi^2 = 0. \tag{35}$$

From Eq.(35) we have the solution

$$\Psi = \frac{-a_3 + (a_3^2 - 4a_2a_4)^{1/2}}{2a_4}. \tag{36}$$

From Eq.(28) with $\eta = 0$, we have

$$2a_2 + 3a_3\Psi + 4a_4\Psi^2 = 0. \tag{37}$$

Substituting Eq.(36) into Eq.(37) gives that

$$2a_2 + 3a_3[\frac{-a_3 + (a_3^2 - 4a_2a_4)^{1/2}}{2a_4}]$$

$$+4a_4[\frac{-a_3 + (a_3^2 - 4a_2a_4)^{1/2}}{2a_4}]^2 = 0. \tag{38}$$

This equation is the NA phase line equation.

2.2. NC phase line

We take the NC transition a first order transition. For the nematic phase we have $\Psi = 0$, $\eta = 0$. For the smectic C phase we have $\Psi \neq 0$, $\eta \neq 0$. Hence, the free energy for the nematic phase is

$$F_N = 0 \tag{39}$$

and the free energy for the smectic C phase is

$$F_C = a_2\Psi^2 + a_3\Psi^3 + a_4\Psi^4 + b_2\eta^2 + b_4\eta^4 + c\Psi^2\eta^2. \tag{40}$$

The condition that $F_N = F_C$ on the phase line gives

$$a_2\Psi^2 + a_3\Psi^3 + a_4\Psi^4 + b_2\eta^2 + b_4\eta^4 + c\Psi^2\eta^2 = 0. \tag{41}$$

By solving η^2 from Eq. (28), we get

$$\eta^2 = -\frac{1}{2c}(2a_2 + 3a_3\Psi + 4a\Psi^2). \tag{42}$$

Substituting Eq. (42) into Eq.(29) gives

$$\Psi = \frac{E + (E^2 - 4DF)^{1/2}}{2D}, \tag{43}$$

where

$$\begin{aligned} D &= c^2 - 4a_4^2 \\ E &= 3a_3a_4 \\ F &= a_2c - 2a_2a_4. \end{aligned} \tag{44}$$

Inserting this equation into Eq.(42) and substituting the resulting equation into Eq.(41) gives

$$\begin{aligned} &2a_4(2a_4^2 - c^2)[\frac{E + (E^2 - 4DF)^{1/2}}{2D}]^4 \\ &+a_3(6a_4^2 - \frac{c^2}{2})[\frac{E + (E^2 - 4DF)^{1/2}}{2D}]^3 \end{aligned}$$

$$+a_4(-2a_2c+\frac{9}{4}a_3^2+4a_2a_4)[\frac{E+(E^2-4DF)^{1/2}}{2D}]^2 \quad (45)$$
$$+3a_2a_3(a_4-\frac{c}{2})[\frac{E+(E^2-4DF)^{1/2}}{2D}]$$
$$+a_2^2(a_4-c)=0.$$

This equation is the NC phase line equation.

3. Phase Diagrams and Discussion

The phase diagrams which we have obtained using our mean field models I and II are given in Figures 1 and 2, respectively. At the NAC point, experimentally when $x = x_{NAC}$, we have $T - T_{NAC} = 1°$C [13]. Therefore, by taking $a = b = 1$ in Eq.(2) we have

$$a_2 = b_2 = T - T_{NAC}$$
$$a_4 = b_4 = x - x_{NAC}.$$

We define the new variables b'_2 or a'_2 as

$$b'_2 = b_2 + 1°C$$
$$b'_2 = a_2 + 1°C.$$

for the temperature axis. Hence, the NAC point is located at $b_4 = 0$ (or $a_4 = 0$) and $b'_2 = 1°C$ (or $a'_2 = 1°C$). For our Figures 1 and 2 we take for the NA transition $b'_2 > 0$, $b_4 > 0$ (or $a'_2 > 0$, $a_4 > 0$); for the AC transition $b_4 > 0$ (or $a_4 > 0$); for the NC transition $b'_2 > 0$, $b_4 < 0$ (or $a'_2 > 0$, $a_4 < 0$).

The graphs of the phase line equations in the phase diagrams for models I and II are drawn using the Mathematica computer programme (Figures 1 and 2).

In these figures the solid lines represent the phase line equations. In Figure 1 (model I) we have taken that $b_3 = -0.001$ and $c = -1$, whereas in Figure 2 (model II) we have taken $a_3 = -0.1$ and $c = -1$. Since the NAC tricritical point is located at $b_4 = 0$, $b'_2 = 1$, when $b_4 = 0$ (or $a_4 = 0$) for the minimizing conditions and $F_A = F_B$ where A and B are two different phases from the first order phase transition it is easy to find that $b_2 = 0$ (or $a_2 = 0$). Therefore, the tricritical point that we find as $b_4 = 0$, $b_2 = 0$ (or $a_4 = 0$, $a_2 = 0$) can be taken as the NAC point. In terms of the new variable b'_2 (or a'_2) the NAC point is located at $b_4 = 0$, $b'_2 = 1$ (or $a_4 = 0$ $a'_2 = 1$). Since the NAC tricritical point is located at $b_4 = 0$, $b'_2 = 1$ for model I, the AC phase line obtained from Eq.(16), which does not pass from the $b'_2 = 1$ when $b_4 = 0$, is cut at a point close to $b_4 = 0$. Starting from that point, we connected the AC phase line to the NAC point which we have denoted by dots in Figure 1. For the NC transition in model I the Mathematica programme gives from Eq.(25) that $b_4 = 0$ for the NC phase line.

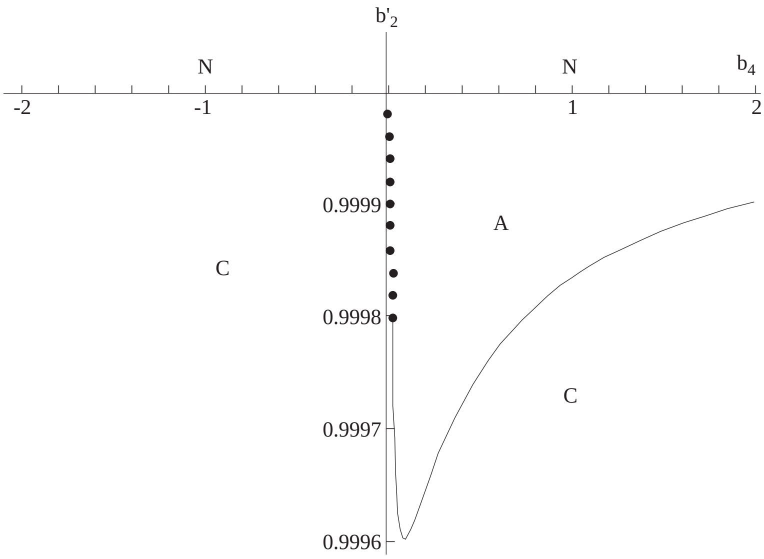

Figure 1. Our theoretical phase diagram near the NAC point using the mean field theory for the model I with $c = -1$ and $b_3 = -0.001$ (see the text)

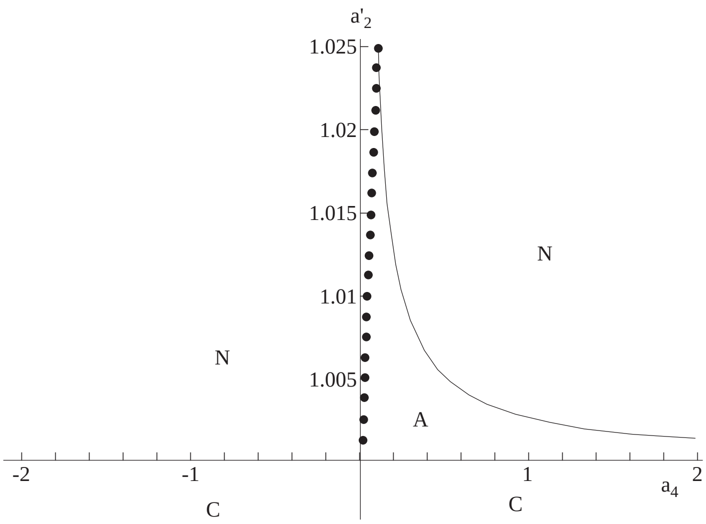

Figure 2. Our theoretical phase diagram near the NAC point using the mean field theory for the model II with $c = -1$ and $a_3 = -0.1$ (see the text)

Since the NAC tricritical point is located at $a_4 = 0$, $a_2' = 1$ for model II, the NA phase line obtained from eq.(38), which does not pass from the $a_2' = 1$ when $a_4 = 0$, is cut at a point close to $a_4 = 0$. Starting from that point we connected the NA phase line to the NAC point, which we have denoted by dots in Figure 2. For the NC transition in model II the Mathematica programme gives from eq.(45) that $a_4 = 0$ for the NC phase line.

5. Conclusions

In this study we have developed two models (model I and II) to obtain the phase diagram near the NAC point in a mixture of liquid crystals. Since both mean field models are the temperature and concentration dependent, the diagrams obtained in this study are the T-x phase diagrams near the NAC point in a mixture of liquid crystalline system.

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