Extension of the Angell Fragility Concept

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We have analyzed and extended the concept of fragility introduced by Angell. Although they often appear to be correlated, we have separated the property of "strength" from that of "fragility." We have taken the measure of "strength" to be the activation free energy at constant density, $E_\infty(\rho)$, for relaxation processes at relatively high temperatures; strong liquids, those with $E_\infty(\rho) \gg kT$ over the relevant temperature range, relax via activated processes, whereas weak liquids do not. As the measure of "fragility" we have taken the curvature of the effective activation energy determined at temperatures well below the melting point where relaxation for all but the most nonfragile liquids appear to be activated. We have discussed a number of examples including weak−fragile and weak−nonfragile systems. We have suggested how these indicators of dynamical behavior might be correlated with thermodynamic indicators (entropy) and structural indicators (intermolecular interactions, structural frustration, collective interactions) as well as with other dynamical indicators such as the degree of nonexponentiality in the relaxation. We have also discussed the limitations of scaling data about the glass-transition temperature, T_g.

Introduction

The concept of fragility, introduced by Angell,[1] has had and continues to have a profound and useful influence on the study of the relaxation behavior of supercooled liquids. One might say that the concept is based upon the observation that strong liquids (specified by the fact that they tend to form strong, directed intermolecular bonds) exhibit Arrhenius behavior with rather large activation energies over the entire accessible temperature range, whereas fragile liquids (specified by the fact that they tend to form rather weak, undirected intermolecular bonds) exhibit super-Arrhenius behavior over the lower part of the accessible temperature range and Arrhenius behavior with rather low activation energy in the upper part of the accessible temperature range. By super-Arrhenius we mean that the activation energy associated with relaxation times or transport coefficients increases appreciably with decreasing T. The activation energy, $E(T)$, for the slow relaxation times, known as α-relaxation times (τ_α), is defined by the relation

$$\ln[\tau_\alpha/\tau_\infty] = E(T)/T \tag{1}$$

where τ_∞ is a temperature-independent parameter. The accessible temperature range stretches from high temperatures well above melting down to the glass transition temperature T_g; below T_g the time $\tau_\alpha > 10^3$ s, and the supercooled liquid converts to a glass. In many cases it is found that

$$\ln[\tau_\alpha(T_g)/\tau_\infty] = E(T_g)/T_g \approx 36 \tag{2}$$

We shall not examine the properties of glasses here. This classification into "fragile" and "strong" has been of value in guiding studies in the field because it appears that the two categories of liquids are indeed distinct in many ways.

As the concept of fragility evolved, it became the character of the activation energy at low temperatures, i.e., at temperatures approaching T_g, rather than the strength or directionality of the bonds (or of their network-forming ability) that became the defining character of fragility. It should be carefully noted that this represented a shift from a thermodynamic or structural specification ("weak" or "strong" or "networked" bonds) to a dynamical specification (super-Arrhenius or Arrhenius activation energy). Indeed, a recent reformulation[2] of the original Angell concept specifies fragility in terms of the temperature variation of a relaxation time or transport coefficient at T_g; it is the steepness index, $m(T_g)$, defined as[2]

$$m(T_g) = \frac{\text{d} \ln[\tau_\alpha(T_g)]}{\text{d}(T_g/T)} \tag{3}$$

that is taken as a measure of fragility, large values corresponding to fragile and small values to strong liquids. It is readily seen that the connection between the temperature-dependent super-Arrhenius activation energy, $E(T)$, and the steepness index, $m(T_g)$, is given by

$$m(T_g) = \frac{E(T_g)}{T_g} - \frac{\text{d}E(T_g)}{\text{d}T_g} \tag{4}$$

where E is actually E/R, i.e., energies are measured in degrees Kelvin. The steepness index clearly focuses the concept of fragility on dynamical behavior at the glass transition temperature, T_g. T_g is a convenient reference point because it is the point at which the super-Arrhenius behavior is most prominent and because it can be operationally well specified. However, T_g does not relate to a fundamental universal state, but rather to an experimentally convenient and qualitatively interesting

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state, and as such it may be operationally useful but of questionable value as a reference point about which one can develop insight leading to a theory. The reason that T_g is not "fundamental" is that it is specified by the fact that below T_g the relaxation time exceeds some arbitrary experimental time constant of 10^3 s.

Attempts have also been made to relate the concept of fragility to the increasingly nonexponential relaxation observed in supercooled liquids as they are cooled further. The degree of nonexponentiality is usually measured by the smallness of the stretching coefficient β for relaxations represented by the stretched exponential $\exp[-(t/\tau)^\beta]$. It is a widely, but not universally, held perception that fragile liquids exhibit greater nonexponentiality than strong liquids. The correlations of fragility with the stretching exponent β have yielded ambiguous answers.[2-4]

We thus have a number of different phenomena and associated questions that are thought to be interrelated but may not be identical. There is the classification of glass-formers according to whether their intermolecular bonds are "weak" or "strong". The entropies of supercooled liquids, particularly those with "weak" bonds, decrease rather anomalously with decreasing temperature (i.e., more rapidly than those of simple liquids above the melting point), and it seems that the most striking thermodynamic signatures by which to classify glass-formers might be found in the entropies rather than the energies.[5] One is then interested in how these structural and thermodynamic signatures carry over to the relaxation or dynamical properties, the latter being characterized by the steepness index as "fragile" or "nonfragile" liquids or else by the stretching exponent β as nonexponential or nearly exponential. It is the basic assertion of the much used Adams−Gibbs model[6] that there is a direct and simple connection between the thermodynamics (entropy) and the dynamics (activation energy),[7] and a similar connection between dynamics and structure is implied in the widespread use of the fragility concept.[1] The possible correlation between fragility and the nonexponentiality of relaxation is one in which all the quantities are dynamical. Finally, there is also the question of the appropriateness of scaling about T_g. It is our contention that the interrelationships of these various concepts require clarification and modification, and that the concept of fragility must be refined if it is to continue to be useful in the current studies of supercooled liquids.

Overview

Weak and Strong Liquids. The way we view the problem is that at high temperatures, above a crossover temperature (T^*), the relaxation times exhibit approximate Arrhenius behavior with an activation energy, E_∞, that is nearly T-independent. Above this T^*, which typically is not far from the melting point, the liquid might be called "simple", while below T^* it is "supercooled" with a T-dependent activation energy, $E(T)$, that increases with decreasing T. We classify liquids as "strong" if they have a large E_∞ and "weak" if they have a small E_∞; thus "weak" and "strong" refer to dynamical properties of "simple" liquids:

$$E_\infty \gg T \text{ defines "strong"} \qquad (5a)$$

$$E_\infty = T \text{ defines "weak"} \qquad (5b)$$

This specification of "weak" and "strong" in terms of the high-T dynamical behavior of liquids is not unique, "weak" and "strong" having been alternatively specified in terms of the strength of intermolecular bonds (nondynamical quantities), and the alternative modes of specification may not be equivalent. As specified, whether a given E_∞ is "strong" or "weak" depends on the T of interest, and indeed, as we discuss below, this is as it should be; moreover, in the study of glass-forming liquids the range of T's is sufficiently small that it makes little difference which midrange temperature one takes as the comparison temperature.

Super-Arrhenius Activation. The activation energy for the supercooled liquid can be written as[8]

$$E(T) = E_\infty \qquad (T \geq T^*) \qquad (6a)$$

$$E(T) = E_\infty + T^*Bf(T/T^*) \qquad (T \leq T^*) \qquad (6b)$$

where $f(T) = 0$ at $T = T^*$, and $f(T) \rightarrow 1$ as $T \rightarrow 0$ K. Of course, the value at $T \rightarrow 0$ is an extrapolated one since one cannot make measurements on supercooled liquids below T_g, and the values of T^*, B, and even of E_∞ depend to a certain extent upon the function $f(T/T^*)$ used to fit the data. One finds[9] empirically that $f(T/T^*)$ may be represented by a universal function, at least to within what we take to be reasonable accuracy.

Fragile and Nonfragile Glass-Formers. In contrast to "weak" and "strong", we classify glass-formers as "fragile" if the parameter B is large and as "nonfragile" if B is small; thus "fragility" is associated with the dynamical properties of the supercooled liquid (well below melting). Above we classified liquids as "strong" or "weak" according to their E_∞ values; thus "strength" is associated with the dynamical properties of the high-T simple liquid and "fragility" with the dynamical properties of the low-T supercooled fluid. This is our extension of the concept of fragility. Both "strength" and "fragility" are dynamical concepts, and our analysis does not, unfortunately, provide a direct link of dynamics to thermodynamics and structure.

Scaling about T^*. In the present picture the crossover temperature, T^*, is the inherent focal temperature relative to which the problem of supercooled liquids should be scaled. In very general terms it is the continuous crossover point from simple liquid to supercooled liquid behavior. In most analyses of supercooled liquids, such a crossover is evident, but just where it occurs is dependent upon the mode of analysis. The approach to the problem that we prefer is that in which an Arrhenius plot of the log of the α-relaxation time (τ_α) is plotted versus T^{-1}, and the crossover from high-T Arrhenius to low-T super-Arrhenius behavior is discerned; of course, the exact positioning of T^* depends on how seriously one tries to make a high-T Arrhenius fit and how one goes about making a low-T super-Arrhenius fit, but the approximate value of T^* is seldom in much doubt.[9] One would, of course, get different T^*'s by fitting the same curves in different ways or by plotting the same data in different ways;[10] one could also look for different signatures of a crossover T^* such as a change from exponential to stretched exponential relaxation or a rapid increase in dS/dT where S is the entropy. We would like to think that an appropriate model, well worked out, would relate all the observations to a single inherent crossover T^*, which could be precisely specified only in terms of that model; this has not yet been achieved.

Although in many cases the melting temperature is close to T^*,[11] except for the necessary avoidance of crystallization it is generally accepted that crystallization has no direct connection with the properties of supercooled liquids.

Mastercurve. The fits to the data that are reported in Table 1 have been made with eq 1, or the analogous equation for the viscosity,[24] with $E(T)$ given by eqs 6a,b and with the universal

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TABLE 1: Material Parameters[a]

substance	B	T*/K	E∞/T*	{E∞(ρ)/T*}	Tg/K	Tm/T*	Tg/T*	E∞/10³ K	{E∞(ρ)/E∞(P)}	γ(Tg)	β(Tg)	m(Tg)
H₂O[16a,b]	790	195	11.7		(136)	1.40	0.70	2.28				
poly(propylene glycol)	558	265	17.0		(197)	4.7	0.74	4.52		20.8	0.52	(75)
poly(p-chlorostyrene)	454	544	11.2				6.3	6.08				
α-phenylcresol	440	293	20.8		(220)	1.12	0.75	6.09		14.5	(0.53)	(83)
o-terphenyl	412	350	9.0	{9.0}	(241)	0.95	0.69	3.25	{1.0}	26.3	(0.57)	(81)
salol	394	304	10.6		(218)	1.05	0.72	3.22		18.4	(0.53/0.6)	(73)
trinaphthylbenzene	288	515	9.8		(337)	0.92	0.65	5.07		26.9	(0.55)	(66)
n-butylbenzene	282	198	7.2			0.93		1.43				
poly(vinyl acetate)	282	454	6.1		(311)		0.68	2.76		19.8	(0.43)	(95)
propylene carbonate	280	235	9.0		(158)	0.93	0.67	2.12		21.7	(0.73)	(104)
triphenyl phosphite	180	311	7.6	{6.1}	189	0.95	0.61	2.35	{0.8}	24.0		
isopropylbenzene	180	210	8.2			0.83		1.72				
dibutyl phthalate	148	288	11.5	{5.8}	(179)	0.83	0.62	3.31	{0.5}	18.1	(0.56)	(69)
toluene[b]	145	192	7.9	{1.6}	118	0.92	0.61	1.52	{0.2}	19.3	0.52	105
ZnCl₂	106	689	9.2		(380)		0.55	6.34		22.9	(0.73)	(30)
glycerol	88.7	322	16.0	{16.0}	(190)	0.91	0.59	5.18	{1.0}	13.9	(0.65/0.7)	(53)
boron oxide	63.4	978	10.7		(554)	0.74	0.57	10.5		11.7	(0.60)	(32)
n-propanol	56.1	192	11.6	{8.1}	(109)	0.76	0.57	2.22	{0.7}	10.4	(1.0)	(40)
GeO₂[d]	12.4	1150	11.8		(818)		0.71	13.6		6.4	(1.0)	(20)
2-component Lennard-Jones[19b]	5.4			(2.5)								
Dzugutov[b,c] referred to argon	1.3	260		{1.1}	≈0							
truncated L-J referred to argon	1.0	95		{0.65}	≈0	≈0						

[a] All data and fits, except those specifcally referenced here, have been transferred from refs 3, 8, 13, and 14; the original data sources are indicated in these references. [b] The fitting leading to the fragility parameter was done in the present work. [c] Private communication from H. Sakai. [d] The Tg in ref 3 was in error.

fitting function

$$f(T/T^*) = (1 - T/T^*)^{8/3} \qquad (7)$$

This function has been found to work quite well,[9] and it also has, to some extent, been justified theoretically;[8] in any case, it is not the specific form of the fitting function nor the exact values of T^* and B that concern us, but rather the general trends with variations in the physical characteristics of the different liquids. It should be noted that these fits involve the four adjustable species-dependent, temperature-independent parameters $\{\eta_\infty, E_\infty, T^*, B\}$; they do not require any cutoff temperatures.[25]

The parameter τ_∞ or η_∞ is a molecular amplitude factor, which, as shown by Angell plots,[1] does not vary much from one simple liquid to another. The parameter E_∞ is also interpreted as a "molecular" quantity dependent only upon interactions and correlations with near neighbors. On the other hand, the parameter B is taken as a measure of the collective effects; in the theory of frustration-limited domains[8] B^{-1} is a measure of "frustration," large B corresponding to small frustration. The temperature T^* is the crossover point from molecular to collective behavior.

Scaling about T_g. In the picture presented above, the crossover T^*, in contrast to T_g, is an intrinsic characteristic point about which one might scale. T_g is indicative of what might be called an isochronic point, one determined by an arbitrarily determined relaxation time (10^3 s) or, almost equivalently, by an arbitrarily determined viscosity (10^{15} cP) or, reasonably equivalently, by a dip in the heat capacity versus T curve measured at a cooling rate of 10 K/min. One can generalize[12] the concept of isochronic points by setting the specifying relaxation time at less than 10^3 s. (It is not currently possible to achieve an isochronic time much in excess of 10^3 s.) We note that if T^* lies below the chosen isochronic point, then liquids both weak and strong, both fragile and nonfragile, will appear Arrhenius-like over the entire temperature range. And if for some substance T_g lies only slightly below T^*, the behavior of that substance will be nearly Arrhenius-like all the way down to T_g whether the liquid is strong or weak, fragile or nonfragile,

as specified above. However, one sees that despite the conceptual possibility of such behavior, the values of T_g/T^* given in Table 1 suggest that in practice T_g lies well below T^*; this accounts for the considerable success of the analyses involving scaling about T_g, in particular of the Angell plots[1] in which $\log[\eta]$ or $\log[\tau_\alpha]$ is plotted versus T_g/T.

Density and Pressure

In practice the $E_\infty(T)$ is usually obtained by fitting eq 1 to a $\log[\tau_\alpha]$ versus $1/T$ plot, and this incorporates information on d $\log[\tau_2]/d(1/T)$. In the analysis above no indication was given as to whether $\tau_\alpha(T)$ was taken at constant pressure (P) or at constant density (ρ). Recent studies[13,14] have focused on the distinction between results obtained at constant P and constant ρ. To summarize and incorporate these considerations into the present discussion we distinguish the parameters $\tau_\infty(P)$, $E_\infty(P)$, $T^*(P)$, and $B(P)$ obtained at constant P from the parameters $\tau_\infty(\rho)$, $E_\infty(\rho)$, $T^*(\rho)$, and $B(\rho)$ obtained at constant ρ. The data available are not sufficient to measure the pressure and density dependences of $T^*(P)$ and $T^*(\rho)$, respectively, or to distinguish between them, so we take them as a constant T^*; the same is true for $\tau_\infty(\rho)$ and $\tau_\infty(P)$. We do not expect the differences between $\tau_\infty(P)$ and $\tau_\infty(\rho)$ to have a significant effect upon our conclusions because, as indicated above, the known small differences in $\tau_\infty(P)$'s for various liquids have little effect upon the ultimate values of the effective activation energies.

Activated Dynamics and Strength. The activation energy $E_\infty(\rho)$ has been associated with actual activated dynamics.[14] On the other hand, the effective activation energy $E_\infty(P)$ can be a composite of contributions from both free volume and activated dynamics, and it is, therefore, not as directly interpretable. The suggested criteria[14] for activated dynamics at high-T (above melting) are

$$E_\infty(\rho) \gg T, \qquad E_\infty(\rho) \approx E_\infty(P) \qquad \text{(activated)} \quad (8a)$$

and those for nonactivated (free-volume or congested) dynamics are

$$E_\infty(\rho) = T, \qquad E_\infty(\rho) \ll E_\infty(P) \qquad \text{(nonactivated)} \quad (8b)$$

It appears that, in most cases, the two criteria for "activated" and "nonactivated" go in concert.[14] This suggests that, in order to make meaningful statements concerning activation energies, one should examine constant density relaxation data and not constant pressure data. Correspondingly, we should alter our specification of "strong" and weak" in eqs 5ab to

$$E_\infty(\rho) \gg T \text{ defines "strong"} \qquad (9a)$$

$$E_\infty(\rho) = T \text{ defines "weak"} \qquad (9b)$$

in which case "strong" and "weak" have a clear correspondence with activated and nonactivated dynamics. As indicated below eqs 5a,b, the inequalities could be altered with changing T, as is indeed the case for the criterion for activated dynamics, but since the actual range of T's is small, one might choose T^* or, equally well, the melting temperature as the comparison temperatures.[14]

Unfortunately, there is a paucity of $E_\infty(\rho)$ data, and we must make do in most cases with knowledge of $E_\infty(P)$. Of course, if $E_\infty(P) \approx E_\infty(\rho)$, we need not be concerned about the differences in $E_\infty(P)$ and $E_\infty(\rho)$. However, unless one has constant density data one does not know whether this equality holds, and it appears that $E_\infty(P) \gg T$ even in those cases where $E_\infty(\rho) \lesssim T$. (By $E_\infty \gg T$ we mean at least several times T, i.e., at least $5T$; by $E_\infty(P) \gg E_\infty(\rho)$ we mean at least $2E_\infty(P)$.)

As expected, one finds[14] that $E_\infty(\rho)$ increases with increasing ρ. By the criteria established here, this means that liquids become stronger at higher densities.

Fragility Independent of P and ρ. At low temperatures, below T^*, the distinction between the activation energy at constant P and that at constant ρ is not significant.[13] It appears that all deeply supercooled liquids relax via activated dynamics.[13] Consequently, whereas the specification of "strong" and "weak" is sensitive to whether E_∞ is measured at constant P or constant ρ, the fragility measure, B, as specified here, is not sensitive to these factors.[13,15]

Summary. We have defined both "fragility" and "strength" as dynamical properties, the first applicable for deeply supercooled liquids and the second for simple liquids above their melting points. Strong liquids relax via activated dynamics; weak ones do not. The various criteria are all focused on the effective activation energies, and for weak simple liquids one must be sure to determine the activation energies at constant density.

The concept of "strength" associated with $E_\infty(\rho)$, is often also associated with the strength of intermolecular bonds, and this asssociation, though clearly not exact, may be reasonable. As to the concept of fragility, which is a description of the non-Arrhenius contributions to the low-T activation energy, it has been associated with structural frustration, the smaller the frustration, the larger the B and the more super-Arrhenius the relaxation.[8] Various models associate the Arrhenius behavior above T^* with molecular relaxation, while the relaxation below T^* may be associated with collective phenomena (domains or clusters).[8]

Conclusions

In Table 1 we have arranged liquids in descending order of B values, i.e., in descending order of fragility. The comments below refer to the data in Table 1.

(1) Good Correlation between B and T_g/T^*. We note that the correlation between the B measure of fragility and the ratio T_g/T^* is high, the latter being the only quantity that correlates

well with B. We shall discuss this further below, but this correlation is somewhat surprising in light of the statements above about the nonuniversality of T_g; at the same time it is supportive of the now conventional method[1,2,4] of measuring fragility by the properties of systems at T_g.

(2) No Correlation between Fragility (B) and Strength (E_∞). We note that there is no particular correlation between the B measure of fragility and the E_∞ measure of strength. We emphasize this because our contention is that these two concepts, though often intermixed, should be kept distinct. The measure of "strength" in our formulation should be $E_\infty(\rho)$, but since these are not always available, we have listed both $E_\infty(P)$ and $E_\infty(\rho)$, where available, in Table 1.

(3) E_∞/T^* Reasonably Constant. We note that there is no particular correlation between the crossover T^* and the fragility B. One might, however, discern a reasonable, but not unambiguous, correlation between T^* and E_∞, as indicated by the fact that E_∞/T^* is of the order of 10 for many of the substances in the table. We might regard both E_∞ and T^* as measures of the intermolecular bond strengths, the former arising by the need to break bonds to permit local motion, and the latter arising as the critical temperature at which short-range interations give rise to collective effects. Here, too, it is $E_\infty(\rho)/T^*$ rather than $E_\infty(P)/T^*$ that should be relevant, but the former is not always available. We have tabulated E_∞/T^*, but we have also tabulated $T^*/T(\text{melt})$, where available.

(4) Why Scaling about T_g Works. The fact that $E_\infty/T^* \approx 10$ for many substances also suggests that most of the increase of viscosity from its high-T limiting value to that at T_g occurs at T's below T^*. Said differently, this guarantees that

$$\tau_\alpha(T_g) \gg \tau_\alpha(T^*) \qquad (10)$$

This, in turn, suggests that the now conventional way of measuring fragility properties at T_g may be a useful procedure despite the fact that the behavior of the system at T_g is not universal. Of course, if instead of T_g one had picked a lower isochronic point (a temperature at which viscosity was less than 10^{15} cP or the relaxation time less than 10^3 s), the procedure would have had less merit because the inequality (10) would not be well satisfied.

(5) More about Why Scaling about T_g Works. Looking further at the astonishingly good correlation between B and T_g/T^*, we are struck by the fact that T_g/T^* decreases with decreasing fragility, i.e., with decreasing B. This is related to item 4 above in the sense that although at high-T the viscosity of a strong liquid increases more rapidly with decreasing T than that of a weak liquid, it is the anomalous or super-Arrhenius behavior (controlled by fragility) that dominates for both weak and strong liquids by the time T has decreased to T_g. Again we point out that this would not be the case if a lower isochronic point were used. GeO_2 does not seem to fit the trend, although the determination of its T^* is very uncertain, and this may also be true for other very strong liquids such as SiO_2.

(6) Unimpressive Correlation of Fragility with Relaxation Stretching. Repeating what was concluded in ref 3, we find the correlation of B with the stretching coefficient $\beta(T_g)$ less compelling than one might have hoped. (The stretching coefficient is the parameter β that appears in a relaxation function of the form, $\exp[-(t/\tau)^\beta]$.) There may perhaps be a general upward trend of $\beta(T_g)$ with a downward trend of B, a trend that suggests that stretching of the relaxation function is associated with fragility, as one might expect. A more careful look at the theory of frustration-limited domains,[5] which incorporates eqs 6a,b and 7, indicates that the quantity that might be expected

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to correlate with the stretching coefficient $\beta(T)$ should be[3,8,15]

$$\gamma(T) = B(T^*/T)(1 - T/T^*)^{8/3} \qquad (11)$$

We therefore look for correlation between $\beta(T_g)$ and $\gamma(T_g)$. As seen from Table 1, the correlations are only modestly encouraging. However, the experimental values of the $\beta(T_g)$'s are uncertain.[26] It is also true that $\gamma(T_g)$ depends sensitively upon the uncertainty in T_g/T^*, as well as upon that of B, and in our opinion, a truly critical analysis of the correlation between $\beta(T_g)$ and $\gamma(T_g)$ has yet to be carried out.

Classifications

(1) Strong−Fragile Liquids. The liquids in the top part of Table 1, those with $B > 150$ might be called fragile. All of them, except toluene, are strong with $E_\infty(\rho)$ at least several times T^*. The fact that systems such as *o*-terphenyl and salol are classified as "strong" is an *unusual feature of our classification*. Note that water is "strong," and if the fits to eqs 6a,b are meaningful, *water is extremely "fragile"* and has an unusually large T_m/T^* ratio.[16]

(2) Strong−Nonfragile Liquids. By our classification scheme $ZnCl_2$, GeO_2, boron oxide, and the others with $B < 100$ could be classified as nonfragile, while their values of E_∞ certainly classify them as "strong." These classifications are quite in keeping with standard practice. Silica is known to be very Arrhenius-like all the way down to T_g; silica has a very large E_∞, and so it is very "strong," but whether it is very nonfragile (small B) or merely has its T^* at or below T_g cannot be determined, although, in analogy with GeO_2, we strongly suspect the former.

(3) Weak−Fragile Liquid. Of the fragile glass-formers listed in Table 1, only toluene is "weak" in the sense that $E_\infty(\rho) \lesssim T$. Toluene also has a small $E_\infty(\rho)/E_\infty(P)$ ratio. For both these reasons we do not expect its dynamics to be activated at high T. However, by our measure, toluene with a B value of about 145 should relax via activated dynamics at low temperatures approaching T_g. In contrast, DPB with a similar B value, and hence similar fragility, is much stronger with $E_\infty(\rho)/T_m \approx 6$ and $E_\infty(\rho)/E_\infty(P) \approx 0.5$.

(4) Weak−Nonfragile Systems. The only such systems that we have been able to identify are computer-simulation liquids. One-component truncated Lennard-Jones systems exhibit only very slight super-Arrhenius behavior before crystallizing, but in Table 1 we have presented the best parameters we could extract from our data. A slightly more fragile and stronger liquid, that has more clearly identifiable super-Arrhenius character and retains the simplicity associated with spherical symmetry, is what we call the Dzugutov liquid.[17] Two-component Lennard-Jones liquids[18,19] can be studied down to lower temperatures, where super-Arrhenius behavior is more evident, without the onset of crystallization or formation of quasicrystals, but the effects of demixing are uncertain and the analysis is more complicated; although more fragile than the other computer-simulation systems, they are nonetheless very nonfragile. We note that for these very nonfragile systems, $T_g \approx 0$, so that $T_g/T^* \approx 0$. (Of course, it is a tremendous extrapolation from computer-limited relaxation time to the 10^3 s relaxation time characteristic of a glass, but it is clear that the extrapolation yields a T_g very near zero.) Since B is very small, the excellent correlation between T_g/T^* and B holds for the simulation systems, too. The parameters are only crudely evaluated for all these systems,[25] but sufficiently well for the present discussion.[27] (Detailed studies of the Dzugutov liquids will be reported

elsewhere.[20]) We find $E_\infty/T^* \approx 1$ for the computer models, values that are comparable to that for toluene. We speculate that argon may also be very weak and very nonfragile.

Additional Remarks

One would like to correlate these dynamical properties with structural or thermodynamic ones. To date, the most striking thermodynamic indicator of specific supercooled liquid behavior is the entropy, which decreases rather rapidly as the liquid is supercooled; in particular, the quantity denoted as the "configurational entropy" S_c decreases rapidly, where S_c is the entropy of the liquid minus that of the crystal.[5,21] The Adam−Gibbs model sets the activation energy proportional to $1/S_c(T)$, and this suggests that $S_c(T_g)$ can be taken as a thermodynamic measure of fragility with small values of $S_c(T_g)$ corresponding to great fragility (large B). This correspondence is under study.[22] A somewhat different picture is given by the theory of frustration-limited domains[23] in which the contribution to the entropy associated with domain formation, $S_D(T)$, in supercooled liquids is proportional to $-(1 - T/T^*)$ while the super-Arrhenius contribution to the activation energy is proportional to $B(1 - T/T^*)^{8/3}$. In this picture, there is no simple proportionality between entropy (thermodynamic) and activation energy (dynamic) properties: within the theory the activation energy depends on the frustration (B); the entropy does not.

Summary

We have introduced a classification scheme, derived from that of Angell but distinguishing between the high-T Arrhenius behavior (simple liquid above T^*) and low-T super-Arrhenius behavior (supercooled liquid below T^*); the high-T behavior is classified as "weak" or "strong," the low-T behavior as "fragile" or nonfragile". We have found examples with all four combinations of these two categories. Of special note is the fact that water has been incorporated into the scheme as the most fragile of liquids, that Lennard-Jones simulation liquids, though "weak" as expected, are exceedingly "nonfragile", and that most good glass-formers are "strong". The weak and strong categories are not merely arbitrary categories, since "strong" strongly suggests activation dynamics whereas "weak" suggests flow-congestion (free volume) dynamics. "Strong" liquids should exhibit activated dynamics below T^* as well as above, and "weak" liquids which are "fragile," such as toluene, should also carry out activated dynamics when sufficiently supercooled; on the other hand, a very nonfragile liquid such as a Lennard-Jones system may or may not ultimately exhibit activation dynamics. Two major conclusions from these studies are that one must be very cautious in generalizing results from Lennard-Jones simulations to laboratory fragile supercooled liquids and that one should be very cautious in applying free volume and mode-coupling theories to any but weak systems above T^* and, perhaps, to weak−nonfragile systems below T^*.

For large effective activation energies to be associated with activated dynamics one must statisfy two criteria: that the effective activation energy at constant density be large compared to kT, at whatever T one is studying, and that the effective activation energy at constant density be comparable to that at constant pressure. The activation energies are "effective" because they are probably activation free energies of some kind and also because they are the results of less than perfect fits. It is the activation energy at constant density that is relevant because, in isolating that part of the dynamics that is attributed to activation, one does not wish to incorporate effects due to volume (free volume) changes. It is only if the activation energy

is large compared to kT that one can talk about activated dynamics. And if the activation energy at constant pressure is appreciably larger than that at constant density, then it is the free volume effects that dominate the relaxation processes. If the activation energy at constant density is not large compared to kT, as it is for "weak" liquids above T^* and for weak−nonfragile liquids even well below T^*, one might go back and fit the relevant data to functions other than Arrhenius forms, perhaps to power-law forms.

There is considerable uncertainty in determining the relevant parameters. Furthermore, there is not much constant-density data. Nevertheless, we believe that the quantitative results are quite sufficient to make the major points stressed in this article, although it is, of course, always possible that additional data may suggest alternative approaches. Furthermore, we hope that other workers will be motivated to collect and analyze more and better constant-density data.

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(24) For fits to the viscosity $\eta(T)$, eqs 1 and 2 are modified by replacing $\tau_\alpha(T)$ by $\eta(T)$ and the constant τ_∞ by the constant η_∞.

(25) The best fits of the parameters τ_∞, E_∞, T^*, and B are made on systems for which data are available over a wide temperature range spanning the high-T Arrhenius behavior and the low-T super-Arrhenius behavior down to T_g, where T_g corresponds to relaxation times of 10^3 s. In this case, the fitting can be construed as applied to two separate sets of experiments, one yielding the high-T Arrhenius behavior and the other the low-T super-Arrhenius behavior; the first depends only upon the two parameters $\{\tau_\infty, E_\infty\}$, and the second makes use of these two high-T parameters and introduces two new ones $\{T^*, B\}$. One can thus think of the fitting procedure as two separate two-parameter fits. Unfortunately, data over a sufficient range are available for only a few liquids, among those not included being computer-simulation liquids. For the latter the relaxation times are many orders of magnitude less than those observed near the experimental T_g's, and neither the Arrhenius nor super-Arrhenius ranges are well-spanned.[14] So in many cases one must make four-parameter fits to one set of limited data. The accuracy is not great, but we believe they are semiquantitatively meaningful.[9]

(26) There are two aspects of uncertainty that concern us in the determination of $\beta(T_g)$. The first has to do with the intrinsic difficulty of quantifying the degree of nonexponentiality or non-Lorentzian character. It is usually a simple matter to distinguish exponential from nonexponential behavior, but the actual quantification of the nonexponentiality is a sensitive function of the mode of analysis. The second difficulty arises from the fact that it appears that the stretching coefficient, even if analyzed in a uniform manner, is somewhat different for different phenomena, e.g., for light scattering and dielectric relaxation. These differences may be physically interesting, but they are not incorporated into the simple search for correlation outlined here.

(27) The Dzugutov liquid[17] is specified by a spherically symmetric interparticle potential energy that is much like the Lennard-Jones potential in the region around and below its minimum of $-\epsilon$ at a distance r_{min} but that has a barrier (maximum) of about $\epsilon/2$ at a distance of about 1.5 r_{min}. Our studies of the Dzugutov liquid extended to a temperature that is 30% below the highest temperature studied, but the diffuson constant divided by T spanned only 1 order of magnitude. In contrast, although our studies of the one-component, truncated Lennard-Jones potential spread over a comparable temperature range, the diffusion constant divided by T changed only by a factor of 3 and exhibited less super-Arrhenius curvature.