# Thermodynamical scaling of the low frequency relaxation time in liquid crystalline phases

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The low frequency relaxation times $\tau_\parallel$, which characterize the flip-flop molecular motions in liquid crystalline phases, recently determined in high-pressure experiments for eight liquid crystalline substances, were reanalyzed considering a relation proposed for the glass-forming liquids [C. Dreyfus *et al.*, Phys. Rev. E **68**, 011204 (2003); R. Casalini and C. M. Roland, Phys. Rev. E **69**, 062501 (2004)]. The data, measured at constant pressure, constant temperature, and constant molar volume, could be rescaled onto a master line in the $\ln \tau_\parallel$ vs $1/(TV_m^\gamma)$ plot, with $\gamma$ as an adjustable parameter ($V_m = 1/\rho$ is the specific volume). The obtained $\gamma$ values are in good agreement with other estimations; here, the value of $\gamma$ parameter was determined for the crystal-like smectic-$E$ phase.

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The rotational freedom of rodlike molecules in liquid crystalline (LC) phases is a common feature of the liquidlike phases [nematic, smectic-$A$ (Sm-$A$), and smectic-$C$ (Sm-$C$)], as well as of the crystal-like phases (smectic $B$, $E$, $K$, $G$, $H$,…) (see, for example, Refs. [1–6]). The motions around the long axes do not change at the phase-transition points separating different LC phases, whereas the flip-flop rotations around the short axes are sensitive to the actual arrangements of molecules in LC phases. Therefore, the determination of the low frequency relaxation time $\tau_\parallel$, which characterizes the latter motion, is very important for understanding the molecular interactions in LC phases [7–10]. Dielectric spectroscopy is one of the most effective experimental methods for studying these motions.

Most of the dielectric relaxation measurements were performed with varying temperature under ambient pressure. These measurements yield $\tau_\parallel(T)_{p=1\ \text{atm}}$, from which the activation enthalpy $\Delta H = R(\partial \ln \tau / \partial T^{-1})_p$ can be calculated ($R$ is the gas constant). An application of pressure and volume (density) as additional experimental variables may bring qualitative information about the dynamical properties of molecules in LC phases. High-pressure relaxation studies combined with the $pVT$ measurements enable separation between the effects of volume (density) and of temperature. We found (Refs. [2,4,10–14], and references therein) that the activation energy, $\Delta E = R(\partial \ln \tau / \partial T^{-1})_V$, is roughly two times smaller than the activation enthalpy, independent of the phase studied ($N$, Sm-$A$, Sm-$E$). This indicates an equivalent influence of the thermal and volume effects on the barrier hindering the flip-flop molecular motions in LC phases. A similar effect was found to occur in the glass-forming liquids [15–22]. Recently, several authors [16–22] have suggested that the relaxation time $\tau(T, V_m)$, where $V_m = 1/\rho$ is a specific volume, can be effectively rescaled onto a master curve using a unit parameter built on temperature and specific volume

$$\tau(T, V_m) = \tau_0 \exp[C/(TV_m^\gamma)], \tag{1}$$

where $\tau_0$ and $C$ are constants. Indeed, the relaxation times determined in different conditions could be rescaled to one curve (linear or nonlinear), assuming $\gamma$ as a fitting parameter in the $\ln \tau$ vs $1/(TV_m^\gamma)$ plots. The parameter $\gamma$ was found to be material-dependent, and in the most cases, it is close to 4. Casalini and Roland found [19] that the value of $\gamma$ can be
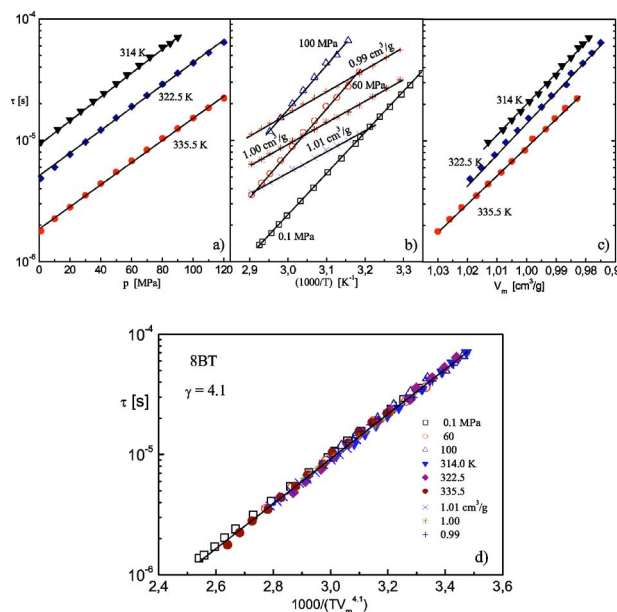


FIG. 1. (Color online) Example of analysis of the data obtained for the smectic $E$ phase of 8BT. (a) Pressure variation of the relaxation time at three constant temperatures. (b) Arrhenius plots at three constant pressures, yielding the activation enthalpy, and at three constant volumes, yielding the activation energy (activation enthalpy $\Delta H = 70 \pm 2$ kJ/mol; activation energy $\Delta E = 34 \pm 2$ kJ/mol). (c) Volume variation of the relaxation times at three constant temperatures [obtained from (a) via an equation of state]. (d) Variation of the relaxation time $\tau_\parallel$ with $(TV_m^{4.1})^{-1}$ for all data displayed in (a)–(c).

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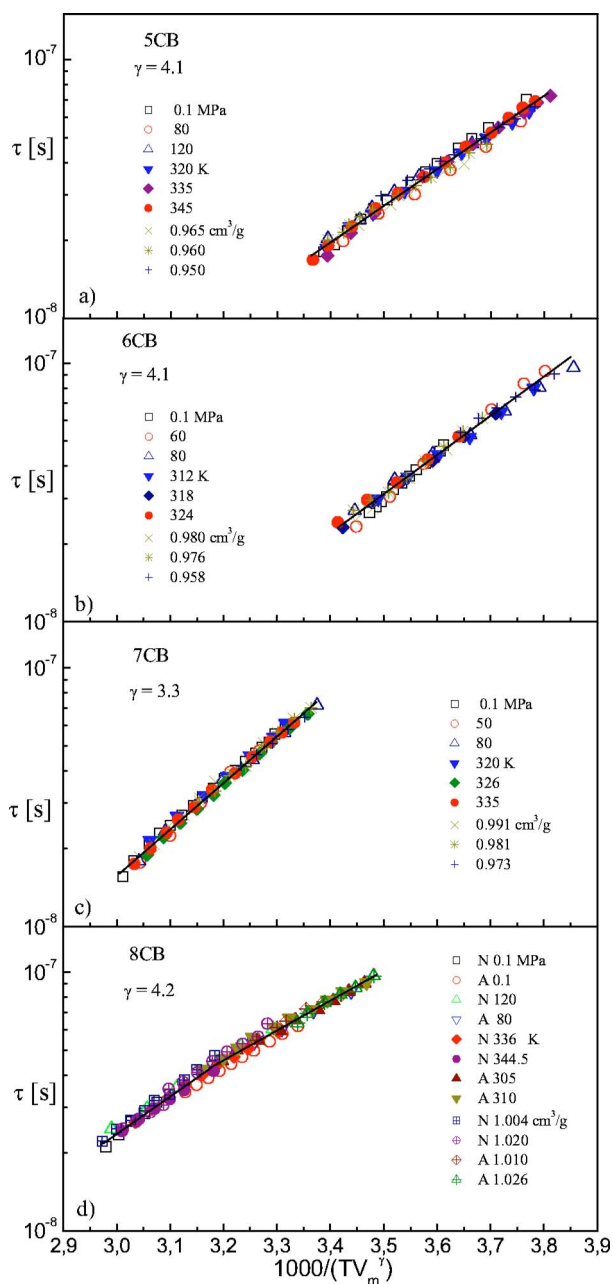†Electronic address: Albert.Wuerflinger@ruhr-uni-bochum.de

FIG. 2. (Color online) Relaxation time vs $1/(TV_m^\gamma)$ for four members of the 4-$n$-alkyl-4′-cyano-biphenyl ($n$CB) homologous series. The $\gamma$ parameters are displayed for particular substances. The scaling procedure was done for three pressures, temperatures, and specific volumes (except 8CB, due to the narrow ranges of the $N$ and $S_A$ phases). Slightly different slopes of the lines in the $N$ and $S_A$ phases can be noted that may be connected with smaller activation parameters for $S_A$ in comparison with $N$ phase.
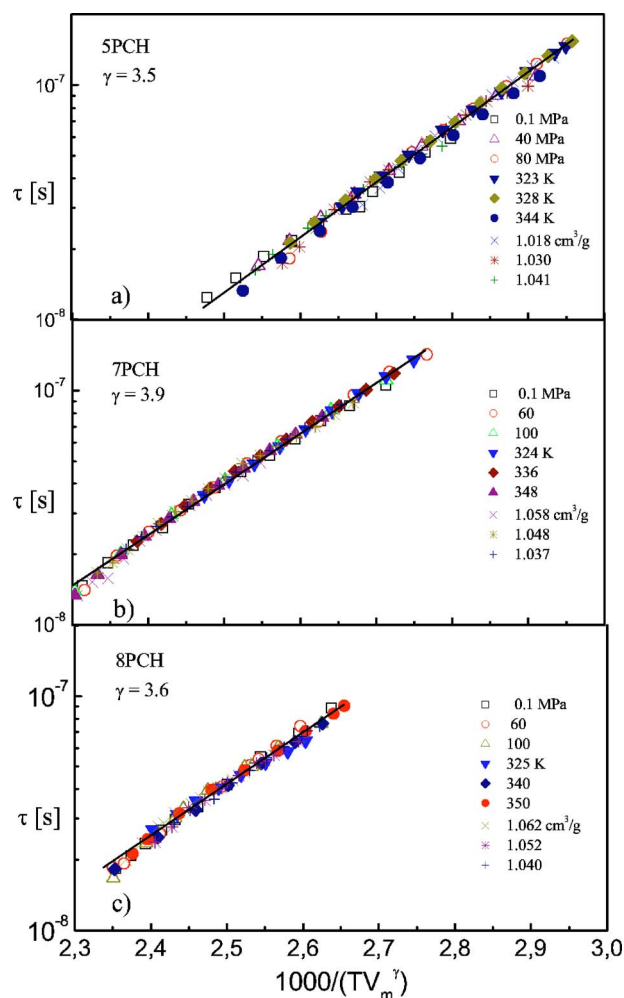


FIG. 3. (Color online) Relaxation time vs $1/(TV_m^\gamma)$ for three members of the *trans*-4-$n$-alkyl-[4-cyanophenyl]cyclohexane ($n$PCH) homologous series. The $\gamma$ parameters are displayed for particular substances. The scaling procedure was done for three pressures, temperatures, and specific volumes.

related to the ratio $\Delta E/\Delta H$. This means that the activation energy is a volume-dependent quantity and can be related to the repulsive part of the interaction potential governed by $r^{-3\gamma}$.

The exponential law used in Eq. (1) was questioned by Dreyfus *et al.* [20] in a discussion of the $\alpha$-relaxation time and by Tarjus *et al.* [21] in a discussion of the viscosity of glass-forming liquids. In both cases, the quantities under

consideration change by several orders of magnitude, contrary to the present case, when $\tau$ is limited, roughly, to one order of magnitude within each LC phase. Therefore the relation (1) seems to be appropriate for our discussion.

In the present paper, we use the preceding scaling procedure on our data for eight LC substances studied by our group during the last decade under elevated pressures with the aid of the dielectric relaxation and $pVT$ methods (Refs. [2,4,12–14,25], and references therein). Having a range of experimental material, we can perform the scaling at the isothermal, isobaric, and isochoric conditions. The parameter $\gamma$ obtained in such a way will be discussed in comparison with those parameters determined using other approaches.

Figures 1(a)–1(c) present the relaxation times $\tau_\parallel$ obtained for 8BT (4-$n$-octyl-4′-isothiocyanato-biphenyl) as functions of (a) pressure at $T$=const, (b) inverted temperature at $p$=const, and $V_m$=const, and (c) molar volume at $T$=const. In Fig. 1(d), the preceding data are rescaled to one master curve with the parameter $\gamma$=4.1. Similar plots for four $n$CBs (4-$n$-alkyl-4′-cyano-biphenyls) and for three $n$PCHs [*trans*-4-
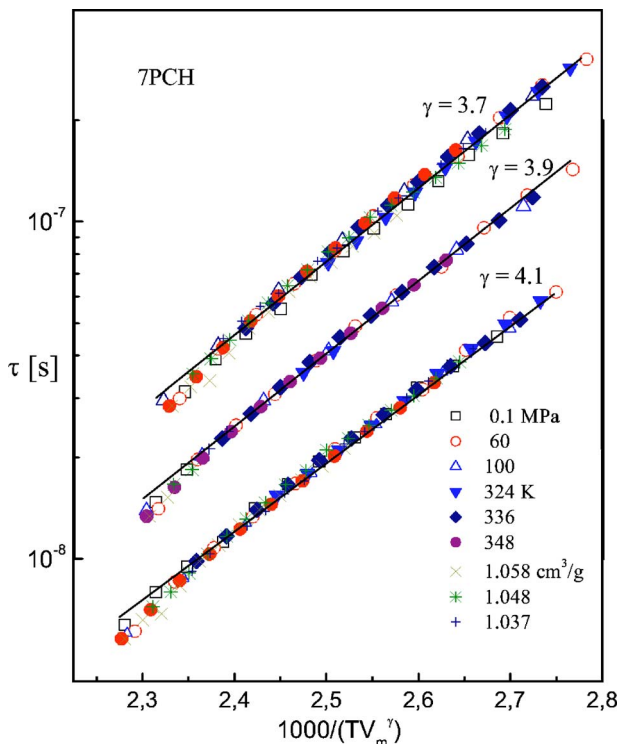
FIG. 4. (Color online) Demonstration of the quality of the scaling procedure in the case of the nematic phase of 7PCH. The vertical scale is valid for the middle plot only; the other plots are shifted up and down by 0.2 in the logarithmic scale. In this way, we could estimate the best value for $\gamma \pm 0.2$. The deviation of points from a straight line at the bottom is due to pretransitional effects in the vicinity of the clearing point.

$n$-alkyl-(4-cyanophenyl)cyclohexanes] are presented in Figs. 2 and 3, respectively. In each case, the longitudinal relaxation time determined in different conditions could be rescaled to one master curve by choosing the proper value of the $\gamma$ parameter. Figure 4 demonstrates how sensitive the scaling procedure is. Changing the $\gamma$ value by $\pm 0.2$ causes the sets of points to spread markedly. A scatter of points is mainly due to the interpolation procedure used when the molar volume data were calculated from the experimental equations of state (the $pVT$ measurements were carried out in 5 K or 10 K steps).

An analysis of the longitudinal relaxation times $\tau_\parallel$ measured for various substances in different phases as functions of temperature, pressure, and density indicates that all these

TABLE I. Values of the $\gamma$ parameter determined in the present work, with the aid of the Maier and Saupe relation (MS) (Ref. [7]) and according to the McColl formula (MC) (Ref. [26]).

| Substance | This work | MS | MC |
|-----------|-----------|-----|-----|
| 5CB | 4.1 | 5.3,[a] 7.62[b] | 5.3[c] |
| 6CB | 4.1 | 6.3,[a] 6.10[b] | |
| 7CB | 3.3 | 4.7,[a] 5.15[b] | |
| 8CB | 4.2 | 4.0,[a] 4.3[b] | |
| 5PCH | 3.5 | 5.24,[a] 3.32[b] | |
| 7PCH | 3.9 | | |
| 8PCH | 3.6 | 3.4[a] | 2.7[d] |
| 8BT | 4.1 | | |

[a]Authors' results [2,3,11,12,25,31,32].
[b]Reference [27].
[c]Reference [31].
[d]Reference [32].

data can easily be rescaled to one master line with only one adjustable parameter $\gamma$. In Table I, the values of the $\gamma$ parameter obtained for various substances in different approaches are gathered. MS indicates the relation predicted in the Maier and Saupe mean-field theory of the nematic state [7], $T_{NI}V_{NI}^\gamma=$const, where NI represents the nematic-isotropic (clearing) point. Maier and Saupe assumed that the stability of the nematic phase came from the dipole-dipole part of the anisotropic dispersion forces. Consequently, they predicted that $T_{NI}\sim V^{-2}$. However, many high-pressure experiments (e.g., [2,10–14,25–32]), as well as theoretical models [33], give distinctly larger $\gamma$ values, which indicate that the repulsive forces play an important role in the creation of the nematic state. It should be mentioned that in the framework of the mean-field approximation, the $\gamma$ values obtained from different experimental data can be treated as equivalent characteristics of the material [28,29,33].

The $\gamma$ values obtained in the present work corroborate other estimations. Therefore, it seems justified to conclude that the energy barrier hindering the flip-flop molecular motions in LC phases is strongly volume dependent. This statement is valid for the nematic as well as for the Sm-$A$ [Fig. 2(d)] and Sm-$E$ [Fig. 1] phases, and so is a determination of the $\gamma$ parameter in the case of a crystal-like smectic phase. Close values of $\gamma$ parameters for the $N$ and Sm-$E$ phases correspond well with the fact that the activation enthalpy and
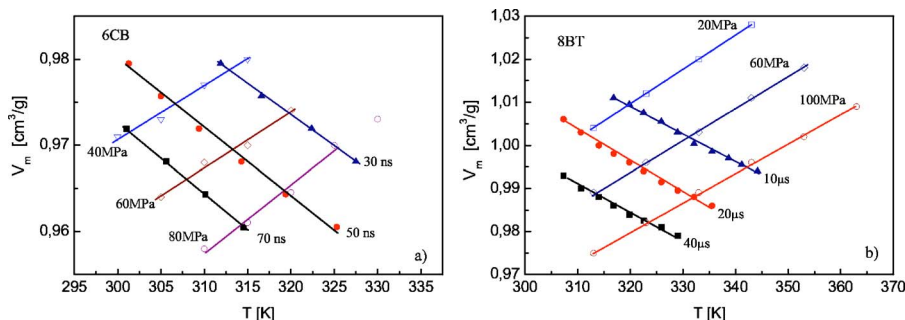


FIG. 5. (Color online) Specific volume-temperature plots (a) for 6CB in the nematic phase and (b) for 8BT in the smectic-$E$ phase at three isobars and at three isochrones.

energy are also similar for both phases [14], in spite of very large differences in the values of the relaxation times (compare Fig. 1 with Figs. 2 and 3).

Recent papers [17–19,21–24] discuss the relative contribution of density and temperature to the dynamics of glass-forming, taking into account the ratio of the absolute value of the isochronic thermal expansion coefficient, $\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$, to the isobaric thermal expansivity, $\alpha_p = -\rho^{-1}(\partial\rho/\partial T)_p$. The ratio $|\alpha_\tau|/\alpha_p = 1$ means equal contribu-

tions to the relaxation times from volume and thermal energies, $|\alpha_\tau|/\alpha_p > 1$ when the temperature dominates, and $|\alpha_\tau|/\alpha_p < 1$ when the volume dominates. Figure 5 displays the $V_m$ vs $T$ plots at $p$=const and $\tau$=const for the (a) nematic and (b) smectic-$E$ phases. For both cases, the ratio $|\alpha_\tau|/\alpha_p = 1.12 \pm 0.05$. This again indicates the equivalence of both thermodynamic quantities in the determination of the relaxation times characterizing the flip-flop motions of molecules in different LC phases.

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