

COMMUNICATIONS

Dynamic crossover in supercooled liquids induced by high pressure

Riccardo Casalini*

*Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375-5342
and Chemistry Department, George Mason University, Fairfax, Virginia 22030*

Marian Paluch

*Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375-5342
and Institute of Physics, Silesian University, Uniwersytwcka 4, 40-007, Poland*

C. Michael Roland

Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375-5342

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The physics underlying the dynamics of molecules near their glass temperature, T_g , comprises one of the major unsolved problems in condensed matter. Of particular interest are the striking changes in relaxation properties observed at temperatures ~ 1.2 times higher than T_g . Herein, we describe experiments in which these changes in dynamics are induced by pressure variations. For several supercooled liquids, the relaxation time associated with the change in dynamics is found to be invariant to both temperature and pressure. That is, the time scale of the molecular motions determines the onset of strong intermolecular cooperativity and the accompanying dynamical changes. While thermodynamic variables such as temperature and pressure influence the crossover in dynamics, the governing variable is the time scale. © 2003 American Institute of Physics.

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The formation of a glass upon cooling of non-crystallizing liquids is a phenomenon known for millennia, glass-making having been practiced in Mesopotamia as early as 3000 BC. Nowadays, the glass transition is recognized as a general property of both simple liquids and polymers, and includes materials having covalent, van der Waals, hydrogen, or ionic bonding. Synthetic development of numerous new glasses has made these materials ubiquitous in everyday life. Notwithstanding the importance of glasses, it remains an unsolved problem how a liquid can be supercooled below its melting point, progressively transforming into a “state” having the rigidity of a solid while maintaining a disordered structure.^{1,2}

Perhaps the most important piece added during last decade to the puzzle of supercooled liquids has been the identification of a qualitative change of the dynamics at a temperature approximately 20% higher than the glass transition temperature, T_g . As temperature is decreased in this range, several phenomena are observed: (1) the breakdown of the Stokes–Einstein relation between the viscosity and translational diffusion,^{3,4} (2) a similar breakdown of the Debye–Stokes–Einstein relation between the viscosity and orientational relaxation times,^{5,6} (3) the loss of ergodicity as predicted by mode-coupling theory (MCT),⁷ (4) broadening of the structural relaxation function,^{8,9} (5) a marked change in temperature dependence of the nanopore (unoccupied volume) radius,¹⁰ and (6) splitting of the high temperature re-

laxation into a slow process, with a relaxation time (τ) which diverges at T_0 ($T_0 < T_g$), and a faster relaxation. The latter exhibits Arrhenius behavior through temperatures well below T_g , and is sometimes identified as a Johari-Goldstein relaxation.^{11–13} The change in dynamics reflected by these phenomena can be seen directly from analysis of the τ , viscosity, or conductivity of supercooled liquids. Derivatives of these quantities exhibit a break at a temperature corresponding to that at which the aforementioned phenomena transpire.^{4,14,15} Parenthetically, these results call to the mind the long-discredited liquid-liquid transition, postulated many years ago from the viscoelastic behavior of polymers.¹⁶

Herein, we describe a change in the dynamics above T_g when glass-formers are subjected to hydrostatic pressure. This finding is important, not only because such a result has not been previously reported, but because it provides insight into the role of different thermodynamic variables in the glass transition.

Dielectric spectroscopy was carried out on four glass-forming liquids, having simple molecular structures and a resistance to crystallization: phenolphthalein-dimethyl-ether (PDE); cresolphthalein-dimethyl-ether (KDE), which is obtained by the addition of a methyl group to each phenyl ring in PDE; and two polychlorinated biphenyls (PCB) having 42% and 62% by weight of chlorine (referred to herein as PCB42 and PCB62, respectively). Spectra were acquired over ten decades of frequency, with variation of either pressure or temperature; a detailed description of the apparatus can be found elsewhere.¹⁷ The samples were in the liquid state (i.e., above the pressure-dependent T_g) during all mea-

*To whom correspondence should be addressed;
e-mail: casalini@ccs.nrl.navy.mil.

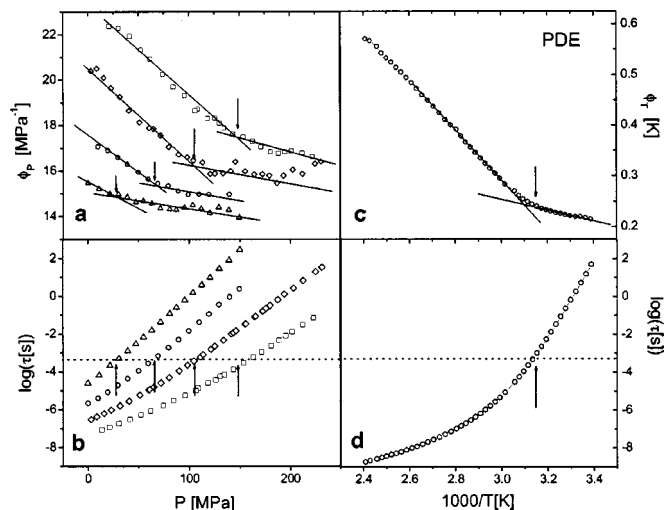


FIG. 1. Dielectric relaxation time data for PDE. (a) Derivative function ϕ_P vs pressure, calculated for isotherms at $T = 327.8$ (Δ), 337.7 (\circ), and 363.1 K (\square); (b) τ vs pressure for $T = 327.8$ (Δ), 337.7 (\circ), 349.5 (\diamond) and 363.1 K (\square); (c) derivative function ϕ_T vs the inverse temperature for atmospheric pressure; (d) τ vs inverse temperature from Stickel *et al.* (Ref. 18).

measurements. The relaxation time, defined from the frequency of the dielectric loss peak, corresponds to the most probable relaxation time. For the materials investigated herein, no secondary relaxation peak was evident.

In the method proposed by Stickel and coworkers,¹⁴ the function $\phi_T = \{d[\log(\tau/s)]/d[1000/T]\}^{-1/2}$ exhibits a change in slope at some characteristic temperature. In Figs. 1(d) and 1(c) we plot, respectively, the relaxation times for PDE, as measured by Stickel,¹⁸ as well as the function ϕ_T . Indicated by an arrow in both figures is the temperature at which ϕ_T deviates from the behavior at lower temperatures. The relaxation time at this temperature, 5×10^{-4} s, is designated by a horizontal dotted line.

In Fig. 1(b) we display the τ measured for PDE under varying pressures, at four fixed temperatures. The Stickel function, ϕ_P , is based on the expectation that the temperature dependence of τ will have the Vogel–Fulcher (or equivalently the Williams–Landel–Ferry) form.¹⁹ Since the pressure dependence of τ can be described by a similar equation, with T replaced by inverse pressure,²⁰ an analogous derivative function for pressure data is $\phi_P = \{d[\log(\tau/s)]/dP\}^{-1/2}$. The ϕ_P corresponding to the τ in Fig. 1(b) is shown in Fig. 1(a). For each isotherm, there is a change in slope of the data, at a pressure (indicated by arrows) that increases with temperature. The relaxation time associated with this change is invariant to pressure. Moreover, as seen in Fig. 1(b) this relaxation time is quite close to the value of τ at which temperature induces a change of dynamics at atmospheric pressure [Figs. 1(c) and 1(d)].²¹ From volume measurements on PDE carried out as a function of T and P , we estimate that the molar volumes yielding the same crossover τ differ by as much as 3%. As seen in a plot of relaxation time versus the volume (Fig. 2), this is twice as large as the volume change accompanying a temperature shift from the crossover to T_g at atmospheric pressure.

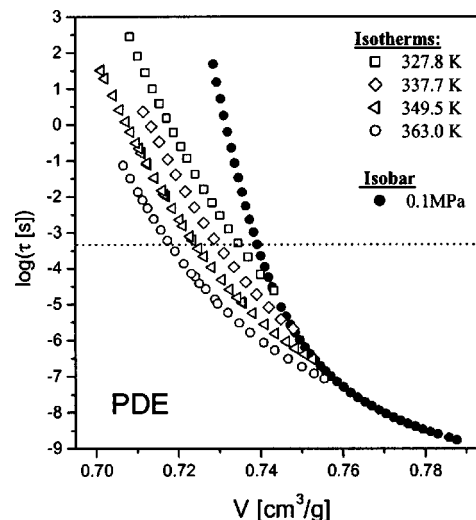


FIG. 2. Dielectric relaxation times for PDE vs specific volume. Both above and below the crossover, the relaxation time is strongly dependent on volume.

Temperature and pressure dependences of τ were also measured for PCB42 and PCB62. Although these liquids have glass temperatures differing by 48° , when we normalize temperature by the respective T_g 's, the relaxation times coincide [Fig. 3(d)]. From the derivative plot, $\phi_T = \{d[\log(\tau/s)]/d[T_g/T]\}^{-1/2}$, departure from the behavior at low temperature can be observed, at the same T_g -normalized temperature [Fig. 3(c)]. The corresponding relaxation time is also the same ($\tau = 5 \times 10^{-5}$ s) for the two PCBs.

The pressure dependence of the relaxation times for PCB62 and PCB42 are shown in Figs. 3(b) and 3(f), respectively. By calculating the function ϕ_P [Figs. 3(a) and 3(e)], we again find that the behavior changes at a temperature-dependent pressure. The value of the relaxation time associated with this change in dynamics is the same for the two

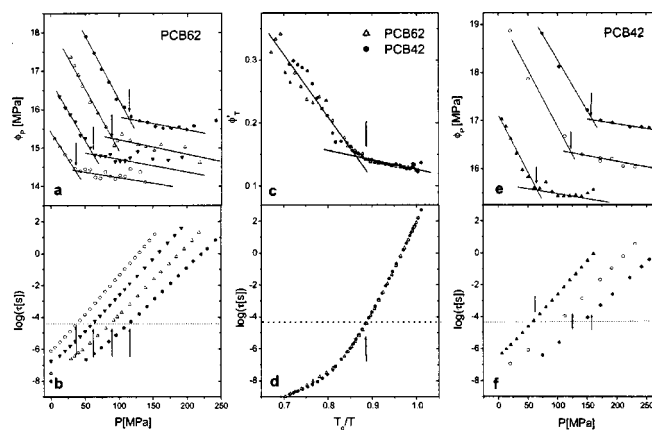


FIG. 3. Dielectric relaxation time data for PCB62 and PCB42. (a) Derivative function ϕ_P for PCB62 vs pressure, calculated for isotherms at $T = 344$ (\circ), 334.5 (Δ), 325.1 (∇) and 317.4 K (\circ); (b) relaxation times for PCB 62 vs pressure at four temperatures $T = 344$ (\circ), 334.5 (Δ), 325.1 (∇) and 317.4 K (\circ); (c) derivative function ϕ_T vs inverse temperature normalized to T_g for PCB62 and PCB42; (d) relaxation time vs inverse temperature normalized to T_g for PCB62 and PCB42; (e) derivative function ϕ_P vs pressure, calculated at $T = 263$ (\blacktriangle), 273.6 (\circ) and 283 K (\bullet); (f) relaxation time vs pressure for PCB42 at $T = 263$ (\blacktriangle), 273.6 (\circ) and 283 K (\bullet).

PCBs, and more importantly is equivalent to the characteristic τ deduced from the isobaric temperature dependences.

For KDE, the characteristic relaxation time at which a change of dynamics occurs at ambient pressure is reported to be $\sim 1 \times 10^{-7}$ s.²² This is beyond the frequency range of our high pressure dielectric measurements. Accordingly, and consistent with the results for PDE and PCB, we find (data not shown) that ϕ_p for KDE exhibits no crossover within the frequency range of our measurements. There is only a monotonic variation of τ with pressure.

As described above, the change in dynamics observed at atmospheric pressure is manifested in properties other than the temperature-dependence of the relaxation time. Similarly, we find herein that both increasing pressure and decreasing temperature cause the relaxation function to broaden. This broadening commences when τ attains its characteristic value. Thus, the shape of the relaxation function is dependent only on the magnitude of the relaxation time, and plots of peak breadth versus τ fall on a single curve.

The present results demonstrate that the time scale of the relaxation is the most important parameter governing the change in dynamics. The crossover can be observed for various conditions of temperature and pressure, but for a given liquid, the unifying feature is the magnitude of τ . The molecular mechanism underlying an abrupt change in dynamics above T_g remains an unsolved problem. Still higher temperatures are required for diffusive motion and Arrhenius temperature dependences, suggesting that the crossover reflects transition from weakly coupled motion to a highly cooperative regime.²³ Our experimental results demonstrate that this crossover arises not at some critical temperature or volume, but rather at a particular value of the relaxation time. This variable denotes the onset of dynamics governed by intermolecular constraints.

A description of cooperativity from the Adam–Gibbs model²⁴ yields the prediction that $\log(\tau) \propto (TS_c)^{-1}$, where S_c is the configurational entropy ($S_c = k \ln \Omega$, Ω = the number of available configurations). The proportionality between $\log(\tau)$ and $(TS_c)^{-1}$ has been verified for τ measured over a range of temperatures and pressures below the crossover.^{17,25,26} Thus, within the framework of this model, our observation that the crossover arises at a constant value of the relaxation time implies a corresponding constancy in the value of the energy TS_c separating the two different dynamic regimes. Of course, the Adam–Gibbs model breaks down at temperatures above (or pressures below) the crossover; this breakdown is implicit in Figs. 1 and 3, and has been shown in previous works.^{8,9,17,27}

It is significant that the changes in dynamics found for the three materials herein have similarities to the behavior reported for other glass formers, for example, orthoterphenyl (OTP).²⁸ In a recent review on OTP,²⁹ Tölle showed that the temperature of the change in dynamics determined using the Stickel function, $T_B \cong 290$ K at $\tau_B \sim 10^{-6}$ s,²⁸ is very close to the critical temperature, T_c , of

mode coupling theory (MCT).³⁰ More relevant, Tölle concluded, from measurements of the pressure and temperature dependence of the static structure factor,^{29,31} that the structure factor does not change significantly along an isochronous line. This implies that the relaxation time at the dynamic singularity of MCT should be independent of pressure and temperature, analogous to the results herein for τ_B . However, the T_c of MCT corresponds to a crossover from liquid-like to hopping dynamics, and it remains to be established whether this can be identified with T_B .

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