# Temperature and volume effects on the change of dynamics in propylene carbonate

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Dielectric relaxation and *PVT* measurements were carried out on propylene carbonate. From these, we show that thermal energy exerts a stronger influence than volume on the temperature dependence of the dynamic properties. Data obtained at all temperatures and pressures superimpose, when expressed as a function of $T^{-1}V^{-3.7}$. The scaling exponent is consistent with more thermally governed dynamics, and can be interpreted as a reflection of the soft nature of the potential. The change of dynamics observed in the conductivity and relaxation data transpires at a fixed value of either quantity, independent of temperature and pressure.

## INTRODUCTION

Glass has been a common material throughout history, yet scientific investigation of its properties, as well as the glass formation process itself, continue unabated. Much effort focuses on understanding the mechanisms underlying the marked loss of mobility, reflected in increasing relaxation times and viscosities, as the glass transition is approached from the equilibrium liquid state [1]. Temperature effects (reducing the energy available for local motion) and density effects (packing molecules into smaller volumes) both drive the system toward vitrification, and the relative significance of these two factors is vigorously debated [2–4]. Both effects lower the configurational entropy of the liquid, and quantifying the connection between this entropy loss and the supercooled dynamics is the objective of many studies [5–9].

An intriguing aspect of this problem is understanding what provokes the change in dynamics occurring *above* the liquid's glass temperature $T_g$. About 40 years ago, Boyer and co-workers proposed the existence of a liquid-liquid transition in polymers, at temperatures approximately 20% larger than $T_g$. Subsequently, Goldstein proposed that a change of dynamics ("dynamic crossover") should occur in supercooled liquids when the structural relaxation time $\tau$ assumed a value of about $10^{-9}$ s [10]. In the 1980s, mode-coupling theory, which relates relaxation behavior to a qualitative change in the motion of molecules within a cage formed by their neighbors, offered specific predictions for the dynamics of supercooled liquids at temperatures about some critical temperature $T_c > T_g$. In the vicinity of $T_c$, several phenomena are observed. (i) There is a breakdown of both the Stokes-Einstein relation between the translational diffusion and viscosity [11,12], and the Debye-Stokes-Einstein (DSE) relation between the viscosity and orientational relaxation time [13,14]. (ii) There is a marked change in the degree of non-exponentiality of the relaxation function below $T_c$ [15,16], usually a diminution with cooling in the magnitude of the stretch exponent of the Kohlrausch-William-Watts relaxation function [17]. (iii) On decreasing temperature below $T_c$, the dependence of the structural relaxation time $\tau$ on the configurational entropy departs from the form of the Adam-Gibbs theory [18,19]. (iv) There is a change in the nature of the temperature dependence of $\tau$, from one Vogel-Fulcher-Tammann-Hesse (VFTH) dependence ($\tau = \tau_0 \exp[C_T/(T-T_0)]$, where $\tau_0$, $C_T$, and $T_0$ are constants) to a second VFTH dependence. This particular change of dynamics is revealed using a derivative analysis of data [20], $\phi_T = \{d[\log_{10}(x)]/d(1000/T)\}^{-1/2}$, where $x$ represents some dynamic variable, such as $\tau$ or the viscosity $\eta$. The temperature associated with this change in $T$ dependence is designated $T_B(\sim T_c)$. (v) A plateau occurs in the apparent pore size (unoccupied volume) versus temperature behavior at $T_B$, as measured by positron annihilation lifetime spectroscopy [21].

From analysis of literature values for $T_c$ (very often determined experimentally as $T_B$), Novikov and Sokolov [22] noted that $\tau(T_c)$ is almost a universal constant, equal to $10^{-6.5\pm0.5}$ s. However, there are at least a few materials, including phenylphthalein-dimethylether [23] and polychlorinated biphenyls, for which the relaxation time corresponding to the change of dynamics is much longer, ca. $10^{-4}$ s. Moreover, measurements at elevated pressure on these materials reveal that $\tau(T_B)$ is independent of temperature and pressure; that is, the change in dynamics is governed by the time scale, not by temperature, pressure, or volume [23,24]. A similar result is found in viscosity measurements on salol and *ortho*-terphenyl—the change in dynamics occurs at a fixed value $\eta(T_B)$ for measurements at various pressures. These results are provocative, and must be reconciled by any theoretical description of the role of thermodynamic and dynamic variables in the behavior of vitrifying liquids.

It is important to determine whether an invariance of $\tau(T_B)$ to thermodynamic variables such as $T$, $P$, and $V$ is a universal characteristic of glass-forming liquids. Herein, we present analysis of the change of dynamics in propylene carbonate (PC), for which the characteristic relaxation time is quite short, $\tau(T_B) = 2 \times 10^{-8}$ s [25]. To acquire data for conditions of small $\tau$, we make use of the ionic conductivity $\sigma$. The relationship between $\tau$ and $\sigma$ is drawn from the Stokes-Einstein [26] and the Debye-Stokes (DS) [27] equations. The former describes the ionic motions according to $D = kT/6\pi\eta r$, in which $D$ is the diffusion coefficient and $r$ the ionic radius. In order to relate $\sigma$ to the diffusion, the Einstein-Nernst equation $\sigma/D = ne^2/kT$ is used. Combining these with the DS relation $\tau = CV\eta/kT$, where $C$ is a constant and $V$ the molecular volume, we get the Debye-Stokes-
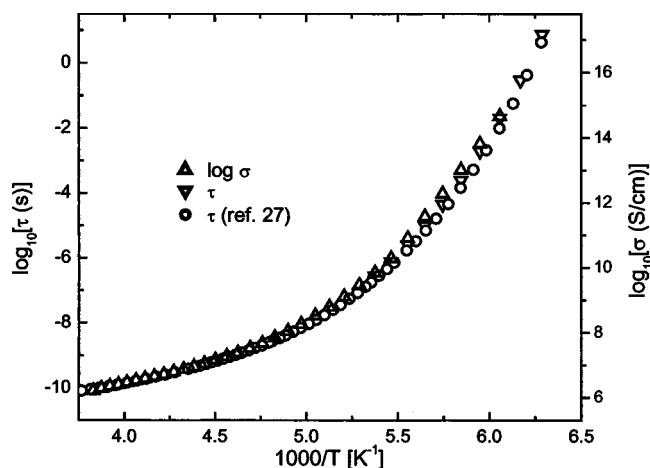
FIG. 1. Arrhenius plot of the $\alpha$-relaxation times measured herein ($\triangle$) and reported by Stickel ($\bigcirc$), along with the dc-conductivity ($\triangledown$). The left and right ordinate scales were chosen to demonstrate the superpositioning at higher temperature.



FIG. 2. $\alpha$-relaxation times ($\triangle$) and dc-conductivities ($\triangledown$) as a function of the hydrostatic pressure at $T=273.2$ K. The dash-dotted line is the fit to the data below 1 GPa [$\log_{10} \sigma = -6.4 + 4.3P/(2.4 - P)$], while the dashed line represents the fit of the data above 1 GPa [$\log_{10} \tau = -11.54 + 17.8P/(5.1 - P)$]. The inset illustrates that the breaks in the volume dependences for the isotherm and the isobar data occur at different values of the specific volume, $0.703 \pm 0.001$ and $0.772 \pm 0.001$ ml/g, respectively.

Einstein equation $\sigma\tau = \text{const}$ [27–29]. For PC at high temperatures, conformance to the DSE relation is observed, so that one VFTH expression accounts for both variables. For lower temperatures ($<T_B$), there is decoupling of the two quantities, which allows the constancy of $\sigma(T_B)$ with respect to $T$ and $P$ to be assessed. We also combine the dielectric spectroscopy data with pressure-volume-temperature ($PVT$) measurements, in order to quantify the contribution of density to the temperature dependence of the properties. This analysis enables the $\sigma$ and $\tau$ data to be expressed as a single function of the temperature and density.

## EXPERIMENT

Dielectric spectra were acquired over ten decades of frequency, with variation of both pressure and temperature; a detailed description of the instrumentation can be found elsewhere [30]. The sample was in the liquid state (i.e., above the pressure-dependent $T_g$) during all measurements. The relaxation time $\tau$, defined from the frequency of the dielectric loss maximum, corresponds approximately to the most probable relaxation time. The $PVT$ measurements employed a Gnomix apparatus.

## RESULTS AND DISCUSSION

Figure 1 shows the variation of $\tau$ and $\sigma$ with temperature at $P=0.1$ MPa. We also include the data of Stickel *et al.* [20,31], which are consistent with our own. Beyond ca. 200 K, which is the value of $T_B$ reported in Refs. [20] and [31], $\sigma$ has the same temperature dependence as $\tau$. In Fig. 2, the relaxation times and conductivities measured herein at 283 K are displayed as a function of pressure. The ordinate scales are chosen to superimpose the data in the overlap region; the respective pressure dependences are the same. At low pressures, $\tau$ is too short to measure herein, so we utilize the conductivity data. The pressure counterpart of the VFTH relation [32], $\tau = \tau_0 \exp[C_p/(P_0 - P)]$, reveals the existence
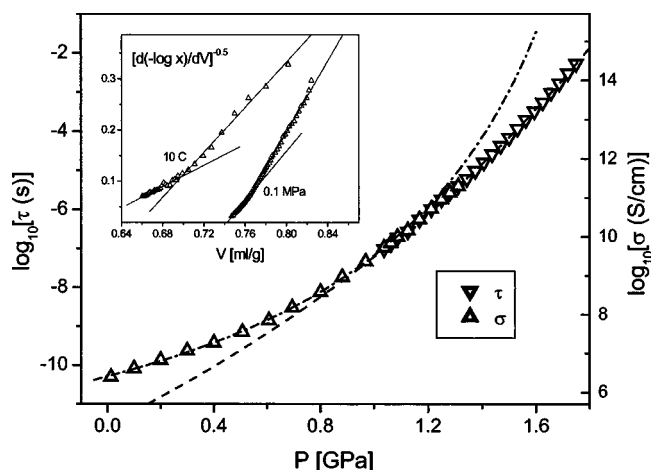
of a change in dynamics in the isothermal results, at a pressure of about 1 GPa. To determine this accurately, we use the pressure derivative function [23] $\phi_P = \{d[\log_{10}(x)]/d(P)\}^{1/2}$, with $x$ defined as $\tau$ or $\sigma$.

The derivative analyses are shown in Fig. 3, the temperature data in the lower panel and the pressure data in the upper. At atmospheric pressure, $T_B = 191$ K, for which $\log_{10}[\tau(\text{s})] = -7.28 \pm 0.2$. The change of dynamics occurs at 283 K for $P = 1$ GPa, at which $\log_{10}[\sigma(\text{S/cm})] = 9.1 \pm 1.0$. This corresponds to $\log_{10}[\tau(\text{s})] = -7.6 \pm 0.8$; thus $\tau(T_B)$ is equivalent for the two conditions. The change in dynamics is governed by the liquid's time scale, independent of the particular combination of $T$ and $P$. This is similar to previous results, in which the relaxation time and the viscosity were found to assume fixed values at the dynamic crossover [20,21].

From the $PVT$ measurements, we obtain an equation of state for the equilibrium liquid. The specific volume of PC can be described by

$$V(T,P) = (0.824 + 6.8 \times 10^{-4}T + 7.5 \times 10^{-7}T^2)$$
$$\times \{1 - 0.0894 \ln[1 + P/210 \exp(-0.0060T)]\},$$
$$(1)$$

where the units are ml/g, with temperature in degrees Celsius and pressure in mega pascals. Using this data, we can express the relaxation times as a function of the specific volume. However, it is well known that volume does not uniquely define the supercooled dynamics, and indeed, the isobaric (Fig. 1) and isothermal (Fig. 2) data do not coincide when plotted versus specific volume. In the inset to Fig. 2, we show the derivative function, defined as $\phi_V = \{d[\log_{10}(x)]/d(V)\}^{-1/2}$. Note that the relaxation data show the characteristic break when plotted in this fashion. For the
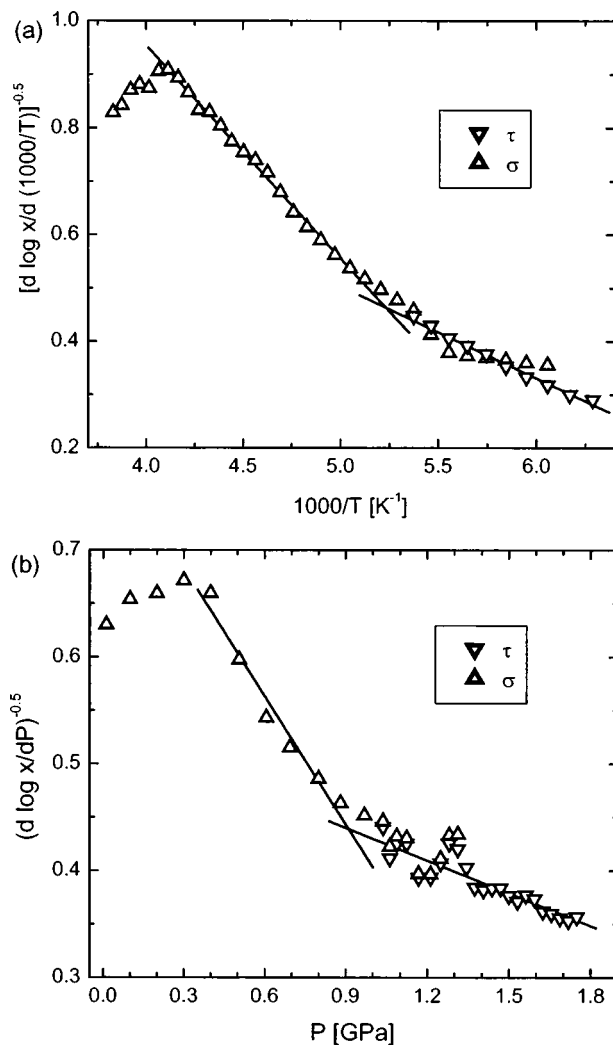
FIG. 3. (a) Derivative analyses of isobar ($P$=0.1 MPa) data from Fig. 1. (b) Derivative analysis of the isotherm ($T$=283 K) data from Fig. 2. Solid lines represent the derivatives of the respective VFTH fits.



FIG. 4. The relaxation times and dc conductivities measured herein for PC, as a function of $T^{-1}V^{-n/3}$. The best-fit value of $n$ = 11.1 yields accurate superpositioning of the data sets from Figs. 1 and 2.

two conditions (0.1 MPa isobar and 10°C isotherm), this change in dynamics occurs at different values of $V$; however, $\log_{10}[\tau(s)] = -7.3 \pm 0.3$ in both cases.

From the combined dielectric relaxation and *PVT* data, we can calculate the thermal expansion coefficient for constant pressure, $\alpha_P$, and for a constant value of the relaxation time, $\alpha_\tau$. From these expansivities, the ratio of the isochoric enthalpy of activation to the isobaric activation energy is obtained using the relation [33]

$$H_V/E_P = (1 - \alpha_P/\alpha_\tau)^{-1}. \qquad (2)$$

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For $P$=0.1 MPa and $163 < T < 188$ K, which corresponds to $10^{-6} < \tau < 10^{-3}$ s, $H_V/E_P = 0.64 \pm 0.02$, decreasing with increasing temperature by ca. 0.0015 K$^{-1}$.

The magnitude of $H_V/E_P$ indicates that temperature exerts roughly twice the effect that volume does, so that while the latter cannot be neglected, thermal energy is the more dominant variable. This suggests that the change with temperature
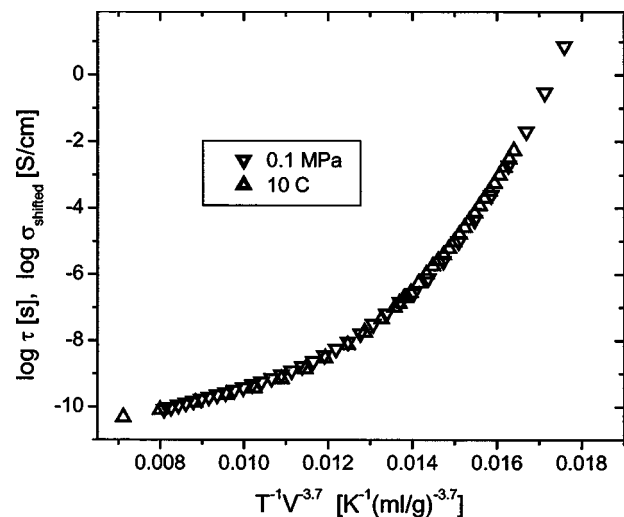
in the relaxation times can be described in terms of the polycarbonate molecule's ability to surmount potential energy barriers [9]. However, given the inestimable complexity of a liquid's potential energy landscape, implementation of an energy landscape approach is usually limited to computer simulations [34,35]. For real molecules, analysis along these lines is necessarily qualitative. On a rudimentary level, the intermolecular interactions can be expressed as a repulsive potential having an inverse power dependence on the distance between molecules, $\varphi(r) \sim r^{-n}$, where $r$ is the molecular separation and $n > 0$, together with an attractive term whose effects are manifested only at higher intermolecular distances (e.g., a mean field term) [36]. The advantage of this idealized form of the potential is that thermodynamic properties of the system, as well as dynamic quantities such as $\tau$ and $\sigma$, depend only on the variable $T^{-1}V^{-n/3}$ [36,37]. This scaling relationship has been demonstrated by Casalini and Roland to accurately superimpose dielectric relaxation times for a number of other glass formers [9,38,39]. The special case of $n$ = 12, the Lennard-Jones potential, was applied to the supercooled dynamics of o-terphenyl measured by both quasielastic neutron diffraction [40] and dynamic light scattering [41].

In Fig. 4 we display the $\tau$ and $\sigma$ data obtained herein on PC as a function of $T^{-1}V^{-n/3}$. We find that $n$=11.1$\pm$0.04 yields accurate superpositioning of the data from Figs. 1 and 2. Note the absence of any discontinuity, such as appears in using the temperature (Fig. 3), pressure (Fig. 3), or volume (Fig. 2) dependences. The exponent is fairly close to the Lennard-Jones value, reflecting the "soft" nature of the PC molecule. We have previously shown that the magnitude of the scaling exponent correlates with the value of the enthalpy ratio, $H_V/E_P = (1 + 0.063n)^{-1}$. For $n$=11.1, this relation yields 0.59, which is close to, but somewhat smaller than, the experimentally determined value of $H_V/E_P = 0.64 \pm 0.02$.

In summary, measurements of the dielectric $\alpha$ relaxation in propylene carbonate at ambient and elevated pressure, in combination with *PVT* data, reveal the factors governing the

vitrification process. The change in the dynamics occurring above the glass transition arises when the liquid acquires a given degree of mobility (reflected in a given value of the relaxation time or ionic conductivity), independent of the particular combination of $T$, $P$, and $V$. However, relaxation time and conductivity data obtained over various temperatures and pressures superimpose when plotted versus $T^{-1}V^{-3.7}$. Such master plots subtend the region over which the change in dynamics is observed. The value of the scaling exponent, 3.7, is consistent with the fact that over this range, thermal energy exerts a stronger influence on the temperature dependence of the dynamics than does volume. These findings represent facts crucial to the formulation of a comprehensive theory of the dynamics of supercooled liquids.

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