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Low frequency relaxation in liquid crystals in relation to structural relaxation in glass-formers[☆]

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ABSTRACT

Liquid crystals (LC) are the state of matter intermediate between isotropic liquids and the crystalline state. LC-forming molecules have strongly anisotropic shapes (rod-like in most cases). This leads to an interaction potential that consists of distance-dependent and orientation-dependent parts. Rotational dynamics of LC molecules falls into two frequency regions. Rotations about the short axes are strongly hindered by the potential barrier and thus coupled to fluctuations of the molecular centers of mass. This in turn causes these longitudinal or “flip-flop” motions, characterized by a relatively large relaxation time $\tau_{||}$, to exhibit considerable temperature, pressure and volume dependences. Experimental relaxation times determined to date for various LC phases (nematic, smectic A, C, and E) for different thermodynamic conditions (isobaric, isothermal and isochoric) are discussed herein, adopting the formulae applied for characterization of the structural relaxation times of glass-formers (GF). This analysis appears fruitful; in particular, the strength parameter characterizing the steepness of the interaction potential can be determined from the relaxation times, and $\tau_{||}$ is independent of temperature and pressure along the nematic–isotropic transition line, similar to the behavior of the structural relaxation time along certain transitions in GFs.

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1. Introduction

Rotational dynamics is an important aspect of molecular systems. The details of the reorientational motion depend strongly on the chemical structure of molecules and on the phase in which they are condensed. Simple molecules, having for example spheroidal shapes and absent pendant moieties, perform fast rotations in the liquid state and in solid rotator phases (called plastic or orientationally disordered phases) [1,2]. The correlation times τ are on the order of picoseconds and depend weakly on temperature (small activation barriers). Molecules having anisotropic shapes and rigid cores (usually rod- or disc-like) have a tendency to form liquid crystalline phases (LC) [3] and have quite different rotational motions. Dielectric relaxation spectroscopy is commonly employed to study the dynamic properties of polar molecules in LCs as functions of temperature T , pressure P and volume V . Rotations about the long axes (i.e., lower inertial moment) are fast and practically insensitive to phase changes [4–6]. On the other hand, rotations about the short axes (having the larger moment of inertia) are relatively slow. These low frequency (l.f.) motions have

relaxation times $\tau_{||}$ on the order of nano- or microseconds and are hindered by high potential barriers [7–10].

A very broad class of compounds, ranging from relatively simple to complex polymers and H-bonded materials, show a tendency to vitrify, with the glassy state characterized by solid-like rigidity but liquid-like disorder [11–13]. A common feature of glass-forming (GF) substances is slow and eventually arrested rotational and translational motions on approaching the glassy state. There are many routes to the glassy state, with cooling or compression the most common.

Several empirical models have been developed to explain the temperature–pressure–volume dependences of the dynamical properties of GF systems (for a review see [13]). Some may be applicable to the l.f. process in LC phases. However, there are two significant differences between the LC and GF systems: (i) the range of T and P in which a LC phase is thermodynamically stable is rather limited, in comparison with the supercooled regime of GF systems; (ii) there is no experimental evidence for non-Arrhenius temperature-dependences of $\tau_{||}$ within LC phases (Fig. 1), whereas such behavior is a common feature of GF substances. Nevertheless, in this paper we concentrate our attention on similarities between the properties of $\tau_{||}$ in LCs and the structural relaxation times in GFs. It should be borne in mind, however, that the number of LC materials studied at elevated pressure is rather limited (about 15), whereas hundreds of GF materials have been investigated at high P . (We ignore herein studies of liquid crystalline glass-formers obtained by fast cooling at ambient pressure from the nematic, smectic or even isotropic phase [15,16].)

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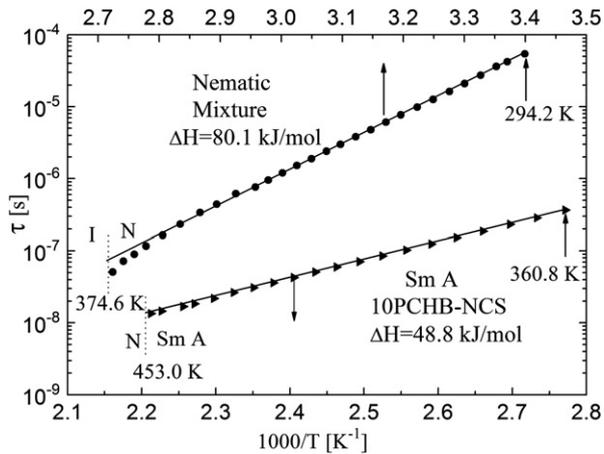


Fig. 1. Arrhenius plots of the low frequency relaxation times determined from dielectric measurements of two substances exhibiting a broad range (> 80 K) of LC phases: nematic mixture (unpublished results) and smectic A phase of 10PCHB-NCS [14]. The symbol size reflects the experimental error. Deviation from linearity is only observed in the vicinity of the clearing point (typical behavior of nematics).

2. Low frequency relaxation process in LCs

To better understand the specific features of the longitudinal rotations of molecules in LC phases, it is useful to look at the molecular arrangements in the smectic phases as determined by X-ray diffraction. Fig. 2 presents the X-ray pattern recorded for *n*-hexylisothiocyanato-biphenyl (6BT) in the smectic E phase [17], together with a sketch of the molecular arrangement in the unit cell. Several Bragg reflections allow determination of the orthorhombic unit cell parameters, which can be compared to the calculated molecular dimensions, with the *c* parameter found to be close to the molecular length *L*. The molecules are loosely packed—only ca. 60% of the volume is occupied. However, the ratio of the distance between the molecular centres to *L* is about 0.4, indicating strong rotation–translation coupling for flip-flop rotation motion in the smectic E layers; that is, rotations occur cooperatively with translational fluctuations. A similar situation seems to prevail in the liquid-like LC phases (N, SmA, and SmC). This illustrates why compression via hydrostatic pressure of a LC sample can effect marked changes in dynamical properties [8–10].

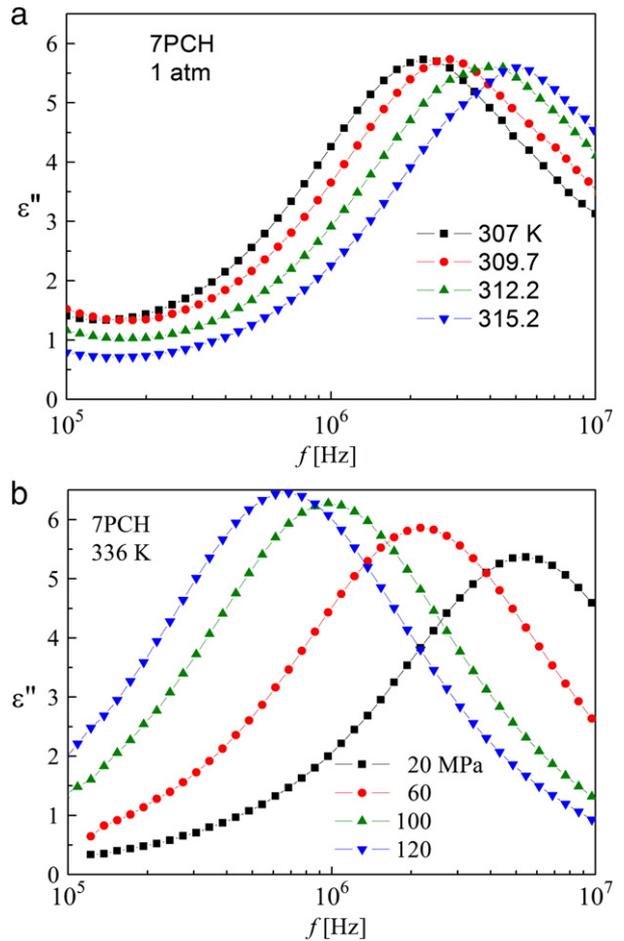


Fig. 3. Dielectric loss spectra for the nematic phase of 7PCH (parallel orientation): a) at atmospheric pressure and different temperatures, b) at constant temperature and different pressures [18]. The reciprocal of the frequency of the loss maximum yields the relaxation time $\tau_{\parallel} = 1/2\pi f_{max}$. The spectra have the Debye shape (exponential temporal response).

The influence of temperature at constant pressure and the influence of pressure at constant temperature on the low frequency relaxation process in the nematic phase of 7PCH (*n*-heptyl-

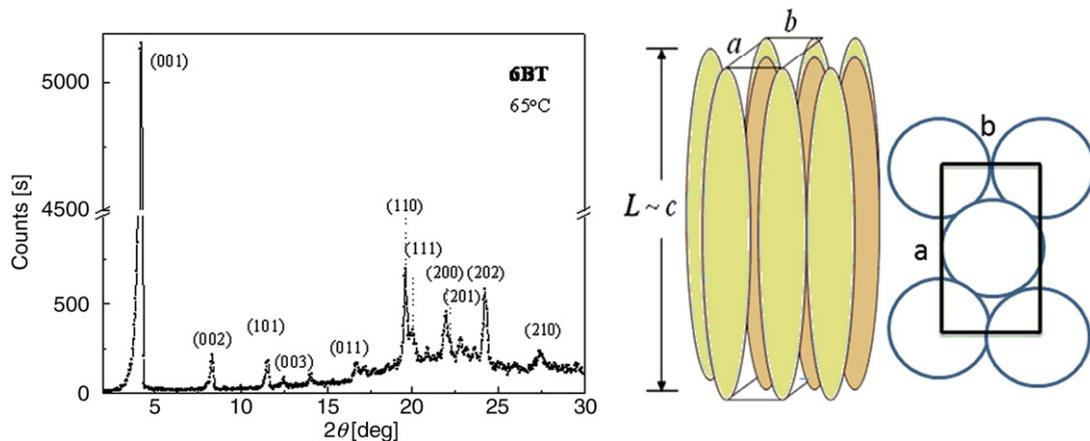


Fig. 2. X-ray pattern for 6BT in the Sm E phase [17] (left) and the sketch of unit cell arrangement. Unit cell parameters are: $a = 8.08 \text{ \AA}$, $b = 5.49 \text{ \AA}$, $c = 21.03 \text{ \AA}$, with $Z = 2$ molecules in the unit cell. Calculated values of $L = 19.1 \text{ \AA}$, unit cell volume $V_{uc} = 732.9 \text{ \AA}^3$, and the molecular volume $V_m = 277.6 \text{ \AA}^3$ yield the packing parameter $p = ZV_m/V_{uc} = 0.60$.

cyclohexyl-cyanophenyl) are shown in Fig. 3 [18]. The variation of $\tau_{||}$ with temperature, pressure and volume can be parameterized in terms of activation quantities:

$$\text{activation enthalpy: } \Delta H = R \left[\frac{\partial \ln \tau}{\partial (T^{-1})} \right]_P \quad (1)$$

$$\text{activation energy: } \Delta U = R \left[\frac{\partial \ln \tau}{\partial (T^{-1})} \right]_V = \Delta H - T(\partial P / \partial T)_V \Delta V \quad (2)$$

$$\text{activation volume: } \Delta V = RT \left[\frac{\partial \ln \tau}{\partial (P)} \right]_T \quad (3)$$

From Eq. (2) and Fig. 4, ΔU is smaller than ΔH ; for many nematics and smectics the activation energy is roughly half the value of the activation enthalpy, whereas the activation volume is ca. 20% of the molar volume [8–10]—see Table 1. These facts suggest that, similarly to GFs [13,19], the barrier hindering the flip-flop motions in LC phases is both temperature and volume (density) dependent

$$\tau(T, V) = \tau_0(V) \exp[E_a(T, V) / RT]. \quad (4)$$

In order to quantify the role of these control variables the relation between the isochronic ($\alpha_\tau = -V^{-1}(\partial V / \partial T)_\tau$) and isobaric ($\alpha_P = -V^{-1}(\partial V / \partial T)_P$) expansivities can be employed, as done for GFs near the glass transition [20,21]. Casalini and Roland [21] found the relation

$$\Delta U / \Delta H = |\alpha_\tau| / (|\alpha_\tau| + \alpha_P) \quad (5)$$

which has been applied to many glass-forming liquids and polymers [13]. The ratio $\Delta U / \Delta H$ equals 1 or 0 in the limit of temperature- or volume-dominated dynamics, respectively.

Fig. 5 shows examples of the volume–temperature plots at constant $\tau_{||}$ and constant P for two LC substances in the nematic phase: pentyl-cyanobiphenyl (5CB) [22] and 4(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanatobenzene (6CHBT) [23]. The obtained expansivity coefficients are listed in Table 1, together with the data for other LCs. In most cases the ratio $|\alpha_\tau| / \alpha_P$ is close to unity, which means $\Delta U / \Delta H \sim 1/2$. This indicates an equivalency in the effects of thermal energy and the volume in determining the low frequency relaxation time in liquid crystalline phases. Values of $\Delta U / \Delta H$ obtained from Eq. (5) agree well with the results obtained directly from Eqs. (1) and (2)—see Table 1.

3. Remarks on the interaction potential in LCs

In some models for GFs [13,24–26], a central parameter is the exponent $\tilde{\gamma}$ in the generalized Lennard–Jones (LJ) potential energy

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{3\tilde{\gamma}} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (6)$$

where r is the molecular separation and ε and σ are constants. In the classic LJ equation $\tilde{\gamma} = 4$. This means that the repulsive part of Eq. (6) dominates the arrangement (liquid structure) and local properties, whereas the attraction interactions are manifested primarily as a uniform background pressure that can be treated as a constant [24,25,27].

In the case of liquid crystals, the intermolecular potential must take into account the anisotropic shapes of the rigid molecules (usually rod-like); i.e., in addition to the separation-dependent $U(r)$, there is an orientation-dependent term, $U(\theta)$, where θ is the angle between the molecular symmetry axes and the director. We briefly review here three representative models of the interaction potential for LCs.

According to the Maier and Saupe (MS) [28] theory of nematics, the potential of mean-torque has the form

$$U(\theta) = -qP_2(\cos \theta). \quad (7)$$

The strength parameter q is related to the order parameter $S = \langle P_2(\cos \theta) \rangle = \langle 3\cos^2 \theta - 1 \rangle / 2$ by $q = vS$. The interaction coefficient is related to the volume by $v = v_0 V^{-2} \sim r^{-6}$. Liquid crystallinity arises due to the anisotropic dispersion forces, and only the attractive part of the potential is considered. The MS theory gives a qualitatively correct description of nematogens (N–I phase transition, order parameter $S(T)$); however, this success of the theory is rather fortuitous, as explained by Luckhurst and Zannoni [29].

Tao et al. [30] assumed an interaction potential of the form

$$U(r, \theta) = U_0(r) + U_2(r) P_2(\cos \theta). \quad (8)$$

$U_0(r) = \varepsilon[\sigma/r^{12} - \sigma/r^6]$ and $U_2(r) = -br^{-n}$ with $n = 6$ (MS) or 12. This mean-field theory correctly predicts the density change at the N–I transition, as well as the slope of the clearing line dT_{NI}/dp for $n = 12$.

In the model proposed by Gay and Berne [31], the potential is a generalization of the standard Lennard–Jones 6–12 potential to molecules of uniaxial symmetry:

$$V_{GB}(\hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j, r) = 4\varepsilon(\hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j, r) (R^{-12} - R^{-6}) \quad (9)$$

$$R = [r - \sigma(\hat{\mathbf{e}}_i, \hat{\mathbf{e}}_j, r) + \sigma_0] / \sigma_0.$$

The unit vectors $\hat{\mathbf{e}}_i$ and $\hat{\mathbf{e}}_j$ describe the orientations of a pair of molecules and $\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$ is the separation vector of their centers of mass; ε is an energy parameter, σ an orientation-dependent

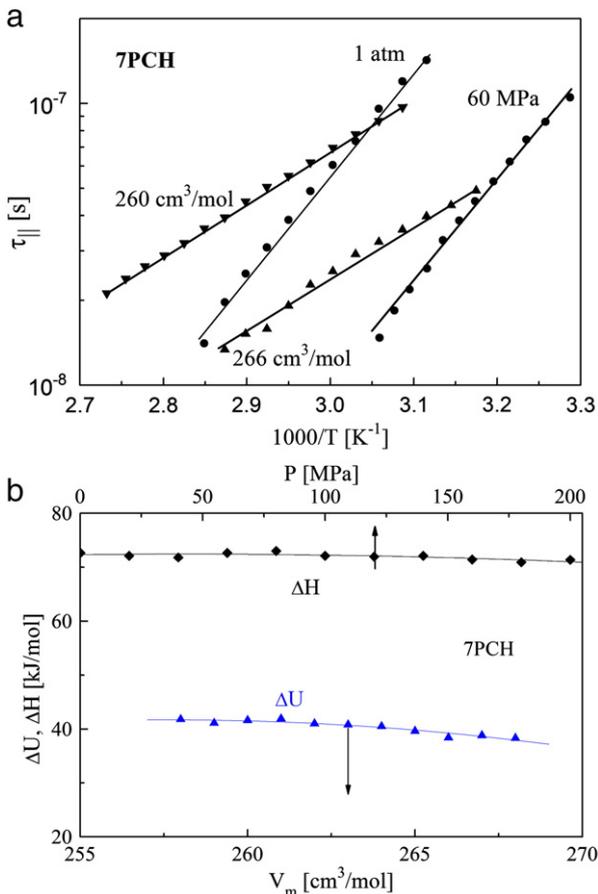


Fig. 4. a) Activation plots at two pressures (yielding the activation enthalpy ΔH) and two specific volumes (yielding the activation energy ΔU). b) Activation enthalpy vs. pressure and activation energy vs. molar volume in the nematic phase of 7PCH [18].

Table 1

The data determined from the DTA, PVT and dielectric spectroscopy measurements of liquid crystalline substances in different phases. The activation parameters ΔH , ΔU and ΔV exhibit some changes within a given phase and tabulated values are the midpoint of the phase.

Substance	T_c [K]	$\partial T_c/\partial P$ [K/MPa]	Phase	ΔH [kJ/mol]	ΔU [kJ/mol]	ΔV [cm ³ /mol]	$\Delta U/\Delta H$		γ	Γ	$10^4\alpha_p$ [1/K]	$-10^4\alpha_\tau$ [1/K]	$-\alpha_\tau/\alpha_p$	Ref.
							Exp.	Eq.(12)						
5CB	308.3	0.424	N	62	38	59	0.61	0.54	4.1	5.3	6.8	6.3	0.92	[22,49]
6CB	301.2	0.390	N	62	27	63	0.44	0.54	4.1	6.3	7.0	8.1	1.15	[48,50]
7CB	314.6	0.370	N	64	30	63	0.47	0.53	3.3	4.7	8.5	9.2	1.15	[48,51]
8CB	313.8	0.370	N/ A	60/40	32/24	60/38	0.53/0.57	0.50	4.2	4.0	7.7	7.7	1.00	[18,52]
5PCH	328.1	0.440	N	69	39	70	0.57	0.58	3.5	5.2	6.3	9.0	1.42	[53,54]
7PCH	331.0	0.420	N	70	35	65	0.50	0.52	3.9	3.3	7.1	7.3	1.03	[18,53]
8PCH	328.3	0.412	N	70	36	60	0.51	0.56	3.6	3.4	6.7	9.2	1.37	[53,55]
6CHBT	316.7	0.419	N	63	33	65	0.52	0.52	5.0	5.0	5.8	6.8	1.17	[23,56]
6DBT	350.1	0.259	A	51	20	42	0.40	0.43	4.0	2.9	9.4	6.6	0.72	[57,58]
60PB8	339.2	0.234	A/C	79/69	52/46	58/45	0.66/0.66	0.61	2.7	2.5	7.0	11.1	1.6	[40,59]
5BT	347.1	0.284	E	74	53	68	0.72	0.72	2.3	2.2	5.1	13.	2.6	[41,60]
6BT	344.7	0.285	E	69	39	65	0.57	0.68	3.1	2.4	4.8	10.	2.1	[41,60]
7BT	345.6	0.241	E	75	53	72	0.71	0.72	2.3	2.2	5.2	13.	2.5	[41,60]
8BT	341.1	0.237	E	70	33	59	0.47	0.48	4.1	2.7	7.4	6.60	0.90	[61,62]

molecular shape parameter, and σ_0 is the contact distance when the particles are orthogonal to the interparticle vector. The theory involves a minimum of six adjustable parameters, although the potential includes the fundamental features essential for liquid crystal formation. It has been successfully applied to describe the main features of many LC phases, as well as their long-range organization [32,33]. For example, in the computer simulations of the N phase, Bates and Luckhurst [34] estimated $\tilde{\gamma} = 5.7 \pm 0.2$, in reasonable accord with experiments.

There is a formal similarity of the interaction potentials given by Eqs. (6), (8) and (9) where the repulsive part, characterized by the parameter γ , is dominating. Larger γ implies a steeper potential.

4. Estimation of the potential strength parameter

It has been shown for dozens of GFs that structural relaxation times (as well as viscosities) measured for different thermodynamic conditions can be rescaled to a single master curve when plotted according to the relation [13,35]

$$\tau(T, V) = f(TV^\gamma) \quad (10)$$

where f is a function and the scaling exponent γ is a material constant. For GFs the value of γ ranges between 0.13 and 8.5 [13]. From the approximation of a LJ potential by an inverse power law, the scaling exponent can be identified with the steepness of the repulsive potential [27,36,37]; thus, $\gamma = \tilde{\gamma}$. This equivalence has been verified by molecular dynamic simulations [25,38].

Recently, relation (10) was successfully applied to $\tau_{||}$ measured as functions of T , P and V for several LC substances exhibiting various polymorphisms (nematic, and smectic A, C, E) [23,39–41]. In Fig. 6 the results of scaling for five LC substances are presented. In all cases the points lie on straight lines in accord with Arrhenius behavior; that is, the function f in Eq. (10) is exponential. This differs from the scaling of relaxation times for GFs, in which such plots are nonlinear [13]. The γ values for these and other LCs are collected in Table 1.

According to the MS mean-field theory of the nematic state [28], the product $T_c V_c^\Gamma$ is a constant, where T_c and V_c refer to the respective temperature and specific volume along the pressure-dependent clearing line (N–I transition). The thermodynamic potential parameter Γ is thus defined as

$$\Gamma = - \left(\frac{d \log T_c}{d \log V_c} \right)_P \quad (11)$$

Using the results for $T_{NI}(P)$ and $V_{NI}(P)$, double logarithmic plots can be constructed with a slope yielding Γ ; this is illustrated for three substances in Fig. 7. Although the MS addressed the nematic–isotropic transition, Eq. (11) has been applied to other LC phase transitions [8,23,40,41]. The obtained Γ are listed in Table 1.

We have pointed out [23,40,41] that the two materials constants, Γ and γ , must be equal if $\tau_{||}$ is constant along the transition line $T_c(P)$. (Note that a constant $\tau_{||}$ at the phase transition is equivalent to constancy of the order parameter S [42].) Fig. 8 shows this constancy for $\tau_{||}$ from Brückert [18] for the N phase of 7PCH (*n*-heptyl-cyclohexyl-cyanophenyl), with the $T(P)$ phase diagram determined by Büsing [18]. The phase transitions points for various isotherms from Fig. 8b are displayed in Fig. 8a. As can be seen, the relaxation time is essentially constant along both the nematic–isotropic and nematic–crystalline transition lines. Similar analyses for several LCs

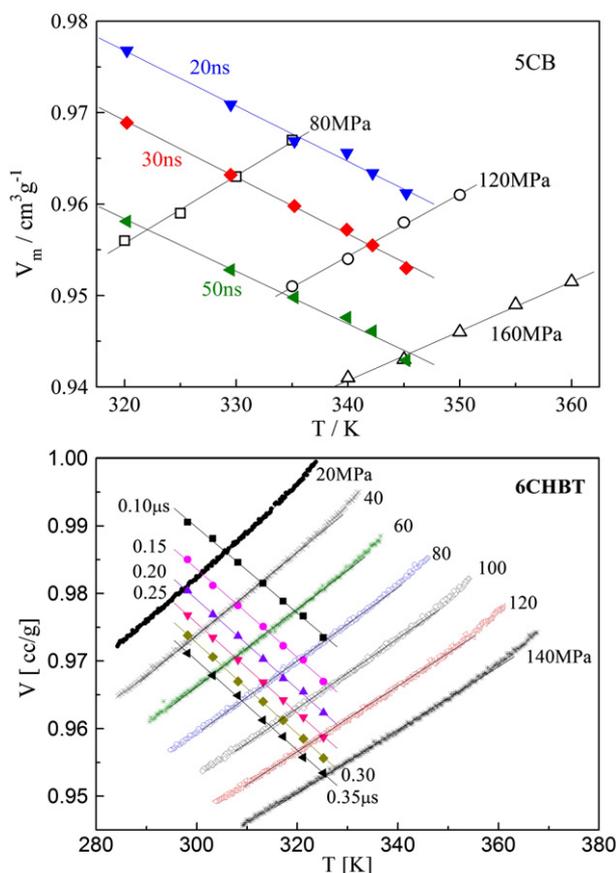


Fig. 5. Volume–temperature plots at constant relaxation time and constant pressure for 5CB and 6CHBT (data from Refs. [22] and [23], respectively).

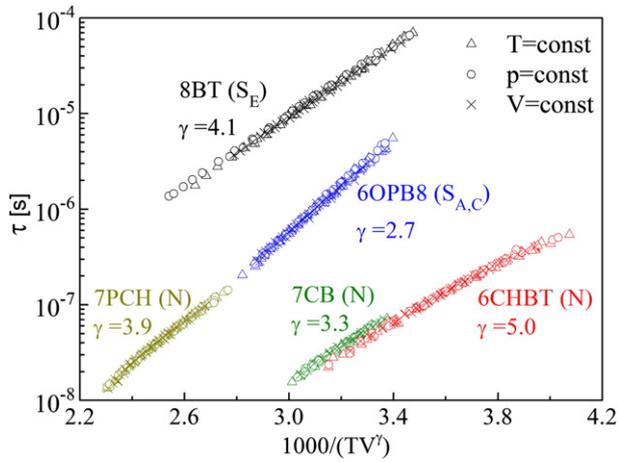


Fig. 6. Dielectric l.f. relaxation times as a function of the reciprocal of temperature times the specific volume, with the latter raised to the indicated power of γ [23,39–41].

have been reported [43], although generally an extrapolation of the relaxation times to the phase transitions is required.

In the case of GFs the structural relaxation time is constant along the glass transition line $T_g(P)$ [13,43], in accord with the kinetic nature of the phenomenon, corresponding to arrest of the molecular motions underlying macroscopic quantities used to define T_g , such as enthalpy and volume. However, the relaxation times at the dynamic crossover of GFs, demarcating the onset of strong intermolecular cooperativity, are also constant for a given material [44,45]. While higher pressure increases the temperature of the crossover, τ remains the same. The same is true for the onset of Arrhenius behavior at high $T-\tau(T)$ begins to conform to Eq. (4) at a material-specific, characteristic value of τ ($\approx 10^{-10}$ s), independent of P or V [43,46]. Thus, there is a striking parallel between ostensibly disparate phenomena. The thermodynamic phase transitions of LC and the changes in relaxation properties of isotropic GFs both have a dynamic signature in the form of a P -, V -, and T -independent τ . While thermodynamic variables such as temperature and pressure influence these transitions, the governing variable appears to be the time scale.

It has been shown [35,47] that Eq. (10) leads to simple relation between the scaling coefficient γ and the ratio $\Delta U/\Delta H$,

$$(\Delta U/\Delta H)_{T_g} = \frac{1}{1 + \gamma T_g \alpha_p}. \quad (12)$$

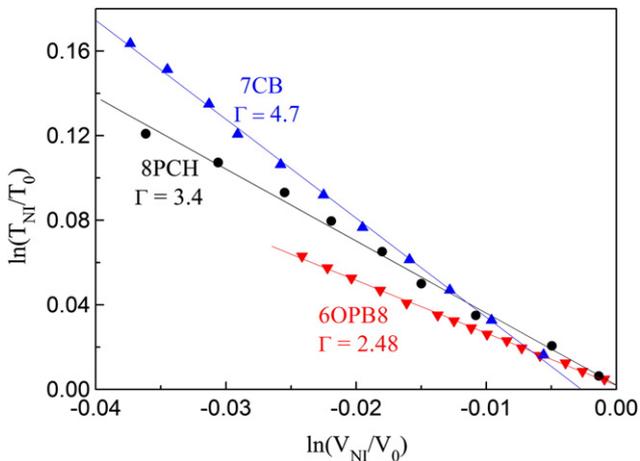


Fig. 7. Double logarithmic plot of the clearing temperature vs. molar volume for three LC at different pressures (T_0 and V_0 correspond to ambient pressure). Data taken from Refs. [48] (7CB), [49] (8PCH), and [39] (6OPB8).

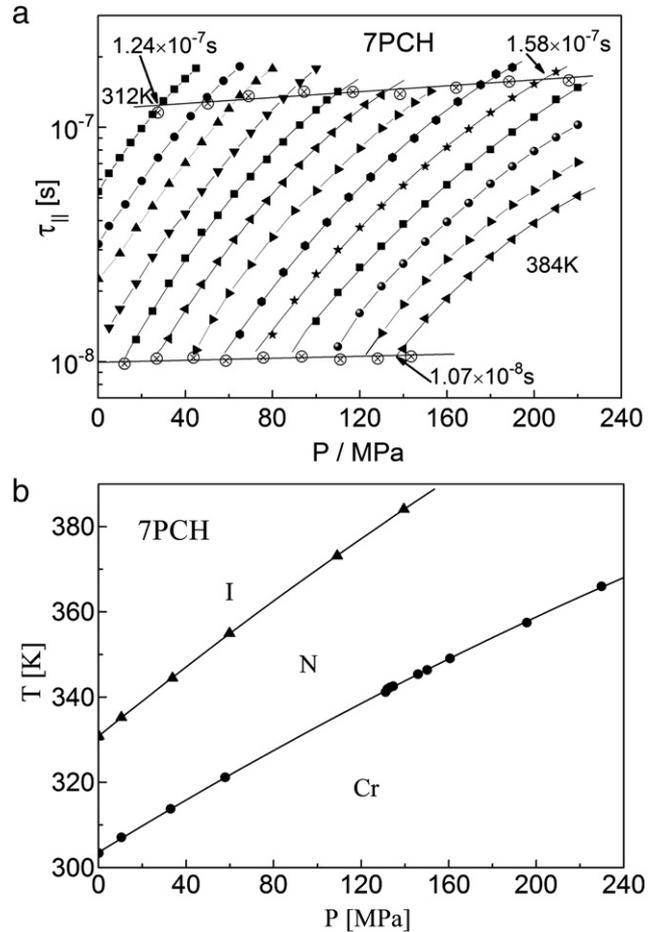


Fig. 8. a) The l.f. relaxation time versus pressure in the nematic phase of 7PCH [18] for isotherms in 6 K steps. The dotted circles denote the phase transition points at a given isotherm, as determined from b) P-T phase diagram from DTA measurements [18]. There is a slight increase of the relaxation time with pressure along the phase transition lines. The experimental points above the phase transition correspond to a superpressed state.

Eq. (12) was fitted to the experimental data at $T \sim T_g$ for 20 glass-formers, yielding 0.19 ± 0.03 for the product $T_g \alpha_p$ [63], consistent with empirical “rules” [64]. In Fig. 9 these γ and $\Delta U/\Delta H$ data for GFs are plotted, together with corresponding results for 14 LCs. The latter show values of γ consistent with the corresponding $\Delta U/\Delta H$ (note LCs

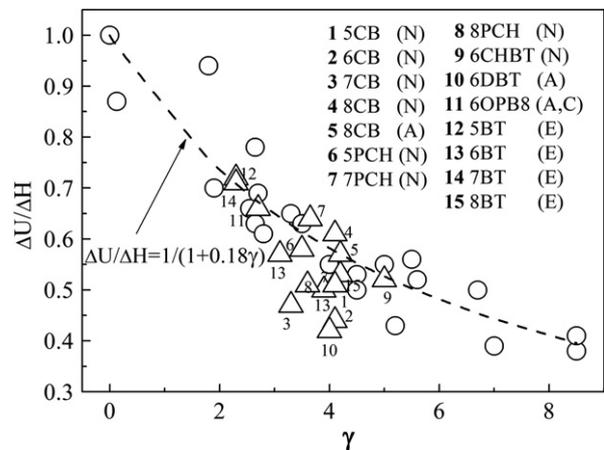


Fig. 9. Ratio of the isochoric activation energy and the isobaric activation enthalpy versus the scaling exponent for glass-formers (circles, see Ref. [13]) and for different phases of liquid crystals (triangles).

span a more restricted range of γ); we find $T_c\alpha_p = 0.23 \pm 0.05$. Table 1 contains the $\Delta U/\Delta H$ values calculated according to Eq. (12), where the clearing T_c was taken as the characteristic temperature. The agreement with the experimental ratios is satisfactory.

5. Conclusions

The actual dynamics of molecules in isotropic and liquid crystalline phases differ considerably—the form of motion, the meaning of cooperativity, and the dependences of their relaxation times on temperature and pressure. Nevertheless, the formalism developed for description of the dynamic properties of GF molecules can be successfully adapted to the reorientational dynamics of rod-like molecules in LC phases. Especially intriguing is the fact that the glass transition for GFs and the clearing point of nematics both transpire at a characteristic value of the relaxation time that, while varying with the material and its phase, is independent of pressure and temperature. This is despite the strong dependence on pressure of the transition temperatures *per se*. (Of course, when T_g is defined by an arbitrary value of the dielectric relaxation time, this invariance for GFs is preordained; however, there remains the fact that different experimental variables used to determine T_g , such as enthalpy, volume, etc., respond differently to changes in thermodynamic conditions, yet $\tau(T_g)$ remains constant.)

The *thermodynamic potential parameter*, Γ , measuring the variation of the interaction energy with volume, is associated with the *stability limits* of the ordered state. The *scaling parameter*, γ , reflects the volume dependence of the dynamical quantities within the *whole range* of a LC phase. Equivalence of the two parameters affirms the connection between the longitudinal dynamics and the repulsive part of the interaction potential. The fact that the thermodynamic conditions associated with the stability limits of the ordered state bear a direct relationship to the time scale of molecular rotations is unanticipated by any LC model and serves as a guide to theoretical progress in this important class of materials.

Acknowledgement

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