

Dielectric and mechanical relaxation of cresolphthalein–dimethylether

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From pressure–volume–temperature measurements, in combination with published dielectric spectroscopy results, we assess the volume dependence of structural relaxation in cresolphthalein–dimethylether (KDE). Structural relaxation in KDE cannot be described as either a volume activated or thermally activated process, and unlike results for some other molecular glass formers, temperature is not the dominant control variable. The inflection point of the PVT data yields a glass temperature, T_g , that corresponds to a dielectric relaxation time equal to 10 s. There is a marked variation with pressure, $dT_g/dP=307$ K/GPa at low pressure. We also carried out dynamic mechanical measurements on KDE near T_g . The shape of the mechanical and dielectric relaxation functions, as well as both the magnitude and temperature dependence of the respective relaxation times, are the same. Such equivalence is not generally expected, and arises herein due to the rigid structure of the KDE molecule. © 2002 American Institute of Physics. [DOI: 10.1063/1.1485965]

INTRODUCTION

Relaxation near the glass temperature is highly cooperative, leading to enormous increases in the viscosity and relaxation time upon cooling towards T_g . While local packing and the spatial correlation of properties underlie all descriptions of the dynamics of glass formers, there are two contrary viewpoints. Free volume approaches embody the idea of congested passage through low-energy pathways in configurational space, as governed by the density and packing considerations.^{1–4} The converse approach emphasizes thermally activated passage over potential barriers, with temperature being the dominant control variable.^{5–7} Molecular dynamics simulations indicate that structural arrest occurs when the density exceeds a critical value, consistent with free volume ideas. On the other hand, from an analysis of the temperature and density dependence of various glass formers, Ferrer *et al.*⁸ concluded that at ambient pressure, relaxation is an activated process, dominated by temperature, with free volume exerting a negligible influence. Of course, since temperature changes *per se* affect the density, apparent activation energies reflect in part the effect of density.^{9,10}

Generally, relaxation properties near T_g are expected to be sensitive to both free volume and temperature, to an extent dependent on the chemical structure of the liquid, as well as pressure. An explicit example of this is found in cresolphthalein–dimethylether (KDE), a nonassociating small molecule glass former. From dielectric measurements,¹¹ it was found that the Kohlrausch stretch exponent,

β , describing the breadth of the relaxation function,¹² is equal to 0.75 at T_g . This is a small degree of nonexponentiality, indicating KDE is a relatively “strong” liquid.¹¹ However the fragility, m (T_g -normalized temperature dependence of τ_α) is 72.5, a relative large value associated with fragile glass formers.¹¹ Thus, the behavior of KDE diverges from the expected correlation of these two parameters, which has been quantified as $m=250(\pm 30)-320\beta$.¹³

This dual nature of KDE persists with respect to the effect of pressure on the relaxation properties. The activation volume displays the weak dependence on pressure expected of strong liquids, although the activation volume *per se* is quite large (230 cm³/mol).¹¹ This means there is a strong dependence of τ_α on pressure. Drawing an analogy to the temperature dependence of the relaxation time, this implies fragile behavior.

It has been proposed¹¹ that the anomalous behavior of KDE has its origin in the competing effects of cooperative dynamics, governed by constraints on the motion from the densely packed liquid structure, and of thermodynamics, whereby a large variation of configurational entropy with temperature contributes to a large fragility. To further investigate this problem, we carried out PVT measurements on KDE. In combination with published dielectric data, these allow a determination of the volume dependence of the relaxation times. Since a given volume can be attained for various conditions of temperature and pressure, the results enable assessment of the relative contributions of density (free volume) and thermal activation to the dynamics. That is, we can use pressure to try to distinguish effects arising from fluctuations in free volume from those due to thermal fluctuations.

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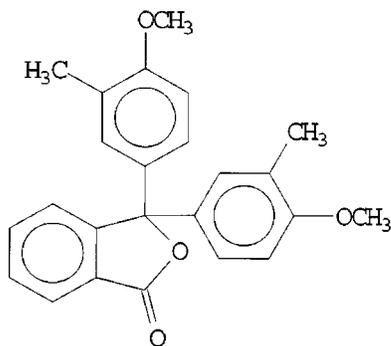


FIG. 1. The chemical structure of cresolphthalein–dimethylether.

We also report dynamic mechanical measurements on KDE, and compare the mechanical properties to the dielectric relaxation. This aspect of the work was motivated by findings that translational and reorientational motions are sometimes decoupled,^{14,15} along with the fact that mechanical relaxation has been shown to be similar to the viscosity, with respect to temperature dependences near T_g .^{16,17} Since KDE is a fairly rigid molecule (the molecular structure of KDE is shown in Fig. 1), we expect that the local motion responsible for the alleviation of stress might be quite similar to the microscopic polarization mechanism.

EXPERIMENT

The cresolphthalein–dimethylether (KDE) used in these studies was synthesized in laboratory of H. Sillescu and obtained from Roland Bohmer of Johannes Gutenberg Universität, Mainz, Germany. The designation KDE derives from the germanic spelling of cresol.

PVT measurements were carried out using a Gnomix instrument, in which the sample is immersed in mercury. A detailed description of the equipment can be found in Ref. 18. Measurements of volume changes were carried out in the isothermal mode. At a fixed temperature, starting at high temperature, the pressure was increased, up through 200 MPa, with data recorded at various intervening pressures. On completion of measurements along one isotherm, the temperature was decreased and the pressure measurements repeated. The quantity of sample used in experiment was equal to 1.523 g.

Dynamic mechanical measurements were carried out using a Rheometrics RMS 800 spectrometer. Shear deformation was applied using 6 mm diameter parallel plates with ca. 1 mm gap, with the strain verified to remain within the range of linear viscoelastic response. The frequency dependences of the storage (G') and loss (G'') modulus were measured at various temperatures, with the sample maintained in a dry nitrogen atmosphere.

RESULTS AND DISCUSSION

PVT results. Figure 2 shows the change in the specific volume with temperature for seven pressures. A change in the thermal expansivity is evident at a temperature that increases with increasing pressure. Above this transition temperature, the data can be described by the Tait equation^{19,20}

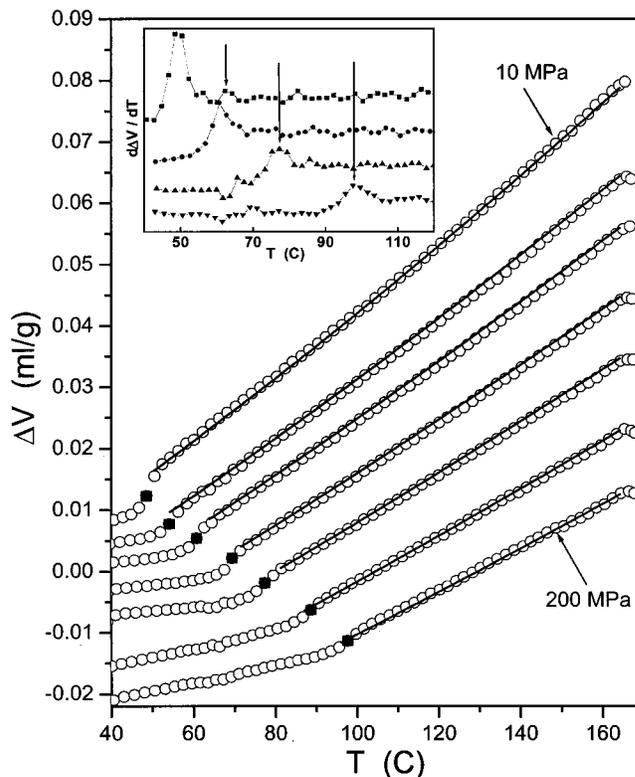


FIG. 2. The temperature dependence of the specific volume change, relative to the volume at 25 C and 0.1 MPa, for KDE at pressures equal to (from top to bottom) 10, 40, 60, 90, 120, 160, and 200 MPa. The solid symbols denote the glass temperature, taken as the inflection point of the curves. The inset shows the derivative used to determine T_g , for $P=10, 60, 160,$ and 200 MPa.

$$V(T, P) = V(T, 0) [1 - C \ln(1 + P/B(T))] - V_{\text{ref}} \quad (1)$$

in which $C(=0.089)$ and $V_{\text{ref}}(=0.9 \text{ ml/g})$ are constants, $V(T, 0) = v_0 + v_1 T + v_2 T^2$, and $B(T) = b_0 \times \exp(-b_1 T)$. The simultaneous fits to the PVT data are shown in Fig. 2, with $b_0 = 331 \text{ MPa}$, $b_1 = 4.46 \times 10^{-3} \text{ K}^{-1}$, $v_0 = 0.895 \text{ ml/g}$, $v_1 = 4.5e-4 \text{ ml/g K}$, with $v_2 = 5.50e-7 \text{ ml/g K}^2$. With a density of unity, we deduce a value for the thermal expansion coefficient equal to $6 \times 10^{-4} \text{ K}^{-1}$. The maxima in the derivatives of the expansivity curves (inset to Fig. 2) yield the glass temperature at each pressure.

It is common in the study of relaxation phenomena to use a “dynamic T_g ,” defined as the temperature at which the relaxation time assumes some arbitrary value. The dielectric relaxation times for KDE were previously shown to conform to the Avramov equation^{21,22}

$$\tau_\alpha = \tau_\infty \exp \left[30 \left(\frac{T_R}{T} \right)^{z_T} \left(1 + \frac{P}{\Pi} \right)^{z_P} \right]. \quad (2)$$

This indicates that the effects of temperature and pressure can be treated separately, and thus the temperature dependence of τ_α of KDE does not depend on pressure.

From fitting dielectric measurements on KDE, the following parameters were obtained:¹¹ $\tau_\infty = 4.0 \times 10^{-13} \text{ s}$, $z_T = 4.9$, $z_P = 1.7$, $T_R = 318 \text{ K}$, and $\Pi = 345 \text{ MPa}$. Solving for T

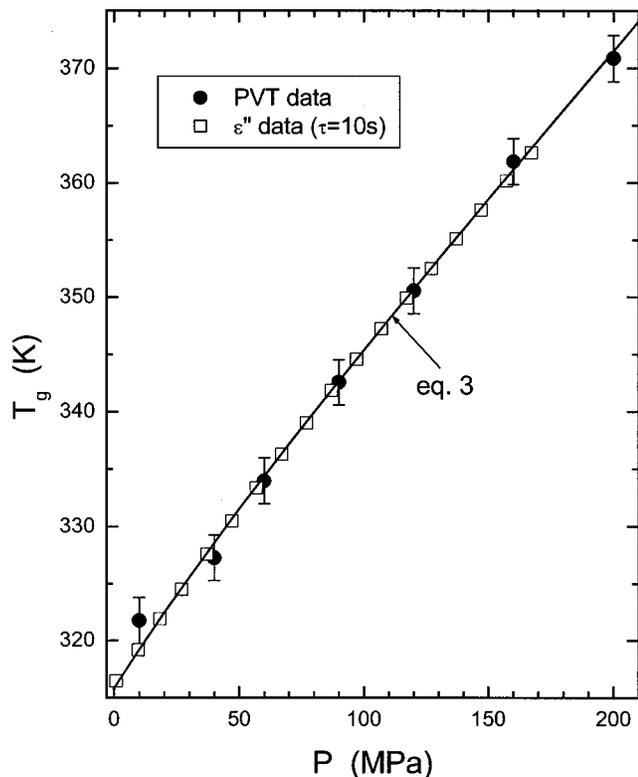


FIG. 3. The glass temperature determined from the *PVT* data in Fig. 2 (●), along with the temperatures at which the dielectric relaxation time equals 10 s (□). The solid line represents the fit to the extended Adam–Gibbs model.

as a function of pressure for $\tau_\alpha = 10$ s yields the results shown in Fig. 3. These are in good agreement with the *PVT* equilibrium determinations of T_g ; that is, while the temperature at which $\tau_\alpha = 100$ s is a commonly used reference temperature for analyzing dynamic data, herein we find for KDE that $\tau_\alpha = 10$ s at T_g . From the initial slope of the combined dielectric and *PVT* data in Fig. 3, we obtain for the pressure coefficient of the glass temperature, $dT_g/dP = 307$ K/GPa. As seen in Table I, this is higher than has been reported for any other small molecule glass former,^{23–26} and for most polymers.^{27–31}

Casalini *et al.*^{32,33} have proposed a model for the pressure dependence of the dynamics of glass formers, based on

TABLE I. Pressure dependence of glass temperature.

| | dT_g/dP (K/GPa) | Reference |
|--------------------------------------|-------------------|-----------|
| KDE | 307 | Herein |
| <i>o</i> -terphenyl | 260 | 23 |
| bis-phenol-cyclohexane-dimethylether | 240 | 24 |
| B ₂ O ₃ | 200 | 25 |
| Selenium | 130 | 25 |
| Glycerol | 35 | 26 |
| Polymethyltolylsiloxane | 370 | 27 |
| Polymethylphenylsiloxane | 280 | 28 |
| Polyisobutene | 240 | 25 |
| Polyvinylacetate | 220 | 25 |
| Polypropyleneglycol | 192 | 29 |
| Polymethylacrylate | 170 | 30 |
| 1,4-polyisoprene | 160 | 31 |

an extension of the Adam–Gibbs model.³⁴ They obtain the following expression for the glass temperature:

$$T_g(P) = T_g(0) [1 + k_1 [- (k_2 + \gamma - 1) P + ((\gamma - 1) B(T) \ln(1 + P/B(T)) + \gamma P) \ln(1 + P/B(T))]]^{-1} \quad (3)$$

in which $T_g(0)$ is the ambient pressure glass temperature, taken to be 315.8 K, the temperature at which the dielectric relaxation time equals 10 s. The quantity γ , the ratio of the thermal expansion coefficient and b_1 (from the Tait equation) is calculated to equal 0.14 for KDE. In principle, k_1 and k_2 can be calculated, respectively, from the configurational entropy and molar volume difference between the crystal and the melt.^{32,33} Herein, we use them as adjustable parameters, to obtain $k_1 = 5.5 \times 10^{-4}$ MPa⁻¹ and $k_2 = 2.0$, with the fit shown as the solid curve in Fig. 3. The agreement with the experimental data is satisfactory. The limiting value of the configurational entropy at high temperature, S_∞ , can then be deduced from the relation^{32,33}

$$S_\infty = \frac{CVb_1}{k_2} \quad (4)$$

in which $V (= 0.37$ l/mol) is the molar volume of KDE. This gives $S_\infty = 270$ J/K mol.

Temperature influences relaxation primarily through its effect on thermal energy, while pressure affects the molecular packing (free volume). This means that a change in temperature has qualitatively the inverse effect of a change in pressure; moreover, a given structural relaxation time can be obtained for different combinations of temperature and pressure. Using the data in Eq. (1), we can compare the volume associated with τ_α for isobaric versus isothermal experiments. Displayed in Fig. 4 are the relaxation times for KDE at ambient pressure and various temperatures [$315 < T$ (K) < 364], along with the τ_α obtained at 364.6 K for pressures up to 167 MPa. Interpolation of the data in Fig. 2 yields the specific volume associated with any T and P .

It is obvious from Fig. 4 that variations in pressure and temperature do not yield equivalent relaxation times. This indicates that the dynamics of KDE near T_g are not a simple volume activated process. Free volume models provide an inadequate description, since volume alone does not uniquely characterize the behavior. Nevertheless, we observe in Fig. 4 that density changes alone exert an enormous effect on the relaxation behavior. Pressure-induced volume changes equivalent to a 50 degree change in temperature cause τ_α to vary by almost three decades. Structural relaxation in the vicinity of T_g is not dominated by thermally activated dynamics, although, of course, thermal energy exerts a substantial effect. However, when compared at equal volume, there are greater changes in τ_α for the isobaric data than for the isothermal results.

We can quantify the relative contributions from temperature and density using a method proposed by Ferrer *et al.*⁸ The change in relaxation time at constant pressure as tem-

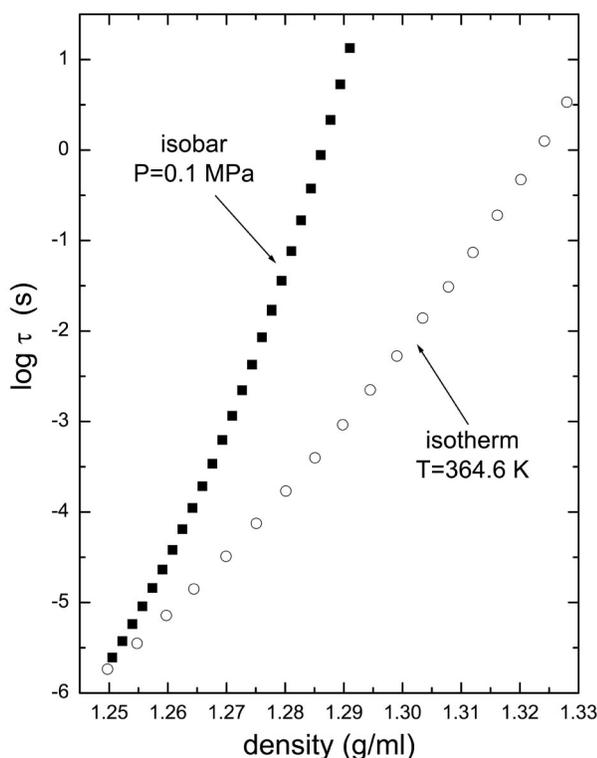


FIG. 4. The dependence of the dielectric relaxation times on the mass density, for measurements in which either pressure (○) or temperature (■) was varied.

perature is decreased from some initial temperature T_i to T_g can be expressed as⁸

$$\ln \left[\frac{\tau(T_g)}{\tau(T_i)} \right] = - \int_{T_i}^{T_g} \left(\frac{\partial \ln \tau}{\partial \ln \rho} \right) (-\alpha_\tau + \alpha_p) dT \quad (5)$$

in which ρ is the mass density, the coefficient of isobaric expansivity $\alpha_p = -\rho^{-1}(\partial \rho / \partial T)_p$, and the coefficient of isochronic expansivity, $\alpha_\tau = -\rho^{-1}(\partial \rho / \partial T)_\tau$. As discussed by Ferrer *et al.*,⁸ the ratio α_τ / α_p reflects the relative contribution of temperature and volume to the relaxation. For all glass formers studied in Ref. 8, $|\alpha_\tau / \alpha_p|$ was substantially larger than unity, leading the authors to conclude that temperature was the dominant control variable.

From the dependence of the relaxation time on pressure and temperature, in combination with the data in Fig. 4, we can calculate the density as a function of temperature, both for constant P and for constant τ . Using the fit of Eq. (2) to the combined T and P dependences for KDE,¹¹ together with the fits to the Tait equation described above, we obtain for $P=0.1$ MPa, $\alpha_p = 8.1 \times 10^{-4} \pm 0.5 \times 10^{-4}$, and for $\tau=1$ s, $\alpha_\tau = 7.9 \pm 0.4$. Thus, $|\alpha_\tau / \alpha_p| = 0.98 \pm 0.11$, suggesting that density and temperature exert a comparable influence on the dynamics of KDE. This is different from previous results on other glass formers. For example, for glycerol $|\alpha_\tau / \alpha_p| = 24$,⁸ indicating that the dynamics are strongly dominated by temperature.

Mechanical results. Displayed in Fig. 5 are the dynamic loss moduli measured for KDE at temperatures from 312 to 323 K. These data encompass the transition from Newtonian flow at low frequencies to the glassy response at higher fre-

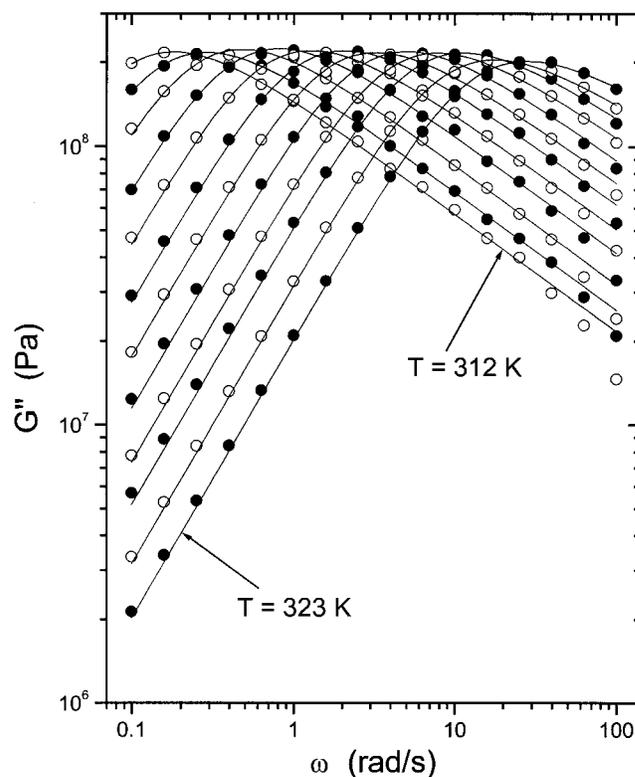


FIG. 5. Dynamic mechanical loss modulus measured isothermally at ambient pressure. There is a one degree temperature difference between each spectrum. The solid lines are only a visual aid.

quencies. For polymers, a breakdown of the time-temperature superposition principle is the norm for mechanical data in this region of the viscoelastic spectrum.^{35–37} Results of this type for small molecule glass formers are sparse.^{16,38} Over the limited frequency range, the KDE data are thermorheologically simple; thus, we can shift along the frequency axis to obtain the master curve of the mechanical modulus shown in Fig. 6.

The inverse circular frequency of the maximum in the loss modulus, ω^{-1} , defines a mechanical relaxation time, which is well known to be shorter than the corresponding τ_α .³⁹ This can be due to the fact that the latter is analogous to a mechanical retardation time. To allow comparison of the mechanical and dielectric spectra, we can calculate the dielectric loss modulus

$$M''(\omega) = \epsilon''(\omega) / (\epsilon'^2(\omega) + \epsilon''(\omega)^2), \quad (6)$$

where ϵ' and ϵ'' are the dielectric constant and loss, respectively.

A master curve for the dielectric loss modulus, at the same reference temperature, 318 K, as the mechanical data, is included in Fig. 6. The dielectric loss exhibits a low frequency peak, due to the conductivity contribution ($\epsilon'' \propto \omega^{-1}$). This corresponds to the flow region for the loss modulus ($G' \propto \omega \times G'' \propto \omega^2$), although there is no terminal peak in the mechanical spectrum.

Note that the frequency of the maximum in the dielectric modulus is quite close to its mechanical counterpart. In Fig. 7, we plot both relaxation times as a function of temperature.

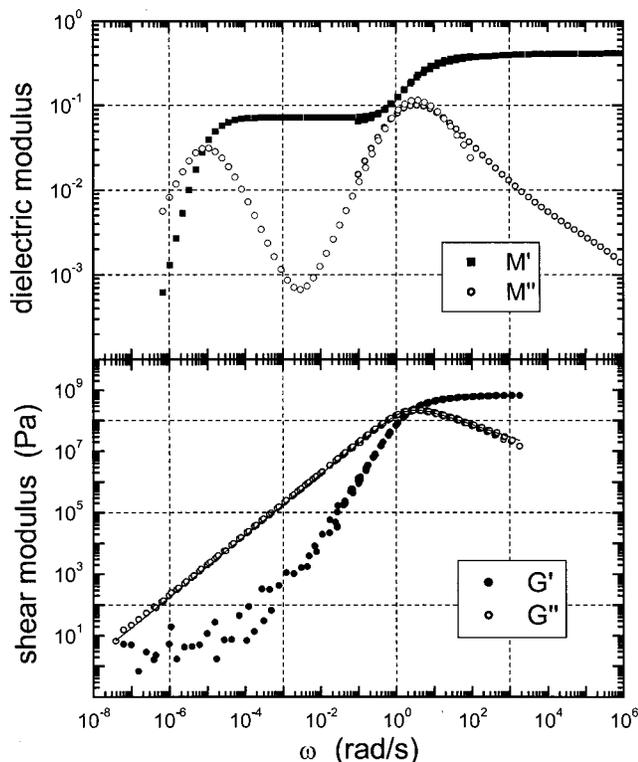


FIG. 6. Master curves of the mechanical modulus (lower) and the dielectric modulus (upper) at the same reference temperature, =318 K. The abscissa represents the shifted, not the measured, frequencies.

It can be seen that the magnitude of the relaxation times as measured by the two spectroscopies, as well as their respective temperature dependences, are nearly the same. Similar cases, at least of equivalence between mechanical and dielectric temperature dependences, have been reported for polyvinylethylene,⁴⁰ polyisoprene,³⁵ and polybutadiene.⁴¹

Of course, there is no requirement that different dynamic variables exhibit identical properties. The equivalence in Fig. 7 suggests that dielectric and mechanical relaxations in KDE arise from the same molecular motion. A free volume interpretation of such a result is that the mean volume of the relaxing entity for each experimental probe must be the same.^{1,2} For a small, rigid molecule such as KDE, it is apparent that any molecular motion that alleviates stress subtends the molecular dipole. For bulkier structures, mechanical and dielectric temperature dependences can differ, as reported for polychlorinated biphenyls,^{39,41} polyvinyl acetate,⁴² and polypropylene glycol.⁴³ Such differences have also been observed in mixtures.⁴⁴

We can extend this comparison to the shape of the respective relaxation functions. As shown in Fig. 8, the peaks are similar in breadth, which is consistent with the expected correlation between time and temperature dependences.¹³ At higher frequencies, an extra intensity (“excess wing”) is observed in the dielectric spectrum.¹¹ Since the primary dispersion shifts to higher frequency upon converting ϵ'' to M'' , the structural relaxation peak is less separated from any secondary peak in the modulus representation of the data. Hence, the excess wing is less prominent in the modulus representation of the dielectric loss.

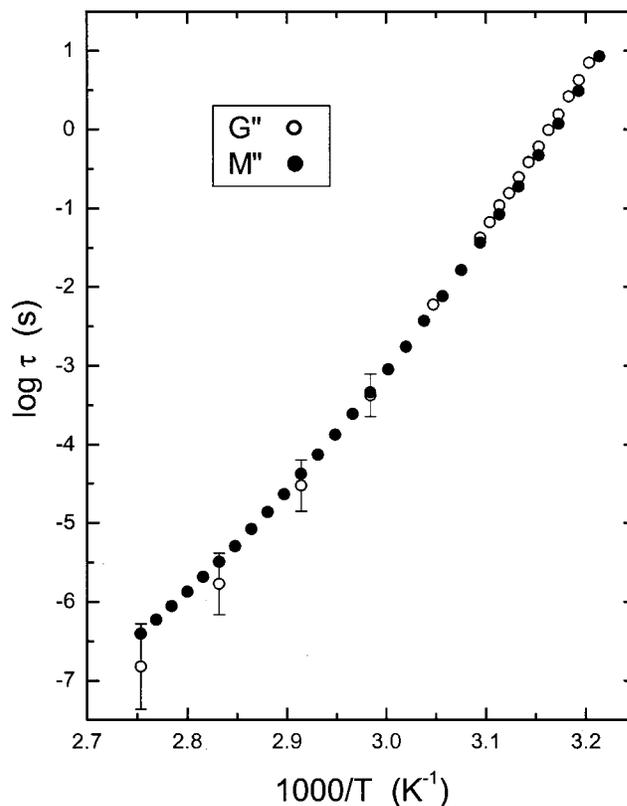


FIG. 7. The relaxation times determined from shift factors for the dynamic shear modulus (○) and from the maximum in the dielectric loss modulus (●).

This may account, in part, for the absence of Johari–Goldstein secondary processes in most mechanical spectra. In principle, the dynamic modulus can be converted to the (less commonly used) compliance function, in order to better resolve any higher frequency process. However, measurement of Johari–Goldstein relaxations typically requires frequencies $\geq 10^7$ Hz; thus, mechanical data, including the present results, do not usually extend to sufficiently high frequencies.

SUMMARY

From equation of state measurements on the glass-forming liquid KDE, we assess the relative contributions of free volume and thermal energy to the dynamics. The variation of the dielectric relaxation time with volume is different for isothermal and isobaric measurements. Analysis of the data indicated, moreover, that temperature is not the dominant control variable. The enormous slowing down of relaxation times as T_g is approached reflects the combined effects of both volume and temperature.

At all pressures, the glass temperature determined for KDE from the PVT data is equal to the temperature at which the dielectric relaxation time equals 10 s. This glass temperature is especially sensitive to pressure; at low pressures, $dT_g/dP = 307$ K/GPa. The pressure dependence up through 200 MPa can be described using an extension of the Adam–Gibbs model, having two adjustable parameters. From fitting

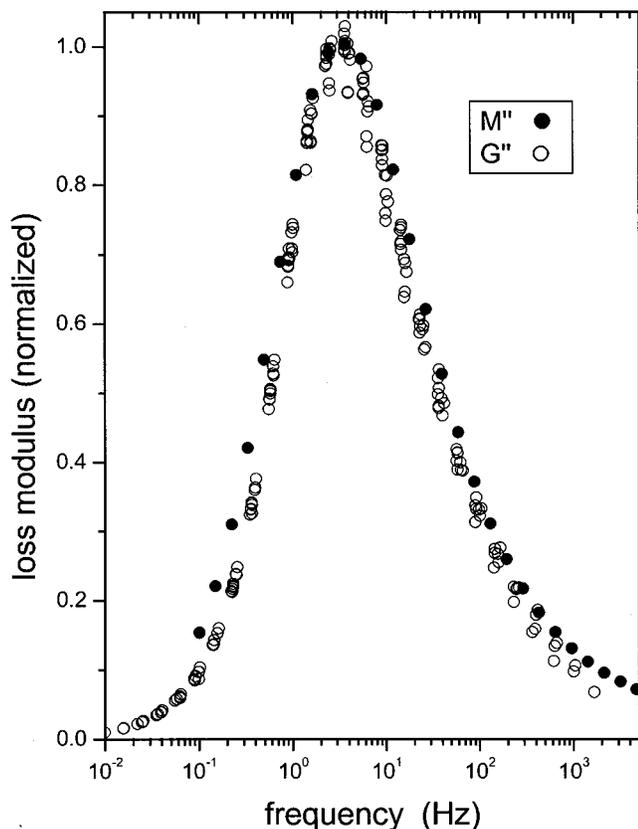


FIG. 8. The dispersion in the mechanical loss modulus at 318 K (○) and in the imaginary component of the dielectric modulus at 317 K (●). The latter was shifted slightly to superimpose the respective maxima, and the data were scaled to unity at the peak.

the experimental data, we estimate 270 J/K mol as the value of the configurational entropy in the limit of high temperature.

The relaxation time determined by mechanical measurement has the same temperature dependence as the dielectric τ_α . Moreover, when the dielectric loss is converted to a dielectric modulus, both the magnitude of the respective relaxation times and the shape of the mechanical and dielectric relaxation functions are the same. This equivalence reflects the rigid structure of KDE, whereby reorientations which alleviate stress necessarily involve motion of the molecular dipole.

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