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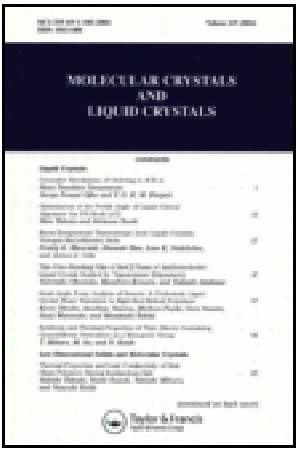

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# Translational Diffusion in Thermotropic Smectic Phases

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# Translational Diffusion in Thermotropic Smectic Phases

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*In this report the translational self-diffusion behavior of calamitic mesogens in smectic phases measured by means of NMR diffusometry will be reviewed. In particular the results reported demonstrate that translational diffusion in smectic phases is strongly dependent on molecular packing in the layered structure, but, in contrast with previous assertions seems to be only slightly affected by the clinicity of the phases, i.e., supporting the second order character of the phase transition going from the synclinic to the anticlinic structure typical in chiral Smectic C* phases.*

**Keywords:** Smectics; translational diffusion; diffusion anisotropy; NMR

## Introduction

Translational self diffusion in calamitic liquid crystals is one of the most representative features of the *liquid* behavior of this peculiar state of matter. Since the first advanced studies of chemico-physical properties in liquid crystalline phases, attempts of measuring molecular diffusion and in particular its anisotropy have been reported [1,2]. Among different techniques, NMR diffusometry seemed to be particularly suitable to investigate this property as it does not require the use of specific probes [3], as it is the case for ESR spectroscopy [4], quasi-elastic neutron scattering [1,5], fluorescence photobleaching [6] optical methods [7] or radio tracers [8], and can measure directly Brownian motions at the thermal equilibrium [9,10].

This technique is based on monitoring the trajectory of NMR active spins during a specific diffusion time by means of spatially dependent magnetic field pulses [11]. The basic experiment is depicted in Fig. 1.

After the first RF pulse, the gradient pulse encodes the spin along its direction making their Larmor frequency position dependent. The second RF pulse stores the magnetization (with its encoded position) along the Z axis of the laboratory frame and during the diffusion time $\Delta$, only spin lattice relaxation affects spins magnetization. The third RF pulse rotates the spins back in the transverse plane and the second gradient pulse "reads" the spins encoded position again. If spin do not move during $\Delta$, the two gradient pulses full

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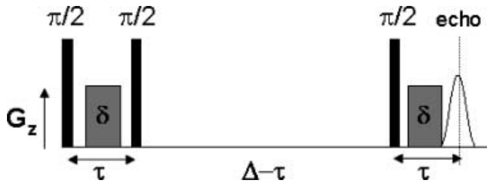


**Figure 1.** Stimulated Echo pulse scheme with pulsed field gradient of intensity $G_z$ and duration $\delta$. Echo is refocused after a time $\Delta + \tau$ after the first $\pi/2$ pulse.

compensate their effects, but if spins changed their positions, i.e., by means of brownian motions, the signal results attenuated [11].

The echo attenuation can be modeled considering a Gaussian distribution of spin displacements leading to the well known expression:

$$A\left(\gamma, \delta, \Delta, G_Z\right) \propto \exp\left[-\left(\gamma G_Z \delta\right)^2 \left(\Delta - \frac{\delta}{3}\right) D\right] \tag{1}$$

Where $\gamma$ is the giromagnetic ratio of the active nucleus.

Here the attenuation depends on spin relaxation, as shown by the second and third term, but also on translational diffusion along the gradient direction through the diffusion coefficient $D$, the gradient strenght $G_Z$ and the time delays $\delta$, gradient pulse duration, and $\Delta$, the previoulsy mentioned diffusion time. As far as $\tau < T_2$ and $\Delta < T_1$ diffusion along the gradient direction can be measured extracting the diffusion coefficient $D$ monitoring the echo attenuation as a function of the gradient strenght $G_Z$.

In principle hence the application of $^1$H NMR diffusometry to liquid crystals seems straightforward. However, it must be noted that the first results published seemed to be affected by a relevant uncertainty due to the intrinsic difficulties faced by the experimenters to measure diffusion in fast relaxing systems as liquid crystals. In this case the problem resides in the limited time of application of the pulsed gradients as transverse relaxation is a strongly competitive process for signal attenuation [9]. Recently different NMR experimental methodologies to measure translational diffusion have been reviewed [10]. Among different approaches, including the exploitation of very high static field gradients [12], sample alignment at peculiar orientations that strongly reduce dipolar interactions [13], the most reliable proved the combination of homonuclear dipolar decoupling and pulsed field gradient stimulated echo [14]. In particular it has been shown that the best efficiency for decoupling is obtained with the Magic Echo pulse scheme, as it provide good line-narrowing at relative low R.F. power irradiation and it does not scale down pulsed field gradient strenght as it is the case for other decoupling pulse schemes [10,14].

Going back to early measurements, despite their limitations, due mostly to the hardware available at that time, early results proved that, as envisaged by theoretical models, translational diffusion anisotropy has an opposite behavior moving from the nematic to the smectic phases in calamitic thermotropics [15]. This can be easily rationalized considering that while rod-like molecules move faster along the phase director in the orientationally ordered nematic phase, in smectic phases the formation of positionally ordered layers creates a potential barrier that slows down the out of plane diffusion making it slower that the in plane one. This behavior is schematically shown in Fig. 2.

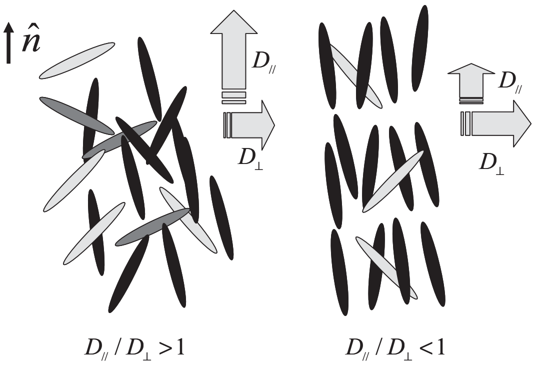


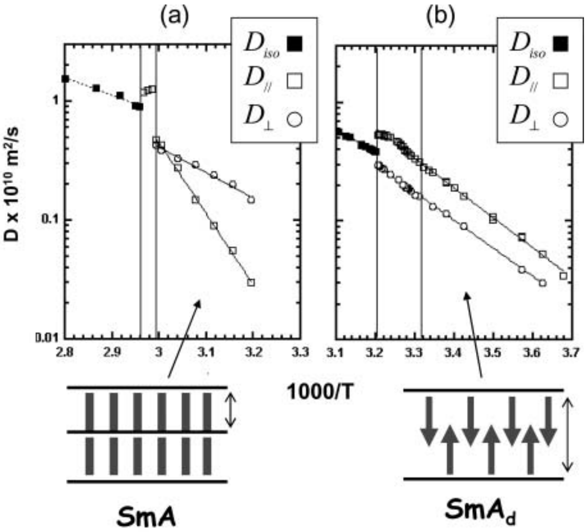
**Figure 2.** Sketch of translational diffusion in nematic (left) and smectic A (right) phases of a calamitic mesogen. In the nematic phase diffusion parallel to the phase director $D_{//}$ is faster than diffusion normal to the phase director $D_{\perp}$ because of the orientational order. In the smectic A phase the opposite is expected as smectic layers slow down out of plane diffusion $D_{//}$ leaving unaffected the in plane one $D_{\perp}$.

In the following, we will discuss in more details the molecular diffusion behavior considering more recent results showing that for smectic phases, the *scenario* is a little more complicated than the simple one depicted above.

### *Diffusion in the Smectic A Phases: Single Molecule vs Interdigitated layers*

Since early measurements in the nematic and smectic A phase, despite the lack of accuracy of the single diffusion coefficient measured, an estimation of diffusion anisotropy was reported, showing that, as expected in plane diffusion should be strongly influenced by the layered structure on smectic phases [15]. This is indeed the case for the translational diffusion of a smectogen OAB (4,4′-di-n-octyl-azoxybenzene) reported in Fig. 3 (on the left), measured by high static field gradient diffusometry under sample rotation for the Smectic A phase [12]. Eventhough direct evaluation of diffusion anisotropy in the nematic phase was not possible, due to fast director re-orientation under sample rotation, it can be assumed to be $D_{//}/D_{\perp} > 1$ as it seems to be a quite general behavior for calamitic nematics [10], while it is evident that the a first order transition occurs from N to SmA and the diffusion anisotropy turns to $D_{//}/D_{\perp} < 1$, accounting for a strongly hindered out of plane diffusion due to a well organized smectic structure [12].

It is however interesting to notice that translational diffusion behavior can be quite different as the smectic phase packing changes. This different behavior was already pointed out by Oishi and Miyajima that reported diffusion anitropy change as a consequence of a chemical substitution [13]. The substitution of a cyano-group as polar moiety along the long molecular axis promotes the formation of a partially interdigitated phase $\mathrm{SmA_d}$ that seems to preserve a relevant nematic-like behavior in terms of diffusion properties. This is quite well shown in Figure 3 (on the right), where accurately measured cyanobiphenyl anisotropic translational diffusion in the nematic and smectic A phase is reported. In the $\mathrm{SmA_d}$ phase of 8CB (n-4-octyloxy-4′-cyanobiphenyl), the diffusion anisotropy remains nematic-like across the whole temperature range, eventhough a change in the activation energy occurs [14]. In particular, for 8CB, if the activation energy is calculated fitting the



hindered out of plane diffusion due to a well organized smectic structure [12].

**Figure 3.** Translational self diffusion measured by means of NMR Diffusometry on the smectogens 4,4′-di-n-octyl-azoxybenzene (a) and n-4-octyloxy-4′-cyanobiphenyl (b); details on the measurements are reported in references [12] and [14] respectively. The lines represent the Arrhenius fittings of the data in the different phases. The two mesogens present the same phase behavior but a different molecular packing for respective smectic A phases. This affect the translational diffusion anisotropy as discussed in the text.

temperature dependence with the well known Arrhenius equation:

$$D(T) = D_{\infty} \exp(-E_i^a E_i^a / RT) \tag{2}$$

with i = // or $\perp$, parallel of perpendicular diffusion is considered respectively, it turns out that in the nematic phase $E_{\perp}^a = 45\,\mathrm{KJ/Mol}$ does not change as phase change occurs. As the activation energy of $D_{//}$ is considered instead, the fitting of the diffusional behavior in the nematic and smectic A phase gives activation energies $E_{//}^a = 42\mathrm{KJ/Mol}$ and $E_{//}^a = 48\,\mathrm{KJ/Mol}$ in the nematic and in the SmA$_\mathrm{d}$ interdigitated phase, respectively. Despite the approximation of fitting the parallel diffusion coefficient in the nematic phase as a simple Arrhenius equation, if the results are compared, it turns out that an inversion of the activation energy anisotropy occurs, however a diffusional *nematic like* behavior is preserved along the whole SmA$_\mathrm{d}$ phase range of stability [13,14].

It seems that a strong intermolecular interaction of the cyano polar groups, pointing along the long axis of the calamitic mesogens inhibits the formation of well defined layers. This can be also related to the small translational order parameter determined for cyanobiphenyls by means of small-angle X ray scattering [16] and to the absence of higher order diffraction patterns [17]. Moreover it is well known that mesogens exhibiting SmA$_\mathrm{d}$ phase also present re-entrant Nematic phase under high pressure [18].

In terms of translational diffusion it's interesting to notice that theoretical models that consider the SmA phase as a nematic with a periodic potential barrier along the phase director to mimic the layer structure works quite well for the SmA$_\mathrm{d}$ [19], but it doesn't fit as well the "normal" SmA phase. In the former case in fact perpendicular diffusion coefficient $D_{\perp}$ monotonously decrease with no variation crossing the N-SmA transition, keeping its *nematic behavior*, while $D_{//}$ slightly changes [14]. However, in the case of monolayer SmA it seems that besides the expected variation of $D_{//}$, also $D_{\perp}$ changes a the N-SmA. This has been shown also by simulations considering the phase diagram of a Gay-Berne mesogen, where discontinous behavior and an increase of Arrhenius activation energy are found for both out of plane and in plane diffusion crossing the nematic and smectic A phases [20].

To our knowledge, a clear theoretical explaination of the diffusional behavior of the smectic A phase in terms different molecular aggregation has still to be reported. Of course the different entropic contributions to phase stabilitity should be taken into account for a detailed comparison. In particular, the different behavior of the two phases under high pressure indeed depends on entropic factors [18], but in a very simple picture limited to dipole-dipole intermolecular interactions the interdigitated structure of $\mathrm{SmA_d}$ phase compared to the single layer SmA seems to promote head to head intermolecular interactions in respect with side to side ones that stabilize smectic molecular packing. These lateral interactions may be strong to affect in plane diffusion also, while the effect is negligible in the $\mathrm{SmA_d}$ that preserves its *nematic like* behavior also in the smectic phase.

### *Diffusion in SmC* Phases: Synclinic vs Anticlinic Molecular Organization*

Quite recenlty the interest on novel ferro-electric chiral smectic phases also involved their translational diffusion properties. In particular first evaluation of the out of plane diffusion by means of angular dependent $^2$H NMR spectra analisys demonstrated that quite slow diffusion process along the helical pitch, with diffusion coefficient of about $10^{-13}$ m$^2$/s occurs in anti-ferroelectric phases [21]. A first explaination of this relevant slow down, in respect with typical diffusion coefficient measured in smectic phase, i.e., $10^{-11}$ m$^2$/s invoked a high energy barrier due to the anticlinic arrangement of molecules in that phase [21].

Further investigations, carried out be means of $^2$H NMR exchange spectroscopy on synclinic ferro-electric smectic phases, seemed to confirm this abrupt change in diffusion that was justified considering a change from the ferro-electric synclinic structure to the anti-ferroelectric anticlinic one [22].

More recently, however, $^1$H NMR diffusometry was applied to measure both in plane and out of plane diffusion in smectic phases formed by chiral smectogens [23,24]. The obtained result for the smectogen (S)-2-methylbutyl-[4′-(4″-heptyloxyphenyl)-benzoyl-4-oxy-(S)-2-((S)-2′)-benzoyl)-propionyl)]-propionate (ZLL7/*) are reported in Fig. 4 as an example of the results obtained.

From the results shown in Fig. 4 it is quite clear that the clinicity of the phases has a little effect on the diffusional behavior of mesogenic molecules. The out of plane diffusion is much slower that the in plane one starting from the smectic A phase and this behavior characterizes the whole mesophasic range.

The discrepancy with previously reported results is quite evident in the SmC* ferro-electric phase with a difference of more than one order of magnitude [22], while a good agreement is present in the anti-ferroelectric one. A possible explaination can be found in the way diffusion coefficient is evaluated from NMR spectroscopy, where the estimation of diffusion is considered as a function of the variation of the azimuthal angle $\phi$ as molecules move in space [21,22]. In the anti-ferroelectric phase the variation is relevant moving from one layer to the other giving rise to a 180° jump that can be correlated to a slow diffusion process [21]. On the other hand, in the ferro-electric phase, the angle $\phi$ changes smoothly along the helical axis with pitch lengths of hundreds of nanometers. As translational

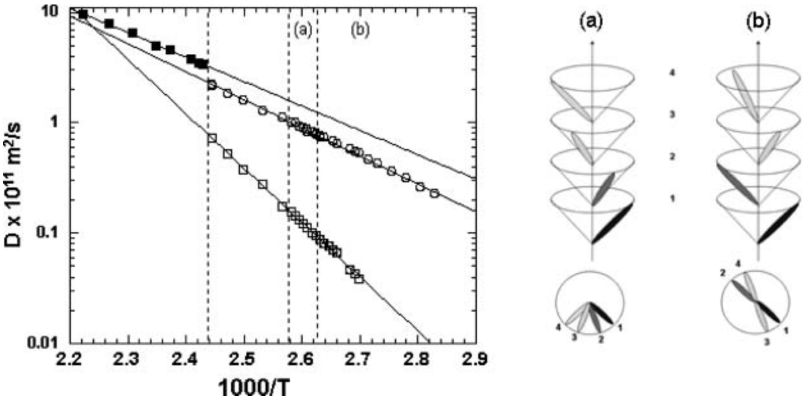


**Figure 4.** Translational diffusion coefficients measured in the isotropic (■) and smectic phases, parallel (□) and perpendicular (○) to the layer normal of the ferroelectric smectogen ZLL7/*. On the right a schematic representation of synclinic (a) and anticlinic (b) tilted structures is also reported for comparison. The anticlinic arrangement consists of two intercalated ferroelectric helices shifted by 180°.

diffusion in not a simple uni- dimensional process, changes of azimuthal angles can occur either as a consequence of out of plane and in plane diffusion as no long range polar order is present in smectic planes. Hence contribution to $\phi$ variations can depend also on the faster in plane translational diffusion, leading to an over-estimation of the out of plane diffusion process.

### *Rotational and Translational Activation Energies*

Another interesting feature that we think it is worth to notice concerns the Arrhenius activation energies of diffusional processes as compared to the anologues determined for single molecule rotational diffusions. An example of this comparison for some selected mesogens is reported in Table 1.

Looking at the table, despite the missing data, for SmA phase rotational activation energies are quite similar to the in plane diffusion one, while $E_{aT}(\perp)$ is always much

**Table 1.** Arrhenius activation energies of rotational ($E_{aR}(//)$, $E_{aR}(\perp)$) and translational ($E_{aT}(//)$, $E_{aT}(\perp)$) diffusion processes of some smectogens in their smectic A phases. HAB and 8CB rotational energies data reported in references [26] and [27] respectively.

| Mesogen | $E_{aR}(//)$ | $E_{aR}(\perp)$ | $E_{aT}(//)$ | $E_{aT}(\perp)$ |
|---|---|---|---|---|
| HAB [26] | 25 | 39.2 | 90 | 35 |
| OAB [26] | 30 | 30 | 111 | 41 |
| 8OCB [27] | 77 | 43 | 45.8 | ? |
| 8CB | ? | ? | 48 | 42 |
| 10B1M7 [24] | 40 | 40 | 101 | 45 |
| 11BE1M7 | 35 | 40 | ? | ? |
| ZLL7/* [24] | ? | ? | 108 | 56 |
| ZLL8/* [24] | ? | ? | 92 | 54 |

higher. This is in agreement with a roto-translational nematic like behavior of molecules in the smectic A planes, while higher value of out of plane diffusion energy accounts for the ordered layered structure. In the case of 8OCB, eventhough the rotational energy values seems not realistic [27], activation energy are all quite similar also including the out of plane diffusion.

A different behavior occurs in the SmC* phase instead. In particular the value of $E_{aR}(//)$, the activation energy of mesogens around their long molecular axis increases in respect of the other activation energies. In this case it seems that the tilted director affects rotational diffusion [28], leaving practically unchanged the translational one [24]. These similarities in the activation energies values can be easily explained considering that rotational and translational dynamics are strongly correlated.

## Conclusions

Translational diffusion in smectic phases formed by thermotropic liquid crystals is reviewed with particular attention to the effect of the supramolecular structure present in these phases. In particular we can point out that features such as tilt angle and clinicity play a little role on molecular translation, while affect relevantly single molecule rotations. On the other hand, the different packing of the layered structure, i.e., single layer or interdigitated, significantly affects the three dimensional translational diffusion processes leaving basically unchanged molecular rotational diffusion within the smectic layers.

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