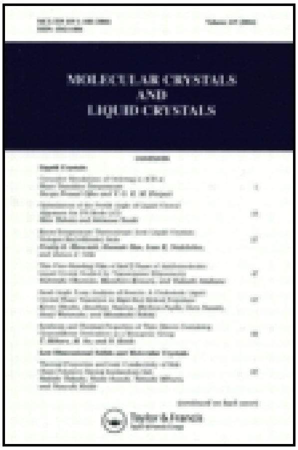

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A Mean Field Model for Reentrant Polymorphism

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A Mean Field Model for Reentrant Polymorphism

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In the earlier intercalation model of the present authors, it was shown how gradual dimerization of polar molecules with lowering of temperature necessitates intercalation of neighboring layers for space filling and how the resulting decrease in layer thickness of S_{Ad} phase brings about a nematic reentrant phase. In the present work, an alternative mechanism for space filling is proposed which can account for S_{Ad}–N_{re} transition with an accompanying increase of layer thickness. It is also shown that the present mechanism of space filling coupled with intercalation can lead to the S_{Ad}–N_{re} transition at constant layer thickness. These are in conformity with experimental observations where the said transition often occurs with virtually no change in layer thickness and in some cases with an increase in layer thickness.

Keywords: mean field, polar sample, reentrant phases

INTRODUCTION

In an earlier work[1] the present authors proposed a molecular mean field model for polar samples and reproduced the phase sequence (as the temperature is lowered) I–N–S_{Ad}–N_{re}–S_{A1}. The model was later applied successfully for the reproduction of the phase diagram of a binary system of polar and non-polar molecules.[2] The proposed model essentially rests on the following idea. The molecules being polar, they form dimers (Figure 1a) with complete overlap of the rigid parts and a symmetric disposition of the chains on either side of the rigid core. These symmetric dimers have much larger layering interaction (i.e., large value of the McMillan

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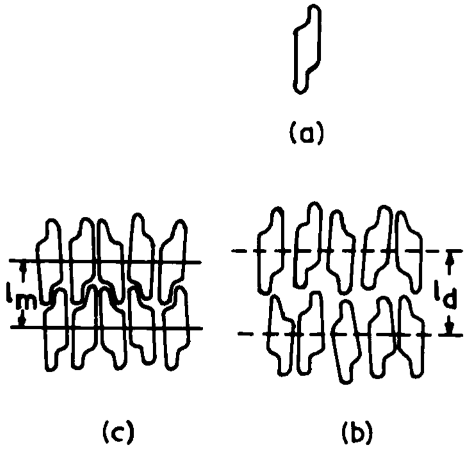

FIGURE 1 (a) A model HH dimer with complete overlap of the rigid parts with a symmetric disposition of chains; (b) SS dimers in bilayer arrangement; (c) Monolayer, smectic phase with layer thickness formed by dimers with a complete intercalation.

parameter α) than that of the monomers. As the temperature of an isotropic sample of these polar molecules is gradually reduced, the monomer–monomer, monomer–dimer and dimer–dimer anisotropic interactions bring about a nematic phase. As the temperature is further reduced, more and more dimers are formed and the large layering interaction stabilizes a S_{Ad} phase. Further dimerization (with lowering of temperature) however poses a problem of packing. It is clear from Figure 1b, that the dimers in a bilayer arrangement cannot fill up the voids left out by the monomers which have been converted to dimers. It was proposed therefore that below a critical volume fraction for monomers (which was connected to l_m/l_d ratio in the theory) the layers intercalate for the sake of space filling. As a result of this intercalation the layer thickness decreases but the core length remains the same (Figure 1c), i.e., there is a gradual diminution in layer thickness to core ratio which in McMillan model is reflected in a decrease in α parameter. This means that there is an effective decrease in layering interaction and hence a nematic (N_{re}) phase reenters. At a lower temperature a S_{A1} phase occurs with a near complete intercalation of pairs of neighboring layers. This intercalation model had thus a remarkable success in reproducing a double reentrant phase sequence. The decrease in layer thickness, a natural outcome of intercalation is not however a universal feature of reentrant polymorphism. There are instances,[3–8] including both pure sample and mixtures, where the layer thickness increases instead of decreasing and in some cases the layer thickness remains a constant.

In the present paper we propose an alternative mechanism of space filling which can cause an increase in layer thickness and at the same instance can bring about a S_{Ad}–N_{re} phase transition. As in our earlier model, here also the polar monomers form dimers with complete overlap of rigid cores (henceforth to be referred to as side by side or SS dimers) and the chains symmetrically disposed on either side. The high temperature nematic phase is a mixture of monomers and side by side (SS) dimers. With lowering of temperature more and more SS dimers are formed and due to large layering interaction a S_{Ad} phase comes into existence. With further increase in SS dimers, when there are not enough monomers to fill in the void in the bilayer arrangement of dimers, the SS dimer changes to a configuration where the monomers are attached head to head (HH) (Figure 2a). These HH dimers when arranged in layers (Figure 2b) leave out no void-space. That is, instead of intercalation of neighboring layers a second type of dimers are pressed into existence for the sake of packing. These HH dimers have a core length twice that of a SS dimer but the length of a HH dimer is not double that of a SS dimer (we assume core length r_c to be smaller than the chain length of the monomer). Hence a conversion from SS to HH dimer means a reduction in length to core ratio, i.e., a reduction in the value of McMillan parameter α. With sufficient conversion, α is so reduced that a nematic phase becomes free energetically favourable. This S_{Ad}–N_{re} transition is naturally associated with an increase in layer thickness (weighted average of SS and HH dimer lengths). Contrary to our earlier model, here a low temperature S_{A2} phase can be obtained when the system is virtually an all HH dimer system.

In this paper we also show that a S_{Ad}–N_{re} transition can be brought about at constant layer thickness by invoking both the space filling mechanisms namely the intercalation and SS to HH dimer conversion in an appropriate manner.

MEAN FIELD AND SELF CONSISTENT EQUATIONS

In our earlier work we assumed the system to consist of monomers and dimers (SS type) in chemical equilibrium ($D \rightleftarrows M + M$). With lowering of temperature more dimers are formed. The large layering interaction of the dimers brings about a S_{Ad} phase. The minimum volume fraction of monomers below which these dimers can not fill up space when arranged in layers[1] is

$$C_m = 1 - l_m/l_d = 1 - 1/s$$

where l_m and l_d are the lengths of a monomer and a SS type of dimer respectively. In that work we assumed that for monomer volume fraction $(1 - a) < C_m$, the neighbouring layers intercalate to fill up space. In the present work we assume exactly the same picture till the monomer volume fraction is reduced to C_m. When

FIGURE 2 (a) A model HH dimer; (b) HH dimers arranged in smectic layer. No void space is left out.

further reduction in $(1 - a)$ occurs, the void left out by monomers, which can not be filled by SS type dimers arranged in layers, is filled up by converting SS type dimers to HH type dimers. It is to be noted that HH type dimers when arranged in layers can fill up space with uniform packing. Only that much HH dimers are however produced which can just fill the void space up. Therefore for $(1 - a) < C_m$ the system becomes a mixture of three components—monomer, SS dimer and HH dimer.

In order to treat this three component system in a mean field approximation we follow our earlier work in reference 2; where also we had a three component system comprised of two types of monomers and one kind of dimer.

Let us consider a situation where there is $(1 - a)$ volume fraction of monomers and out of the rest a, x fraction i.e., $a.x$ volume fraction (of the whole system) is HH type dimers and a $(1 - x)$ volume fraction is SS type dimers.

The mean field experienced by the monomers and the dimers of two kinds can be written as

$$\begin{aligned} V_M = -\Bigg[&(1 - a)V_{mm}\left(\eta_m + \alpha_{mm}\sigma_m \cos\frac{2\pi Z_m}{d}\right) \\ &+ a(1 - x)V_{ms}\left(\eta_s + \alpha_{ms}\sigma_s \cos\frac{2\pi Z_m}{d}\right) \\ &+ ax\, V_{mh}\left(\eta_h + \alpha_{mh}\sigma_h \cos\frac{2\pi Z_m}{d}\right)\Bigg] P_2(\cos\theta_m) \end{aligned} \tag{1a}$$

$$\begin{aligned} V_S = -\Bigg[&(1 - a)V_{sm}(\eta_m + \alpha_{sm}\sigma_m \cos\frac{2\pi Z_s}{d}\Big) \\ &+ a\,(1 - x)V_{SS}\left(\eta_s + \alpha_{SS}\sigma_S \cos\frac{2\pi Z_s}{d}\right) \\ &+ ax\, V_{sh}\left(\eta_h + \alpha_{sh}\sigma_h \cos\frac{2\pi Z_s}{d}\right)\Bigg] P_2(\cos\theta_s) \end{aligned} \tag{1b}$$

$$\begin{aligned} V_H = -\Bigg[&(1 - a)V_{hm}\left(\eta_m + \alpha_{hm}\sigma_m \cos\frac{2\pi Z_h}{d}\right) \\ &+ a(1 - x)V_{hs}\left(\eta_s + \alpha_{hs}\sigma_s \cos\frac{2\pi Z_n}{d}\right) \\ &+ axV_{hh}\left(\eta_h + \alpha_{hh}\sigma_h \cos\frac{2\pi Z_h}{d}\right)\Bigg] P_2(\cos\theta_h) \end{aligned} \tag{1c}$$

In the above equations suffixes M and m refer to the monomers, S and s refer to SS dimers, H and h are for the HH type of dimers. V_{mm}, V_{ms} etc. are the coupling constants; where the first suffix indicates the mean field experiencing component and the latter index refers to the mean field producing agent. α_{mm}, α_{ms} etc. are the McMillan parameters with the suffixes used in the sense just stated. The other notations are as in references 1 and 2.

In this case, if we assume that the volume of the two types of dimers is the same and is twice that of monomers, the number of molecules of respective components, in terms of the total number N of monomer units present, are

$$N_m = N(1 - a);\ N_s = 0.5\,Na(1 - x) \text{ and } N_h = 0.5\,Nax$$

The free energy of the system is

$$F = 0.5\,N(1 - a)\langle V_M\rangle + 0.25\,Na(1 - x)\langle V_S\rangle + 0.25\,Nax\langle V_H\rangle$$
$$- \ln[Z_m^{N(1-a)} Z_s^{Na(1-x)/2} Z_h^{Nax/2} / \{N(1 - a)!0.5\,Na(1 - x)!0.5Nax!\}]$$

where Z's are the partition functions. F above is in units of KT and V_I's V_{ij}'s here and henceforth are also in units of KT.

As in Reference 2, we write these partition functions as product of translational (Z_t), vibrational (Z_v) and orientational cum layering (Z_o) partition functions.

$$Z_m = Z_{mo}Z_{mt},\quad Z_s = Z_{so}Z_{st}Z_{sv},\quad Z_h = Z_{ho}Z_{ht}Z_{hv}$$

The self consistent equations for the order parameters are,

$$\eta_j = \int P_2(\cos\theta_j)\exp(V_J)\,d(\cos\theta_j)/Z_{jo} \tag{3a}$$

$$\sigma_j = \iint \cos\frac{2\pi Z_j}{d} P_2(\cos\theta_j)\exp(V_J)\,d(\cos\theta_j)\,d(2\pi Z_j/d)/Z_{jo} \tag{3b}$$

With $j = m, s, h$ and correspondingly $J = M, S, H$.

Next we write the free energy of the system explicitly in terms of Z's, x, a etc. (please see Appendix I). Equating to zero the derivative of free energy with respect to "a" we get the following self consistent equations for the equilibrium volume fraction (detail of the calculation given in Appendix I)

$$\begin{aligned} a/(1 - a)^2 = {} & [2.0/\{x^x(1 - x)^{(1-x)}\}](NZ_{st}/Z_{mt}^2)(Z_{ht}/Z_{st}).^x \\ & \{Z_{ho}^x Z_{so}^{(1-x)}/Z_{mo}^2\}Z_{sv}^{(1-x)}Z_{hv}^x \exp\{(1 - x)\,X + xY\} \end{aligned} \tag{4}$$

where

$$X = V_{ms}(\eta_m\eta_s + \alpha_{ms}\sigma_m\sigma_s) - 0.5\,V_{sm}(\eta_s\eta_m + \alpha_{sm}\sigma_s\sigma_m)$$

$$Y = V_{mh}(\eta_m\eta_h + \alpha_{mh}\sigma_m\sigma_h) - 0.5\,V_{hm}(\eta_h\eta_m + \alpha_{hm}\sigma_h\sigma_m)$$

Further reduction can be made by the following simplifying assumptions. We assume that the translational partition function of the two types of dimers are the same. This eliminates the $(Z_{ht}/Z_{st})^x$ term. For the vibrational partition function we assume that the dimers are in the ground state of vibrational motion and the ground state energies of the two types are same. As discussed in Reference 2, it is not possible to write Z_{st} and Z_{mt} explicitly. However, assuming their temperature dependence as that of a perfect gas and lumping the rest of the partition functions in "WI" we define

$$NZ_{st}/Z_{mt}^2 = (NZ_s^e/Z_m^{e2})T^{-3/2} = WIT^{-3/2}$$

where Z_s^e and Z_m^e are the translational partition functions without the temperature factor. Equation (4) now becomes

$$\begin{aligned} a/(1-a)^2 = {} & [2.0/\{x^x(1-x)^{(1-x)}\}]WIT^{-3/2} \\ & \{Z_{ho}^x Z_{so}^{(1-x)}/Z_{mo}^2\}\exp(\epsilon_s/kT)\exp\{(1-x)X + xY\} \end{aligned} \tag{5}$$

Some of the α_{ij}'s can be related in the following way.

Equating the potential energy of dimers in the field of monomers with the potential energy of monomers in the field of dimers we get

$$\begin{aligned} & 0.5\,N(1-a)\{a(1-x)V_{ms}(\eta_m\eta_s + \alpha_{ms}\sigma_m\sigma_s) + axV_{mh}(\eta_m\eta_h + \alpha_{mh}\sigma_m\sigma_h) \\ & = 0.25\,Na(1-x)(1-a)V_{sm}(\eta_s\eta_m + \alpha_{sm}\sigma_s\sigma_m) \\ & \quad + 0.25\,Nax(1-a)\,V_{hm}\,(\eta_h\eta_m + \alpha_{hm}\sigma_h\sigma_m) \end{aligned}$$

In absence of HH dimers (for $a \leq 1 - \mathrm{Cm}$) and for the system in nematic phase,

$$0.5\,N(1-a)a\,V_{ms}\eta_m\eta_s = 0.25\,Na(1-a)V_{sm}\eta_s\eta_m$$

$$\therefore V_{ms} = 0.5\,V_{sm} \tag{6a}$$

With this in the smectic phase (with $x = o$) we have

$$\alpha_{sm} = \alpha_{ms} \tag{6b}$$

When we consider $x \neq o$ in the nematic phase and use relation (6a) and (6b) we get

$$V_{mh} = 0.5\,V_{hm} \tag{6c}$$

Further considering the smectic phase we get

$$\alpha_{hm} = \alpha_{mh} \tag{6d}$$

Out of the 9 α_{ij}'s there are six dependent ones. We further use

$$\alpha_{ms} = \alpha_{sm} = \alpha_{hs} = \alpha_{ss} \tag{7a}$$

and

$$\alpha_{mh} = \alpha_{sh} = \alpha_{hm} = \alpha_{hh} \tag{7b}$$

Therefore only three independent "α" parameters remain in our model. Out of these three, α_{mm} is assumed to retain its value throughout the temperature range of interest. In our calculation we put a small input value for α_{mm} as it is assumed that the layering interaction of monomers is quite weak. The other α's change due to change in the layer thickness. The values of these parameters are obtained, at any temperature, from some self consistent equations to be established next.

At N–I transition temperature T_{N-I} we assume an input value "α_{in}" for α_{ss}. In the application of McMillan's model of ordinary smectics it is assumed that "α" calculated from T_{S-N} corresponds to core length usually smaller than the geometrical size of the core i.e., the core length relevant to α is a fraction K_c of r_c, which is the geometrical length. With this possibility α_{in} can be written as

$$\alpha_{in} = 2 \exp\left[-\pi^2 Kc^2 r_c^2/(2lm - r_c)^2\right]$$

where $(2l_m - r_c)$ is the length of a SS dimer and also the smectic layer thickness. As the temperature is lowered and when there is "x" fraction of HH dimers, the layer thickness "l" becomes

$$l = (1 - x)(2l_m - r_c) + x\, 2l_m = (2l_m - r_c) + xr_c \tag{8}$$

and then

$$\alpha_{ss} = 2 \exp\left[-\pi^2 K_c^2 r_c^2/l^2\right]$$

This can be written in terms of "α_{in}" as

$$\alpha_{ss} = 2 \exp\left[ln(\alpha_{in}/2).\ (2l_m - r_c)^2/(2l_m - r_c + xr_c)^2\right] \tag{9}$$

Now $S = (2l_m - r_c)/l_m = 2 - r_c/l_m$.

Then equation (9) becomes

$$\alpha_{ss} = 2 \exp[ln(\alpha_{in}/2).\ s^2/\{s + x(2 - s)\}^2] \tag{10a}$$

Similarly for the HH dimers, the core being 2 r_c,

$$\alpha_{hh} = 2 \exp[ln(\alpha_{in}/2).4s^2/\{s + x(2 - s)\}^2] \tag{10b}$$

The volume fraction "x" of the HH dimer can be related to association parameter in the following manner. The void space corresponding to $(1 - C_m)$ fraction of SS dimer is C_m which is to be filled by monomers.

For $a > 1 - C_m$ there are not enough monomers. The fraction x of the dimers is converted to HH type to fill up this void space. There will still be a $(1 - x)$ fraction of SS dimers with associated void space to be filled in by monomers.

Therefore, $1 - a = [C_m/(1 - C_m)]a(1 - x)$ which gives

$$x = 1 - (1 - a)(1 - C_m)/(aC_m) \text{ for } a > 1 - C_m \tag{11}$$

The equations (1a) to (1c), (3a), (3b), (5), (8), (10a), (10b) and (11), the set of self consistent equations, are to be solved and the stable solution is to be picked up by looking at the minimum of the free energy (please see appendix I).

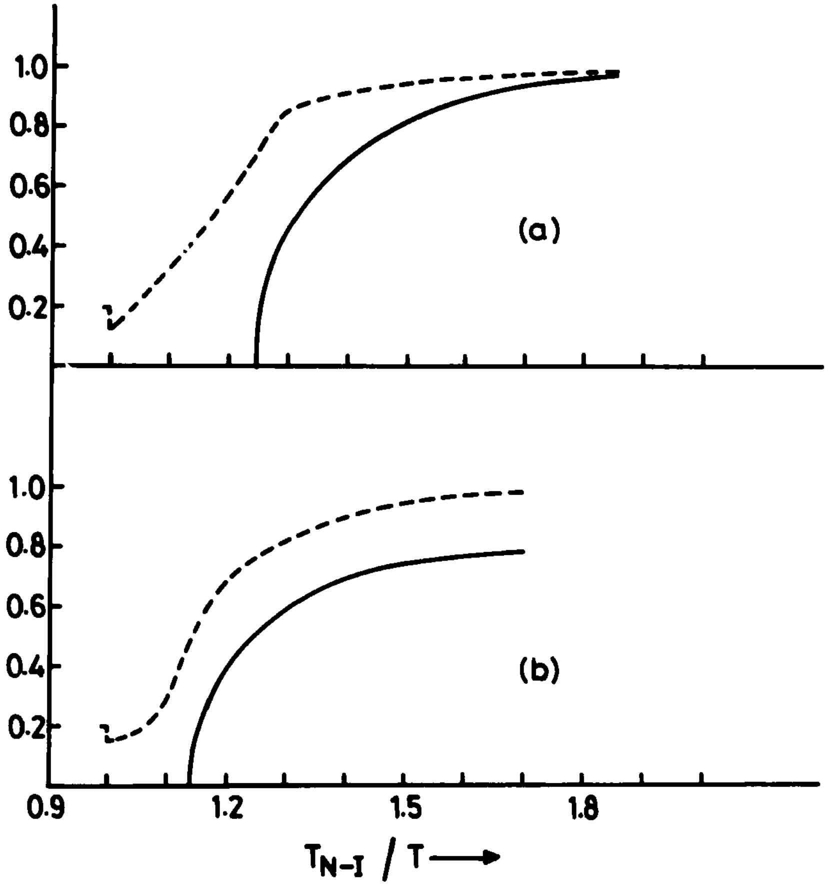

FIGURE 3 Fraction of dimers in HH configuration "x" vs. T_{N-I}/T shown by continuous line; the dotted lines show corresponding variation of "a". (a) Layer thickness variable, S = 1.3; (b) Layer thickness constant, S = 1.8.

RESULTS

For numerical evaluation we have taken (as in Reference 1) $V_{mm} = V_{dd} = 2\ v_{md} = V_{dm} = 4.54\ kT_{N-I}$ and $\epsilon_s/kT = 10.0$ (It has already been stated that for the sake of simplicity we have assumed the same value of ϵ_s/kT for both the SS and HH dimers). Taking the value of WI to be such that "a" at T_{N-I} is 0.2 we have solved the self consistent equations for $S = 1.3$ and over a range of reduced temperature from 1 to 1.9 and for different values of α_{in}.

Variation of x, fraction of dimers in HH configuration and of association "a" with reduced temperature is shown in Figure 3a. Typical variations of layer thickness and order parameters with reduced temperature are shown in Figures 4a, 4b and 4c. It is observed that the phase sequence I-N-S_{Ad}-N_{re}-S_{A2} is observed for the range $0.615 \leq \alpha_{in} < 0.685$.

CONSTANT LAYER THICKNESS FORMULATION

The filling up of void space by conversion of SS dimers to HH dimers entails an increase in the layer thickness whereas the intercalation of neighboring layers fill up void space and causes a decrease in layer thickness. If we assume that both these mechanisms of packing are operative in a sample, we can make an appropriate combination such that the layer thickness remains constant. It has been made amply clear that both the methods of space filling give rise to a fall in value of α parameter in the S_{Ad} phase. Therefore even if the layer thickness be kept constant by invoking appropriate amount of intercalation and conversion of SS to HH dimers, the S_{Ad} phase can give way to a N_{re} phase.

For $a \geq 1 - C_m$, if x fraction of dimers are converted to HH dimers and if the SS dimers intercalate to a length l, then the constancy of layer thickness requires

$$2l_m - r_c = (1 - x)l + x\,2l_m \tag{12}$$

with core length

$$\begin{aligned} r_e' &= (1 - x)r_c + x\,2r_c \\ &= (1 + x)r_c \end{aligned} \tag{13}$$

Therefore,

$$\begin{aligned} \alpha_{ss} &= 2\exp[-\pi^2(1 + x)^2 r_c^2 Kc^2/(2l_m - r_c)^2] \\ &= 2\exp[(1 + x)^2 ln(\alpha_{in}/2)] \end{aligned} \tag{14a}$$

$$\alpha_{hh} = 2\exp[4(1 + x)^2 ln(\alpha_{in}/2)] \tag{14b}$$

The volume fraction remaining to be filled up by the monomers is given below which provides us with the relation connecting "x" and "a"

$$1 - a = (1 - ax)(1 - l_m/l) \tag{15}$$

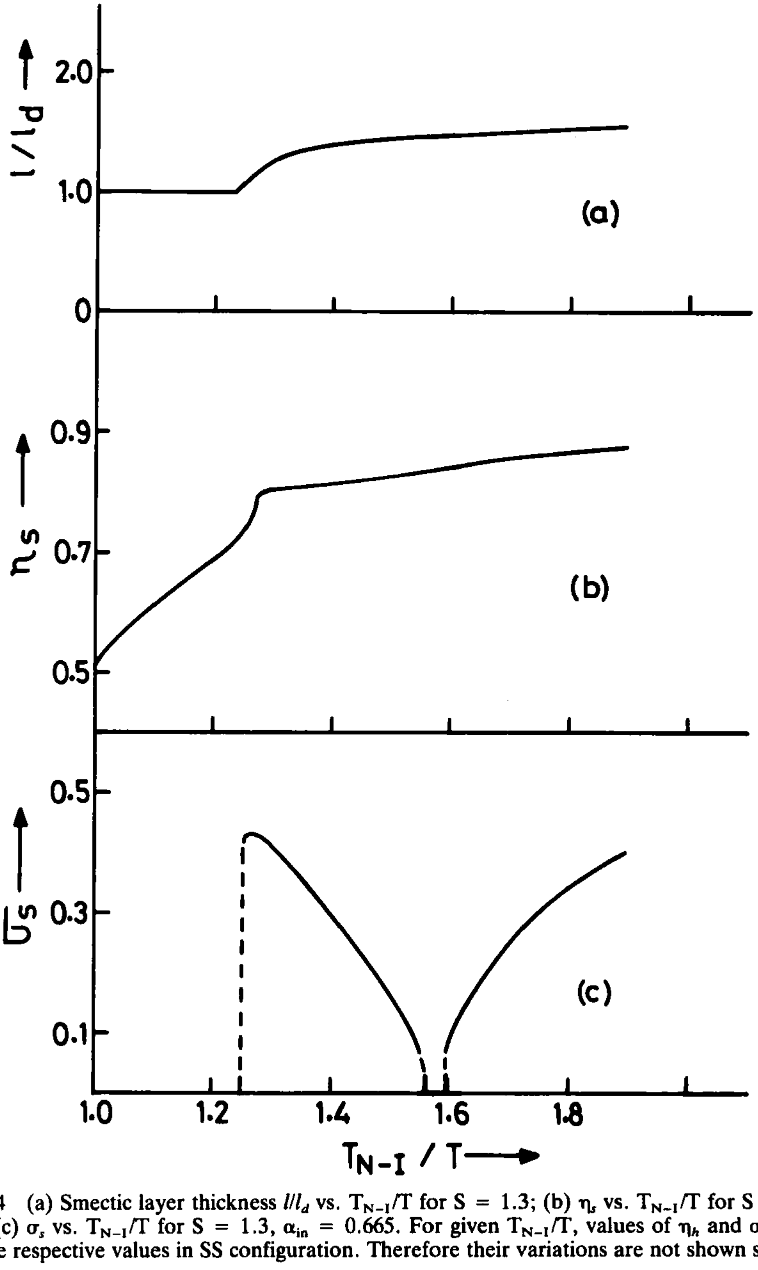

FIGURE 4 (a) Smectic layer thickness l/l_d vs. T_{N-I}/T for S = 1.3; (b) η_s vs. T_{N-I}/T for S = 1.3, α_{in} = 0.665; (c) σ_s vs. T_{N-I}/T for S = 1.3, α_{in} = 0.665. For given T_{N-I}/T, values of η_h and σ_h are very close to the respective values in SS configuration. Therefore their variations are not shown separately.

For the mean field and the self consistent equation of the association parameter, we can still use the equations (1a) to (1c), (3a), (3b) and (5) respectively. We thus have the new set of self consistent equations (1a) to (1c), (3a), (3b), (5) and (12) to (15). Figures 3b, 5a, 5b, 5c show the results of the numerical calculation. It depicts the usual phase sequence I-N-S_{Ad}-N_{re}-S_{re}.

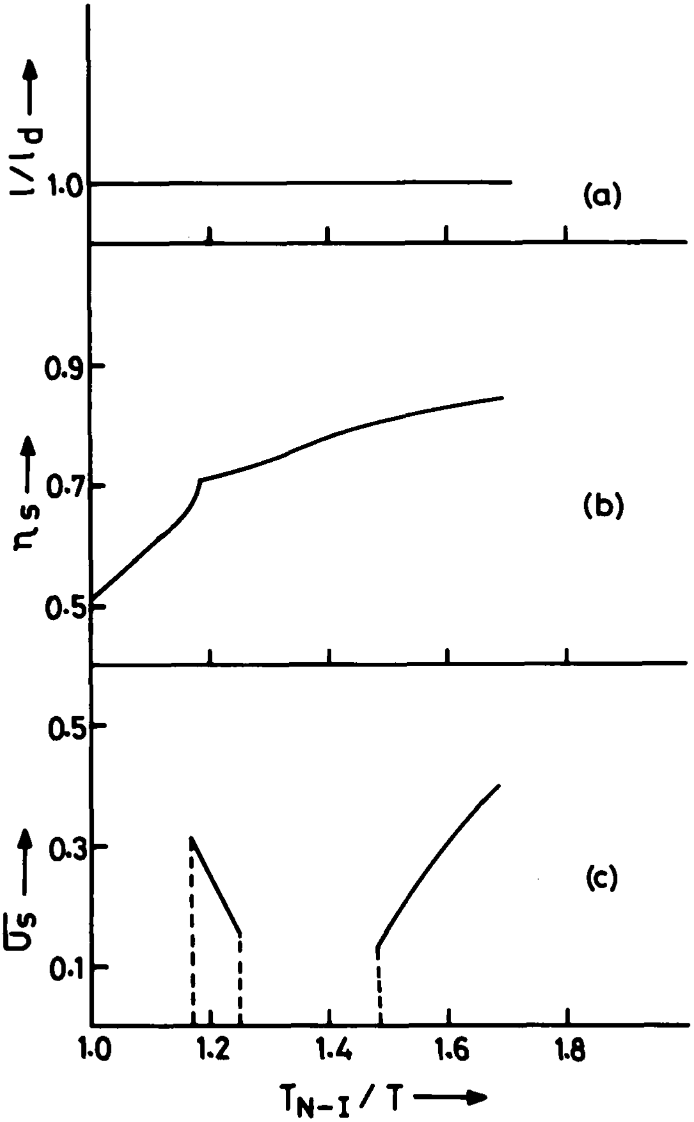

FIGURE 5 Smectic layer thickness l/l_d vs. T_{N-I}/T for $S = 1.8$ (layer thickness remains constant); (b) η_s vs. T_{N-I}/T for $S = 1.8$, $\alpha_{in} = 1.085$; (c) σ_s vs. T_{N-I}/T for $S = 1.8$, $\alpha_{in} = 1.085$. For given T_{N-I}/T, values of η_h and σ_h are very close to the respective values in SS configuration. Therefore their variations are not shown separately.

CONCLUSION

The earlier and the present work, though based on different modes of space filling rest on the common single basic idea that the reentrant phase sequence is due to the inability of dimers (SS type) to fill up space. This filling up of space may proceed in either way—intercalation or conversion to HH type of dimers. It is difficult to ascertain, a priori, for a particular sample which mode of space filling will be operative. However, we think that if the dipole–dipole interaction in forming a SS type dimer is very strong a large scale conversion to HH type will be prohibited and intercalation will be the primary mode of space filling. In the other case where the binding of the SS type dimer is weak a copious conversion to HH type is likely. It is also clear from our calculation for the constant layer thickness that a combination of the two modes can also give rise to a reentrant polymorphism. The two modes so to say are complementary to each other and together can reproduce the different types of layer thickness variation with temperature observed experimentally.[3–8] It is worth noting that this work and the work in Reference 1 are based on the basic framework of McMillan's model[9] and the numerical calculation, particularly of association parameter are done in a thoroughly self consistent manner.

Acknowledgement

The use of IRIS 80 computer at VEC site in Calcutta is thankfully acknowledged.

APPENDIX I

The free energy F can be written as a sum of two terms,

$$F = A + B$$

where

$$\begin{aligned}
A &= -0.5N(1-a)\langle V_M\rangle - 0.25Na(1-x)\langle V_S\rangle - 0.25Nax\langle V_H\rangle \\
&= 0.5N(1-a)[(1-a)V_{mm}(\eta_m^2 + \alpha_{mm}\sigma_m^2) \\
&\quad + a(1-x)V_{ms}(\eta_m\eta_s + \alpha_{ms}\sigma_m\sigma_s) + axV_{mh}(\eta_m\eta_h + \alpha_{mh}\sigma_m\sigma_h)] \\
&\quad + 0.25\,Na(1-x)[(1-a)V_{sm}(\eta_s\eta_m + \alpha_{sm}\sigma_s\sigma_m) \qquad \text{(A-1)} \\
&\quad + a(1-x)V_{ss}(\eta_s^2 + \alpha_{ss}\sigma_s^2) + axV_{sh}(\eta_s\eta_h + \alpha_{sh}\sigma_s\sigma_h)] \\
&\quad + 0.25\,Nax[(1-a)V_{hm}(\eta_h\eta_m + \alpha_{hm}\sigma_h\sigma_m) \\
&\quad + a(1-x)V_{hs}(\eta_h\eta_s + \alpha_{hs}\sigma_h\sigma_s) + axV_{hh}(\eta_h^2 + \alpha_{hh}\sigma_h^2)
\end{aligned}$$

(use has been made of equations 1(a), 1(b) and 1(c)), and

$$
\begin{aligned}
B = & -\ln \left[Z_m^{N(1-a)} Z_s^{Na(1-x)/2} Z_h^{Nax/2} / \{N(1-a)!0.5Na(1-x)!0 \cdot 5\, Nax!\}\right] \\
= & -N(1-a)\ln Z_m - 0.5\, Na(1-x)\ln Z_s - 0.5\, Nax \ln Z_h \\
& + N(1-a)\ln\{N(1-a)\} - N(1-a) + 0.5Na(1-x)\ln\{0.5Na(1-x)\} \\
& - 0.5Na(1-x) + 0.5\, Nax\ln(Nax/2) - 0.5\, Nax \\
= & -N(1-a)\ln Z_{mt} - N(1-a)\ln Z_{mo} - 0.5\, Na(1-x)\ln Z_{st} \\
& -0.5Na(1-x)\ln Z_{so} - 0.5\, Na(1 \quad x)\ln Z_{sv} - 0.5Nax\ln Z_{ht} \\
& -0.5\, Nax\ln Z_{ho} - 0.5\, Nax\ln Z_{hv} + N(1-a)\ln N \\
& + N(1-a)\ln(1-a) - N(1-0.5a) + 0.5Na(1-x)\ln\{Na(1-x)/2\} \\
& + 0.5\, Nax \ln (Nax/2) \\
= & -N\ln Z_{mt} - 0.5\, Na \ln (Z_{st}/Z_{mt}^2) - N(1-a)\ln Z_{mo} \\
& + 0.5\, Nax \ln (Z_{st}/Z_{ht}) - 0.5\, Na(1-x)\ln Z_{so} - 0.5\, Na(1-x)\ln Z_s \\
& - 0.5\, Nax \ln Z_{ho} - 0.5\, Nax\ln Z_h + N\ln N - Na\ln N \\
& + N\ln(1-a) - Na\ln(1-a) - N(1-0.5a) + 0.5\, Na\ln N \\
& + 0.5\, Na\ln(a/2) + 0.5\, Na\ln(1-x) - 0.5\, Nax\ln\{Na(1-x)/2\} \\
& + 0.5\, Nax\ln(Nax/2) \\
= & -N\ln Z_{mt} - 0.5\, Na\ln(NZ_{st}/Z_{mt}^2) - N(1-a)\ln Z_{mo} \\
& + 0.5\, Nax\ln(Z_{st}/Z_{ht}) - 0.5\, Na(1-x)\ln Z_{so} \\
& - 0.5\, Na(1-x)\ln Z_{sv} - 0.5\, Nax\ln Z_{ho} \\
& - 0.5\, Nax\ln Z_{hv} + N\ln N + N\ln(1-a) - Na\ln(1-a) \\
& - N(1-0.5a) + 0.5\, Na\ln(a/2) + 0.5\, Na\ln(1-x) \\
& - 0.5\, Nax\ln\{Na(1-x)/2\} \\
& + 0.5\, Nax\ln(Nax/2) \qquad \text{(A-2)}
\end{aligned}
$$

Using (A-1) and (A-2), the equation $\partial F/\partial a = 0$ can be written explicitly as

$$\begin{aligned}
&-0.5\,N\,2(1-a)\,V_{mm}(\eta_m^2+\alpha_{mm}\sigma_m^2)\\
&+0.5\,N\,(1-2a)(1-x)V_{ms}(\eta_m\eta_s+\alpha_{ms}\sigma_m\sigma_s)\\
&+0.5\,N\,(1-2a)\,xV_{mh}\,(\eta_m\eta_h+\alpha_{mh}\sigma_m\sigma_h)\\
&+0.25\,N\,(1-x)(1-2a)V_{sm}(\eta_s\eta_m+\alpha_{sm}\sigma_s\sigma_m)\\
&+0.25\,N\,(1-x)^2\,2a\,V_{ss}\,(\eta_s^2+\alpha_{ss}\sigma_s^2)\\
&+0.25\,N\,2a(1-x)x\,V_{sh}(\eta_s\eta_h+\alpha_{sh}\sigma_s\sigma_h)\\
&+0.25\,Nx(1-2a)V_{hm}(\eta_h\eta_m+\alpha_{hm}\sigma_h\sigma_m)\\
&+0.25\,N\,2a\,x(1-x)V_{hs}(\eta_h\eta_s+\alpha_{hs}\sigma_h\sigma_s)\\
&+0.25\,N\,2a\,x^2\,V_{hh}(\eta_h^2+\alpha_{hh}\sigma_h^2)-0.5\,N\ln(NZ_{st}/Z_{mt}^2)\\
&+N\ln Z_{mo}-N(1-a)[-V_{mm}(\eta_m^2+\alpha_{mm}\sigma_m^2)\\
&+(1-x)V_{ms}(\eta_m\eta_s+\alpha_{ms}\sigma_m\sigma_s)+x\,V_{mh}\,(\eta_m\eta_h+\alpha_{mh}\sigma_m\sigma_h)]\\
&+0.5\,Nx\ln(Z_{st}/Z_{ht})-0.5\,N(1-x)\ln Z_{so}\\
&-0.5\,Na(1-x)\,[-V_{sm}(\eta_s\eta_m+\alpha_{sm}\sigma_s\sigma_m)\\
&+(1-x)\,V_{ss}(\eta_s^2+\alpha_{ss}\sigma_s^2)+xV_{sh}(\eta_s\eta_h+\alpha_{sh}\sigma_s\sigma_h)]\\
&-0.5\,N\,(1-x)\ln Z_{sv}-0.5\,N\,x\ln Z_{ho}\\
&-0.5\,Nax\,[-V_{hm}\,(\eta_h\eta_m+\alpha_{hm}\sigma_h\sigma_m)\\
&+(1-x)\,V_{hs}\,(\eta_h\eta_s+\alpha_{hs}\sigma_h\sigma_s)+xV_{hh}(\eta_h^2+\alpha_{hh}\sigma_h^2)]\\
&-0.5\,N\,x\ln Z_{hv}-N/(1-a)-N\ln(1-a)+Na/(1-a)\\
&+0.5\,N+0.5\,N\ln(a/2)+0.5\,N\\
&+0.5\,N\ln(1-x)-0.5\,N\,x\ln\{Na(1-x)/2\}\\
&-xN\,(1-x)/\{2(1-x)\}\\
&+0.5\,N\,x\ln(Nax/2)+0.5\,Nx=0
\end{aligned}$$

Introducing a parameter $W = NZ_{st}/Z_{mt}^2$ and after some straightforward rearrangement and cancellation of terms we get

$$\begin{aligned}
&\ln [(Z_{mo}/W^{1/2})(Z_{st}/Z_{ht})^{x/2}/\{Z_{so}^{(1-x)/2}Z_{s}^{(1-x)/2}Z_{ho}^{x/2}Z_{hv}^{x/2}\}] \\
&+ \ln [(0.5a)^{1/2}(1-x)^{1/2}(0.5\,Na)^{x/2}(x)^{x/2}/\{(1-a)(0.5\,Na)^{x/2}(1-x)^{x/2}\}] \\
&+ V_{ms}(\eta_m\eta_s + \alpha_{ms}\sigma_m\sigma_s)(-1/2)(1-x) \\
&+ V_{mh}(\eta_m\eta_h + \alpha_{mh}\sigma_m\sigma_h)(-1/2)x \\
&+ V_{sm}\,(\eta_s\eta_m + \alpha_{sm}\sigma_s\sigma_m)(1/4)(1-x) \\
&+ V_{hm}\,(\eta_h\eta_m + \alpha_{hm}\sigma_h\sigma_m)(1/4)x \\
&= 0
\end{aligned}$$

or

$$\begin{aligned}
&\ln [(1/W^{1/2})(Z_{st}/Z_{ht})^{x/2}Z_{mo}/\{Z_{ho}^{x/2}Z_{so}^{(1-x)/2}Z_{sv}^{(1-x)/2}Z_{hv}^{x/2}\}] \\
&+ \ln [(0.5a)^{1/2}/(1-a)] + \ln [(1-x)^{(1-x)/2}(x)^{x/2}] \\
&= \{(1-x)\,X + xY\}/2
\end{aligned}$$

where

$$X = V_{ms}(\eta_m\eta_s + \alpha_{ms}\sigma_m\sigma_s) - 0.5V_{sm}(\eta_s\eta_m + \alpha_{sm}\sigma_s\sigma_m)$$

and

$$Y = V_{mh}(\eta_m\eta_h + \alpha_{mh}\sigma_m\sigma_h) - 0.5V_{hm}(\eta_h\eta_m + \alpha_{hm}\sigma_h\sigma_m) \qquad \text{(A-3)}$$

From (A-3) we get

$$\begin{aligned}
(0.5a)^{1/2}/(1-a) &= [1/\{(x)^{x/2}(1-x)^{(1-x)/2}](W^{1/2}/Z_{mo})(Z_{ht}/Z_{st})^{x/2} \\
&\quad Z_{ho}^{x/2}Z_{so}^{(1-x)/2}Z_{s}^{(1-x)/2}Z_{hv}^{x/2}\,\exp[\{(1-x)X + xY\}/2]
\end{aligned}$$

or (Putting back the expression for W)

$$\begin{aligned}
a/(1-a)^2 &= [2.0/\{(x)^x(1-x)^{(1-x)}\}](NZ_{st}/Z_{mt}^2)(Z_{ht}/Z_{st})^x \\
&\quad \{Z_{ho}^{x}Z_{so}^{(1-x)}/Z_{mo}^{2}\}\,Z_{s}^{(1-x)}Z_{hv}^{x}\,\exp\{(1-x)X + xY\}
\end{aligned}$$

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