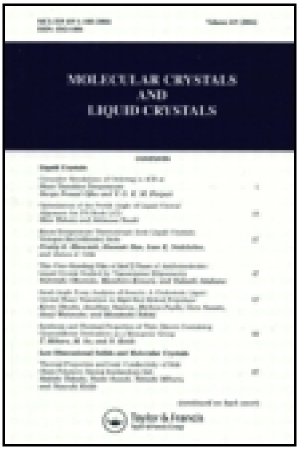

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

# A Mean Field Model for the Phase Diagram of a Discotic Liquid Crystalline System

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Version of record first published: 19 Dec 2006.

To cite this article: D. Ghose , T. R. Bose , M. K. Roy , M. Saha & C. D. Mukherjee (1988): A Mean Field Model for the Phase Diagram of a Discotic Liquid Crystalline System, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 154:1, 119-125

To link to this article: http://dx.doi.org/10.1080/00268948808078727

*Mol. Cryst. Liq. Cryst.*, 1988, Vol. 154, pp. 119–125
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Printed in the United States of America

# A Mean Field Model for the Phase Diagram of a Discotic Liquid Crystalline System

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(*Received February 9, 1987; in final form June 15, 1987*)

In an earlier work the present authors extended the variational method of Lee *et al.* for rod-like molecules to obtain the phase diagram of a discotic liquid crystal system. In the present work, the phase diagram of a discotic system is reproduced in a single particle potential model. It is seen that the single particle potential approach reproduces results very similar to those of the variational method but with considerable ease in computation. The equivalence of the two approaches is discussed.

*Keywords: discotic phase, single particle potential*

## INTRODUCTION

In an earlier paper[1] we extended the variational technique of Lee *et al.*[2] to the discotic phase. The calculated phase diagram shows better agreement with experiment[3] in comparison to earlier models.[4,5] Though

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the method is a powerful one, it takes a formidable amount of time for computation. To overcome this difficulty we have developed a single particle potential approach which is being presented in this paper. The present model reproduces the phase diagram having the same qualitative features of the results obtained from the variational approach, yet the computation time is appreciably reduced. It is really surprising to note that the results of the single particle potential approach, which requires an order of magnitude less computation time, are virtually as good as those of the variational method. Moreover, we tried a similar single particle potential approach for the rod-like molecular system and the calculated phase diagram has all the essential qualitative features of the phase diagram obtained by the variational approach of Lee *et al.*

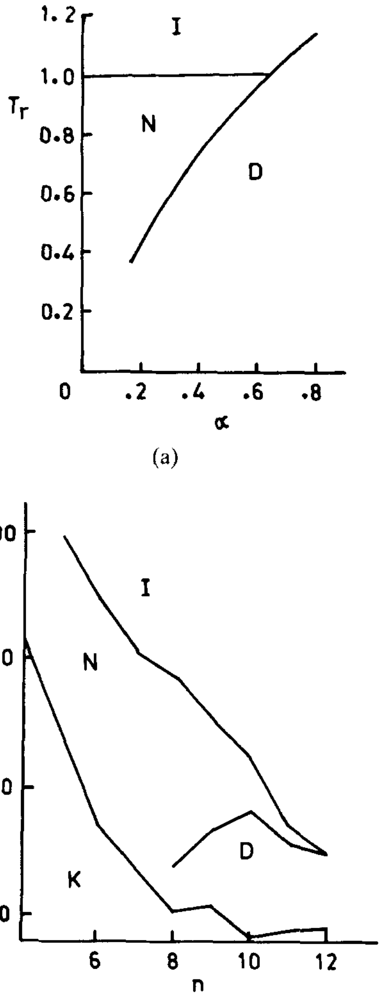
Thus, besides reproducing the phase diagram of a discotic system, this paper demonstrates that the variational method as proposed by Lee *et al.* is really not essential to improve the calculated phase diagram.

## THEORY

The earlier models[4,5] are essentially a generalisation of McMillan's[6] model of smectic ordering to the two dimensionally periodic discotic phase. Chandrasekhar's model[5] starts directly from the single particle potential and Feldkamp *et al.*[4] have assumed, following McMillan,[6] a short range anisotropic two particle interaction potential.

$$v_{12}(r_{12},\theta_{12}) = -(v_0/nr_0^3\pi^{3/2})\exp[-(r_{12}/r_0)^2]\cdot P_2(\cos\theta_{12}) \quad (1)$$

where $r_{12}$ is the distance between molecular centres, $\theta_{12}$ is the angle between molecular short axes [usually normal to the plane of the disc], $n$ is the molecular number density, $v_o$ is the strength of interaction and $r_o$ the range of interaction. Because of the presence of the Gaussian term $[\exp\{-(r_{12}/r_0)^2\}]$, the strength of the orientational potential diminishes as the average distance between molecules increases with increasing chain length. However, there is a term $n$, in the denominator, which gradually decreases with increasing size of the molecule in higher members of a homologous series. Therefore, the effective strength of interaction increases monotonically as a homologous series is ascended and this is the reason for the unusual increase of calculated $t_{N-D}$ with chain length contrary to experimental observation [Figure 1(a) and 1(b)].



(a)

(b)

FIGURE 1 (a) Phase diagram for discotic mesophase obtained by Feld Kamp *et al.* [Reference 4]. Reduced transition temperature ($T_r = T/T_{N-I}$) is plotted against model parameter $\alpha$. (b) Experimental phase diagram of HBT [Reference 3]. 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.]

In our earlier work on variational approach, we assumed a pair interaction potential

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

Here $n_z$ is the linear density of molecules along the $z$-axis (i.e. the director) which remains more or less constant with increasing chain length. Straightforward mean field calculation gives the single particle potential as

$$v_1(x,y,\cos\theta) = -(v/R_L^2)$$

$$[\eta + \alpha\sigma\{\cos(\mathbf{R}_1 \cdot \mathbf{r}) + \cos(\mathbf{R}_2 \cdot \mathbf{r}) + \cos(\mathbf{R}_3 \cdot \mathbf{r})\}] \cdot P_2 (\cos\theta) \quad (3)$$

where, $v = v_0\pi$, the modified strength of interaction
$R_L = d/r_0$, reduced length
$\alpha = 2 \exp[-(2\pi r_0/\sqrt{3}\, d)^2]$

$\eta$ and $\sigma$ are the orientational order parameter and the orientation-like layering order parameter respectively.

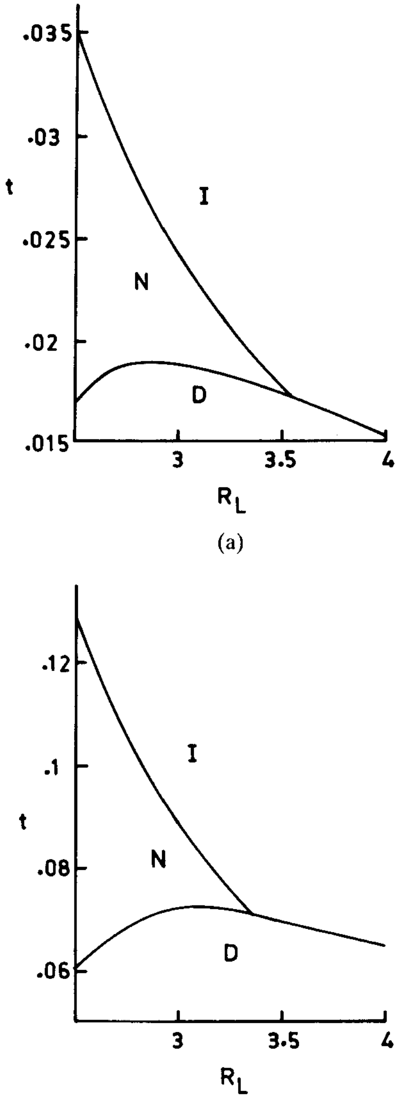
Here $d$, the molecular diameter, is the same as the direct lattice parameter for close packing of molecules in a two dimensional hexagonal lattice. Corresponding reciprocal lattice vectors are $\mathbf{R}_1$, $\mathbf{R}_2$ and $\mathbf{R}_3$ [defined in Reference 1].

The phase diagram, obtained by utilizing the above mean field [Equation (3)] is shown in Figure 2(a), where reduced transition temperature [$t = kT/v$] is plotted against the reduced length $R_L$. Here, unlike the Maier-Saupe result, the *N–I* transition temperature is given by

$$t_{N-I} = 0.22/R_L^2 \quad (4)$$

[This is a direct reflection of the fact that the present single particle potential varies as $(1/R_L^2)$.]

The columnar–nematic transition temperature initially rises with $R_L$ and after attaining a maximum near $R_L \approx 2.9$ it decreases slowly. For $R_L > 3.56$ there is a direct *D–I* transition. All these features agree very well with the basic trend of the experimental findings for Hexa-alkoxy benzoates of triphenylene (HBT) [Figure 1(b)].



(a)

(b)

FIGURE 2 (a) Phase diagram reproduced by the present mean field theory for the discotic mesophase. Reduced temperature ($t = kT/v$) is plotted against reduced length. (b) Phase diagram reproduced by our earlier variational theory [Reference 1] for the discotic mesophase.

## CONCLUSION

It is to be emphasized that the present theory reproduces the same type of phase diagram [Figure 2(b)] as was obtained earlier by the variational method.[1] For the *N–I* transition both the theories give $R_L^{-2}$ dependence of $t_{N-I}$. For *D–N* and *D–I* transitions, except for a difference in curvature (which partially may be due to the computational inaccuracy), the basic features are quite the same. Since the present work is a single particle potential theory, it has the usual computational advantage over the variational method.

It is evident from the similarity of the two phase diagrams [Figure 2(a) and 2(b)] that the merit of our earlier work[1] (which is an extension of Lee's work[2] to the discotic phase) does not really lie on the variational approach but on the ingenious choice of the pair interaction potential. This similarity in the phase diagrams is not quite obvious as the pair potential, in the variational method, is not approximated by a truncated Fourier series as is done in the single particle potential approach. However, in this type of variational method, the trial distribution function contains only the lowest order Fourier components of the density wave. So the result is in a sense approximate up to the lowest order Fourier components only and this we think is the reason behind the similarity of two phase diagrams. This

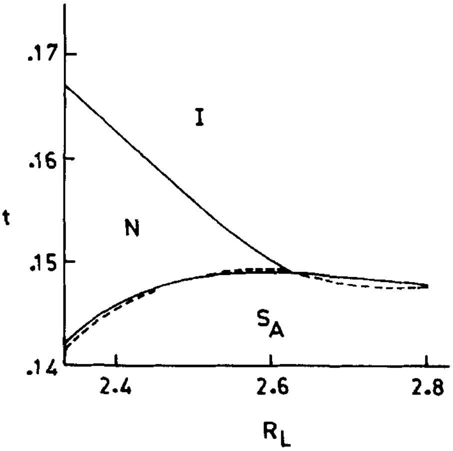


FIGURE 3 Phase diagram obtained for rod-like molecules (1) by Lee *et al.* [Reference 2] represented by continuous line and (2) by mean field method represented by dotted line. Reduced temperature ($t = kT/v_0$) is plotted against $R_L$. $R_L$ is related to $\zeta_0^{-1}$ used as abscissa in [Reference 2] by $R_L = 2\pi\zeta_0^{-1} = d/Z_0$. [$I$ = Isotropic, $N$ = nematic, $S_A$ = smectic A.]

aspect of the variational approach of Lee *et al.*, has been extensively discussed by Tan[7] for the *N–I* transitions of rod-like molecular systems. In order to be sure that the variational method itself is of no avail in improving the phase diagram even in $S_A$–$N$ transitions, we obtained the single particle potential from the pair interaction potential of Lee *et al.*[2] and calculated the phase diagram. A comparison of this phase diagram (Figure 3) with that of Lee *et al.* shows the validity of our contention.

It should also be pointed out that the assumption made in the paper regarding the dependence of pair interaction potential on $R_L$ is valid only if the $T_{N-I}$ of the series is relatively high (150°C) so that the conformational statistics of the chains can be ignored.

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