Kasetsart J. (Nat. Sci.) 41 : 192 - 197 (2007)

# Extension of Mean Field Theory and General Form of Order Parameter

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## ABSTRACT

In this work we study the phase transition of liquid crystal between nematic and isotropic phases by introducing the general form of order parameter, $s_i = a\cos^2\theta_{\mathrm{i}} - b$, then applying mean field theory (Maier-Saupe Theory) to calculate the free energy of the system, and considering the phase transition. We obtain the values of *a* and *b* that satisfy the conditions at the transitions.

**Key words:** order parameter, phase transition, nematic liquid crystals

## INTRODUCTION

In the Maier-Saupe Theory, they use the definition of order parameter by using the second order Legendre polynomial (Colling and Hird., 1997) , $P_2(\cos\theta_i) = (3/2)\cos^2\theta_i - 1/2 = s_i$, then study the phase transition by means of statistical mechanics solved for the free energy of the system, and get the values of order parameter $s_c = 0.429$, that mean that for all kinds of nematic liquid crystal the values of $s_c$ have only one value that does not hold for all kinds of nematic liquid crystals. In the experimental data the values of those are different. So in this work we try to extend Maier – Saupe theory by introducing the order parameter of the molecule i<sup>th</sup> in the general form.

## MATERIALS AND METHODS

### Part I. The helmholtz free energy of the system

In mean field theory (Maier and Saupe, 1958) assume that a molecule i is embeded in the sea of other molecules and has potential energy, $u_i$, in the form

$$u_i = -\frac{A}{V^2}s(a\cos^2\theta_{\mathrm{i}} - b) \tag{1}$$

where A is the constant not depending on volume and pressure (Chandrasekhar, 1977), V is the molar volume, *s* is the thermal average of order parameter, *a* and *b* are parameters depending on types of nematic liquid crystal , and $\theta_i$ is the angle which the molecule i th making angle with the director and

$$s = \langle a\cos^2\theta - b\rangle \tag{2}$$

According to statistical mechanics (Reif, 1988), we consider partition function for the i th molecule in the form

$$z_i = \int_0^1 \exp[-\beta u_i]dx_i \tag{3}$$

Where $x_i = \cos\theta_i$, and thermal average of order parameter defined by

$$s = \frac{\int_0^1 (ax_i^2 - b)\exp[-\beta u_i]dx_i}{\int_0^1 \exp[-\beta u_i]dx_i} \tag{4}$$

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Received date : 21/07/06 Accepted date : 11/01/07

To consider the partition function $Z$ of the system composed of 1 mole, we obtain

$$Z = [\int_0^1 \exp[-\beta u_i]dx_i]^{N_A} \tag{5}$$

where $N_A$ is the Avogardo Number and $\beta$ = $1k_BT$ and $k_B$ is the Boltzmann constant. Next we calculate the average Helmholtz free energy can be calculated by using the formula

$$F = \frac{1}{2}\frac{\partial}{\partial\beta}\ln Z - k_BT\ln Z \tag{6}$$

Finally, we obtain the free energy

$$F = N_Ak_BT\{\frac{1}{2}Bs(s+2b) - \ln(\int_0^1 \exp [Bsax_i^2]dx_i)\} \tag{7}$$

where

$$B = \frac{A}{k_BTV^2} \tag{8}$$

**Part II. The phase transition between isotropic and nematic phase**

The transition between isotropic and nematic phase must satisfy two conditions.

First, the free energy must be zero at the transition point

$F$ ($s_c$, $B_c$) = 0 (9)

Second, the partial derivative of the free energy with respect to $s$ at $T = T_c$ must be zero

$$(\frac{\partial F}{\partial s})_{V,T_c} = 0 \tag{10}$$

From these two conditions, we have

$$\frac{1}{2}Bs(s+2b) = \ln(\int_0^1 \exp[Bsax_i^2]dx_i) \tag{11}$$

and

$$\frac{s+b}{a} = \frac{\int_0^1 x_i^2 \exp[Bsax_i^2]dx_i}{\int_0^1 \exp[Bsax_i^2]dx_i} \tag{12}$$

Solving equation (11) and (12), we obtain $s_c$ and $B_c$ , then we get $T_c$ from the equation

$$B_c = \frac{A}{k_BT_cV^2} \tag{13}$$

where $A = 1.3 \times 10^{-27}$ $J \cdot m^6$ and $k_B = 1.38 \times 10^{-23}$ $J/K$

## RESULTS AND DISCUSSION

From equation (11) and (12), In case of $a$ = 1.5 and $b$ = 0.5 by solving the two equations simultaneously, we obtain $s_c$ = 0.429 and $B_c$ = 4.5461 which correspond to Maier-Saupe theory. To calculate $a$ and $b$ for each type of the nematic liquid crystals , we have the series of experimental results (Phaovibul *et al*., 1981) as Table 1.

And we plot the curves between F/ $NK_BT_c$ against $s$ for each type of those as shown in the **Figure** 1-6.

To consider the state of phase changes while the temperature changing we need to know the two conditions. At the point that the energy of the two phases is equal, the free energy is equal to zero and the derivative of the free energy with

**Table 1** Valaes of $S_c$, $B_c$, *a* and *b* at the transitions for each type of the rematic ligquid crystal.

| Types | $s_c$ | $B_c$ | $a$ | $b$ |
|---|---|---|---|---|
| p-azoxyanisole (PAA) | 0.43 | 4.5312 | 1.50187 | 0.50067 |
| p-azoxyphenetole (PAP) | 0.50 | 3.8968 | 1.63408 | 0.54909 |
| 4,4′-di-n-propyloxyazoxybenzene(PDPAB) | 0.44 | 4.4282 | 1.52104 | 0.50758 |
| 4,4′-di-n-butyloxyazoxybenzene(PBAB) | 0.55 | 3.5426 | 1.72636 | 0.58403 |
| 4,4′-di-n-pentyloxyazoxybenzene(PPAB) | 0.48 | 4.0592 | 1.59673 | 0.53522 |
| 4,4′-di-n-hexyloxyazoxybenzene(PHAB) | 0.56 | 3.4793 | 1.74467 | 0.59108 |

respect to the order parameter must equal to zero. We found that when the structure of the molecules are changed a little bit from the main structure the temperature and the order parameter at the transition are changed that means the flexibility of molecules of nematic liquid crystal depending on the structure of the molecule (de Jue, 1976), another word the strength of the inter action between the molecules is changed.

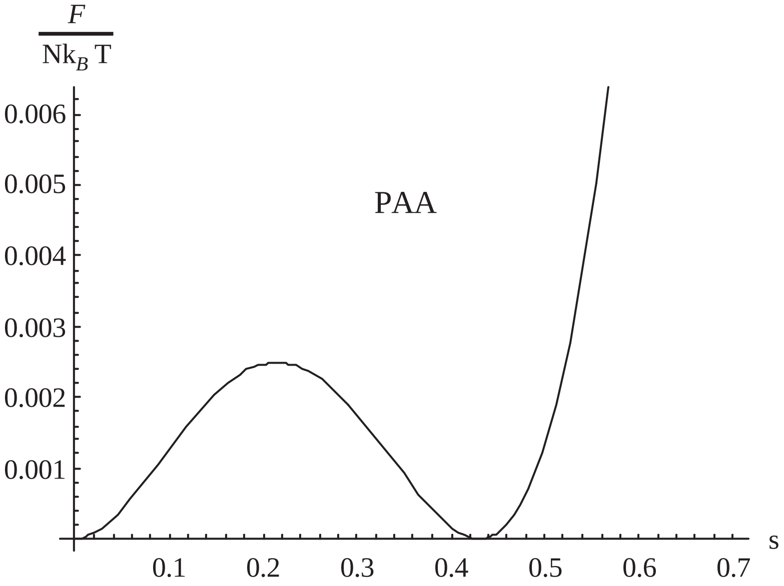

**Figure 1** Plot of $F / Nk_BT_c$ against $s$ at the transition point for PAA with $V = 225\ ml / mole$, $T_{NI} = 408\ K$ and $s_c = 0.43$

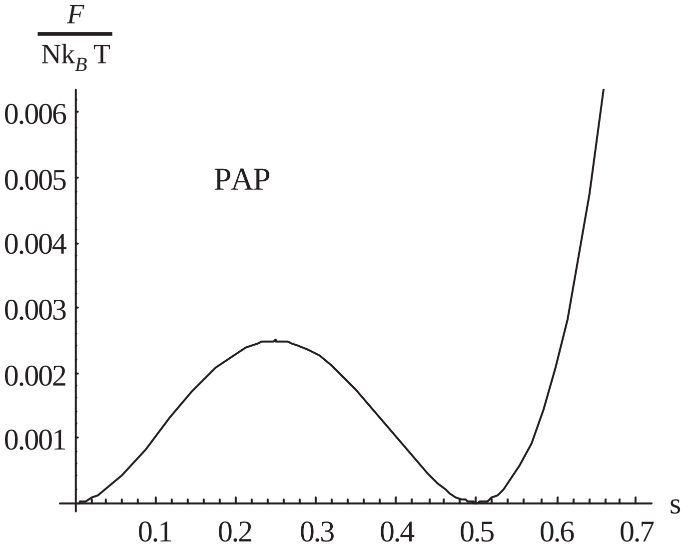

**Figure 2** Plot of $F / Nk_BT_c$ against $s$ at the transition point for PAP with $V = 267.3\ ml / mole$, $T_{NI} = 441\ K$ and $s_c = 0.50$

## CONCLUSION

From the calculations we found that the phase transitions of nematic liquid crystal between nematic-isotropic depending on the parameter *a* and *b*. In the experiments the range of order parameter at the transition between 0.3 and 0.8 . In other word if we know the values of $s_c$ and $B_c$ from the experiments we can calculate the values *a* and *b*, that means we know the potential energy for each molecule of the nematic liquid crystals.

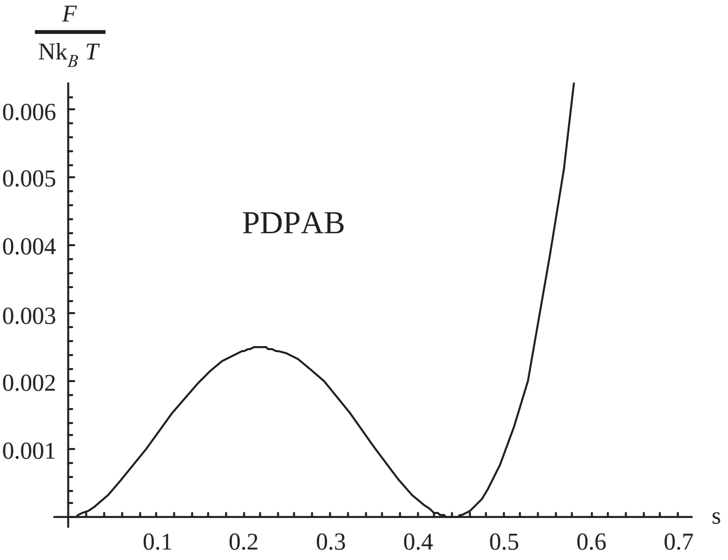

**Figure 3** Plot of $F / Nk_BT_c$ against *s* at the transition point for PDPAB with $V = 229$ *ml / mole*, $T_{NI} = 396$ *K* and $s_c = 0.44$

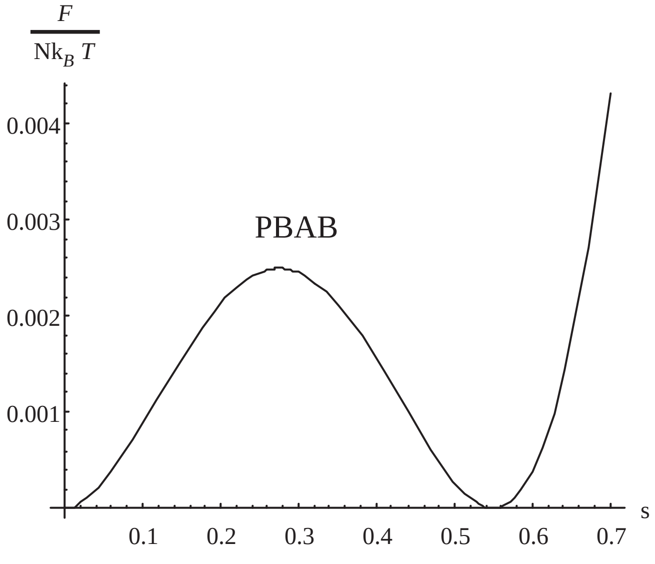

**Figure 4** Plot of $F / Nk_BT_c$ against *s* at the transition point for PBAB with $V = 338.5$ *ml / mole*, $T_{NI} = 409$ *K* and $s_c = 0.55$

## ACKNOWLEDGEMENTS

The author would like to thank Prof. I Ming Tang at Department of Physics, Mahidol University, Thailand and Prof. Till Daniel Frank at Institute for Theoretical Physics, University of Muenster, Germany.

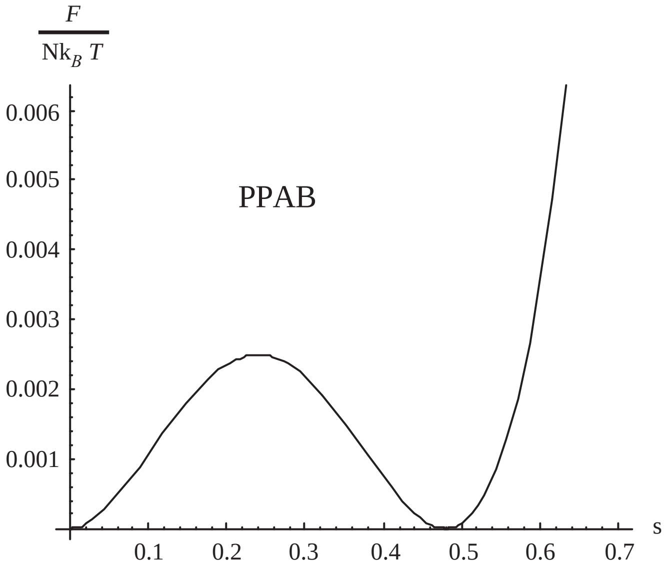

**Figure 5** Plot of $F / Nk_B T_c$ against $s$ at the transition point for PPAB with $V = 368.9$ *ml / mole*, $T_{NI} = 396$ $K$ and $s_c = 0.48$

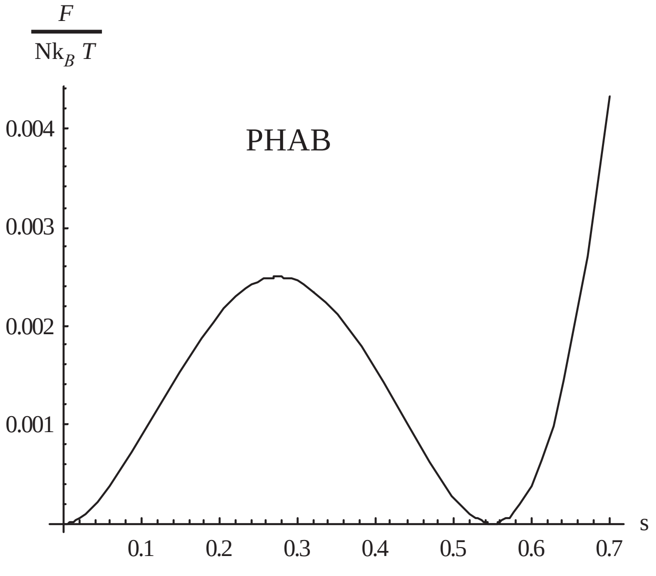

**Figure 6** Plot of $F / Nk_B T_c$ against $s$ at the transition point for PHAB with $V = 406$ *ml / mole*, $T_{NI} = 402$ $K$ and $s_c = 0.56$

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