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Supercooled Liquids and Glasses

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Selected aspects of recent progress in the study of supercooled liquids and glasses are presented in this review. As an introduction for nonspecialists, several basic features of the dynamics and thermodynamics of supercooled liquids and glasses are described. Among these are nonexponential relaxation functions, non-Arrhenius temperature dependences, and the Kauzmann temperature. Various theoretical models which attempt to explain these basic features are presented next. These models are conveniently categorized according to the temperature regimes deemed important by their authors. The major portion of this review is given to a summary of current experimental and computational research. The utility of mode coupling theory is addressed. Evidence is discussed for new relaxation mechanisms and new time and length scales in supercooled liquids. Relaxations in the glassy state and significance of the "boson peak" are also addressed.

I. Introduction

In spite of the impression one would get from an introductory physical chemistry text, disordered solids play a significant role in our world. All synthetic polymers are at least partially amorphous, and many completely lack crystallinity. Ordinary window glass is obviously important in building applications and, in highly purified form (vitreous silica), is the material of choice for most optical fibers. Amorphous silicon is being used in almost all photovoltaic cells. Even amorphous metal alloys are beginning to appear in technological applications. Off our world, the role of disordered solids may be equally important. Recently, it has been argued that most of the water in the universe, which exists in comets, is in the glassy state.

Liquids at temperatures below their melting points are called supercooled liquids. As described below, cooling a supercooled liquid below the glass transition temperature T_g produces a glass. Near T_g, molecular motion occurs very slowly. In molecular liquids near T_g, it may take minutes or hours for a molecule less than 10 Å in diameter to reorient. What is the primary cause of these very slow dynamics? Are molecular motions under these circumstances qualitatively different from motions in normal liquids? For example, do large groups of molecules move cooperatively? Or are supercooled liquids merely very slow liquids?

In this article, we describe selected aspects of recent progress in the fields of supercooled liquids and glasses. Section II describes several basic features of the dynamics and thermodynamics of supercooled liquids and glasses. We have attempted to summarize enough material in this section so that readers with no previous knowledge of this area will be able to profit from the later sections. Section III describes various theoretical models which attempt to explain the basic features of section II. Here our goal was not to review the most recent theoretical work, but rather to describe those approaches (whether recent or not) which influence current research in this area. Section IV describes areas of current experimental and computational activity. Most of the material in this section is organized in response to five questions. These questions are important from both a scientific and technological viewpoint; the answers can be expected to influence important technologies.

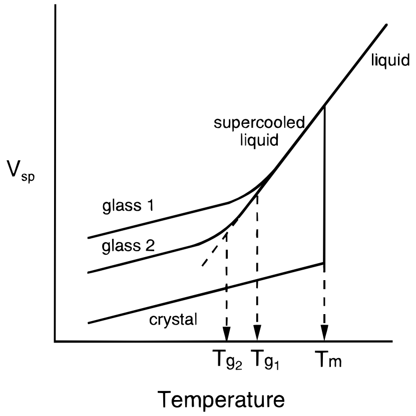

Figure 1. Schematic representation of the specific volume as a function of temperature for a liquid which can both crystallize and form a glass. The thermodynamic and dynamic properties of a glass depend upon the cooling rate; glass 2 was formed with a slower cooling rate than glass 1. The glass transition temperature T_g can be defined by extrapolating V_{sp} in the glassy state back to the supercooled liquid line. T_g depends upon the cooling rate. Typical cooling rates in laboratory experiments are 0.1−100 K/min.

Because this is a review for nonspecialists, a great deal of exciting new material could not be included. We refer the interested reader to other recent reviews[1] and collections[2] which will contain some of this material and offer other perspectives on the questions addressed here.

II. Basic Features of Supercooled Liquids and Glasses

What Are Supercooled Liquids and Glasses? Figure 1 shows the specific volume V_{sp} as a function of temperature for

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a typical liquid. Upon cooling from high temperatures, a liquid may crystallize at T_m. This first-order phase transition usually results in a decrease in the specific volume (water is a notable counterexample). A liquid that manages to get below T_m without crystallizing is called a supercooled liquid. The specific volume and other thermodynamic properties of a supercooled liquid are what would be expected from extrapolating to lower temperature the properties of the liquid above T_m.

As a supercooled liquid is cooled to lower temperatures, its viscosity increases and the molecules which comprise it move more and more slowly. At some temperature the molecules will be moving so slowly that they do not have a chance to rearrange significantly before the temperature is lowered further. Since these rearrangements are necessary for the liquid to find the equilibrium V_{sp} for that temperature, the experimentally observed V_{sp} will begin to deviate from the equilibrium value at this point. At temperatures not much lower than this, the time scales for molecular rearrangements become hopelessly long compared to the time scale of the experimental observations. The structure of this material is "frozen" for practical purposes, and we call it a glass. V_{sp} continues to decrease as the temperature is lowered, but the thermal expansion coefficient ($=[d(\ln V_{sp})/dT]_p$) in the glassy state is significantly smaller than in the liquid and supercooled liquid states. Thermal expansion in the glassy and crystalline states is similar; in each case, expansion is dominated by atomic vibrations which are very similar in the two states.

The glass transition temperature T_g can be defined in many different ways. One convenient method uses the change in the thermal expansion coefficient. As shown in Figure 1, this change does not occur suddenly, but rather over a range of temperatures which has been called the "transformation range" by glass scientists. T_g is different for different cooling rates. A smaller cooling rate allows the sample to stay in equilibrium (i.e., the supercooled liquid state) until lower temperatures. Typically, the dependence of T_g upon cooling rate is relatively weak; an order of magnitude change in cooling rate may change T_g by only 3−5 K. Notwithstanding its dependence on cooling rate, T_g is an important material property; when defined consistently, it is the single parameter which is most useful in estimating the mechanical properties of a polymeric material.

It is important to emphasize that the glass transition is not a first-order phase transition. Indeed, the glass transition observed in the laboratory is not any kind of phase transition. It is a kinetic event which depends upon the crossing of an experimental time scale and the time scales for molecular rearrangements. Furthermore, glasses are not crystals or liquid crystals. They are liquids which are "frozen" on the time scale of experimental observation. As indicated by Figure 1, there is not a single glassy state; the thermodynamic (and dynamic) properties of a glass depend upon how it was formed.

In the preceding discussion, we have referred to the supercooled liquid as being in equilibrium. Conventionally, the crystal is regarded as the equilibrium state below T_m. The supercooled liquid and glassy states are considered metastable and unstable, respectively. Nevertheless, the supercooled liquid may be regarded as the equilibrium state as long as no crystal nuclei are present. Although this may sound odd, chemists often make similar statements. A mixture of oxygen gas and benzene vapor reaches equilibrium very quickly at room temperature—unless one considers the very slow chemical reaction (i.e., combustion) which will eventually occur. In the absence of a catalyst, however, one can ignore the more stable equilibrium state if no significant reaction occurs on the time scale of the experiment. Similarly, a supercooled liquid which has not crystallized may be regarded as being at equilibrium.

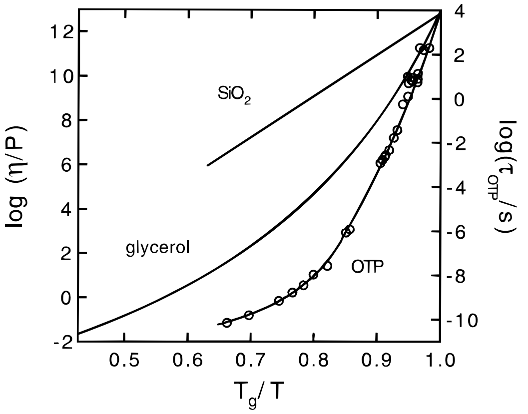

Figure 2. Viscosity as a function of reduced inverse temperature for three liquids: SiO$_2$, glycerol, and *o*-terphenyl. Reorientation times are shown for *o*-terphenyl only (○). A nearly Arrhenius temperature dependence for relaxation times and the viscosity is characteristic of *strong* liquids, while *fragile* liquids show quite non-Arrhenius behavior. Data from refs 4−7.

The characterization of the glassy state as unstable also requires a brief comment. This is a thermodynamic statement. For a single-component glass at constant T and P, for example, the Gibbs free energy will not be at a local minimum. In constrast to a supercooled liquid, a glass is continually relaxing, possibly too slowly to measure, toward a more stable state, i.e., a local free energy minimum. If experimental observations are made on time scales fast compared to the molecular motions which allow the glass to relax, then the glass is mechanically stable for practical purposes, even though it is thermodynamically unstable.

Supercooled liquids may be stable for very long times. For example, a pure sample of liquid *o*-terphenyl will not crystallize for years in a test tube at room temperature even though this is 35 K below its melting point. Very pure liquid water is easily supercooled in a capillary to 30 K below its melting point. Some liquids, such as *m*-fluoroaniline, have never been crystallized at atmospheric pressure. For atactic polymers (i.e., polymers with random stereochemistry), the crystalline state is often never obtained and may be higher in free energy than the liquid state at all temperatures. The likelihood that a liquid remains in the supercooled state rather than crystallizing during cooling depends upon cooling rate, the cleanliness of the liquid, the viscosity at T_m, the similarity of the liquid packing to that of the crystal, and other factors.[3]

Dynamics as T_g Is Approached. The viscosity of a liquid is a macroscopic measure of its resistance to flow. In Figure 2, the solid lines show the logarithm of the viscosity as a function of temperature for three liquids which are easily supercooled: *o*-terphenyl,[4] glycerol,[5] and SiO$_2$.[6] Temperature is scaled in this plot so that T_g for each liquid occurs at the right edge of the graph. The viscosity at T_g for nonpolymeric glass formers is typically near 10^{13} P; in this plot, this value of the viscosity is used to define T_g. Liquids such as water, benzene, and ethanol have viscosities near 10^{-2} P at room temperature. Clearly supercooled liquids near T_g flow very slowly and behave as solids for many purposes.

The time scale for molecular motion increases dramatically as a supercooled liquid is cooled toward T_g. This is illustrated in Figure 2, where rotation times for *o*-terphenyl are shown as open circles.[7] The rotation time at T_g is about 10^4 s; values between 10 and 10^4 s are typical for many materials. This is an astoundingly long time compared to the picosecond or nanosecond rotation times observed in "typical" liquids and in *o*-terphenyl itself above T_m. Other measures of molecular

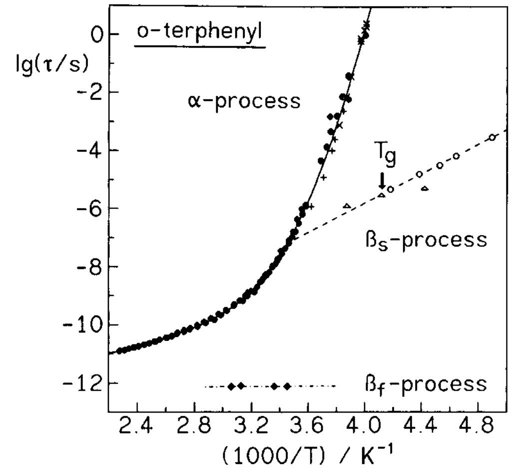

Figure 3. Compilation of various relaxation times measured for *o*-terphenyl. α-relaxation: dielectric relaxation (+); dynamic Kerr effect (×); light scattering (⊕); NMR (●). β_s-relaxation: dielectric relaxation (○); time-resolved optical spectroscopy (△). β_f-relaxation: neutron scattering (◆). The ordinate is the base 10 logarithm. Solid and dashed lines are guides for the eye. Different experimental techniques often give similar relaxation times in one-component supercooled liquids. Data sources are given in ref 10. Reproduced with permission from ref 9. Copyright 1994 North-Holland.

mobility also show very large changes as the temperature is lowered toward T_g.

The three liquids shown in Figure 2 have different temperature dependences as T_g is approached. The viscosity of SiO_2 has almost an Arrhenius dependence while the viscosity and rotation times for *o*-terphenyl are quite non-Arrhenius. On this type of plot, almost all materials would fall in between these two curves.[8] On the basis of this property and others, supercooled liquids have been classified as strong or fragile.[8] *Strong* liquids (e.g., SiO_2) show Arrhenius relaxation processes and typically have three-dimensional network structures of covalent bonds. *Fragile* liquids (e.g., *o*-terphenyl) have quite non-Arrhenius relaxation properties and typically consist of molecules interacting through nondirectional, noncovalent interactions (e.g., dispersion forces).

The temperature dependence of relaxation times (or the viscosity) for supercooled liquids is often described at least approximately by the Vogel–Tammann–Fulcher (VTF) equation:

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_\infty}\right) \tag{1}$$

When $T_\infty = 0$, the familiar Arrhenius equation results. In this case, the constant B is equal to E/k, where E is the activation barrier. When $T_\infty > 0$, the temperature dependence is non-Arrhenius, and the relaxation time is predicted to become infinite at T_∞. At any given temperature, non-Arrhenius relaxation processes can be characterized by an apparent activation energy ($=k[\mathrm{d}(\ln \tau)/\mathrm{d}(1/T)]$). Fragile liquids may have apparent activation energies of 500 kJ/mol or more near T_g, corresponding to changes in dynamics of 1 decade for a temperature change of 3–5 K. The Williams–Landel–Ferry (WLF) equation often used to describe viscosity or relaxation times in polymers is mathematically equivalent to the VTF equation.

Usually supercooled liquids show more than one relaxation process at temperatures near T_g. Figure 3 illustrates the behavior of *o*-terphenyl.[9,10] For nonpolymeric liquids, the slowest relaxation process is called the *alpha* (α) process and roughly corresponds to molecular rotation. Secondary relaxation processes occur on shorter time scales. Unfortunately, the designation of these secondary processes in the literature is not uniform. In Figure 3, two secondary processes are marked as the slow and fast *beta* (β) processes.[11] The β_s process is believed to be due to partial reorientation of *o*-terphenyl molecules.[12] For decades this process was called simply the β relaxation; "slow" has recently been added to distinguish it from much faster processes. One of these, labeled as the β_f process in Figure 3, is thought to be a complex collective anharmonic cage rattling process.[13] The β_s process has also been called the Johari–Goldstein process.

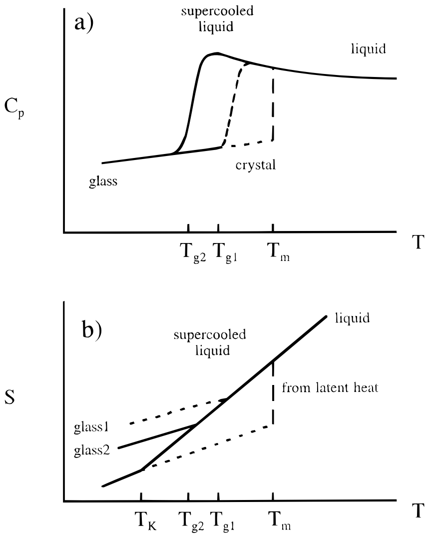

Figure 4. A schematic diagram of the temperature dependence of (a) the specific heat, c_p, and (b) the specific entropy, s, of a crystal, liquid, supercooled liquid, and glass. Glasses 1 and 2 are obtained with different cooling rates and have different apparent glass transition temperatures. Glass 1, shown by the dashed curve, represents the result of a faster cooling rate than that used to produce glass 2, the solid curve.

Thermodynamics as T_g Is Approached: The Entropy Crisis. The specific entropy, s, of a supercooled liquid, even though it is not the state of lowest free energy, can be calculated in the usual way by integrating over the measured specific heat. Figure 4a shows a schematic graph of a typical specific heat curve for the crystal, liquid, supercooled liquid, and glass.[14] The specific heat $c_p(T)$ is largest in the supercooled liquid and drops to a lower value, close to the value found in the crystal phase, near T_g. The temperature at which the specific heat drops rapidly depends sensitively on the rate of cooling of the liquid. The two separate curves in the figure indicate the result of cooling at two different rates. Upon even slower cooling, the curve would shift even farther to lower temperatures. The thermodynamic relation

$$s(T_2) - s(T_1) = \int_{T_1}^{T_2} \frac{c_p(T)}{T}\, \mathrm{d}T \tag{2}$$

allows a determination of the entropy from such data. The crystal entropy at the melting point T_m can be calculated if the specific heat of the crystal is measured from $T = 0$ to T_m. The entropy of the liquid at T_m is obtained by adding the entropy of fusion to the crystal entropy. Upon recooling the liquid below T_m, one again measures c_p and uses eq 2 to determine the entropy of the supercooled liquid. This is shown schematically in Figure 4b. The slope of s versus T must be largest in the liquid and supercooled liquid phases since that is where c_p is largest. Thus, as the temperature drops, the entropies of the supercooled liquid and the crystal must quickly approach one another.

If the specific heat did not drop at T_g, and the rapid decrease of the liquid entropy were to continue to arbitrarily low temperature, then the liquid would eventually have the same entropy as the crystal. This extrapolated point is known as the "Kauzmann temperature", T_K.[15] Below this temperature the crystal would then have the larger entropy. Although it is counterintuitive that a liquid could have an entropy smaller than that of the ordered crystal, it does not violate any law of thermodynamics. However, the third law of thermodynamics would be violated if the liquid entropy continued to decrease much below T_K without any change in slope since then we would find that s becomes negative well above $T = 0$. This chain of reasoning due to Kauzmann effectively puts a limit on how low a value of T_g one can imagine since the glass transition must intervene at a temperature above T_K in order for the entropy of the glass to remain positive.[15] Thus, we expect that T_K, while not a rigorous bound, must stand as a good estimate for how far a liquid can conceivably be supercooled before the glass transition must intervene: $T_g \geq \approx T_K$. No matter how slowly one cools the liquid, one should always expect a specific-heat anomaly (i.e., a drop in c_p) at a temperature above the Kauzmann temperature.

The Kauzmann argument is more relevant for fragile than strong glass-forming liquids. In fragile liquids the difference between the liquid and crystalline specific heat is relatively large so that T_K often falls not far below the temperature range where experiments can still detect relaxation phenomena. On the other hand, in a strong liquid, such as SiO_2, the specific heats of the liquid and solid are nearly the same so that the value of T_K is almost indistinguishable from $T = 0$ K. The fragile liquids have therefore been the systems of choice for experimentalists seeking to investigate the importance of the Kauzmann argument and the nature of the glass transition in general.

Nonexponential Relaxation Functions. A striking feature of many supercooled liquids is the nonexponential nature of the response of the liquid to various perturbations. If the temperature of a typical fragile supercooled liquid is suddenly dropped by 0.5 K, the volume does not approach the new equilibrium volume exponentially. Likewise, if some net orientation is given to the molecules (possibly by an electric field), the molecules will not randomize their orientations exponentially. As shown in Figure 5, this behavior can be explained in two fundamentally different ways.[16] One can imagine that a heterogeneous set of environments exists in a supercooled liquid; relaxation in a given environment is nearly exponential, but the relaxation time varies significantly among environments. Alternatively, one can imagine that supercooled liquids are homogeneous and that each molecule relaxes nearly identically in an intrinsically nonexponential manner.

Often the Kohlrausch−Williams−Watts (KWW) or stretched exponential function is used to characterize response functions:

$$\phi(t) = e^{-(t/\tau)^{\beta}} \qquad (3)$$

The smaller the value of β, the less exponential the response function. If $\beta = 1$, a single exponential is recovered. (Other functional forms, such as the Cole−Cole and Cole−Davidson functions, are also commonly used; these functions are also nonexponential in the time domain.) Although the KWW function can be "derived" if certain assumptions are made,[17,18] many investigators use it simply as a flexible two-parameter fitting function. Data often exhibit some deviations from eq 3. In particular, this equation does not have the correct short-time (high-frequency) behavior.[19,20] In many systems, β decreases as the temperature is lowered toward T_g. β values near 0.5 are often observed near T_g for fragile supercooled liquids. A rough correlation has been noted between the value of β and the extent to which the temperature dependence of the relaxation time is non-Arrhenius.[21,22] Generally, systems whose temperature dependences show the largest deviations from Arrhenius behavior also have very nonexponential relaxation functions.

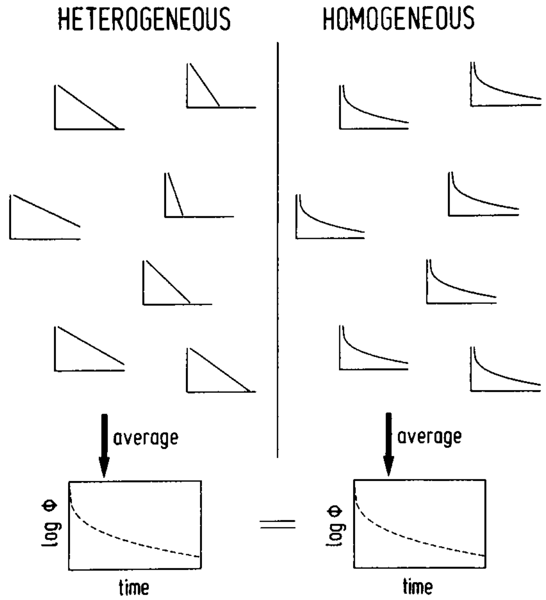

Figure 5. Heterogeneous and homogeneous explanations for a nonexponential relaxation function. Different locations in the figure represent different locations in the sample. Observation of only the ensemble averaged relaxation function cannot distinguish between these explanations. Reproduced with permission from ref 16. Copyright 1994 North-Holland.

State-Dependent Relaxation Properties. Relaxation in the glass transformation range and the glassy state is even more complicated (and more interesting!) than in the supercooled liquid. As shown in Figures 1 and 4b, the thermodynamic state of the system deviates from that anticipated by extrapolations of higher temperature measurements and it is said that "equilibrium has been lost", or in more recent, more sophisticated terms, "ergodicity has been broken".[23] What this means is that molecules have become "stuck" relative to their neighbors so that the volume occupied at the higher temperature tends to be retained, and therefore a change is observed in the system's expansion coefficient. Likewise, the potential energy of the higher temperature configuration is retained (so the heat capacity at lower temperatures is smaller, as shown in Figure 4). It is said that the higher temperature "structural state" has been frozen in. The final frozen-in state has an important influence on the properties of the system at lower temperatures. The freezing-in process occurs in the transformation range; this range may be many tens of degrees in the case of strong liquids.

Such a freezing-in of a structural state during cooling is not unique to liquids and is certainly not a particular consequence of the nonexponential relaxation processes common in liquids. It also happens in ionic and molecular crystals as the defect concentration becomes frozen at some value characteristic of higher temperatures, and it happens in chemical reactions when the barrier opposing the process is too high relative to the thermal energy for any further reaction to occur. However, it is especially noticeable in liquids because of the large changes in heat capacity and other thermodynamic properties which accompany the freezing-in, and it is most noticeable in liquids which have highly nonexponential relaxation functions.

Because this arrest is purely kinetic in nature, a period of waiting at a temperature not too far below T_g will allow the system to catch up with the state that is preferred by the thermodynamic driving forces, so the system will be observed to "relax". This means that any property of the system (e.g.,

S) will show a time dependence. Because relaxation times depend upon the values of properties like S (see eq 5), the rate at which relaxation occurs will also vary with time. Provided T is not too far below T_g, and after sufficient time, all properties will attain values expected from extrapolation of liquid properties above T_g. This process is called "annealing" when it is something which we can manipulate to our advantage (for instance, in stabilizing a refractive index or enhancing mechanical strength), or "aging" when it is happening naturally under conditions in which we would prefer it not to happen at all.

Aging constitutes a serious practical problem in systems which have strongly nonexponential relaxation[24] and T_g not too far above ambient, which unfortunately is the case with many chain polymers used in practical applications.[25] Because of aging, the polymer properties will change over time to the detriment of such things as the original molded dimensions and in some cases the mechanical strength. More will be said of this phenomenology and the factors which control it in a later section.

III. Theories of Viscous Slowdown and the Glass Transition

> "The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade. The solution of the problem of spin glass in the late 1970s had broad implications in unexpected fields like neural networks, computer algorithms, evolution, and computational complexity. The solution of the more important and puzzling glass problem may also have a substantial intellectual spin-off. Whether it will help make better glass is questionable."—P. W. Anderson [*Science* **1995**, *267*, 1615]

Although there have been many attempts to understand the nature of the glass transition, no theory has yet been proposed that captures all the salient features of this phenomenon. Because glass transitions occur in almost all classes of liquids, any complete theory must account for the related phenomena seen in all these different materials. We recognize, however, that the precise nature of some of these phenomena is not clear. For example, we have noted that the viscosity, or any of a wide variety of relaxation times, gets extremely large as the temperature is lowered. We often fit this temperature dependence with the VTF equation (eq 1) or a power law equation:

$$\tau = \tau_0[(T - T_0)/T_0]^{-\beta} \tag{4}$$

One vital issue in all the work on the glass transition is whether equations of this sort predict correctly that these relaxation times actually diverge (i.e., approach infinity) at a temperature which is well above 0 K. Arguments for such an assertion require an extrapolation of the data over what is admittedly a very large range. Even though measurements of a relaxation time τ may extend over the whole practical range of 10^{-10} to 10^4 s, one is still rather far from infinitely long times and, perhaps more relevant, still typically many tens of degrees above T_∞ or T_0, where eq 1 or eq 4 predicts a divergence. The situation is much different for most thermodynamic transitions where one can approach the transition temperature within a fraction of a degree. The fact that relaxation times get so large at temperatures so far above T_∞ or T_0 is a major obstacle for determining the nature of the glass transition experimentally. Thus, it cannot be definitely concluded that there is a divergent time scale in the problem although there are many indications that this may be the case.

In order to provide some framework for this review, we will classify theories according to the temperature regime deemed important by their authors. In this scheme, there are three types of theories. The first assigns a phase transition to a low temperature ($<T_g$) where the viscosity and relaxation times appear to diverge (see eqs 1 and 4). The second class of theory focuses attention on a range of temperature far above T_g. Theories in this class attempt to understand the initial features of the slowing down of the liquidlike processes. As the temperature is lowered, the system passes close to, but not through, a critical point. This narrowly avoided critical point is responsible for the dramatic increase in relaxation times. These theories do not predict a true divergence of time scales below T_g. A third class of theory does not find any temperature of unique importance. All three classes of theory view the *laboratory* glass transition as kinetic in origin.

Theories with Low-Temperature Phase Transitions. Many of the early theories postulated a true phase transition near T_∞ or T_K. Among these were free volume theories which divided the supercooled liquid into solidlike and liquidlike regions.[26] In such models, the free exchange of volume between liquidlike atoms is responsible for the fluid properties. At low temperatures, a lack of free volume leads to large solidlike regions. In these models, the glass transition occurs when the solidlike regions span the entire sample (i.e., at the percolation threshold). In a rival theory, appropriate for polymers, a second-order phase transition was predicted to occur as the number of occupied sites on a lattice became sufficiently large and the configurational entropy vanished.[27] (The configurational entropy is that part of the entropy which is due to configurational rather than vibrational degrees of freedom. It can be calculated by subtracting the entropy of the crystal from the that of the supercooled liquid.) The theory of Adams and Gibbs then explained the temperature dependence of relaxation behavior in glass-forming liquids in terms of the temperature variation of the size of "cooperatively rearranging regions".[28] This leads to

$$\tau = \tau_0 \exp(C/TS_c) \tag{5}$$

where τ_0 and C are constants and S_c is the configurational entropy. If S_c goes to zero at a finite temperature [i.e., $S_c = a(T - T_K)/T$], then one obtains the VTF equation with the identification of the Kauzmann temperature with T_∞. The observation that T_∞ and T_K are often similar lends support to eq 5.

A more recent theory with a low-temperature phase transition computes the number and types of rearrangements necessary to produce macroscopic flow behavior in a liquid made up of very long, thin rods.[29] A VTF law for relaxation times could be obtained by calculating the cooperative motion of rods in a large ring. Still other approaches concentrate on the time dependence of relaxation but couple this with an underlying phase transition below T_g.[32] Other theories argue for a thermodynamic transition at T_∞ by making an analogy with the spin-glass problem where it is known that a true second order phase transition exists.[30,31] Using scaling ideas for the dynamics near the glass transition, it was recently argued that a random first-order transition occurs at low temperatures;[33] the supercooled phase is composed of glassy clusters separated by domain walls. A second, higher temperature is also important in this approach. In this respect, this theory has some similarities with the second class of theory, which we now discuss.

Theories with High-Temperature Critical Points. In recent years, much of the theoretical attention has shifted away from concern with the underlying phase transition concept. This may be because, despite intriguing hints at diverging time scales and susceptibilities (ΔC_p, $\Delta\kappa_T$, $\Delta\epsilon$, etc.) at T_∞[34] and a continuing accumulation of thermodynamic data associating the Kauzmann temperature with T_∞ values[8,14] or their equivalent,[35] there has so far been no success in detecting *directly* a diverging correlation length, or even the diverging susceptibility which is the hallmark of the second-order phase transitions of common experience.

Mode coupling theory provides a way of understanding diverging correlation times in the absence of diverging correlation lengths or susceptibilities.[36−38] The idea is based on a nonlinear feedback mechanism for the density correlations in a fluid. The original work from 1984, now known as the "idealized" mode coupling theory, indicated that there would be a divergence of relaxation times at a temperature T_c. In fact, this does not occur; the T_c predicted on the basis of the first stages of viscous slowdown is greater than T_g. Later revisions of the "idealized" theory argued that the absence of a divergence at T_c could be understood by the existence of secondary couplings which allow activated processes to occur below T_c so that relaxation can continue down to much lower temperatures. This crossover of relaxation mechanisms complicates the observation of critical behavior at T_c, and as a result, there has been much debate in recent years about the experimental evidence for the existence of T_c.

One of the great successes of mode coupling theory has been its prediction of a relaxation scenario consisting of several different, distinct regimes.[39] The quantity calculated by the theory is the normalized density autocorrelation function $\phi(t)$; this function describes the time dependence of the relaxation of density fluctuations of particular wavelengths. $\phi(t)$ first decays via a fast microscopic process which is followed by a power-law decay [$\phi(t) \approx f + A_1 t^{-a}$]. At longer times this decay then crosses over to another power-law regime with $\phi(t) \approx f - A_2 t^b$. Finally, at very long times, the decay appears as the α relaxation, which is described quite well by a stretched exponential $\phi(t) \approx \exp[-(t/\tau)^\beta]$. This sequence of relaxations has been verified experimentally for fragile liquids, and many of the quantitative details of the β_f to α crossover have also been demonstrated, using light scattering[40−43] and neutron scattering.[44,45] The applicability of mode coupling theory to strong liquids has also been discussed.[46,47]

Particularly searching investigations of mode coupling theory have been made using molecular dynamics computer simulations on Lennard-Jones spheres.[48] While some predictions of the theory were found to be inconsistent with simulation results on this fragile liquid, a number of predictions for both the time and temperature dependence were verified for this system.

Recent dielectric relaxation measurements[20,49a] have been interpreted as being inconsistent with mode coupling theory. The electric field couples to the motions involved in the α and β_s relaxations, and the dielectric response shows no sign of a critical temperature in either quantity. In fact, the dielectric data scale for all temperatures above and below the T_c identified with other techniques.[20] The minimum in the susceptibility seen so prominently in the light scattering spectra is hardly visible[49b] or possibly completely missing[49c] in the corresponding dielectric response. This is apparently related to the exceptionally weak absorption of the probe electromagnetic field at far-IR or phonon frequencies.

The major weakness of mode coupling theory is that the idealized theory does not describe real systems below the crossover at T_c. Furthermore, the still-more-complex extended theory has only been supported by scattering experiments on systems in which density fluctuations may not dominate the scattering. In contrast to some claims to the contrary, it is our view that mode coupling theory in its present form is not a useful theory of the laboratory glass transition. It is however a remarkable theory of the initial stages of viscous slowdown for fragile liquids, predicting among other things a complex series of relaxations which has subsequently been observed.

A more recent theory which also relies on an avoided critical point can be motivated by the idea that the preferred local structure in a liquid could give rise to an "ideal" crystal structure except that it is not possible to perfectly fill space by repeating this local structure.[50] For attracting spheres, the ideal crystal structure would consist of an infinite cluster/array of icosahedra. Such a crystal cannot exist in three dimensions since icosahedra do not tile space. Thus, if such a crystal were to start to nucleate, it could only grow to a limited size before it would be frustrated by the inability to fit further icosahedra into the lattice. Nevertheless, clusters of such an "ideal crystal" could start to grow at a temperature above the ordinary melting temperature. For spheres, the ideal freezing temperature would be the important temperature for this theory. In general, the important temperature corresponds to a transition from the disordered liquid to an ordered state. Slow relaxation of the frustrated domains gives rise to the slow relaxation of the supercooled liquid. Reasonable agreement between one model prediction (i.e., the temperature dependence of the viscosity) and experimental data has been demonstrated. Experimental detection of thermodynamic anomalies associated with the avoided critical point or structural evidence for clusters would support the viewpoint taken by this theory. In this theory the behavior of the liquid below the critical temperature is still governed by the critical behavior which is in contrast to the extended mode-coupling theory where a new mechanism is invoked which dominates the dynamics in this temperature range.

A mean field theory has recently been constructed which has a spinodal instability where the system becomes heterogeneous and spontaneously forms clumps.[51] The clump dynamics become arrested at T_g whereas the single particle motion does not. Evidence for such clusters has been found in a 2-d Lennard-Jones molecular dynamics simulation.

It is worth noting that, with one exception,[33] the theories in this class provide no insight into how to resolve the Kauzmann entropy crisis described in section II.

Theories without Dynamic or Thermodynamic Transitions. Finally, we note the possibility of theories without singularities at any temperature. For instance, the simplest possible statistical mechanical treatments of configurational excitation in an initially solid amorphous phase—the classical two-state models[52,53]—account simply (though not quantitatively) for many features of glass-forming liquids (including variable fragility and order parameter freezing). These treatments predict no singularities near T_K in the infinitely slow cooling limit, only a continuous entropy decrease and relaxation time increase. Cooperative versions of these approaches could perhaps model the experiments accurately without invoking singularities at any stage although a rapid drop in c_p would still be needed to avert the entropy crisis. A glass transition would still occur, but merely as a consequence of molecular relaxation times crossing the experimental time scale.

IV. Areas of Current Experimental and Computational Activity

The past decade has witnessed a remarkable increase of activity in this field. Progress has been made in addressing a number of important questions, and we have organized this section in terms of these questions. Naturally, the selection of these particular questions reflects to some extent the authors' prejudices. First, however, it is appropriate to comment on the increased capabilities of experimental methods. Particular progress has been made in expanding the time range of observations which can be brought to bear on "slow dynamics" problems. Because of a lack of space, we will simply list a number of techniques and the time windows which can now be accessed with them: dielectric relaxation[19,20,54,55] (10^{-11} to 10^{+4} s); dynamic light scattering[56−59] (10^{-12} to 10^{+2} s); NMR[60,61,72] (relaxation times from 10^{-11} to 10^{+3} s; diffusion coefficients from 10^{-5} to 10^{-10} cm^2/s); dynamic neutron scattering[62] (10^{-12} to 10^{-7} s); atomistic computer simulations[48,63−65] (10^{-14} to 10^{-7} s); optical probe methods[66−68] (relaxation times from 10^{-12} to 10^{+5} s; diffusion coefficients from 10^{-5} to 10^{-17} cm^2/s).

Is There a High-Temperature Change in Relaxation Mechanism? A quarter century ago, Goldstein argued that diffusion in liquids occurs by different mechanisms at high and low temperatures.[69] In this view, molecules at low temperature move by crossing substantial potential energy barriers (i.e., activated transport or hopping). At high temperatures, thermal energies will be comparable to the barrier heights, and translational motion will have a fundamentally different character (free diffusion). Goldstein used three independent arguments to conclude that the transition from free to activated diffusion should occur when the relaxation time for the shear viscosity is about 10^{-9} s and the viscosity is about 10 P. The idealized mode coupling theory considers only a high-temperature diffusion mechanism. Thus, one can reasonably associate T_c, the temperature at which free diffusion ceases in this theory, with the temperature at which activated processes of various types become important in Goldstein's picture.[70]

The clearest evidence that a change in mechanism occurs at high temperature comes from dielectric and other spectroscopies in the splitting of a single high-temperature relaxation process into the α and β_s processes at lower temperatures (see Figure 3). This pattern was established more than two decades ago.[11] The β_s process can often be given a specific and local molecular origin,[12] while the α relaxation is general and apparently of cooperative origin. The splitting off of the cooperative component is well illustrated in a recent analysis of calorimetric and other relaxation data.[71]

Recent experiments indicate changes in the mechanism of translational diffusion about where Goldstein predicted. At low temperatures, translational self-diffusion in supercooled liquids can have a significantly *weaker* temperature dependence than that of the viscosity or molecular reorientation. Figure 6 shows results for *o*-terphenyl[72] and indicates that a change in the relationship between translation diffusion and viscosity occurs at about 10 Pa•s (=100 P). Results from probe studies on *o*-terphenyl[73] and other supercooled liquids[7,74] are broadly consistent with these trends.

Although these experiments indicate a high-temperature change in relaxation mechanism, they do not provide a direct molecular interpretation. In contrast, computer simulations can provide an extremely detailed view of high-temperature relaxation processes in supercooled liquids. Simulations on atomic liquids provide very strong evidence for a transition from free to activated diffusion.[65,75] At very high temperatures, the simulations indicate that translational motion fits the diffusion equation starting at very short times and very small distances; thus, the motion is accurately described by small-step free diffusion. At lower temperatures, hops from one "site" to another are seen; sometimes correlated motions of 3−4 particles are observed. While these observations from *atomic* simulations match Goldstein's predictions, the evidence from molecular simulations is less clear.[13,76,77] Low-temperature "jumps" are observed, but these jumps often involve reorientation without substantial center-of-mass translation.[13] Thus, for molecular systems, the relationship between activated processes, Goldstein's predictions, and data such as those shown in Figure 6 has yet to be fully established.

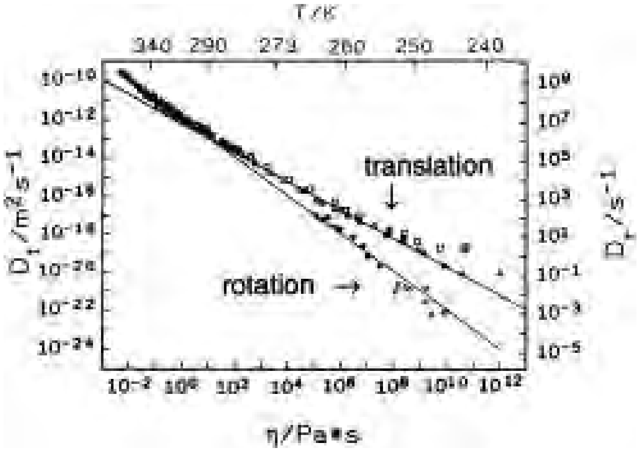

Figure 6. Translational (D_t) and rotational ($D_r = 6/\tau_c$) diffusion coefficients in *o*-terphenyl as a function of viscosity and temperature. Translation: self-diffusion (●); tracer diffusion for two probes (□ and △). Rotation: self-diffusion for deuterated *o*-terphenyl (◆ and ◇). Full lines show $\eta^{-0.75}$ and η^{-1} dependences. Translational diffusion has a weaker dependence on viscosity below 290 K than above. Translational and rotational diffusion have different dependences on viscosity below 290 K. Reproduced with permission from ref 7. Copyright 1994 North-Holland.

Is Mode Coupling Theory a Correct Description of the Behavior of Glass-Forming Liquids? A great deal of recent experimental and computational work has been motivated by this question. Our assessment of the answer has been described in section III. To summarize, mode coupling theory appears to be a remarkable theory of the initial stages of viscous slowdown in fragile supercooled liquids. In our view, it is not yet a useful theory for describing dynamics closer to the glass transition, where the viscosity is many orders of magnitude greater than in the liquid state.

One α Process or Many? To what extent do the observables from different experiments show the same temperature dependence for the α process? Relaxation processes in supercooled liquids will be much easier to understand (although still challenging!) if all processes slow down together. If this is the case, the particular relaxation process probed in an experiment is not so important, and a "universal" explanation of supercooled liquid dynamics will be more likely.

It is certainly the case that different temperature dependences can be observed for various processes if the supercooled liquid has multiple components. This is illustrated in Figure 7, which shows relaxation times for enthalpy, shear, conductivity, and some reorientational process (presumably for the NO_3^- ion), for $2Ca(NO_3)_2{\cdot}3KNO_3$. It is reasonable that the rotation of a nearly spherical ion should occur without structural relaxation of its surroundings. One can also imagine that electrical conductivity is controlled by a small ion which can slip (or hop) through a slowly relaxing structure of larger ions, thus allowing the relaxation time for conductivity to be much shorter than that for shear.[78] Indeed, the existence of "superionic glass" solid electrolytes (currently being used in thin film batteries) depends upon this mechanism.

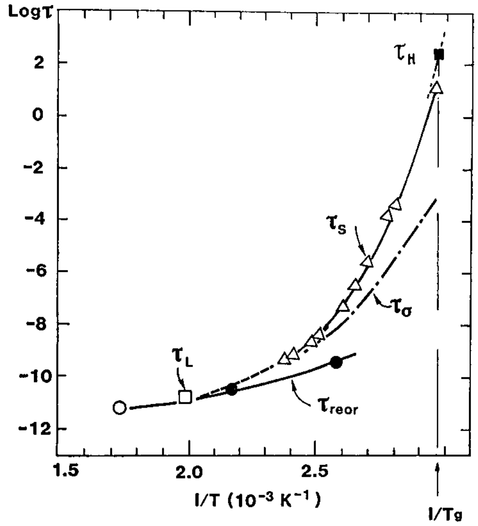

Figure 7. Variation of several relaxation times with temperature in $Ca(NO_3)_2 \cdot 3KNO_3$: longitudinal relaxation time for phonons (τ_L); reorientation time (τ_{reor}); conductivity relaxation time (τ_σ); shear viscosity relaxation time (τ_s); enthalpy relaxation time (τ_H). In this multicomponent system, different relaxation processes show quite different temperature dependences. Reproduced with permission from ref 8. Copyright 1991 North-Holland.

The question of one or many α processes is most relevant to a fundamental understanding of supercooled liquids in the case of single-component systems. Figure 3 shows that four different experimental techniques give very similar results for the α process in *o*-terphenyl. Very nearly this same temperature dependence is also observed for probe molecule reorientation[66] and viscosity[4] over 14 decades in each of these quantities. For this well-studied system and others,[79] the connection between the viscosity and various measures of molecular reorientation seems well established, at least to a good approximation. In some cases, small differences between the temperature dependences of these variables have been interpreted as evidence for a diverging length scale as T_g is approached.[80] Others have criticized this approach, showing that similarly small differences can arise from a temperature-dependent change in the shape of the *distribution* of relaxation times.[79]

How do relaxation times associated with thermodynamic variables (e.g., enthalpy, volume) compare with those for the "mechanical" (molecular rotation and viscosity) variables discussed above? While the notion of a relaxation time associated with the volume, for example, may be unfamiliar, it is simply a characteristic time for the volume to return to its equilibrium value after a small perturbation. Figure 8 shows a comparison between the peak frequencies ($\nu_p \approx (2\pi\tau)^{-1}$, where τ is a relaxation time) observed in dielectric relaxation and specific heat relaxation experiments for four supercooled liquids.[81] In these four cases, excellent agreement is observed between the relaxation time associated with the enthalpy and the dielectric relaxation time (which is closely related to molecular reorientation). In another recent study, it was shown that five fragile liquids had very similar viscosities at the T_g determined by volume relaxation.[4] A good correspondence between relaxation times for shear and volume can be inferred from these results.

One can also ask how relaxation times associated with the structure of a supercooled liquid compare to mechanical and thermodynamic relaxation processes. By "structural relaxation" we mean the process by which a liquid forgets its structure from some earlier time, e.g., the decay of the density autocorrelation function. At high temperatures, where structural relaxation times are on the order of a nanosecond or less, this question can be answered using quasi-elastic neutron scattering. In nonpolymeric liquids, "structure" at high temperatures exists only on time scales short compared to molecular reorientation.[82,83] Unfortunately, at present there are no experiments which directly probe structural relaxation on time scales much longer than a nanosecond (on the relevant length scale of 0.5–10 nm). The appropriate time scales can be probed on longer length scales with visible light photon correlation spectroscopy.[84] X-ray photon correlation spectroscopy probes structural relaxation on the relevant length scales but for the present lacks sensitivity.[85]

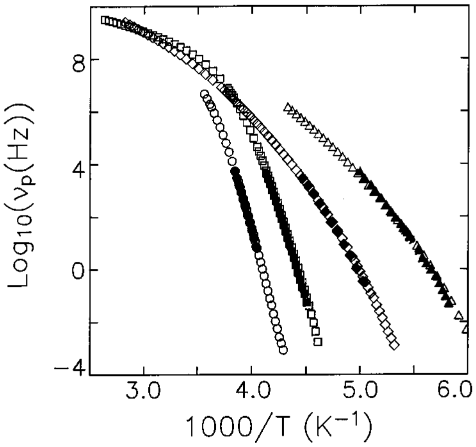

Figure 8. The log of the peak frequency ν_p as a function of inverse temperature for four samples: glycerol (◇), propylene glycol (△), salol (□), and *o*-terphenyl mixed with 33% *o*-phenylphenol (○). The open symbols show dielectric relaxation data, and the corresponding solid symbols show results from specific heat spectroscopy. For these samples, excellent agreement is observed between these two techniques. Reproduced with permission from ref 81. Copyright 1991 North-Holland.

Recent experiments indicate that some relaxation times associated with structure may be considerably longer than the time scale for molecular rotation near T_g. This implies that structural relaxation has a stronger temperature dependence than molecular rotation or viscosity. Optical measurements have been used to show the presence of spatially heterogeneous dynamics in *o*-terphenyl and to estimate the time required for the local environments to reequilibrate.[86] For these experiments, a chromophore similar in size to *o*-terphenyl was dissolved in *o*-terphenyl at very low concentration. Most of the probes were then destroyed by intense laser light. Surprisingly, the probes which survived had rotation times about 40% longer than the average probe rotation time prior to the intense laser illumination, indicating that probes in more mobile environments had been selectively destroyed. As shown in Figure 9, the average rotation time of the remaining probes gradually returned to equilibrium over 100–1000 rotation times. This time can be interpreted as the lifetime for dynamic heterogeneities in *o*-terphenyl. These observations indicate that nonexponential relaxation functions in *o*-terphenyl are at least partly a result of spatial heterogeneity (see Figure 5).[87]

Further evidence for long-lived heterogeneity in supercooled liquids is shown in Figure 6 and in related work.[7,73,74,88] The comparison between rotation and translation allows strong conclusions since both experiments measure single particle correlation functions. The results in Figure 6 indicate that *o*-terphenyl molecules near T_g, on the average, rotate many fewer times in the time required to translate a fixed distance than they do at high temperatures. In contrast, simple hydrodynamics predicts that this quantity is independent of temperature and viscosity. The experimental results can be explained either by

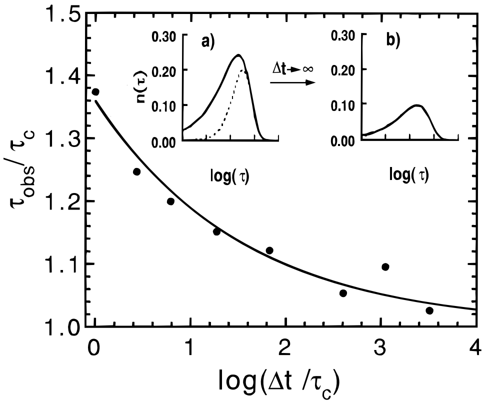

Figure 9. Evolution of probe rotation times in *o*-terphenyl after selective destruction of probes in more mobile environments. Inset (a) schematically illustrates the initial distribution of relaxation times (full line) and the distribution of relaxation times after destruction of some mobile probes. With time, the nonequilibrium distribution returns to equilibrium as shown in inset (b). The main figure indicates that this reequilibration takes 100−1000 rotation times. Thus, for *o*-terphenyl, the nonexponential relaxation function observed in a rotation experiment is partially due to spatially heterogeneous dynamics. Adapted from ref 86.

invoking extremely anisotropic translational motion or, more plausibly, by assuming that the local translational diffusion coefficient is a spatially varying quantity.[7,73,89−91] These results support the view that structure relaxation near T_g occurs on a longer time scale than molecular reorientation.

Are New Length Scales Important as T_g Is Approached from Above? There are several reasons why one might suspect that the answer to this question is "yes". The high apparent activation energies near T_g for molecular motion and viscous flow have often been interpreted in terms of cooperative molecular motion. If this is true, the length scale associated with this cooperativity might be expected to grow with decreasing temperature. If a second-order thermodynamic phase transition underlies the kinetic laboratory glass transition, then a critical length scale for dynamic fluctuations may be observable at temperatures sufficiently close to the phase transition temperature. Likewise, if dynamics near T_g are spatially heterogeneous, the length scales associated with these heterogeneities might provide a new length scale.

Computer simulations and scattering experiments have been used to search for new length scales in *structural* properties. These investigations have not produced any undisputed evidence for a growing length scale with decreasing temperature. For example, in computer simulations, only minor changes have been observed in the pair correlation function $g(r)$ at various temperatures.[92,93] Computer simulations can monitor more exotic correlations which are not directly observable in experiments. These simulations have typically used soft spheres which might approximate the behavior of liquid argon. Early work indicated increasing icosahedral ordering as the temperature was lowered below T_m;[94] in one case, an apparent divergence at T_g was reported.[95] More recent simulation work has contradicted the report of divergence.[93] Very recent direct spatial imaging of colloidal glasses supports the conclusion that there is no increasing length scale associated with icosahedral ordering at low temperatures.[96] Light scattering experiments of supercooled liquids have uncovered no dramatic changes in scattering intensity as a function of temperature;[97] such changes would have indicated a significant change in molecular ordering. Small-angle X-ray scattering on *o*-terphenyl has shown only statistical density fluctuations near T_g on length scales from 3 to 25 nm, providing no evidence of a new length scale in this range.[98] Low-angle neutron scattering has likewise found no structure growing on these length scales.[99]

Dynamic properties have also been investigated in an effort to find a new length scale. Although initial experiments[100] indicated that such a new length scale might be sensed by the diffusion of small spheres (10−100 nm) in supercooled liquids, more complete measurements showed that the diffusion of such spheres is well predicted by the macroscopic viscosity.[101] Unfortunately, even 10 nm spheres diffuse so slowly that such experiments cannot be performed near T_g. Very precise dielectric relaxation measurements on a variety of liquids have been interpreted as possibly indicating a diverging length scale near the Kauzmann temperature T_K.[34] Although based on observation of dielectric data covering more than 14 orders of magnitude in frequency, this prediction necessarily involves a considerable extrapolation in frequency and temperature.

Some experiments indicating slow structural relaxation were described in the previous section. What are the length scales associated with these structures, and does this length scale increase with decreasing temperature? NMR spin diffusion experiments on amorphous polycarbonate indicated mobile regions roughly 3 nm in size at $T_g + 50$ K.[102] Light scattering[103] and calorimetric[104] measurements performed on nonpolymeric liquids during temperature scanning have been reported as indicating dynamic heterogeneities of roughly this size at T_g. A similar length scale has been inferred for *o*-terphenyl at T_g on the basis of probe rotation studies.[66] It is possible that all these observations are fundamentally due to an increasing time scale (the structural relaxation time relative to viscosity or molecular reorientation) as opposed to an increasing length scale.[86] They provide no clear evidence of a *new* length scale near T_g.

Evidence of density fluctuations on a new, very large length scale (20−200 nm) has been detected by visible light scattering.[98,105] In some cases, these fluctuations relax very slowly on time scales 10^4−10^7 longer than the α relaxation. The relationship between these fluctuations and the glass transition is not clear. In *o*-terphenyl, molecular reorientation near T_g has been shown to be insensitive to their presence;[106,107] for this system, the implication is that these fluctuations have little to do with the glass transition. These large length scale fluctuations have been implicated in transmission losses in polymeric optical fibers.[108]

Relaxation in the "Frozen" State—Is It a Contradiction? All of the above discussion has referred to supercooled liquids which we defined earlier as systems in metastable states, i.e., states in which the properties are independent of time. Supercooled liquid properties depend only on T and P for a single-component system, so long as a crystal nucleus does not form. Is there anything useful that can be said about the properties of this same collection of molecules when the temperature has dropped below the glass transition temperature, causing the structure to become at least partly frozen; e.g., has it become truly trapped in some thermodynamically unstable state? It would be nice if the answer could be "yes" because so many of the "plastics" we use in our technological society are noncrystalline substances which are below their T_g's at room temperature—but not so far below that they are truly frozen like optical glasses. Unfortunately, unless they have been engineered to be largely crystallized, the properties of these plastics are usually changing slowly with time—which, for engineering materials, is a very undesirable way to behave. For example, this is why an old plastic ruler has a different length than one that is newly made. Fortunately, much of this time-dependent behavior can be described more or less quantitatively using quantities which have been measured in the metastable state. This is quite a complex subject, but its essentials can be understood in fairly simple terms.

The key is to appreciate the role of the structural disorder in controlling rates of processes in both liquids and glasses. For instance, it has already been pointed out that the non-Arrhenius behavior of most liquids can be attributed to the increase in structural disorder (as opposed to vibrational disorder) which occurs with increasing temperature above T_g. With some provisos, the fragile liquids are those with rapidly changing configurational entropies. This idea is captured in the Adam–Gibbs equation (eq 5) for liquid relaxation processes which fortunately also provides a basis, the best we currently have, for understanding the out-of-equilibrium behavior. Consider a system far below T_g in which the configurational entropy S_c is frozen. If the response for which τ is the relaxation time can still be measured, then the Adam–Gibbs equation predicts that an Arrhenius law should apply. It predicts, furthermore, that the Arrhenius activation energy will depend on the frozen-in entropy. Figure 10 shows that the prediction of Arrhenius relaxation below T_g is fulfilled for three different properties in three different systems.[109–112] The "fictive temperature", a quantity much used by glass scientists in the description of out-of-equilibrium states, is defined as the temperature at which the value of S_c of the glass would be its equilibrium value.

If the temperature is only a little below T_g, S_c will change in time as the structure evolves toward equilibrium. In this case, the system properties will change with a time-dependent τ which can be predicted if the time evolution of S_c is known. Since the time dependence of S_c is itself a structural relaxation process governed by eq 5, the ingredients are in place for a general treatment of far-from-equilibrium, i.e., nonlinear, relaxation.[35] The relaxation of glasses formed by quenching of liquids, and of glasses of the same substance made with much higher excess entropies by a vapor deposition process, has been shown to be well described by this approach. This is also the basis of an important modification[22,113] of the Tool–Narayanaswamy–Moynihan[114] analysis of out-of-equilibrium relaxation. The fictive temperature of the latter is replaced by the frozen-in entropy in the former. An interesting aspect of this development is that the quantity S_c needed to describe the nonlinear aspect of the process is itself a quantity determined from equilibrium measurements. An excellent review of this subject has been given recently.[35]

A question of interest which can be answered by out-of-equilibrium measurements concerns the dependence of the nonexponentiality parameter β of eq 3 on the liquid structure (as distinct from a dependence on some coupling determined by absolute temperature). In metastable state measurements, fictive temperature and absolute temperature are the same, and the two change simultaneously. Both mechanical[115] and dielectric[116] studies of out-of-equilibrium behavior of glasses in which the relaxing structure is one characteristic of a higher temperature appear to be described by the β value for the higher temperature equilibrium system. This suggests that the β value is determined by the structure directly and presumably related to domain size distributions or microheterogeneities as various authors have suggested.[18,86,103]

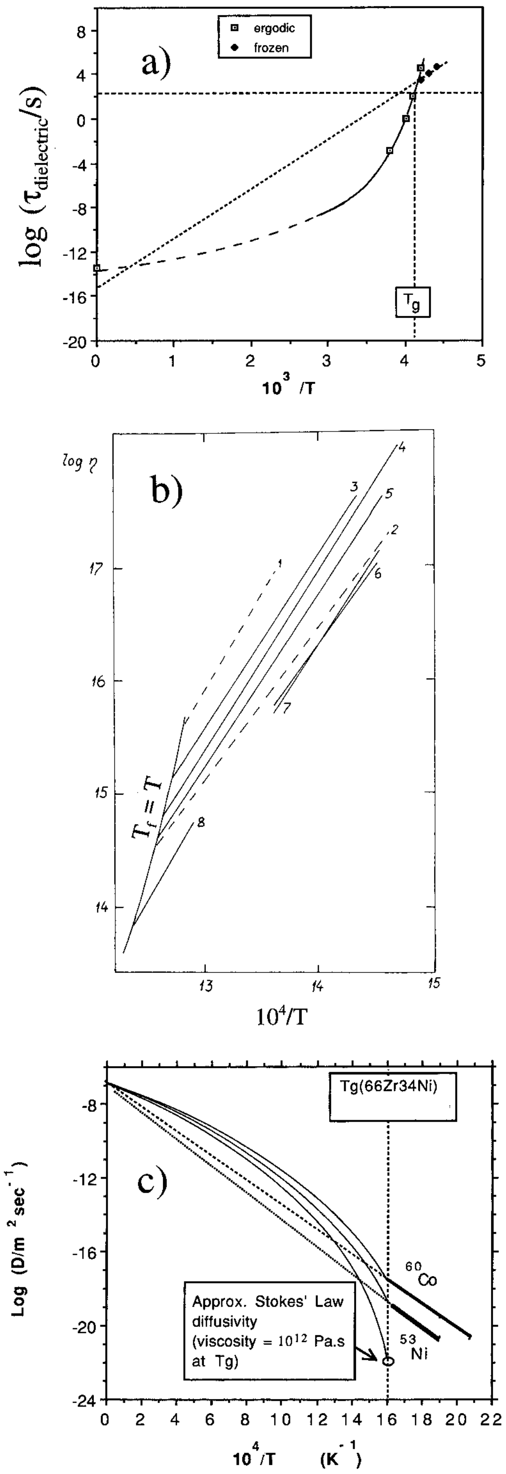

Figure 10. Effect on relaxation and transport properties of freezing the structure at T_g. In each case, properties are well described by an Arrhenius temperature dependence below T_g. (a) Dielectric relaxation times in poly(vinyl methyl ether); from ref 109. Enthalpy relaxation data show similar behavior.[109] (b) Shear viscosity in window glass (Na_2O–CaO–SiO_2). The line labeled $T = T_f$ indicates the behavior of the equilibrium supercooled liquid. The numbers indicate glass preparations with different fictive temperatures. From ref 110. See also ref 111. (c) Tracer diffusivities of ^{60}Co and ^{53}Ni in the metallic glass Zr_{50}-Ni_{50}. The value of T_g for this composition is uncertain; the value for $Zr_{66}Ni_{34}$ was used in the construction of the figure. Both diffusivities are quite high at T_g. This behavior is closely related to the enhanced transport of some ionic species in "superionic" glasses (see discussion of Figure 7). Data from ref 112.

Boson Peaks and the Correlation of Early Time and Long Time Dynamics. Another benefit of out-of-equilibrium studies of glassy dynamics has been the attention it has brought to possible links between very short time and very long time dynamics. For instance, it has been suggested on the basis of measurements on glass formers of different fragilities that the behavior of a controversial low-frequency vibrational mode, or group of modes, known collectively as the "boson peak" is predictive of the fragility.[117] The boson peak is determined by neutron or Raman *inelastic* scattering studies[117,118] and is located in the range 10−60 cm^{-1}. Systems with strong boson peaks which can be observed even above T_g tend to be those with "strong" liquid character; fragile glass formers have weak boson peaks which can only be observed below T_g. The origin of the boson peak is poorly understood. However, it can be seen in molecular dynamics studies of glasses of simple constitution, e.g., SiO_2.[119] Since the eigenvectors associated with these modes can in principle be identified by dynamical matrix analyses, it will presumably not be long before they will be well characterized. There is a strong suggestion that these modes are also closely linked to the cryogenic anomalies of glasses that have received so much attention from the physics community over the two decades since the discovery that glasses violate the Debye T^3 law.[120] Since the fragility of glass formers is also generally correlated with both the nonexponentiality of relaxation and the nonlinearity of relaxation, there now seems to be some possibility that key characteristics of the slow relaxing liquid and glassy systems might be at least qualitatively predicted from proper determinations of the characteristic dynamics in the first few picoseconds.

Other Recent Developments. Almost undiscussed in the article so far is the behavior of metastable liquids and unstable glasses under conditions of high compression. There is growing evidence that liquid properties might be very sensitive to the molecular packing conditions. At this time it is not known whether liquids which are extremely fragile at atmospheric pressure owe their fragility to structural factors which would be affected by compression. However, the possibility exists that a canonical behavior for glass formers exists which will be discovered only by systematic measurements under conditions where the product PV becomes of the order of the intermolecular attractive potential. That is, by comparing liquids at different pressures, it may be possible to superpose the relaxation properties of all liquids onto a single curve in Figure 2. The exploration of this question has now become possible with the development of diamond anvil cell techniques capable of studying extreme pressure properties. Already there have been reports on structural relaxation from Brillouin line width studies[121] and nuclear spin−lattice relaxation from NMR studies,[122] as well as direct viscosity measurements[123] above 5 GPa, and much more activity in this important area may be anticipated in the near future.

Recent dielectric relaxation work suggests that relaxation functions from various liquids may have universal features. A scaling procedure has been found empirically that allows the collapse of the dielectric data from one sample on top of that from another.[20,81] The data, for all measured temperatures for a series of simple glass-forming liquids, can be successfully superposed onto a single "universal" curve. This superposition is possible, however, only when the ordinate and abscissa used in the scaling procedure are somewhat complicated functions which include a dependence upon the width of the dielectric dispersion. (There have been some suggestions that the scaling does not work for all liquids.[49a] This is as yet still unclear.[124]) It is evident from this scaling procedure that none of the functional forms that have been suggested in the literature can fit the data over its entire range. There is, as yet, no adequate explanation for the existence of this master curve or for the unconventional scaling procedure that was used to bring the data onto a single curve although there have been some efforts in this regard.[125]

A number of recent investigations have examined experimental systems which might serve as models for the supercooled and glassy states of liquids. Some orientationally disordered crystals (called "glassy crystals" by Seki and co-workers,[126] who first recognized their relation to normal glasses) show nonexponential relaxation functions, non-Arrhenius relaxation times,[127] and the same strong/fragile pattern discussed in section II.[128] Thus, randomness in translational degrees of freedom is not an essential requirement for this behavior. Suspensions of ≈1 μm colloidal spheres can be viewed as models for atomic liquids and glasses. These systems can be studied both by standard methods[129] used on molecular systems and by optical microscopy.[96] The latter provides direct visualization of particle motion in three dimensions. The interactions between the spheres can be systematically altered by changing their surface charges and the solvent. Work on these relatively simple systems may provide critical insights into relaxation processes in molecular and polymeric liquids.

V. Concluding Remarks

The past decade has been one of tremendous vitality for the study of supercooled liquids and glasses. New experimental techniques have been developed, and the time windows of several existing methods have been significantly increased. Likewise, the power of computer simulations has increased dramatically, to the point where simulations are beginning to provide quite definitive tests of certain types of theoretical models. New theoretical ideas have also come to the forefront. The introduction of mode coupling theory and other theories which invoke high-temperature critical points has, to a certain extent, shifted attention away from the laboratory glass transition to the initial stages of viscous slowdown.

This is an exciting field with a long history and a rich phenomenology. The problems are complex, and major issues are not easily sorted out. As an illustration of this, we mention that, even among the present authors, there is not complete agreement about the importance of the mode coupling theory. Some of us are not convinced that focusing on the initial stages of viscous slowdown will eventually lead to an adequate description of the laboratory glass transition. We hope that this review has conveyed the impression that recent discourse on this and other issues in the field has been intense and spirited.

Much of the excitement and interest of the past decade is due to the enormous progress made in increasing the power of relevant experimental tools. Because dynamics in supercooled liquids and glasses span an extremely wide range of time scales (more than 17 decades), the development of new experimental methods and the improvement of existing ones must surely continue to play a crucial role in this field. With further development, we expect X-ray photon correlation spectroscopy to provide critical information about structural relaxation near T_g. Extremely high-pressure measurements can similarly be expected to advance our understanding of these relaxation processes.

What scientific issues will galvanize activity in this field in the next decade? At the risk of looking foolish in retrospect, we mention several areas as candidates for special attention. The strikingly different temperature dependences for rotational and translational motion in supercooled liquids will certainly be more fully explored. This observation may be linked to the study of heterogeneities in the liquid. Recent experimental evidence has indicated the importance of such heterogeneities as the viscosity becomes large. Experiments using a wide range of techniques will likely test these results and attempt to characterize the size and nature of the observed heterogeneities. Another possible focal point may be the issue of whether relaxation functions in supercooled liquids have universal features. In this vein, work will probably continue on model systems, which are more easily studied theoretically and which can be seen as analogous in some respects to structural glasses. One example of such a system is the spin glass for which a Hamiltonian and an order parameter for the spin-glass transition exist. Such work should help to clarify the role of thermodynamics in glass transition phenomena.

Relaxation in liquids and glasses is one of oldest and most thoroughly studied (yet unsolved!) problems in condensed matter physics and chemistry. Our predictions about the future paths of development in this area may or may not be correct. Even so, we have no doubt that this field will have an exciting and productive future with many intellectual advances resulting from the rich interplay of theory, simulation, and experiment.

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References and Notes

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