

# Thermodynamic scaling and the characteristic relaxation time at the phase transition of liquid crystals

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(Received 5 March 2008; accepted 28 April 2008; published online 10 June 2008)

The longitudinal relaxation time  $\tau$  of a series of alkyl-isothiocyanato-biphenyls (*n*BT) liquid crystals in the smectic E phase was measured as a function of temperature  $T$  and pressure  $P$  using dielectric spectroscopy. This relaxation time was found to become essentially constant, independent of  $T$  and  $P$ , at both the clearing point and the lower temperature crystalline transition.  $\tau(T, P)$  could also be superposed as a function of the product  $TV^\gamma$ , where  $V$  is the specific volume and  $\gamma$  is a material constant. It then follows from the invariance of the relaxation time at the transition that the exponent  $\gamma$  superposing  $\tau(T, V)$  can be identified with the thermodynamic ratio  $\Gamma = -\partial \log(T_c) / \partial \log(V_c)$ , where the subscript  $c$  denotes the value at the phase transition. Analysis of literature data on other liquid crystals shows that they likewise exhibit a constant  $\tau$  at their phase transitions. Thus, there is a surprising relationship between the thermodynamic conditions defining the stability limits of a liquid crystalline phase and the dynamic properties reflected in the magnitude of the longitudinal relaxation time. © 2008 American Institute of Physics. [DOI: [10.1063/1.2931541](https://doi.org/10.1063/1.2931541)]

## INTRODUCTION

Although the relaxation properties of liquid crystals and supercooled liquids obviously differ (e.g., Debye relaxation with Arrhenius behavior for the former versus stretched relaxation and non-Arrhenius behavior for the latter), there are interesting parallels between the two classes of liquids. For example, theoretical developments on both were based either on energetic or steric effects. Mean field theories assumed that liquid crystallinity arose from long range, anisotropic attractive forces between molecules,<sup>1,2</sup> whereas local packing effects are paramount in models<sup>3,4</sup> in which the excluded volume governs orientational order. The latter idea is central to lattice models,<sup>5,6</sup> especially appropriate for polymers, which have very large aspect ratios. In analogous fashion, structural relaxation of liquids was interpreted historically in terms of either thermally activated transport over local potential barriers<sup>7</sup> or, particularly for polymers, free volume.<sup>8,9</sup> Current understanding has evolved to a common recognition of both factors. Liquid crystalline order results from both long range energetic attractions and short range steric repulsions,<sup>10–14</sup> and similarly, the dynamics of supercooled liquids and polymers reflects both temperature and density effects.<sup>15–17</sup>

At the clearing temperature  $T_c$  above which the liquid crystal becomes an isotropic fluid, the product  $T_c V_c^\Gamma$ , where  $V_c$  is the specific volume at  $T_c$ , is constant.  $T_c$  and  $V_c$  both vary with pressure. The material constant  $\Gamma$  is presumed to

depend on the nature of the intermolecular interactions; i.e., how the effective anisotropic pair potential varies with intermolecular separation  $r$ . Consistent to a good approximation with experimental results,<sup>14,18</sup> this mean field approximation leads to the prediction that the order parameter describing the degree of orientation of the liquid crystal is constant at  $T_c$ .<sup>19</sup> This, in turn, implies constancy of  $\Gamma$ , which is referred to as the thermodynamic ratio

$$\frac{d \log T_c}{d \log V_c} = -\Gamma = \text{const.} \quad (1)$$

For nematic ordering due solely to anisotropic dispersion forces, as in the model of Maier and Saupe,<sup>1</sup>  $\Gamma=2$ . Chandrasekhar and Madhusudana<sup>20</sup> introduced additional contributions to the volume dependence of the radial distribution function to obtain  $\Gamma=3$ . More generally,  $\Gamma$  can be taken as an adjustable parameter in applying Eq. (1) to experimental data. The value of  $\Gamma$  reflects the volume dependence of the orientational contribution to the internal energy, without *a priori* assumptions about the nature of the anisotropic intermolecular potential;<sup>21</sup> larger  $\Gamma$  implies stronger steric repulsions relative to the attractive interactions. Experimentally,  $\Gamma$  is found to lie in the range of 2–8,<sup>22–24</sup> dependent on the molecular structure.<sup>25–28</sup> Although the original Maier–Saupe theory<sup>1</sup> considered only the nematic-isotropic clearing line, this method of analysis has been extended to other liquid crystal phase changes, which are found to yield somewhat smaller values of  $\Gamma$  than for the nematic-isotropic transition.<sup>23,25,29,30</sup>

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There is a scaling law for the dynamics of supercooled liquids analogous to Eq. (1) for liquid crystals. Structural relaxation times  $\tau_\alpha$  (as well as viscosities) measured versus temperature and pressure superpose as a function of the quantity  $TV^{\gamma_\alpha}$ ; i.e.,

$$\tau_\alpha(T, V) = f(TV^{\gamma_\alpha}), \quad (2)$$

where  $f$  is a material-specific function and the exponent  $\gamma_\alpha$  is a material constant.<sup>16,31–33</sup> Since  $\tau_\alpha$  for a glass-forming material at  $T_g$  is constant,<sup>16</sup> Eq. (2) implies that at the glass transition,  $T_g V_g^\gamma$  is constant; thus, analogous to Eq. (1)

$$\frac{d \log T_g}{d \log V_g} = -\gamma_\alpha. \quad (3)$$

Equations (1) and (3) are less general than Eq. (2) since the latter applies throughout the dynamic range, not just at the transition point. The scaling of  $\tau_\alpha$  [Eq. (2)] is an empirical fact, demonstrated for dozens of glass-forming materials.<sup>16</sup> It was motivated by the assumption that the intermolecular potential  $U(r)$  can be approximated by

$$U(r) \sim r^{-3\gamma_\alpha} + \text{const} \sim V^{-\gamma_\alpha} + \text{const}. \quad (4)$$

To the extent this approximation is valid, the entire range of thermodynamic states could be characterized by the single parameter  $\gamma_\alpha$ .<sup>34</sup> Such an approximation to  $U(r)$  is popular in models of crystallization,<sup>35</sup> and over the length scales associated with structural relaxation of supercooled liquids, it leads to the expectation that the local motion of nonassociated molecules depends only on  $TV^{\gamma_\alpha}$ .<sup>31,36,37</sup>

Of course, the experimental fact of Eq. (2) does not mean that Eq. (4) is an accurate representation of the potential nor that the scaling exponent  $\gamma_\alpha$  can be identified with the repulsive power law exponent. However, in a typical experiment in which Eq. (2) has been applied, the volume changes only a few percent, which corresponds to even smaller changes in the intermolecular distance; therefore, even if eq. (4) is not entirely accurate, it can describe the “local” shape of the potential, with the scaling parameter  $\gamma_\alpha$  a measure of the effective steepness. This correspondence was suggested in molecular dynamic simulations on 1,4-polybutadiene<sup>38,39</sup> and shown explicitly in simulations of Lennard–Jones (LJ) systems (neutral particles interacting via a two-body, spherically symmetric potential), carried out using the standard value of 4 for the repulsive power law exponent<sup>40</sup> (i.e.,  $U \sim r^{-12}$ ) or systematically varying it over a range from 3 to 12.<sup>36</sup> The simulation results conform to Eq. (2), with the interesting finding that the scaling exponent is related to, but numerically larger than, one-third the repulsive exponent in the LJ potential. The obtained value of  $\gamma_\alpha$  corresponds to the power law slope on the repulsive side of  $U(r)$  in the region of closest approach between particles. The attractive forces make the effective potential steeper close to the minimum than in the (purely repulsive) limit of small  $r$ . The implication is that the scaling of structural relaxation times can provide information about the steepness of the intermolecular potential,<sup>36,38,39</sup> in the same manner that  $\Gamma$  in Eq. (1), derived from models of the thermodynamic stability of liquid crystalline phases, is related to the anisotropic potential governing orientational order.

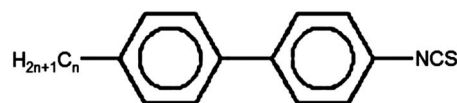


FIG. 1. Chemical structure of  $n$ BT.

Equation (2) can also be derived from the assumption that  $\tau_\alpha$  is governed by the configurational entropy, with the scaling exponent given by the thermodynamic Grüneisen parameter.<sup>41</sup> In turn, the (mode) Grüneisen parameter is approximately equal to  $\gamma_\alpha$  when  $U(r)$  has the form of Eq. (4).<sup>42</sup>

Molecules in the liquid crystalline state undergo longitudinal reorientations (rotation about the short axis), due to coupling with translational motions; that is, fluctuations in molecular centers of mass confer some rotational freedom.<sup>19</sup> (Note that transverse rotations also transpire but usually are too short to measure dielectrically.) Recently the dynamic scaling [Eq. (2)] was extended to the longitudinal relaxation times  $\tau$  of liquid crystals.<sup>43,44</sup> Thus, there exists an exponent  $\gamma$  that superposes the relaxation times in the ordered state, thereby quantifying the volume dependence of the dynamics

$$\tau(T, V) = f(TV^\gamma). \quad (5)$$

It is not necessarily the case that the exponent  $\Gamma$  [Eq. (1)] that quantifies the effect of volume on the order-disorder transition temperature equals the scaling exponent for the longitudinal relaxation times. However,  $\Gamma$  and  $\gamma$  would be equal if  $\tau$  were constant at  $T_c(V_c)$  (i.e., at the pressure-dependent transition temperature). In analogous fashion, Eq. (3) follows from the fact, together with Eq. (2), that the structural relaxation time at the glass transition is independent of  $V$  or pressure  $P$ .<sup>45</sup>

We pursue this idea herein, analyzing dielectric longitudinal relaxation times together with  $V(T, P)$  measurements for the ordered phase of several liquid crystals, including new measurements on three materials from the homologous series of alkyl-isothiocyanato-biphenyls ( $n$ BT), whose structure is depicted in Fig. 1. The transitions include the clearing point, demarcating the ordered and isotropic phases, and in some cases lower temperature transitions between different liquid crystal phases. We use  $T_c$  generally to refer to the temperature of these transitions. For the  $n$ BT materials, we determine both scaling exponents,  $\Gamma$  and  $\gamma$ , and find for the odd  $n$ BT that they are equal to within the experimental error and for 6BT they are nearly equal. Consistent with this equivalence, the longitudinal relaxation times at the liquid crystal transitions are constant. Thus, remarkably the thermodynamics conditions defining the stability limits of the liquid crystalline phase correspond to an essentially fixed value of  $\tau$ .

Beyond the clearing point, the loss of orientational order speeds up reorientation about the short axis, whereby the longitudinal relaxation times became too short to measure with the available dielectric instrument. Accordingly, for selected samples we measured the viscosity  $\eta$  in the isotropic state as a function of  $T$  and  $P$ . As found previously for various liquids,<sup>39</sup>

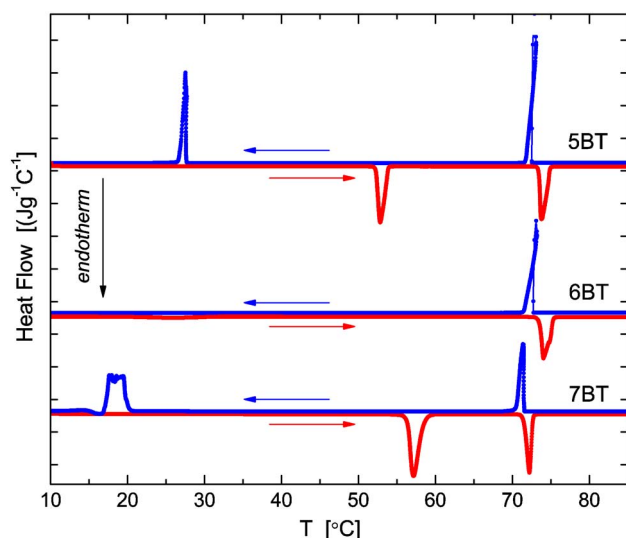


FIG. 2. (Color online) DSC curves for the  $n$ BT homologous series, displaced on the ordinate scale for clarity (tic marks every 25 J/g °C). For 6BT the transition from the SmE to crystal phase at  $-22.4$  °C and the corresponding melting at  $-1.5$  °C are not shown. Note the brief loss of temperature control during the cooling of 5BT and 6BT through the isotropic liquid to smectic liquid crystal transition due to the strong exotherm.

$$\eta = f(TV^{\gamma_{\eta}}), \quad (6)$$

but we find that the value of  $\gamma_{\eta}$  for the isotropic liquid, dominated by the intermolecular repulsive potential, differs from  $\gamma$  for the ordered phase reflecting the anisotropy of this potential.

## EXPERIMENTAL

The alkyl-isothiocyanato-biphenyls were synthesized starting from biphenyl, with the preparative details published elsewhere.<sup>46</sup> Differential scanning calorimetry (DSC) employed a TA Q100. Samples were initially melted at 100 °C, with data taken during subsequent cooling below the crystallization temperature, followed by reheating through the clearing point. Temperatures were varied at 1 °C/min.

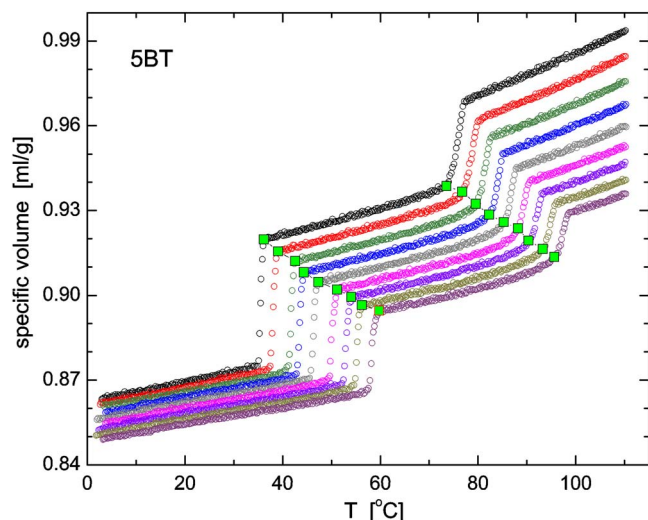


FIG. 3. (Color online)  $V$  vs  $T$  for 5BT at  $P$  from 10 to 90 MPa (top to bottom) in increments of 10 MPa. The bounds of the SmE phase are indicated by the squares.

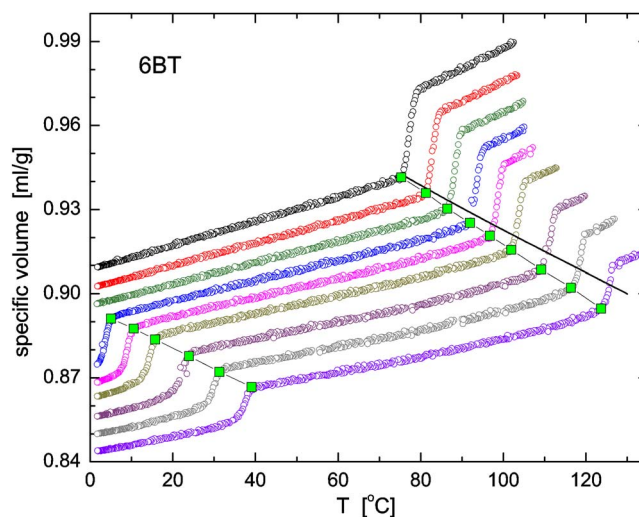


FIG. 4. (Color online)  $V$  vs  $T$  for 6BT at  $P$ =from 10, 30, 50, 70, 90, 110, 140, 170, and 200 MPa (top to bottom). The bounds of the SmE phase are indicated by the squares, with the solid line indicating the  $V_c(T_c)$  calculated using  $\gamma=3.1$ , as determined from scaling the longitudinal relaxation times measured dielectrically.

The volume changes of  $\sim 1$  ml samples were measured as a function of pressure and temperature with a Gnomix instrument, utilizing mercury as the confining fluid. At each pressure, the sample was cooled at 0.5 °C/min from above the clearing temperature to  $-10$  °C. For the next isobaric run, the temperature was raised prior to increasing the pressure. The differential volume data were converted to specific volumes using the value determined at ambient conditions by the buoyancy method.

Dielectric measurements were carried out with the samples in a parallel plate geometry (2 cm diameter and 50  $\mu$ m thick Teflon spacers). The applied field was too weak to orient the material or influence the relaxation spectra, all

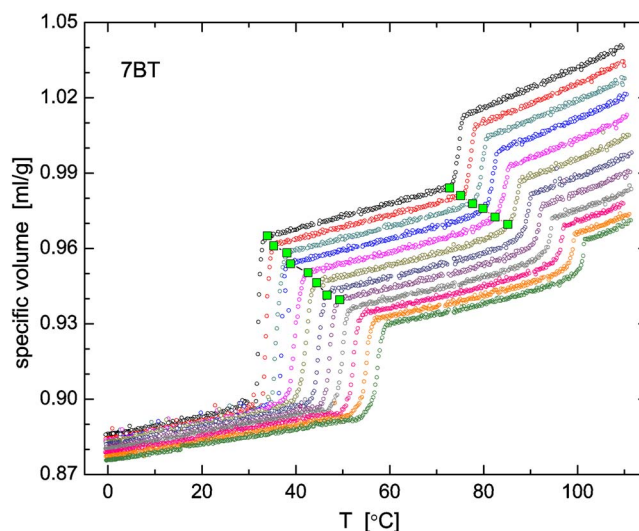


FIG. 5. (Color online)  $V$  vs  $T$  for 7BT for  $P$  from 10 to 120 MPa (top to bottom) in increments of 10 MPa. The bounds of the SmE phase are indicated by the squares. Note the rounded nature of the higher temperature transition, especially evident at the highest pressures after repeated melting and recooling of the sample. This is an indication of thermal degradation, but the extent of such deterioration was not sufficient to significantly affect  $T_c(P)$  or the measured volumes.



of which were described by the well-known Debye equation. Spectra were obtained with a Novocontrol Alpha Analyzer ( $10^{-2}$ – $10^6$  Hz), at ambient pressure using a Delta Design oven ( $\pm 0.02$  K stability) and at elevated pressure with a Tenney Jr. temperature chamber ( $\pm 0.1$  K precision at the sample). Pressure was applied by an Enerpac hydraulic pump in tandem with a pressure intensifier (Harwood Engineering). Pressure was measured with a Sensotec tensometric transducer (resolution = 150 kPa). Viscosities were determined for 5BT and 6BT with a falling body viscometer.<sup>47</sup> (For 7BT there was insufficient sample to do the experiment.) At various fixed temperatures, the viscosity measurements were carried out at pressures from ambient to the condition at which flow ceased ( $\leq 140$  MPa); the shear stress was 5.7 Pa.

## RESULTS

Calorimetry, PVT, and dielectric measurements were carried out on three members of the homologous series of *n*BT with *n* = 5, 6, and 7. Figure 2 shows the transitions seen by DSC at ambient pressure. These materials are crystalline solids at low temperature, isotropic liquids at high temperatures, and exist in the smectic E (SmE) phase at intermediate temperatures (appearing at about 73 °C on cooling). The smectic phase is the only liquid crystalline phase exhibited by *n*BT.<sup>46,48</sup> The  $T_c$  at ambient pressure are within 2° from one another for these three *n*BT samples. The range of stability of the ordered state is larger when there is an even number of carbon atoms in the alkyl side chain, i.e., 6BT. This is a well-known phenomenon in liquid crystals:<sup>19</sup> The hexyl end chain in the *all-trans* orientation lies largely along

the major molecular axis, enhancing the anisotropy underlying liquid crystallinity. For this reason the crystal to smectic transition for 6BT falls  $\sim 20^\circ$  below that for the odd *n*BT.<sup>46,49</sup>

The variation in the specific volume with temperature for various pressures is shown in Figs. 3–5 for 5BT, 6BT, and 7BT, respectively. (Recently Jasiurkowska *et al.*<sup>48</sup> determined from x-ray diffraction measurements the orthorhombic unit cell parameters for *n*BT in the SmE phase, which can be used to infer the specific volumes; these results are 5–8% smaller than the present direct volumetric measurements.) We determined the onset temperature for disappearance of the SmE phase both at higher *T* (clearing temperature) and lower *T* (due to crystallization); these  $T_c$  correspond to the ambient pressure transitions seen in Fig. 1. The pressure-dependent transition temperatures could be described by a quadratic function (units are °C and MPa):

5BT

$$T_c = 32.3 + 0.323P - 2.7 \times 10^{-4}P^2 \quad \text{cryst-SmE}, \quad (7a)$$

$$T_c = 73.9 + 0.284P - 1.9 \times 10^{-4}P^2 \quad \text{SmE-iso}, \quad (7b)$$

6BT

$$T_c = -22.2 + 0.406P - 6.8 \times 10^{-4}P^2 \quad \text{cryst-SmE}, \quad (7c)$$

$$T_c = 74.0 + 0.285P - 1.9 \times 10^{-4}P^2 \quad \text{SmE-iso}, \quad (7d)$$

7BT

$$T_c = 26.4 + 0.273P - 1.2 \times 10^{-4}P^2 \quad \text{cryst-SmE}, \quad (7e)$$

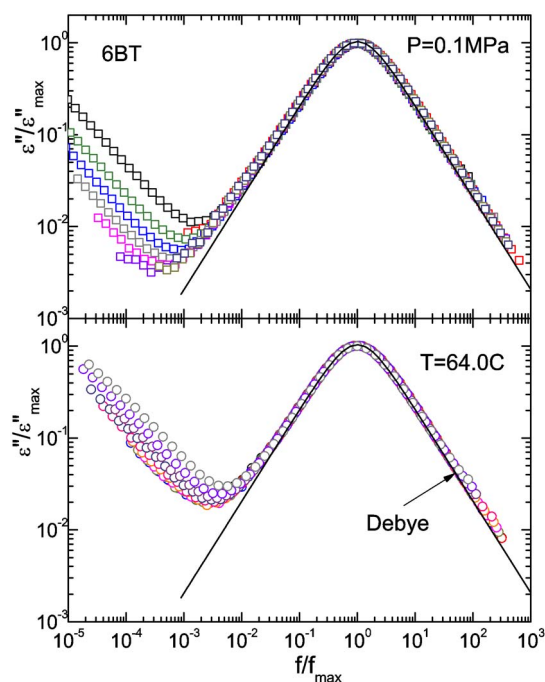


FIG. 6. (Color online) Representative dielectric loss curves for 6BT; upper panel (top to bottom): 63.6, 54.5, 45.5, 36.9, 28.1, 19.5, 10.4, 0.7, and  $-5.6^\circ\text{C}$  at ambient pressure; lower panel (top to bottom): 7.7, 27.6, 49.7, 72.6, 95.9, 118.0, 143.7, 169.7, 196.5, 220.2, 245.4, and 269.2 MPa at  $64.0^\circ\text{C}$ . The solid lines are the Debye function, which describes the peaks well.

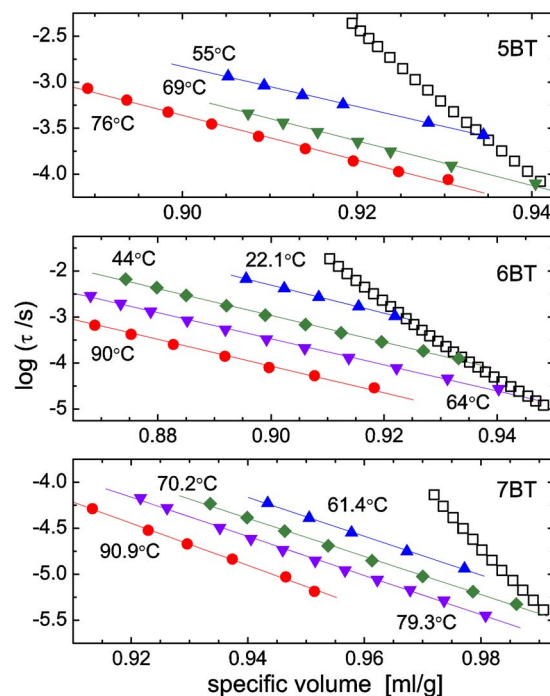


FIG. 7. (Color online) Longitudinal relaxation times measured for the SmE phase of *n*BT as a function of *V*, showing results for both the isobaric (open symbols, 0.1 MPa) and isothermal (solid symbols, *T* as indicated) experiments; all measurements were obtained with the samples in equilibrium. The solid lines are only to guide the eyes.

TABLE I. Scaling exponents for  $n$ BT.

		5BT	6BT	7BT	8BT
$\Gamma$ [Eq. (1)]	SmE-iso	$2.2 \pm 0.2$	$2.4 \pm 0.2$	$2.2 \pm 0.2$	$2.7^a$
	SmE-cryst	$2.2 \pm 0.2$	$4.1 \pm 0.2$	$2.2 \pm 0.2$	...
$\gamma$ [Eq. (5)]	SmE phase	$2.3 \pm 0.1$	$3.1 \pm 0.2$	$2.3 \pm 0.1$	$4.1^b$
$\gamma_\eta$ [Eq. (6)]	Isotropic phase	$4.2 \pm 0.2$	$5.8 \pm 0.2$	...	...

<sup>a</sup>Reference 29.<sup>b</sup>Reference 43.

$$T_c = 72.4 + 0.241P - 9 \times 10^{-6}P^2 \quad \text{SmE-iso.} \quad (7f)$$

Comparable results for 6BT were reported from differential thermal analysis measurements.<sup>50</sup> In Table I are listed  $\Gamma$  values for the three materials, determined from the slopes of double logarithmic plots of  $T_c$  versus  $V_c$ .

Dielectric relaxation measurements were carried out on the  $n$ BT liquid crystals as a function of temperature at ambient pressure and as a function of pressure at various fixed temperatures. As illustrated in Fig. 6 for 6BT, under all measurement conditions, the spectra have the Debye form (exponential relaxation), as reported previously from measurements at only ambient pressure.<sup>46</sup> From the frequency of the maximum in the dielectric loss  $f_{\max}$  we obtain a relaxation time  $\tau = (2\pi f_{\max})^{-1}$  for the longitudinal rotational motion. These are plotted in Fig. 7 as a function of  $V$  for the three samples, with the specific volume calculated for each measurement condition by interpolating the  $V(T, P)$  data using the Tait equation of state (EOS)

$$V(T, P) = V_0 \exp(\alpha_0 T) \{1 - 0.0894 \ln[1 + P/B(T)]\}, \quad (8)$$

where  $\alpha_0$  is the thermal expansion coefficient at zero pressure,

$$B(T) = b_0 \exp(-b_1 T) \quad (9)$$

and  $V_0$ ,  $b_0$ , and  $b_1$  are material constants. The Tait parameters for the three liquid crystals in the SmE phase are tabulated in Table II. We found the Tait EOS described well  $V(T, P)$  for the odd  $n$ BT, but was somewhat less accurate for 6BT.

The viscosities of 5BT and 6BT were measured as a function of pressure at three temperatures, and using the Tait fit to  $V(T, P)$  above the clearing point (Table II), we obtain the plot of  $\eta$  versus  $V$  in Fig. 8. The curvature of the data reflects departure from a simple volume activated process. This is normal behavior for nonhydrogen bonded liquids; both volume and temperature govern the dynamics so that simple models based on activated dynamics fail.<sup>16</sup>

## DISCUSSION

### Thermodynamic scaling

The relationship [Eq. (1)] between  $T_c$  and  $V_c$ , developed originally for the clearing point of nematics,<sup>1</sup> has been applied to other transitions in various liquid crystals including  $p$ -azoxyanisole, heptyloxazoxybenzene, octyloxycyanobiphenol, octylisothiocyanatobiphenyl, and a series of di-alkylazoxybenzenes.<sup>23,25,29,30,49</sup> From the PVT data (Figs. 3–5), the thermodynamic ratio for the transition from the

SmE phase to the isotropic phase is essentially the same for the three  $n$ BT,  $\Gamma = 2.2$  (Table I). For the octyl-substituted thiocyanatobiphenyl 8BT, Urban and Würflinger<sup>43</sup> reported a slightly higher value of  $\Gamma = 2.7$ . For the nematic to isotropic transition in 4'-alkyl-4-cyanobiphenyls ( $n$ CB), which differ from the present materials by the absence of a terminal sulfur atom. Shirakawa *et al.*<sup>51</sup> reported that  $\Gamma$  decreases with increasing alkyl chain length, while Urban and Würflinger<sup>43</sup> found no systematic variation of  $\Gamma$  with  $n$ . For alkoxyazoxybenzenes, Tranfield and Collings<sup>52</sup> observed a systematic decrease in the exponent with alkyl chain length, while for 4-alkyl-(4'-cyanophenyl)cyclohexane ( $n$ PCH) Urban and Würflinger<sup>43</sup> found no effect of  $n$  on  $\Gamma$ . Aside from the effect of alkyl chain length, the presence of such an end tail or greater flexibility of the molecular core seems to lead to smaller values of  $\Gamma$ .<sup>43,44</sup> Note also in Table I that for 5BT and 7BT, the value of  $\Gamma$  is the same for the transition of the SmE phase to the crystalline phase at lower temperature as for the clearing transition at higher  $T$ . However, for 6BT crystallization from the SmE phase gives a significantly larger  $\Gamma$  than for the clearing transition (Table I). Thus, although it is tempting to draw inferences from the magnitude of the exponent in Eq. (1) concerning the effect of molecular structure on the anisotropic potential, the situation at present is too complicated.

As described in the Introduction, there is an alternative scaling exponent,  $\gamma$  [Eq. (5)], that we expect to be related to  $\Gamma$ . We replot the data from Fig. 7 in Fig. 9 versus the product variable  $TV^\gamma$ , with the exponent  $\gamma$  determined empirically to superpose the longitudinal relaxation times for each sample. As can be seen, for the odd  $n$ BT the  $\tau$  are uniquely determined by  $TV^\gamma$  with a common value of  $\gamma = 2.3 \pm 0.1$ . This is equivalent within the error to the value of  $\Gamma$  (Table I). However, superpositioning for 6BT is obtained with a higher value of  $\gamma = 3.1 \pm 0.2$ ; this is too large to be consistent with the slope of the transition ( $\Gamma$  from  $V_c$  versus  $T_c$ ) in the PVT data in Fig. 4. Similarly, Urban and Würflinger<sup>43</sup> obtained  $\gamma = 4.1$  for 8BT; thus, the scaling exponent for the longitudinal relaxation times in the SmE phase is larger for the even  $n$ BT than for the odd  $n$ BT.

Commonly, activation parameters are used as measures of the effect of changing thermodynamic conditions on the frequency of the dynamics; these parameters quantify the change of the relaxation time with  $T$  or  $P$  under conditions of constant  $T$ ,  $P$ , or  $V$ .<sup>16</sup> Some values of the activation parameters for  $n$ BT materials have been reported in the literature.<sup>29,46,50</sup> These parameters and the scaling law [Eq. (5)] contain the same information. For example, the ratio of

TABLE II. EOS parameters for the *n*BT liquid crystals.

Phase	5BT		6BT		7BT	
	SmE	Isotropic	SmE	Isotropic	SmE	Isotropic
$V_0$ (ml/g)	$0.909 \pm 0.004$	$0.921 \pm 0.001$	$0.913 \pm 0.001$	$0.922 \pm 0.001$	$0.954 \pm 0.008$	$0.947 \pm 0.005$
$\alpha_0 \times 10^4 (\text{C}^{-1})$	$5.06 \pm 0.04$	$7.90 \pm 0.05$	$4.83 \pm 0.02$	$7.86 \pm 0.06$	$5.23 \pm 0.05$	$9.90 \pm 0.18$
$b_0 (\text{MPa}^{-1})$	$141 \pm 1$	$98.9 \pm 2.1$	$211 \pm 2$	$178 \pm 6$	$157 \pm 2$	$212 \pm 14$
$b_1 \times 10^3 (\text{C}^{-1})$	$0.73 \pm 0.14$	$2.17 \pm 0.21$	$3.57 \pm 0.06$	$3.54 \pm 0.04$	$1.74 \pm 0.16$	$9.1 \pm 0.7$

the isobaric activation enthalpy  $H_p$  and the isochoric activation energy  $E_V$  is related directly to the scaling exponent, according to<sup>53</sup>

$$H_p/E_V = 1 + \alpha_p T \gamma, \quad (10)$$

where  $\alpha_p$  is the pressure-dependent, isobaric thermal expansion coefficient. While the activation parameters change with  $T$ ,  $P$ , and  $V$ , the scaling exponent is strictly constant, which makes it more amenable to analysis.

It has been shown for various fluids<sup>39</sup> that the viscosity of isotropic liquids is in accord with Eq. (6). As shown in Fig. 10, a similar result is obtained for  $\eta$  for 5BT and 6BT from Fig. 8. The scaling exponent for the isotropic state is larger than  $\gamma$  for the SmE phase. Of course, these exponents characterize different things— $\gamma$  reflects the anisotropy of the intermolecular potential, whereas  $\gamma_\eta$  depends on the steepness of the isotropic repulsive potential.<sup>36,39,38</sup>

### Longitudinal relaxation time at the phase transition

The expectation that the exponents  $\Gamma$  and  $\gamma$  should be the same follows from the idea that both are a measure of the anisotropic intermolecular potential, values greater than 2 reflecting the increasing importance of the repulsive interactions in governing both the ordering and motions of molecules in the liquid crystalline state. As pointed out above, if  $\Gamma$  and  $\gamma$  are equal, it follows that  $\tau$  assumes a constant value at  $T_c(V_c)$ ; that is, the longitudinal relaxation time is indepen-

dent of pressure. Using the scaling function [Eq. (5)] we extrapolate the measured relaxation times for the SmE phase to  $T_c$ , with the results plotted as a function of pressure in Fig. 11. At both the lower and higher temperature transitions,  $\tau$  for the odd *n*BT are sensibly independent of pressure (Table III). For 6BT there is a weak change with  $P$ , on the order of one decade per gigapascal. This change in  $\tau$  for 6BT is consistent with the fact that  $\gamma$  is not equal to  $\Gamma$ .

It can be seen in Table III that longitudinal reorientations at the clearing point become faster with increasing size of the pendant alkyl chain;  $\tau$  decreases by about half a decade per additional carbon atom in *n*BT. This is counterintuitive and arises from the fact that as  $n$  increases, the “unoccupied volume” per unit cell volume increases,<sup>48</sup> leading to the unexpected effect of faster molecular rotation for the larger *n*BT molecules.

In Fig. 12 are collected data for other liquid crystals, calculated from published results<sup>54–56</sup>. A general invariance of  $\tau(T_c)$  to thermodynamic conditions is evident. The average value of the relaxation time of the liquid crystal at the transition and its variation with pressure are tabulated in Table III. It is striking that the thermodynamic conditions defining the stability limits of a liquid crystalline phase should correspond to any particular property of the dynamics, such as a fixed value of  $\tau$ .

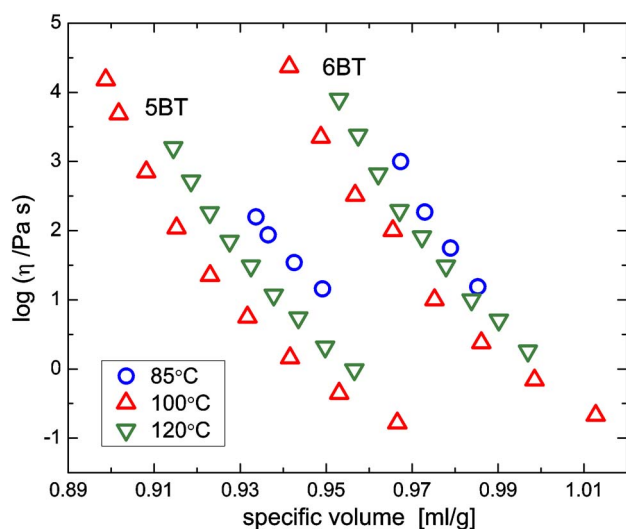


FIG. 8. (Color online) Viscosities of 5BT and 6BT in the isotropic state measured as a function of  $P$  at the indicated  $T$  and plotted vs  $V$ .

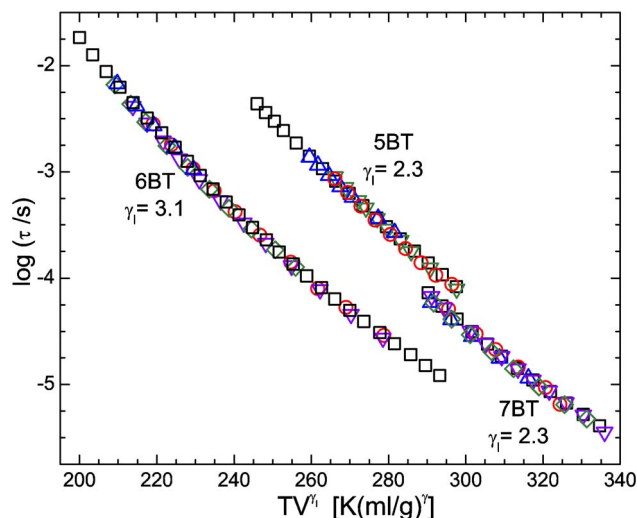


FIG. 9. (Color online) Longitudinal relaxation times for the SmE phase of *n*BT as a function of  $TV^\gamma$ , with the respective scaling exponents as indicated. The symbols are the same as in Fig. 7.

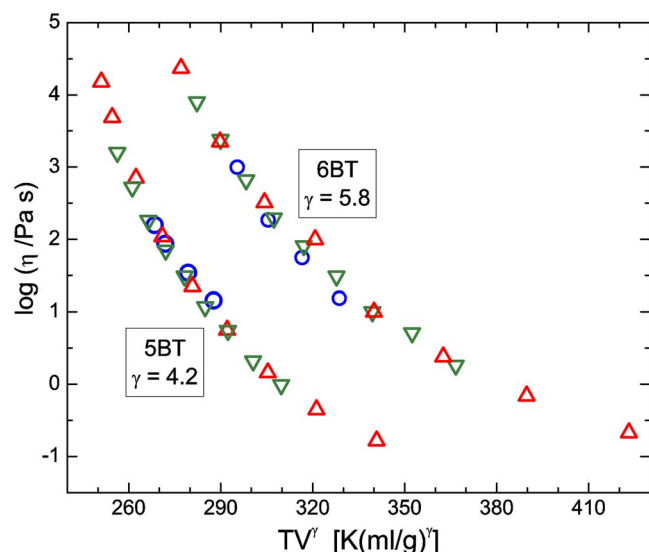


FIG. 10. (Color online) Viscosities of 5BT and 6BT from Fig. 8 plotted as a function of  $TV^\gamma$ , with superpositioning obtained for the indicated values of the scaling exponent.

### Thermodynamic properties at the clearing point

The increase in specific volume upon transition to the isotropic phase  $\Delta V_c$  was determined in the usual manner as the mean of the extrapolated volumes of the adjacent phases at  $T_c$ . The changes in the enthalpy  $\Delta H_c$  and entropy  $\Delta S_c$  for the transition can be calculated using the  $PVT$  data and the Clapeyron equation

$$\Delta S_c = \Delta V_c \frac{dP}{dT_c}, \quad (11)$$

where  $dP/dT_c$  is the isochoric thermal pressure coefficient. The enthalpy change at the clearing point is then obtained from

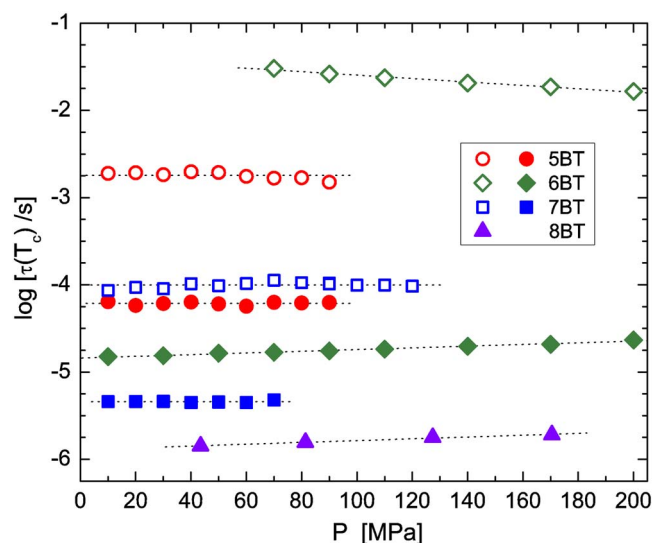


FIG. 11. (Color online) Longitudinal relaxation times in the SmE phase at the low (open symbols) and high (solid symbols) temperature transitions of  $n$ BT. Only 6BT exhibits even a weak pressure-dependence.

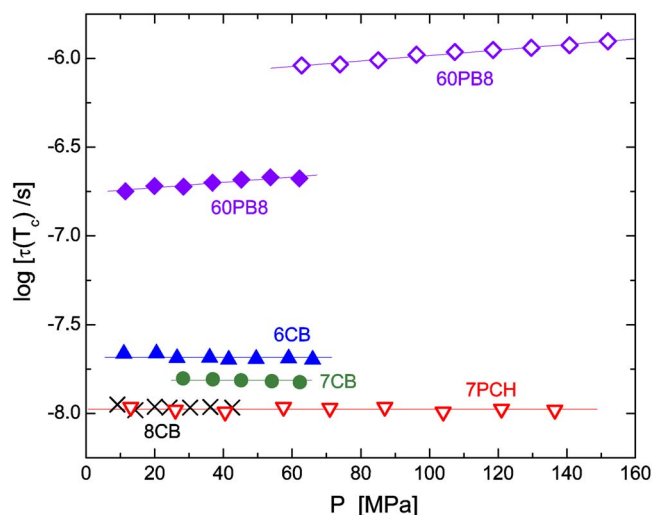


FIG. 12. (Color online) Longitudinal relaxation times in the ordered state vs pressure for various liquid crystals (data from Refs. 26 and 54–56).

$$\Delta H_c = T_c \Delta S_c. \quad (12)$$

The results are in Table IV.

Integration of the heat capacity and its ratio with  $T$  from the DSC measurements yields alternative determinations of  $\Delta H_c$  and  $\Delta S_c$ , respectively. The strongly exothermic nature of the transition (see Fig. 2) introduces some uncertainty into the cooling data, so we integrate the heating runs to obtain the results in Table IV. These are consistent with the  $PVT$  determinations, although the DSC experiments were carried out at 0.1 MPa, whereas the  $PVT$  results are for 10 MPa.  $\Delta V_c$ ,  $\Delta H_c$ , and  $\Delta S_c$  all decrease weakly with  $P$ , for the present materials and generally,<sup>30,52,57</sup> however, the effect of the modest change from 0.1 to 10 MPa is less than the experimental uncertainty. Published enthalpy changes determined by DSC for 5BT and 6BT (Ref. 46) are equivalent to those in Table IV, but the value reported for 7BT (Ref. 46) is substantially smaller than herein. The reduced accuracy of DSC determinations for liquid crystal phase changes compared to  $PVT$  methods has been pointed out previously.<sup>57</sup>

Finally, the isochoric entropy change can be obtained from

$$\Delta S_V = \frac{\alpha_P}{K_T} \Delta V_c \quad (13)$$

in which  $K_T$  is the isothermal compressibility.  $\Delta S_V$  avoids complications due to changes in the intermolecular potential with volume and is a measure of the entropy change at the transition due primarily to conformational changes. Values for these various quantities are listed in Table IV for the three  $n$ BT; there is no significant change with length of the alkyl end group. This implies similar degrees of disorder in the smectic phase. Theoretical models predict that the nature of the alkyl tail can affect the thermodynamic property changes at the transition, but the magnitude and even the sign of these changes with alkyl group size (e.g., with  $n$ ) seem to depend on the flexibility of the end group.<sup>58,59</sup>



TABLE III. Relaxation times at the liquid crystal transition.

liquid crystal	Transition	$\log(\tau(T_c)s)$	Ref. <sup>a</sup>
4- <i>n</i> -pentyl-4'-thiocyanatobiphenyls (5BT)	Crystal-SmE	$-2.75 \pm 0.04$	Herein
	SmE-isotropic	$-4.21 \pm 0.01$	
4- <i>n</i> -hexyl-4'-thiocyanatobiphenyls (6BT)	Crystal-SmE	$-1.65 \pm 0.10$	Herein
	SmE-isotropic	$-4.75 \pm 0.06$	
4- <i>n</i> -heptyl-4'-thiocyanatobiphenyls (7BT)	Crystal-SmE	$-4.00 \pm 0.01$	Herein
	SmE-isotropic	$-5.34 \pm 0.02$	
4- <i>n</i> -octyl-4'-thiocyanatobiphenyls (8BT)	SmE-isotropic	$-5.78 \pm 0.06$	Refs. 29 and 43
2-(4-hexyloxyphenyl)-5-octyl-pyrimidine (60PB8)	SmC-SmA	$-5.97 \pm 0.05$	Ref. 54
	SmA-nematic	$-6.70 \pm 0.03$	
4'- <i>n</i> -pentyl-cyanobiphenyl (5CB)	Nematic-isotropic	$-7.85 \pm 0.20$	Ref. 55
4'- <i>n</i> -hexyl-cyanobiphenyl (6CB)	Nematic-isotropic	$-7.68 \pm 0.01$	Ref. 26
4'- <i>n</i> -heptyl-cyanobiphenyl (7CB)	Nematic-isotropic	$-7.81 \pm 0.01$	Ref. 56
4'- <i>n</i> -heptyl-cyanobiphenyl (8CB)	Nematic-isotropic	$-7.97 \pm 0.01$	Ref. 26
4- <i>trans</i> -heptylcyclohexylcyanobenzene (7PCH)	Nematic-isotropic	$-7.97 \pm 0.01$	Ref. 54

<sup>a</sup>Source of  $\tau$  and  $PVT$  data used to calculate  $\tau(T_c, P_c)$ .

## SUMMARY

$PVT$ , dielectric, and viscosity measurements were obtained on three members of the  $nBT$  series of liquid crystal forming materials. We show that both the longitudinal relaxation times in the SmE phase and the viscosity in the isotropic phase are determined by the product of temperature and specific volume, with the latter raised to a constant  $\gamma$ . The dynamics in the ordered and isotropic phases have different scaling exponents, since the respective  $\gamma$  is determined by the steepness of the anisotropic or the isotropic intermolecular potential. With the observation that  $\tau$  assumes a constant value at the phase transition of the liquid crystal, the constant  $\gamma$  can be identified with the thermodynamic ratio,  $\Gamma$  [Eq. (1)]. Similar results are found for other liquid crystals for which elevated pressure data are available in the literature. The implication of these findings is that the control parameter (e.g., the Gibbs free energy) driving the transitions of a liquid crystal has the same functional dependence on  $T$ ,  $P$ , and  $V$  as does the longitudinal relaxation time.

TABLE IV. Thermodynamic parameters for the  $nBT$  ( $P=10$  MPa except for DSC results).

		5BT	6BT	7BT
$T_c$ (K)		350.2	350.3	348.1
$\alpha_T(T_c)$ (K <sup>-1</sup> )		$6.32 \times 10^{-4}$	$6.11 \times 10^{-4}$	$6.48 \times 10^{-4}$
$\kappa_P(T_c)$ (MPa <sup>-1</sup> )		$6.26 \times 10^{-4}$	$4.90 \times 10^{-4}$	$6.08 \times 10^{-4}$
$\Delta V_c$ (ml/mol)		8.37	8.56	8.34
$dP/dT_c$ (MPa/K)		$3.53 \pm 0.19$	$3.70 \pm 0.22$	$4.04 \pm 0.48$
$\Delta S_c$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Eq. (11)	$29.6 \pm 1.8$	$31.7 \pm 3.1$	$33.8 \pm 2$
	DSC	$29.5 \pm 0.2$	$30.6 \pm 0.2$	$28.3 \pm 0.5$
$\Delta H_c$ (kJ/mol)	Eq. (12)	$10.4 \pm 0.6$	$11.1 \pm 1.1$	$11.8 \pm 0.7$
	DSC	$10.4 \pm 0.1$	$10.7 \pm 0.1$	$10.3 \pm 0.1$
$\Delta S_V$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Eq. (13)	$8.5 \pm 0.4$	$10.7 \pm 0.3$	$8.9 \pm 1.3$

## ACKNOWLEDGMENTS

The work at NRL was supported by the Office of Naval Research. R.B.B. acknowledges an NRL-ASEE postdoctoral fellowship. Viscosity measurements at Georgia Tech were supported by the National Science Foundation (Grant No. EEC#0540834).

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