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Vibrational and orientational relaxations in complex liquids: The case of ME6N liquid crystal in the isotropic phase

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Abstract

In the context of the dynamical characterisation of liquid systems, in this paper we critically compare methodological approaches formulated for the determination of the dynamics in complex molecular liquids. We will show that the experimental vibrational relaxation of the ν(CN) mode of the ME6N liquid crystal in the isotropic phase is successfully reproduced, at long times ($t > 3$ ps), by the non-Markovian modelling of the perturbation modulation proposed by Rothschild et al.. The non-hydrodynamic behavior of the orientational relaxation times obtained for the same normal mode confirms the picture of pseudo-nematic domains persisting in the isotropic phase of this liquid crystal well above the nematic–isotropic (N-I) transition. Finally, the comparison of the time and frequency domain methods for the determination of dynamical parameters indicates their qualitative equivalence.

Keywords: Raman spectroscopy; Molecular liquids; Liquid crystals; Vibrational time correlation functions; Orientational time correlation functions

1. Introduction

In the framework of an extended activity addressed to the determination of structural [1,2] and dynamical aspects [3–5] in condensed-phase molecular systems by steady-state vibrational spectroscopic experiments, we have recently moved our attention from simple to complex molecular liquids [6].

In this contribution we specifically refer to liquid crystals, a state of soft condensed matter with properties intermediate between those of liquids and crystals. From a microscopic point of view, they are featured by orientational and positional order induced by the long alkyl chain of their molecules. Investigations on the orientational organization at molecular level and on the molecular dynamics on the picosecond time scale may help to unveil some intimate peculiarities of this state of condensed matter.

It was just the peculiarity of liquid crystals of being featured by a strong orientational organization that directed, at the very beginning, our attention to these complex liquids. The idea was put forward, in fact, that, thanks to the high orientational order persisting even in the isotropic phase above the N-I transition in these systems, the manifestation of a spectroscopic phenomenon strongly dependent on the molecular orientational order, called the noncoincidence effect (NCE) [7], could be favoured [8,9]. It is frequently observed in the band of the ν(C=O) stretching mode [10,11] of molecular liquids locally ordered by dipole–dipole interactions. Extended investigations carried out on this phenomenon in ME6N liquid crystal [12] have somehow frustrated this expectation and precluded the achievement of any conclusive evidence of its orientational organization.

With regard to the characterization of the picosecond dynamics of molecular liquids, recourse can be made to the use of the time correlation function methodology [13–16]. Within this approach, the Raman spectral band-shapes may be analysed in terms of vibrational and orientational relaxation processes in the assumption of their statistical independence. The application of the stochastic treatment to the perturbation fluctuations [14–16], based on the assumption that the perturbation relaxation is a Markovian process (Kubo theory), gives a modellistic interpretation of the vibrational time

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correlation functions in terms of two parameters, (i) the perturbation modulation time τ_c and (ii) the perturbation amplitude Δ^2. This procedure, very popular among liquid phase vibrational spectroscopists, thanks to its rather easy applicability, has represented for many years the only way to extract the dynamical regime of the intermolecular interactions in several (simple and complex) liquids from vibrational band profiles [3,17]. However, this theory does not seem to be completely adequate to model the experimental vibrational correlation functions for complex liquids as Rothschild et al. have observed in several occasions [18,19]. Modelling the perturbation modulation through a non-Markovian process proved to be an effective way to include the effects of the fluctuating aggregate species present in complex liquids in the formulation of the vibrational relaxations.

Orientational dynamics in simple liquids is generally discussed within the general framework of hydrodynamic theory, which predicts a linear increase with the inverse temperature of the orientational relaxation times in semilog plots (the Arrhenius plot) [20]. However, the orientational relaxation times obtained from the signal decay of the diffusive component (the same extracted from the band-shape analysis of the anisotropic component of a Raman band) in transient grating OKE experiments have indicated that, in liquid crystals in the isotropic phase, the Arrhenius law is no longer followed even at high temperature [21]. Liquid crystals above the N-I transition, even though behaving like isotropic systems at macroscopic level, may be structurally anisotropic at microscopic level for the persistence of short-lived, fluctuating nematic domains with temperature dependent sizes. It was pointed out that the observation of a non-hydrodynamic regime in liquid crystals in the isotropic phase can be traced back to their structural anisotropy at microscopic level [22].

There are advantages and disadvantages in the application of the correlation function approach to the determination of vibrational and orientational relaxation processes of liquid crystals, and generally to complex liquids which have, typically, long reorientation times ($\tau_{or} \gg 10$ ps) [23]. The advantage is that these relaxation processes, occurring at very different time scales, can reliably be experimentally separated since they naturally fulfil the required statistical independence. The disadvantage is that of the limited sensitivity of the steady-state (frequency domain) vibrational spectroscopy experiments regarding the dynamics outside the picosecond time domain. Additionally, since the correlation function approach of the band-shape analysis is based on the discrete Fourier transformation of band profiles in the time domain, only marginally overlapping vibrational bands and only bands with widely extended wings can be considered. Methods overcoming both these limitations have been proposed for studying molecular dynamics directly in the frequency domain [24].

The purposes of this paper are (1) to address the interpretation of the vibrational relaxations of the ν(CN) normal mode of ME6N liquid crystal in the isotropic phase within the non-Markov model of the perturbation modulation proposed by Rothschild et al. [18]; (2) to check the sensitivity of this method to follow the progressive change of the equilibrium between aggregates of different sizes up to their possible complete disruption by the use of the distribution function of the relaxation times (a central statistical quantity within this theory); (3) to compare the dynamical picture given by the analysis of vibrational relaxations with that obtained from the orientational relaxations.

This paper is organized as follows: in Section 2.1 we will comparatively illustrate the Kubo and Rothschild theoretical methodologies with the help of a tabular description of the different quantities involved in the two methods. Additional theoretical considerations necessary for the analysis of the reorientational relaxations will be included in Section 2.2. In Section 3.1, we shortly describe the material properties, in Section 3.2 the experimental procedures and in Section 3.3 the computational details and the fitting strategy for the determination of the dynamical parameters according to the Kubo and Rothschild models. In Section 4.1 we compare the results of the application of the two models to the interpretation of the experimental vibrational relaxations and we check the sensitivity of the probability distribution function of the relaxation times to follow the progressive achievement of the simple liquid condition with increasing temperature or dilution. In Section 4.2 we illustrate the temperature dependence of the orientational relaxation times and we will discuss its non-hydrodynamic behavior. In Section 5 some final remarks and future perspectives of this activity will be given.

2. Theoretical background

2.1. Vibrational correlation functions

The vibrational correlation function $\hat{C}_v^k(t)$ is obtained by Fourier transformation of the isotropic Raman profile and represents the time decay of the phase coherence of the normal coordinate of a given (k) oscillator, $\langle Q^k(t)Q^k(0)\rangle / \langle |Q^k(0)^2|\rangle$, in the present case that of the ν(CN) oscillator of ME6N liquid crystal.

According to the Kubo theory [14,16], in fact, the oscillator vibrational amplitude $Q^k(t)$ subjected to a modulation $\omega_1(t)$ (as that brought about by intermolecular interactions and thermal motions) temporally evolves, and, in the assumption that $\omega_1(t)$ is a random Gaussian process (i.e., $\langle\omega_1(t)\rangle = 0$), the vibrational time correlation function $\hat{C}_v(t)$ (from now on the superscript k will be omitted) takes the following analytical expression:

$$\hat{C}_v(t) = \frac{\langle Q(t)Q(0)\rangle}{\langle |Q(0)^2|\rangle} = \exp\left[-\langle|\omega_1(0)|^2\rangle \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \hat{F}(t)\right] \quad (1)$$

Here $\hat{F}(t)$ represents the (normalized) time correlation function of the frequency shifts $\langle\omega_1(t)\omega_1(0)\rangle / \langle|\omega_1(0)|^2\rangle$, and $\langle|\omega_1(0)|^2\rangle (=\Delta^2)$ represents the frequency modulation variance and then the perturbation amplitude in the limit of a static environment (i.e., when the dynamics is switched off). It has been shown [16] that Δ^2 coincides with the frequency second