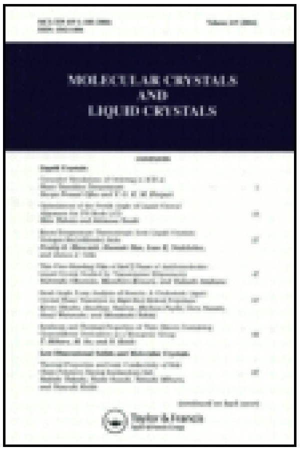

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The Implications of the Diffuse-Cone Model for Smectic A and C Phases and A-C Phase Transitions

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THE IMPLICATIONS OF THE DIFFUSE-CONE MODEL FOR SMECTIC A AND C PHASES AND A-C PHASE TRANSITIONS*

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ABSTRACT: The diffuse-cone model, developed on the basis of the existence of orientational disorder in smectic phases, is valid for all smectic A and C phases, and also, with appropriate modifications, for all other smectic phases. The fundamental angular parameter is not the optical tilt angle τ, but the preferred molecular tilt angle θ_m. This explains why τ does not follow the $(T_{A-C}-T)^{0.35}$ dependency predicted by De Gennes whereas θ_m does. The diffuse-cone model also explains why the tilt angle obtained from measurements of the smectic layer thickness will in general not be equal to τ, and thus invalidates arguments based on such differences which were used to support a particular structural model.

Definition of the Model

In two other papers,[1,2] we have developed a diffuse-cone model for the description of smectic A and C phases. In this

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model, the probability of finding in a monodomain a molecule in the direction (θ,ϕ)--where θ and ϕ are polar angles, θ being the angle between the molecular long axis and the normal to the smectic plane, and ϕ the angle between the projection of the molecular long axis on the smectic plane and a reference direction in this plane--is given by $\{P(\theta)P(\phi) + P(-\theta)P(180^{o} + \phi)\}\, d\theta d\phi$, where[2]

$$P(\theta) = c_1 |\sin\theta| \exp \{(aS)/(TV^2) \cos^2(\theta-\theta_m)\}$$

and

$$P(\phi) = c_2 \exp \{f(T) \cos^2\psi\}$$

with

$$\cos\psi = \cos^2\langle\theta\rangle + \sin^2\langle\theta\rangle \cos\phi.$$

In these equations, c_1 and c_2 are normalization factors, _a_ is a constant, $S = 1/2\langle 3\cos^2\theta - 1\rangle$ is the orier ational order parameter, _T_ is the absolute temperature, _V_ is the molecular volume, θ_m is the preferred angle between the molecular long axis and the layer normal, i.e., θ_m is the angle for which the energy of a molecule has its minimum value, f(T) is a function of temperature, and ψ is the angle between the directions $(\langle\theta\rangle, \phi)$ and $(\langle\theta\rangle, 0)$.

A formula* for f(T) has been suggested[2] and will be tested with experimental data. The main requirement is that

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* $f(T) = (bS_2)/(TV^2)$, where _b_ is a constant and $S_2 = \langle 2\cos^2\phi - 1\rangle$.

short-range orientational disorder, however, may be expected to be much less in A as well as in C phases, and this would apply to neighboring molecules within a layer as well as to neighboring molecules in adjacent layers.

θ_m as the Fundamental Angular Parameter

From a consideration of the diffuse-cone model it appears that the angle θ_m, the preferred molecular tilt angle, is the fundamental angular parameter. Angles like the optical tilt angle τ, or the tilt angle α calculated from the smectic layer thickness, are merely averages dependent upon a number of other, more basic, parameters, as is shown below.

The tilt angle α, for instance, is often calculated by comparing the layer thickness d(T) in the C phase at a given temperature T with the layer thickness d_A in the A phase at temperatures close to T_{A-C}. Assuming that $\alpha = 0$ in the A phase, this yields $\alpha(T) = \arccos\{d(T)/d_A\}$. From the diffuse-cone model it follows[1] that at each temperature $d = \ell(T)\langle\cos\theta\rangle$, where $\ell(T)$ is the molecular length at temperature T, and $\langle\cos\theta\rangle$ is calculated with the $P(\theta)$ given above. Thus it is clear that the temperature dependence of α is a function of the temperature dependence of several parameters: ℓ, S, V, and θ_m.

The optical tilt angle τ is the angle between the smectic layer normal and the average direction of the molecules. In

$f(T) = 0$ in the _A_ phase and $f(T) \neq 0$ in the _C_ phase. The temperature at which $f(T)$ becomes non-zero is the _A-C_ transition temperature T_{A-C}, where the material becomes optically biaxial. When $f(T) \neq 0$, $\phi = 0$ is the direction of overall tilt in the monodomain.

General Applicability

In the other papers[1,2] on the diffuse-cone model we have shown the applicability of the model to some specific _A_ and _C_ phases. Here we want to emphasize the _general_ applicability of this model. Earlier[3] we made distinctions between different kinds of _A_ and _C_ phases (A_1-A_4, C_1-C_4), and so one might suppose that the diffuse-cone model is meant only for some of these phases, and not for others. This is not so, however. The model is primarily based on the existence of orientational disorder in smectic _A_ and _C_ phases, and since this disorder is present in all phases, the model also applies to all phases.

Long-Range Versus Short-Range Order

The long-range orientational order in a monodomain is given by the parameter _S_, and we have shown[1,2] that common _S_ values for _A_ and _C_ phases correspond to quite large angular fluctuations around the average direction of the long axis. In _A_ phases, for instance, $\langle\theta\rangle$ appears to be about 20°. The

the diffuse-cone model, this angle is given by $\tau = \int\beta(\phi)P(\phi)d\phi$, with $\beta(\phi)$ = arc tan $(\tan\langle\theta\rangle \cos\phi)$, where $\langle\theta\rangle$ is calculated with the $P(\theta)$ given above. Thus, the temperature dependence of τ is also a function of the temperature dependence of several parameters: S, V, θ_m, and f(T).

Since θ_m, not τ or α, is the fundamental angular parameter, and since θ_m is the angle of minimum energy, we have proposed[2] that the $(T_{A-C}-T)^{0.35}$ temperature dependency, derived by De Gennes[4] on the basis of an energy argument, applies to θ_m and not to τ or α. This explains why measurements[5] of the temperature dependency of τ do not give the 0.35 exponent, whereas our analysis[2] of θ_m for an A-C transition did give the 0.35 exponent.

The difference in formulas for α and τ also explains why these two "tilt angles" in general will be different.[6]

Importance of Incorporating Orientational Disorder

In the first paper[1] on the diffuse-cone model we have already emphasized the importance of the model for the analysis of smectic layer-thickness data in smectic A phases. Conclusions which were drawn from these data without taking into account the influence of orientational disorder, and which led to models proposing interpenetration of molecules of adjacent layers, or kinking of the alkyl chains, or special tilted arrangements, were found to be without ground.

Now we find the same situation for studies of the tilt angle in smectic C phases. The diffuse-cone model indicates that comparisons of the exponent of the $(T_{A-C}-T)$ dependency of τ or α with the value of 0.35 predicted by De Gennes are irrelevant. Finding that τ and α are different from each other is merely confirming the obvious. Drawing conclusions[6] about the orientation of the molecules in the layers from these differences without making appropriate allowances for orientational disorder is premature.

The Diffuse-Cone Model in Various Phases

The formulas for $P(\theta)$ and $P(\phi)$, given above, revert back to the Maier-Saupe model[7] for the nematic phase if $f(T) = 0$ and $\theta_m = 0$. If $f(T) = 0$ but $\theta_m \neq 0$, they describe the smectic A phase. With $f(T) \neq 0$ and $\theta_m \neq 0$, they describe the smectic C phase. The other smectic phases can be described with the same $P(\theta)$ and appropriate modifications of $P(\phi)$. A phase with a hexagonal lattice in the smectic layer, for instance, would have a $P(\phi)$ with hexagonal symmetry. The appropriate symmetries of the currently known smectic phases have been described elsewhere.[8]

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