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Local dynamics around structural order-disorder phase transitions

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Résumé. — La dynamique locale autour d'une transition de phase structurale de type ordre-désordre est étudiée en particulier en analysant l'influence des fluctuations collectives prétransitionnelles sur la dynamique individuelle. Nous utilisons les résultats expérimentaux de résonance magnétique nucléaire du proton et de diffusion incohérente de neutrons du p-terphényle. La combinaison des deux techniques donne une description plus complète de la dynamique locale critique et non-critique dans de tels systèmes et confirme notre première interprétation des résultats R.M.N., différente de celle d'autres auteurs.

Abstract. — Local dynamics around an order-disorder structural phase transition is studied in particular by analyzing the influence of pretransitional collective fluctuations on individual dynamics. We use experimental results from proton nuclear magnetic resonance and incoherent neutron scattering on p-terphenyl. The combination of both techniques yields a more complete description of the local critical and non-critical dynamics in such systems and confirms our first interpretation of the N.M.R. results, different from that of other authors.

1. Introduction.

The collective aspect of pretransitional fluctuations around structural phase transitions has been extensively studied. In parallel, much attention was given to the way these critical fluctuations modify local properties such as individual relaxational functions, phonon density of states, Debye-Waller factor, heat capacity, etc. The clearest experimental evidence of local critical dynamics usually comes from resonance techniques. In this paper we present an analysis of a molecular crystal around its order-disorder phase transition discussing in parallel Nuclear Magnetic Resonance and Incoherent Neutron Scattering results. The combined use of both techniques actually appears necessary to elucidate both the local critical and non-critical dynamics in such systems.

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This paper is divided in five parts. First we recall the formalism used to describe critical dynamics around an order-disorder phase transition. In the second part we briefly review the experimental techniques. In the following two parts local dynamics is analysed in the absence of critical phenomena in the disordered and in the ordered phase, respectively. The last part deals with local critical dynamics in the neighbourhood of the phase transition.

Experimental techniques that analyse local dynamics probe an autocorrelation function of the local variable $s_i(t)$:

$$g(t) = \frac{1}{N} \sum_{\text{sites}} \langle s_i(t) s_i(0) \rangle = \langle s(t) s(0) \rangle . \quad (1)$$

In the simplest case of dynamical disorder in a double-well potential, the local variable $s_i(t)$ may be defined as a pseudo-spin variable (± 1). The time average of this critical variable $\overline{s_i}$ can be directly related to the order parameter η :

$$\eta = \frac{1}{N} \sum_{\text{sites}} \overline{s_i} e^{i\mathbf{q}_c \cdot \mathbf{r}_i} \quad (2)$$

where \mathbf{q}_c is the critical wavevector defining the static periodicity of the ordered phase. Pretransitional effects around such phase transitions are associated with the formation of short range ordered clusters of finite lifetime. In both phases they correspond to collective fluctuations of the local order parameter around its mean value. A description of the spatial and time variation of these fluctuations is possible by introducing the Fourier components $s_{\mathbf{q}}(t)$ of the local variable :

$$s_i(t) = \sum_{\mathbf{q}} s_{\mathbf{q}}(t) e^{i\mathbf{q} \cdot \mathbf{r}_i} \quad (3)$$

The relaxational collective fluctuations are governed by :

$$\langle s_{\mathbf{q}}(t) s_{-\mathbf{q}}(0) \rangle = \langle |s_{\mathbf{q}}|^2 \rangle \cdot e^{-t/\tau_{\mathbf{q}}} \quad (4)$$

where $\langle |s_{\mathbf{q}}|^2 \rangle$ is the mean square amplitude and $\tau_{\mathbf{q}}$ the relaxation time of the critical fluctuation of wavevector \mathbf{q} . On approaching the transition, the mean square amplitude becomes larger and larger (divergence of the static susceptibility, i.e. of the correlation lengths ξ which characterize the spatial range of the critical fluctuations at \mathbf{q}_c) and the latter live longer and longer (critical slowing down of the fluctuations, i.e. divergence of the correlation time τ_c which characterizes the lifetime of the critical fluctuations at \mathbf{q}_c). Coherent neutron scattering appears to be the best suited technique for the study of the collective aspect of the pretransitional phenomena around structural phase transitions measuring the pair correlation function $\langle s_i(t) s_j(0) \rangle$ [1-3]. Let us note that the number of direct observations, by this technique, of critical slowing-down of the fluctuations around order-disorder phase transitions remains small [4-6].

The general expression of the autocorrelation function may be given by a summation over the Brillouin zone of the collective fluctuations of wavevector \mathbf{q} :

$$g(t) = \frac{1}{N} \sum_{\text{sites}} \langle s_i(t) s_i(0) \rangle = \frac{1}{N} \sum_{\mathbf{q}} \langle s_{\mathbf{q}}(t) s_{-\mathbf{q}}(0) \rangle . \quad (5)$$

The spectral density of the autocorrelation function $G(\omega)$, Fourier transform in time of $g(t)$ is normalised to unity :

$$\int d\omega G(\omega) = g(0) = 1. \quad (6)$$

Up to now, almost all the studies of local critical dynamics have been carried out by using resonance methods such as N.M.R., N.Q.R., E.P.R. [7-10]. These techniques are sensitive to slow fluctuations and thus have been very fruitful in observing and analysing these pretransitional local critical dynamics. However, the problem remains quite complex because in such cases the spectral density of the fluctuations has a very complicated energy shape. Resonance methods only allow the analysis of a very limited number of points (the resonance frequencies) of this function, whereas its observation as a whole would be necessary. By its principle incoherent neutron scattering allows the observation of the complete spectral autocorrelation function [11-15]. Several conditions must be fulfilled however to obtain this result and up to now this technique was seldom applied for analysing local critical dynamics. The most elaborate work concerning an order-disorder transition has been done on ammonium chloride, with a description of the single particle dynamics in both phases [16-18]. Unfortunately, as we will see later, the superposition of different types of motions makes the problem complicated, and may perhaps have hidden the effect of the pretransitional fluctuations. We have therefore retained a compound where no such a problem exists : p-terphenyl. This compound is particularly suited for the study of local critical dynamics for several other reasons :

- the geometry of the molecular motion is simple,
- it exhibits an almost continuous structural phase transition with large pretransitional phenomena, previously studied by coherent neutron scattering,
- total or selectively deuterated compounds are easily obtained as large single crystals which permits all types of experiments to be made.

p-terphenyl is made of three phenyl rings connected by simple C-C bonds. In the gaseous and the liquid state, the repulsion of ortho hydrogen atoms induces a non-planar conformation of the molecule. In the crystal X-ray and neutron diffraction experiments have revealed a doubly peaked probability density function for the phenyl rings, associated to a double-well potential for the conformations of p-terphenyl [19]. These non planar conformations may be described by the torsional angles of the phenyl rings relative to the mean planar conformation. These angles are about $\pm 13^\circ$ for the central ring of p-terphenyl and $\mp 5^\circ$ for the external rings. In the low temperature phase, the molecules stabilize in one of the two non-planar conformations and the critical wavevector is $(1/2, 1/2, 0)$ [19-20]. Our previous results concerning local dynamics in this compound have been described in references [21-24].

2. Experimental techniques.

The two techniques which will be very briefly reviewed here are Incoherent Neutron Scattering (I.N.S.) and Nuclear Magnetic Resonance (N.M.R.). Both are extensively presented in books or review articles [7-12, 25-26].

2.1 INCOHERENT NEUTRON SCATTERING. — It is well known that incoherent scattering of neutrons from hydrogen nuclei results from spin incoherence between the neutron and the scatterer. The experimental separation of coherent from incoherent neutron scattering in molecular compounds with a high concentration of hydrogen atoms is not trivial but somewhat facilitated due to the very large incoherent scattering cross-section of the protons.

The description of the « individual dynamics » of the atom is performed by introducing the Van Hove autocorrelation function, $g_a(\mathbf{r}', t)$, Fourier transform in space of the intermediate scattering function $I_{\text{inc}}(\mathbf{Q}, t)$. The total incoherent intensity is the sum of the intensities of the individual incoherent scatterers. The intermediate incoherent neutron scattering function reads :

$$I(\mathbf{Q}, t) = \frac{1}{N} \sum_{i=1}^N \langle e^{i\mathbf{Q} \cdot \mathbf{r}_i(t)} e^{-i\mathbf{Q} \cdot \mathbf{r}_i(0)} \rangle . \quad (7)$$

Let us now consider the simple case of a relaxational motion of the atoms in a double-well potential, whose minima for each atom are defined by the vectors $-\mathbf{a}$ and $+\mathbf{a}$. The local pseudo-spin variable may here be defined as :

$$\begin{aligned} s_i &= +1 \text{ if } \mathbf{r}_i = +\mathbf{a} \\ \text{and} & \\ s_i &= -1 \text{ if } \mathbf{r}_i = -\mathbf{a} . \end{aligned} \quad (8)$$

The intermediate incoherent scattering function for this relaxational process is then :

$$I_{\text{inc}}^{\text{R}}(\mathbf{Q}, t) = \frac{1}{2} [1 + \cos(2\mathbf{a} \cdot \mathbf{Q})] + \frac{1}{2} [1 - \cos(2\mathbf{a} \cdot \mathbf{Q})] \cdot \left[\frac{1}{N} \sum_i \langle s_i(t) s_i(0) \rangle \right] . \quad (9)$$

The first time-independent, term, is the well-known Elastic Incoherent Structure Factor (E.I.S.F.) $A_0(\mathbf{Q})$. All the information concerning the dynamics is included in the pseudo-spin variable autocorrelation function $g(t)$ defined by equation (1). The complete expression of the incoherent scattering function is :

$$S_{\text{inc}}(\mathbf{Q}, \omega) \sim e^{-\frac{\hbar\omega}{2kT}} e^{\langle U \cdot \mathbf{Q}^2 \rangle} \{ S_{\text{inc}}^{\text{R}}(\mathbf{Q}, \omega) + S_{\text{inc}}^{\text{inel}}(\mathbf{Q}, \omega) \} . \quad (10)$$

The first term is the detailed balance factor, the second term is the Debye-Waller factor. $S_{\text{inc}}^{\text{R}}(\mathbf{Q}, \omega)$ is the time Fourier transform of the reorientational intermediate scattering function $I_{\text{inc}}^{\text{R}}(\mathbf{Q}, t)$. The last term corresponds to inelastic processes and is directly related to the scatterer-weighted phonon density of states. In the case of an order-disorder phase transition the local dynamics mainly affects the reorientational scattering function $S_{\text{inc}}^{\text{R}}(\mathbf{Q}, \omega)$. Let us mention here that in the displacive case, not further treated in this paper, $A_0(\mathbf{Q})$ and consequently $I_{\text{inc}}^{\text{R}}(\mathbf{Q}, t)$ is \mathbf{Q} -independent and always equal 1. Local critical dynamics, which in the displacive case results from a softening of a phonon branch, will modify $S_{\text{inc}}^{\text{inel}}(\mathbf{Q}, \omega)$ and consequently the associated Debye-Waller Factor.

2.2 NUCLEAR MAGNETIC RESONANCE. — In this paper we will only consider nuclear magnetic resonance of nuclei having spin $I = 1/2$ because this technique is the closest to incoherent neutron scattering. In molecular solids, dipolar interactions yield the main broadening of the resonance lines. Van Vleck [27] has shown that in the rigid lattice the second moment of this line is directly related to the geometrical arrangement of the spins i, j in the crystal :

$$M_2^{\text{R}} = \frac{3}{2N} \gamma^2 h^2 I(I+1) \sum_{i=1}^{N-1} \sum_{j>i}^N \left[\left(\frac{3 \cos^2 \theta_{ij} - 1}{|\mathbf{r}_{ij}|^3} \right) \right]^2 \quad (11)$$

θ_{ij} is the angle between the vector \mathbf{r}_{ij} and the direction of the applied magnetic field.

Through the time dependence of the interactions, the motions narrow the resonance line when their characteristic frequencies are of the same order of magnitude as the frequency strengths of the dipolar interaction. The reduction of the second moment of the line is $\Delta M_2 = M_2^R - \overline{M}_2$ with :

$$\overline{M}_2 = \frac{3}{2N} \gamma^2 h^2 I(I+1) \sum_{i=1}^{N-1} \sum_{j>i}^N \overline{[(3 \cos^2 \theta_{ij} - 1) \cdot |r_{ij}|^{-3^{\text{motion}}}]^2} \quad (12)$$

The information concerning the spectral function of the thermal fluctuations of the crystal is obtained by measuring the spin-lattice relaxation rate T_1^{-1} . This value is proportional to the transition probability W_{km} between the states k, m of the system of the spins, resulting from the interaction with the lattice :

$$W_{km} = \frac{1}{h^2} \int dt e^{-i(\omega_m - \omega_k)t} G_{mk}(t). \quad (13)$$

$G_{mk}(t)$ is the autocorrelation function of the perturbing time dependent part of the dipolar interaction Hamiltonian $\mathcal{H}(t)$:

$$G_{mk}(t) = \langle \mathcal{H}_{mk}(t) \mathcal{H}_{mk}(0) \rangle = |\mathcal{H}_{mk}|^2 j(t) \quad (14)$$

$J(\omega)$, time Fourier transform of $j(t)$, is the spectral density for the involved autocorrelation function of the variables coupling the nuclear spins and the lattice.

In conclusion of this experimental presentation, one sees the analogy between the dynamical spectral autocorrelation function $G(\omega)$ defined for I.N.S. and $J(\omega)$ defined for N.M.R.. However, one has to keep in mind that $G(\omega)$ probes the local dynamics of a given nucleus whereas $J(\omega)$ probes the local dynamics of vectors connecting a given nucleus with the interacting nuclei interacting with it.

3. Local dynamics in the disordered phase far above T_C .

In the high temperature phase, the mean value $\langle \eta \rangle$ of the order parameter is zero. Furthermore, the fluctuations of the order parameter around this mean value are also assumed to be negligible. This is the case around a first order phase transition or around a second order phase transition far above the transition temperature T_C . Then the motion of one molecule in its double-well potential is not correlated with the motion of its neighbours. The description of such non dispersive dynamics may be done in real space. In the case illustrated in figure 1 of a relaxational process between two equivalent sites with a mean residence time τ_R on each site, the calculation of the eigenvalues of the equation of motion gives the well known expression for the dynamical part of the autocorrelation function $g(t)$:

$$g(t) = e^{-\frac{2t}{\tau_R}} \quad (15)$$

The incoherent scattering function is then composed of an elastic peak and a quasielastic line of Lorentzian shape with a half width at half maximum $2/\tau_R$.

$$S_{\text{inc}}^R(\mathbf{Q}, \omega) = A_0(\mathbf{Q}) \cdot \delta(\omega) + [1 - A_0(\mathbf{Q})] \cdot G(\omega) \quad (16)$$

with

$$G(\omega) = \mathcal{L} \frac{2}{\tau_R}(\omega) = \frac{1}{\pi} \frac{2/\tau_R}{(2/\tau_R)^2 + \omega^2}. \quad (17)$$

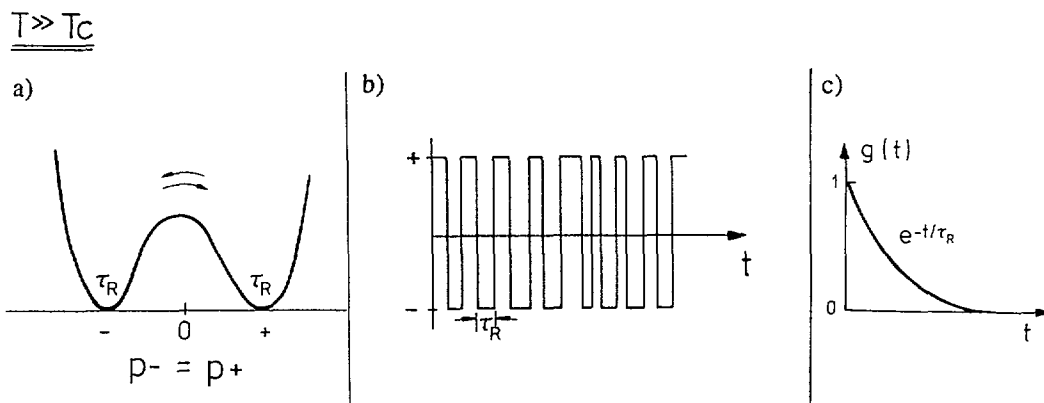


Fig. 1. — Random relaxational motion in a double-well potential with mean residence time τ_R in a well. Schematic representation a) of the double well potential, b) of the time evolution of the conformation of the molecule and c) of the autocorrelation function.

The I.N.S. experimental study of p-terphenyl has been performed at the Institut Laue Langevin combining the time of flight spectrometer IN5 and the high resolution backscattering spectrometer IN13. In order to amplify the decrease in Q of the EISF, a selectively deuterated p-terphenyl $C_6D_5-C_6H_4-C_6D_5$ was synthesised. Diffraction and coherent neutron scattering studies have shown that this compound presents a similar phase transition as $C_{18}H_{14}$ or $C_{18}D_{14}$. The only difference observed (isotopic effect) concerns the transition temperature ($T_C = 193.3$ K for $C_{18}H_{14}$, $T_C = 185.3$ K for $C_6D_5-C_6H_4-C_6D_5$ and $T_C = 178$ K for $C_{18}D_{14}$).

Figure 2 presents the I.N.S. results measured on the spectrometer IN5 above 245 K, that is, far above the transition temperature of the selectively deuterated p-terphenyl. At these temperatures, the random reorientational model gives a very good description of these data. From this analysis, the reorientation rate $1/\tau_R$ was found to follow an Arrhenius law. The activation energy, associated to the height of the barrier of the double-well potential is $E_a = 1.1$ kcal/mole [24]. At room temperature the reorientation rate $1/\tau_R$ equals 84 GHz in this compound.

The same kind of information may be extracted from a proton Nuclear Magnetic Resonance Study. This was performed using a Bruker SXP spectrometer operating at the Larmor resonance frequency $\nu_L = 90$ MHz. The spin-lattice relaxation times have been measured by the saturation 90° - pulse method. The second moment M_2 of the resonance line was derived from the free induction decay by a least squares fit. All measurements were performed on powdered samples. Far above T_C , the random reorientational motion of the molecule induces the same kind of motion for the proton-proton vectors which carry the dipolar interaction :

$$j(t) \sim e^{-t/\tau} \quad (18)$$

In the case of p-terphenyl $\tau^{-1} = \tau_R^{-1}$ for a pair of protons of the same molecule whereas $\tau^{-1} = 2 \cdot \tau_R^{-1}$ for pairs of protons of different molecules. Considering the well known B.P.P. model, the spin-lattice relaxation rate is simply expressed as a function of the spectral density $J(\omega)$ at the Larmor resonance frequency ω_L .

$$T_1^{-1} = \frac{2}{3} \gamma^2 \Delta M_2 \cdot [J(\omega_L) + 4J(2\omega_L)]. \quad (19)$$

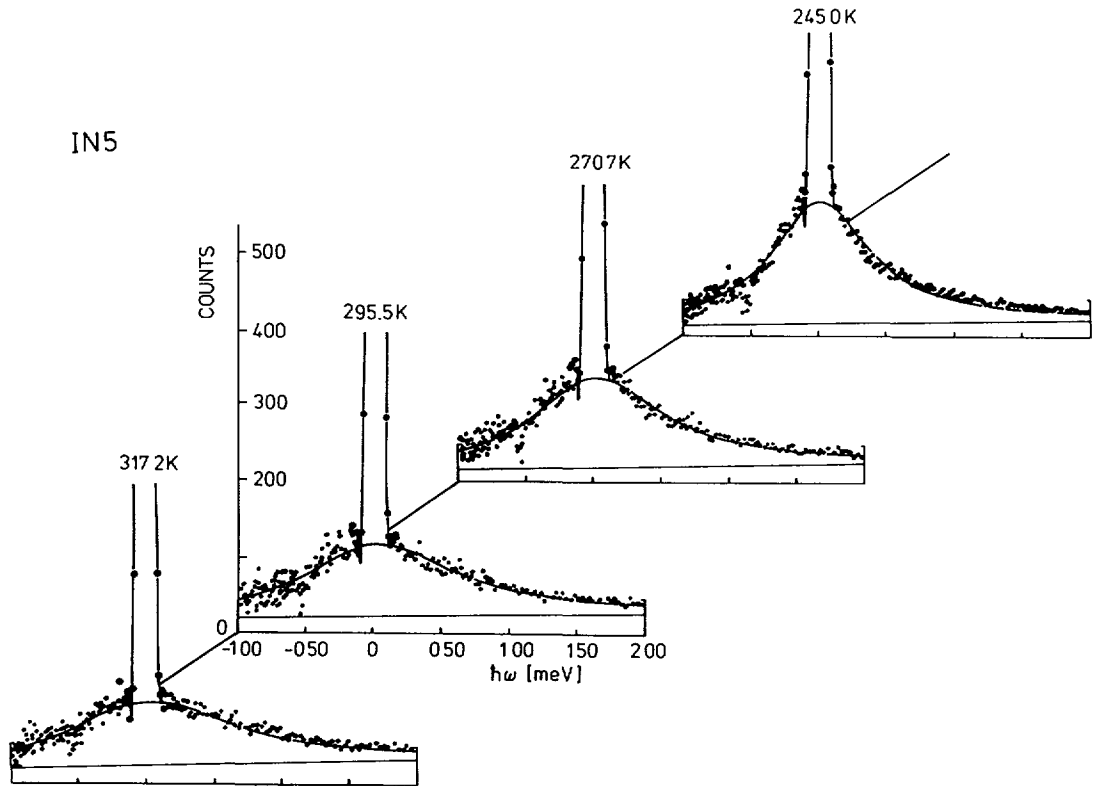


Fig. 2. — Fit of the incoherent scattering spectra (points) with the model of random relaxational jump motion in a double-well potential. These results were obtained on IN5 on powdered p-terphenyl C_6D_5 - C_6H_4 - C_6D_5 at a scattering angle $\phi = 96^\circ$ ($Q_0 = 1.5 \text{ \AA}^{-1}$).

In the fast motion limit defined by $1/\tau \gg \omega_L$, the spin-lattice relaxation rate T_1^{-1} is directly proportional to τ and thus follows the same Arrhenius law :

$$T_1^{-1} = \frac{10}{3} \cdot \gamma^2 \Delta M_2 \cdot \tau . \quad (20)$$

Such a behaviour is observed in p-terphenyl in the high temperature phase above 240 K, as illustrated by the straight line in figure 3. The activation energy is $E_a = 1.05 \text{ kcal/mole}$, in very good agreement with I.N.S. results. The difference between the second moment of the resonance line in the completely ordered phase and in the disordered phase is $\Delta M_2 = 2.2 G^2$ (Fig. 6). Using this value, the characteristic rate $1/\tau$ is found to be equal to 160 GHz, at room temperature. This value is in rather good agreement with that found by incoherent neutron scattering, keeping in mind the differences pointed out above. It should be mentioned here that this interpretation [21] is different from the interpretation given by other authors [28, 9-10]. As we will see later, these authors assume that critical dynamics dominates the spin-lattice relaxation process in the whole high temperature phase. By analogy with magnetic systems, where indeed individual Arrhenius processes do not exist, these authors did not consider the molecular jumps.

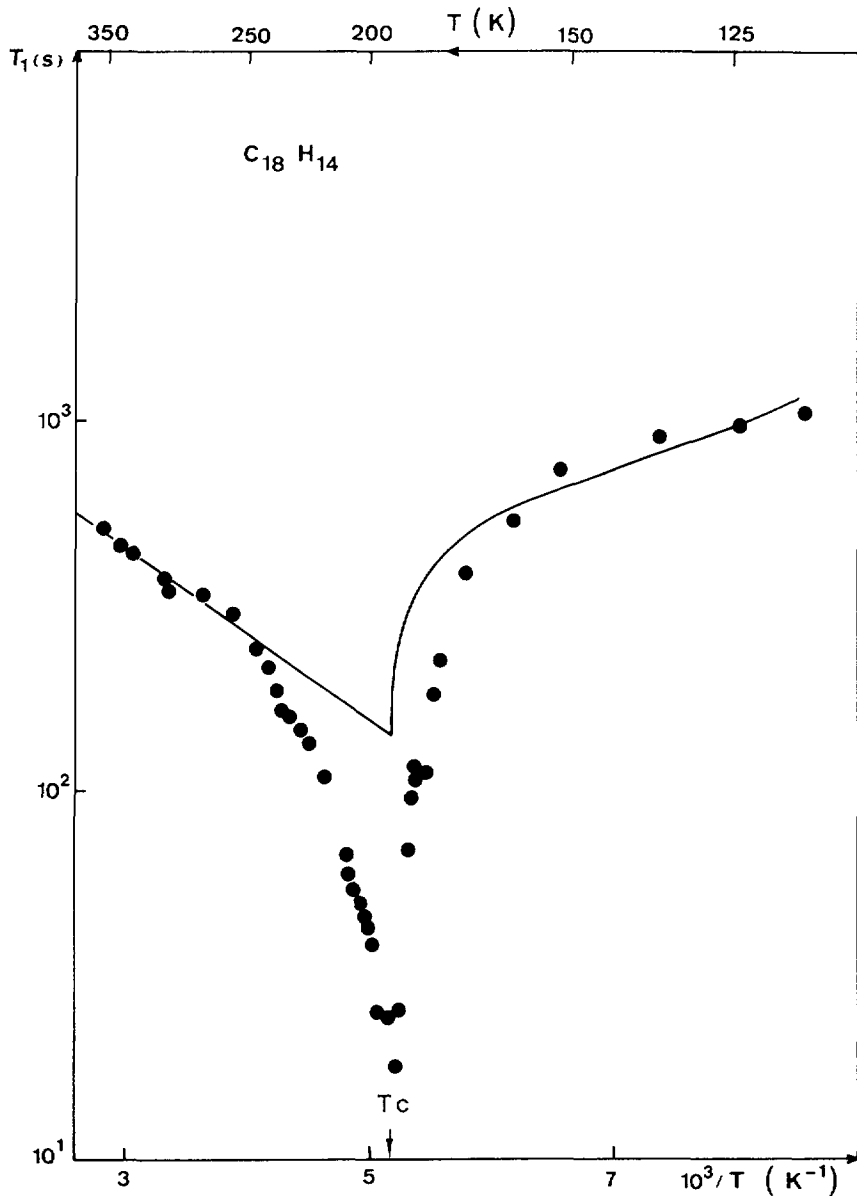


Fig. 3. — Semi-logarithmic plot of the ^1H N.M.R. spin-lattice relaxation time T_1 versus inverse temperature, measured at $\nu_L = 90$ MHz in p-terphenyl $\text{C}_{18}\text{H}_{14}$. The line is the theoretical behaviour of T_1 for a model which neglects local critical dynamics.

4. Local dynamics in the ordered phase far below T_c .

The low temperature phase corresponds to long range order at infinite time, as illustrated in figure 4. This phase may be described in terms of an asymmetric local potential (Fig. 4a). The mean probabilities p_+ and p_- to find the molecule in the (+) and (-) well, respectively, are directly related to the mean residence times τ_+ and τ_- in these wells :

$$\frac{p_+}{p_-} = \frac{\tau_+}{\tau_-} \quad (21)$$

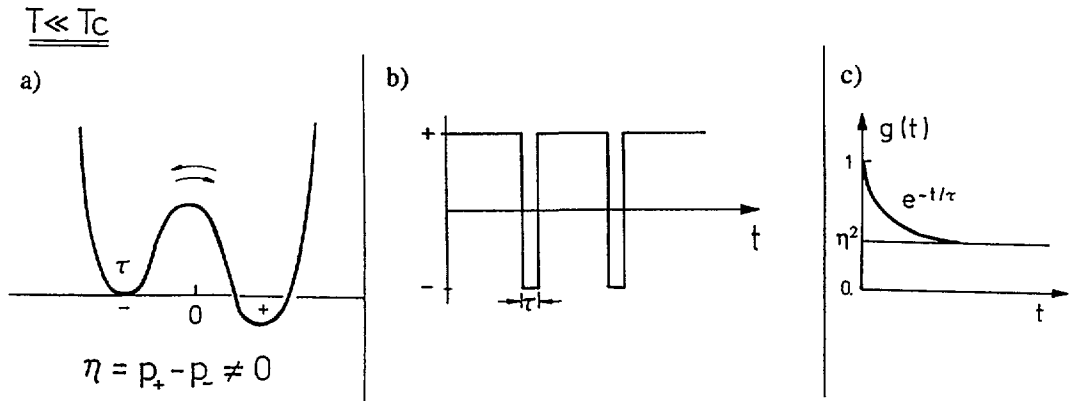


Fig. 4. — The low temperature phase, neglecting the fluctuations of the order parameter : schematic representation a) of the double-well potential whose asymmetry is governed by the order parameter η , b) of the individual dynamics of the molecule in this potential and c) of the resulting autocorrelation function $g(t)$.

The asymmetry of the local potential, characterised by the energy difference ΔV between the two minima, is then a simple function of the order parameter [29] :

$$\Delta V(\eta) = kT \cdot \ln \frac{(1 + \eta)}{(1 - \eta)} \tag{22}$$

Neglecting the fluctuations of the order parameter η around its mean non-zero value, one can again calculate the dynamical autocorrelation function $g(t)$ in real space :

$$g(t) = \eta^2 + (1 - \eta^2) \cdot e^{-t/\tau'} \tag{23}$$

with

$$\tau'^{-1} = \tau_+^{-1} + \tau_-^{-1} \tag{24}$$

This function is still exponential but it no longer tends to zero at infinite time (Fig. 4c). In the low temperature phase, the reorientational incoherent scattering function is then :

$$S_{inc}^R(\mathbf{Q}, \omega) = \{A_0(\mathbf{Q}) + [1 - A_0(\mathbf{Q})] \cdot \eta^2\} \cdot \delta(\omega) + \{[1 - A_0(\mathbf{Q})] \cdot [1 - \eta^2] \cdot \mathcal{L}\tau'^{-1}(\omega)\} \tag{25}$$

This result was first developed to describe the II to III phase transition of NH_4Cl [16, 17]. There the problem is experimentally more complex because there are two types of statistically independent motions for the NH_4 tetrahedron : the fourfold and the threefold jumps. At this transition, the ordering process concerns the first motion only while the second one, essentially not affected, continues to yield a quasi-elastic scattering in phase III. The main advantage in p-terphenyl is that the ordering phenomenon is directly associated with a unique reorientational motion. Actually the use of a single crystal of the selectively deuterated compound $\text{C}_6\text{D}_5\text{-C}_6\text{H}_4\text{-C}_6\text{D}_5$ even reduces the problem to the simplest case treated in part 2.1 of one proton in a double-well potential ; in this case the temperature dependence of the purely elastic incoherent scattering is directly given by formulae 10 and 25, as shown at different Q values in figure 5. The quasi-elastic line measured in the low temperature phase is found to be Lorentzian with an integral which decreases quickly upon cooling down. However

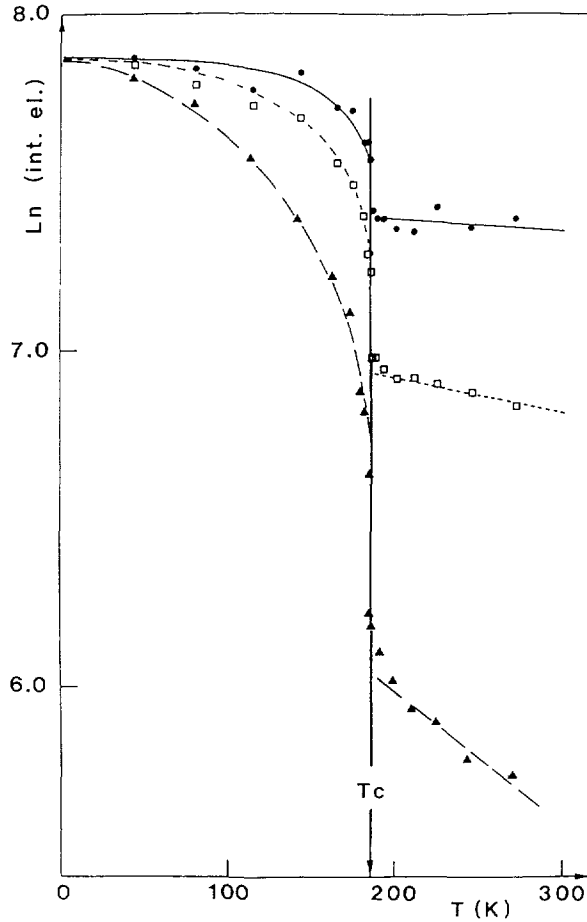


Fig. 5. — Semi-logarithmic plot of the elastic incoherent scattering intensity measured on the spectrometer IN13 at the ILL using a single crystal of selectively deuterated p-terphenyl $C_6D_5-C_6H_4-C_6D_5$. ((●) $|Q_0| = 1.19 \text{ \AA}^{-1}$, (□) $|Q_0| = 1.79 \text{ \AA}^{-1}$, (▲) $|Q_0| = 3.76 \text{ \AA}^{-1}$ with Q_0/a^* .) The straight lines in the high temperature phase take the temperature dependence of the Debye-Waller factor into account. Below T_C , the lines are meant as a guide to the eye.

this component remains quite broad as its width is essentially dominated by the inverse of the mean residence time τ_-^{-1} in the non-favorable well [29-30]. The relaxational process may even become faster in the low temperature ordered phase than in the disordered phase as found in p-terphenyl using formulae 22 and 25. Ten degrees below T_C , the reorientational rate $1/\tau'$ in this compound is found to be of the order of 30 GHz.

A similar calculation in nuclear magnetic resonance yields the same kind of result for the second moment of the resonance line :

$$M_2(t) = \overline{M}_2 + \eta^2(t) \cdot [M_2^R - \overline{M}_2]. \quad (26)$$

The temperature dependence of the order parameter is determined through neutron diffraction experiments from the intensities of superlattice reflections in the low temperature phase [20], and it may be described by a power law : $\eta^2 \sim ((T_0 - T)/T_0)^{2\beta}$ with $\beta = 0.14$.

Note that this small value of β probably indicates a weakly first order phase transition within a mean field theory [31]. Indeed the metastability limit T_C of the disordered phase is found some 0.1 K below the transition temperature T_0 . The resulting values of $M_2(T)$ are plotted in full line in figure 6, showing a good agreement with the experimental data. Quite clearly the increase of the second moment in the low temperature phase occurs because of the ordering process of this phase and although we are still in the fast motion limit ($1/\tau' \gg \nu_L$). The general expression of the spin-lattice relaxation rate is then :

$$T_1^{-1} = \frac{2}{3} \gamma^2 \Delta M_2 (1 - \eta^2) [J(\omega_L) + 4J(2\omega_L)]. \quad (27)$$

By analogy with the analysis of the incoherent neutron scattering results in the low temperature phase, the N.M.R. process may be interpreted in terms of a spectral function whose integral behaves as $(1 - \eta^2)$. However the behaviour of the spin-lattice relaxation time T_1 is governed by the order-parameter below the transition temperature only when the contribution of the collective fluctuations in this phase becomes negligible (Fig. 3). Other authors [28] have taken the measurements between T_C and $T_C - 5$ K, and only them, to determine the temperature dependence of the order parameter using the following formula :

$$T_1^{-1} = T_{1C}^{-1} \cdot (1 - \eta^2). \quad (28)$$

This expression is wrong since the spin-lattice relaxation rate determined at T_C , T_{1C}^{-1} , is governed by the critical pretransitional fluctuations of the order parameter. Formula (28) corresponds to formula (27), if T_{1C}^{-1} is the value of the spin-lattice relaxation rate extrapolated at T_C without considering the contribution of the critical fluctuation (Fig. 3). This description is based on the assumption that the local potential is actually not much deformed by the collective fluctuations.

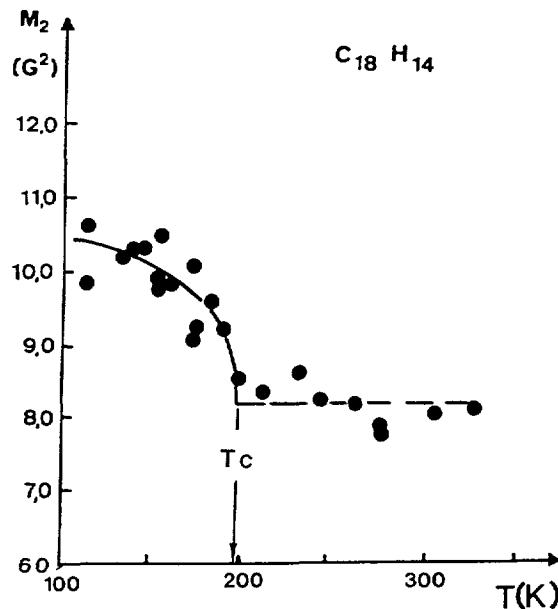


Fig. 6. — Temperature dependence of the second moment of the proton resonance line measured in p-terphenyl $C_{18}H_{14}$. The lines correspond to the theoretical description (see text).

5. Local critical dynamics ($T \rightarrow T_c$).

In the presence of pretransitional phenomena, around continuous or almost continuous phase transitions the influence of the conformation of a molecule on its neighbours becomes important. This local order may be described by a larger occupation probability for one of the wells during the finite lifetime of the fluctuations in « clusters » characterized by the correlation lengths (Fig. 7). The autocorrelation function must integrate all these collective fluctuations over the whole Brillouin zone :

$$g(t) \sim \sum_q^{BZ} \langle |s_q|^2 \rangle \cdot e^{-t/\tau_q} \tag{29}$$

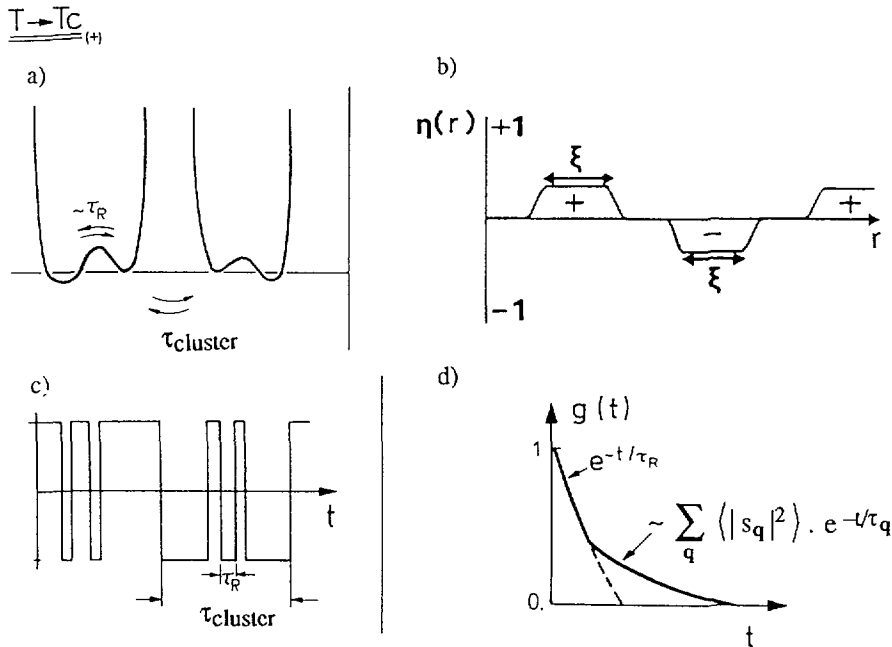


Fig. 7. — Schematic representation of the influence of the collective critical fluctuations on the local properties : a) the time evolution of the double-well potential for a given molecule, b) the spatial fluctuation of the order parameter around its mean value, c) the dynamics of a molecule and d) the resulting autocorrelation function.

The mean square amplitude of a collective relaxational mode of wavevector \mathbf{q} is :

$$\langle |s_q|^2 \rangle = \frac{kT}{q^2 + \xi^{-2}} \tag{30}$$

In the absence of collective fluctuations ($T \gg T_c$ and $T \ll T_c$), there is a negligible dispersion in the correlation times τ_q . On the contrary, the collective fluctuations introduce a strong dispersion in these correlation times close to T_c (Fig. 8). In a mean field description close to the critical wavevector $\mathbf{q}_c = 0$, one has

$$\tau_q^{-1} = \tau_c^{-1} + D \cdot q^2 \tag{31}$$

with

$$\tau_c^{-1} \sim \xi^{-2} \sim (T - T_c) \tag{32}$$

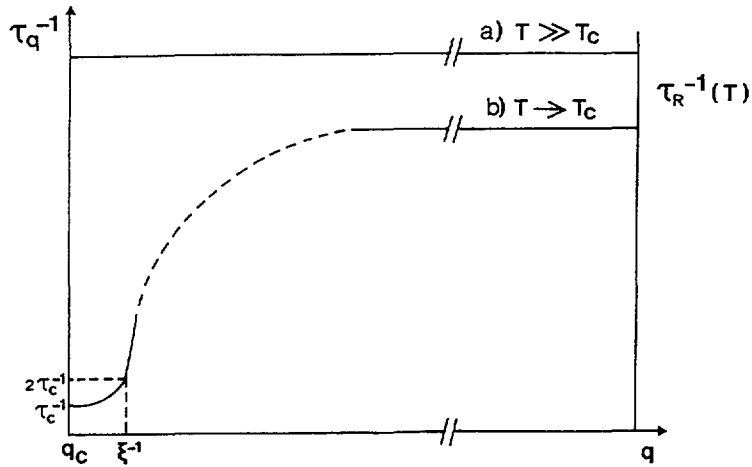


Fig. 8. — Schematic representation of the dispersion relation of the correlation times in reciprocal space, a) neglecting the collective fluctuations ($T \gg T_c$) and b) in the presence of the collective fluctuations ($T \rightarrow T_c$).

From coherent neutron scattering experiments performed on the high resolution spectrometers IN10 and IN11 at the I.L.L. we found for deuterated p-terphenyl :

$$\tau_c^{-1} \cong [0.25 \cdot (T - T_c)] \text{ GHz} . \tag{33}$$

The anisotropy in the correlation lengths were $\xi_a : \xi_b : \xi_c \cong 3 : 8 : 1$ [32]. Considering an isotropic description, the mean diffusion coefficient $D = \xi^2 / \tau_c$ was found to be of the order of $2 \times 10^4 \text{ \AA}^2 \text{ \mu eV}$. The calculation of the critical part of the dynamical autocorrelation function may be done analytically in the isotropic case :

$$g^{\text{crit}}(t) \sim kT \int_0^{q_m} dq \frac{q^2}{q^2 + \xi^{-2}} \cdot e^{-t/\tau_q} \tag{34}$$

q_m defines the critical volume in the reciprocal space where the dispersion given by formula (31) is assumed valid. Let us note that this is the same calculation as that performed to determine the fluctuation correction for the specific heat [33]. For a second order phase transition, at $T = T_c$ ($\xi^{-1} = 0$ and $\tau_c^{-1} = 0$), $g^{\text{crit}}(t)$ has this simple expression :

$$g_{T=T_c}^{\text{crit}}(t) \sim kT_c \int_0^{q_m} dq \cdot e^{-(Dt)q^2} \tag{35}$$

For very long times ($t \gg \tau_R$), one can only consider fluctuation modes $q \ll q_m$, i.e. $q_m \rightarrow \infty$, and one has

$$g_{T=T_c}^{\text{crit}}(t) \sim kT_c \cdot \frac{1}{\sqrt{t}} \tag{36}$$

corresponding to the spectral function

$$G_{T=T_c}^{\text{crit}}(\omega) \sim kT_c \cdot \frac{1}{\sqrt{\omega}} . \tag{37}$$

At the transition temperature, the low energy part of the autocorrelation function ($\omega \ll \tau_R^{-1}$) behaves as $\omega^{-1/2}$. Even if it probes a local property, the point at zero energy transfer diverges for a second order phase transition. The experimental evidence of the latter result has often been reported by N.M.R. through the divergence, in the fast motion limit, of the spin-lattice relaxation rate T_1^{-1} at T_C [7, 9-10]. The temperature dependence of this divergence is much dependent of the anisotropy of the correlations. If d characterizes this spatial dimension, one finds :

$$J(0) \sim T_1^{-1} \sim (T - T_C)^{\frac{d-4}{2}} \quad (38)$$

Thus, in principle, N.M.R. measurements give the dimensionality of the correlations. However the determination of the exponent governing T_1^{-1} is not obvious at all because here one has to consider both critical and non critical dynamics. If, like Guillon *et al.* [28], one considers that the critical phenomena govern the N.M.R. process at all temperatures, the fluctuations are found to have a 2-dimensional character. But if, as shown in part 3, the critical phenomena actually dominate the spin-lattice relaxation process only up to 30 K or

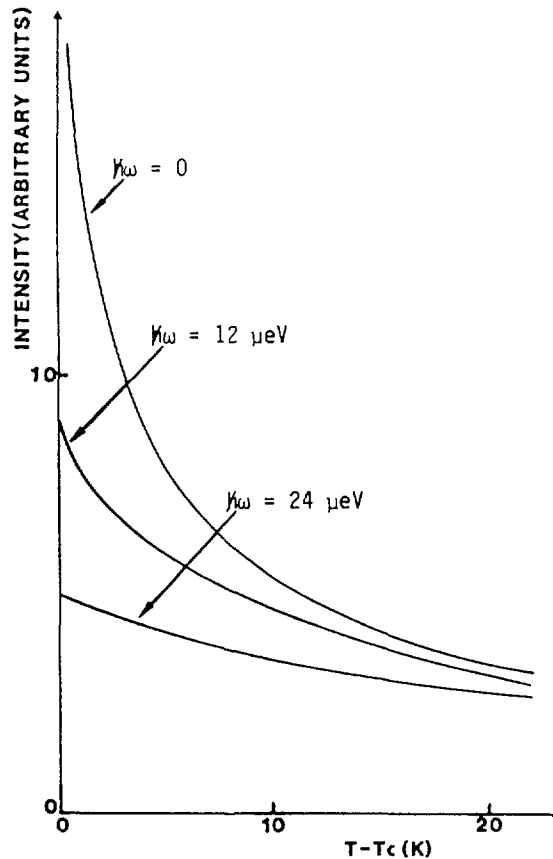


Fig. 9. — Theoretical temperature dependence of the spectral density of the autocorrelation function at points $h\omega = 0$, $h\omega = 12 \mu\text{eV}$ ($\nu \cong 6 \text{ GHz}$) and $h\omega = 24 \mu\text{eV}$ ($\nu \cong 12 \text{ GHz}$) in p-terphenyl, in the presence of collective fluctuations. The phase transition is assumed to be continuous and is described in the frame of a mean field theory.

40 K above the transition temperature, the fluctuations are found to have essentially a 3-dimensional character [17, 19]. The analytical calculation of local critical dynamics considering the actual anisotropy of the correlation is quite complicated. The numerical simulation, however, shows that the spectral shape of this critical part is essentially not different from that obtained in the isotropic case, its relative weight being simply increased [34]. The theoretical behaviour of the different points of the critical part of the autocorrelation function is shown in the isotropic case in figure 9. The experimental evidence of this result for these three frequencies is given in reference [24]. The complete observation of the spectral autocorrelation function has been obtained by incoherent neutron scattering [23]. Contrary to N.M.R., the analysis of these data require a realistic description of the dispersion of the collective correlation times over the whole reciprocal space [23, 30].

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