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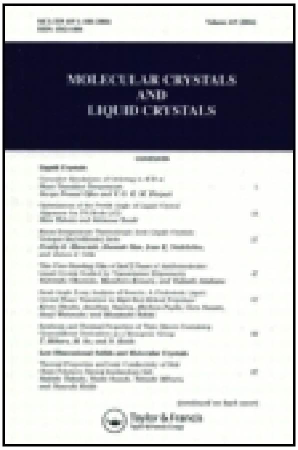

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Polymeric liquid crystals: Frank elasticity and light scattering

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Polymeric liquid crystals : Frank elasticity and light scattering

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(Submitted for publication March 18, 1977)

Abstract : We discuss some theoretical features of a nematic phase made of long, partially flexible chains. The bend constant K_3 is dominated by the rigidity of the chains. The twist constant K_2 is mainly related to the anisotropic couplings between chains. The splay constant is very large (increasing like the square of the molecular mass M). An interesting limit is obtained when the length of the extended chains is larger than the optical wavelength used in a light scattering experiment : then the scattering laws should differ qualitatively from what is known in usual nematics.

The existence of nematic phases made of polymeric materials has been announced for various systems (1-3) - although a complete identification is still lacking in many cases. The limit of completely rigid chains (corresponding to the hard rod model initiated by Onsager (4)) has been known for some time with polypeptides (5) and will not be discussed here. The case of partly flexible chains is more novel : the coupling between chains may react on the effective rigidity of each, so that chains which are flexible in dilute solutions may become very stiff in concentrated systems. A crude theory of this effect has been constructed (6).

In the present note we consider only the elasticity and the thermal fluctuations in an ordered phase of strongly extended chains (fig. 1 a). Our description includes two variables : the director $\underset{\sim}{n}$ and the density (or

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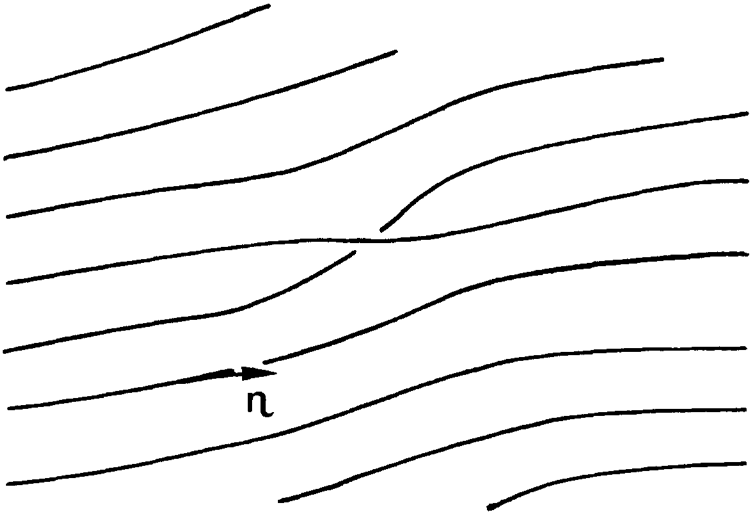

FIG. 1a

concentration) ρ. Our central assumption is that the local chain axis varies only slowly from point to point ; it can hold only if "hairpin defects" - of the type shown in fig. 1 b - are very few in number.

Let us start with the limit of very long chains ($M \to \infty$) then the concentration of chain ends vanishes, and the "current" $\underset{\sim}{J} = \rho \underset{\sim}{n}$ is conserved (7) :

$$\text{div } \underset{\sim}{J} = 0 \tag{1}$$

This implies that $\underset{\sim}{n}$ and ρ are coupled by the condition

$$\text{div } \underset{\sim}{n} = - \underset{\sim}{n} \, . \, \nabla\rho/\rho \tag{2}$$

Thus a splay deformation imposes local changes in ρ, and requires large energies. The detailed form of the elastic free energy is

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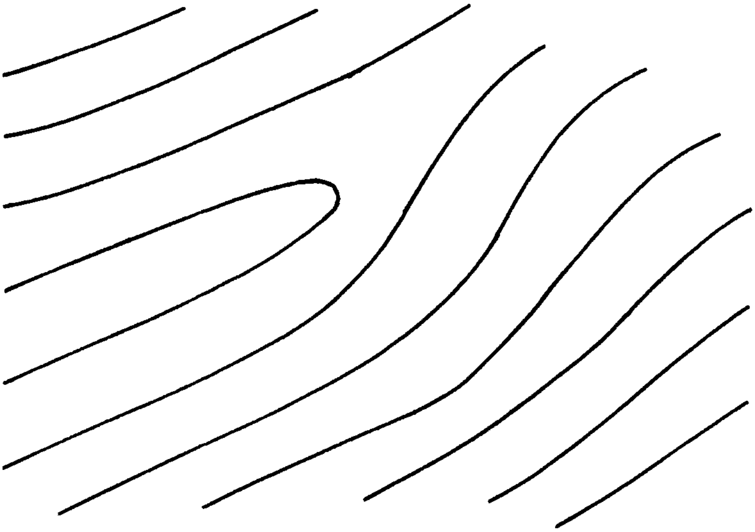

FIG.1b

$$F = \frac{1}{2} K_1 \ (\text{div}\ \underset{\sim}{n})^2 + \frac{1}{2} K_2 \ (\underset{\sim}{n}.\text{curl}\ \underset{\sim}{n})^2$$

$$+ \frac{1}{2} K_3 \ [\ (\underset{\sim}{n}.\nabla)\ \underset{\sim}{n}|^2 + \frac{1}{2} E \ \left(\frac{\delta\rho}{\rho} \right)^2 \qquad (3)$$

Here K_1, K_2, K_3 are "bare" Frank constants, and E^{-1} is a compressibility (or an osmotic compressibility if we are dealing with a solution). These 4 coefficients are independent of M.

Let us now look at small fluctuations of wave vector $\underset{\sim}{q}$, setting $\underset{\sim}{n} = \underset{\sim}{n}_o + \underset{\sim}{v}$ where $\underset{\sim}{n}_o$ is parallel to (z) and $\underset{\sim}{v}$ is in xy plane. For a given $\underset{\sim}{q}$ (with transverse components $\underset{\sim}{q}_\perp$ in the xy plane) we split $\underset{\sim}{v}_q$ into a component v_{1q} parallel to $\underset{\sim}{q}_\perp$ and v_{2q} normal to $\underset{\sim}{q}_\perp$: our notation follows ref (8). We find :

$$2\ F = \sum_q \{ |v_{1q}|^2 \ (q_z^2\ K_3 + \frac{E\ q_\perp^2}{q_z^2} + K_1\ q_\perp^2) + |v_{2q}|^2\ (q_z^2\ K_3 + K_2\ q_\perp^2) \} \qquad (4)$$

We see on eq. (4) that the splay constant undergoes a $\underset{\sim}{q}$ dependent renormalisation

$$K_1 \quad \tilde{K}_1 = K_1 + \frac{E}{q_z^2} \cong \frac{E}{q_z^2} \qquad (5)$$

the E term being dominant since q_z is always small on the atomic scale. From (4) we can find the thermal fluctuations (setting $F_q = \frac{1}{2}\ k_B\ T$ for each q). The result on v_{2q} is unchanged (see ref. 8). But for the splay-bend mode v_{1q} we find now :

$$< |v_{1q}|^2 > \cong \frac{k_B\ T\ q_z^2}{K_3\ q_z^4 + E\ c_\perp^2} \qquad (6)$$

For most $\underset{\sim}{q}$ directions the light scattering described by (6) is very weak : only when $\underset{\sim}{q}$ is very near the nematic axis (deviation angle $\theta_q < q\ b$) do we recover an intensity of the usual magnitude for v_{1q}. (Here $b = (K_3/E)^{1/2}$ is a microscopic length).

It is also possible to Fourier transform eqs such as (6) and to obtain the static correlation functions

$$<v_\alpha\ (o)\ v_\beta\ (\underset{\sim}{r})> = C^{(1)}_{\alpha\beta}\ (r) + C^{(2)}_{\alpha\beta}\ (\underset{\sim}{r}) \qquad (7)$$

where (α, β = x, y). The $C^{(1)}$ term describes the splay-bend contribution and $C^{(2)}$ describes the twist-bend. $C^{(2)}$ behaves as in a conventional nematic, and decreases essentially like $\frac{1}{r}$ (8). But $C^{(1)}$ is very different :

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$$\sum_{\alpha} C^{(1)}_{\alpha\alpha}(\underset{\sim}{r}) = \sum_{q} \langle |v_{1q}|^2 \rangle \, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}$$

$$= \frac{T}{\pi E} \frac{1}{|z|^3} f\ (z^2/r_{\perp}\, b) \qquad (8)$$

The function f (u) is equal to 1 for $u \gg 1$, and is proportional to $u^{3/2}$ for $u \to 0$. If r is at a finite angle from the nematic axis, and if $r \gg b$, we have $u \sim r/b \gg 1$ and $C^{(1)}$ (r) decreases like $|z|^{-3}$. If $\underset{\sim}{r}$ is very nearly normal to $\underset{\sim}{n}_o$ $C^{(1)}$ varies like $|r|^{-3/2}$. Thus the $C^{(1)}$ correlations decrease much more rapidly than in a conventional nematic.

Let us now consider chains of finite length L (L M). We assume here that the chain ends tend to be distributed statistically, and do not coalesce into bound pairs (the latter possibility would correspond to chains whose effective length is a multiple of L). What is the splay constant K_1 in this case ?

Under a given splay, eq (2) still applied locally (except near the cahin ends). At a distance z from the midpoint of one chain (z measured along $\underset{\sim}{n}_o$) the dilation is then

$$- \frac{\delta\rho}{\rho} = z \text{ div } \underset{\sim}{n} \qquad (9)$$

and the corresponding energy/cm^3 is

$$\frac{1}{2} E \ \overline{\left(\frac{\delta\rho}{\rho}\right)^2} = \frac{1}{2} E \ \overline{z^2} \ (\text{div } n)^2$$

giving

$$\tilde{K}_1 = E \ \overline{z^2} = \frac{1}{12} \ E \ L^2 \qquad (10)$$

Eq (10) applies for wave vectors $\underset{\sim}{q}$ such that $q_z L \ll 1$. In the opposite limit, eq (10) crosses over into eq (5).

We conclude that measurements of $\tilde{K}_1/K_3 = \mu$ may help to discriminate between a rigid rod model (where $\mu \sim 1$) and a model based on partly flexible chains ($\tilde{K}_1/K_3 \gg 1$).

Finally, we must stress that these may be other ways to adjust to a splay - e.g. allowing each chain to wander somewhat around the local director $\underset{\sim}{n}$. This may be described by writting, instead of $\underset{\sim}{J} = \rho\, \underset{\sim}{n}$, the more complete form

$$J = \lambda\, \rho\, \underset{\sim}{n}$$

where λ (<1) measures the local level of alignment. In the free energy (3) we must than add a term $\frac{1}{2}\, G \left(\frac{\delta\lambda}{\lambda}\right)^2$. If $G > E$ our discussion is unchanged, but if $G < E$, the coupling to λ is dominant, and in all later equations (6, 10, etc.) we should replace E by G.

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