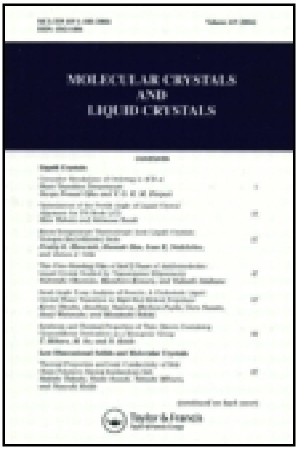

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phase Diagram for Discotic Liquid Crystals

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Version of record first published: 17 Oct 2011.

To cite this article: D. Ghose , T. R. Bose , C. D. Mukherjee , M. K. Roy & M. Saha (1986): Phase Diagram for Discotic Liquid Crystals, Molecular Crystals and Liquid Crystals, 138:1, 379-392

To link to this article: http://dx.doi.org/10.1080/00268948608071771

Mol. Cryst. Liq. Cryst., 1986, Vol. 138, pp. 379–392
0026-8941/86/1384-0379/$20.00/0

Printed in the United States of America

Phase Diagram for Discotic Liquid Crystals

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(*Received August 19, 1985; in final form December 23, 1985*)

The variational method of Lee *et. al.*, for calculating the phase diagrams of systems consisting of rod-like molecules, has been extended to the discotic systems. Compared to the existing models of the discotic phase, the present results are in much better agreement with experimental observations. According to this theory the N–I transition temperature (T_{N-I}) varies inversely as the square of the molecular diameter whereas in the work of Lee *et. al.*, on rod-like molecules, T_{N-I} varies inversely as the molecular length.

Keywords: discotic liquid crystal, phase diagram, variational method

INTRODUCTION

In some recent works,[1,2] McMillan's mean field theory[3] for the rod-like molecules has been fruitfully extended to the mesophases of disc-shaped molecules. By introducing a two dimensional spatial order parameter, similar to McMillan's mixed order parameter 'σ', Feldkamp[1] reproduced the phase sequence, hexagonal discotic (D_h)—Nematic (N_D)—Isotropic (I), with increasing temperature. Chandrasekhar's model,[2] besides reproducing the above phase sequence, can account for the possible existence of the rectangular discotic (D_{rd}) phases. In both these models, a 'length parameter', which is virtually identical with the McMillan parameter 'α', can be varied to take into consideration the variation of the end chain length and a phase diagram can thus be obtained. The calculated phase diagrams (Figure 1) show the essential qualitative aspects of the ex-

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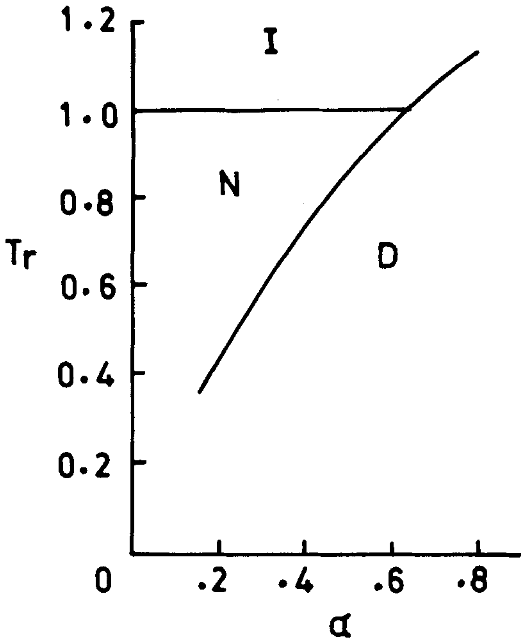

FIGURE 1 Phase diagram for discotic mesophase obtained by Feldkamp *et. al.*, [Ref. 1]. Reduced transition temperature (T_r = T/T_{N-I}) is plotted against model parameter α. [*I*—Isotropic, *N*—Nematic, *D*—Columnar].

perimentally observed results, but suffer from the same shortcomings of the McMillan model. Instead of an expected (as observed in experiments)[4] decrease of T_{N-I}'s with increasing chain length the calculated T_{N-I}'s are found to be constant, independent of chain length. Moreover, the calculated columnar-nematic transition temperature (T_{D-N}) rises monotonically with chain length whereas in experiment there is an initial rise at short chain lengths and after attaining a maximum it decreases again for long chain lengths (Figure 2). For rod-like molecules, Lee *et. al.*[5] had a spectacular success in reproducing the phase diagrams which are in excellent agreement with experiments (Figure 5). Their approach had three new features (in comparison to McMillan's mean field model):

i) the complete Kobayashi form of the pair interaction potential with an orientation independent term was used,

ii) the pair potential was not approximated by a truncated Fourier series, and

iii) the theory was based on a variational principle for determining the parameters of an assumed distribution function.

In the present work, we have applied the variational approach of Lee *et. al.*[5] to the discotic systems. The calculated phase diagrams (Figure 4) show marked improvement over the earlier results. It is seen that the phase diagrams are qualitatively similar to the results of Lee *et. al.* The N–I transition temperature has, however, a steeper fall with increase in chain length. To be precise, the present calculation shows an inverse square dependence on diameter whereas for rod-like molecules Lee *et. al.* obtained a fall proportional to the inverse of length. Moreover, it is shown in the present paper that the N–I phase diagram can be obtained analytically without lengthy numerical computations which are endemic to the variational approach. A considerable amount of computation is however unavoidable for the columnar to nematic (D–N) or columnar to isotropic (D–I) calculations.

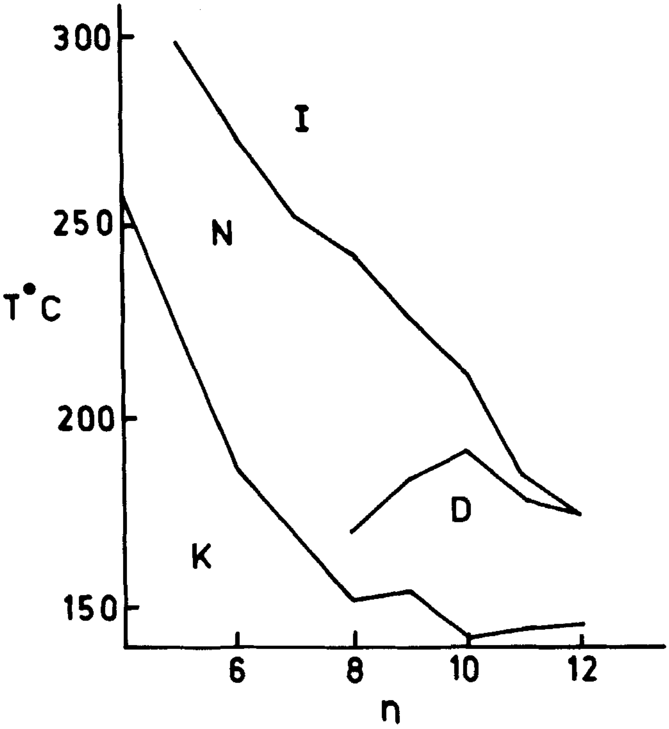

FIGURE 2 Experimental phase diagram of HBT [Ref. 4]. Transition temperature (T) in °C is plotted against number of carbon atom (n) in the alkoxy chain of HBT. [*I*—Isotropic, *N*—Nematic, *D*—Columnar, *K*—Crystal].

FORMULATION OF THE VARIATIONAL METHOD

We choose, as in Feldkamp,[1] the following two order parameters relevant for the description of a hexagonal columnar to nematic transition.

The orientational order parameter $\eta = \langle P_2(\cos\theta)\rangle$ where θ is the angle between the axis of polarizability of the disc-like molecules (this axis is usually normal to the plane of the disc) and the laboratory Z-axis (the director).

The other order parameter, an orientation cum layering order parameter, is given by

$$\sigma = \left\langle \frac{1}{3}\{\cos(\vec{R}_1 \cdot \vec{r}) + \cos(\vec{R}_2 \cdot \vec{r}) + \cos(\vec{R}_3 \cdot \vec{r})\} P_2(\cos\theta) \right\rangle \tag{1}$$

where $\vec{r}$ denotes the position of the center of a disc.

The vectors $\vec{R}_1$ and $\vec{R}_2$ are the reciprocal lattice vectors of the two dimensional hexagonal lattice and given by

$$\vec{R}_1 = (2\pi/d)[\hat{i} - \hat{j}/\sqrt{3}] \tag{2a}$$

$$\vec{R}_2 = (2\pi/d)[\hat{j} \cdot 2/\sqrt{3}] \tag{2b}$$

and

$$\vec{R}_3 = \vec{R}_1 + \vec{R}_2 = (2\pi/d)[\hat{i} + \hat{j}/\sqrt{3}] \tag{2c}$$

The corresponding direct lattice parameters are

$$\vec{r}_1 = \hat{i}d \quad \text{and} \quad \vec{r}_2 = (d/2)[\hat{i} + \hat{j}/\sqrt{3}] \tag{3}$$

With the above choice of order parameters a trial single particle distribution function can be written as

$$f(x, y, \theta) = \frac{1}{A} \exp\left[\frac{v_0}{kT}\left\{a \cdot P_2(\cos\theta) + b \cdot \left(\cos(\vec{R}_1 \cdot \vec{r}) + \cos(\vec{R}_2 \cdot \vec{r}) + \cos(\vec{R}_3 \cdot \vec{r})\right) P_2(\cos\theta)\right\}\right] \tag{4}$$

where 'a' and 'b' are the variational parameters, 'A' is the normalizing constant. The essence of the variational technique lies in obtaining a global minimum (by varying 'a' and 'b') at a given temperature of the following free energy functional

$$F(f(x,y,\theta)) = F_0 + NkT\int f_1 \ln f_1 \, d^5\tau_1 + \frac{1}{2}N^2\int f_1 f_2 v_{12} d^5\tau_1 d^5\tau_2 \quad (5)$$

where τ's are the five component vectors denoting the positions and orientations of a molecule. The suffixes '1' and '2' refer to the first and second particle respectively.

Generalising the pair interaction potential used by Lee *et. al.*, to the discotic phase we choose it as

$$v_{12}(r_{12}, \theta_{12}) = -(v_0/r_0 n_z\sqrt{\pi}) \cdot \exp[-(r_{12}/r_0)^2]P_2(\cos\theta_{12}) \quad (6)$$

where 'v_0' and 'r_0' are the measures of the strength and range of interaction respectively and 'n_z' is the linear density of molecules along Z axis (director).

In the above expression we did not include any orientation independent term for the sake of simplicity. We would like to emphasize that the orientation independent term is not really the reason behind the success of the work by Lee *et. al.* The present calculation shows it clearly as we could reproduce the phase diagram without including such a term in the pair potential. Moreover, we have checked that the pair potential of Lee *et. al.*[5] without the orientation independent term does give rise to a phase diagram for rod-like molecules which is not qualitatively different from the one reported in their work.[5] It has been observed that the inclusion of the orientation independent term has no influence on the T_{N-I}'s and only marginally flattens the S–N transition curve of the phase diagram for rod-like molecules.

CALCULATION AND RESULTS

For the evaluation of the free energy functional the region of integration of the first particle is over the unit cell (shown by the dotted line in Figure 3) and for the second particle it is over the entire x-y plane. For the sake of convenience in calculation we choose an oblique co-ordinate system (s, p) parallel to $\vec{r}_1$ and $\vec{r}_2$. The relation between (x, y) and (s, p) systems is given by

$$x = d(s + p/2) \quad \text{and} \quad y = d(\sqrt{3}p/2) \quad (7)$$

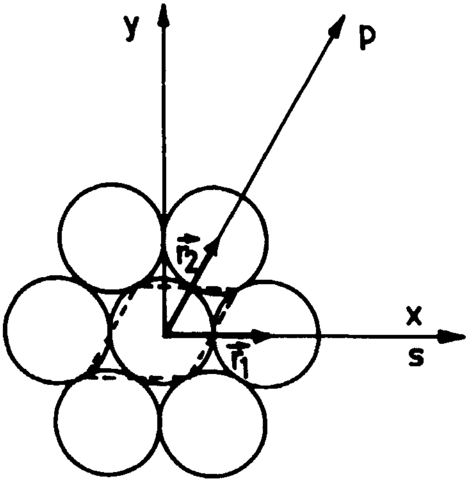

FIGURE 3 Arrangement of molecules in hexagonal columnar (D_h) phase. Dotted region shows the unit cell of the hexagonal lattice.

The range of integration (over the unit cell) in the new system will be from $s = -(1/2)$ to $+(1/2)$ and $p = -(1/2)$ to $+(1/2)$. In the transformed system the spatial part of the two dimensional translational order is represented by

$$\begin{aligned} &\cos(\vec{R}_1 \cdot \vec{r}) + \cos(\vec{R}_2 \cdot \vec{r}) + \cos(\vec{R}_3 \cdot \vec{r}) \\ &= \cos(2\pi s) + \cos(2\pi p) + \cos(2\pi(p + s)) \\ &= R(s, p) \qquad \text{say} \end{aligned} \tag{8}$$

Accordingly, the free energy functional $F(f)$ will be

$$F(f) = \text{Const.} + F_1 + F_2 \tag{9}$$

where,

$$\begin{aligned} F_1/NkT = &-\ln B + (1/Bt) \\ &\cdot \int_0^1 d\mu \int_{-1/2}^{1/2} ds \int_{-1/2}^{1/2} dp\, [\{a + b \cdot R(s, p)\} P_2(\mu)] \\ &\cdot \exp[\{a + b \cdot R(s, p)\} P_2(\mu)/t] \,, \end{aligned}$$

$$F_2/NkT = -(1/2B^2t)$$

$$\cdot \int_0^1 d\mu_1 \int_{-1/2}^{1/2} ds_1 \int_{-1/2}^{1/2} dp_1 \cdot P_2(\mu_1)$$

$$\cdot \exp[\{a + b \cdot R(s_1, p_1)\}P_2(\mu_1)/t] \cdot I(s_1, p_1)$$

and
$$I(s_1, p_1) = \int_0^1 d\mu_2 \int_{-\infty}^{\infty} ds_2 \int_{-\infty}^{\infty} dp_2 \cdot P_2(\mu_2)$$

$$\cdot \exp[\{a + b \cdot R(s_2, p_2)\}P_2(\mu_2)/t]$$

$$\cdot \exp[-R_L^2\{(s_1 - s_2)^2 + (p_1 - p_2)^2 + (s_1 - s_2)$$

$$\cdot (p_1 - p_2)\}]$$

In the above expressions

Reduced temperature $`t' = kT/v_0\,,$ (10)

Reduced length $`R_L' = d/r_0\,,$ (11)

$$\mu = \cos\theta \qquad (12)$$

and

$$B = \int_0^1 d\mu \int_{-1/2}^{1/2} ds \int_{-1/2}^{1/2} dp \cdot \exp[\{a + b \cdot R(s, p)\}P_2(\mu)/t] \qquad (13)$$

For a particular R_L, the free energy functional is evaluated for different values of 't'. For each 't', the minimum of 'F' is sought over a wide range of values of parameters 'a' and 'b'. If we denote the values of the parameters at the minimum by $\tilde{a}$ and $\tilde{b}$, then the different phases are characterised by:

Isotropic phase : $\tilde{a} = \tilde{b} = 0$

Nematic phase : $\tilde{a} \neq 0, \tilde{b} = 0$

and Columnar phase : $\tilde{a} \neq 0, \tilde{b} \neq 0$

Once the variational parameters are fixed, the order parameters can be calculated from the following expressions:

$$\eta = \frac{1}{B}\int_0^1 d\mu \int_{-1/2}^{1/2} ds \int_{-1/2}^{1/2} dp \cdot P_2(\mu) \cdot \exp[\{\tilde{a} + \tilde{b} \cdot R(s, p)\} P_2(\mu)/t] \tag{14}$$

and

$$\sigma = \frac{1}{B}\int_0^1 d\mu \int_{-1/2}^{1/2} ds \int_{-1/2}^{1/2} dp \cdot \{P_2(\mu) \cdot R(s, p)/3\} \cdot \exp[\{\tilde{a} + \tilde{b} \cdot R(s, p)\} P_2(\mu)/t] \tag{15}$$

The phase transition temperatures are ascertained from the equality of free energy of two phases. Varying R_L we obtained the phase diagram depicted in Figure 4. A comparison with Figure 5 shows that

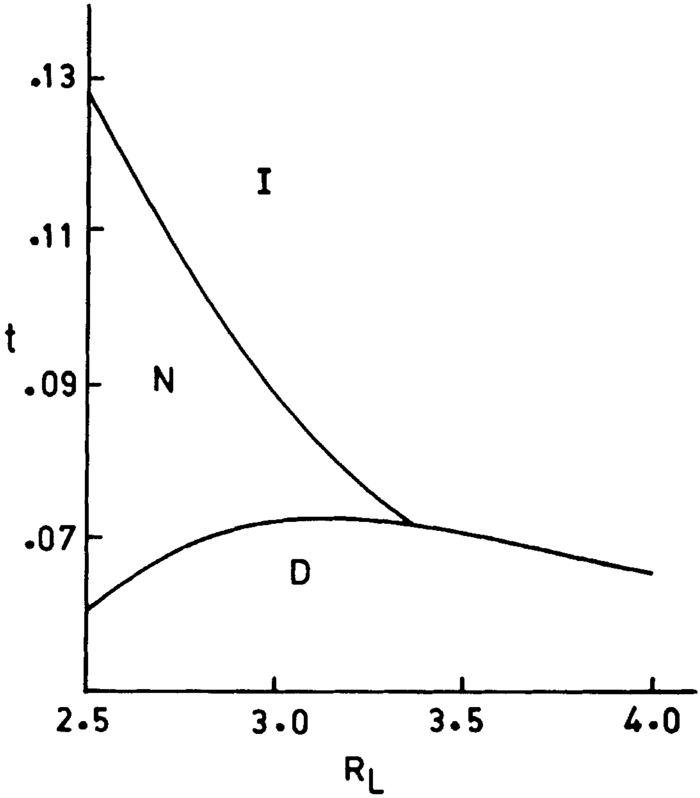

FIGURE 4 Phase diagram reproduced by the present theory for the discotic mesophase. Reduced temperature ($t = kT/v_0$) is plotted against reduced length ($R_L = d/r_0$). [*I*—Isotropic, *N*—Nematic, *D*—Columnar].

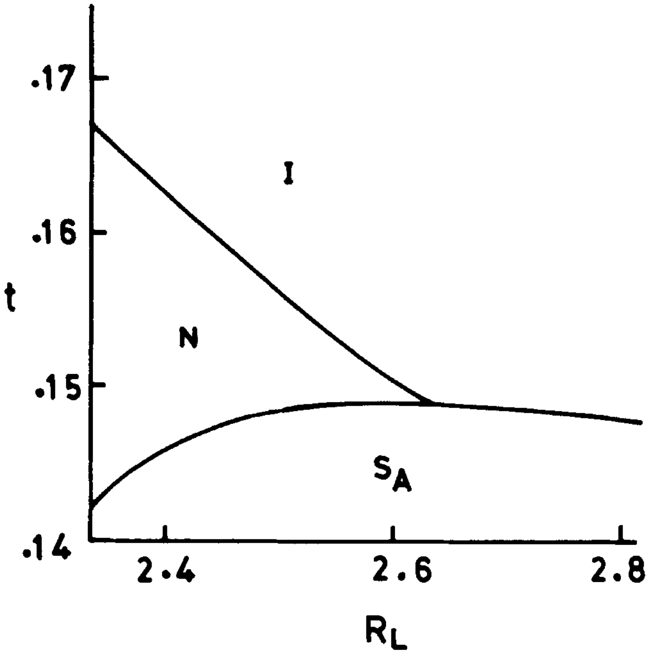

FIGURE 5 Phase diagram obtained by Lee *et. al.* [Ref. 5] for rod-like molecules. Reduced temperature ($t = kT/v_0$) is plotted against 'R_L'. R_L is related to ζ_0^{-1} used as abscissa in Ref. 5 by $R_L = 2\pi\zeta_0^{-1} = d/Z_0$. [$I$—Isotropic, N—Nematic, S_A—Smectic A].

in the discotic phase we get a steeper decrease of T_{N-I}'s with increasing R_L. The columnar-nematic transition temperature (T_{D-N}) vs. R_L curve initially rises, attains a maximum and then slowly decreases. The N–I and D–N curves meet near about $R_L = 3.4$, which indicates a direct columnar to isotropic transition. All these features agree with the experimental phase diagram of HBT (Figure 2). The entropy of discotic-nematic transition has also been calculated for various values of R_L and the results are shown by a ΔS_{D-N} vs. T_{D-N}/T_{N-I} curve in Figure 6. We could not, however, compare this result with any experimental observations as we have not come across any measurement of ΔS_{D-N} for a homologous series.

While discussing the results some comments on the accuracy of the results are called for. It is understandable that the accuracy of the calculated results depend on the number of points used for the Gauss-quadrature method of integration. For the columnar phase, the two particle term needs considerable computation time as the term contains a six dimensional integral. In IRIS-80 computer for each set of '*a*', '*b*' and '*t*' in 8 point Gauss quadrature method we require ~19 mins,

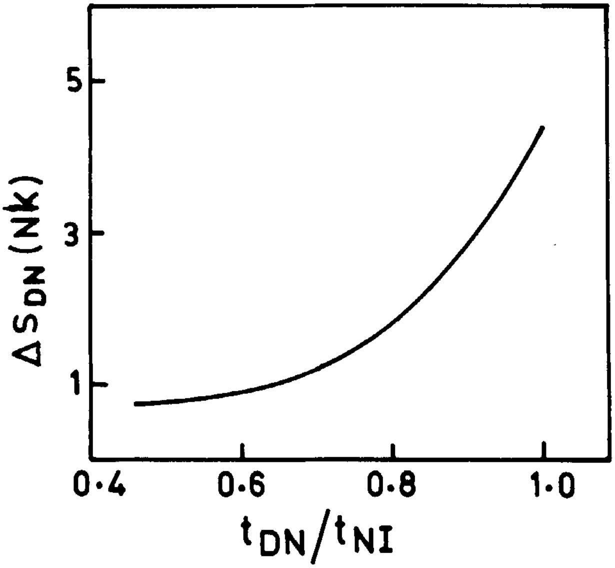

FIGURE 6 Molar transition entropy ΔS_{DN} for columnar-nematic transition is plotted against t_{DN}/t_{NI}.

whereas in a twelve point calculation time is higher by a factor of ~12. A very judicious search for a transition temperature for a given R_L can take as much as 10 to 15 hours on the IRIS-80, if we use 8 point Gauss method. Naturally being restricted to a 8 point calculation, we utilize some symmetries of the functions to convert the integration limit $-(1/2)$ to $+(1/2)$ (which naturally leads to -1 to $+1$ in Gauss quadrature technique) to 0 to 1. From equation (8) it is evident that

$$R(s, p) = R(-s, -p) \quad \text{and} \quad R(s, -p) = R(-s, p) \qquad (16)$$

Hence the distribution function

$$f(\mu, s, p) = \exp[\{a + b \cdot R(s, p)\} P_2(\mu)/t]$$

also satisfies the conditions

$$f(\mu, s, p) = f(\mu, -s, -p)$$

and

$$f(\mu, s, -p) = f(\mu, -s, p)$$

So,

$$B = \int_0^1 d\mu \int_{-1/2}^{1/2} ds \int_{-1/2}^{1/2} dp \cdot f(\mu, s, p) \tag{17}$$

$$= \frac{1}{2}\int_0^1 d\mu \int_0^1 ds \int_0^1 dp \left[f\left(\mu, \frac{s}{2}, \frac{p}{2}\right) + f\left(\mu, \frac{-s}{2}, \frac{p}{2}\right) \right] \tag{18}$$

Evaluating equations (17) and (18) both with 8 points Gauss quadrature method, we have seen that the results of equation (18) have a much better agreement with a 12 point result. This is due to a closer spacing of the Gauss points in the latter case (Eqn. (18)). Even with this change of limit the results obtained are not as accurate as a twelve point calculation. However, so far as the qualitative features of the phase diagrams are concerned we feel that the results are quite indicative.

For the N–I transitions, we can overcome this limitation on accuracy by calculating the transition temperatures analytically using only the Maier-Saupe result as shown in the following section.

NEMATIC-ISOTROPIC TRANSITION

For the nematic phase the space dependent part of the second particle integration in $F(f)$ can be evaluated analytically due to the absence of 'b' containing term.

So

$$F_2/NkT = -[\pi/(\sqrt{3} \cdot R_L^2 \cdot t)] \cdot \eta^2$$

$$= -[C/t]\eta^2 \tag{19}$$

where,

$$C = \pi/\sqrt{3} \cdot R_L^2 \tag{20}$$

and

$$\eta = \frac{1}{B}\int_0^1 d\mu \cdot P_2(\mu) \cdot \exp[a \cdot P_2(\mu)/t] \tag{21}$$

Then

$$F/NkT = F' = -\ln B + (a/t) \cdot \eta - (c/t) \cdot \eta^2 \tag{22}$$

At the minimum of F'

$$\left.\frac{\partial F'}{\partial a}\right|_{a=\tilde{a}} = 0 \tag{23}$$

Or,

$$-\frac{1}{B}\left.\frac{\partial B}{\partial a}\right|_{\tilde{a}} + \frac{\eta}{t} + \frac{\tilde{a}}{t}\left.\frac{\partial \eta}{\partial a}\right|_{\tilde{a}} - \frac{2C}{t}\cdot\eta\cdot\left.\frac{\partial \eta}{\partial a}\right|_{\tilde{a}} = 0\,. \tag{24}$$

at the minimum, $B(\tilde{a})$ = partition function Z

From the expression of $B(a)$
We have

$$\frac{1}{B}\left.\frac{\partial B}{\partial a}\right|_{\tilde{a}} = \frac{\eta}{t} \tag{25}$$

Therefore Eqn. (24) becomes

$$\frac{1}{t}\left.\frac{\partial \eta}{\partial a}\right|_{\tilde{a}} (\tilde{a} - 2\eta C) = 0 \tag{26}$$

Since

$$\left.\frac{\partial \eta}{\partial a}\right|_{\tilde{a}} \neq 0\,, \quad \text{so} \quad \tilde{a} = 2\eta C \tag{27}$$

Putting the value of $\tilde{a}$ from equation (27) to equation (22) we obtained the free energy for the nematic phase

$$F = NkT[-\ln Z + (C/t)\eta^2] \tag{28}$$

and the distribution function takes the form

$$f(\mu) = (1/A)\exp[\eta\cdot P_2(\mu)/t'] \tag{29}$$

Where

$$t' = t/2C \tag{30}$$

It is quite evident from the above expression that for nematic phase this variational method reduces to a Maier-Saupe type mean-field approximation with only differences of having a strength of potential inversely proportional to R_L^2. From M–S theory we know that at the N–I transition

$$\eta_{\text{tran}} = 0.429 \tag{31}$$

and

$$v_0/kT_{\text{N-I}} = 1/t_{\text{N-I}} = 4.54 \tag{32}$$

So here we have

$$1/t'_{\text{N-I}} = 4.54$$

or,

$$2C/t_{\text{N-I}} = 4.54$$

or,

$$t_{\text{N-I}} = 2C/4.54$$

or,

$$t_{\text{N-I}} = 0.799/R_L^2 \tag{33}$$

The equation (33) gives the N–I transition curve straight way (Figure 4).

CONCLUSION

In the present work, the phase diagrams of discotic liquid crystal systems have been reproduced by extending the variational method applied by Lee *et. al.* for the rod-like molecules. The phase diagrams reproduced have the correct qualitative features and show a definite improvement over the earlier results by Feldkamp or Chandrasekhar. It has been stressed that the present variational method requires a considerable amount of computation. This difficulty stems from the use of a pair interaction potential rather than a single particle potential. Efforts are underway to develop a single particle potential approach which can reproduce the correct qualitative features of the phase diagrams without being handicapped by enormous amount of computations. It is to be mentioned that S. Changquing and Lin Lei,[6] generalizing the McMillan Hamiltonian and using a single particle approach, have been successful in reproducing the results of Lee *et. al.* They have stated that their model can be extended to the case of discotic liquid crystals. Their model might therefore provide a single particle potential approach for calculating the phase diagrams for discotic liquid crystals.

Acknowledgments

D. Ghose, one of the authors, wishes to thank the governing body of the R. K. Mission Vidyamandira for allowing him a study leave [under the Faculty Improvement Programme of U.G.C.] during which the major portion of the work was performed. We thankfully acknowledge the use of the IBM 1130 computer at C.U. and IRIS-80 computer at VECC in Calcutta.

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