Cohen-Grest model for the dynamics of supercooled liquids

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Recent experiments have established that, at least for van der Waals glass formers, volume fluctuations contribute significantly to the slowing down of the dynamics near T_g. Accordingly, we use the Cohen-Grest (CG) free-volume model to analyze dielectric relaxation data for six van der Waals liquids. The CG equation accurately describes the structural relaxation times over broader ranges of temperature than the more common Vogel-Fulcher relation. Moreover, the CG equation requires two less adjustable parameters when the data span the Stickel temperature T_B associated with a change in the dynamics. The characteristic temperature T_0 of the CG model can be identified with T_B, suggesting that the crossover reflects onset of percolation of the free volume. The CG parameters used to fit the structural relaxation times allow the free volume per liquidlike molecule to be calculated. These results, however, are at odds with free-volume estimates extracted from pressure-volume-temperature data.

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INTRODUCTION

Amorphous liquids near their glass transition display complex relaxation and transport properties, making their investigation especially interesting. Experiments measuring the dependence of the dynamics on both pressure and temperature enable assessment of the relative contributions of thermal energy and volume (density) to the behavior. Although for associated liquids, such as hydrogen-bonded polyalcohols [1,2], and perhaps for polymers [3], temperature may be the variable governing the structural relaxation times, for van der Waals molecular glass formers, thermal energy and density have a comparable effect on τ [4–8]. In fact, for 1,1′-bis(*p*-methoxyphenyl)cyclohexane (BMPC) and 1,1′-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC), density exerts a *stronger* influence than does thermal energy [9]. Recent positron annihilation lifetime spectroscopy (PALS) measurements on BMMPC were interpreted in terms of free volume and its influence on the local dynamics [10]. These developments in our understanding of the properties of glass-forming liquids suggest that free-volume models, however long discredited [1,3,11–13], perhaps deserve reexamination.

Various theoretical approaches to the dynamics of supercooled liquids provide an equation to describe the temperature dependence of τ. Far and away the most common are the Vogel-Fulcher (VF) equation [14]

$$\ln \tau(T) = \ln \tau_\infty + \frac{b}{T - T_V} \tag{1}$$

and the Williams-Landel-Ferry (WLF) equation [14]

$$\ln \tau(T) = \ln \tau(T_R) - \frac{c_1(T - T_R)}{c_2 + T - T_R}. \tag{2}$$

In these expressions, b, τ_∞, c_1, and c_2 are constants, while T_V and T_R are, respectively, the Vogel temperature and an arbitrary reference temperature. Although the VF is an empirical equation, it can be obtained either from the theory of Adam-Gibbs, a thermal activation model [11], or derived from a free-volume model [15]. On the other hand, the WLF equation reflects a free-volume approach [16]. Notwithstanding their different origins, the two equations are mathematically equivalent, viz., $b = c_1/c_2$ and $T_V = T_R - c_2$ [14].

Although these equations are routinely used to fit experimental data, their accuracy is known to be limited to a range of temperatures. Stickel *et al.* [17] have shown that two VF equations are required to describe τ from just above T_g up to very high temperatures, where Arrhenius behavior ($T_V = 0$) is obtained for temperatures beyond those considered herein. At some intermediate temperature, $T_B \sim 1.2 T_g$, a change in the VF parameters is required, evidently reflecting some change in the dynamics. This aspect of the behavior of supercooled liquids has evoked much interest. It has been shown from high pressure measurements that for a given liquid, the change transpires at a fixed value of τ, independent of T and P [18,19]. It has also been shown that other alterations in properties transpire at the temperature associated with the change from one to another VF fitting function [17,19,20–24]; nevertheless, the molecular mechanisms underlying this "dynamic transition" are unknown. The general consensus is that below T_B, the dynamics become "fully cooperative," although the non-Arrhenius character of $\tau(T)$ above T_B indicates that the intermolecular cooperativity remains extant.

To describe fully the relaxation times of glass formers throughout the supercooled regime requires additional parameters beyond the three found in Eq. (1) or (2). In particular, as many as six parameters would be necessary for the use of two VF equations (without taking into account Arrhenius behavior at very high temperatures). In this paper, we examine the Cohen-Grest (CG) model [25,26], which treats the supercooled dynamics considering diffusion to be governed

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by free volume. The system is divided in liquidlike and solidlike cells, only the former having free volume. The model expresses the temperature dependence of the relaxation times as

$$\log_{10}\tau(T)=A+\frac{B}{T-T_0+[(T-T_0)^2+CT]^{1/2}}, \qquad (3)$$

in which A, B, C, and T_0 are material constants. T_0 is identified as the temperature at which continuity of the liquidlike molecules is attained. This percolation threshold is reached when each liquidlike molecule is proximate to at least two other liquidlike molecules. Since Eq. (3) has one parameter more than the VF or WLF equations, superior data fitting is expected, and has in fact been demonstrated [25,27,28]. Of course, over a sufficiently broad temperature range, the dynamics of supercooled liquids requires two VF equations for a good description, so that the number of parameters in the CG approach is fewer.

Since an ability to fit experimental relaxation times is not unique to the CG model, an assessment must rely on interpretation of the physical significance of the obtained parameters. Specifically, we examine whether the threshold for percolation of liquidlike domains can be associated with any experimental observable. T_0 has been interpreted as being equal to the glass temperature [15,28] or to the Vogel temperature [21], but as shown herein, these suggestions are not borne out by analysis of data on various van der Waals glass formers. Instead, we show that the characteristic temperature of the CG model can be identified with the temperature at which supercooled liquids exhibit a change in their dynamics.

A more important consideration is whether free volume can serve as a tenable basis for a theory of the glass transition. This issue has a long history, with recent opinion siding with the notion that temperature is overwhelmingly the dominant control variable [1,3,12,13]. However, experiments have established that volume fluctuations contribute substantially to the dynamics near T_g, at least for van der Waals glass formers [4–9]. Thus, we investigate application of the CG model, not only how well it can describe experimental results, but the significance of the obtained parameters.

RESULTS AND DISCUSSION

Temperature dependence of dielectric relaxation times

In Figs. 1–6 are the structural relaxation times versus temperature, as reported [29] for the supercooled liquids BMPC, BMMPC, phenylphthalein-dimethylether (PDE), cresolphthalein-dimethylether (KDE), phenyl salicylate (salol) and orthoterphenyl (OTP). We choose these six glass formers because each has been shown to have $\tau(T)$ which are governed to a significant extent by volume.

This is seen in Table I, which lists two quantities reflecting the relative contribution of density and thermal energy to the structural relaxation. The first is the ratio of the isobaric expansion coefficient, $\alpha_P=-\rho^{-1}(\partial\rho/\partial T)_P$, to the isochronal coefficient of expansivity, $\alpha_\tau=-\rho^{-1}(\partial\rho/\partial T)_\tau$ [1]. A large $|\alpha_\tau|/\alpha_P$ reveals that temperature (thermal energy) dominates the relaxation, a value of zero that density dominates, and equal contributions to $\tau(T)$ would yield a ratio close to unity. The highest value in Table I is for PDE, for which $|\alpha_\tau|/\alpha_P=1.25$, while for all others the ratio is less than 1.

A second measure of the relative significance of temperature and volume is the ratio of the activation energy at constant volume, E_V, to that at constant pressure, E_P [3,7]. A predominance of the effect of temperature gives $E_V/E_P\approx 1$, of volume a value close to zero, and $E_V/E_P=0.5$ if the two

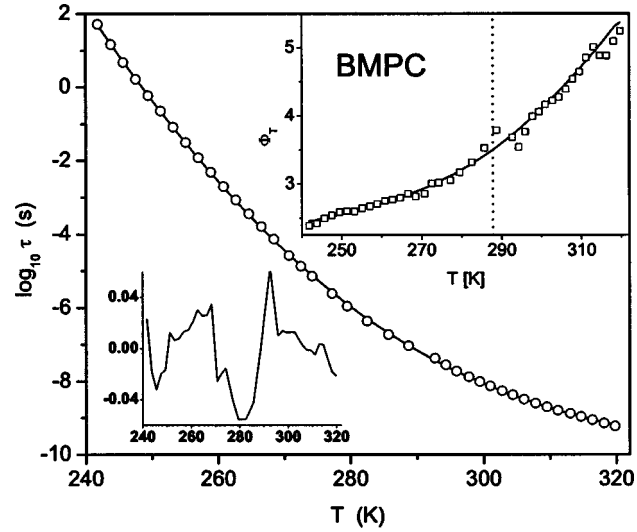

FIG. 1. Dielectric α-relaxation times for 1,1′-bis(p-methoxyphenyl)cyclohexane (○), along with the fit of Eq. (3) using the parameters in Table I. The derivative function [Eq. (4)] is shown in the upper inset, with the value of T_0 indicated by the vertical dotted line. The lower inset displays the difference between the experimental and calculated τ.

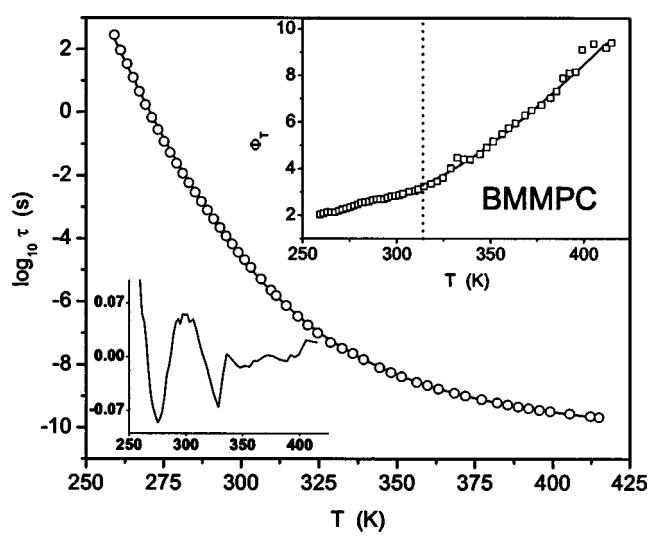

FIG. 2. Dielectric α-relaxation times for 1,1′-di(4-methoxy-5-methylphenyl)cyclohexane (○), along with the fit of Eq. (3) using the parameters in Table I. The derivative function [Eq. (4)] is shown in the upper inset, with the value of T_0 indicated by the vertical dotted line. The lower inset displays the difference between the experimental and calculated τ.

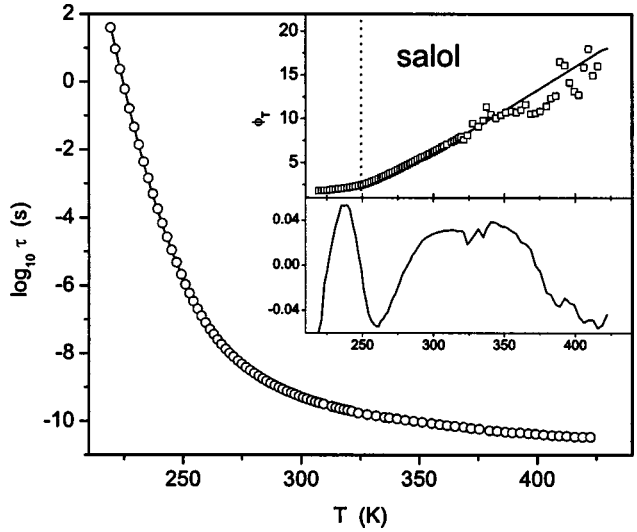

FIG. 3. Dielectric α-relaxation times for phenyl salicylate (○), along with the fit of Eq. (3) using the parameters in Table I. The derivative function [Eq. (4)] is shown in the upper inset, with the value of T_0 indicated by the vertical dotted line. The lower inset displays the difference between the experimental and calculated τ.

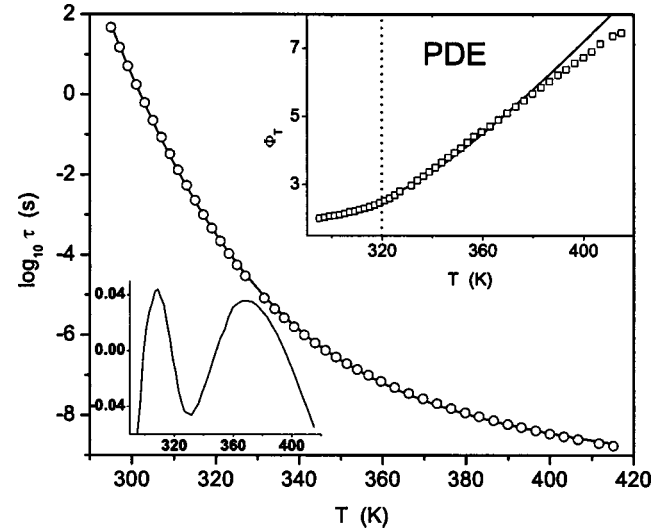

FIG. 5. Dielectric α-relaxation times for phenylphthalein-dimethylether (○), along with the fit of Eq. (3) using the parameters in Table I. The derivative function [Eq. (4)] is shown in the upper inset, with the value of T_0 indicated by the vertical dotted line. The lower inset displays the difference between the experimental and calculated values.

factors govern $\tau(T)$ equally. Among the liquids in Figs. 1–5, PDE again has the largest contribution from thermal energy, $E_V/E_P=0.52$. For the other four liquids, the ratio is less than 0.5, indicating that the structural relaxation times are controlled somewhat more by volume than by thermal energy.

Such glass formers are the most appropriate candidates for application of a free-volume model. Accordingly, we fit Eq. (3) from the CG model to the experimental $\tau(T)$ in Figs. 1–6. As shown by the solid lines, a satisfactory description is obtained for these data, which cover as much as 12 decades of relaxation time. Shown in the inset to the figures is the difference between the measured and calculated τ. Generally, these deviations are small and randomly scattered. For OTP, we have included viscosities [29] in order to extend the range of the data. The obtained fitting parameters for all liquids are listed in Table I. Note that dielectric relaxation times for salol have previously been fit to Eq. (3), with

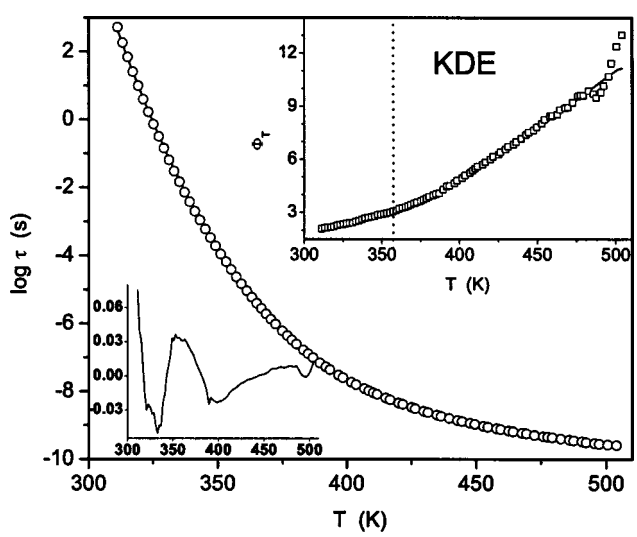

FIG. 4. Dielectric α-relaxation times for cresolphthalein-dimethylether (○), along with the fit of Eq. (3) using the parameters in Table I. The derivative function [Eq. (4)] is shown in the upper inset, with the value of T_0 indicated by the vertical dotted line. The lower inset displays the difference between the experimental and calculated τ.

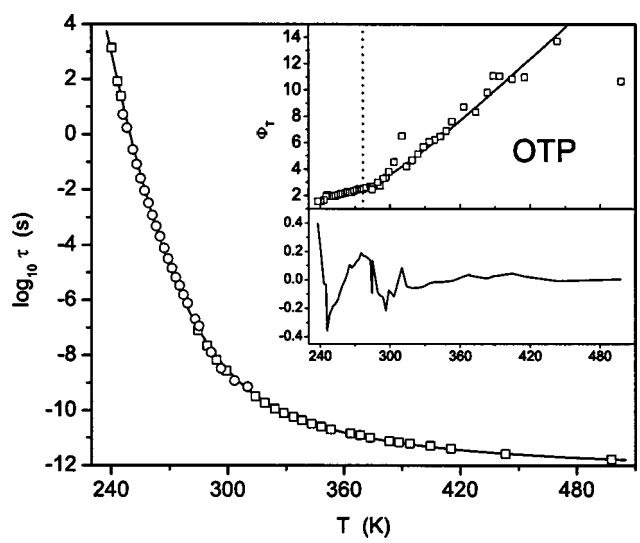

FIG. 6. Dielectric α-relaxation times for (○) and viscosities (□, shifted vertically by 8.77 decades to superpose on the τ ordinate scale) for *o*-terphenyl, along with the fit of Eq. (3) using the parameters in Table I. The derivative function [Eq. (4)] is shown in the upper inset, with the value of T_0 indicated by the vertical dotted line. The lower inset displays the difference between the experimental and calculated τ.

TABLE I. Glass-forming liquids whose $\tau(T)$ are governed by both temperature and volume.

	T_g (K)	A	B (K)	C (K)	T_e (K)	T_B (K)	$\lvert\alpha_\tau\rvert/\alpha_P$	E_V/E_P
BMPC	243	−11.43	197	6.64	288	270[a]	0.58[b]	0.39[b]
BMMPC	263	−10.97	285	10.82	314	320[c]	0.72[b]	0.41[b]
salol	220	−10.96	190	5.15	249	265[a]		0.43[d]
KDE	313	−10.87	397	11.5	357	385[c]	0.98[e]	
PDE	249	−10.26	319	6.85	320	325[a]	1.25[f]	0.52[f]
OTP	244	−12.44	296	7.35	276	290[a]		0.55[g]

[a]Reference [17].
[b]Reference [9].
[c]Reference [29].
[d]Reference [8].
[e]Reference [5].
[f]Reference [4].
[g]Reference [7].

equivalent results [30].

Characteristic temperatures T_0 and T_B

As discussed above, when the VF relation [Eq. (1)] is fit to experimental τ, a different set of fitting parameters is required above and below a characteristic temperature, T_B ($>T_g$) [17]. This temperature is a function of pressure, such that $\tau(T_B)$ is constant for a given liquid [18,19]. It is obviously of great interest to understand the fundamental mechanism giving rise to this apparent change in dynamics.

Deviation from the VF equation can be assessed from plots of the derivative function [17]

$$\phi(T)=\left(\frac{-d\log_{10}\tau}{dT}\right)^{-1/2}, \tag{4}$$

wherein the VF behavior appears as a straight line. Although there is no discontinuity in $\tau(T)$ at T_B, the derivative function identifies the presence of the two distinct dynamical ranges. We have included $\phi(T)$ in an inset to Figs. 1–6, with the obtained T_0 denoted by a vertical dotted line. Its correspondence to T_B is evident.

In Fig. 7, the characteristic temperature T_0 is plotted versus T_B, the latter obtained from the literature [17,19,29]. We have also included the T_0 obtained by CG [25] from fitting viscosities for both salol and OTP. [25] There is a good correspondence between the two parameters. Excepting the datum for KDE, we find that $T_0 \approx T_B$.

The identification of T_0 with T_B implies that the change in dynamics, accompanied by changes in various properties [17,19,20,23,24], is a reflection of the high-density percolation of free-volume containing sites; that is, at T_B, each liquidlike molecule (i.e., molecules associated with free volume) is adjacent to at least two other liquidlike molecules. Identification of T_B with the percolation of free-volume clusters is reminiscent of positron PALS experiments showing that the T_B is associated with a change in the temperature dependence of the free-volume hole size [31].

This concept of T_B in terms of free volume naturally implies a pressure dependence, as has been observed [18,19]. Cohen and Grest incorporate the effect of pressure in their

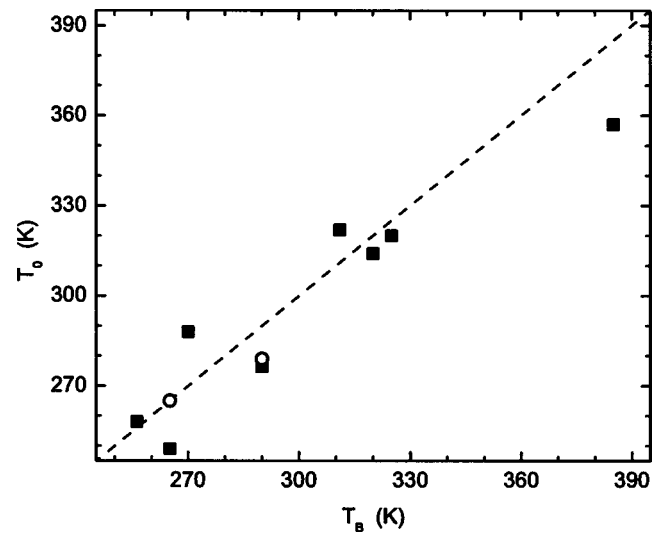

FIG. 7. The characteristic temperature of the CG model obtained from fitting Eq. (3) to the experimental relaxation times of the liquids in Tables I and II (■), plotted vs the temperature at which $\tau(T)$ departs from the lower temperature VF function. The latter values were taken from the literature [17,18,29]. Also shown are the T_0 from fits to viscosity data for salol and OTP (○) [25]. The dashed line represents $T_0=T_B$, which describes the data well, except for the highest point for KDE.

theory by introducing an additional term, proportional to pressure, into their expression for the local free energy [25]. It has been shown that this overpredicts the effect of pressure on the relaxation times [32]. Notwithstanding, herein we examine the proposed relation for the dependence of the percolation temperature on pressure [25],

$$T_0(P)=T_0+KP, \tag{5}$$

where K is a constant. Since the data in Fig. 7 suggest a correspondence between T_0 and T_B, Eq. (5) in effect offers a prediction for the variation of the latter with pressure.

High pressure measurements have been carried out on PDE and two polychlorinated biphenyls, PCB42 and PCB62, having chlorine contents of 42% and 62%, respectively [18,19]. Although the relative contributions from temperature and density to the structural relaxation times of the PCB have not been determined, we expect from their chemical structure that molecular interactions will be primarily of the van der Waals type. Thus, the expectation is that volume plays a significant role, justifying application of the CG model. The $\tau(T)$ reported for atmospheric pressure for PCB42 and PCB62 are displayed in Fig. 8. As can be seen, the data are well described by Eq. (3), with the results summarized in Table II.

High pressure measurements on the PDE and PCB extend to sufficiently high frequencies to allow a determination of the crossover temperature, associated with the change in dynamics. This crossover temperature is a couple of degrees above T_B, when the latter is defined as the temperature at which the data deviate from a low temperature VF fit. In Fig. 9, the crossover temperatures determined for the three liquids are displayed as a function of pressure. The variation devi-

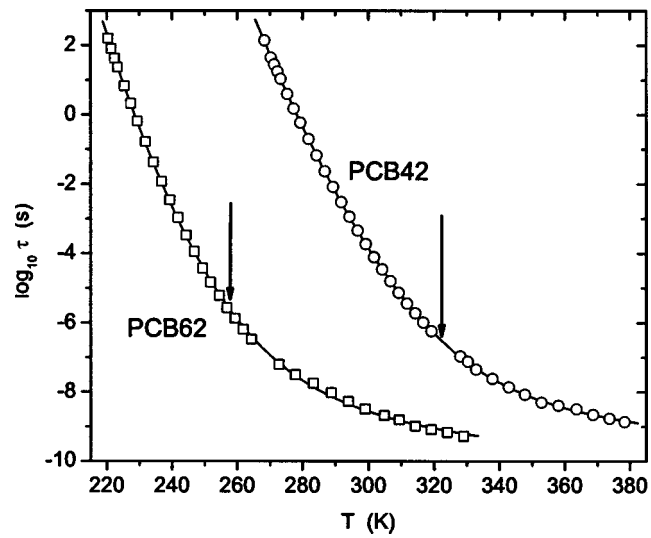

FIG. 8. Dielectric α-relaxation times for polychlorinated biphenyl having 42% chlorine content (○) and 62% chlorine (□), along with the fit of Eq. (3) using the parameters in Table II. The arrows denote the values of T_0.

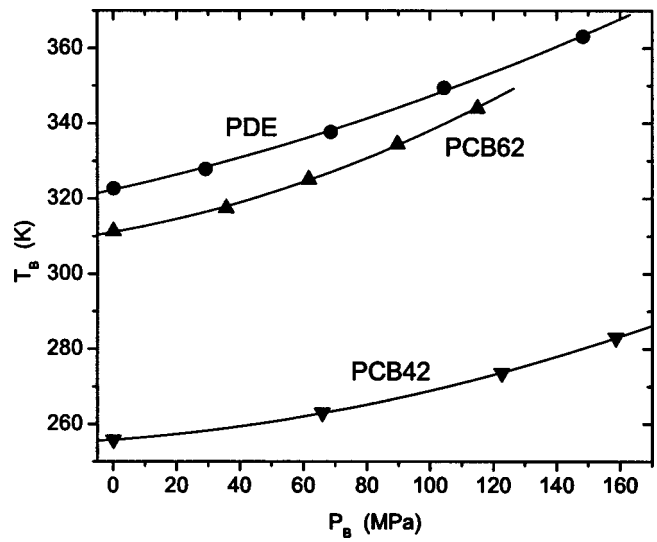

FIG. 9. The temperature associated with the change in dynamics (crossover temperature) for PDE (■), PCB62 (▲), and PCB42 (▼) vs pressure. The data were taken from Ref. [18]. The lines through the data represent second-degree polynomial fits.

ates from the linear relationship predicted by Eq. (5). Note that for both PDE [33] and the polychorinated biphenyls [19], the variation of T_g with pressure is also nonlinear over this range of P.

Fitting the data in Fig. 9 to a second-order polynomial, the linear term (i.e., the pressure dependence of T_B at low pressure) is set equal to the K in Eq. (5). Using the parameters from Eq. (3), the molecular volume, v_m, can then be calculated as [25]

$$v_m = K\frac{2B}{C\ln e}. \tag{6}$$

We obtain $v_m = 563$ Å^3 for PDE, which corresponds to a molecular radius equal to 5.1 Å. For PCB42 and PCB62, $v_m = 122$ and 254 Å^3, respectively, with molecular radii equal to 3.1 and 3.9 Å.

Free volume

The mean free volume per liquidlike molecule in the CG model is given by [25]

$$v_f = \frac{v_m \ln(e)}{B}\{T - T_0 + [(T-T_0)^2 + CT]^{1/2}\}, \tag{7}$$

TABLE II. Results for polychlorinated biphenyls.

	M_w (g/mol)	T_g (K)	A	B (K)	C (K)	T_e (K)	T_B (K)	r (A)
PCB42	258	221	−10.44	193	6.22	258	256[a]	3.1
PCB62	396	269	−9.91	137	5.07	322	311[a]	3.9

[a]Reference [19].

enabling its calculation using the fitting parameters of Eq. (3) to $\tau(T)$ data [34]. The total free volume of a liquid can be obtained from experimental pressure-volume-temperature (PVT) data, using an equation of state derived from a lattice model. The Simha-Somcynsky (SS) lattice model [35], originally developed for polymers, places each molecule in a cell. Lattice imperfections give rise to empty cells, constituting the free volume. For atmospheric pressure, the SS equation of state is [36]

$$\overline{T} = \frac{2y}{(y\overline{V})^2[1-2^{-1/6}y(y\overline{V})^{-1/3}]\left[1.2045 - \frac{1.011}{(y\overline{V})^2}\right]}, \tag{8}$$

where y is the fraction of lattice cells containing molecules, and thus $1-y$ is the fractional free volume. The reduced variables are defined as ratios of the experimental quantities to constants characteristic of the particular fluid, $\overline{V} \equiv V/V^*$ and $\overline{T} \equiv T/T^*$, where V is the molar volume.

Published PVT data for BMPC and BMMPC [9] were fit to Eq. (8). The total free volume per molecule, v_0, is then obtained as the product of $(1-y)V$. Results are shown in Fig. 10 for BMPC and in Fig. 11 for BMMPC. These are the two glass formers in Table I for which density is most dominant relative to the effect of temperature. Included in these figures are the v_f calculated from Eq. (7) using the parameters obtained from fitting the $\tau(T)$ data (Table I). For the occupied cell volume in Eq. (7), we use the molar volume at the temperature for which the free volume goes to zero ($y=1$); that is, when $v_0 = 0$, $V = v_m$. According to a free-volume derivation of Eq. (1), this occurs at T_V [15]. For both BMPC and BMMPC, $v_0 = 0$ at roughly 100° below T_g. This result of the SS model, that the free volume becomes negli-

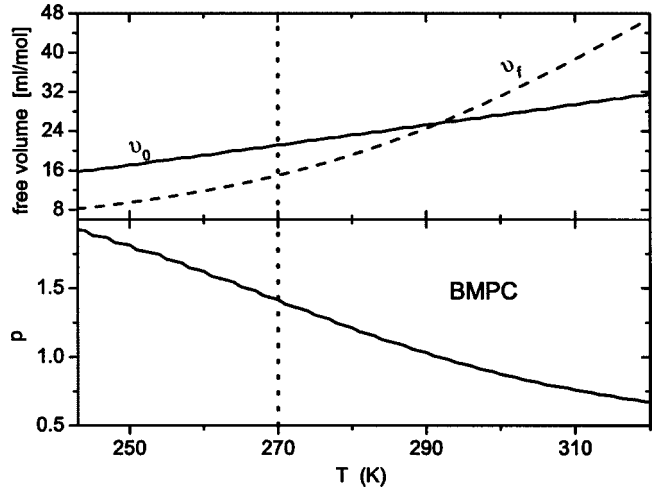

FIG. 10. The free volume per mole of liquidlike molecules (dashed line) calculated from the fits of Eq. (3) to the experimental $\tau(T)$, and the free volume per mole of all molecules (solid line) calculated from fits of Eq. (8) to PVT data for BMPC. The lower panel shows the fraction of molecules which are liquidlike (i.e., have free volume), as calculated from the ratio of υ_m/υ_f. The data are for $T>T_g$, with T_B indicated by the vertical dotted line.

gible above absolute zero, differs from the CG model, wherein an absence of free volume is only attained at 0 K.

It can be seen in Figs. 10 and 11, that at high temperatures, υ_f varies in proportion to $T-T_0$ and, as pointed out by Cohen and Grest [25], there is no distinctive aspect of the free-volume data at $T=T_0$. More significant, however, is the fact that the change in υ_f with temperature is greater than the change in υ_0. This means that the ratio, $p\equiv\upsilon_0/\upsilon_f$, equal to the fraction of liquidlike molecules [25], decreases with increasing temperature, as shown in Figs. 10 and 11. Such a

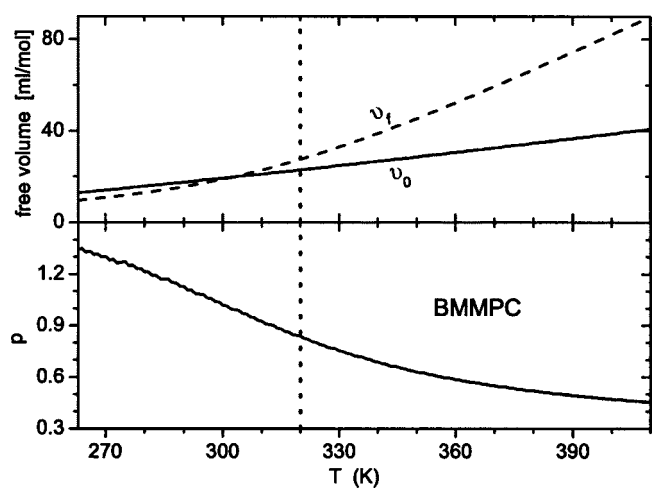

FIG. 11. The free volume per mole of liquidlike molecules (dashed line) calculated from the fits of Eq. (3) to the experimental $\tau(T)$, and the free volume per mole of all molecules (solid line) calculated from fits of Eq. (8) to PVT data for BMMPC. The lower panel shows the fraction of liquidlike molecules, calculated as υ_m/υ_f. The data are for $T>T_g$, with T_B indicated by the vertical dotted line.

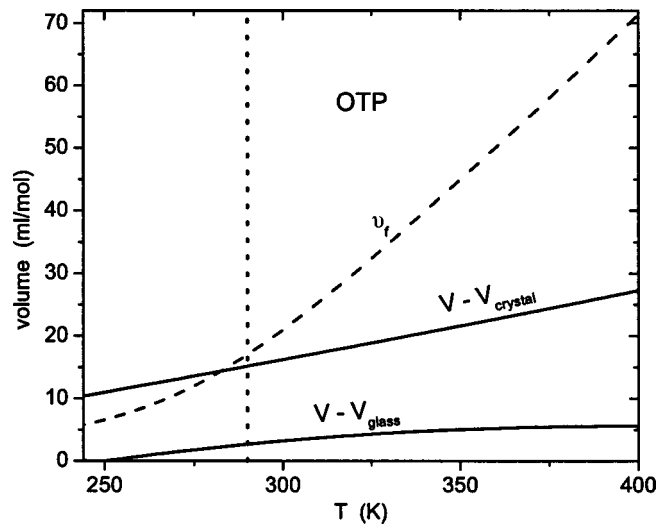

FIG. 12. The free volume per mole of liquidlike molecules (dashed line) calculated from the fits of Eq. (3) to the experimental $\tau(T)$ for OTP, along with the free volume estimated as the difference in the molar volume and the crystal volume (upper solid curve) and the difference in the molar volume and the extrapolated glassy volume (lower solid curve). The data are for $T>T_g$, with T_B indicated by the vertical dotted line.

result is unphysical, and at odds with a basic premise of the CG model.

It can also be seen that $p>1$ at lower temperatures, which of course is not possible. However, the magnitude of p (but not the sign of its temperature dependence) depends on the value assumed for υ_m, which is a constant in the CG theory. In a precursor to the CG model, Turnbull and Cohen [37] allowed the occupied cell volume to vary with temperature; that is, they introduced some ''softness'' into the molecular core. A υ_m which decreases with increasing temperature is plausible, and moreover, would enable adjustment of the $p(T)$ result in Figs. 10 and 11 to yield consistency with PVT measurements. We eschew this approach herein in order to maintain fidelity with the CG model.

To examine whether the anomalous results of Figs. 10 and 11 are a consequence of using the SS lattice model to calculate the total free volume, we can estimate υ_0 as the difference between the molar volume of the liquid and the volume of the glass extrapolated above T_g [14]. Since the PVT data for BMPC and BMMPC do not extend down to the glassy state, we do this for OTP, using published PVT results [38]. The results are shown in Fig. 12, along with the υ_f calculated from Eq. (7) using the parameters in Table I. Clearly, the dependence of υ_f on T is much steeper than that of υ_0; hence, the unphysical result that p decreases with increasing temperature remains. Alternatively, we can calculate υ_0 as the difference between the liquid and crystalline states of OTP. This yields a larger value for the total free volume, but does not change the sign of dp/dT (Fig. 12).

SUMMARY

The CG equation can describe structural relaxation times over broader ranges of temperature than the more common

Vogel-Fulcher relation, and requires fewer adjustable parameters if $\tau(T)$ spanning T_B are analyzed. From the fact that T_0 of the CG model corresponds to the crossover temperature associated with myriad property changes [17–24], it is tempting to identify the change in dynamics as reflecting the threshold for dense percolation of the free volume. According to the CG model, free-volume fluctuations below T_0 entail an energy expenditure, which inhibits molecular rearrangements. However, molecular diffusion and reorientation are not frozen ($T_0 > T_g$), although energy barriers begin to exert a role below T_0. Conceptually, this result accords with the data in Table I showing that thermal energy does contribute to the structural relaxation times of the van der Waals liquids studied herein; that is, $|\alpha_\tau|/\alpha_P$ and E_V/E_P are greater than zero. Since temperature cannot be neglected, modification of the CG model to include explicitly temperature-dependent parameters [39,40] is necessary for a more general description of the supercooled dynamics. Mode coupling theory (MCT) [21] identifies the glass transition as occurring well above the observed T_g, if not for the intervention of activated processes [22]. However, unlike the CG model, MCT offers no prediction for τ over the range encompassing the crossover temperature.

The predicted effect of pressure on T_0 ($\approx T_B$) is in accord with the limited available experimental results, even though previous work has shown that the CG prediction for the variation of τ with pressure is incorrect [32]. Notwithstanding the utility of the CG model in parametrizing relaxation data and identifying the crossover temperature, the deduced parameters yield unphysical results. Specifically, the basic idea underlying the model, that the concentration of liquid-like molecules increases with temperature, giving rise to enhanced fluidity of the supercooled liquid, is contradicted by the free volume calculated using the model parameters obtained from fitting $\tau(T)$ data.

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