

# Characteristic relaxation times and their invariance to thermodynamic conditions

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The dynamics of molecular liquids and polymers exhibit various “transitions”, associated with characteristic changes in properties. With decreasing temperature or increasing pressure, these transitions include (i) the onset of intermolecular cooperativity with consequent non-Arrhenius and non-Debye behavior; (ii) the dynamic crossover at which derivatives of the relaxation time and strength exhibit breaks; (iii) vitrification, corresponding to cessation of translational and rotational motions; and (iv) for anisotropic molecules the development of liquid crystallinity. At each of these transitions of a liquid, the structural or reorientational relaxation time is constant, independent of thermodynamic conditions; that is, while the temperature of the transition depends on pressure, the relaxation does not.

## Introduction

The study of molecular motions in dense fluids is of long-standing interest to physicists, chemists, and biologists. How the time scale of the dynamics varies with temperature, pressure, entropy, *etc.*, reflects the nature of the intermolecular potential, thus providing fundamental insights into chemical structure and the forces between molecules. The relaxation behavior also governs to a large extent the physical and mechanical properties underlying many applications of materials, so that such studies facilitate material engineering and development.

Both small molecules and polymers exhibit a spectacular variation of their “structural” relaxation time,  $\tau$ , over the range of the liquid state. This relaxation

time is a measure of the time scale for reorientation of the molecule or, in the case of polymers, correlated conformational transitions of a couple of backbone bonds (“local segmental dynamics”). Large changes in  $\tau$  are especially evident when crystallization is avoided (for example, by quenching); temperature changes near the glass temperature  $T_g$  of one degree can shift  $\tau$  by decades, corresponding to apparent activation energies that are two or more orders of magnitude larger than the van der Waals bond energy between molecules. Representative data are shown in Fig. 1 for a polymer, *atactic*-polypropylene (aPP),<sup>1</sup> and a molecular liquid, polychlorinated biphenyl (PCB).<sup>2</sup> Their respective  $\tau$  show quite similar behavior; indeed, near the glass transition differences between polymers and molecular liquids are not easily discerned. However, for polymers another relaxation time can be measured

that relates to the motion of the chain. This global process has a weaker temperature dependence than the local segmental dynamics.<sup>3</sup> There is no corresponding global relaxation time for small molecules, large scale (translational) motion having properties related to the reorientational dynamics; for example, the Maxwell equation

$$\tau = \eta/G_\infty \quad (1)$$

relates  $\tau$  to the viscosity,  $\eta$ , and the shear modulus at infinite frequency,  $G_\infty$  (usually approximated by the glassy modulus, although the latter decreases somewhat with temperature). Eqn (1) is similar to the Debye–Stokes–Einstein equation.<sup>4</sup>

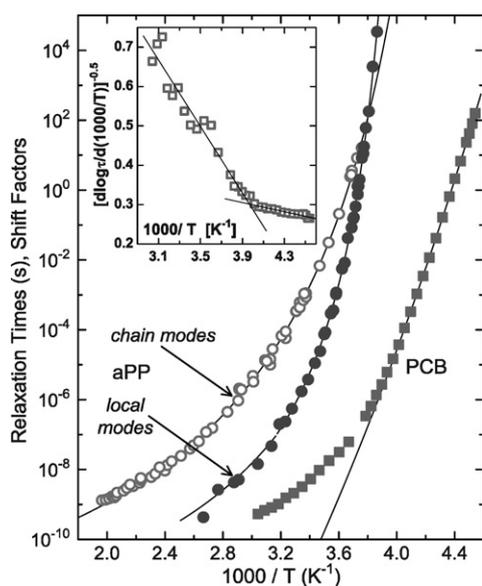
Analysis of liquid motions is simplest for non-interacting species, and solutions were obtained in the early 20th century for translational Brownian diffusion<sup>5</sup> and rotational diffusion<sup>6</sup> in dilute solution. When neighbors exert a reciprocal influence, interpretation of the behavior becomes much more complex, with quantitative, predictive, first-principles theories as yet unattained. Efforts remain at the model-building stage, primarily addressing how molecular motions vary with thermodynamic variables.

Our focus herein is on the time scale of molecular motions, the central importance of which is seen in the correlation of  $\tau$  with other properties. For example, the shape of the relaxation function (or equivalently, the breadth of the absorption peak in the spectrum) is uniquely determined by

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**Fig. 1** Local segmental and global chain relaxation times (the latter multiplied by a constant to superpose on the local  $\tau$  at lower  $T$ ) for atactic-polypropylene<sup>1</sup> and the reorientational relaxation times for 42% chlorinated biphenyl.<sup>2</sup> The solid lines are fits to eqn (4), which for the molecular liquid only describes  $\tau(T)$  up to  $T_B$ . The inset shows the Stickel derivative function [eqn (5)] for the PCB.

$\tau$ ; thus, if increases in  $P$  are compensated by increases in  $T$  such that  $\tau$  remains constant, the relaxation function is constant.<sup>7,8</sup>  $\tau$  also conforms to the scaling law<sup>9–12</sup>

$$\tau = f(TV^\gamma) \quad (2)$$

in which  $f$  represents a function,  $V$  is the specific volume, and  $\gamma$  a material constant related to the steepness of the intermolecular repulsive potential.<sup>13–15</sup> An explicit form for the dependence of  $\tau$  on  $TV^\gamma$  can be derived from the assumption that the configurational entropy drives the mobility.<sup>16</sup> The issue we examine herein is the behavior of  $\tau$  at the various dynamic transitions of the liquid state. As described below, different ranges of temperature and pressure are associated with different dynamical behaviors. We show that there is a particular magnitude of the relaxation time associated with the transition of a given liquid from one dynamic regime to another, and this value of  $\tau$  does not change with thermodynamic conditions. Variations in pressure or density will change the transition temperature, but for a given material  $\tau$  at the transition remains the same. In turn, from eqn (2) the quantity  $TV^\gamma$  at the transition will also be a material constant.

These dynamical regimes within the liquid state include:

(i) At high temperatures molecular interactions are sufficiently small that the

relaxation is exponentially fast and is often described by the Debye function. (Exceptions would be when chain motions contribute to the decay. The global chain dynamics do not exhibit exponential relaxation, even for isolated chains.<sup>17</sup>) Debye behavior implies the motion entails a single activation barrier with an Arrhenius temperature dependence of the relaxation times

$$\tau = \tau_0 \exp(E_a/RT) \quad (3)$$

where  $R$  is the gas constant and the prefactor  $\tau_0$  and activation energy  $E_a$  are temperature-independent constants. As a liquid or polymer is cooled, the loss of thermal energy and concomitant molecular crowding constrain the dynamics, making them more intermolecularly cooperative; the motion of each molecule is affected by the motion of neighboring molecules.<sup>18</sup> The temperature,  $T_A$ , associated with the onset of non-Debye and non-Arrhenius behaviors<sup>19</sup> characterizes the first dynamic transition.

(ii) The intermolecular cooperativity developing as temperature is lowered or pressure increased has many manifestations, all related to heterogeneity of the dynamics (*i.e.*, spatial fluctuations of the relaxation time for durations comparable to its average value<sup>20,21</sup>). These effects include: non-Gaussian distribution of the molecular displacement, seen for example

in dynamic correlation functions such as the van Hove function for molecular diffusion,<sup>22</sup> non-Debye relaxation commonly described by the Kohlrausch-William-Watts function,<sup>23</sup> and, as illustrated in Fig. 1, a non-Arrhenius temperature dependence, conforming to the Vogel-Fulcher (VF) equation<sup>23</sup>

$$\tau = A \exp\left(\frac{B}{T - T_0}\right) \quad (4)$$

where  $A$ ,  $B$  and  $T_0$  are constants. As the relaxation time of the liquid becomes longer with further cooling or densification, a change occurs in the nature of the non-Arrhenius temperature dependence of  $\tau$ . Eqn (4) still describes the behavior, but with different values for the 3 VF parameters.<sup>24</sup> This “dynamic crossover” from one VF form to another is the second characteristic of liquid motions.

(iii) Ultimately fluidity is lost due to vitrification at the glass transition.<sup>12</sup> The material retains the microscopic disorder of the liquid state, but behaves as a solid because its viscosity is so large; that is, the relaxation time is much longer than the experimental time scale (see Fig. 1). This freezing is observed in most non-crystallizing materials and terminates the liquid regime.

(iv) The presence of long range order distinguishes liquid crystals from isotropic fluids.<sup>25</sup> The phenomenon requires anisotropy of the intermolecular potential, resulting from molecules having an anisotropic shape or polarity. Both short range repulsive forces and long range dipolar and van der Waals attractions can contribute to the formation of orientational (nematic) or positional (smectic) structure. Despite the long range order of the liquid crystal phase, a degree of fluidity is retained: in nematics the molecules slide past one another while remaining aligned; in smectic liquid crystals the ordered layers slide over one another, although there is substantial resistance. The orientation of molecules to form a liquid crystal, or the change from one phase to another, represents the final characteristic of liquid behavior considered herein. With further cooling or pressurization, liquid crystals usually attain the three-dimensional order of a crystalline solid.

In this short review we review a broad range of experimental data to bring out a unifying feature of the dynamics of

liquids, that at each of these four characteristic transitions,  $\tau$  for a given material is essentially constant, independent of  $T$ ,  $P$ , and  $V$ . The relaxation time is not universal at any transition, but it is a material constant. This property must be taken into account by theory, since  $\tau$  is a key parameter for fundamental understanding of the dynamics of complex liquids (reorientation motion in the case of molecular liquids and segmental dynamics for polymers). In the following sections we review the experimental facts establishing the near invariance of  $\tau$  at these transitions.

## 1. Onset of Arrhenius behavior

At sufficiently high temperature the logarithm of the relaxation time becomes inversely proportional to temperature [eqn (4) with  $T_0 = 0$ ]. Such Arrhenius behavior indicates an absence of inter-

molecular cooperativity of the motions. Arrhenius plots of the relaxation times for five liquids are shown in Fig. 2, with the data converging at the highest temperatures to linear behavior. The value of  $T_A$  can be determined using the derivative function<sup>19,26</sup>

$$\phi_T = \left[ \frac{d \log(\tau)}{d(1000/T)} \right]^{-\frac{1}{2}} \quad (5)$$

which is model-independent and yields lines of different slope and intercept for Arrhenius *versus* VF behavior.<sup>27</sup>

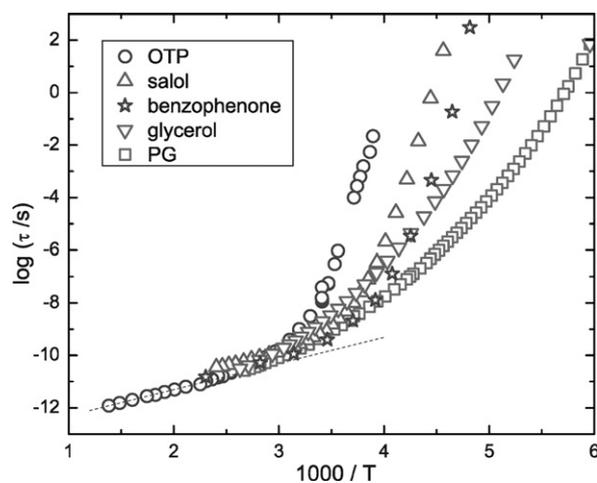
In Table 1 are listed the relaxation times at the onset of Arrhenius behavior for several liquids and one polymer. The  $\tau$  values were either directly measured by dielectric spectroscopy or obtained from  $\eta$  *via* eqn (1). (Since the relaxation times at high temperature are very small, experimentally it is sometimes easier to measure

$\eta$  rather than  $\tau$ . However, this procedure only applies to low molecular weight materials, since for entangled polymers  $\tau$  would reflect the chain dynamics not the local segmental motion.) The  $\tau(T_A)$  in Table 1, determined by applying eqn (5), span the range from 5 to 150 ps, indicating that its value is not universal. The mean of  $\sim 30$  ps is 3 orders of magnitude longer than the Debye frequency, since the relevant length scale for liquid motions is the intermolecular distance, rather than interatomic distances. Interestingly,  $\tau(T_A)$  is within about one decade of the characteristic time for the onset of cooperative motions according to the coupling model of relaxation.<sup>28,29</sup> This correspondence is consistent with the idea that the loss of Arrhenius behavior upon cooling is due to development of intermolecular cooperativity, which according to the coupling model transpires around 2 ps. Note also that at a time of the order of  $\tau(T_A)$ , the time dependence of the correlation function begins to have the linear exponential form.<sup>30–34</sup>

The relatively narrow spread of  $\tau(T_A)$  for the different liquids in Table 1 indicates only a weak sensitivity to chemical structure; therefore, a reasonable inference is that the relaxation time at the onset of Arrhenius behavior is a material constant. Unfortunately there is no data available for a single material as a function of pressure or volume. However, we can use the scaling relation, eqn (2), together with the equation of state for a liquid to calculate  $\tau(T_A)$  for various combinations of  $T$  and  $P$ . Results are shown in Fig. 3 for salol, using the experimental data from Fig. 2 for 0.1 MPa, with values of  $\tau$  for  $P = 100$  and 500 MPa obtained from eqn (2) with  $\gamma = 5.2$ .<sup>9</sup> The specific volume of salol (in  $\text{ml mol}^{-1}$ ) is given by<sup>35</sup>

$$V(T, P) = (140 + 0.133T)[1 - 0.087 \ln\{1 + P/[790 \exp(-0.047T)]\}] \quad (6)$$

with  $T$  in Kelvin and  $P$  in MPa. The calculation is done only over the range of measured  $\tau$ , to avoid any extrapolation when applying eqn (2). Thus, the only assumption is that the scaling law is valid for salol up through 500 MPa, and it has been shown for many materials that eqn (2) is very accurate over broad ranges of thermodynamic conditions.<sup>12</sup> Determination of  $\tau(T_A)$  is done again using eqn (5). The analysis for salol in Fig. 3 confirms

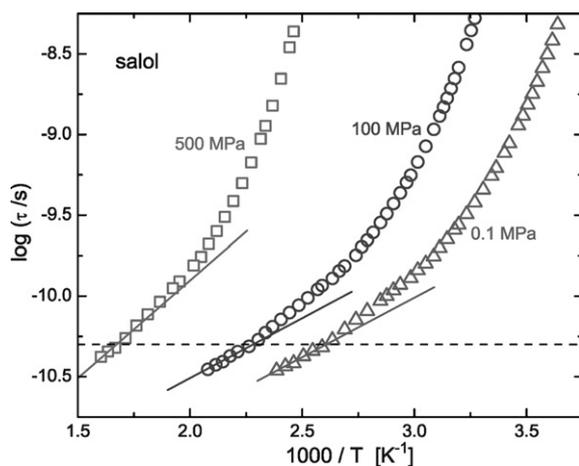


**Fig. 2** Relaxation times for OTP (circles; from the viscosity<sup>4</sup> using eqn (1) and  $G_\infty = 1 \times 10^{-8.1}$  Pa, which gives superposition with  $\tau$  for lower temperatures<sup>27</sup>), salol (triangles<sup>27</sup>), benzophenone (stars<sup>31</sup>), glycerol (down triangles<sup>27</sup>), and propylene glycol (squares<sup>27</sup>).

**Table 1** Relaxation times at the onset of Arrhenius behavior

| Material                                      | $T_A/\text{K}$ | $\log[\tau(T_A)]/\text{s}$ | Ref. |
|---|----------------|----------------------------|------|
| Salol   | 348            | -10.3                      | 19   |
| Butyl benzene                                 | 268            | -10.2                      |      |
| Propyl benzene                                | 240            | -10.1                      |      |
| Propylene carbonate                           | 290            | -10.3                      |      |
| $\alpha$ -Polypropylene                       | 476            | -10.3                      | 1,34 |
| DGEBA   | 352            | $(-10.3 \pm 0.2)$          | 33   |
| Poly[(phenyl glycidyl ether)-co-formaldehyde] | 390            | $(-11.0 \pm 0.3)$          |      |
| Trinaphthylbenzene                            | 588            | -10.7                      | 38   |
| Benzophenone                                  | 309            | $-9.8 \pm 0.1$             | 31   |
| Glycerol                                      | 413            | $-11.3 \pm 0.3$            | 32   |
| OTP   | 443            | $-10.8 \pm 0.2^a$          |      |

<sup>a</sup> using  $\log(G_\infty/\text{Pa}) = 8.1$ .



**Fig. 3** Relaxation times for salol, including experimental data for ambient pressure<sup>2</sup> and calculated  $\tau$  for two higher pressures using eqn (2). The deviation from the Arrhenius slopes at high temperature, determined from the change of slope of the derivative plots, occurs at a constant value of  $\tau = 5 \times 10^{-11}$  s, as indicated by the horizontal dashed line.

our expectation that for a given material, the characteristic relaxation time at the onset of Arrhenius behavior is invariant to pressure.

## 2. Dynamic crossover in supercooled liquids

The non-Arrhenius behavior below  $T_A$  is complicated. As first discovered by Plazek and Magill,<sup>36</sup> liquids exhibit a qualitative change in their dynamics at temperatures approximately 10 to 50% above the glass transition temperature. As this dynamic crossover temperature  $T_B$  is traversed by cooling or pressurization, several effects become apparent: (i) the breakdown of the inverse proportionality between the viscosity and translational diffusion known as the Stokes–Einstein relation;<sup>37,38</sup> (ii) a similar breakdown of the relation between the viscosity and orientational relaxation times [*viz.* eqn (1)],<sup>39,40</sup> (iii) the structural relaxation function, or its counterpart, the dispersion in the frequency domain, begins to broaden, deviating strongly from Debye behavior;<sup>41,42</sup> and (iv) the structural relaxation splits into a fast, secondary relaxation, identified as the Johari–Goldstein process,<sup>43–45</sup> and the slower primary  $\alpha$ -relaxation.

The dynamic crossover can be detected in plots of  $\tau$  versus the reciprocal of the KWW stretch exponent<sup>46</sup> or more usually from the departure of  $\tau(T)$  from one set of VF parameters [eqn (4)] prevailing at higher temperatures to a second set of VF

parameters at lower temperatures.<sup>24</sup> This change can be readily detected using eqn (5), which linearizes eqn (4) with a change in slope observed at  $T_B$ .<sup>26,38,47</sup> The corresponding equation for the isothermal variation of  $\tau$  with pressure is<sup>48</sup>

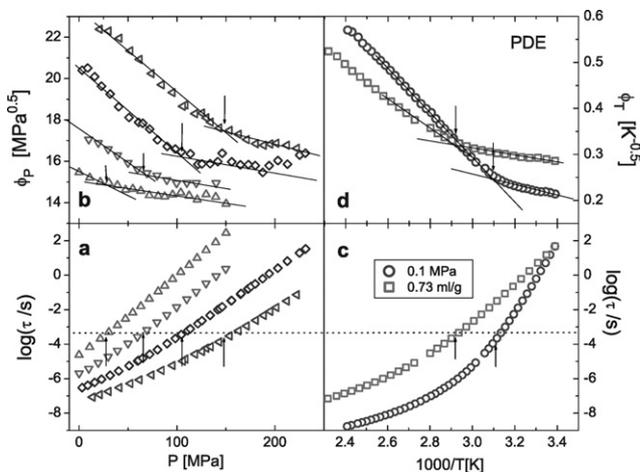
$$\phi_P = \left[ \frac{d \log(\tau)}{dP} \right]^{-\frac{1}{2}} \quad (7)$$

Equivalent expressions are obtained for  $\eta$ , since the two quantities are related [eqn (1)].

In the inset to Fig. 1, eqn (5) is plotted for  $\tau$  of PCB.<sup>2</sup> Although the relaxation times vary smoothly over the entire temperature

range, the derivative shows a clear break, denoting the dynamic crossover. More comprehensive results are shown for phenolphthaleindimethylether (PDE) in Fig. 4.<sup>49</sup> Whether  $T_B$  is traversed isothermally by variation of  $P$ , or by either isobaric or isochoric variation of  $T$ , the relaxation time at the crossover is constant. It is noteworthy that this invariance of  $\tau$  prevails for values of  $T_B(P)$  for which the density of PDE differs by as much as 3%. For comparison, the density change accompanying cooling from  $T_B$  down to  $T_g$  at atmospheric pressure is only half this amount, yet  $\tau$  changes by more than 5 orders of magnitude. Calculations show that if the effects of intermolecular cooperativity are removed, the change in dynamics at  $T_g$  disappears, suggesting its direct connection to many-body effects.<sup>50</sup>

It was proposed that  $\tau(T_B)$  might be a universal constant, equal to  $1 \times 10^{-6.5 \pm 0.5}$  s for all materials,<sup>51</sup> in a manner similar to  $\tau(T_A)$  as described above. In fact, reported values range from  $\tau(T_B) = 2 \times 10^{-4}$  s for propanol<sup>52</sup> to  $5 \times 10^{-11}$  s for polymethylacrylate,<sup>53</sup> a span of more than six decades.  $\tau(T_B)$  is constant only for a given material. Results are shown in Table 2 for 8 molecular and polymeric liquids, including some viscosity data. The values of  $T_B$  in the table are for zero (atmospheric) pressure, and increase with  $P$ , while  $\tau(T_B)$  [or  $\eta(T_B)$ ] in each case remains the same. Using the scaling law [eqn (2)],  $\tau_B$  can be calculated for any  $T$  and  $P$ . This enables examination



**Fig. 4** Relaxation data for PDE<sup>49</sup> with the dynamic crossover indicated by the vertical arrows: (a) isothermal variation of  $\tau$  with pressure; (b) Stickel derivative [eqn (7)] of  $\tau(P)$  showing the break at the crossover; (c) isobaric (circles) and isochoric (squares) variation of  $\tau$  with temperature; (d) Stickel derivative [eqn (5)] of  $\tau(T)$  showing the break at the crossover.

**Table 2** Relaxation times or viscosities at the dynamic crossover

| Material             | $P$ range/GPa | $T$ range/K | $\log[\tau(T_B)]/s$ | $\log[\eta(T_B)]/Pa\ s$ | Ref. |
|----------------------|---------------|-------------|---------------------|-------------------------|------|
| PDE                  | $\leq 0.23$   | 295–363     | $-3.4 \pm 0.1$      | –                       | 49   |
| PCB62                | $\leq 0.24$   | 325–344     | $-4.4 \pm 0.2$      | –                       | 2    |
| PCB42                | $\leq 0.25$   | 263–283     | $-3.82 \pm 0.2$     | –                       | 2    |
| KDE                  | $\leq 0.16$   | 313–455     | $-5.9 \pm 0.2$      | –                       | 49   |
| PC                   | $\leq 1.7$    | 159–270     | $-7.4 \pm 0.2$      | –                       | 56   |
| Salol                | $\leq 0.95$   | 303–363     | $-6.3 \pm 0.7^a$    | $1.3 \pm 0.1$           | 57   |
| OTP                  | $\leq 0.8$    | 383–423     | –                   | $1.5 \pm 0.4$           | 57   |
| Polyphenyl thioether | $\leq 0.85$   | 293–373     | –                   | $2.0 \pm 0.1$           | 55   |

<sup>a</sup> ref. 54.

of  $\tau_B$  in the absence of experimental measurements (which are difficult when  $\tau_B < 1 \times 10^{-7}$  s). Such determinations confirm the invariance of  $\tau_B$  to thermodynamic conditions.<sup>54</sup> The only exception that has been found is a cycloaliphatic hydrocarbon, for which  $\eta$  at  $T_B$  decreased about one decade for a 250 MPa increase in pressure.<sup>55</sup> Thus, fairly generally, experimental results demonstrate that the dynamic crossover phenomenon arises not at some critical temperature or volume, but rather it is governed by the time scale of the molecular motions.<sup>56,57</sup>

### 3. Glass transition dynamics

If crystallization is avoided, the “supercooled” liquid or polymer eventually becomes a glass at sufficiently low  $T$  or high  $P$ . Commonly  $T_g$  is determined as the pressure-dependent temperature at which the heat capacity or thermal expansion coefficient exhibits a step change; thus, the glass transition is sometimes loosely referred to as a second order phase transition, corresponding to marked changes in second derivatives such as specific heat, compressibility, and the thermal expansion coefficient. The particular value of  $\tau$  measured upon vitrification depends on the experimental technique; typically  $\tau(T_g)$  is in the range from 0.1 to 1000 s. With increasing pressure  $T_g$  increases, as shown in Fig. 5 (filled symbols) for polymethylmethacrylate (PMMA),<sup>12</sup> diglycidylether of bisphenol A (DGEBA),<sup>58</sup> and two molecular liquids, *p*-phenylene<sup>59</sup> and cresolphthalein–dimethylether (KDE).<sup>60</sup> These glass transitions were determined as the temperature at which the  $V(T)$  data change slope. Dielectric relaxation measurements on these two materials yield the value of  $\tau(T)$  over this same range of pressures. For example,  $\tau$  of PMMA = 100

s at  $T_g$  (= 380 K at ambient  $P$ ) and Fig. 5 shows the temperatures at which  $\tau$  maintains the value of 100 s at various elevated pressures. A correspondence between  $T_g$  and  $T(\tau = 100\text{ s})$  is apparent. Although the value of  $\tau$  at the glass transition temperature will vary depending *inter alia* on the cooling rate used in determining  $T_g$ , at any pressure  $T_g$  is associated with a fixed value of the local segmental relaxation time for polymers and the reorientational time of molecular liquids.

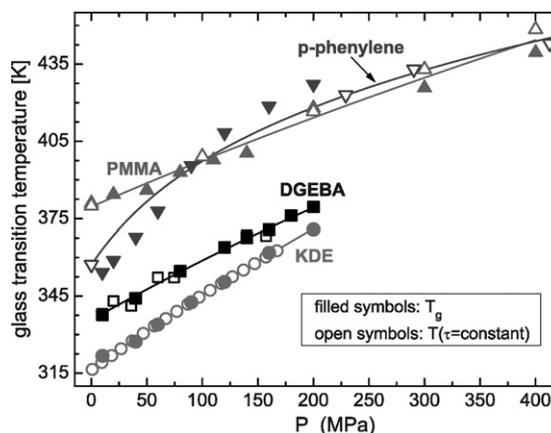
For many materials, especially when the pressure is not too large,  $T_g$  varies linearly with  $P$ . This is the case for both DGEBA<sup>58</sup> and KDE,<sup>60</sup> with their respective pressure coefficients, determined from PVT measurements, listed in Table 3. Also in the table are the corresponding pressure coefficients for the temperature at which  $\tau$  measured dielectrically remains constant; that is, for a given increase in pressure, the amount by which  $T$  must be increased in order to maintain a fixed  $\tau$ . For both DGEBA and

KDE, the pressure dependences of the two quantities are the same within the experimental uncertainty. This means that for any value of relaxation time at  $T_g$ , as determined by the experimental protocol,  $\tau(T_g)$  will remain constant as  $T_g$  is varied.

Although the value of  $\tau$  at  $T_g$  remains unchanged as  $P$  is varied, the actual value of  $\tau(T_g)$  depends on the experiment, specifically the rate at which temperature (or pressure) is varied during the determination of  $T_g$ . Traditionally in the study of lubricants  $T_g$  has been defined as the temperature at which the viscosity reaches the value of  $1 \times 10^{12}$  Pa s [since  $G_\infty$  is typically a couple of GPa, from eqn (1) this  $\eta$  corresponds to  $\tau_\alpha$  in the range 100–1000 s]. Defining  $T_g$  in this manner, of course, guarantees that  $\eta(T_g)$  is constant with pressure, *by definition*. However, such a kinetic value of  $T_g$  is not expected to coincide with the glass transition temperatures obtained from other experiments, such as calorimetry or thermal expansion measurements. This is seen, for example, in comparisons of the pressure-dependent glass transition determined from the viscosity *versus* that from the bulk modulus.<sup>61</sup> But the point remains that for those materials for which results are available,  $\tau(T_g)$  is indeed invariant to pressure.

### 4. Order–disorder transition in liquid crystals

Thermotropic liquid crystallinity describes the development of long range



**Fig. 5** The glass transition temperature determined from the temperature dependence of the volume (filled symbols) and the temperature at which  $\tau = 100$  s (open symbols), as a function of the pressure for KDE (circles<sup>60</sup>), DGEBA (squares<sup>58</sup>), polymethylmethacrylate (triangles<sup>12</sup>) and *p*-phenylene (downward triangles<sup>59</sup>).

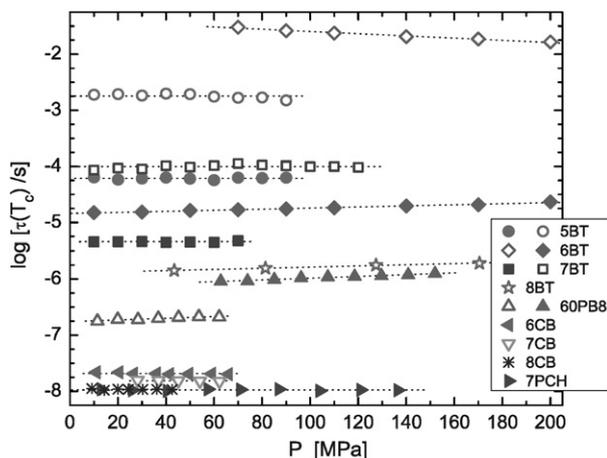
**Table 3** Pressure coefficient of the glass transition temperature and of the temperature at which the relaxation time = 100 s

|                     | $dT_g/dP/K \text{ GPa}^{-1}$ | $dT(\tau = 100 \text{ s})/dP/K \text{ GPa}^{-1}$ |
|---------------------|------------------------------|--|
| DGEBA <sup>58</sup> | $224 \pm 16$                 | $218 \pm 22$                                     |
| KDE <sup>60</sup>   | $273 \pm 7$                  | $277 \pm 2$                                      |

order when a liquid is cooled to a pressure-dependent temperature,  $T_c$ . Along with more sluggish translational motions, the molecules in the liquid crystal state continue to rotate, both rapidly about their long axis and more slowly about their short axis.<sup>25</sup> The latter “flip-flop” motion, facilitated by coupling to fluctuations of the centers of mass, is the process of interest herein.

The transition from one liquid crystalline phase to another and the loss of long range order at higher temperature (“clearing point”) are governed in the usual manner by minimization of the free

energy. We use  $T_c(P)$  to refer to the pressure-dependent temperature of a transition between two ordered phases, as well as clearing point temperature. There is no *a priori* reason to expect the thermodynamic conditions associated with a phase change to bear any relationship to the time scale of molecular rotations; nevertheless, dielectric measurements at high pressure on various materials reveal that the longitudinal relaxation time,  $\tau(T_c)$ , at a liquid crystal transition is independent of pressure and volume.<sup>62</sup> This surprising result is illustrated in Fig. 6, showing  $\tau(T_c)$  as

**Fig. 6** The pressure-invariance of the longitudinal relaxation times (flip-flop motion) at the phase transitions of various liquid crystals.<sup>62</sup> The transitions are identified in Table 4.**Table 4** Relaxation times at transitions of various liquid crystals.<sup>62</sup>

| Liquid crystal                                       | Transition        | $\log[\tau(T_c)]/s$ |
|--|-------------------|---------------------|
| 4- <i>n</i> -Pentyl-4'-thiocyanatobiphenyls (5BT)    | Crystal-SmE       | $-2.75 \pm 0.04$    |
|  | SmE-isotropic     | $-4.21 \pm 0.01$    |
| 4- <i>n</i> -Hexyl-4'-thiocyanatobiphenyls (6BT)     | Crystal-SmE       | $-1.65 \pm 0.10$    |
|  | SmE-isotropic     | $-4.75 \pm 0.06$    |
| 4- <i>n</i> -Heptyl-4'-thiocyanatobiphenyls (7BT)    | Crystal-SmE       | $-4.00 \pm 0.01$    |
|  | SmE-isotropic     | $-5.34 \pm 0.02$    |
|  | SmE-isotropic     | $-5.78 \pm 0.06$    |
| 4- <i>n</i> -Octyl-4'-thiocyanatobiphenyls(8BT)      | SmC-SmA           | $-5.97 \pm 0.05$    |
|  | SmA-nematic       | $-6.70 \pm 0.03$    |
|  | SmE-isotropic     | $-7.85 \pm 0.20$    |
| 2-(4-Hexyloxyphenyl)-5-octyl-pyrimidine (60PB8)      | Nematic-isotropic | $-7.68 \pm 0.01$    |
|  | Nematic-isotropic | $-7.81 \pm 0.01$    |
| 4'- <i>n</i> -Pentyl-cyanobiphenyl(5CB)              | Nematic-isotropic | $-7.81 \pm 0.01$    |
| 4'- <i>n</i> -Hexyl-cyanobiphenyl(6CB)               | Nematic-isotropic | $-7.97 \pm 0.01$    |
| 4'- <i>n</i> -Heptyl-cyanobiphenyl(7CB)              | Nematic-isotropic | $-7.97 \pm 0.01$    |
| 4'- <i>n</i> -Heptyl-cyanobiphenyl(8CB)              | Nematic-isotropic | $-7.97 \pm 0.01$    |
| 4- <i>trans</i> -Heptylcyclohexylcyanobenzene (7PCH) | Nematic-isotropic | $-7.97 \pm 0.01$    |

a function of pressure for various liquid crystals, with the value of the relaxation times at the transitions tabulated in Table 4. Note that some data exhibit a weak slope, but this might arise from systematic error in the measurements. This is the case for 60PB8, yet  $\tau(T_c)$  varies less than 10% over the range of  $P$ . There is no model that predicts that the thermodynamic conditions associated with a phase change, reflecting competition between the anisotropic interaction energy and the orientational entropy, should also correspond to a specific value of the longitudinal relaxation time. The experimental result that the stability limits of a liquid crystalline phase have a fixed value of  $\tau$  offers an insight into the relationship between molecular structure and motion in anisotropic materials that should serve as a guide to theoretical progress. For example, since the order parameter is almost constant at  $T_c$ , it has an apparent relationship with the relaxation time at  $T_c$ .

## 5. Conclusions

The fact that phenomena relating directly to molecular motions, such as the onset of Arrhenius behavior and the dynamic crossover, have a dynamic signature (in the form of  $P$ -,  $V$ -, and  $T$ -independent relaxation times) is interesting and significant for the development of quantitative theories of relaxation in liquids. More remarkable is that the vitrification of molecular liquids and polymers and the order-disorder transition of liquid crystals would be associated with a specific value of  $\tau$ , independent of temperature or pressure. Although thermodynamics and

dynamics must be related in the linear response regime (fluctuation–dissipation theory), models of the glass transition and liquid crystallinity do not anticipate that the stability limits might be associated with fixed values of  $\tau$ .

The significance of  $\tau$  is underscored by the fact that the shape of the relaxation function depends only on the relaxation time.<sup>7,8</sup> Moreover, since  $\tau$  is uniquely a function of  $TV^\gamma$  [eqn (2)], the implication from the present results is that the various transitions (onset of activated dynamics, dynamic crossover, order–disorder transition, vitrification) are characterized by a fixed value of this same product variable. For liquid crystals, such a result follows from Maier–Saupe type models of liquid crystallinity.<sup>25,63</sup> Thus,  $T_c V_c^m$  is a constant with the exponent, referred to as the thermodynamic potential parameter, a measure of the strength of the steric repulsions relative to that of the attractive interactions.<sup>63</sup> A connection to the dynamic scaling [eqn (2)] is apparent; *i.e.*,  $m = \gamma$ .<sup>62</sup> Models of the glass transition often address  $T_g$  from a thermodynamic basis;<sup>16,64–66</sup> however, it is not obvious that if  $\tau$  is determined by the configurational entropy, the latter should be the same for any  $T_g(P)$ . The inference is that the control parameter (free energy, configurational entropy, ...) driving these transitions has the same functional dependence on  $T$ ,  $P$ , and  $V$  as the relaxation time.

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- Note in Fig. 1 that the quantity plotted for the chain dynamics is the shift factor, which is the relaxation time multiplied by a constant in order to bring them into coincidence with the segmental  $\tau$ . The chain relaxation times are actually much longer, their exact value being strongly dependent on the molecular weight of the polymer.
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