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LATTICE THEORY FOR HELIX-COIL INDUCED REENTRANT ISOTROPIC-NEMATIC TRANSITIONS

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A lattice model is proposed to study reentrant isotropic-nematic phase transitions mediated by helix-coil transformations within individual liquid crystal molecules. The system consists of a racemic mixture of molecules in solution with a solvent capable of hydrogen bonding. We first introduce a model to describe helix-coil transformations in the presence of such a solvent. This model displays not only normal helix-coil transformations, but also inverted transformations (i.e. reentrant), as well as reversion to the coiled state at high temperatures. Secondly, we develop a model for the isotropic-nematic phase transition which incorporates intermolecular interactions on the same footing with the intramolecular interactions. Reentrance of the isotropic phase is driven by the inverted helix-coil transformation. Within the nematic phase the effect of induced rigidity is observed. In addition, when solvent-solvent bonding is important in the system, doubly reentrant phase diagrams are predicted. We study our model using renormalization-group and other partial-trace methods.

I. Introduction

Reentrant phase transitions are those in which a given system displays a reversed sequence of phases as a function of some external parameter. Such transitions have been observed in systems as diverse as binary liquid mixtures,[1] adsorbed films,[2] metal hydrides,[3] superconductors,[4] and liquid crystals,[5] to name a few. For example, in liquid crystals we expect that as temperature is lowered the system may undergo a transition from the isotropic to nematic phase, since the nematic is characterized by more order. In contrast, a reentrant system may actually exhibit a transition from the nematic to isotropic phase on cooling; this is counterintuitive, at least on a superficial level, and as such demands a more detailed microscopic understanding. In this paper we study a reentrant isotropic-nematic transition which is driven by the underlying reentrant behavior of helix-coil transformations in the individual molecules. Thus, we first present a model for the inverted, or reentrant, helix-coil transformation, and then apply these results to the liquid crystal system of which they constitute an integral part.[6]

The type of systems we shall focus on here are those involving polypeptide molecules in solution. An example of such a polypeptide is poly-γ-benzyl-L-glutamate (PBLG), which, in suitable solvents such as methyl chloride or chloroform, can form intramolecular hydrogen bonds between amide groups resulting in a rigid spiral structure known as an α-helix.[7] Of crucial importance for the liquid crystal phases to be discussed below is the rigidity of the α-helix, as opposed to the floppy, amorphous form the molecule takes in the coiled state.

The normal helix-coil transformation can readily be understood in terms of arguments involving energy and entropy.[8] Thus, at high temperatures the polypeptide will seek to maximize its entropy, which means it will be in the coiled, or random, state. At low temperatures the system will go into the state of lowest energy. This is accomplished by forming the molecule into the helical structure, which allows for hydrogen bonding between the amide groups. The competition between energy and entropy results in a transformation from the coiled to helical state[9] at a temperature which is set by the strength[10] of the hydrogen bonds.

We now extend the above considerations by including the role of the solvent molecules. Imagine, then, that the solvent can form hydrogen bonds, so that the amide groups on the polypeptide can bond either to one another, or to a solvent molecule. If the solvent-amide bonding is weaker than amide-amide bonding the qualitative argument given above is unaltered. However, when the system is such that solvent-amide bonding is strongest, it is clear that the polypeptide will bond to the solvent at low temperatures, so that energy will be minimized, and unravel the helix in the process. Thus, at high temperature the polypeptide is coiled and unbonded, so as to maximize entropy, while at low temperatures it is again coiled, though now it is bonded to the solvent.

From the above discussion it might seem that the coiled state, which appears at both high and low temperatures, is always present and that helical molecules never occur. However, the argument just given related only to the energetics of the solvent-amide bonding, whereas the entropic considerations are equally important. In

particular, it is clear that the amide groups are constrained to rotate only about the local molecular chain axis, in contrast to the solvents which can rotate freely. As a result, when solvent-amide bonds are formed there is a greater loss of entropy than when amide-amide bonding occurs. Therefore, we see that the solvent-amide bonds, though energetically the most favorable in the system, nonetheless are entropically disfavored and thus become important only at rather low temperatures. For intermediate temperatures the free energy can be lowered by entering the helical state, thereby lowering energy through amide-amide bonding, while at the same time maintaining a large entropy due to the freely rotating, nonbonded solvents. In the next section these qualitative arguments will be verified and made quantitative in terms of our microscopic model.[11]

Finally, when the hydrogen bonding solvents are also able to bond to one another, as well as to the amide groups, doubly reentrant effects can be expected. We shall return to this possibility in Sec. III.

We are now in a position to understand the reentrant isotropic-nematic transition exhibited by polypeptides in solution with the appropriate solvents. We note in passing that an equal mixture of right- and left-handed enantiomers is envisaged; that is, we consider a racemic mixture. Recall, as mentioned above, that molecules in the α-helical states are long, rigid and rod-like - these are the molecules that can participate in liquid crystalline ordering, in contrast to the floppy molecules in the coiled state. At intermediate temperatures we expect the fraction of polypeptides in the helical state to be large, and thus a transition to the nematic, or even smectic, phase is possible. As temperature is lowered, however, the helical

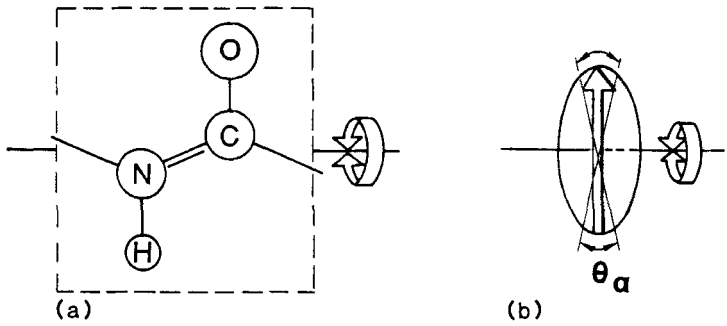

FIGURE 1 (a) Amide group of a polypeptide molecule. The group is free to rotate about the axis shown. (b) Schematic representation of the amide group; arrow "tip" represents the oxygen.

molecules unravel as amide groups bond to the solvent, thus leaving fewer and fewer rod-like molecules to maintain the liquid crystal order. Finally, most molecules will again be in the coiled state, causing the system to revert perforce to an isotropic liquid.

The remainder of this paper is organized as follows: In Sec. II we introduce a microscopic lattice model for the helix-coil transition with strongly-bonding solvents. In Sec. III we combine the intra- and intermolecular interactions in a microscopic model of the reentrant isotropic-nematic liquid crystal.

II. HELIX-COIL TRANSFORMATION

We now turn to constructing a quantitative model of the intramolecular interactions guided by the qualitative ideas discussed in the Introduction. Consider a line of bonding sites representing the amide groups on the polypeptide chains. Since each amide group can rotate in a plane perpendicular to the local chain axis (Fig. 1a), we ascribe an orientational variable α_i to each site i. In the

simplest case, we partition the orientational phase space into q_α segments (we envisage setting $q_\alpha = 2\pi/\theta_\alpha$; where θ_α is the angular width of each segment in the unit circle, Fig. 1b). Hence, α_i labels the orientation of the particular segment in question; $\alpha_i = 1,2,3,\ldots,q_\alpha$. We can think of the amide group as an "arrow" (the "tip" being the oxygen for example) that "points" in one of the q_α segments (see Fig. 1b).

Since the hydrogen bond is highly directional,[7] we model the interaction energy between neighboring sites by $-E_1\delta_{\alpha_i\alpha_{i+1}}$, where δ is the Kronecker delta symbol and $-E_1$ is the attractive ($-E_1<0$) hydrogen bonding energy. Thus, bonding occurs only if neighboring sites are in the same orientational state; the rotational analogue of a square-well potential. Hence the total energy of N bonding sites is given by the Hamiltonian,

$$H_1 = -E_1 \sum_{i=1}^{N-1} \delta_{\alpha_i\alpha_{i+1}} \tag{2.1}$$

In writing this energy we have assumed that the conformational (strain) energy is much weaker than E_1, thus allowing the proper conformations for helical formation and hydrogen bonding to take place.

Strictly speaking, bonding does not occur between neighboring sites but rather between every third site.[7,9] In such a case one should actually consider three separate interpenetrating sublattices, each with a Hamiltonian of the form (2.1), where neighboring pairs i and i+1 would refer to those on the same sublattice. In addition, some form of interaction between the sublattices might be of interest. However, in what follows we shall study a single sublattice only, an approximation we feel certain still

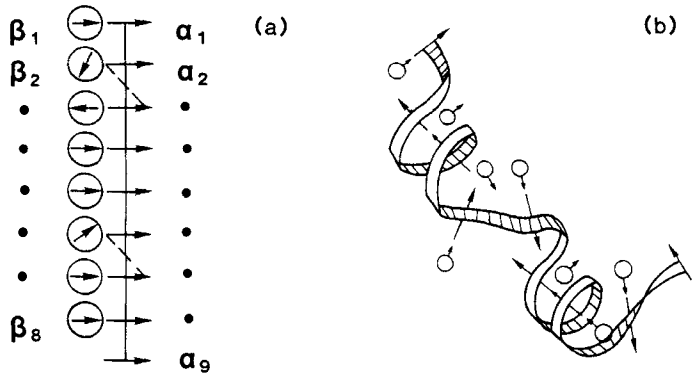

FIGURE 2 (a) Lattice model of polypeptide chain plus bonding solvent. Intrachain hydrogen bonding indicated by dashed lines. (b) Polypeptide solvent conformation shown in (a).

contains the essential physics. The model is illustrated schematically in Fig. 2.

Next, we consider effects associated with the addition of a strongly-bonding solvent. Further, we assume that the solvent interacts strongly with only one member of the amide group, for example the "tail" of the arrow (see Fig.2a). A way to visualize the solvent interaction is to imagine that the solvent gets "in between" two adjacent amide groups (Fig. 2b). If there are N sites, then N-1 solvents will saturate the chain. This is topologically equivalent to allowing the N-1 solvents to act at the first N-1 sites, as illustrated in Fig. 2a.

As with the amides, each solvent's orientation is also specified by a variable, which we will label β_i. However, in contrast to the amides, the solvent can rotate freely over all solid angles. Thus we divide the unit sphere into q_β solid angle segments (where $q_\beta = 4\pi/\Omega_\beta$, with $\Omega_\beta = 2\pi(1-\cos\theta_\beta)$; $2\theta_\beta$ the polar width of the solid angle), with

$\beta_i = 1,2,3,\ldots,q_\beta$. We note that the solvent can bond to an amide group only if the amide is not bonded with its neighbor (to the "right"). Hence, the interaction energy can be written as,

$$H_2 = -E_2 \sum_{i=1}^{N-1} \delta_{\alpha_i \beta_i} (1 - \delta_{\alpha_i \alpha_{i+1}}) . \tag{2.2}$$

The solvent-amide attractive interaction energy is $-E_2$ ($-E_2 < 0$) and we expect the ratio $R = E_2/E_1$ must be greater than unity in order for the solvent to unravel the helical structure at low temperatures, as mentioned in the Introduction.

However, it is also crucial for this mechanism that the phase space for nonbonding of the solvent be much greater than the corresponding phase space for the amide groups, i.e., $q_\beta >> q_\alpha$. This can be expected from the following simple physical arguments. Typically, the spread in hydrogen bonding angles is small, approximately 10° ($\pi/18$ radians),[7] so that $\theta_\beta \simeq \pi/36 << 1$. Thus, we can expand $\cos\theta_\beta$ to obtain $q_\beta \simeq 4/\theta_\beta^2$. Since $\theta_\alpha \simeq 2\theta_\beta$, we have $q_\beta \simeq 4q_\alpha^2/\pi^2$. Typically $q_\beta \simeq 500$, as has been observed in many binary liquid mixtures,[1,12] yielding $q_\alpha \simeq 35$. Hence, $q_\beta >> q_\alpha$ as expected.

The total interaction energy of the polypeptide-solvent system is $H = H_1 + H_2$. All relevant equilibrium quantities may be obtained once the partition function Z is known, where

$$Z = \sum_{\{\alpha_i\}} \sum_{\{\beta_i\}} e^{\mathcal{H}} , \tag{2.3}$$

with $\mathcal{H} = -H/k_B T$ (T the absolute temperature, k_B Boltzmann's constant) the reduced Hamiltonian,

$$H = \sum_{i=1}^{N-1} [K_1 \delta_{\alpha_i \alpha_{i+1}} + K_2 \delta_{\alpha_i \beta_i} (1 - \delta_{\alpha_i \alpha_{i+1}})] , \qquad (2.4)$$

and $K_\ell = E_\ell / k_B T > 0$, $\ell = 1,2$. The sum in (2.3) is taken over all $q_\alpha^N q_\beta^{N-1}$ configurations of the system. The remaining part of this section will be concerned with the exact solution of (2.3).

Of utmost interest is the end-to-end orientational correlation function,

$$\langle \delta_{\alpha_1 \alpha_N} \rangle = Z^{-1} \sum_{\{\alpha_i\}} \sum_{\{\beta_i\}} \delta_{\alpha_1 \alpha_N} e^H , \qquad (2.5)$$

which will be important in determining the degree of helicity in a given molecule. We begin by noting that the sum over all configurations of the solvents, $\{\beta_i\}$, can be carried out exactly for fixed $\{\alpha_i\}$. This follows since each β_i is independent of the other β's for a fixed $\{\alpha_i\}$. The result is an effective interaction between the α_i given by $Z = \zeta^{N-1} \tilde{Z}$, where $\tilde{Z} = \sum_{\{\alpha_i\}} e^{\tilde{H}}$, with

$$\tilde{H} = \tilde{K}_1 \sum_{i=1}^{N-1} \delta_{\alpha_i \alpha_{i+1}} \qquad (2.6)$$

and

$$\tilde{K}_1 = \ln\{q_\beta e^{K_1} / [(q_\beta - 1) + e^{K_2}]\} , \qquad (2.7a)$$

$$\zeta = (q_\beta - 1) + e^{K_2} . \qquad (2.7b)$$

Note that the high temperature limit, $K_1, K_2 \to 0$, gives $\tilde{K}_1 \to 0, \zeta \to q_\beta$, as expected, and that $K_2 = 0$ yields $\tilde{K}_1 = K_1$ as it must. The interesting result of (2.7) is that for $K_1, K_2 > 0$,

and $R=K_2/K_1>1$, we find that $\tilde{K}_1$ will eventually become negative, asymptoting to $\tilde{K}_1 \to -(R-1)K_1$ as $K_1 \to +\infty$. This indicates that the system favors $\alpha_i \neq \alpha_{i+1}$ for all i (unbonding) at low temperatures, i. e. the molecule is in the coiled state. For $R<1$ the solvent-amide interaction is weaker than the amide-amide bonding, therefore the polypeptides eventually become perfectly helical at zero temperature. When R is equal to unity, $\tilde{K}_1$ becomes $\ln(q_\beta)$ at zero temperature, indicating incomplete helix formation.

Next, we can sum over the $\{\alpha_i\}$ in $\tilde{Z}$. There are many ways this can be done. The method we use is an exact renormalization-group (RG) decimation.[13] This involves summing out every $b^{\underline{th}}$ site between 1 and N. The aim is to iterate this process until only two sites, 1 and N, are left. The resulting two-site problem is then solved exactly. We emphasize that no approximations are made; the entire procedure is exact.

The result of the RG transformation is that $\tilde{K}_1$ becomes renormalized, so that after n iterations the coupling between α_1 and α_N is $K_1^{(n)}$. We can easily study chain-length dependent effects since this simply involves varying the number of iterations, n. A detailed study of these effects will be presented in a forthcoming work.[14] Here we shall focus on the basic features of the problem, thus it will be sufficient to consider the very simple illustrative case of N=2. The solution for the correlation function can be written in closed form,

$$\langle \delta_{\alpha_1 \alpha_N} \rangle = 1/\{1+[(q_\alpha-1)/q_\beta][(q_\beta-1)+e^{K_2}]e^{-K_1}\} . \qquad (2.8)$$

Let us investigate various limits. First, note that the high temperature limit, $K_1, K_2 \to 0$, is $\langle \delta_{\alpha_1 \alpha_N} \rangle \to 1/q_\alpha$, i.e.,

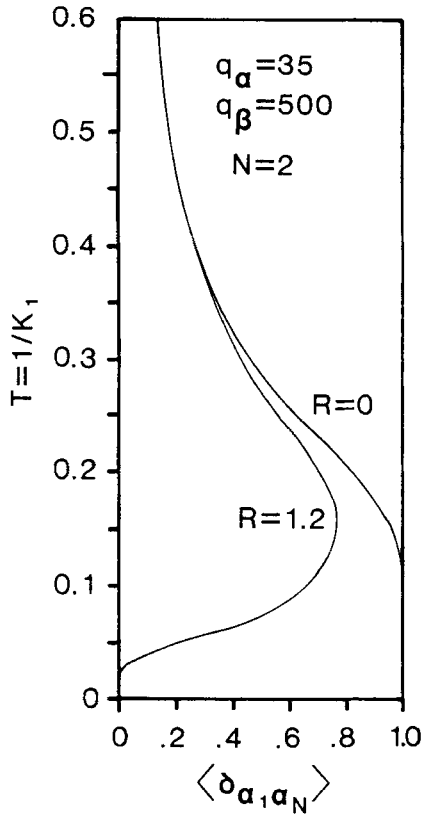

FIGURE 3 End-to-end orientational correlation function $\langle\delta_{\alpha_1\alpha_N}\rangle$ for N=2. q_α=35, q_β=500.

simply the random chance of α_1 and α_N being in the helical state. This is true for any N since $K_1^{(n)}\to 0$ in this limit. For $K_2=0$ (R=0), $\langle\delta_{\alpha_1\alpha_N}\rangle=1/[1+(q_\alpha-1)e^{-K_1}]$, which monotonically increases to unity as $T\to 0$. For R>1, (2.8) monotonically increases with decreasing temperature to a maximum at $K_1^*=(1/R)\ln[(q_\beta-1)/(R-1)]$. For $K_1>K_1^*$ (lower temperatures), the correlation function falls off exponentially to zero, $\langle\delta_{\alpha_1\alpha_N}\rangle\to[q_\beta/(q_\alpha-1)]e^{-(R-1)K_1}$ as $K_1\to+\infty$. When R is less than one the zero temperature limit is unity since solvent bonding is disfavored energetically. Fig. 3 gives an illustration of the above remarks. These trends are general for any N; the larger the N, the more suppressed to lower temperatures these effects become.

III. REENTRANT ISOTROPIC-NEMATIC TRANSITION

In this section we go beyond the intramolecular system studied thus far, and include interactions between different polypeptide chains. Imagine, then, a three

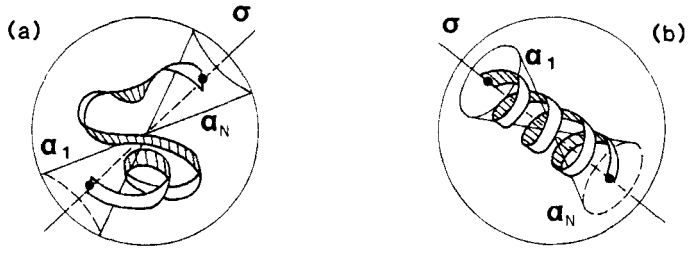

FIGURE 4 Illustration of the variable σ. (a) Orientation of a coiled conformation. (b) Orientation of a rigid, helical structure.

dimensional cubic lattice, each cell of which is occupied by a polypeptide and its satellite solvents. The behavior within each of these cells has been described in Sec. II. In addition, when the chain molecules in neighboring cells are helical they interact so as to prefer parallel alignment. This interaction is not nearly as orientationally specific as hydrogen bonding, since it is due primarily to induced quadrupolar forces;[15] these are generally represented by $P_2(\cos\theta)$, where θ is the angle between the long axis of the two molecules.

To describe these interactions we introduce a new statistical variable, σ_m, to represent the orientation of the molecule in the m^{th} cell, analogous to the variables α and β used in the intramolecular context. This is illustrated in Fig.4. As before, the unit sphere is divided into Q solid angle segments, labeled by σ_m=1,2,3,...,Q. Further, we again employ a square-well type of potential, only now our square-well approximates $P_2(\cos\theta)$. We find that a value of Q=5 is appropriate, because then the angular width of the attractive and repulsive regions of $P_2(\cos\theta)$ and $\delta_{\sigma_m\sigma_{m'}}$ are approximately the same.

Finally, since the interaction favoring alignment acts only if both polypeptides involved are in the helical

state, we need a way to determine whether a given molecule is helical or not. However, we've already seen that the correlation of the 1^{st} and N^{th} amide groups, $C_{1N}=\langle\delta_{\alpha_1\alpha_N}\rangle$, represents the helicity fraction, therefore $\delta_{\alpha_1\alpha_N}$ is unity for a helical molecule and zero for one that is coiled. With these comments in mind we see that the intermolecular interaction can be represented by $-E_N\delta_{\sigma_m\sigma_{m'}}(\delta_{\alpha_1\alpha_N})_m(\delta_{\alpha_1\alpha_N})_{m'}$, where $-E_N$ is the energy associated with the nematic phase, and $(\ldots)_m$ means the quantity in brackets refers to the m^{th} cell. If we now label the intramolecular Hamiltonian (2.4) with the subscript m, for the m^{th} cell, we obtain for the full Hamiltonian,

$$H = \sum_m H_m + \sum_{<mm'>} K_N \delta_{\sigma_m\sigma_{m'}}(\delta_{\alpha_1\alpha_N})_m(\delta_{\alpha_1\alpha_N})_{m'} \qquad (3.1)$$

where $K_N=E_N/k_BT$.

To see that our Hamiltonian contains the correct basic physics for the isotropic-nematic transition, we first note that the only true phase transition implied by (3.1) involves the σ variables, since it is only these that interact as part of a three dimensional system. In fact, the nematic phase is characterized by a condensation into a single one of the Q states available to σ_m, implying a director which singles out a particular direction. This transition will be first order (as is the isotropic-nematic transition) because the interaction is simply that of a Q-state Potts model,[16] which for Q=5 and three dimensions is known to exhibit a discontinuous phase change. It now remains for us to obtain at least an approximate solution to (3.1).

To do this we introduce a new method of analyzing Potts models, based on the observation that in the Potts interaction, $\delta_{\sigma_m\sigma_{m'}}$, all that really matters is whether $\sigma_m=\sigma_{m'}$ or not. Since this is simply a yes-no proposition, it reminds us of the basic symmetry inherent to an Ising model.[17] With this in mind, we would like to "project out" of (3.1) the essential "Ising-like" quality it contains; basically, if $\sigma_m=\sigma_{m'}$ we project to an Ising variable s=+1, while for $\sigma_m\neq\sigma_{m'}$ we project to s=-1. This method has been found to provide a very simple and accurate means of treating Potts models.[18] In this application of the basic idea we must also add the condition that the polypeptide in the site m is helical, i.e., $(\alpha_1)_m=(\alpha_N)_m$. The resulting projection operator, then, is simply,

$$P_m(s_m;\sigma_m,\sigma_{m'},(\alpha_1)_m,(\alpha_N)_m)=\tfrac{1}{2}\{1+[2(\delta_{\alpha_1\alpha_N})_m\,\delta_{\sigma_m\sigma_{m'}}-1]s_m\} \quad (3.2)$$

which applies independently to each site.

In principle, the mapping defined by this projection could be carried out exactly, but in order to make the calculation manageable we approximate the complete transformation by its effects on a single "bond", i.e., on a single pair of nearest-neighbor cells, m and m'. Each such bond is mapped to the Ising interaction

$$H_I = K_I s_m s_{m'} + H_I(s_m+s_{m'}) + K_o \quad (3.3)$$

where K_o represents a shift in the free energy. The single-bond transformation is then defined by

$$e^{H_I} = \sum_{\{(\alpha)_m,(\alpha)_{m'}\}}\sum_{\{\sigma_m,\sigma_{m'}\}} P_m P_{m'} \times \exp[H_m + H_{m'} + K_N\delta_{\sigma_m\sigma_{m'}}(\delta_{\alpha_1\alpha_N})_m(\delta_{\alpha_1\alpha_N})_{m'}]. \quad (3.4)$$

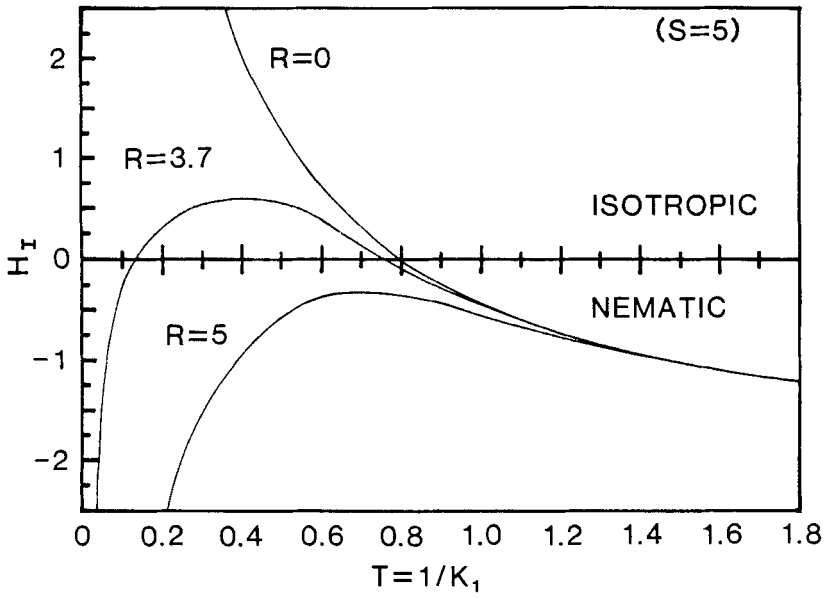

FIGURE 5 Ising magnetic field, H_I versus temperature. Note that $H_I<0(>0)$ corresponds to the isotropic (nematic) phase. $Q=5$, $q_\alpha=35$, $q_\beta=500$, $S=K_N/K_1=5$.

This yields,

$$H_I = \tfrac{1}{2}\tilde{K}_1 + \tfrac{1}{4}K_N - \tfrac{1}{4}\ell n[(q_\alpha-1)^2+(Q-1)(e^{\tilde{K}_1}+q_\alpha-1)^2] \quad (3.5a)$$

$$K_I = \tfrac{1}{4}K_N + \tfrac{1}{4}\ell n[1+(Q-1)(e^{\tilde{K}_1}+q_\alpha-1)^2/(q_\alpha-1)^2] \quad (3.5b)$$

and a similar result for K_o. Here we have assumed the case of $N=2$. For general N, $\tilde{K}_1$ is simply replaced by $K_1^{(n)}$.

From these results we find that K_I is greater than the Ising critical coupling for all $\tilde{K}_1$ and K_N. This means that a phase transition occurs each time H_I crosses zero, and this transition is first order. Since molecules that are aligned, i.e. $\sigma_m=\sigma_{m'}$, map to $s=+1$, it follows that the $H_I>0$

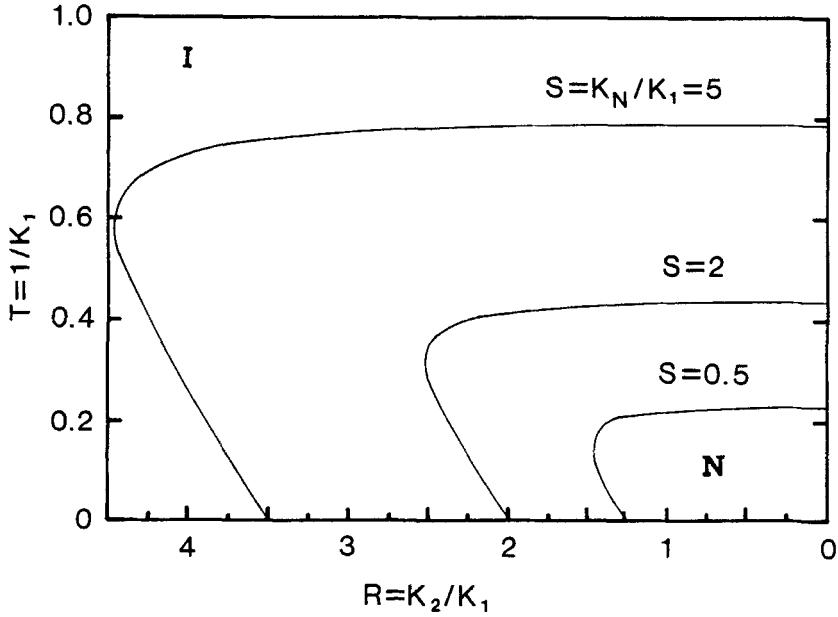

FIGURE 6 Reentrant isotropic-nematic transitions for various values of S. In this figure I denotes isotropic and N the nematic phase. Q=5, q_α=35, q_β=500.

phase is the nematic, whereas the $H_I<0$ phase is isotropic. The behavior of H_I versus temperature, which we choose to measure as $1/K_1$, is shown in Fig. 5. For R=0, and S>0, a single transition from isotropic to nematic is observed. The case R=3.75 illustrates a reentrant transition, whereas R=5 displays no transition at all.

Fig. 6 shows our results as T versus R for various values of S. Note that for T=0 the phase boundaries come down at R=1+S/2, a direct result of ground-state energetics. One can easily see how R might be varied in a physical system. First, changing the type of solvent being used clearly should give R a new value. More interesting is a system in which two types of solvents are used in a mixture; one solvent hydrogen bonds, the other does not, for example. Then one would expect the effective value of R

for this mixture to vary monotonically with concentration of the bonding solvent. Thus, these results show qualitatively what could be expected in such a T versus concentration phase diagram.

Recall from our earlier discussion that for R>1 the polypeptides will be coiled at T=0. However, in the range $1<R<1+S/2$ the nematic phase is stable even at zero temperature, and in order for the system to be nematic the polypeptides must be helical. This is an extreme example of induced rigidity (helicity),[19] where the nematic phase causes the molecules to be more helical than they would have been on their own.

Finally, we point out the possibility for doubly reentrant transitions in these types of systems. Imagine a solvent which is a mixture of two types of molecules, both of which can hydrogen bond either to the polypeptide, or to one another. The interaction strength for solvent-solvent bonding will be referred to as $K_3=E_3/k_BT$. With two types of solvent variables at each site, β and γ, we expect a new interaction to be added to $\mathcal{H}_m$; namely, $K_3\,\delta_{\beta_i\gamma_j}\delta_{\alpha_i\alpha_j}$. This interaction takes place only when amide groups bond to one another, thus freeing up the solvents to bond to themselves, and allowing the polypeptides to become helical again at very low temperatures. The calculation indicated in (3.4) is performed with this additional interaction in place, the results of which are shown in Fig. 7 for various values of the parameters. We note that in contrast to the singly reentrant case, where the reentrance effect occurs over a wide range of parameters, double reentrance is much more sensitive to the details of the model. As such, these phase diagrams may be rather difficult to realize in a physical situation.

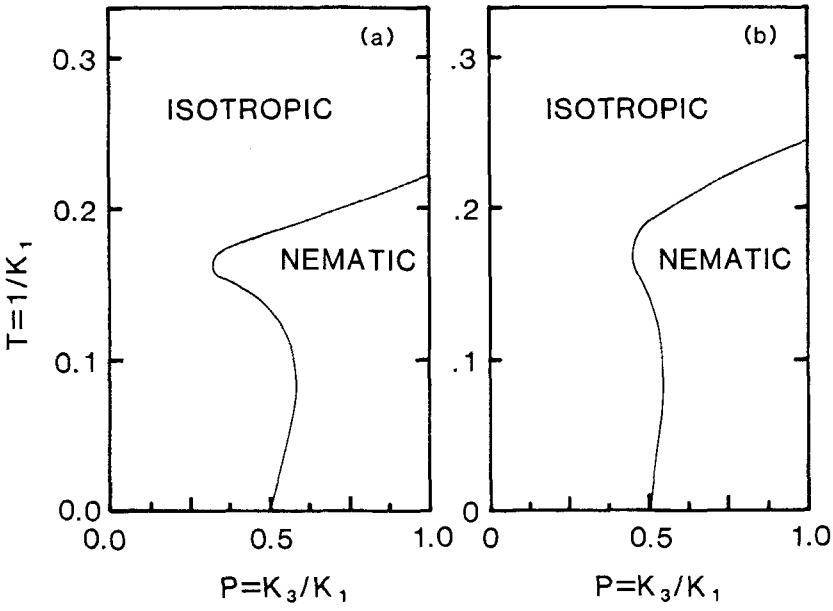

FIGURE 7 Doubly reentrant isotropic-nematic phase transitions for R=S=1. (a) Q=10, q_α=100, q_β=105. (b) Q=20, q_α=20, q_β=45.

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