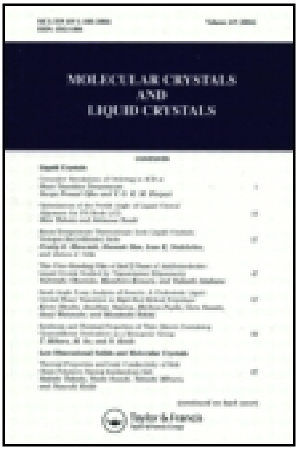

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Bowlic and Polar Liquid Crystal Polymers

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BOWLIC AND POLAR LIQUID CRYSTAL POLYMERS

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Abstract Bowlic liquid crystals are made up of polar molecules. Both main-chain and side-chain bowlic polymers are possible. Exactly solvable discrete models describing the phases and conformations of these bowlic and other polar liquid crystal polymers are presented. For the ideal one-dimensional case the model is equivalent to the 1D Ising model. Susceptibility and other properties are calculated. Wave propagation and solitons in these polar polymers are discussed. Possible highly conducting and high T_c superconducting liquid crystal polymers are proposed.

INTRODUCTION

Bowlic liquid crystals[1,2] are made up of polar molecules with up-down asymmetry. The even-$\vec{n}$ symmetry may be broken leading to many novel properties, including real ferroelectricity. They have been synthesized[3] and studied by x-rays[4]. These bowlics can be made into polymers[2] - both main-chain and side-chain are possible (Fig.1).

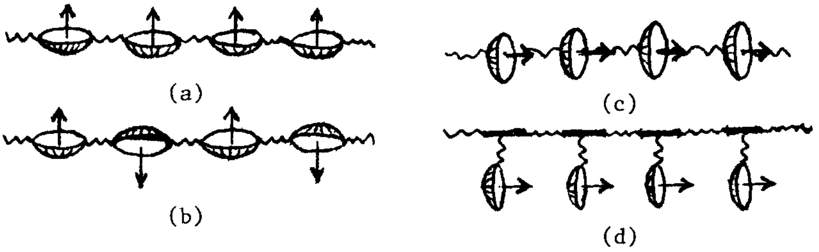
(a)
(b)
(c)
(d)

FIG.1. Main-chain (a-c) and side-chain (d) bowlic polymers.

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Depending on whether the separation between two bowlic molecules are large or small, one may have ferroelectric (a) or antiferroelectric (b) main-chains. In the semiflexible abstraction these polymers may be considered as chains with dipoles attached. In this sense they are no different from polar polymers made up of rod-like molecules, except that bowlics like case (c) can be much stronger in strength due to the stacking of the molecules which is absent in the rodic polymers.

In the following, our discussions are valid for both bowlic and rodic polar polymers.

THE DISCRETE MODEL

To describe the conformations of a polar main-chain in external electric field E, a possible model is shown in Fig.2. For a chain of L repeatible units (each of which has length b and may be longer than a monomer) we consider a biased random walk of L steps such that the energy for a bond (step) parallel (antiparallel) to $\vec{E}$ causes energy $-\varepsilon(\varepsilon)$, a bond perpendicular to $\vec{E}$ causes zero energy, each corner causes energy α, and a pair of antiparallel (parallel) adjacent bonds have energy $-\gamma(\gamma')$. All ε, α, γ and γ' are positive, with

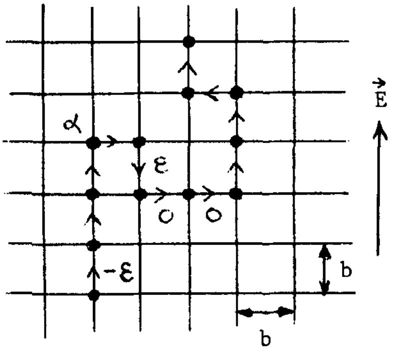

FIG.2. The discrete model. E is external electric field. The lattice may be 1-3D.

$\varepsilon \equiv \mu E$ where μ is the dipole moment of each repeatible unit. In general, the lattice is 3D, but may be 2D or 1D for simplicity or special cases.

As far as we know there is no analytic solution for this model. But it can be solved easily by Monte Carlo method with computers. For $E = 0$ and in 1D continuum limit this model reduces to that of Zwanzig and Lauritzen[5] which was exactly solved in the $L \rightarrow \infty$ limit resulting in a second-order phase transition with the number of hairpins acting as the order parameter. For $E \neq 0$ and $\gamma = \gamma' = 0$ and in the 1D continuum limit the model reduces to that of Gunn and Warner[6] which has exact solution but no phase transition. However, as shown by Lauritzen and Zwanzig[7] the continuum version of a physically discrete model may contain spurious results.

To render the model solvable let us consider a simplified version (Fig.3). Here, the model is 2D (or 1D) and the horizontal bonds are in one direction only. For $E = 0$, it reduces to that of Ref.7. In the $L \rightarrow \infty$ limit the exact solution[7] gives a second-order phase transition. For general E and $\gamma = 0$ we found exact solutions. The partition function is given by

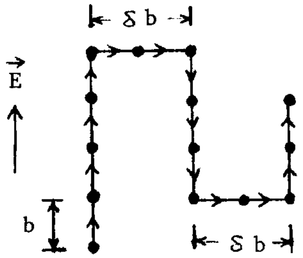

FIG.3. The 2D simplified discrete model. δ is a constant. $\delta = 0$ reduces the model to 1D.

$$Z(L) = 2[H_L - (\cosh\beta\varepsilon)H_{L-1} + fH_{L-\delta}] \qquad (1)$$

where $\beta \equiv 1/k_B T$, $f \equiv \exp(-\beta h)$, $h \equiv 2\alpha$ and

$$H_m = \frac{1}{m!} \lim_{z \to 0} \frac{d^m}{dz^m}[1/G(z)] \tag{2}$$

with

$$G(z) \equiv z^2 - (2\cosh \beta \varepsilon)z + 1 - f^2 z^{2\delta} \tag{3}$$

Here, L, δ and m are integers with $L \geqslant 1$, $L \geqslant \delta \geqslant 0$.

For $\delta = 1$, in particular, the free energy $F = -(L/\beta) \times \ln(1+f) - (1/\beta)\ln 2$ for $E = 0$. The average number of hairpins $n \square \partial F/\partial h \square Lf/(1+f)$ which increases monotonically from zero to $L/2$ as temperature T increases from zero to infinity. The susceptibility χ is obtained for arbitrary L and E. As $E \to 0$,

$$\chi \sim \beta \mu^2 L \exp(\beta h) \tag{4}$$

which is identical to Eq.(5) of Gunn and Warner[6] if the length l there is identified with b.

For $\delta = 0$, our simplified discrete model is mapped onto the 1D Ising model. This can be seen easily by considering the up segments (in Fig.3) to be spin-up and the down ones as spin-down with spin 1/2; parallel adjacent spins have energy zero and antiparallel pair having energy h. If periodic boundary condition is used (which is valid for large L) χ is the same as in Eq.(4), both of which are valid for all temperatures.

Several remarks are in order. (i) The Z of Ref.6 depends on an arbitrary parameter l which has to be related to some physical quantities separately.[6] We note that l comes in in the "density of states factor"[8] when one takes the continuum limit of the physical discrete model. In the discrete model, this problem is avoided. (ii) We note that Eq.(4) and hence the giant dielectric response[6] is the same as the mean-field results of the Ising model as $T \rightarrow 0$. (iii) The fact that in our simplified model the influence of the other molecules is ignored in calculating the conformations of a single molecule implies that the result is valid for a single molecule or in very dilute solution; it is not for nematic polymers. This can be remedied easily by treating the other molecules in a mean-field manner and treating the conformation of a molecule exactly as done here. For this purpose one simply replace E by E + aP, where a is a proportional constant and P is the polarization given by $P = -\partial F/\partial E$. In this way we did find phase transitions even though the adjacent segment interaction γ is ignored. However, the behavior of χ is drastically changed. This is confirmed by an alternative description which maps the problem to a quantum mechanical differential equation.[9] For example, instead of Eq.(4), at low temperature one has

$$\chi \sim \beta^{-1}\exp(c/\beta), \quad c = \text{constant} > 0 \qquad (5)$$

In short, the giant dielectric response of Eq.(4) is modified when intermolecular interaction in a nematic is taken into account.

PHASE TRANSITIONS

It is worth to point out that the columns in the columnar phase of bowlic (as well as discotic) mesophases may be considered as polymers. In the crystal phase of polymers chain packing is important. Helical chains as well as hexagonal or rectangular packing can be understood from simple geometrical considerations.[10] The similar cases in liquid crystal columnar phases (including the helical low-temperature phase observed in bowlics[4]) may be understood this way.

WAVE PROPAGATION AND SOLITONS

For a main-chain (polar or non-polar) polymer the motion of the hairpins along the chain may be described by the sine-Gordon equation which is the Lagrange equation of the free energy,

$$F = \int [M\dot{\theta}^2 + Q\sin^2\theta + B(\partial\theta/\partial s)^2]\tfrac{1}{2}ds \qquad (6)$$

The hairpins may be understood as solitons.[11] In the polar case, when $E \neq 0$ one has the additional term $\sim \cos\theta$ in the integrand of Eq.(6). One then has the double-sine-Gordon equation and still has solitons (which do not maintain their identities after pair-wise collision). Here θ is the angle between the tangent of the semiflexible chain at a point with the director (or the electric field).

For dipoles transverse to the chain as in cases (a) and (b) of Fig.1, one may consider the chain to be twistable as well as flexible. The mechanical property of such a chain may be described by the Kowteweg-deVries equation which is also a soliton equation.[11]

CONDUCTING AND HIGH T_c SUPERCONDUCTING LC POLYMERS

The bowlic molecules do have holes in their centers.[3] [In contrast, the discotics may[12] or may not have holes[13]. The former is called tubular.[12]] To make the bowlics conducting there are two ways of doing it. One is to make new molecules by connecting a metal or transition metal atom in the center of the original (or modified) bowlic molecule. This has been shown to be possible for the discotics[14] and should be so for the bowlics too, in our opinion. The second is to put in the metal or transition metal elements into the empty tube of the columns in the columnar phase of the bowlics. The size of the atoms will depend on how large the tube diameter is. We will then have a conducting and possibly highly conducting liquid crystal (or crystal below the mesophase-crystal transition temperature). The fact that one will have parallel conducting filaments capable of sliding against each other is peculiar to these liquid crystal conductors. The consequences are worth further investigation. All these remarks of course apply also to the discotics.

The conducting polymers (or columnars) may become superconducting through three possible mechanisms. In the case of the atom which is capable of some motion inside the tube (manufactured by the second method above) there may be Peierls transition and then charge-density wave. One then has the Frohlich mechanism. The second is by hopping as in the Hubbard model.[15] This may work for the two cases of manufacturing. The third is by the exciton mechanism.[16] It is the last one that may lead to high T_c superconductors.

In fact, hypothetical organic molecule with Pt in the center had been proposed by Davis, Gutfreund and Little[17] before for the excitonic mechamism to work. Superconducting T_c above 1000 K is possible, in theory.[17] The difficulty is that this molecule is very difficult if not impossible to synthesize; more importantly, even one has such a molecule there is no guarantee that they will stack up to form one-dimensional or quasi-one-dimensional filament as required by the theory. In contrast, in our case the stack up of the molecules is natural; the synthesis is possible. In this regard the bowlics should have advantage over the discotics. With the bowlics the separation between the conducting columns can be more close to each other due to the inclined configuration of the benzene rings in the molecule. The interchain coupling[18] would be more favorable.

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