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Fitting of viscosity: Distinguishing the temperature dependences predicted by various models of supercooled liquids

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In an effort to assess the applicability of various competing theoretical models, we have examined the temperature dependence of the viscosity $\eta(T)$ and of the α-relaxation times of a wide variety of supercooled liquids. The overall best fits over the entire temperature range above the glass-transition temperature and for all the diverse supercooled liquids investigated are given by the expression $T\ln[\eta(T)/\eta_\infty]=E_\infty+BT^*[(T^*-T)/T^*]^{8/3}\Theta(T^*-T)$, where $\Theta(T^*-T)$ is a step function that is 1 for $T<T^*$ and 0 for $T>T^*$, and T^* is usually greater than the melting point temperature. Our analysis supports the notion that there is a single dominant species-independent, nonmolecular mechanism underlying α relaxation for all supercooled liquids, throughout the entire T-range characteristic of supercooled liquids.

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INTRODUCTION

The salient feature characterizing a supercooled liquid is the dramatic increase of viscosity (η) with decreasing temperature, an increase which may encompass 15 orders of magnitude over a temperature range of perhaps 150 K. Structural relaxation times (the so-called α-relaxation times) are more or less proportional to the viscosity, and so also increase rapidly with decreasing temperature [1]. Below a temperature T_g, called the glass-transition temperature, the relaxation times are so long that in most experiments equilibrium cannot be attained, and the system is said to be a glass rather than a supercooled liquid. Although T_g does not represent a true phase transition, but rather a dynamical crossover, the properties of nonequilibrated glasses are quite different than those of quasiequilibrated supercooled liquids. (We say quasiequilibrated because below the melting point the crystal is presumably the thermodynamically stable phase.)

At the heart of most theories of supercooled liquids is a description of the temperature dependence of the viscosity and the α-relaxation times. In fact, the description one gives for these quantities predetermines the nature of the theory one chooses, or, conversely, the theory determines the manner in which one analyzes the data. Here we shall examine in some detail the relationship between fitting forms and theories, and shall consider the feasibility of using these studies to discriminate among theories. Although in our discussion we focus on viscosity, the α-relaxation time, which can be determined through properties such as dielectric relaxation, can also be treated in the same way; in fact, some of the data used in Figs. 1 and 4 were obtained by relaxation measurements. See Table I. Previous studies of the kind reported here were carried out by Rössler [2] and by Stickel, Fischer, and Richert [3].

STRATEGY

(1) *What to plot?* We are interested in the temperature dependence of the coefficient of shear viscosity η. Plot-

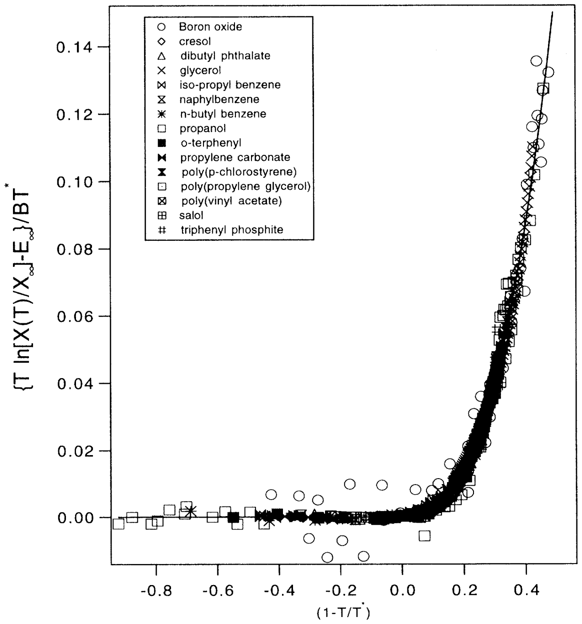

FIG. 1. Scaled viscosity or α-relaxation activation energy vs $[(T^*-T)/T^*]$ for all liquids indicated in Table I. $X=\eta$ or τ. Parameters given in Table I are determined by means of Eqs. (1), (7a), and (7b). The line is the fit of Eqs. (7a) and (7b).

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ting η versus T is not useful, since η may change by as much as 15 orders of magnitude over a 150-K temperature range. One is, therefore, more interested in the T dependence of $\ln[\eta]$, even though, or rather because, it is a far less sensitive measure of the correspondence between fitting formulas and experiment. Because of this, η is often expressed in terms of a T-dependent activation energy, $E(T)$, according to

$$\ln[\eta(T)]=\ln[\eta_\infty]+E(T)/T\ , \tag{1}$$

where η_∞ is a T-independent but species-dependent parameter. Plots of $\ln[\eta]$ versus T, or versus T^{-1}, are also frequently given. We believe that the most insightful plots are not the customary $\ln[\eta/\eta_\infty]$-versus-T plots, but $T\ln[\eta/\eta_\infty]$-versus-T, i.e., $E(T)$-versus-T plots.

The most noticeable feature of many supercooled liquids is the fact that the activation energy $E(T)$ is very temperature dependent, increasing appreciably as the temperature is lowered toward T_g. This is clearly seen in Fig. 1. It is, of course, a fact that merely an appreciable increase in $E(T)$ can account for the observed stupendous increase in $\eta(T)$.

TABLE I. Material parameters and fits to Eqs. (7a) and (7b).

	B	T^* (K)	E_∞ (10^3 K)	T_{melt} (K)
n-butyl benzene[a,b]	282	198	1.43	185
triphenyl phosphite[c]	180	311	2.35	295
isopropyl benzene[a,b]	180	210	1.72	174
propylene carbonate[d]	280	235	2.12	218
salol[e]	394	304	3.22	318
dibutyl phthalate[a,b]	148	288	3.31	238
o-terphenyl[f,g]	412	350	3.15	331
s-trinaphthyl benzene[f]	288	515	5.07	472
n-propanol[b]	56.1	192	2.22	147
α-phenyl-cresol[f]	440	293	6.09	327
glycerol[h]	88.7	322	5.18	293
boron oxide[i]	63.4	978	10.5	723
poly(p-chlorostyrene)[j]	454	544	6.08	
poly(propylene-glycol)[j]	558	265	4.52	
poly(vinyl acetate)[j]	282	454	2.76	

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Analyses in terms of $d\ln[\eta]/dT$, and even $d^2\ln[\eta]/dT^2$, have been carried out by Stickel, Fischer, and Richert [3]. These analyses (although very uncertain in the vicinity of and above the melting temperature T_m) require fewer adjustable parameters and provide a more challenging test for the various fitting formulas and theories; too challenging, we believe. Most of the theories and fitting formulas are designed to describe the leading temperature behavior of the viscosity, and the requirement that they also describe the derivatives properly is a heavy one, one that goes beyond the design of the various proposed descriptions. We believe that the behavior of $E(T)$ is commensurate with the design of the descriptions, and so it is this quantity that we study. To clarify the point made here, suppose that the "exact" viscosity were $\eta=aT^x\exp[E/T]$, where a, x, and E are constants. So long as $|x|<1$, we would be content, at our current level of understanding, with a "theory" that described η by an Arrhenius function, i.e., $x=0$. However, if, as in Ref. [3], we tested for Arrhenius behavior by plotting $d(T^2d\ln[\eta]/dT)/dT$, which would be 0 for Arrhenius behavior, we would find that it was equal to x, and we might therefore conclude, unconstructively, that our "theory" was poor.

(2) *Parameter count.* Counting of adjustable parameters is not always a trivial task. Temperature- and species-dependent parameters are adjustable for each T, and each species. Although such parameters are used in the universal susceptibility fits of Dixon *et al.* [4], in studies of viscosity one does not usually encounter such parameters because the fitting formulas explicitly address the problem of the T dependence. T-independent, but species-dependent parameters must be adjusted for each substance. Cutoff temperatures enter as adjustable parameters, be they high-T or low-T cutoffs or both. Where a species-dependent crossover temperature T_{co} is introduced to separate two regimes of qualitatively different behavior, T_{co} must be counted as a parameter. (This crossover temperature appears as an upper or lower cutoff temperature for the fits in each individual region.) Finally, there are the universal dimensionless constants, which ideally should be given by theory, but even when obtained by empirical adjustment they contribute little to the parameter count if the analysis involves many different substances.

(3) *Corresponding states.* By corresponding states we mean that relevant quantities [for all substances, at all temperatures, frequencies (ω) and times] can be scaled in terms of a small number of adjustable parameters and placed on a single, nontrivial master curve. Figure 1 is such a curve for the T dependence of $E(T)$, and Dixon *et al.* [4] have obtained such a curve for the imaginary part of the dielectric susceptibility $\varepsilon''(T,\omega)$. The search for corresponding states may come at the cost of small deviations due to specific molecular behavior. An important goal in the present case is that the description should apply to all supercooled liquids: network (strong), molecular (fragile), hydrogen-bonded, and polymeric liquids.

(4) *Physical implications of fits.* If a fitting formula incorporates a temperature T_0 at which properties diverge, there is an implicit assumption that there is a phase transition at that temperature. If a fitting formula changes character at a temperature T^*, there is an implication of a crossover of dominant relaxation mechanisms. Such implications should be subject to independent tests.

(5) *Occam's razor or the principle of parsimony.* We proceed with the principle that all things being equal, the most compelling fits to the viscosity and relaxation times are as follows.

(i) Those with as few adjustable parameters as possible, i.e., those that exhibit the best corresponding states.

(ii) Those with as few phase changes and crossovers as possible, e.g., with as few divergences and discontinuities (even in the derivatives) as possible, unless these can be independently and thermodynamically established.

(iii) Those with as few novel and specific aspects as possible, i.e., those that remain as simple as possible unless the complicating features are independently substantiated.

Except for the rapid increase in η and relaxation times as T decreases toward T_g, the behavior of supercooled liquids as functions of T (and even of ω), though distinctive, is devoid of sharp features; as a consequence, theories based on phase changes and the crossover of dominant mechanisms are difficult to confirm. Nevertheless, a careful analysis of the data can cast light on the subject, even though a definitive determination of whether there is a phase transition at temperatures below T_g, or a crossover point between T_g and the melting temperature T_m, must await a convincing theory. The master curve in Fig. 1 does not require that there be a low temperature (T_0) phase transition. It suggests that there need not be a change in relaxation mechanism between T_g and T_m. This last conclusion is also reached by examining the susceptibility scaling curve of Dixon *et al.*; their master curve fits the data at all temperatures between T_g and the melting temperature.

Despite this implied continuity of mechanism, most of the fitting formulas and theoretically inspired expressions that have been used to describe the temperature dependence of the viscosity data have been applied successfully only over a limited part of the supercooled-liquid temperature range, the implication being that there is a change of dominant structural relaxation mechanism. We count this as an argument against most of these fitting expressions.

ACTIVATION ENERGY AND THE ARRHENIUS FUNCTION

If the activation energy in Eq. (1) is taken as a species-specific, T-independent constant, $E(T)=E_\infty$, the expression is then that of Arrhenius. A glance at the scaled data in Fig. 1 and that obtained from orthoterphenyl (OTP) data [6,7] in Fig. 2 indicates that an Arrhenius expression describes the viscosity and relaxation time well at temperatures above a cutoff temperature $T_{\rm co}$, which is usually above the melting temperature T_m. A fit to just this high-T data contains the adjustable species-dependent parameters, η_∞ and E_∞, as well as the lower cutoff temperature $T_{\rm co}$, which for OTP is about 350 K.

Alternatively, one might attempt to fit an Arrhenius expression to the low-temperature data below a high-T cutoff, $T_{\rm co}$ [7]. However, care must be exercised in analyzing a fitting formula with a particular choice of effective activation energy $E_0(T)$ that is restricted to use below a cutoff temperature:

$$\eta(T)=\eta_0\exp[E_0(T)/T]\ , \quad T<T_{\rm co}\ , \tag{2a}$$

where η_0 is independent of T. In this case, η_0 need not equal η_∞, and in the limit $T\to\infty$ the activation energy $E_0(T)$ need not go to E_∞, so that $E_0(T)$ usually differs from the $E(T)$ in Eq. (1), as indicated by the relation

$$E(T)=E_0(T)+T\ln[\eta_0/\eta_\infty]\ , \quad T<T_{\rm co}\ . \tag{2b}$$

Of course, such a fit cannot describe data over the entire temperature range. The $E(T)$ resulting from a low-T Arrhenius fit, i.e., one with constant $E_0(T)$, is shown for

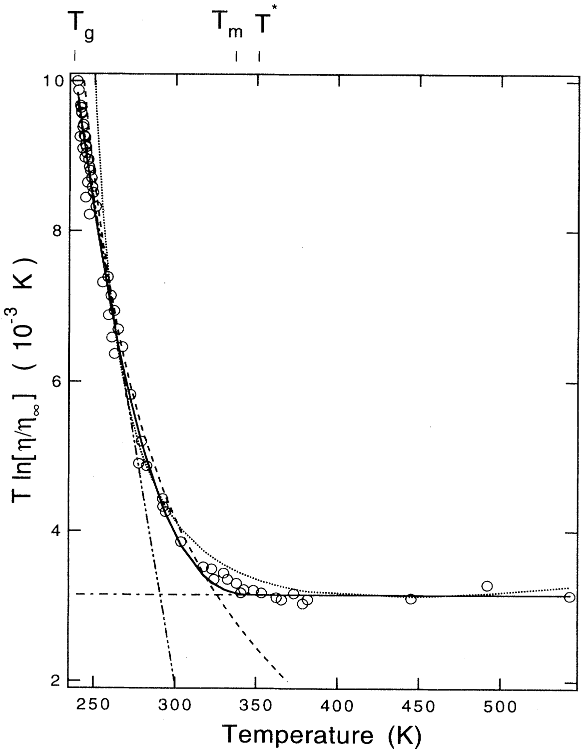

FIG. 2. Viscosity activation energy $E(T)$ for orthoterphenyl vs T. See Eqs. (1), (2a), and (2b). $\eta_\infty=1.03\times10^{-5}$ P and $E_\infty=3150$ K. ○, experimental points [6,7] [Eq. (1)]. ——, frustration-limited domains [Eqs. (7a) and (7b)]. See Table I. —·—·—·, high-T Arrhenius: $E(T)=E_\infty$; $\eta_0=\eta_\infty$. ----, low-T Arrhenius: $E(T)=E_0+T\ln[\eta_0/\eta_\infty]$. · · · ·, high-$T$ VFT: $D=2.98$, $T_0=231$ K, and $\eta_0=4.65\times10^{-4}$ P. Fitted between 257 and 523 K [7]. — — —, low-T VFT: $D=10.4$, $T_0=200$ K, and $\eta_0=1.1\times10^{-8}$ P. Fitted between 243 and 293 K [7].

OTP in Fig. 2; the cutoff temperature is in the vicinity of 275 K, well below the melting temperature $T_m = 331$ K. This fit depends upon the three parameters $\{\eta_0, E_0, T_{co}\}$, and additional parameters are required to fit the data above T_{co}.

VOGEL-FULCHER-TAMMANN

One method of describing the temperature-dependent activation energy is by means of a generalized Vogel-Fulcher-Tammann expression

$$E_{\mathrm{VFT}}(T) = DT[T_0/(T-T_0)]^x , \tag{3}$$

where D, T_0, and x are temperature-independent constants. D and T_0 are species dependent, whereas x is assumed to be universal. Although it is by no means clear what exponent x gives the best fit [8], for simplicity in the face of the fact that this expression gives only modestly good fits regardless of the value of x, one normally chooses $x=1$. Thus what is often used is the simple Vogel-Fulcher-Tammann (VFT) equation [1]

$$E_{\mathrm{VFT}}(T) = DT[T_0/(T-T_0)] . \tag{4}$$

The use of Eq. (3) or (4) implies much about one's view of supercooled liquids. In particular, it implies a divergence, and hence a phase change at T_0. A phase change to what? Although its structure is usually not specified, the resultant phase is sometimes called an ideal glass. The ideal-glass phase-transition temperature T_0, also called the VFT temperature, lies well below T_g, and so it is dynamically inaccessible. By this one means that if the temperature is lowered to T_0, the system will have been nonequilibrated from T_g downward. Because of the very rapid increase of η with decreasing T, it is not unreasonable to fit the data to Eq. (4), but such a divergence is not required because a rather modest, nondiverging increase in $E(T)$ can account for the observed rapid increase in $\eta(T)$. The parameter D is sometimes called the fragility constant: liquids with small values of D, under about 12, are called fragile, while those with large values, above 20, are called strong. The former are often molecular glass formers, whereas the latter are often network systems [1].

Although it can be rationalized in terms of a number of models, including a free-volume approach [9], there is at present no generally accepted theory that yields the VFT equation. But the postulate that there is a divergence at (or near) T_0, and consequently a phase transition is supported by the observed temperature dependence of the entropy of melting, ΔS_{melt}. This quantity decreases quite markedly as the temperature is lowered below the melting point, being reduced at T_g to about 20% of its value at the melting point [1]. Furthermore, an extrapolation of the data to temperatures below T_g suggests that the entropy of melting vanishes at a temperature (the Kauzmann temperature) in the vicinity of T_0 [1]. It has been thought, quite reasonably, that the correspondence of this thermodynamic divergence, i.e., of $\Delta S_{\mathrm{melt}}^{-1}$, together with the dynamic VFT divergence, i.e., of η, argued for a low-temperature phase change near T_0. But no critical theory built about this low temperature critical point has been fully successful [10–12]. Not only do conventional critical theories predict less dramatic increases than observed in $\eta(T)$, they predict diverging correlation lengths and corresponding divergences in the order parameter susceptibility and in associated thermodynamic quantities, none of which have been observed. In fact, no rapidly increasing correlation length has been unambiguously distinguished [13]. However, recently Menon and Nagel [14] have presented an analysis that leads to a divergence near T_0 in the dielectric constant (a nondynamic, structural quantity), provided one assumes a corresponding divergence (such as that given by the VFT expression) in the α-relaxation time.

Use of the VFT equation involves an activation energy given by the expression in Eq. (2b), with $E_0(T)$ given by the expression in Eq. (4). The VFT equation has been fitted separately to both the high- and low-T viscosity data [15]. Fits to the data below an upper cutoff T_{co} depends upon the four adjustable parameters $\{\eta_0, D, T_0,$ and a high-T cutoff temperature $T_{co}\}$, and it yields T_0's that are comparable to the Kauzmann temperatures. The fit of this low-T VFT activation energy $E(T)$ for OTP, with the parameters given in Ref. [7], is shown in Fig. 2. The fit below the cutoff $T_{co} = 293$ K is quite good, but, of course, in this case it requires the four adjustable parameters $\{\eta_0, D, T_0, T_{co}\}$ just to describe the data at temperatures below T_{co}. To fit the high-T data above T_{co}, one would need additional parameters.

The VFT fits to the high-T data also depend upon the four adjustable parameters $\{\eta_0, D, T_0, T_{co}\}$, where T_{co} is now a low-T cutoff temperature. (Note that $\eta_0 \neq \eta_\infty$.) The results for OTP, obtained with the parameters given in Ref. [7], are shown in Fig. 2; the cutoff temperature used [5] in the fits is 257 K, but even the fits above this temperature are, at best, only fair.

T^{-z} ACTIVATION ENERGY

Fits with Eq. (2a) and $E_0(T)$ given by

$$E_0(T) = A/T^z , \quad T < T_{co} , \tag{5}$$

where A is a species-specific parameter and z a universal exponent, have also been attempted [16–19]. No critical divergence at any nonzero temperature is implied in this expression. In particular, Bässler [18] investigated the fits with $z=1$. He obtained good fits for the viscosity data above about 10^4 P; this implies an upper-cutoff temperature T_{co}, which for OTP is about 275 K. Furthermore, he set $A = (CT_g)^2$ and $\eta_0 = \eta_g \exp(-C^2)$, where η_g is the measured viscosity at the glass temperature T_g. Thus, in addition to the cutoff temperature T_{co} above which this formula does not work, one can make use of either C and T_g, or of η_0 and A, as the adjustable parameters. Bässler found that the C's were fairly constant for classes of liquids, i.e., fragile and strong, but we nevertheless believe it must be taken as an adjustable parameter.

We have used the parameters given in Ref. 2 to construct an $E(T)$-versus-T-curve for the Bässler model for OTP; see Fig. 3. Besides the fact that this formula has a theoretical basis, it is interesting because it gives reasonable fits at T's below 275 K with only the three species-specific adjustable parameters, $\{A, \eta_0, T_{co}\}$. However, to fit the data at T's above T_{co}, more parameters are needed, at least two if one requires that the temperature derivative of $\eta(T)$ be continuous at T_{co}. Note that in Fig. 3 we present $E(T)$, not $E_0(T)$.

A scaling procedure that is similar to that of Bässler, but that does not depend on a particular fitting form, is that proposed by Rössler [2]. In this approach, $\ln[\eta]$ for a group of fragile liquids is plotted versus T/T_r, where T_r is an adjusted glass transition temperature, adjusted for each substance so as to obtain the best single-curve representation of all the liquids for viscosities in excess of 10^3 P. To the extent that such a single curve represents the data, the procedure is equivalent to a fit with two adjustable and one or more universal parameters (e.g., Bässler's adjustable T_g and T_{co}, and his "universal" C and z); of course, if one includes nonfragile liquids in the study, then the single-curve scaling no longer holds (e.g., Bässler's parameter C is no longer universal). For viscosities below 10^3 P, this scaling procedure breaks down, and more adjustable parameters are needed.

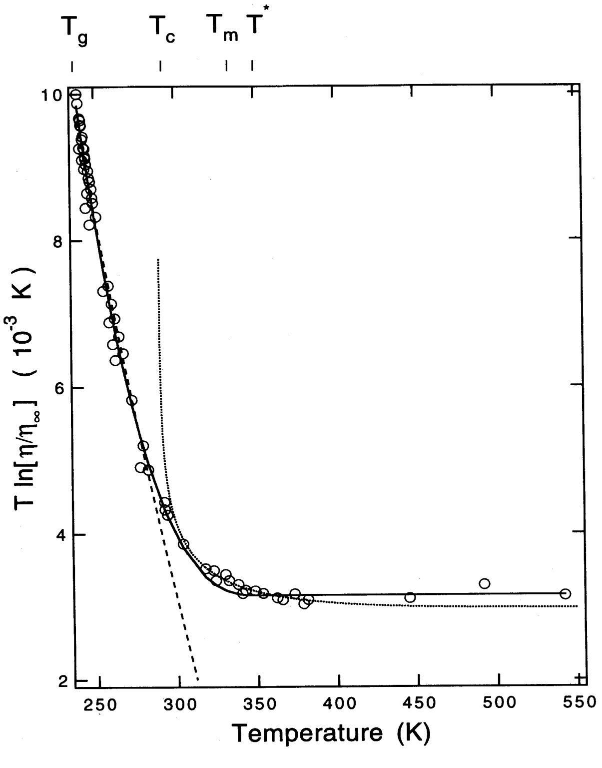

FIG. 3. Viscosity activation energy $E(T)$ for orthoterphenyl vs T. See Eqs. (1), (2a), and (2b). $\eta_\infty = 1.03 \times 10^{-5}$ P and $E_\infty = 3150$ K. ○, experimental points [6,7] [Eq. (1)]. ——, frustration-limited domains [Eqs. (7a) and (7b)]. See Table I. · · · ·, MCT power law [Eq. (6)]: $E(T) = T\{-\gamma \ln[(T-T_c)/T_c] + \ln[\eta_c/\eta_\infty]\}$, where $T_c = 290$ K, $\gamma = 2.55$, and $\eta_0 = 1.74 \times 10^{-3}$ P [29]. — — —, Bässler model: $E(T) = T\{\ln[\eta_0/\eta_\infty] + AT^{-2}\}$, with $\ln[\eta_0] = -53.8$ and $A = 4.73 \times 10^6$ K^2 [2].

POWER-LAW FITS

Since ordinary critical theories tend to yield power-law divergences, one might also try to fit the viscosity to a power law:

$$\eta(T) = \eta_c[(T-T_c)/T_c]^{-\gamma}, \quad T > T_c, \tag{6}$$

where η_c and T_c are species-dependent, temperature-independent parameters, and $\gamma > 0$ may or may not be species dependent. It has been reported that better fits to the viscosity data in a low-temperature range (but still above T_g) can be obtained with Eq. (6) than with the VFT formula, but the exponent γ takes on values of about 11 or 12 [20]. Such large exponents are not compatible with ordinary critical theories. Although the T_c's so obtained are not equal to the T_0's of VFT fits, they are also below T_g.

A different outlook on supercooled liquids is given by mode-coupling theories (MCT). These are dynamical (rather than the usual thermodynamic) critical theories, and in their extended form they are built about an avoided dynamic critical point T_c. In common with usual thermodynamic critical theories, the MCT predicts power-law divergences with rather modest exponents γ. Because, as explained above, fits to Eq. (6) for data near T_g yield very large values of the exponent γ, early versions [21] of the MCT, which associated T_c with a temperature at or below T_g, were discarded. However, more recently, Götze [22] has suggested that the dynamical critical temperature should not be associated with a temperature as low or lower than T_g, but with a temperature T_c that lies below the melting point T_m, but well above T_g. Well above such a T_c, one can fit the data to Eq. (6) with an exponent γ between 2 and 3, as is suggested by MCT at its simplest level. This fit requires four parameters: γ, T_c, η_c and a low-T cutoff temperature T_{co}, which lies above T_c and below which the fit is clearly poor [23]. Thus, from a purely fitting point of view, this expression does little, particularly since it excludes from consideration the most rapidly varying $\eta(T)$ data at temperatures below T_{co}. But to the extent that the theory can yield independent or interdependent values of γ and T_c, Eq. (6) remains interesting. Values of MCT fits of $E(T)$ for OTP are given in Fig. 3.

Of course, it is clear that η does not actually diverge at an intermediate temperature T_c, and an extended MCT introduces hopping mechanisms which lead to an avoidance of the critical point at T_c [22,24]. Near and below T_c, where the collective α modes relax very slowly, hopping is thought to compete effectively with the collective modes. Thus, although the simple theory predicts a critical divergence in η as one approaches T_c from above, the extended theory allows hopping to take over at temperatures somewhat above T_c, and allows it to keep both the relaxation time and η finite at and below T_c. Although there is no theory for the hopping motions, the characteristic relaxation times are generally thought to vary as an Arrhenius function, $\eta_0 \exp[E_0/T]$ [24]. The total picture is then equivalent to describing the intermediate-T regime ($T_m > T > T_c$) by the MCT curve

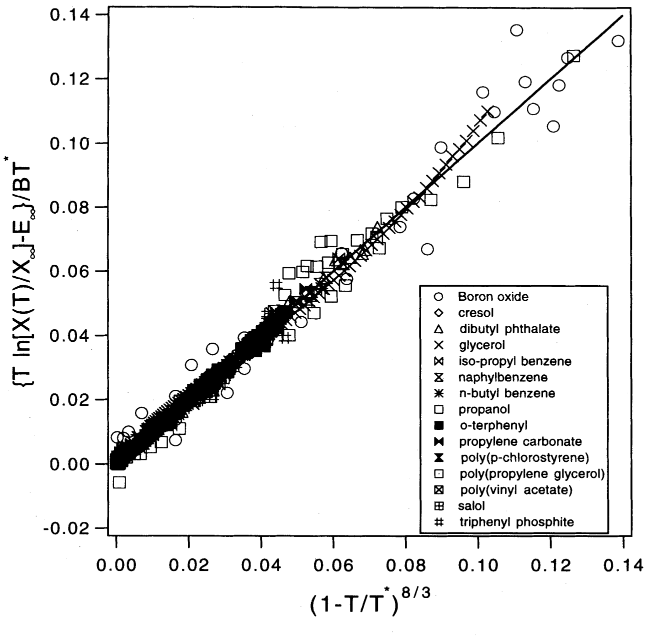

FIG. 4. Scaled viscosity or α-relaxation activation energy vs $[(T^*-T)/T^*]^{8/3}$ for all liquids indicated in Table I. $X=\eta$ or τ. Parameters given in Table I are determined by means of Eqs. (1), (7a), and (7b). See Fig. 1 for symbols. The line is the fit of Eqs. (7a) and (7b).

in Fig. 3 and the low-T regime ($T<T_c$) by the low-T Arrhenius curve in Fig. 2. Thus, in addition to the parameters needed to fit Eq. (6) in the temperature regime well above T_c, at least two extra parameters are needed to extend the fits down to T_g, even if one excludes from consideration the crossover temperature regime in the vicinity of the avoided critical point T_c, and the behavior for $T>T_m$.

MCT fits suggest a change in relaxation mechanism as reflected in power-law T dependence above and Arrhenius dependence below a T_c that lies between the melting point and T_g; such changeover behavior has been reported [2,7,24], but the smoothly varying, strongly temperature-dependent, experimentally determined activation energies, reported in Figs. 1–4, argue for a different interpretation. Other analyses [25] of data also argue against a change in relaxation behavior at a temperature between T_m and T_g.

FRUSTRATION-LIMITED DOMAINS

A rather different fitting formula, which does not imply a low-temperature divergence, has been presented in which the activation energy has the form [5,26,27]

$$E(T)=E_\infty+T^*B[(T^*-T)/T^*]^y\Theta(T^*-T)\ , \quad (7a)$$

where $\Theta(T^*-T)$ is a step function which is 1 for $T<T^*$ and 0 for $T>T^*$. E_∞, B, and T^* are species dependent, but temperature-independent parameters, and y is a universal exponent which seems, both empirically and theoretically, to be

$$y\approx\tfrac{8}{3}\ . \quad (7b)$$

This formula fits the data well over the entire measured temperature range. See Figs. 1 and 4 and Table I. It leads one to a very different picture than do the fitting formulas discussed above, one in which an appreciable increase in $E(T)$ occurs as T is lowered, along with a corresponding dramatic increase in $\eta(T)$, but in which there are no divergences.

So one turns to a very different theory if one accepts the fits in Eqs. (7a) and (7b) than if one accepts the fits with the other equations given above. A theory that focuses on self-forming frustration-limited domains (without the imposition of quenched disorder), and on an avoided high-temperature critical point T^* (in contrast to the low-T critical points associated with the other formulas) has recently been presented [27]; in this theory T^* represents not the ultimate congestion, as do the critical points in the other theories, but the temperature below which collective motions begin to play a role. Below T^* this approach, supported by the success of Eqs. (7a) and (7b) in fitting the data, as well as by statistical mechanical model calculations, suggests a single dominant structural relaxation mechanism all the way from T^* down to T_g. The theory also suggests that $T^*\geq T_m$ [5,27]. See Table I.

Fits to the data with Eqs. (7a) and (7b) can be made over the entire measured temperature range. These fits involve the four species-dependent parameters $\{\eta_\infty, E_\infty, B, T^*\}$, and the universal parameter $y=\frac{8}{3}$ which we shall take as given. In those liquids (such as o-terphenyl depicted in Figs. 2 and 3), for which data are available over a wide temperature range from well above the melting temperature down to T_g, one can fit the two parameters η_∞ and E_∞ by using only data at temperatures well above T^*, and once these parameters are determined one can fit B and T^* to the low-temperature data; this is equivalent to fitting two parameters in each of two independent experiments. Unfortunately, for many liquids the temperature range of available data is somewhat limited, and all four parameters must be evaluated simultaneously.

In examining the fits of Eqs. (7a) and (7b) we can also take a different point of view by trying to establish the value of y empirically. We have done the latter by fitting the available data for 14 liquids with different values of the parameter y. Fits with $y=3$ were given in Ref. [5], and fits with $y=\frac{8}{3}$ were given in Ref. [27] and in Figs. 1 and 4 and Table I of this article. We have also made fits with other nearby values of y. The fits are not very sensitive to the value of y, provided y is in the range $\frac{7}{3}$ to 3, with the best fits obtained with $y\approx\frac{8}{3}$. The sum of the squares of the deviations was about 10% smaller for $y=\frac{8}{3}$ than for $y=3$ or $\frac{7}{3}$; in this range of y values, B and T^* change only slightly, but, of course, their changes are interrelated. Thus the value $y \approx \frac{8}{3}$ can be established experimentally as well as theoretically.

Of course, the conclusion concerning the success of the fits in Fig. 4 is, to some extent, a matter of judgment. One sees that the glycerol data appear to deviate somewhat from the scaling curve at low T's. It should also be mentioned that the theory underlying Eq. (7a) is valid only for $T < T^*$, and for temperatures just around T^* it is merely an interpolation formula.

GLOBAL FITS

We have compared various fitting formulas for viscosity and α-relaxation times in what we believe to be a consistent manner that is useful in discriminating between various models. All our fits are semilog fits with no other weighting. Rather than examining $\ln[\eta]$, $\ln[\eta/\eta_0]$, or $E_0(T)$, we have examined $E(T) = T\ln[\eta/\eta_\infty]$, where all these quantities are specified in and around Eqs. (1), (2a), and (2b). Where fits are made to data from a limited range of temperatures, the cutoff temperature must be included as an adjustable parameter.

In this paper Eqs. (7a) and (7b) have been used as a four-parameter global fit, i.e., a fit over the entire temperature range for which data are available from well above the melting point down to T_g. All other fitting formulas are explicitly restricted to limited temperature ranges for which cutoff temperatures become part of the set of adjustable parameters; consequently, global fits that require continuity but allow adjustable cutoff temperatures have a large number of adjustable parameters. A number of these have been discussed by Fischer [28] and by Stickel, Fischer, and Richert [5].

For *global fits* that use different fitting formulas for the high- and low-temperature regimes two parameters (the two cutoff temperatures) can be eliminated by imposing the condition of continuity at the crossover temperature T_A, the temperature at which the high- and low-T expressions cross. (T_A is not an independent adjustable parameter.) Only five adjustable parameters are then needed for such global fits with procedures consisting of (a) a low-T VFT plus a high-T Arrhenius function, or (b) a high-T VFT plus a low-T Arrhenius function, or (c) a high-T mode coupling and a low-temperature Arrhenius function. (A high-T mode-coupling plus a low-T VFT fit requires six parameters.) Reasonable fits to the data (but not necessarily reasonable physics) can sometimes be obtained in this way, but since they involve five or more parameters we shall not pursue them further.

There are, however, a number of global fitting procedures that require fewer parameters. Procedures that use (d) a low-T Arrhenius plus a high-T Arrhenius function or (e) a low-T Bässler plus a high-T Arrhenius function incorporate only four parameters. Fits making use of these procedures, as well as those obtained by using Eqs. (7a) and (7b), are illustrated for OTP data in Fig. 5. The χ^2 values (the square of the differences between fitted curve and data points) are 24, 11, and 6 for the double-Arrhenius, the Bässler plus Arrhenius, and Eqs. (7a) and (7b) fits, respectively. (These numbers are meaningful only when compared to fits over the same data points.) It can also be seen in the caption to Fig. 5 that the preexponential factors are not physically reasonable for the double-Arrhenius and Bässler plus Arrhenius fits.

Additionally, a global fit that makes use of (f) a low-T VFT plus a high-T Arrhenius function, and which also requires that the preexponential factors be equal, makes use of only four parameters. This fit is also indicated in Fig. 5. For this procedure, the χ^2 value for OTP is 12, while, as indicated above, for the Eqs. (7a) and (7b) procedure it is 6. [Because there is considerable high-quality dielectric data available for the fragile liquid salol, we also compared its $\chi^2 = 3$ for procedure (f) with its $\chi^2 = 0.2$ for Eqs. (7a) and (7b).]

One can conceive of three-parameter global fitting procedures. One can develop such a procedure with two Arrhenius functions or with a low-T Bässler plus a high-T Aarhenius, in which one additionally equates the low- and high-T preexponential factors. However, we were unable to obtain reasonable fits with thes procedures, the χ^2 values for OTP being in excess of 50.

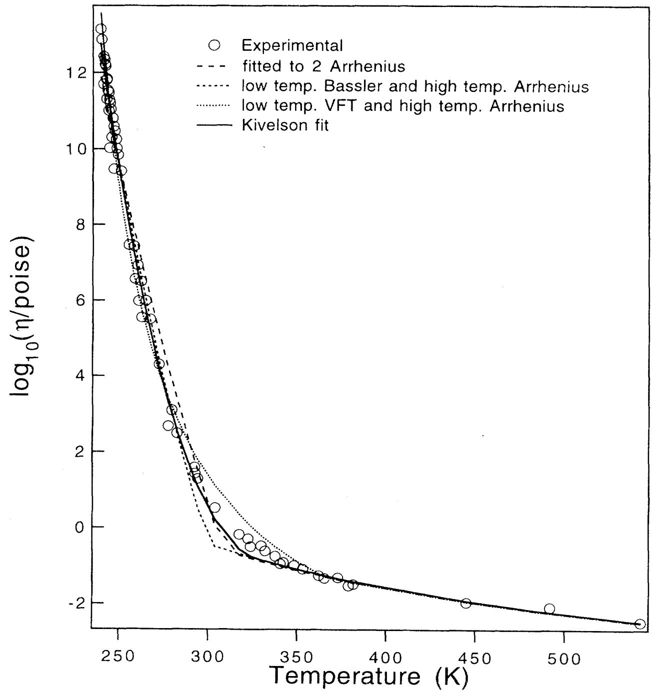

FIG. 5. Four-parameter fits for $\log_{10}[\eta]$ vs temperature for orthoterphenyl. ○, experimental points [6,7]. ——, frustration-limited domains [Eqs. (7a) and (7b)], with $\eta_\infty = 1.03 \times 10^{-5}$ P, $E_\infty = 3150$ K, $B = 412$, and $T^* = 350$ K. $\chi^2 = \mathbf{6}$. · · · ·, $\eta = \max\{\eta_\infty \exp(DT_0)/(T - T_0)]$ for $T < T_A$, $\eta_\infty \exp[E_\infty/T]$ for $T > T_A\}$. $T_A = 363$ K, $T_0 = 208$ K, $\eta_\infty = 1.03 \times 10^{-5}$ P, and $E_\infty = 3125$ K. $D = 6.48$, $\chi^2 = \mathbf{12}$. —·—·—·, $\eta = \max\{\eta_0 \exp[E_0/T]$ for $T < T_A$, $\eta_\infty \exp[E_\infty/T]$ for $T > T_A\}$. $T_A = 308$ K, $\eta_\infty = 1.03 \times 10^{-5}$ P, $\eta_0 = 1.12 \times 10^{-44}$ P, $E_\infty = 3150$ K, and $E_0 = 30\,791$ K. $\chi^2 = \mathbf{24}$. — — —, $\eta = \max\{\eta_0 \exp[CT_A/T^2]$ for $T < T_A$, $\eta_\infty \exp[E_\infty/T]$ for $T > T_A\}$. $T_A = 300$ K, $\eta_\infty = 1.03 \times 10^{-5}$ P, $\eta_0 = 8.2 \times 10^{-24}$ P, $E_\infty = 3150$ K, and $C = 1.6 \times 10^4$ K. $\chi^2 = \mathbf{11}$.

It seems reasonable, therefore, to conclude that to date the best global fit to the data is provided by Eqs. (7a) and (7b). Not only when applied over the entire studied temperature range above T_g is this form *parameter lean* in comparison with most other fitting formulas, and better than other extant four-parameter fitting procedures, but this procedure also implies that below T_m the *viscosity, as well as its temperature derivative, are continuous functions of T,* that below T_m there is *no temperature at which a divergence* (not even an inaccessible or avoided one) need be incorporated, and that there is *no need to postulate a change from one α-relaxation mechanism to another in the range between melting and* T_g. A single mechanism appears to dominate over the entire range below T^*, and if this is the case, the mechanism is likely to be a collective, nonmolecular one. This point of view is taken by the theory of self-forming frustration-limited domains [27].

In Figs. 1 and 4 we have illustrated the corresponding-state character of the fits to Eqs. (1), (7a), and (7b) over a large temperature range. Because of this scaling, we focused only on the single liquid OTP, a liquid that exhibits the full range of liquid and supercooled liquid behavior, i.e., Arrhenius behavior above a crossover and non-Arrhenius behavior below it. Many studies of liquids have been limited to one region or the other, and so can be described adequately by one of the many limited-range fitting formulas, but the full-range problem is the topic of study here.

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