

## Viscosity at the Dynamic Crossover in *o*-Terphenyl and Salol under High Pressure

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The viscosities of two prototypical glass formers, *o*-terphenyl and phenyl salicylate (salol), are shown to exhibit a change in their temperature and pressure dependences at a constant value of the viscosity. This is the first evidence of a dynamic crossover in the viscosity induced by pressure. The characteristic value associated with the change in dynamics is material dependent, but independent of temperature and pressure. These results are in accord with the previous finding, for other glass formers, that the dielectric relaxation time assumes a density-independent value at the dynamic crossover.

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The vitrification of liquids has been known since antiquity, with silicate glass artifacts dating back to at least 2500 B.C. In the last half century, the appearance of numerous new types of glasses (e.g., metal alloys, polymers, etc.) have made such materials ubiquitous, and of inestimable importance to material engineering and science. The glass transition is now recognized as a general property of both simple liquids and polymers, with diverse and often spectacular changes in properties occurring upon approach to the glassy state.

Many theoretical models have been proposed to describe the glass transition; however, presently none provide accurate predictions, or even a full accounting, of the myriad properties associated with glass formation. Part of the difficulty is the lack of experimental data completely characterizing these properties. One of the most notable glass transition phenomena is the progressive increase of the viscosity  $\eta$  whereby the material behaves as a solid, while retaining the microscopic disorder of the liquid state. This viscosity increase is accompanied by an increase in the characteristic time for molecular motions,  $\tau$ , from nanoseconds to literally an eon.

Although investigations of vitrification naturally tend to focus on temperatures in the vicinity of the glass transition temperature  $T_g$  (at which  $\tau$  becomes larger than the laboratory time scale, ca. 100 s), there are indications that a first signature of the glass transition appears at some significantly higher temperature, ca.  $\geq 1.2 T_g$ . Phenomena observable, or at least anticipated by models, at this characteristic temperature include the following: (i) the liquid-liquid transition postulated for polymers by Boyer [1] (note some of his work has been discredited [2]); (ii) the crossover from free diffusion to landscape dominated diffusion at  $\tau \sim 10^{-9}$  s, as predicted by the energy landscape model, first proposed by Goldstein [3]; (iii) the loss of continuity among “liquidlike cells,” according to the Cohen-Grest free-volume model [4]; (iv) a marked increase in the degree of intermolecular cooperativity, according to the coupling model [5,6]; (v) the bifurcation of the structural and Johari-Goldstein secondary relaxation times [7] (although the determination

of this hypothetical splitting temperature is problematic [8]); (vi) the divergence of the viscosity according to mode coupling theory [9] (this divergence may be unobserved in practice because of a transition to hopping dynamics [10]); (vii) a change in the temperature dependence of the dielectric strength [11]; (viii) the onset of dynamic freezing above the phase transition temperature in disordered ferroelectrics [12]. From an experimental point of view, the existence of such a characteristic temperature, referred to *inter alia* as  $T_B$ , is commonly evidenced by a change in temperature dependence of the relaxation time or the viscosity [13–15]. How such a change in dynamics supports any particular model of the glass transition remains to be clarified.

Although cooling is the usual route to the glassy state, compression of a liquid has proven useful in distinguishing the different secondary processes preceding structural relaxation [16], and also to assess the relative importance of density and temperature to the dynamics [17,18]. Recent results for three supercooled liquids showed that the dielectric relaxation time,  $\tau_B$ , associated with the change in dynamics at  $T_B(P)$ , is invariant to both temperature and pressure [19,20]; that is,  $\tau_B$  is a density-independent, material property [21]. In this Letter, previously published viscosities for two glass formers, ortho-terphenyl (OTP) and phenyl salicylate (salol), measured at atmospheric [7,22] and higher pressures [23], are analyzed in order to examine the effect of pressure on the dynamic crossover.

Close to  $T_g$ , the temperature behavior of supercooled liquids can usually be described by the Vogel-Fulcher (VF) equation [24,25]

$$x(T) = x_0 \exp\left(\frac{DT_0}{T - T_0}\right), \quad (1)$$

where  $x$  may represent  $\eta$ ,  $\tau$ , ionic conductivity, etc., and  $T_0$ , the Vogel temperature,  $D$ , the fragility parameter, and  $x_0$  are constants. Although the VF equation has been successfully applied to many data, when measurements are carried out over many decades, at higher temperatures [roughly  $(1.2-1.5)T_g$ ] the property  $x$  progressively

deviates from Eq. (1). This behavior is generally referred to as the dynamic crossover. Such a change in dynamics was first observed by Plazek and Magill for the viscosity of 1,3-bis(1-naphthyl)-5(2-naphthyl)benzene [13,26], and was also seen in viscosities measured for OTP and salol by Laughlin and Uhlmann [22]. These early works made clear that a single VF equation cannot describe the data over the entire range. An alternative function is the Cohen-Grest equation [4], which can accurately fit relaxation times and viscosities over a range encompassing  $T_B$  [4,27,28]. The Cohen-Grest equation has one more adjustable parameter than the VF expression, and its fitting to experimental  $\tau$  or  $\eta$  data directly yields a determination of  $T_B$  [28]. However, the model's applicability to high-pressure measurements is problematic [28–30], and moreover our interest is to examine the general conditions associated with  $T_B$ . Thus, herein we eschew any specific model.

To clearly demarcate the change in dynamics occurring at high temperature, Stickel *et al.* [14] proposed use of the derivative function

$$\phi_T = \{d[\log(x)]/d[1000/T]\}^{-1/2}. \quad (2)$$

$\phi_T$  transforms VF behavior into a linear dependence on inverse temperature. The pressure behavior close to  $T_g$  can be described by a function similar to Eq. (1) [31],

$$x(P) = x_p \exp\left(\frac{D_p P}{P_0 - P}\right), \quad (3)$$

in which  $x_p$  is obtained from isobaric data measured at atmospheric pressure, and  $P_0$  and  $D_p$  are constants. Another derivative function, similar to  $\phi_T$ , can be defined [19,20],

$$\phi_P = \{d[\log(x)]/d[P]\}^{-1/2}. \quad (4)$$

This linearizes data that conform to Eq. (3), whereby deviations in the pressure dependence of  $\tau$  or  $\eta$  are unambiguously revealed.

Hansen *et al.* [7] used the function  $\phi_T$  to analyze extensive atmospheric pressure viscosity and dielectric relaxation data for OTP. They obtained  $T_B \approx 290$  K, with  $T_B$  defined as the temperature at which the data deviate from the low temperature VF. For OTP at  $T_B$ ,  $\eta_B \approx 10$  Pa s and  $\tau_B = 2.3 \times 10^{-8}$  s [28]. Isothermal viscosity measurements on OTP at pressures as high as 1 GPa were reported by Schug *et al.* [23]. Three isotherms at higher temperatures are shown in Fig. 1(a). We calculate the function  $\phi_P$  for these data [Fig. 1(b)], and observe a change in the pressure dependence of  $\eta$ . The pressure at which this change in  $P$  dependence occurs is constant to within the experimental error,  $\log \eta_B(\text{Pa s}) = 1.5 \pm 0.4$ . This is close to the value for atmospheric pressure; thus, for OTP, we conclude that  $\eta_B$  is independent of temperature and pressure. These viscosity results call to mind the

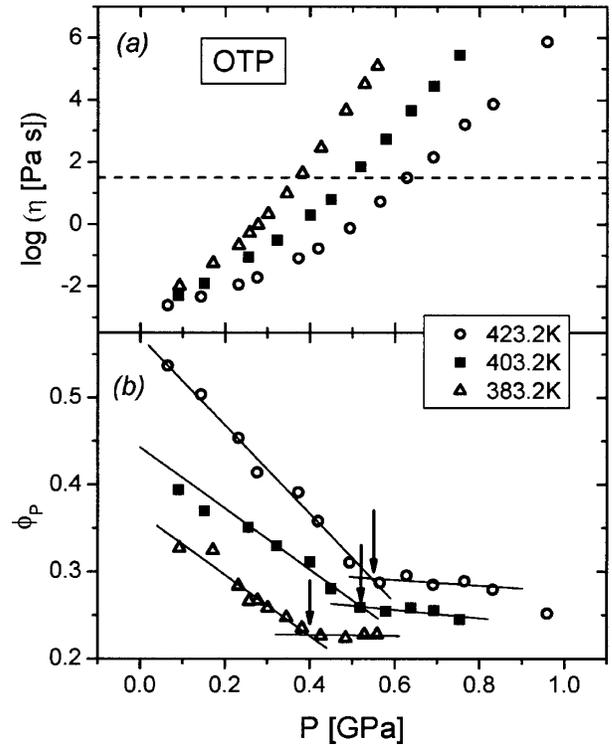


FIG. 1. (a) Isothermal viscosities of OTP from Ref. [23]. The horizontal dashed line indicates the value at the crossover,  $\log \eta_B(\text{Pa s}) = 1.5 \pm 0.4$ . (b) The derivative function,  $\phi_P$ , for the three isotherms, along with the fitted Eq. (3) (solid lines). The arrows denote the pressure associated with the change of dynamics.

fact that the characteristic value of the relaxation time at the glass transition temperature (as measured, for example, volumetrically) has been found to be independent of pressure, that is,  $T_g$  varies with  $P$ , but  $\tau(T_g)$  may not [32–34].

The pressure dependence of  $T_B$  for OTP is shown in Fig. 2, along with a fitted polynomial,  $T_B(P) = (290 \pm 1) + (258 \pm 10) \times P - (56 \pm 7) \times P^2$  (units are K and GPa). Note that pressure exerts a similar effect on  $T_B$  as on  $T_g$ . For example, in the limit of low pressure,  $dT_B/dP = 258$  K/GPa, equivalent to the pressure coefficient of  $T_g$ , which equals 260 K/GPa [35]. In this same plot are shown the neutron scattering data of Tölle [36], corresponding to the pressures at which there is a change in the Debye-Waller factor. Interestingly, the respective data correlate well, notwithstanding recent criticism [37] of the neutron results.

Viscosity measurements on salol over a broad range of temperatures at atmospheric pressure were reported by Laughlin and Uhlmann [22] [see Fig. 3(a)]. Calculating  $\phi_T$  [see Fig. 3(b)], we find  $T_B \approx 254$  K [38], at which  $\log \eta_B(\text{Pa s}) = 1.7 \pm 0.1$ . The relaxation time at this temperature is  $5 \times 10^{-7}$  s [14]. High-pressure viscosity measurements on salol by Schug *et al.* [23] are displayed in Fig. 4, along with the calculated  $\phi_P(P)$ . A crossover is

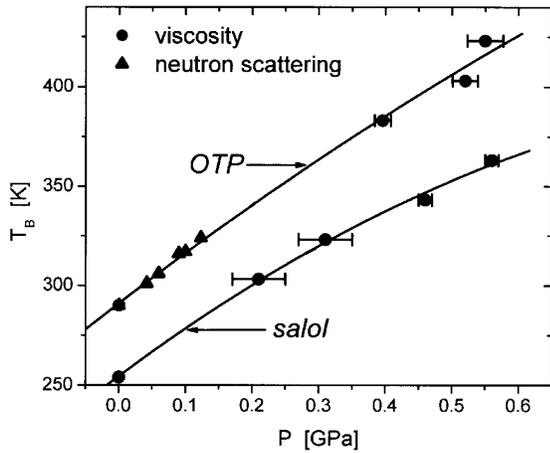


FIG. 2. Crossover temperature for OTP (upper curve) and salol (lower curve) determined from viscosity data (●) at atmospheric pressure (varying temperature) and at high pressure (constant temperature). Also shown are the  $T_B$  deduced from the neutron-scattering Debye-Waller factor (▲) (from Ref. [36]). The solid lines represent fitted quadratic polynomials.

evident in both the isothermal and isobaric data, and we find that, at the crossover,  $\log \eta_B(\text{Pa s}) = 1.3 \pm 0.4$ , equal within the error to the value of  $\eta_B$  determined from the atmospheric-pressure data in Fig. 3(b). The pressure

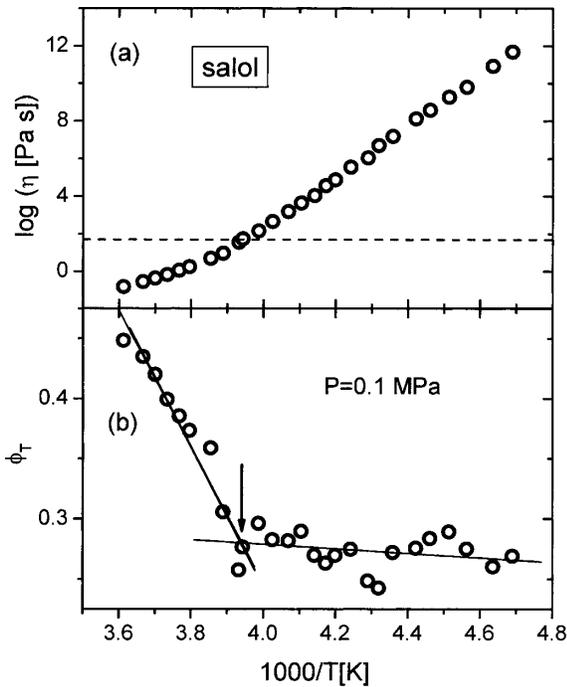


FIG. 3. (a) Viscosities at atmospheric pressure for salol (from Ref. [22]). The horizontal dashed line corresponds to the value at  $T_B$ ,  $\log \eta_B(\text{Pa s}) = 1.3 \pm 0.1$ . (b) The derivative function,  $\phi_T(T)$ , along with the fit to Eq. (1). The arrow denotes  $T_B = 254$  K.

dependence of the crossover temperature is shown in Fig. 2, along with the best-fit polynomial,  $T_B(P) = (254 \pm 3) + (250 \pm 25) \times P - (106 \pm 43) \times P^2$  (units are K and GPa). For salol,  $T_B$  changes somewhat more with pressure than does  $T_g$ . At low pressure,  $dT_B/dP = 250$  K/GPa vs  $dT_g/dP = 204$  K/GPa [40].

In conclusion, the analysis of isothermal and isobaric viscosity data for the glass formers OTP and salol, using the derivative function introduced by Stickel *et al.* [14] together with a modification for high-pressure data [19,20], reveal a crossover in the dynamics. This is the first evidence for such a crossover in viscosity data under elevated pressure. The crossover temperature shows a nonlinear dependence on pressure, as previously seen in neutron scattering measurements on OTP [36].

The value of the viscosity at the crossover is sensibly independent of pressure or temperature, and therefore also of density. These results agree with earlier findings for polychlorinated biphenyls and phenolphthalein-dimethyl ether, in which the dielectric relaxation time at the crossover was likewise independent of temperature and pressure [19,20,40]. At atmospheric pressure, this crossover is known to occur at the same temperature, when determined using either viscosities or dielectric relaxation times [41]. Accordingly,  $\tau_B$  for OTP and salol

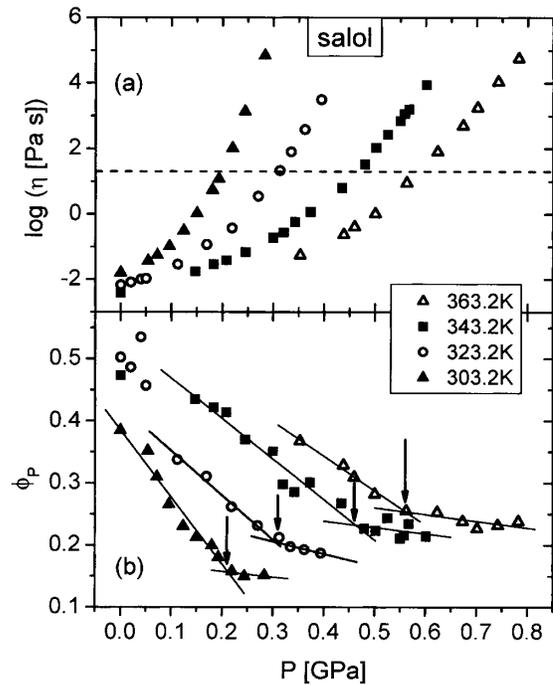


FIG. 4. (a) Isothermal viscosities versus pressure for salol at four temperatures (from Ref. [23]). The horizontal dashed line indicates the value at the crossover,  $\log \eta_B(\text{Pa s}) = 1.3 \pm 0.4$ . (b) The derivative function,  $\phi_P$ , for the four isotherms, along with the fit of Eq. (3) (solid lines) to the data for  $\log \eta > -1.3$ . The arrows denote the pressure associated with the change of dynamics.

are expected to be independent of density. Given the myriad phenomena associated with the dynamic crossover, our finding that  $\eta_B$  (or  $\tau_B$ ) serves as the control variable governing the crossover is a salient fact that must be accounted for by any theory of the supercooled dynamics of glass-forming liquids.

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