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Static and dynamic properties of smectic liquid crystal side chain polymers

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On the basis of models for the conformation of liquid crystal side chain polymers in the smectic phase, some dynamic aspects of such systems are considered using the reptation approach. The overall diffusion constants of the polymer along and perpendicular to the director of the side chains are derived.

1. Introduction

Liquid crystal side chain polymers (comb-like polymers) consist of a flexible polymeric backbone to which the mesogenic side chains are attached via flexible relatively short spacers [1, 2]. The mesogenic units are responsible for the occurrence of one or more of the typical liquid crystal phases, whereas the backbone supplies the samples with a mechanical stability unknown to classical liquid crystal samples. Recently much interest has developed in liquid crystal side chain polymers (LSP) both with a view to possible applications [3–5] and with regard to the more academic question [6–8] of how the competition between the tendency of the backbone to coil up and the tendency of the side chains to order in a mesophase balances out.

In order to examine the static properties of LSP systems in the smectic (S_A) phase the author proposed recently several models for the conformation of the backbone [9, 10]. These models are briefly reviewed in §2 for a better understanding of §3, where a model for the dynamics of the backbone in the smectic phase is proposed.

It is emphasized that the discussion is restricted to LSP systems where the side chains are oriented preferably perpendicular to the backbone. This is the smectic analogue to the nematic N_I and N_{II} system according to Warner's classification [7], and implies explicitly that the N_{III} systems which also seem to have a smectic counterpart [11, 12] are excluded.

2. Models for the main chain conformation

The following experimental results are significant for the following considerations.

(*a*) Small angle neutron experiments revealed that the radius of gyration $R_{g,\parallel}$ of the backbone along the director of the side chains is much smaller than the radius of gyration $R_{g,\perp}$ perpendicular to that direction [13–16].
(*b*) Both $R_{g,\parallel}$ and $R_{g,\perp}$ are temperature dependent [14–16].
(*c*) Wide angle neutron scattering data indicate that the backbone is mainly located between the smectic lamellae built by the side chains [17].
(*d*) The smectic order is somewhat disturbed by the presence of the polymeric backbones [18].

Very little is known yet about the small scale configurational properties of the backbone. I examined a hierarchy of conformation models [9] in order to see whether

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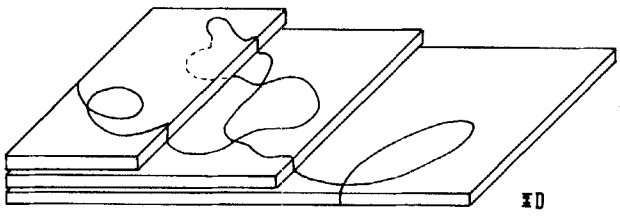
it might be possible to differentiate between the models by comparison with the experimental data. It turned out, however, that despite the large difference of the underlying models (with respect to the available number of degrees of freedom) the difference in the final expression for the anisotropy factor $\alpha = R^2_{g,\parallel}/R^2_{g,\perp}$ is amazingly small. In the following the hierarchy of models is sketched and the final result recapitulated. For all details and for a discussion of the problem of non-equilibrium effects which in the author's opinion are likely to occur in experiment, see [9].

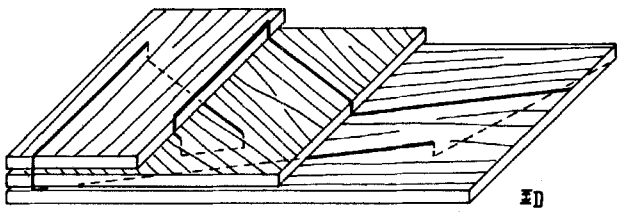
The basic ingredients of the present models are the following. The backbone is modelled by a type of random walk of length L. This random walk is placed on a stack of parallel two-dimensional planes, viz. the planes between the smectic lamellae. The distance between two adjacent planes is D, the lamellar thickness. The random walk is allowed to jump from one plane to its adjacent planes. Such a jump (crossing of the lamella) requires a random walk segment of length D and is weighted by a factor $\exp(-\beta E_C)$ in the respective configuration sum, where $\beta = (kT)^{-1}$ and E_C is the free energy of a crossing. Obviously $E_C > 0$, since the backbone with its appending side chains locally destroys the smectic order of the lamella through which it passes (unless the side chains fit in some way into register during such a crossing, which might be the case for the above mentioned N_{III}-type LSP).

The proposed hierarchy consists of the following types of random walks for the conformations of the backbone in the interlamellar planes.

Model A (see figure 1 (*a*)). A k step segment of the backbone between two crossings is described by ideal random walk statistics, i.e. $\Omega = q_0^k$, where Ω is the number of possible configurations of the segment and q_0 is some coordination



(*a*)



(*b*)

Figure 1. A typical (highly idealized) configuration of the backbone of a liquid crystal side chain polymer in the smectic phase is shown for (*a*) the case where the backbone is assumed to behave as a quasi-two dimensional random walk and (*b*) the case where the backbones of the polymers have a tendency to lie parallel to each other in one interlamellar plane. In the latter case backbones of other polymers lying in the respective planes are also depicted to clarify the assumed bundle-like structure. The side chains are omitted for the sake of clarity. In both cases D is the thickness of one smectic lamella.

number. This model attributes to the backbone the maximum conceivable number of configurational degrees of freedom but is unrealistic, as it does not consider excluded volume effects. In a more sophisticated model such effects can be taken into account [9]. It should be recalled that excluded volume effects are dominant in two dimensions. The neglect of these effects is a severe shortcoming of model A and of models proposed by other authors [6, 19]. We might consider the present simple random walk model as one extreme in the hierarchy of theoretically possible models.

Model B (see figure 1 (*b*)). This is the other extreme case: the backbone describes a straight path in the interlamellar plane between two crossings. The directional fields of the paths in the different interlamellar planes are assumed to be uncorrelated. Furthermore, the backbone does not activate its configurational degrees of freedom contained in a segment between two crossings. This case is unrealistic in so far as the backbone will always show some lateral wiggling. Furthermore, a certain probability of crossing the backbones which are neighbouring in the interlamellar planes is always sure to occur.

In [9] intermediate situations are also discussed. The important point now, however, is that all easily conceivable models are assumed to lie between model A and model B with respect to the number of degrees of freedom of the backbone. Thus, the respective anisotropy factors are also assumed to lie between α_A and α_B, where α_i is the anisotropy factor for model i (i = A, B). In [9] it is shown that α_i can be represented in the general form

$$\alpha_i \sim q_i^{-D} \exp(-\beta E_i), \tag{1}$$

where $q_A > 1$, $q_B = 1$ and $E_A = E_C$, $E_B = 2E_C$. The negative aspect implied by this result is that it seems to be impossible to decide from the knowledge of the small angle scattering data which model is realized in nature since, presently, almost nothing is known about the value of E_C. However, the gratifying implication of this result to the development of theories on LSP in the smectic phase might be that it is indeed justified to use simple random walk models to describe approximately large scale static properties of these systems.

It may be worthwhile to mention here that there exists experimental indication [20] on the small scale structure of the backbone, that the backbone exhibits in the interlamellar planes an approximately straight configuration. This result favours, of course, a model which is similar to our model B.

3. A reptation model for the dynamics of the main chain

On the basis of the models discussed earlier and using the reptation approach to the dynamics of the backbone, in the following a derivation of the diffusion constants for the centre of gravity of the LSP along the direction of the director ($D_\parallel$) and perpendicular to that direction ($D_\perp$) is proposed. (For all details concerning the reptation model the reader is referred to the original paper by deGennes [21] and to [22]). The following assumptions are made.

(*a*) The backbone diffuses longitudinally along a tube which is defined by the instantaneous configuration of the backbone. A justification for the use of the tube picture is given below.

(*b*) This diffusion is mediated by so-called kinks [21], i.e. surplus length of the backbone diffusing along the curvilinear length of the backbone.

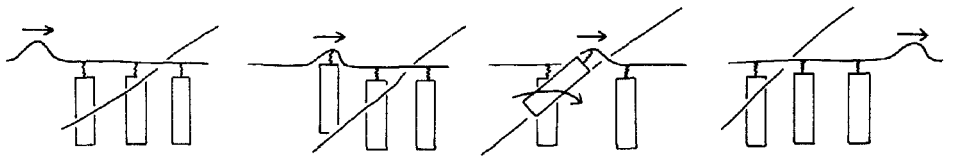


Figure 2. The propagation of a kink along the backbone, and the resultant process of one side chain hopping over the topological barrier imposed by the backbone of another polymer, or by a remote segment of the same polymer to which the side chain is attached.

(*c*) If a diffusional step involves a transfer of a side chain over the backbone of another LSP (see figure 2) the transition rate for such a process is given by $\Gamma_1 = \nu_0 \exp(-\beta E_H)$; in all other cases it is $\Gamma_0 = \nu_0$, where ν_0 is a typical frequency of the unhindered kink diffusion. E_H is the activation energy of a jump process.

(*d*) Along the backbone on the average a fraction of $\langle\kappa\rangle$ 'monomers' are in a position where a diffusion of a kink involves a side chain jump. For model A it may be assumed that $\langle\kappa\rangle_A \approx \langle n_\perp\rangle/N$ where $\langle n_\perp\rangle$ is the average number of monomers of the backbone in the interlamellar planes and N is the number of backbone monomers ($L = Na$). For model B it is safe to assume a similar relationship with $\langle\kappa\rangle_B \ll \langle\kappa\rangle_A$, since neighbouring backbones are much less frequently crossed than in the case of model A.

With these assumptions the kink diffusion constant D_k is readily found by mapping the present model onto the one dimensional random barrier model [23] where it is assumed that the statistics of a particle (i.e. of a kink) are governed by the master equation

$$\partial_t p_n(t) = \omega_{n,n+1}[p_{n+1}(t) - p_n(t)] + \omega_{n-1,n}[p_{n-1}(t) - p_n(t)]. \tag{2}$$

Here $p_n(t)$ is the probability of finding a particle at position n at time t ($n = 1, 2, \ldots, N-1$). $\omega_{n,n+1}$ denotes the transition rate between sites n and $n+1$ and is a random variable. In the present model there are two transition rates: either $\omega_{n,n+1} = \Gamma_1$ with probability $\langle\kappa\rangle$ or $\omega_{n,n+1} = \Gamma_0$ with probability $1 - \langle\kappa\rangle$. According to [23] D_k is given by $D_k \sim \langle\Gamma^{-1}\rangle^{-1}$, where $\langle\Gamma^{-1}\rangle$ is the geometrical mean of the transition rates. For the present case we obtain

$$D_k \sim [\langle\kappa\rangle \exp(\beta E_H) + 1 - \langle\kappa\rangle]^{-1}. \tag{3}$$

Using the fact that for $\langle\kappa\rangle = 0$ the friction coefficient ζ of the whole backbone along the tube must scale as $\zeta = N\zeta_0$, where ζ_0 is the friction coefficient per monomer, we obtain for the diffusion constant D^* of the backbone along the tube $D^* = N^{-1}D_k$. The respective diffusion constants $D_\parallel$ and $D_\perp$ are computed using the relationships

$$\left.\begin{aligned} D_\parallel &\sim \tfrac{1}{2}\,\overline{(\Delta\mathbf{R}_g \cdot \mathbf{e}_z)^2}\,\nu_0, \\ D_\perp &\sim \tfrac{1}{4}\,\overline{[\Delta\mathbf{R}_g \times \mathbf{e}_z]^2}\,\nu_0, \end{aligned}\right\} \tag{4}$$

where $\Delta\mathbf{R}_g$ is the displacement of the centre of gravity due to the migration of one kink from one end of the backbone to the other [22], $\mathbf{e}_z$ is the unit vector pointing into the direction of the director of the side chains and the overbars indicate time averaging. Assuming that in each time interval ν_0^{-1} a segment of the backbone of length δ is transferred from one end of the backbone to the other it is found that the relationships

$\overline{[\Delta \mathbf{R}_g \cdot \mathbf{e}_z]^2} = \delta^2 R_z^2/L^2$ and $\overline{[\Delta \mathbf{R}_g \times \mathbf{e}_z]^2} = \delta^2 R_\perp^2/L^2$ hold, where R_z^2 and $R_\perp^2$ are the mean-squared end-to-end distances in the z direction and the direction perpendicular to the z axis, respectively. Furthermore, making use of the relationship $v_0 = 2D^*/\delta^2$ [22] we obtain the final results for the diffusion constants

$$\left.\begin{aligned} D_\perp &\sim kT\zeta_0^{-1}N^{-3}R_\perp^2[\langle\kappa\rangle \exp(\beta E_H) + 1 - \langle\kappa\rangle]^{-1}, \\ D_\parallel &\sim [R_z^2/R_\perp^2]D_\perp . \end{aligned}\right\} \tag{5}$$

In the case of model A (the pure random walk model) we assume that $N\langle\kappa\rangle \sim \langle n_\perp\rangle$ (see earlier). Considering furthermore the limiting case $\langle n_\perp\rangle \gg \langle n_z\rangle$, because of the small α observed [13] we obtain

$$D_\perp^A \sim N^{-2}\exp(-\beta E_H). \tag{6}$$

In the case of model B we assumed earlier that $\langle\kappa\rangle \ll 1$ and find

$$D_\perp^B \sim N^{-3}R_\perp^2[\langle\kappa\rangle \exp(\beta E_H) + 1]^{-1}. \tag{7}$$

For a comparison of these results with the expression for the diffusion constant in the case of a linear polymer in the isotropic melt, recall that the reptation model yields $D \sim N^{-3}R^2$ with $R^2 \sim N$ [21].

A further deviation from the usual reptation behaviour occurs when considering the local diffusion of one kink. In the reptation model it is explicitly assumed that the kinks diffuse unhindered [21]: $\langle r^2\rangle \sim D_k t$, where $\langle r^2\rangle$ is the mean-squared distance that the kink travels along the polymer chain during a time interval t. In the random barrier model which we apply a long-time tail appears [23]:

$$\langle r^2\rangle \sim 2D_k t + 2\gamma\pi^{-1/2}[D_k t]^{1/2} + \cdots, \tag{8}$$

where $\gamma = D_k^2\langle(\Gamma^{-1} - \langle\Gamma^{-1}\rangle)^2\rangle$. For our model we obtain

$$\gamma = \frac{(\langle\kappa\rangle - \langle\kappa\rangle^2)[1 - 2A^{-1} + A^{-2}]}{A^{-1} + \langle\kappa\rangle[2A^{-1} - 2A^{-2}] + \langle\kappa\rangle^2[1 - 2A^{-1} + A^{-2}]}, \tag{9}$$

where $A = \exp(\beta E_H)$. In the two limiting cases where $\langle\kappa\rangle = 0$ or $\langle\kappa\rangle = 1$, γ vanishes as expected, since in these cases there is no disorder along the backbone with regard to the transition rates. In our models we have $0 < \langle\kappa\rangle < 1$ and due to this fact the additional long-time tail in equation (8) comes into play.

The modified diffusional behaviour derived above affects the form of the incoherent scattering function $S(q, \omega)$ in the ω range where $N^{-2}\langle\Gamma^{-1}\rangle^{-1} \ll \omega \ll \Gamma_1$. Because of the non-gaussian statistics underlying equation (8) it seems to be impossible to derive an analytical expression for $S(q, \omega)$. This is a point that is open for future work.

Finally, we make an attempt to justify the assumption of a tube, i.e. a region to which the backbone is confined because of energetic and topological reasons, and which prevents large transverse excursions of chain segments. (For a thorough discussion of the tube model, see [24].) The following points are noted:

(*a*) Because of the large free energy penalty the backbone suffers if it tries, starting with a segment embedded in one interlamellar plane, to build a loop reaching an adjacent interlamellar plane with a part of this segment, transverse wiggling in the z direction is highly improbable when exceeding the length scale of a few Ångströms.

(*b*) When considering the lateral wiggling in the interlamellar planes one has to discriminate between model A and model B. In the case of model A one finds that large excursions of segments of a backbone (say BB1) in the xy plane are prevented by the fact that very effective topological barriers are frequently built up at points where two backbones (neither of which may be identical with BB1) cross their paths (see the discussion in §2 of [9] and also figure 1 of [9]). In model B it is assumed that the state which minimizes the free energy of the LSP sample is given by a state where the backbones have a strong tendency to align in a bundle-like structure when regarding one interlamellar plane. Again it is very improbable (in the statistical sense) that the backbone will perform large random walk-like motions when looking at a segment between two adjacent crossings.

(*c*) An effect which competes, as regards relaxational processes, with 'classical' reptation along the tube is the tube renewal mechanism. This effect was discussed for the case of dense linear polymers: the chains which build the tube of one 'test' polymer are themselves reptating and therefore destroying locally parts of the tube if one of their ends passes the 'test' polymer [25, 26]. Recently it was argued [26] that self-diffusion and relaxation of ordinary polymers are dominated by reptation if the polymers are sufficiently long, i.e. if $L \gg L_C$, where L_C is the typical distance between entanglements. In that case it is assumed that the tube renewal effects are negligible. Because we discuss here the case of long backbones, it might be justified to neglect in the proposed model tube renewal effects. Furthermore, it must be stressed that the tube picture which is used in this paper differs somewhat from the usual conception. (i) In the direction parallel to the director the 'walls' of the tube are built by the repelling smectic lamellae. This is an energetic and not a topological effect. (ii) In the case of model B we assumed that there is, apart from topological hindering, an energetic barrier against large lateral excursions of the backbone in the plane perpendicular to the director, cf. point (*b*) above. In the case of model A and 'short' backbones ($L \approx L_C$) tube renewal effects might be important.

4. Conclusion

The static properties of two extreme models for the conformation of liquid crystal side chain polymers in the smectic phase were reviewed. It was stressed that with regard to the anisotropy of the radii of gyration $\alpha = R_z^2/R_\perp^2$ which is measured in small angle scattering experiments the difference between the resultant expressions for α obtained for these two models seems to be relatively small. Little is currently known about the microscopic parameters of the LSP systems as, for example, the crossing energy, and it is thus not possible to differentiate, from a knowledge of small angle scattering data, between the proposed models. The positive aspect of this finding is that it seems to be justified to use in a first approximation the simple random walk approach in further theoretical work on the statistics of LSP systems.

On the basis of the two models and employing the reptation theory formulae for the diffusion constants of the polymer in the z direction perpendicular to the smectic lamellae and in the xy plane, respectively, were derived. It was obtained that $D_\parallel/D_\perp = R_z^2/R_\perp^2$ as expected, and furthermore a dependence of $D_\parallel$ and $D_\perp$ on the activation energy for the hopping of a side chain over the topological barrier of the

backbone of another LSP crossing the path of the LSP to which this side chain is attached. A material difference between the usual reptation approach and the present model was found, viz. the diffusion of a kink along the backbone is no longer given by a simple diffusion law but a long-time tail occurs which is assumed to affect the dynamical structure factor.

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