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A Molecular Mean Field Theory of Reentrant Phases

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The observed phase transition sequence $N - S_A - N_{re} - S_{re}$ with a lowering in temperature in pure compounds of molecules with a strongly polar end group is reproduced in a mean field model which is taken as an extension of the McMillan potential. This model shows how the dimers in presence of space filling monomers can account for the high temperature S_A phase. As the temperature is lowered, more and more monomers form dimers leaving empty spaces and this initiates an intercalation of dimers belonging to the neighbouring layers. This intercalation is responsible for the lowering of the strength of layering interaction in a McMillan type potential and thus a reentrant nematic phase occurs. This model for the first time successfully accounts for the thickness of the low temperature smectic phase.

INTRODUCTION

Ever since the first observation of the reentrant phenomenon by P. E. Cladis[1] in a mixture of two paracyano substituted compounds a large number of experimental works[2,3,4] were done to study the liquid crystals consisting of molecules with strongly polar end groups (usually CN or NO_2). The unusual phase sequence $N - S_A - N_{re} - S_{re}$ with a decrease in temperature was then observed in pure compounds under pressure[5,6,7] and later in pure compounds at atmospheric pressure.[8,9] A considerable amount of progress in understanding this phenomenon has been achieved through the works of Cladis,[1]

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Luckhurst and Timimi,[10] Longa and de Jeu,[11] Pershan and Prost[12] and Prost and Barois.[13] The work by Prost and coworkers[12,13,14] based on a phenomenological Landau theory, reproduced the reentrant phase sequence but is lacking in an explanation at the molecular level. In contrast, the other works provide us with a microscopic picture of the phenomenon. Elaborating on a model suggested by Cladis, de Jeu has shown that the high temperature smectic phase is stabilized because of dimers with a stronger layering interaction than that of monomers. With the lowering of temperature more dimers are formed. However, because of the bulky central parts all the dimers can not be accommodated in the central plane of a layer and a reentrant nematic phase occurs. Luckhurst has shown how a proper choice of variation of the McMillan parameter 'α' with temperature can give rise to a reentrant phase. These works, though pioneering, are by no means complete. The main drawback of de Jeu's model is that it can not satisfactorily explain the low temperature smectic phase with a layer thickness equal to that of monomers. It is also unlikely that the repulsion between the bulky central parts is solely responsible for the reappearance of nematic phase. If so, any system of mesogenic molecules with bulky central parts would, at low temperature, have a reentrant phase sequence irrespective of the fact whether these molecules are polar or not. Moreover, the equilibrium concentration of dimers at a given temperature in this model is an input from the permittivity data i.e., this fraction is not brought into the fold of self consistency. Luckhurst's work, on the other hand, is far less detailed and the temperature variation of 'α' is rather ad hoc. He suggested the cause of the variation of 'α' as due to a structural change in dimers, but he did not elaborate on this point.

In the present work we propose a model along with some quantitative results, which furnishes a consistent explanation of the reentrant phenomenon. The essential aspect of this model is that the high temperature smectic phase is an 'induced' smectic phase of a mixture of dimers and monomers in chemical equilibrium. The molecules under consideration have the permanent dipoles at one end. The monomers associate themselves with an antiparallel arrangement. The dimers thus have a bulky central part and two chains attached on either side of it. These dimers can be considered as symmetric molecules with individual chains having half the cross section of the central part (Figure 1a). The dimers when arranged in layers leave out 'void' space (Figure 1b) which is filled up by monomers thus establishing a smectic phase with a layer thickness equal to the length of dimers (Figure 1c). With the lowering of temperature more and

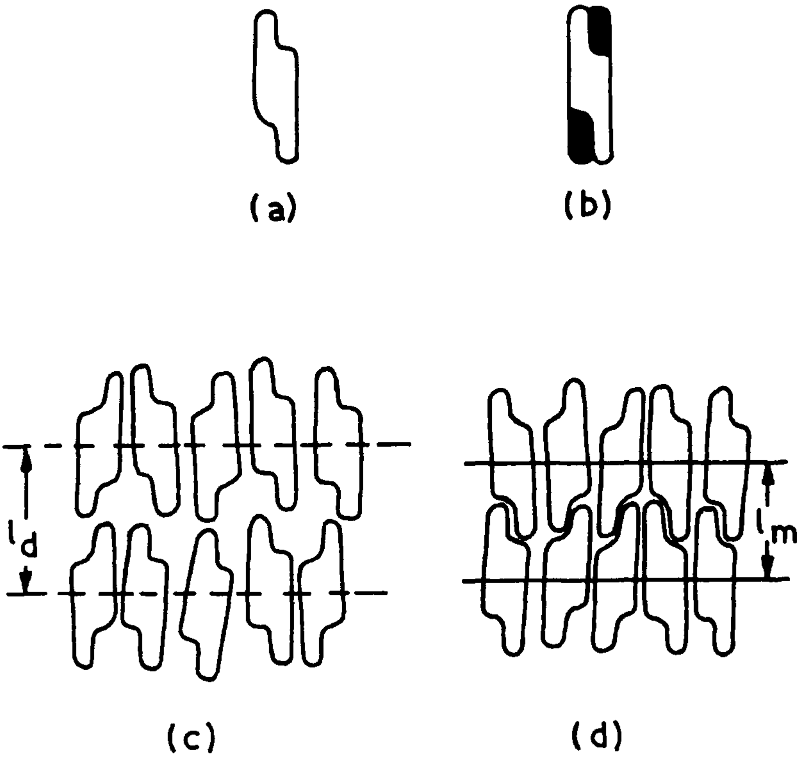

FIGURE 1 (a) A model dimer with individual chains on either side having half the cross section of the central part. (b) Shaded part shows void space per dimer. (c) Dimers forming diffuse bilayer smectic phase with layer thickness ℓ_d, however the spacefilling monomers are not shown. (d) Low temperature, monolayer, smectic phase, with layer thickness ℓ_m, formed by dimers with a complete intercalation. The figures are typical for $\ell_d/\ell_m = 1.3$.

more monomers combine to form dimers. Above a critical concentration of dimers (to be calculated later in this paper) there is not enough monomers to fill the void spaces. Then the neighbouring layers intercalate for better packing and the layer thickness gradually decreases. The core length of the dimers remaining unchanged and the layer thickness diminishing, the McMillan 'α' decreases and reaches a stage where a nematic phase is free-energetically favoured over the smectic phase. As the temperature is lowered further a low temperature smectic, virtually an all dimer phase, occurs with a complete intercalation (Figure 1d) and the layer thickness is the same as the length of the monomers.

MEAN FIELD FORMULATION

In the following calculation we considered the system to be a mixture of monomers and dimers in chemical equilibrium (written symbolically $D \rightleftarrows M + M$), the interaction between them being described by an extension of McMillan type potential. Variation in equilibrium fractions with temperature of these two types of entities are numerically evaluated self consistently from the chemical equilibrium considerations. The void space per dimer is taken to be the difference of the actual dimer volume and the volume of a cylinder with a dimer length and cross section equal to the cross section of the central part of a dimer. It is assumed that so long as the volume fraction of monomers is large enough to fill up this void space the layering interaction (between dimers or between monomers and dimers) is unchanged and described by an input value of α_{in}. As the temperature is lowered, layer thickness decreases for want of the spacefilling monomers and the decrease is only that much which is needed for uniform packing. This decrease causes a decrease in 'α' (corelength remaining the same and the layer thickness decreasing) thus affecting the mean field. The appropriate value of layer thickness or for that matter 'α' is determined by incorporating a self consistent equation for 'α' in the total system of self consistent equations. It is seen that with a proper choice of parameters the reentrant phase sequence is reproduced. The scheme of intercalation ensures the thickness of the low temperature smectic phase to be of monomer length. The variation of dimer fraction with temperature is seen to be consistent with the permittivity data.

With the above preliminary remarks let us proceed to write down the self consistent equations.

The mean field experienced by a monomer in the field of other monomers and dimers can be written as

$$V_M = -[(1 - a)V_{mm}\eta_m + aV_{md}(\eta_d + \alpha_d\sigma_d \cos(2\pi z/d))]P_2(\cos\theta) \qquad (1a)$$

The corresponding expression for a dimer is

$$V_D = -[aV_{dd}(\eta_d + \alpha_d\sigma_d \cos(2\pi z/d)) + (1 - a)V_{dm}(\eta_m + \alpha_m\sigma_m \cos(2\pi z/d))]P_2(\cos\theta) \qquad (1b)$$

In the above expressions η_m and η_d are the orientation order parameters of the monomers and dimers respectively. σ_m, σ_d are the corresponding 'mixed' order parameters. α_m and α_d are the respective McMillan length parameters of monomers and dimers. V_{mm}, V_{dd}, V_{dm} and V_{md} are the coupling constants of the interaction mean fields. In each case the first suffix indicates whether a monomer (m) or a dimer (d) is experiencing the mean field and the latter suffix refers to the mean field producing units. We have ignored the smectic interaction in the monomer–monomer interaction as it is believed to be small for assymmetric molecules. The fraction of the total volume of the system occupied by the dimers is denoted by 'a', henceforth to be referred as the association parameter. With a simple assumption that the volume of a dimer is twice that of a monomer (ϑ) we get

$$1 - a = N_m\vartheta/(N_m + 2N_a\vartheta) = N_m/(N_m + 2N_d) = N_m/N \quad (2)$$

where N_m and N_d are the number of monomers and dimers respectively. N stands for the total number of monomer units (in monomer and dimer form) in the system. The association parameter which depends both on the mean field and the temperature is to be determined from the criteria of chemical equilibrium. With the above mean field the free energy per unit volume (in units of monomer volume)

$$F/N = [(1 - a)^2V_{mm}\eta_m^2 + (1 - a)aV_{md}(\eta_m\eta_d + \alpha_d\sigma_m\sigma_d)]/2$$
$$+ [a^2V_{dd}(\eta_d^2 + \alpha_d\sigma_d^2) + (1 - a)aV_{dm}(\eta_m\eta_d + \alpha_m\sigma_m\sigma_d)]/4 + A \quad (3)$$

where,

$$A/KT = (1 - a)\ln(N_m/Z_m) + [a\ln(N_d/Z_d) + a]/2 - 1 \quad (4)$$

In the above expression Z_m and Z_d are the partition functions of monomers and dimers respectively. As we are considering dissociation of dimers, Z_m and Z_d contain contributions other than the orientation cum layering partition functions. Assuming the translational, the vibrational and the orientation cum layering parts to be independent of one another[15] we get

$$Z_m = Z_{mo}\,Z_{mt} \qquad \text{and} \qquad Z_d = Z_{do}\,Z_{dt}\,Z_{dv}$$

where subscripts 'o', 't' and 'v' refer to the orientation-layering, translation and vibration respectively. Z_{dv} is taken as $\exp(\epsilon_s/KT)$ where $-\epsilon_s$ is the vibrational ground state energy. Excitation of vibrational levels is ignored for the sake of simplicity.

The part A of the free energy expression can now be written as

$$A/KT = (1 - a)[\ln(1 - a) - 1 - \ln Z_{mo} + (\ln W)/2] + a[\ln(a/2) - 1 - \ln Z_{do} - \epsilon_s/KT]/2 - (\ln Z_{dt})/2 + (\ln N)/2 \tag{5}$$

where $W = N Z_{dt}/Z^2_{mt}$. The last two terms are independent of phase (I, N or S) and can be ignored. Minimizing the free energy expression the following self consistent equations are obtained.

$$\eta_m = \iint P_2(\cos\theta)\exp(-V_M/KT)d(\cos\theta)d(2\pi z/d)/Z_{mo} \tag{6a}$$

$$\eta_d = \iint P_2(\cos\theta)\exp(-V_D/KT)d(\cos\theta)d(2\pi z/d)/Z_{do} \tag{6b}$$

$$\sigma_m = \iint \cos(2\pi z/d)P_2(\cos\theta)\exp(-V_M/KT)d(\cos\theta)d(2\pi z/d)/Z_{mo} \tag{6c}$$

$$\sigma_d = \iint \cos(2\pi z/d)P_2(\cos\theta)\exp(-V_D/KT)d(\cos\theta)d(2\pi z/d)/Z_{do} \tag{6d}$$

and,

$$a/(1 - a)^2 = 2W(Z_{do}/Z^2_{mo})\exp(\epsilon_s/KT)\exp[V_{dm}(\eta_m\eta_d + \alpha_m\sigma_m\sigma_d)/2 - V_{md}(\eta_m\eta_d + \alpha_d\sigma_m\sigma_d)] \tag{7}$$

In our calculation we assumed the volume of a dimer to be twice that of a monomer. Equating the potential energy of dimers in the field of monomers with the potential energy of monomers in the field of dimers we get

$$V_{md}[\eta_m\eta_d + \alpha_d\sigma_m\sigma_d]a(1 - a)/\vartheta = V_{dm}[\eta_m\eta_d + \alpha_m\sigma_m\sigma_d]a(1 - a)/2\vartheta$$

In the nematic phase phase (where $\sigma_m = \sigma_d = 0$) we get $V_{md} = V_{dm}/2$. With this relation valid in the smectic phase we get $\alpha_d = \alpha_m$ from the above relation. The eqn. (7) becomes now

$$a/(1 - a)^2 = 2W(Z_{do}/Z_{mo}^2) \exp(\epsilon_s/KT) \tag{8}$$

The translation part of the partition function is contained in W. It is not possible to write Z_{mt} and Z_{dt} exactly. We assumed for simplicity[15] the temperature dependence of Z_t's to be the same as that of a perfect gas. The eqn. (8) can now be written as

$$a/(1 - a)^2 = W1T^{3/2}(Z_{do}/Z_{mo}^2) \exp(\epsilon_s/KT) \tag{9}$$

The contributions to Z_t from factors other than temperature (e.g., volume) are lumped together in the factor $W1$. As the volume change in the system is neglected we can fix $W1$ by fitting this to the experimental data of dimer volume fraction (obtained from permittivity data) at the $N - I$ transition temperature. Once this is fixed we can evaluate the variation of 'a' with temperature. The self consistent equation 'α' however has to be framed separately. The variation of 'α' with temperature is governed by the association parameter 'a' and can be calculated in a self consistent manner.

Let ℓ_m and ℓ_d be the lengths of a monomer and a dimer respectively. The minimum volume fraction C_m required to fill in the gaps in a dimer layer is

$$1 - \ell_m/\ell_d = 1 - 1/s$$

where s is the length ratio ℓ_d/ℓ_m. Starting from the $N - I$ transition temperature and going downward in temperature, α_d is taken to be a constant (equal to the input value α_{in}) until the monomer volume fraction reaches C_m. As the monomer fraction drops below this C_m the intercalation starts and the layer thickness decreases. Assuming the variation of 'α' with layer thickness to be of the McMillan form

$$\alpha = 2 \exp(-\pi^2 r_c^2/\ell^2) \tag{10}$$

where r_c is the core length and ℓ is the layer thickness. We have thus

$$\alpha_{in} = 2 \exp(-\pi^2 r_c^2/s^2 \ell_m^2) \tag{11}$$

The layer thickness ℓ corresponding to the association parameter 'a' is given by $\ell_m/\ell = a$ for $a \geqslant 1 - C_m$. Therefore the length parameter α is

$$\alpha = 2\exp(-\pi^2 r_c^2/\ell^2) = 2\exp(-\pi^2 r_c^2 a^2/\ell_m^2) \tag{12}$$

Using eqns. (11) and (12) we get the self consistent eqn. for α as

$$\alpha = 2\exp[a^2 s^2 \ln(\alpha_{in}/2)] \qquad \text{for } a \geqslant 1 - C_m \tag{13a}$$

$$\alpha = \alpha_{in} \qquad \text{for } a < 1 - C_m \tag{13b}$$

The set of self consistent eqns. (6a) to (6d) and (13) can be solved at different reduced temperatures and the free energies of nematic solutions are compared with those of the smectic solutions to ascertain the stable phase. For numerical evaluation we have taken V_{mm} =

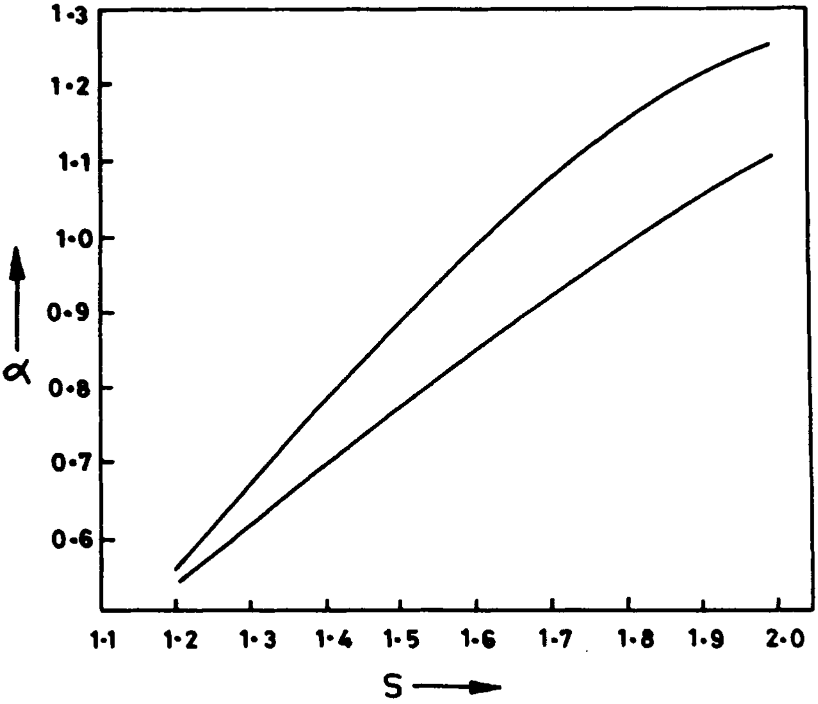

FIGURE 2 Range of α_{in} vs. 's' for reentrant solution with upper bound of 's' ≃ 1.6, above which solution is virtual.

$V_{dd} = V_{md} = V_{dm}/2 = 4.54\ KT_{N-I}$ (Maier-Saupe value) and

$$\epsilon_s/KT = 10.0$$

RESULTS

Calculations were done for several values of 's'. For each value of s we took a series of values of α_{in}. For all the cases we assumed $W1$ to be such that 'a' at T_{N-I} is $= 0.2$. For specific values of α_{in} and 's' we obtained reentrant phase sequence. The Figure 2 shows the regions of α_{in} and 's' for which a reentrant solution was obtained. Figure 3 and Figure 4 respectively show typical variation of σ_d and 'a'. The results clearly show that for low length ratio, there cannot be any reentrant phase sequence. This is corroborated by the experimental results that the layer thickness of the high temperature smectic phase is larger than the monomer length. Our results show reentrant behaviour even for large 's', but it is noticed that the required α_{in} values are not commensurate. For 's' values close to 2.0 (the core length

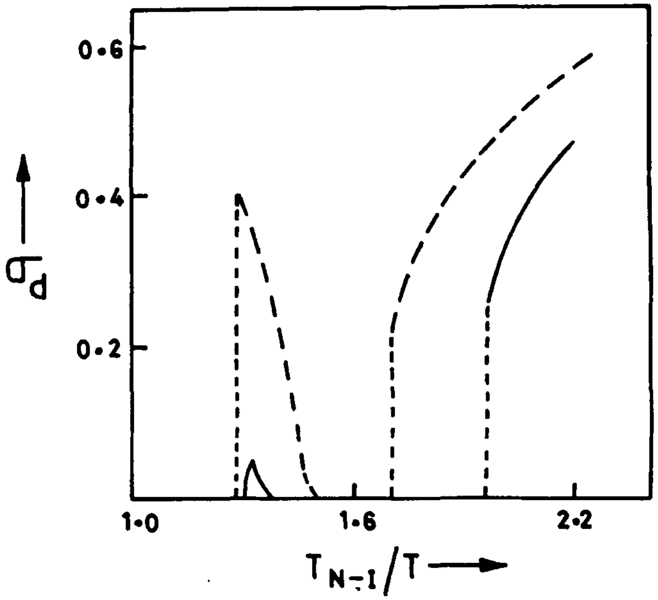

FIGURE 3 σ_d vs. T_{N-I}/T for $s = 1.3$. (i) ——— with $\alpha_{in} = 0.625$, note that the high temperature smectic phase transition is second order. (ii) - - - - with $\alpha_{in} = 0.675$.

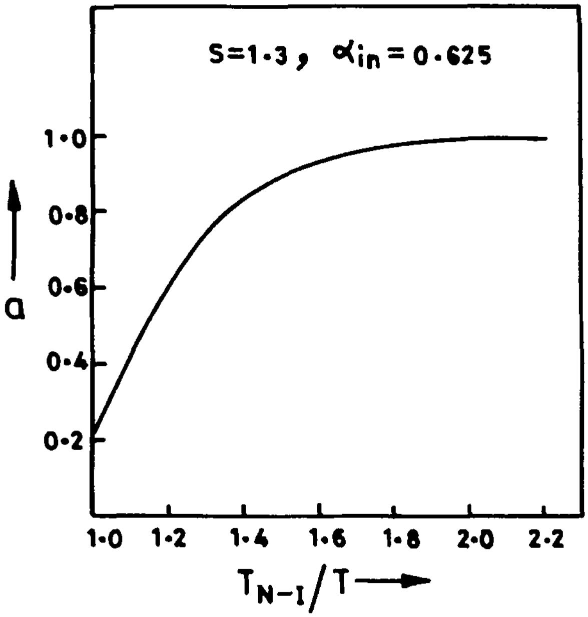

FIGURE 4 Dimer association parameter '*a*' vs. T_{N-I}/T for $s = 1.3$, $\alpha_{in} = 0.625$; for $\alpha_{in} = 0.675$ the curve falls very close to the above and is not shown separately.

negligible compared to layer thickness), α_{in} should be quite large and hence a reentrant phase sequence is not likely to be observed. A simple estimate of an upper limit of '*s*' can be made in the following way. In the applications of McMillan's model to ordinary smectic phases it is observed that 'α' calculated from T_{S-N} corresponds to core length usually smaller than the geometrical size of the core. In our calculation the maximum value of 'α' for a reentrant phase sequence is $\simeq$ 1.25. The core to length ratio for this value of 'α' is 0.218. This may be taken to be the minimum geometrical size of the core and the corresponding '*s*' is $\simeq$ 1.6. Therefore, we see that the present model is consistent with the experimental observation that the '*s*' values are seen to lie between 1.1 and 1.6 for samples showing the reentrant phase sequence.

In our model the lower smectic phase is found to have layer thickness value close to monomer length. This is because this phase stabilizes for '*a*' nearing 1.0 i.e., at complete intercalation.

CONCLUSION

In conclusion we would like to mention that this work shows how an extension of McMillan's model for ordinary smectics coupled with the idea of intercalation can reproduce a doubly reentrant phase sequence.

With the help of a few simplifying assumptions the evaluation of numerical values of the relevent parameters can be done selfconsistently. Because of the simple choice of coupling constants and dissociation energy ϵ_s, the input value of association parameter at T_{N-I}, it is not possible to ascribe the calculated values to a particular sample. However the strength of the model lies in the fact that once the initial values are chosen, the temperature variations are calculated in a thoroughly self consistent manner. The model also points out the fact that the repulsion between the central parts is not absolutely essential for the reentrant phenomenon. In this respect the present work can be considered to be similar in vein to that of Luckhurst. Above all the low temperature smectic phase with monomer thickness follows naturally in this model.

The idea of intercalation of neighbouring layers and the ensuing decrease in layer thickness is however the crucial premise on which the model is based. The decrease in layer thickness with lowering of temperature is supported by experiments, e.g., Hardouin and Levelute[16] and Suresh et al.[17] Depending on the values of α_{in} and 's' we get in our model various amounts of decrease in the layer thickness (typical examples are shown in Figure 5 and Figure 6 for $s = 1.3$).

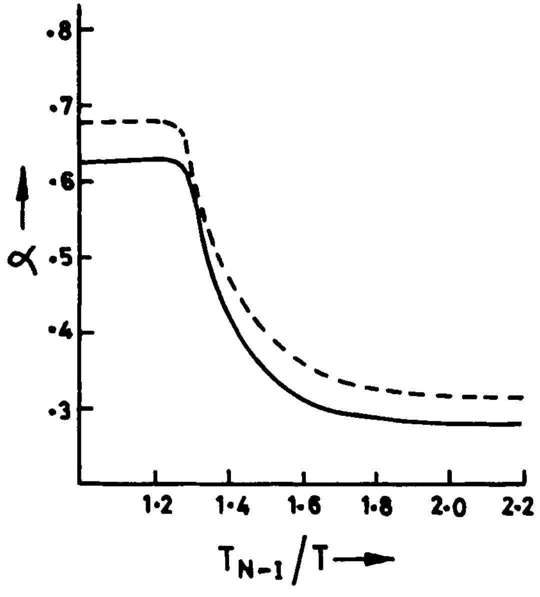

FIGURE 5 Smectic layering interaction parameter α vs. T_{N-I}/T. (i) —— represents $s = 1.3$ $\alpha_{in} = 0.625$. (ii). ---- represents $s = 1.3$ $\alpha_{in} = 0.675$.

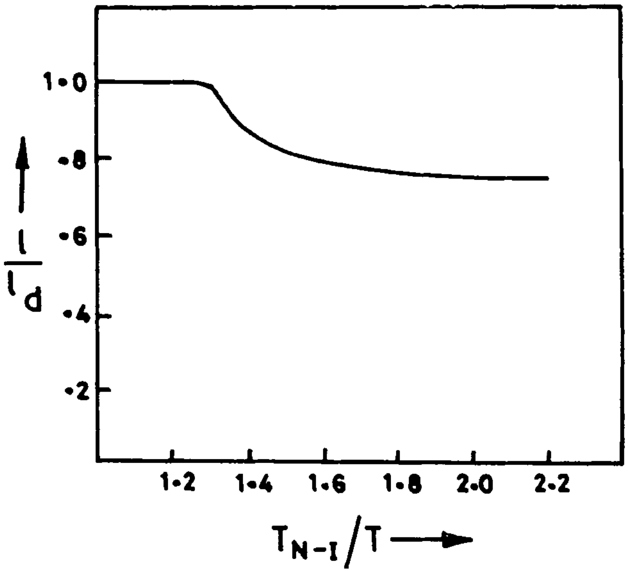

FIGURE 6 Variation of smectic layering thickness with T_{N-I}/T for $s = 1.3$ and $\alpha_{in} = 0.625$. For $\alpha_{in} = 0.675$ the curve falls very close to the above and is not shown separately.

It should be mentioned that there are attempts to explain the decrease in layer thickness as due to an increase of overlap of monomers forming a dimer[18] rather than an intercalation of neighbouring layers. The mathematical formulation of the present model can in principle be applied to this alternative interpretation of the decrease in layer thickness. The only change which has to be made is that a variation of ϵ_s with temperature should be incorporated. This will certainly make the calculations more cumbersome without significantly changing the qualitative aspects of the results.

Lastly, in the present model, the occurrence of two smectic phases in the doubly reentrant phase sequence can be looked at as the manifestation of a natural tendency of the system to stabilize at two differing lengths (layer thickness corresponding to a dimer or a monomer). The intervening nematic phase results, so to say, as a compromise when the layer thickness is not favourable to either of the smectic phases. In this respect, we think that the present approach provides a molecular background for the 'two lengths' theory developed by Prost and coworkers.[12,13,14]

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