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Relaxation in glassforming liquids and amorphous solids

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Abstract

The field of viscous liquid and glassy solid dynamics is reviewed by a process of posing the key questions that need to be answered, and then providing the best answers available to the authors and their advisors at this time. The subject is divided into four parts, three of them dealing with behavior in different domains of temperature with respect to the glass transition temperature, T_g , and a fourth dealing with “short time processes.” The first part tackles the high temperature regime $T > T_g$, in which the system is ergodic and the evolution of the viscous liquid toward the condition at T_g is in focus. The second part deals with the regime $T \sim T_g$, where the system is nonergodic except for very long annealing times, hence has time-dependent properties (aging and annealing). The third part discusses behavior when the system is completely frozen with respect to the primary relaxation process but in which secondary processes, particularly those responsible for “superionic” conductivity, and dopant mobility in amorphous silicon, remain active. In the fourth part we focus on the behavior of the system at the crossover between the low frequency vibrational components of the molecular motion and its high frequency relaxational components, paying particular attention to very recent developments in the short time dielectric response and the high Q mechanical response.

Keywords

Amorphous solids, Annealing, Liquid solid interfaces, Viscosity, Amorphous metals, Amorphous semiconductors, Dielectric response, Glass transitions

Disciplines

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APPLIED PHYSICS REVIEWS

Relaxation in glassforming liquids and amorphous solids

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The field of viscous liquid and glassy solid dynamics is reviewed by a process of posing the key questions that need to be answered, and then providing the best answers available to the authors and their advisors at this time. The subject is divided into four parts, three of them dealing with behavior in different domains of temperature with respect to the glass transition temperature, T_g , and a fourth dealing with “short time processes.” The first part tackles the high temperature regime $T > T_g$, in which the system is ergodic and the evolution of the viscous liquid toward the condition at T_g is in focus. The second part deals with the regime $T \sim T_g$, where the system is nonergodic except for very long annealing times, hence has time-dependent properties (aging and annealing). The third part discusses behavior when the system is completely frozen with respect to the primary relaxation process but in which secondary processes, particularly those responsible for “superionic” conductivity, and dopant mobility in amorphous silicon, remain active. In the fourth part we focus on the behavior of the system at the crossover between the low frequency vibrational components of the molecular motion and its high frequency relaxational components, paying particular attention to very recent developments in the short time dielectric response and the high Q mechanical response. © 2000 American Institute of Physics. [S0021-8979(00)02213-1]

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INTRODUCTION

The understanding of noncrystallizing liquids and the formation of glasses by viscous slowdown at temperatures near $2/3$ of the melting point, is currently seen as a major intellectual challenge in condensed matter physics. The amorphous products of this slowdown process in polymers, ceramics, and metallic systems provide a variety of important materials which are, in many cases, already in widespread use. In other cases, they offer exciting possibilities for the future. Amorphous solids formed by other more exotic routes, and their relation to liquid-formed glasses, are likewise under intense study.

The task of this workshop team was to define the range of problems which is impeding the full understanding of this rather broad range of materials.

In our considerations, both for reasons of time and of the expertise of those involved, we had to omit some important aspects of the subject. For instance, while no one would deny the essential need for proper theory of this phenomenology, nor the considerable excitement, not to say controversy, generated by recent developments in the theory of moderately viscous liquids, we do not seek to define the status of theory in this area. Rather we felt it more appropriate to define the key aspects of the phenomenology which must ultimately be successfully addressed by theorists.

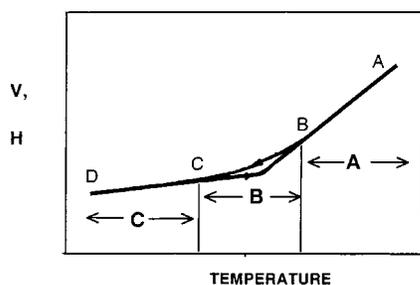


FIG. 1. Definition of the regions of glassformer phenomenology A, B, and C defined in text based on the variation with temperature of extensive thermodynamic properties such as volume and enthalpy during heating and cooling cycles without annealing. In domain A, the system is in internal equilibrium at all temperatures. In domain B, it is relaxing during the experiment, and in domain C, it is totally frozen except for secondary relaxations.

Likewise we did not attempt to address the subject of electronic conduction in semiconducting or metallic glasses. Rather the focus was on the nature of atomic and molecular motion in the amorphous phase and the manner in which it determines the responses of viscous liquids or glasses to various perturbations. In other words we focused on the subject of relaxation. And within the field of atomic motion and relaxation we deliberately did not address that major aspect of the subject which involves the relaxation of the system out of the liquid state into the stable crystalline state.

A good coverage of both of these excluded areas, as well as much information on topics we do consider, is contained in the recent monograph “Metastable Liquids” by Debenedetti (Princeton University Press, 1996).

THE SCOPE OF THE PROBLEM: SUBDIVISIONS

Research in the general area covered by the description “Glasses and Glassforming Liquids” tends to divide up into subareas which are distinguished by the relation of the temperature range covered to the glass transition temperature T_g . To define these subareas, we refer to the canonical glass-science diagram Fig. 1, which illustrates the variation of the volume of a glassformer as it is cycled from liquid to glassy state and back to liquid. We define first a subarea A by the temperature range in which the properties of the system have no history dependence; i.e., the system is always ergodic—except with respect to crystal formation.

A second subarea is that defined as C in Fig. 1 in which interest is focused on the properties of systems which are truly frozen (truly “glassy,” if formed from an initial liquid state). Unless prepared by an atypical method, a glass in region C will show behavior which is essentially reversible with respect to temperature changes unless the temperature excursion crosses the area boundary at point C (although the location of point C depends on time of exposure). In subarea C, however, the properties of the system depend strongly on the initial path taken into the glassy state; i.e., on what happened with respect to time and temperature during the initial passage from temperature range AB through BC to CD—if the glass was formed by liquid cooling. In many interesting cases, the glassy state under study in range C will have been

accessed without ever being a liquid, in which case the properties will depend on the precise mechanism by which it was formed (unless some carefully controlled exposure to the range BC has been imposed to “erase the memory” of the formation route).

A third area is that defined as B in Fig. 1, in which researchers are specifically interested in the difficult temperature range BC. Here not only do the properties depend on the arrival pathway into the region but also on the duration of the actual measurement. This is because, so long as the system does not recover the equilibrium state, it is subject to continuing evolution—called relaxation—at all stages of whatever measurement is being performed. This is an important region to understand but also one where difficulties are considerable, at both the experimental and theoretical levels.

The organization of this review will follow the above-outlined division of interest, although not in the order in which they were introduced. Rather, the order will be the order of increasing departure from equilibrium, i.e., $AB \rightarrow BC \rightarrow CD$. The sections and contents in brief will be as follows.

A. Glassformers in internal equilibrium

The review of area A will be subdivided into three major sections, the first dealing with the temperature dependence of transport properties or relaxation times. The second will deal with the frequency dependence and nonexponentiality of relaxation processes. The third section will address the recently discovered complex behavior in some systems in which more or less sudden transitions from one type of behavior to another, including first order phase transitions, occur within the liquid. This relates to the subject of polyamorphism recently discovered in the glassy state.

B. Relaxing glassformers out of equilibrium

This section will be divided into two sections, according to how far below the onset of range BC the studies are conducted:

- (1) near and somewhat below T_g : structural relaxation, annealing and aging,
- (2) rather far below T_g : constant structure relaxation and its implications.

C. Dynamic processes in amorphous solids

This section will deal with motion of mobile species in otherwise fully frozen glasses.

D. Short time dynamics

This special section will address the problems posed by recent studies of very short time events reflected in studies of Boson peaks, Debye–Waller factors, and localization studies.

Within each of these sections, we have recognized a number of questions regarding the phenomenology which need to be addressed, and give in each case the best answer

we can provide from our own resources. In some cases, the best answer is “we don’t know,” and we try to be brief about saying it.

The review will take an unconventional form. In each section, we issue a challenge to current and potential workers in the field in the form of a series of questions which we feel cut to the core of the phenomenology. The questions are posed at the beginning of the section and are followed by a narrative account of that aspect of the phenomenology which is intended to contain answers to the questions as far as they can currently be given within the reviewers’ knowledge. The incompleteness of the narrative will measure some combination of the state of the field in that area and the ignorance of the reporting authors.

The questions that arose, and which are partially answered below, can be arranged by the relaxation domains shown in Fig. 1.

Domain A: Internal equilibrium

A.1. The temperature dependence of the average relaxation time for various types of perturbations, and probes

- A.1.1. What are the most appropriate measurements for characterizing the temperature dependence?
- A.1.2. What equations have been used and how good a job do they do? Is there a pattern to the failure of the Vogel–Fulcher (VF) equation? Does it fail in a systematic way for different relaxing perturbations?
- A.1.3. Does the VF equation apply better for the relaxation time than for the related transport property? (The former is usually taken as the most probable relaxation time while the latter is determined by the average relaxation time: in general they will not have the same temperature dependence.)
- A.1.4. Is the VF equation worse or better for individual probes; e.g., large rotators (Ediger) that sample a large region within the liquid; or are such probes always slaved to the liquid suspending them? What are the dangers of probe measurements? Which are the most interesting types of probes? To what extent are probes a substitute for neutron scattering q -dependent studies? How important to this temperature dependence problem is the q dependence of the property under study? Are the probes detecting growing lengthscales near T_g ?
- A.1.5. How do the properties of high temperature inorganic systems compare with those of low temperature molecular liquids? What are the chemical/structural factors that determine

whether a liquid of a given class (molecular, metallic, ionic, and covalent) will exhibit a large or a small deviation from Arrhenius law?

- A.1.6. Is there a change of relaxation mechanism at high temperatures?
- A.1.7. What scaling relations can help rationalize the observations?
- A.1.8. What is the relevance of the “energy landscape?”
- A.1.9. What are the circumstances under which the relaxation of a given species in the viscous liquid can become much faster than the host? Examples: gases in liquid polymers, small ions in silicate glasses and liquid superionic glasses in general; small atoms, and/or metalloids in liquid metallic glassformers? Which are the chemical types, or structural types, which lead to such behavior?

A.2. How and why does the relaxation function differ from an exponential?

- A.2.1. What is the most appropriate and economical form for describing the deviation?
- A.2.2. How does the stretching exponent vary with temperature? Are there systems in which time–temperature superposition (TTS) really works? What distinguishes these cases from other liquids (or other perturbations of the same liquid)? How should the vertical shifts needed to obtain TTS be interpreted? Where do secondary relaxations fit into all this? What is it that makes it possible for some systems like normal alcohols to have non-Arrhenius relaxation times but exponential relaxation? Are there any systematic differences between polymers and nonpolymeric liquids in the above respects?
- A.2.3. How does stretching differ for different relaxing properties?
- A.2.4. Are there any other approaches to this problem area?
- A.2.5. What is the relation of “susceptibility spectroscopy” to “modulus spectroscopy?” Do such differences depend on whether or not TTS is violated?
- A.2.6. What is the relevance of domain structures and their temperature dependence to this problem? Are the inhomogeneities growing in length scale with decreasing temperature?

- A.2.7. How can the Adam–Gibbs equation be consistent with stretched exponential relaxation?
- A.2.8. How can spectral broadening effects due to composition fluctuations be separated from that due to intrinsic stretching?

A.3. Are there systems that fall outside the pattern of behavior under which the “normal glassforming systems” are discussed?

- A.3.1. What is polyamorphism?
- A.3.2. Where does amorphous silicon fit in?

Domain B: Out of equilibrium, relaxing

B.1. Not far below—nonlinear relaxation, annealing, aging

- B.1.1. What are the current approaches to the nonlinear relaxation problem?
- B.1.2. How serious is it in each of the above to neglect variation of β , the stretching parameter, with T , when we know in some cases it is changing?
- B.1.3. Is there any conceptual or analytical advantage of the Tool–Narayanaswamy–Moynihan approach over the Scherer–Hodge approach?
- B.1.4. What are the best conditions under which to critically compare alternative models?
- B.1.5. How well do we understand the τ_{eff} paradox these days? Is the “expansion gap” a consequence of incomplete modeling or merely inadequate data?
- B.1.6. Is the description of relaxation *far* from equilibrium our biggest problem?
- B.1.7. Can nonlinearity be correlated with any other canonical glass characteristics? Can microscopic heterogeneity be invoked to explain nonlinear effects?
- B.1.8. Can nonlinear effects be much more pronounced for some relaxing variables than for others? Are the differences systematic in any way?
- B.1.9. Are there any systematic relations between fast relaxing and slowly relaxing perturbations? Is entropy relaxation always the slowest? Is shear relaxation always faster than bulk relaxation in the nonlinear regime?

B.2. Rather far below T_g (where relaxation occurs at more or less constant structure)

- B.2.1. What is the temperature dependence of relaxation at constant structure?
- B.2.2. What is the relation of β , the stretching parameter, under constant structure conditions far from equilibrium to β measured when structure is equilibrated; i.e., is β simply an index of structure, hence of fictive temperature?
- B.2.3. Is the relation between bulk and shear relaxation very different under “constant structure” conditions? Are there special differences between “strong” and “fragile” glassformers under these conditions? What are the best techniques for examining the kinetics of relaxation at constant structure?

Domain C: Very far below T_g (primary relaxations completely frozen: only decoupled motion is possible). Dynamics in glasses

C.1. What types of processes remain active in the glass when the α relaxation has been completely frozen?

C.2. What is the source of the high ionic conductivity seen in some glasses?

- C.2.1. What is the theoretical maximum conductivity?
- C.2.2. What are the physical and chemical factors which determine whether ions will migrate freely through the structure?
- C.2.3. What is the nature of the “constant loss” in glassy relaxation spectroscopy?

C.3. Is there a similar decoupling possible for nongaseous elements in the so-called met-glasses (metallic alloy glassformers)?

C.4. What about gas molecules in glasses and polymers?

C.5. What about decoupling of water molecules in biopolymers?

C.6. What about dopant elements in amorphous silicon?

C.7. What is the relation between secondary relaxation in glasses due to fast-translating species, on the one hand, and nontranslating entities (e.g., side chains) on the other?

C.8. Other questions

- C.8.1. Can comparisons of *dielectric relaxation* of small dipolar molecules in molecular or polymer glasses, and of ions in ionic glasses, throw light on the origin of nonexponential relaxation in ionic glasses; e.g., does CO in o-terphenyl (OTP) give a nonexponential relaxation like Na^+ in $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$?
- C.8.2. Can we compare *mechanical* relaxation due to small atoms in met glasses, small molecules in polymers, and small ions in ionic glasses?
- C.8.3. What is the relation of the high frequency constant loss in conducting glasses to the high frequency loss in dielectric relaxation, given that the first is a secondary relaxation and the second one a primary relaxation?

Domain D: Short time dynamics

D.1. Boson peaks in raman and neutron scattering

- D.1.1. How good are the data?
- D.1.2. Is there a correlation of Boson peaks with strong/fragile behavior in the longer-time properties?
- D.1.3. Is there a correlation with the structural features responsible for the first sharp diffraction peak (FSDP)?
- D.1.4. Do Boson peaks measure cluster dynamics or cage rattling dynamics?
- D.1.5. Are there relaxation dynamics at time earlier than the Boson peak?

D.2. Extrapolated breaks in the Debye–Waller factor versus temperature plot—what do they signify? Are they related to FSDPs?

D.3. What is vibrational localization? What special dynamical characteristics are associated with localized modes? And how might it be related to relaxation? Are there fractal dynamics in disordered but Euclidean structures? How helpful are photon echo studies?

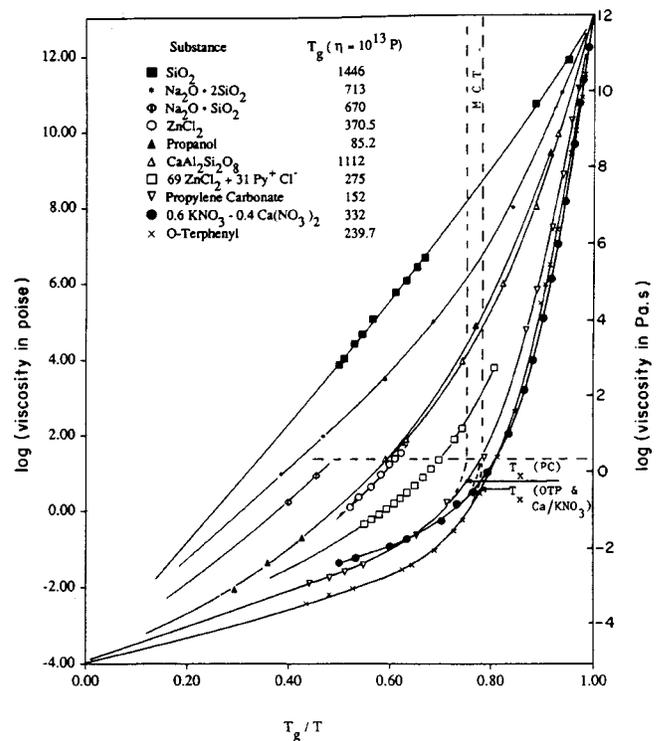


FIG. 2. T_g scaled Arrhenius plots for viscosities of different glassforming liquids showing spread of data between strong and fragile extremes. Predictions of mode coupling theory power law are shown by dashed line for two cases. Inset shows the pattern of behavior obtained by varying the D parameter in the modified Vogel–Fulcher equation, Eq. (6).

D.4. What is the decay time for the FSDP in relation to the wave vector Q_0 , at the peak of the structure?

D.5. What are the newest, and most important steps forward?

A. RELAXING GLASSFORMERS IN INTERNAL EQUILIBRIUM

A.1. The temperature dependence of transport constants and relaxation times for various types of perturbations and probes

A.1.1 Relevant measurements

(What are the most appropriate measurements for characterizing the temperature dependence?)

Liquids of all classes, now including even liquid metals, have been extensively characterized with respect to the temperature dependence of their transport properties and their relaxation times down to, and often below, their T_g . The transport properties studied have been mainly viscosity η to a lesser extent diffusivity D , and also conductivity σ , where appropriate.¹

The relaxation times studied have been dielectric τ_D ,² longitudinal τ_1 , and sometimes shear mechanical τ_s relaxations,³ and (with modeling) nuclear spin lattice correlation $\tau_{c,n}$, and electron spin correlation $\tau_{c,e}$.⁴ Recently, en-

thalpy relaxation times τ_H ,⁵ both by frequency domain^{5(a)–(c)} and time domain^{5(d)–(f)} measurements, have been added. With very few exceptions, these properties have been found to, deviate more or less strongly from the Arrhenius behavior familiar in most physical processes. The pattern of behavior is best seen by plotting the data for viscosity, etc. or relaxation on a scaled Arrhenius plot using the temperature of some common high value of the viscosity (e.g., 10^{13} P), or T_g itself, as the temperature scaling parameter. An example is given in Fig. 2.⁶

A.1.2. Mathematical representations

(What equations have been used and how good a job do they do? Is there a pattern to the failure of the VF equation? Does it fail in a systematic way for different relaxing perturbations?)

The deviations from Arrhenius behavior seen in Fig. 2 have been described by a wide variety of equations, all of which fit selections of the data rather well. Some have stronger theoretical bases and more predictive utility than others do. A selection of such equations is presented below, along with references to their origins where theoretical foundation or empirical basis can be found.

(i) For simple liquids and computer simulated systems with density linear in absolute temperature, T see^{7–9}

$$\tau = A + B(T - T_0)^{-1}. \quad (1)$$

(ii) For supercooled water¹⁰ and liquids in the highly fluid to moderately viscous regime (theoretical results from mode coupling theory¹¹)

$$\tau = A([T - T_0]/T_0)^{-\gamma}. \quad (2)$$

(iii) For light oils and normal alcohols¹²

$$\tau = A \exp(E_a/RT). \quad (3)$$

(iv) For all liquids^{13,14}

$$\tau = A \exp(E/RT^2). \quad (4)$$

(v) For molecular glassforming liquids¹⁵

$$\tau = A \exp(B/T^3). \quad (5)$$

(vi) For all liquids (see Vogel,^{16(a)} Fulcher,^{16(b)} Tammann and Hesse,^{16(c)} Cohen and Turnbull.¹⁹ Equation (6) is mathematically equivalent to the Williams–Landel–Ferry equation^{17,18} which is constructed to eliminate the pre-exponential term of Eq. (6) and deals only with the temperature dependence

$$\eta = A \exp(B/[T - T_0]) = A \exp(DT_0/[T - T_0]); \quad (6)$$

(vii) Theoretical result for random walkers^{20,21}

$$\eta = A \exp(B/[T - T_0]^{3/2}). \quad (7)$$

(viii) Theoretical result for random packed spheres²²

$$\eta = A \exp(B/[T - T_0]^2). \quad (8)$$

(ix) Theoretical result for cooperatively rearranging systems,²³ also Potts-like system with forced scaling²⁴

$$\eta = A \exp(C/TS_c), \quad (9)$$

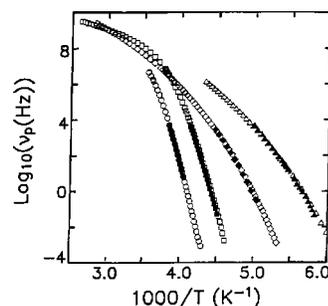


FIG. 3. Variation of the peak frequency for the imaginary part of the specific heat and dielectric relaxation spectra for various molecular liquids, showing coincidence of relaxation times for these two properties. [From Wu *et al.* [Ref. 29(a)], by permission of J. Non-Cryst. Solids.]

which becomes either

$$\eta = A \exp(B/[\ln T/T_0]) \quad (9a)$$

or Eq. (6) depending on the functional form assumed for excess heat capacity in evaluating the configurational entropy S_c ($\Delta C_p = \text{constant}$ gives Eq. (9a)²³ while $\Delta C_p = K/T$ (which is commonly true for low temperature liquids but rarely for liquids with T_g above ambient) gives Eq. (6).²⁵

(x) Theoretical result for model in which displacement of molecule requires uniform local volume expansion²⁶

$$\eta = \eta_0 \exp\left(\frac{C}{G_\infty(T)}\right), \quad (10)$$

where G_∞ is high frequency shear modulus, and changes rapidly with T for fragile liquids and slowly for strong liquids.

Of the above, the most frequently applied are the VF law, [Eq. (6)], the Bässler law [Eq. (4)] and the power law [Eq. (2)].

It is perhaps surprising how similar the responses to quite different types of perturbations are; i.e., for how many properties of a given liquid one equation with the same parameters (adjusted for unit differences, of course) describes the different data. An example from the literature^{27(a)} is given in Fig. 3. Figure 3 suggests that for these liquids, there is strong coupling among the relaxation modes of the system, at least for enthalpy relaxation and polarization relaxation, in a variety of molecular liquids. For glycerol, at least, shear relaxation times τ_s also coincide in temperature dependence with τ_D and τ_H .

On the other hand, such coupling is by no means complete. For instance, for chain polymers such as PVAc, sizable differences among τ_s , τ_D , and τ_H have been observed.^{27(b)} In some cases, particularly those in which the liquid contains more than one type of particle, the decoupling of the small particle motions from those of the bulk may be very pronounced. Examples are the motion of small ions in ionic liquids, gas molecules in polymers, and small molecules doped into molecular liquids composed of large molecules. For all of these, a “fractional Stokes–Einstein equation” is found to apply over limited temperature ranges. Their behavior in region A of Fig. 1 is discussed in Section A.1.9.

This decoupling phenomenon leads to the possibility of various important relaxation and transport phenomena in glasses; e.g., “solid electrolytes,” which are discussed in Sec. C of this review. Thus the possibility of qualitatively different responses for different measurements must be borne in mind. Even for similar responses, it is a valid and to date an unanswered question whether or not Eq. (1) or any of its rivals does a better job for one response than for another. Most measurements, however, have been performed on properties which probe the bulk or matrix response. In particular, viscosity and dielectric relaxation measurements which probe the bulk response have been extensively reported. Recently valuable measurements of the dynamic behavior of dilute optically active probes, which seem to follow the bulk response temperature dependence faithfully if the probe is large, have been reported.²⁸

1.2.1. Vogel–Fulcher equation. Without question, the most frequently applied equation is Eq. (6), the Vogel (Vogel–Fulcher (VF); Vogel–Fulcher–Tammann (VFT); Vogel–Tammann–Fulcher (VTF); or Vogel–Fulcher–Tammann–Hesse (VFTH)) equation, particularly when the application of its equivalent, the Williams–Landel–Ferry (WLF) equation to polymer liquids and rubbers is taken into account. Like several of the others, it is provocative because of its implication that a nonzero K singular temperature T_0 (VF) or $T_g - C_2$ (WLF) exists where relaxation times diverge. The equation performs best for liquids which show only small deviations from Arrhenius behavior;²⁹ i.e., for the so-called “strong” and “intermediate” liquids⁶ which include most of the common liquids of the geochemical and technological world and now includes also the most easily vitrifying of the metallic glasses.^{1(a),30}

On the other hand, for most of the molecular liquids studied by scientists interested in the phenomenology of the glass transition—liquids which tend to be “fragile” in their behavior; i.e., which show very large deviations from the Arrhenius equation—Eq. (6) does not apply at all well; neither does any other simple three-parameter equation. For most of its applications, the equation has only been used to account for curvature in the Arrhenius plots of data covering some 2–4 orders of magnitude, and in such cases, it usually performs well. Increasingly, however, data are being obtained over much wider ranges, up to 14 decades,^{1,2} and it is found, invariably for fragile liquids, that the whole range cannot be fitted with a single set of parameters. Systematic deviations commonly are found, with a tendency to smaller curvature approaching the glass transition temperature and also in the highest temperature range (which may be either Arrhenius or power law in character) and excess curvature in between.^{31–34}

The most critical analysis in recent times has been the derivative analysis of Stickel *et al.*³² The analytical procedure weights most heavily the temperature regions which, on an ordinary Arrhenius plot, have the greatest curvature. Stickel *et al.* find that quite frequently this region, which involves the first 3–4 decades of data, obeys the VF equation well but with unphysical values of both T_0 ($T_0 > T_g$) and the pre-exponent (τ_0 or η_0), a consequence of its failure at lower temperatures. The Stickel analysis of data on salol^{32(b)} pro-

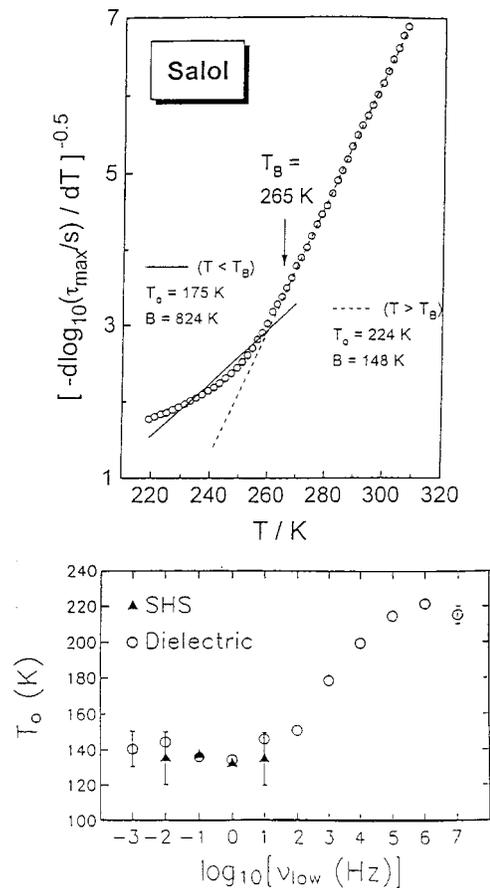


FIG. 4. Comparison of the Stickel *et al.* and Dixon procedures for testing the applicability of the Vogel–Fulcher equation to relaxation data for molecular liquids. The Stickel plot emphasizes the validity in the region of largest curvature while the Dixon plot tests validity over the widest range of relaxation times.

vides an interesting contrast with the analytical strategy of Dixon³⁴ who tested the utility of the VF equation on the same liquid by dividing the available 14 decades of data (of precision comparable to that of Stickel) into 3 decade segments, and examined the behavior of the best fit T_0 for each segment against the mid-range temperature. This procedure gives equal weight to each decade of τ . To contrast the conclusions of the two authors based on their alternative diagrammatic representations of data on salol we reproduce the latter in Fig. 4.

Stickel concludes that VF is only useful for fitting data at $T > T_g + 50$ K while Dixon concludes that only near T_g does the equation gain physical meaning (although the very large values of the pre-exponent obtained in the fit of these data leave this in doubt).³⁵ An element of investigator taste inevitably intrudes into the assessment of data fits via different axis choices, as seen most clearly from the way 14 orders magnitude of data of equal precision can be compressed into the baseline of plots “testing” the application of linear or power law equations for transport properties.

While the case of salol, which has now been studied so carefully, illustrates the problems to be dealt with in deciding how to approach data fitting, it should be pointed out that salol is the sort of system which probably should be avoided in this sort of test because of the heterogeneous nature of the

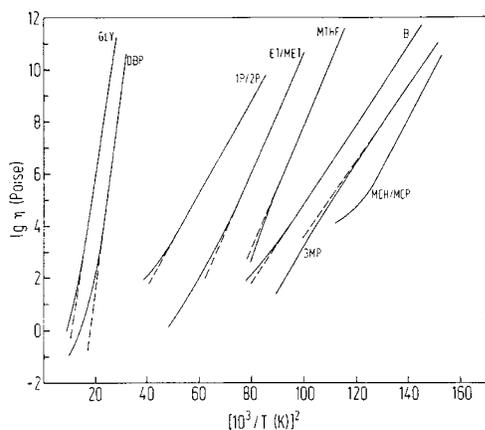


FIG. 5. Representation of experimental data for molecular liquids by Eq. (4) (Bässler equation). The equation performs best in the high viscosity regime, as would be seen more clearly if available data in the normal fluid range around 10^{-2} P were included in the plot. Glycerol (gly), di-(*n*-butyl)-phthalate (DBP), 1-propanol+2 (1:1) (1P/2P), ethanol-methanol (1:1) (Et/Met), methyltetrahydrofuran (MTHF), methylcyclohexane + 3-methylpentane (1:1) (B), 3-methylpentane (3MP), methylcyclohexane + methylcyclopentane (1:1), (MCH/MCP).

interactions between molecules. Both hydrogen bonds and van der Waals interactions play a role, and they will influence the dynamics differently in different temperature domains. A good example of the sort of problems this can cause is provided by *m*-cresol (3 methyl phenol).³⁶ Here also the intermolecular interactions contain hydrogen bonding and van der Waals contributions, but the H-bond component remains unexcited until above T_g . It then contributes an additional component to the total heat capacity of the Schottky anomaly form, providing a marked contrast with the behavior of other molecules of the same shape but with less disparate interactions. The dynamic consequences of this situation are unfortunately not yet known, but they can be expected to lead to greater complexity than observed in salol.

In contrast to the salol and cresol cases, when the interactions are dominated by hydrogen bonds, as in glycerol, or by van der Waals interactions of a uniform type, as in saturated hydrocarbons, then even the Stickel analysis finds the Vogel–Fulcher equation fitting the data over wide relaxation time ranges with physically intelligible parameters. For cases in which the pre-exponent has a physically acceptable value, $\sim 10^{-14}$ s (the quasilattice vibration period which is the time between successive assaults on the rearrangement energy barrier), Angell³⁵ has found that the divergence temperature T_0 falls within 2% (variance of 2%) of the independently evaluated Kauzmann temperature T_K (at which the configurational entropy vanishes for ergodic systems³⁷ for some 30 different substances for which both the transport (relaxation) and thermodynamic data are available.

By fixing the pre-exponent at 10^{-14} s and T_0 at T_K , the VF equation becomes a one-parameter equation which has physical significance but doesn't fit the data very well except for intermediate and stronger liquids. VF apparently works well as an empirical form for the classical oxide liquids but can only be approximately rationalized in terms of the Adam–Gibbs equation because the hyperbolic temperature dependence of ΔC_p needed to convert Eq. (10) to Eq. (6) is

not observed experimentally over a wide temperature range.³⁸

1.2.2. Ferry–Bässler equation. The Ferry equation which was later derived by Bässler¹³ has the advantage of having only two parameters and a theoretical base in the random energy model which has physical appeal. The random energy model as developed by Derrida³⁹ also gives an account of the temperature dependence of the excess heat capacity. Data fitted by this equation are shown in Fig. 5. Because of its weaker temperature dependence, Eq. (4) deals better with substances that approach their T_g with a tendency to return to Arrhenius laws (or Vogel–Fulcher laws with lower T_0), as indicated by the changes of slope in Fig. 4(a).

1.2.3. Power law (model coupling). Power laws with three parameters have been shown to fit the data over wide relaxation time ranges near T_g with a precision equal to that of the VF equation.^{40,41} In fact, for values of the exponent near 12, the two equations are mathematically indistinguishable (the Bardeen identity).⁴² The problem is that exponents of this magnitude have no theoretical interpretation. Power law fits of a limited range of very high temperature low viscosity data give much smaller exponents and are in a range consistent with the expectations of mode coupling theories.

1.2.4. Other equations: equations with >3 parameters. Equations exist, which fit all the data available for a given substance, and also have a theoretical basis, but they contain four or more parameters. For instance, the Cohen–Grest equation⁴³ provides an excellent fit to data on fragile ionic fluoride glasses which are very badly fit by the VF equation.⁴⁴ The Cohen–Grest equation does a slightly better job at fitting the data on salol, discussed earlier, than does another recent entry, the Kivelson–Tarjus–Kivelson (KTK) equation.⁴⁵ Based on the notion of an avoided critical point, the KTK equation assumes an Arrhenius form in the high temperature domain and then a weak power law in the lower temperature domain. The theory predicts a power of 8/3 which is close to the experimental finding. Comparisons of fitting prowess have been made by Cummins.⁴⁶

A.1.3. Average versus most probable relaxation time behavior

(Does the VF equation apply better to properties like viscosity (which are determined by the average relaxation time) than to properties like relaxation times (which are reported as the most probable relaxation times?)

It is not obvious, from the available data, that frequency-independent properties like macroscopic viscosity give better fits to any of the above equations than do relaxation times. Transport properties such as the viscosity or dc conductivity are determined by averages over a spectrum of relaxation times, whereas the “dielectric relaxation time” usually plotted is the most probable time. These should have essentially the same temperature dependence unless the distribution function changes rapidly with temperature. Such cases exist with fragile liquids, but we are not aware of comparative tests of fitting functions. In such cases, the average time will exhibit a stronger temperature dependence than that of the most probable time. Relaxation data are generally preferable

because of the extra kinetic information contained in the spectrum.

A.1.4. Probe relaxation time measurements

(Does the VF equation apply better to relaxation measurements made with molecular probes? etc.)

The question of whether relaxation times measured by probe methods tend to be more tractable than bulk measurements can be answered by reference to the data from the groups of Sillescu, of Ediger and of Richert,^{28(a)–(c)} and also that of Leporini,⁴ all of which trace back to dielectric and optical probe studies in the 1970s.^{28(d)–(f)} Certainly with larger probes, the problem of differences in T dependence between average and most probable relaxation times goes away because in these cases the relaxation processes become exponential at all temperatures. An early example is the work of Williams and co-workers,^{28(a)–(b)} in which high dipole moment molecules additives were used as probes for the dynamics of dielectrically weak OTP,^{28(a)} and the massive ion dipole probe tri-*n*-butyl ammonium picrate was found to yield slow and exponential relaxation,^{28(b)} except near T_g . The recent measurements employing molecular probes of variable dimensions give much clearer behavior, and the largest probes give exponential relaxation at all temperatures.^{28(b)} In all these cases, the probe relaxation time is longer than that of the host. A contrasting case is that of the probe ion Co^{2+} in the model system $0.4\text{Ca}(\text{NO}_3)_2 \cdot 0.6\text{KNO}_3$ CKN,^{28(c),(f)} in which the glass transition detected by the probe is lower, hence the relaxation time shorter, than that detected by the conventional calorimetric route. This showed that the probe relaxation is not only faster than the host relaxation, but again is more exponential, as if it samples only a part of the distribution rather than averaging over the whole of it. This phenomenology can, in principle, be studied by an ac structure spectroscopy technique,^{28(f)} but heat flow problems restrict its application.

Probe measurements must be applied with caution. If supercooled liquids become microheterogeneous with decreasing temperature approaching T_g , then a probe result will depend on where the probe is. For instance if the probe, for reason of size or interaction, tends to segregate in the mobile component of the structure then it may give a temperature dependence quite different from the average value being sensed by the viscosity or by a large probe which spans the heterogeneities. This is seen for some of the optically excitable probes,²⁸ and also electron spin resonance (e.s.r.) probes⁴ used in such studies. For these same reasons, however, strategically chosen probes can offer potentially vital details on relaxation (and structure) in viscous systems; e.g., by providing insights into the dimension of microheterogeneities^{28(b)} and by revealing various types of decouplings.^{4(c)} These are discussed further in a later section.

A.1.5. High temperature systems (liquid oxides and chalcogenides)

(How do the properties of high temperature inorganic systems compare with those of low temperature molecular liquids? What are the chemical/structural factors that deter-

mine whether a liquid of a given class (molecular, metallic, ionic, and covalent) will exhibit a large or a small deviation from Arrhenius' law?)

Some particular note should be made of the wealth of data, particularly viscosity data, which have become available for the ionic liquids of interest to geochemists and glass technologists. The data available cover the whole range of known fragilities. Furthermore, in many cases, thermodynamic data of good quality are now also available, and this permits direct testing of equations like the Adam–Gibbs equation.

Richet and co-workers^{38,47,48} in particular have tested the application of the Adam–Gibbs equation to silicate melts of a variety of fragilities and consider the equation successful. Thus the connection between entropy and relaxation time which we have seen supported by the T_K , T_0 coincidence for transport and relaxation in low temperature molecular liquids, applies equally well, and indeed more reliably, to high temperature ionic liquids.⁴⁹

The liquid oxides cover the entire known range of liquid fragility values. Broadly, the simpler (“less polymerized”) the liquid structure is, the more fragile it is,⁵⁰ consistent with proposed importance of intermediate range order (hence structural fluctuations) in controlling fragility. Comparable changes of fragility with composition are seen in the liquid chalcogenides⁵¹ where again extended covalently bonded clusters control the fragility. These tend to percolate at a particular bond density (mean coordination number) of 2.4.^{51,52}

A.1.6. High frequency crossovers

(Is there a change of relaxation mechanism at high temperatures?)

There have been suggestions over the years that some change of transport or relaxation mechanism occurs at high temperatures in the vicinity ~ 1 Pa s viscosity. It was argued in a 1969 paper by Goldstein,⁵³ now a classic, that as molecules in the liquid pack more closely with decreasing temperature, there should come a point where free diffusion, characteristic of simple liquids and dense gases, can no longer occur because the molecules begin to “jam up,” and energy fluctuations, whose probability is a Boltzmann function of temperature, are needed to free them; i.e., the molecular mobility becomes activated. This change in mechanism has been much discussed recently,^{1,32(c),41,42} and evidence for its reality is accumulating - see also Sec. A.1.9.

The most direct evidence for some change in mechanism is probably the splitting off, in most fragile liquids at least, of a weak (called secondary or β -) dielectric relaxation from the main α relaxation.⁵⁴ It may also be observed by low frequency mechanical relaxation studies. The β relaxation sometimes appears to be a simple continuation of the high temperature, approximately Arrhenius process, but more often the splitting has the aspect of a bifurcation. This is seen most clearly in the Fujimori–Oguni scaling scheme discussed below.

The idea of a high temperature crossover to activated transport has been strongly reinforced through more recent evaluations of mode coupling theories (MCTs) of the glass

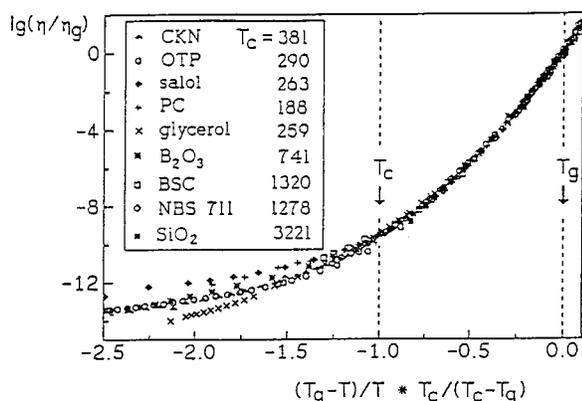


FIG. 6. Scaling of viscosity data for a variety of liquids showing how fragile and strong liquids can be collapsed onto a master curve by using a second scaling temperature at T_c , which coincides closely with the mode coupling theory of critical temperature. (CKN)= $Ca_{0.4}K_{0.6}(NO_3)_2$; (OTP)=*o*-terphenyl; (PC)=propylene carbonate; (BSC)=boron silicate crown glass. (From Rössler and Sokolov, Ref. 54, by permission).

transition which have provided an interesting and detailed prediction of the transition from free diffusion to a dynamically jammed state identified with the glass. Because the jammed state is not found, but many other predicted features of the initial slowdown are, a natural conclusion has been that the jamming is avoided by the intervention of activated processes which are not provided for in the idealized theory. Finally, at a temperature close to this T_c , breakdowns in the Stokes–Einstein relation between diffusion and viscosity, and the Debye–Einstein relation between reorientation time and viscosity, have been reported. This decoupling phenomenon is of much importance and is discussed in detail in Sec. A.1.9. The crossover phenomenon and its characteristic temperature T_x has provided the basis for another of the several scaling schemes discussed in the next section.

A.1.7. Scaling relations, fragility, and cooperativity

(What scaling relations can help rationalize the observations?)

Much effort has been made to find appropriate ways of highlighting the general or universal features of the glass-forming systems. We now describe four alternative schemes for collecting together in a single diagram the kinetic properties of a wide variety of systems in ways which stimulate thinking about the origin of their special behavior.

The first is the T_g -scaled Arrhenius plot introduced by Oldekop in 1957,^{55(a)} reintroduced by Laughlin and Uhlmann,^{55(b)} and by Angell^{55(c)} in the 1970's and popularized under the title of “strong and fragile” liquids in the 1980s.⁶ An example of this data presentation has already been provided in Fig. 2. “Strong” liquids are those with approximately Arrhenius transport behavior, and tend to be of tetrahedral network structure. Interestingly enough, the recently developed bulk glassforming metal systems based on Zr-rich Zr–Cu alloys prove to be strong liquids^{1(a)} and may contain a quasicovalent four-coordinated Zr network. Fragile liquids, on the other hand tend to be more highly coordinated ionic liquids, or aromatic hydrocarbons.

The second, a recent variant of this scaling, is that due to Rössler and co-workers⁵⁶ in which all data are collapsed onto a single curve by introducing the above-discussed crossover temperature into the scaling. For strong liquids, the crossover temperature identified by Rössler and co-workers lies far above T_g for strong liquids, but close to T_g for fragile liquids. In each case it also lies close to the T_c derived from fits to MCT equations, T_c in turn usually corresponds to the α – β bifurcation temperature. By plotting the data of Fig. 2 against the new temperature variable $(T_g - T)/T [T_c / (T_c - T_g)]$, the difference between strong and fragile liquids is removed and a universal behavior is obtained, as shown in Fig. 6.⁵⁴ The fragility should thus be represented by the quantity $T_g / (T_c - T_g)$. As a crossover temperature, T_c in this scaling would be better written T_x . The manner in which T_c is obtained by Rössler and colleagues is a little complex.⁵⁴ Since T_c lies near the temperature of the α – β bifurcation in many cases, the possibility arises of using this temperature ($T_{\alpha\beta}$), obtained from the experiments on secondary relaxations, as the second scaling parameter to produce a plot like that of Fig. 6. While this has not yet been attempted, the β relaxation has been invoked in the third of the proposed scaling relations, which is discussed next.

The third scaling proposal, which introduces new empirical information into the total picture, is that suggested by Fujimori and Oguni.⁵⁷ It is based on their calorimetric identification of the β –glass transition. This is a calorimetric manifestation of the Johari–Goldstein β relaxation,⁵⁵ and is found at temperatures far below that of the α –glass transition. Fujimori and Oguni then used $T_{g,\beta}$ as the temperature-scaling parameter in their Arrhenius plot of relaxation time data. The value of the Fujimori–Oguni scaling is the emphasis it gives to the concept of the α process as a process which grows out of a background “sea” of simpler activated processes as a result of the increasing cooperativity forced on the system by its increasingly dense packing. The liquids which are most fragile by the Fig. 2 scaling are seen, in the Fujimori–Oguni picture, to be those in which the α process first splits off from the background—hence which are the most cooperative—although this does not always seem to be the case. The possible connection between this phenomenology and the microheterogeneity being detected near the glass transition temperature will be discussed later. The overall scenario is strongly reminiscent of that described in spin model analogs by Harrowell^{58(a)} and recently developed into an interpretation of strong and fragile liquid patterns by Perera and Harrowell.^{58(b)}

Finally, in this section, is the most recent scaling proposal, due to Kivelson and co-workers.⁵⁹ Where the scaling temperature used by Fujimori and Oguni falls far below T_g , the Kivelson scheme uses a scaling temperature which lies far above it and even far above T_c . The Kivelson scaling is based on the notion that viscous slowdown is a consequence of packing frustration which, in higher dimensional spaces, would not occur. Rather, an ordering in the higher dimensional space reference system would be completed at a critical temperature T^* . In three dimensions this is sensed by the system as a narrowly avoided transition, and the properties of the liquid, now dominated by the domain structure, scale

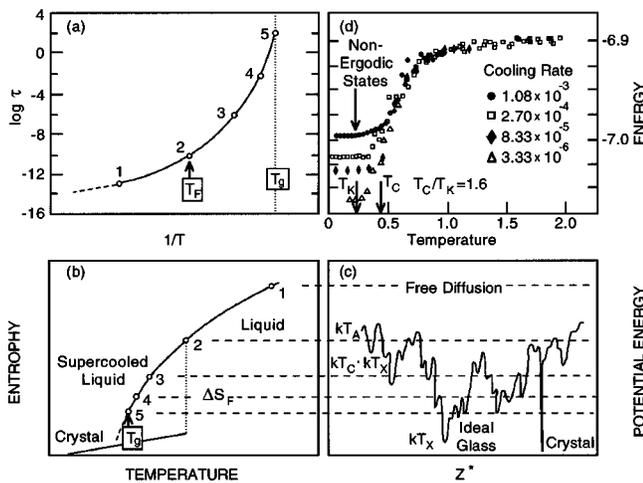


FIG. 7. Summary of phenomenology of glassformers showing (a) diverging relaxation times related, by points 1, 2, 3,... on the plot to (b) vanishing excess entropy which is in turn related to (c) the energy minima on the potential energy hypersurface. The temperature T_K corresponds to the energy of the lowest minimum in the amorphous phase megabasin. Many vertical spikes, corresponding to configurations in which particle core coordinates overlap, are excluded from this representation for clarity. (d) quantifies the landscape for the case of the mixed Lennard Jones (LJ) system according to the study of Ref. 60(c), by showing the potential energy of the inherent structures sampled with highest probability at each temperature. The energy profile is extended to the inaccessible Kauzmann temperature by [Ref. 60(e)] linearly extrapolating to satisfy the condition $T_c/T_K=1.6$.

by T^* . A scaling relation based on an approximate theory for this phenomenology seems rather successful⁵⁹ although a critical analysis shows it is not superior⁴⁶ (see Sec. 1.2.4).

A.1.8. The landscape paradigm

(What is the relevance of the “energy landscape”?)

A qualitatively (and recently quantitatively) useful way of thinking about the complex behavior discussed in the previous section is in terms of the potential energy hypersurface representative of the liquid.^{53,60} This is a $3N+1$ dimensional map of the system potential energy as a function of its particle coordinates. In a glass, the system clearly resides within a local minimum (or “basin”) on this hypersurface and executes \leftarrow collective vibrational modes of motion in accord with basin shape. Near but below T_g ; i.e., during annealing, the system can slowly explore nearby lower energy minima while lowering its entropy. At very high temperatures, it either “sees” no energy wells at all or relaxes by mechanisms which avoid them. In consequence, vibrational modes of excitation pass over to independent binary collisions via a regime described very well by mode coupling theory.¹¹ This situation, in which entropy and relaxation time are connected to the topology of the energy “landscape,” is depicted in Fig. 7. It shows how diverging relaxation times and vanishing excess entropy (i.e., the entropy in excess of the crystal vibrational entropy) are linked to the shortage of configurational states at energies near RT_g/mole (R the gas constant).

For every potential of interaction there is, according to the “landscape paradigm,” an energy of order RT_K below which there are no states other than vibrational states and those involved in the β relaxation. Thus any property linked to the availability of configurational states will show anomalous

behavior as T_K is approached. Whether the liquid is strong or fragile will depend on how densely packed these states are.

The temperature T_x in the Rössler scaling of Fig. 6 seemed a likely candidate for the temperature which “floats” the system point to the “top of the landscape”,^{6(d),56(c)} However, the recent quantitative evaluation of the relation between temperature and the energy of the basins being “visited with highest probability”,^{60(c)} shows that $T_x (=T_c)$ lies well down on the “excitation profile” for the system studied. The results of that study are shown in Fig. 7(d) in an adaptation which includes an extension of the profile to T_K for the systems.^{60(e)} An “instantaneous normal mode” analysis of the dynamics of typical liquid configurations in this system near and above T_c ^{60(d)} shows that T_c is the temperature at which (by extrapolation) no more unstable modes exist in the system at that temperature. This means that at lower temperatures all samplings of different basins by the system point must involve activated jumps, as apologists for MCT have argued for some time. Quantification of the “landscape approach” to the thermodynamic and relaxational aspects of supercooled liquids is now proceeding rapidly.^{60(c)–(f)} Although complex, it is ultimately the only correct way to deal with the many-body disordered systems under consideration. Progress at a simpler level will depend on formulating real space models that approximately capture essential features of the collective model. The evaluation of landscape characteristics for systems with different pair potentials^{60,61} and for given pair potentials at different densities is a pressing need.

A.1.9. Decoupled modes above T_g

(What are the circumstances under which the relaxation in a given viscous liquid can become multimodal; i.e., that one mode of transport can occur on a quite different time scale from others?)

The notion of decoupled transport in liquids above T_g was introduced in Sec. 1.2, and is now treated in more detail. There are important subdivisions of this general problem. While it has been realized for a long time that electrical conductivity in some molten salts could proceed on much shorter time scales, and with quite different temperature dependences than the viscosity, the realization that somewhat similar decouplings could occur rather generally in liquids consisting of a single molecular species is a fairly recent development. Although the decoupling of dielectric and mechanical relaxation processes in propanol and other normal alcohols has been recognized since Litovitz’ studies¹⁵ this was considered a special case caused by H-bonded microheterogeneities of the structure. Now, however, it seems that decouplings of one sort or another may be common to most, if not all, fragile liquids and may be directly associated with the strong departures from exponential relaxation common to these systems.^{62,63} We consider this case first.

1.9.1 Decoupling of diffusion from viscosity and in molecular liquids. The discovery that below the crossover temperature T_x (i.e., the Stickel temperature or $T_{\alpha-\beta}$), diffusivity of systems like o-terphenyl and toluene slows down less rapidly than does the fluidity (violating the Stokes–Einstein relation) has been predominantly the work of the groups of

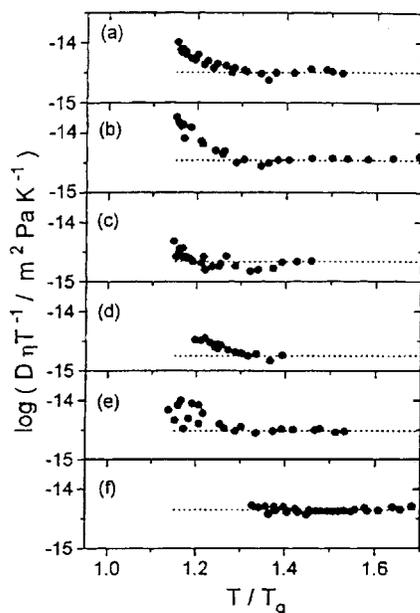


FIG. 8. Decoupling of diffusivity from viscosity as assessed by the Stokes–Einstein form of the diffusivity/viscosity relation as a function of T/T_g for a selection of molecular liquids: (a) OTP, (b) salol, (c) CDE, (e) *m*-tricresyl phosphate, (f) glycerol. The horizontal lines are drawn through the experimental points in the high temperature region where the Stokes–Einstein equation is valid (after Chang and Sillescu, Ref. 60(e) by permission).

Sillescu⁶² and Ediger.⁶³ The gap between the actual diffusivity and that predicted from the Stokes–Einstein equation grows by almost an order of magnitude between $1.25 T_g$ and $1.15 T_g$ (the limit of the diffusivity measurement) in *o*-terphenyl and comparable fragile liquids^{62(a),(b),63(a)} and is comparable in the case of toluene.^{62(c)} The findings are displayed in Fig. 8 taken from Ref. 62(e). Since this decoupling is not observed for the diffusivity of probe molecules which are larger than the host solvent molecules, the authors argue that it is due to the onset of microheterogeneity in the structure near and below T_x . It also may be correlated to the crossover from continuous to episodic diffusive displacements which are being revealed by molecular dynamics simulations approaching T_x . The difference has been recognized empirically in the finding that diffusivity in highly viscous liquids is better related to the viscosity by the Eyring (jump diffusion) equation than by the Stokes–Einstein equation.⁶⁴ The latter predicts diffusivities that are larger by about an order of magnitude. The decoupling can also be described using a fractional Stokes–Einstein equation analogous to the fractional Walden rule long applied to molten salts (see below). In some stronger liquids like glycerol, the Stokes–Einstein relation apparently remains valid to the lowest temperatures studied. The stronger liquids also have smaller, and less temperature-dependent, departures from exponential relaxation, and show less evidence for growing microheterogeneity near T_g ; e.g., polyisobutylene PIB in the study of Cicerone and Ediger.^{1(d)} In very strong liquids, like SiO_2 , the diffusivity for the slowest (network center) species Si also has the value $10^{-18} \text{ cm}^2 \text{ s}^{-1}$ expected from the viscosity by the Eyring equation.^{64(b)} [The Eyring equation holds better at all temperatures than does the Stokes–Einstein

equation in the case of the (high temperature) oxide glass-formers.] The onset of microheterogeneity and the related findings of long-lived “slow” regions, will be considered further in Sec. A.2. where the relaxation function is considered in more detail.

Models to account for the relation between decoupling and dynamic heterogeneity have been given.^{62(d),63(c)}

1.9.2. Decoupling of relaxation modes in liquid ionic compounds. The case of liquid ionic compounds is to be distinguished from that of other pure liquids because of the presence of distinct cationic and anionic species which can have different mobilities. The same could be said of covalent and metallic liquids like GeSe_2 and GaSb , but they have not been characterized yet in this respect. SiO_2 mentioned in the previous section provides an example. The diffusivity of the oxide species in liquid SiO_2 near T_g is two orders of magnitude larger than that of the silicon species.⁶⁴ Normally it is the cation which is the faster species. In silver metaphosphate, AgPO_3 , near T_g the difference amounts to some 10 orders of magnitude,⁶⁵ to judge by the conductivity. These cases are not difficult to understand. The decoupling occurs in the liquid because the barrier opposing the rearrangements which permit irreversible displacements of the smaller species is smaller.

It is found that, at high temperatures, the conductivity follows the VF equation with the same value of T_0 , within fitting error as the viscosity, but with a smaller value of B (making the system appear more fragile by conductivity measurements).⁶⁵ In terms of the Adam–Gibbs equation, this would imply that the energy barrier for a cooperative rearrangement, which permits small ion displacement, is smaller while the cooperative group remains the same or at least has the same dependence on temperature as for structural relaxation. At lower temperatures, the curvature of the Arrhenius plot decreases, and by T_g , it is following an Arrhenius law but with an unphysical pre-exponent.^{65(c)} About T_g , the slope changes as the electrical relaxation begins to occur within a fixed structure, and the pre-exponent returns to a value close to, but slightly above, the far infrared (IR) phonon cycle time; i.e., a physical value. This low temperature regime will be considered further in Sec. C.

The extent to which the other decoupled long range diffusion processes follow the above phenomenology is not known at this time. It might be anticipated that the less coupled the process to the structural relaxation, the earlier it will depart from the VF equation.

In terms of the landscape paradigm for characterizations of relaxing systems, these phenomena are interesting since they remind us of a complexity which is quite underrepresented in the usual version of Fig. 7. Below T_g , when the system is trapped in a single minimum, subsystems of its particles can still execute long range motions over an intrabasin landscape.

1.9.3 Decoupling phenomena in solutions. (What is it that leads to very large mobility differences within the liquid state?)

The occurrence of fast species, and large deviations from the Stokes–Einstein equation has most frequently been observed in solutions of different types. The subject has not

been treated systematically although it might be expected that such a treatment would reveal common patterns. Probably the earliest cases studied would be those of small molecules diffusing through polymers.⁶⁶ The fast diffusion of water through polymers, both organic and inorganic,⁶⁷ is a more recent example. The interest content ranges from contact lenses through dehydration preservation of biopolymers to explosive volcanic eruptions. It also appears to be an occurrence in metallic glassformers and in doped amorphous silicon and germanium. These systems have been studied mainly in the glassy state and accordingly will be considered in Sec. C of this review. The solutions on which some detailed liquid state data are available are the ionic liquids, and we provide additional information on these in the following.

Addition to a high viscosity liquid like SiO₂ of a component like Al₂O₃ in which the bonding is of the same type and strength as that in SiO₂ does not produce any differentiation in microscopic relaxation times: aluminosilicate liquids viscoelastically exhibit unimodal relaxation despite widely changing fragility. On the other hand, with additions of small cation alkali oxides such as Li₂O or Na₂O, in which the bonding interactions are significantly weaker than those of the host liquid, a new set of microscopic relaxation times can be spawned—those of the weakly bound alkali cations. The extent to which the relaxation times of these species are different from those of the host liquid is a function of the difference in the strength of interaction of the cation with the host liquid structure, and the size of the alkali cation.

The time scale for this “secondary” relaxation, which may be far below the host liquid’s average viscoelastic relaxation time, depends in the simple case upon two factors: the energy (bonding) and the volume (steric) interactions impeding the relaxing entity. In the first of these, the stronger the bonding, the closer the time scales for relaxation. In the latter, the greater the activation volume; i.e., the volume required for the cation to reach the activated relaxation state, the closer the time scales for the relaxations. For ions, these requirements tend to conflict, and greatest decoupling is obtained by compromise. Thus Li⁺ is mobile, but the smaller isoelectronic species Be²⁺ is not. Likewise, the weakly interacting but large cation Cs⁺ is immobile.

The “decoupling” of the relaxation times in these and other systems can be quantified by a “decoupling index” R_τ ^{68(a)–(d)} which measures the extent to which different relaxing modes in a multicomponent viscoelastic liquid are differentiated in time. $R_\tau (= \tau_S / \tau_\sigma)$ ratios the average relaxation time for structural relaxation, bulk viscous relaxation time τ_S , and the average relaxation time for conductivity relaxation τ_σ . Since the structural relaxation time becomes difficult to quantify below T_g where the glass is an elastic solid, it is convenient to define the decoupling index at the lowest possible temperature at which the structural relaxation time can be easily characterized; namely, the glass transition temperature T_g . At this temperature, significantly, τ_S takes a nearly universal value of ~ 100 s. Hence, by simply measuring T_g , one can determine the temperature where τ_S is accurately known. Then τ_σ is determined from the conductivity at T_g (by a Maxwell relation $\tau_\sigma = \epsilon_\infty e_0 / \sigma$; ϵ_∞ is the high frequency dielectric constant; e_0 is the permittivity of a

vacuum) to obtain R_τ which can then be used for comparisons of decouplings among different systems. Variations covering some 13 orders of magnitude have been recorded. In the case of the system of the much studied fragile molten salt system known as CKN,^{3(i)(b),3(iie),5(c),28(e)(f),65(c)} the index is small, only 10³; i.e., the decoupling is weak. Similar behavior for other glass types will be reviewed in Sec. C.

A similar system of quantification has been applied to diffusion-rotation decoupling in single component systems by Ediger.^{63(a),(c)}

A.2. The relaxation function

(How and why does the relaxation function differ from an exponential?)

Next in importance to the characteristic time itself, is the function that this characteristic time represents. In the simplest case the relaxation function is an exponential so that there is a unique time τ characterizing the process. In viscous liquids and glasses, however, exponential responses are rare, and the process has to be characterized by some more complex function, or distribution of different τ s, the nature of which is the subject of this section. Just as there were different processes whose time scales were discussed in Sec. A.1, and whose time scales could, in principle, be different due to different couplings to the structure, so will there be different functions describing the total process. Most of what follows in this section will be focused on the dielectric response function because this is the one that is most simply and accurately measured. However, for every relaxing variable there is a function that can be measured and whose relation to other relaxation functions is of interest to this field.

The electric field (or alternatively the displacement) response, while the most simply measured because of the ease of generating and detecting oscillating fields, is not the most fundamental. The most fundamental are those which relate to the volume and the entropy, and are determined by the decay of fluctuations about the equilibrium thermodynamic states. Volume and entropy fluctuations are statistically independent and hence may have different time correlation functions (tcf). Volume tcf is measured most directly by neutron scattering methods, but the time scales are limited. Oscillating isotropic pressure techniques are in their infancy.^{83(b)} Other methods, which are less direct, are the different mechanical spectroscopies including ultrasonics, Brillouin scattering, etc., represented in Ref. 4 (i)–(iv). Entropy fluctuation tcf is measured by specific heat spectroscopy which has only been practiced in the past 15 years.^{5(a),(b)} Most recent of all is the study of the entropy-volume cross fluctuations, the tcf for which is measured in terms of the frequency-dependent expansivity.^{5(c)} Finally, there is the least direct but the most powerful spectroscopy, based on nuclear magnetic resonance. While frequency variations are difficult to achieve, the amount of information on time-dependent processes that becomes available from time domain studies using different types of perturbations at different delay times, is enormous, and even bewildering to the nonexpert. Many examples will be referenced below.

A.2.1. The description of nonexponential relaxation

(What is the most appropriate and economical form for describing the deviation?)

It is now well known that, except at the highest temperatures, relaxation processes in glassforming liquids cannot be described as simple exponentials. The most economical form for describing the deviation is the Kohlrausch (1847) function

$$\theta(t) = \exp[-(t/\tau)^\beta], \quad \text{with } 0 < \beta \leq 1 \quad (11)$$

in the time domain. There are only two parameters: the stretch exponent β and the relaxation time τ in this form. In many glassformers in internal equilibrium, this Kohlrausch or stretched exponential form describes rather well a major portion of the primary relaxation process that is responsible for the glass transition.⁶⁹ Frequently deviations from the Kohlrausch form are found in the short time ($t \ll \tau$) and in the long time ($t \gg \tau$) regions. The deviation at long times seems to come from extra but identifiable relaxation processes such as electronic or ionic conductivity in the case of electrical field stresses and for polymers responding to mechanical stresses from the motion of the polymer chain with a length scale that is longer than the local segmental motion. It is generally believed, as well as achieved in practice, that when the contribution from the extra process is removed, there is no deviation from the Kohlrausch function at long times. There are many substances which do not have the complication of the presence of an extra process at $t \gg \tau$. In these cases, deviation from the Kohlrausch function at long times is usually not found. On the other hand at short times, the actual correlation or relaxation function always deviates from the Kohlrausch function. This deviation is not trivially due to the presence of a different mechanism such as a secondary relaxation. The deviation occurs in a way which suggests that an additional broad loss mechanism that slowly decreases and extends indefinitely over many decades to high frequencies $\omega \gg \tau^{-1}$ is always present. A full understanding of the origin of this high frequency broad loss mechanism is presently lacking.

There are many other ways of describing the deviations from exponentiality.⁷⁰ The earliest ways of accounting for the spectral characteristics of dielectric loss spectra were given by Cole and co-workers.^{70(a),(b)} The Cole–Cole and Cole–Davidson distributions, between them, offered good accounts of most of the recorded loss functions with the same number of parameters as the stretched exponential function. Both are empirical functions.

In an alternative approach, Dixon *et al.*^{2(b)} scale the dielectric loss function $\epsilon''(\omega)$ by the width in a special manner to obtain a universal shape for many small molecule glass-forming liquids of various chemical types. This is shown in Fig. 9(a). This procedure, although successful, has so far not been justified on a theoretical basis. However, an almost indistinguishable form comes out of a relaxation function based on percolation theory due to Chamberlin.^{70(c)} The agreement with this function of data for three molecular liquids studied by Richert and co-workers^{70(d)} is exemplified in Fig. 9(b). Both seem to be related to the “constant loss” seen, but unexplained, in all relaxing systems⁷¹ (including

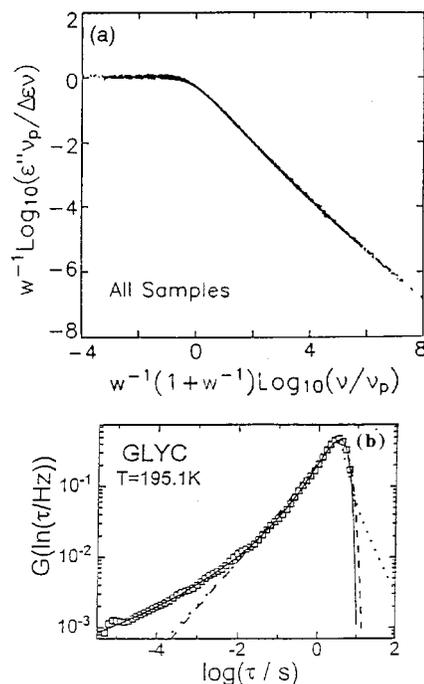


FIG. 9. (a) Example of the Dixon–Nagel scaling of relaxation spectra obtained from dielectric relaxation studies of a variety of different liquids [from Ref. 2(b), by permission of Phys. Rev.]. (b) Scaling of relaxation data for three liquids by the Chamberlin relaxation function (from Ref. 71 by permission of J. Non-Cryst. Solids).

ionically conducting systems above the electrical relaxation frequency) and which persists up to the crossover to the $\sim \omega^2$ dependence of the lattice (libron) frequency. Both of these functions, like the popular Havriliak–Negami (HN) function,^{70(c)} have one more parameter than the Kohlrausch function.

Empirical functions that have more than two parameters naturally provide a better fit than the Kohlrausch function. The (HN) function, $\epsilon''(\omega) \propto 1/[1 + (i\omega\tau)^\alpha]^\gamma$, has three parameters and has been more widely applied than any other, but again a theoretical justification is lacking. The possibility of better fitting with more parameters carries with it the danger of including extraneous relaxation mechanisms or substances which have additional complications beyond that of a glassforming liquid. An example would be the poly(vinyl ether) and polystyrene mixture, a miscible binary polymer blend in which concentration fluctuations inhomogeneously broaden the relaxation function of the individual components of the blend.⁷² The fit to the dielectric relaxation of each component by the HN function, though successful, has incorporated more than one physical origin for the nonexponentiality of the component dynamics in the blend. The HN function does not account for the deviations seen in the data at high frequency.

It has been shown⁷³ that less economical but more powerful forms for the relaxation function may become inappropriate for glassforming liquids when they violate certain requirements. For example, in the low frequency limit, the relaxation function must lead to well-defined transport coefficients including viscosity [$\omega G''(\omega)/\omega \rightarrow \eta$ in the small ω limit] and conductivity [$\omega \epsilon_D \epsilon''(\omega) \rightarrow \sigma$ in the small ω limit].

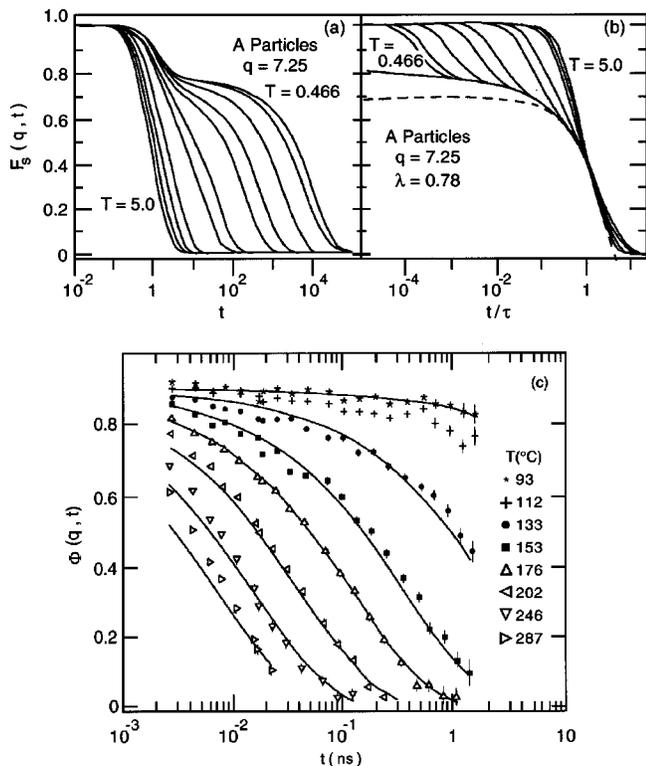


FIG. 10. Structural relaxation as represented by the intermediate scattering function obtained by computer studies (a), (b) and, experimentally by neutron spin echo studies (c). The scaling (TTS) of the simulation results is shown in (b) reproduced from Refs. 73 and 74, with permission of Am. Inst. Phys. In strong liquids a dip in $F_s(q, t)$ develops between the fast step and the plateau, and this is the time domain manifestation of the boson peak discussed in Sec. D.

In contrast, the Kohlrausch function is perfectly appropriate in this respect.

A.2.2. Temperature dependence of nonexponentiality

2.2.1. *The question of time–temperature superposition (TTS).* (What is normal and what is predicted? When should time–temperature superposition (TTS) hold?)

It seems to be a general rule that the stretching exponent β , if temperature dependent, increases monotonically with increasing temperature^{2(b),33} and approaches unity in the high fluidity range. However, the circumstances surrounding this dependence seem to be variable and also to change with the temperature range considered. The increase of β with temperature seems to be correlated with the departure from temperature dependence of the relaxation time τ . The challenging problems are: (1) the origin of the temperature dependence of β and its correlation with the temperature dependence of τ or η ; (2) the physical meaning of the energy barrier in the high temperature/frequency limit; (3) why the temperature variation of β in some substances is more pronounced than in others, (4) whether there is a correlation with chemical structure; and (5) like the value of β , why the temperature dependence of β , as well as the T dependence of τ , depends on the probe; i.e., with the correlation function being monitored.

TTS has been predicted by mode coupling theory¹¹ for temperature ranges in which two-step relaxation occurs. The

predictions are borne out for a considerable range of relaxation times (at temperatures above T_c) by computer simulation studies of the most fundamental relaxation process, the structural relaxation. This is represented by the intermediate scattering function $F(k, t)$, which monitors the decay of density fluctuations. An example⁷³ is seen in Figs. 10(a) and 10(b) and experimental studies showing the same behavior^{3(ii)(e)} are given in Fig. 10(c). The complex motions underlying the simple scaling behavior seen in this super- T_x regime [Fig. 10(b)] are described and analyzed in Ref. 74. A crossover from high temperature exponential relaxation to intermediate temperature stretched exponential relaxation is incorporated in the coupling model of Ngai and co-workers.⁷⁵ This important crossover is examined in some detail in Sec. D which is devoted to short time behavior.

The scaling seen in Fig. 10(b) pertains to relatively short relaxation time behavior; specifically, behavior in the “slow dynamics” regime but above the “landscape-controlled regime” (specifically, above T_x in Fig. 7 and in particular above the temperature at which secondary relaxations have split off). At longer times a still more complicated situation prevails⁷⁶ and the observed behavior depends, among other things, on whether or not a strong β relaxation exists, (see Sec. 2.2.3. below).

Some polymer systems seem to show TTS over wide frequency ranges from both dielectric and photon correlation studies; e.g., polypropylene oxide and poly(methyl phenyl) siloxane.⁷⁷ It would be interesting to know whether there are simpler systems in which β is constant at all temperatures; i.e., time–temperature superposition really holds. However, until very recently, there have been no data for the same correlation function extending over the entire time range, from picoseconds to hours relaxation times (near and below) T_g for any single substance. Short time dynamics can be measured by dynamic light scattering and quasielastic neutron scattering. Unfortunately, at this time, there is no consensus on what dynamic light scattering is measuring. Neutron scattering measures density–density correlations at large q . In principle, such data can be combined with another technique (such as photon correlation spectroscopy) which measures density–density correlation at long times down to near 100 s in order to check TTS over all time scales. A candidate substance for ideal TTS seems to be ZnCl_2 in which there is agreement between dynamic light scattering in the short time range and photon correlation spectroscopy in the long time range.⁷⁸ Neutron scattering measurements are needed for confirmation. However, even if ZnCl_2 survives the additional test, it has the disadvantage that, like many intermediate liquids, it has a relatively large β value ~ 0.8 . A molecular liquid which is interesting in this respect is propylene carbonate, which is very fragile, but also has a large and temperature-insensitive β value.^{32(d)} This may be peculiar to the high dielectric constant of this liquid since the mechanical relaxation is much less exponential.

If TTS is found for a certain correlation function, then the next question to ask is whether the same holds for the other correlation functions. Are there substances in which TTS works for some correlation functions and fails for an-

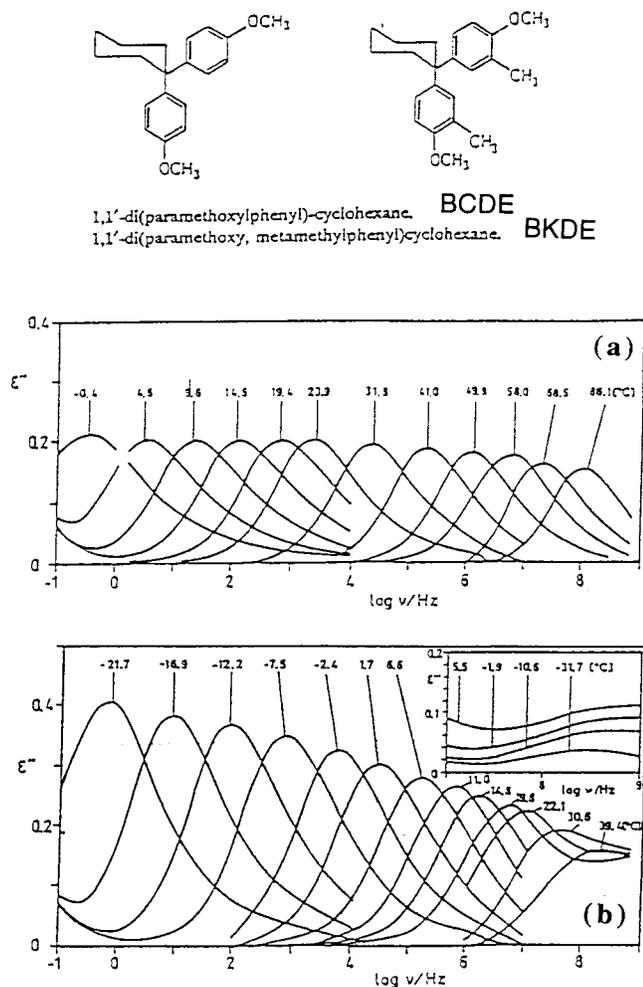


FIG. 11. Demonstration of the effect of a strong β relaxation on the time-temperature superposition (TTS) of the dielectric relaxation spectrum for two very similar molecules which differ by the presence of a strong β relaxation in the case of BCDE (from Ref. 76 by permission of J. Non-Cryst. Solids).

other correlation function? Some cases are addressed in the following sections.

2.2.2. The case of normal alcohols. The normal alcohols have exponential relaxation according to dielectric relaxation measurements performed at long times. Judging from the monotonic increases in β toward unity at high T seen with most molecular liquids, the relaxation function in alcohols should remain exponential even at microscopic times, and this has been directly observed in microwave studies of methanol.⁷⁹ Thus the normal alcohols are systems in which TTS really works for one process, dielectric relaxation. However, the relaxation of mechanical stress,⁸⁰ and also of enthalpy,⁸¹ is very nonexponential and faster,⁸² so these are special cases. Propylene carbonate seems to belong partly in this group, since the anomalously large value of β found for dielectric relaxation^{141(c)} does not hold for mechanical relaxation, at least at high frequencies.^{82(b)} The value of β obtained from the detailed NMR study of this substance by Qi *et al.*^{82(c)} is also the lower value expected from its fragility. However, a gap between τ_D and τ_{mech} only seems to open up at the highest temperatures in this case (see Sec. D.5, Fig. 28).

2.2.3. Influence of secondary relaxation. In the investigation of TTS, it is important to exclude possible effects due to the presence of the secondary relaxation which has a different and much weaker temperature dependence than that of the primary relaxation with which we are most concerned. If the β relaxation carries significant dielectric strength, then if it is merging with or separating from the primary relaxation in the range of measurement, TTS will obviously not hold. The scaling of Fujimori and Oguni⁵⁹ would suggest that the best cases for ensuring that secondary relaxations do not interfere would be the most fragile liquids, although this scaling has not yet been tested with sufficient cases to be considered reliable.

An excellent example of secondary relaxation interference is described by Meier *et al.*⁸³ and shown in Fig. 11 for the closely related molecules BKDE and BCDE defined by the structures shown in Fig. 11, one of which has a strong secondary relaxation (due to phenyl ring flipping), and the other of which does not. Because of this complication, the question of the temperature dependence of the stretching exponent of the primary relaxation will be more difficult to settle. On the other hand, a data analysis using precise dielectric data, with careful removal of intensity due to secondary relaxations, using annealing strategies, has led Olsen *et al.*⁸⁴ to find that, once the effect of β -relaxations is removed, the α -relaxation scales precisely for most of the several liquids examined, and particularly for those whose high frequency loss goes as $\omega^{1/2}$ in the Havriliak–Negami function, as is often found, i.e., TTT usually holds when secondary relaxations are properly extracted. Currently, it is being found^{84(b)} that systems which were thought *not* to have a β -relaxation, but rather only a broad high frequency wing on the α -relaxation spectrum (e.g. propylene carbonate) may exhibit a β -relaxation if the glass is sufficiently annealed. It seems that in such cases it is only in the deeper minima of the potential energy surface (Fig. 7) that sufficient substructure within the minima develops for the high frequency features to be resolved as differentiable features. This case makes a contrast with (a) systems such as OTP^{84(c)} in which annealing of the glass causes the β -relaxation to disappear and (b) other systems in which sufficiently fast quenching causes β -relaxations to appear.^{84(d)} There is clearly room for additional systematic work in this area, particularly for cases in which there is a clear connection between the β -relaxation and a structural element (the phenyl ring flip) as in the case of the system described in Fig. 11.

2.2.4. Polymer versus nonpolymeric liquids. If consideration is limited to the local segmental motions in polymers that are responsible for their calorimetric glass transitions, then there are no systematic differences between polymers and nonpolymeric liquids in the above respects. One observes, however, that the stretching exponents of known amorphous polymers are usually smaller, and no case of an amorphous polymer with β larger than 0.6 is known. For the majority of nonpolymeric liquids, on the other hand, the value of 0.5 for β can be considered small.

A.2.3. Dependence of nonexponentiality on the function under study

(How does stretching differ for different relaxing properties?)

The case of normal alcohols mentioned above for their exponentiality, hence automatic conformation to time-temperature superposability, raises the question of the dependence of the response function on the perturbation to which the system is responding. Does the response depend on whether it is a thermal stress (e.g., a cyclic temperature change C_p^*), an electrical stress (e.g., a voltage jump or a periodic electric field ϵ^*) or some mechanical stress?

It is interesting that, for such comparisons of results for different stresses, it is alcohols that provide the examples at each extreme. For instance glycerol, in which hydrogen bonding groups occur on all carbons, couples to other molecules in all directions, setting up a structure which seems to respond to all stresses in the same way. Reference 85 shows a correspondence of three different relaxation functions with coincidence equal to those seen in Fig 3, and Ngai⁷⁴ shows that the relaxation functions, observed in the frequency domain, are also the same. This is an unusually simple case, of which there are few other examples.

In striking contrast is the normal alcohol, 1-propanol, in which only one end of the molecule is hydrogen bonding, and the dielectric and mechanical responses are totally different both in average time, in which they differ by $\sim 10^2$ s,^{15,82} and also in shape. The exponential character of the dielectric response has been mentioned above. However, the mechanical response recorded in the early ultrasonic studies of Litovitz and Sette^{80(a)} is so nonexponential as to present a problem in even defining the most probable relaxation time for comparison with the dielectric response. (A new molecular probe method for measuring mechanical responses^{80(b)} may improve knowledge of this relaxation mode in the future.) Various explanations have been advanced for such a response difference^{82,86} but they will not be discussed here beyond the caution that where single hydrogen bonds are present in a molecule which otherwise interacts with its neighbors by van der Waals forces, then anomalies in relaxation functions can be expected. It is notable in this respect that salol, which has been selected frequently as a test substance, is such a molecule and it is not surprising that its behavior has been particularly problematic.^{32,33}

An extensive comparison of enthalpy and dielectric responses has been given by Nagel and co-workers,⁸⁵ and the spectral shapes are usually different. Comparisons have been made by half width rather than by stretched exponential fitting. Apart from the important observation that spectral widths tend to Debye values at high temperatures, and that fragile liquids tend to have more rapidly changing widths than do intermediate liquids, few generalizations can be made (but, see Ref. 84, Sec. A.2.2.3). The expectation that the enthalpy spectrum would be the broadest^{82(a)} is rarely borne out,³³ however, see Ref. 87.

It should be noted here that the comparison of susceptibilities is not necessarily always the most appropriate. One analysis of the set of response functions needed to fully char-

acterize a relaxing substance⁸⁸ leads to the conclusion that in one case the inverse should apply: specifically, the thermal modulus (C_p^{-1}) should be compared with the adiabatic compressibility (although this conclusion requires the assumption that no structural relaxation can occur at constant volume which is, at best, an approximation). Unfortunately, appropriate data are not available to test this proposition. This analysis is discussed further in the next section.

A.2.4. Thermoviscoelastic response functions. An irreversible thermodynamics approach.

(Are there any other approaches to this problem area?)

We give here an abbreviated account of a systematic approach to the description of linear response functions in isotropic liquids, which has only been published in part.⁸⁸ The description commences with an account of the six response functions that an isotropic liquid can exhibit in an interaction with its surroundings.

For a simple dipolar liquid the interactions are mechanical, electrical, and thermal (magnetic interactions are not considered here). The properties are determined by tensorial interactions, the rank of which may vary. Electrically there is the vector interaction between field and response which defines the dielectric constant ϵ . Mechanically there is a scalar interaction defining the bulk modulus K , or its inverse, the compressibility κ , and also a tensor interaction defining the shear modulus G . Finally there are thermal interactions, one a vector defining the thermal conductivity and the other a scalar defining the specific heat C .

For isotropic liquids, only the scalar properties can couple. Thus, thermomechanical coupling is allowed giving rise to the expansivity in the response matrix

$$\begin{pmatrix} ds \\ dv \end{pmatrix} \begin{pmatrix} C_p/T & \alpha_p \\ \alpha_p & \kappa_T \end{pmatrix} \begin{pmatrix} dT \\ -dP \end{pmatrix},$$

where two variables ds and dv are small changes in entropy and volume associated with the small changes in temperature and pressure, dT and dP . The elements in the matrix, C_p , α_p , and κ_T are the isobaric specific heat, the thermal expansivity, and the isothermal compressibility (κ and C have two variants each, adiabatic and isothermal, and isochoric, isobaric, respectively). The symmetry of the matrix is an expression of the Onsager relations.

A complex macroscopic description of a dipolar liquid then requires specification of six independent properties, three thermomechanical, one thermal, one shear mechanical, and one electrical. Thus, a minimum of six independent response functions must be measured. In this respect no liquid has been fully characterized to date. Furthermore, arguments have been advanced to suggest that some of the responses have not been measured as definitively as had been thought.⁸⁸

The best characterized response is the dielectric response which has been studied over wide ranges of temperature and frequency as discussed already. However it has recently been proven possible to use piezoelectric materials to greatly expand the range of frequency dependent shear mechanical and bulk mechanical properties. These can now be measured

over 8 decades of frequency⁸⁷ although there is some dispute about the accuracy of the different techniques.

The presence of thermomechanical coupling effects requiring a correction factor in the thermal diffusivity whenever $C_p/C_v > 1$ and/or $G > 0$ complicates the measurement of the frequency-dependent specific heat.⁸⁷

A.2.5. Modulus spectroscopy versus susceptibility spectroscopy

(What is the relation of “susceptibility spectroscopy” to “modulus spectroscopy?” Do differences depend on whether or not TTS is violated?)

The representation of system responses is clear in principle but not too clear in practice. This is because, although the same molecular motions determine the observations, different parts of the complete correlation function are emphasized in the different measurements. The consequences are particularly pronounced in the case of properties for which there is not a static zero frequency state. Examples are: (a) the response to shear stress in the case of a liquid of any type, and (b) the response to an electric field in the case of a conducting liquid. In these cases, the usual cyclic stress or step stress measurement produces continuous dissipation of energy and, in consequence, responses which are dominated by the dc components of the response; i.e., the viscosity and the conductivity, respectively, and no relaxation peak can be seen. If the dc component is measured separately and subtracted out, then a component of the response remains and can be analyzed and assigned to mechanical or electrical “dipolar” processes. Since these turn out to have the same activation energy as the dc component, many workers think they are an inseparable part of the same process and so prefer not to make the above separation. Rather they prefer to convert the data to the modulus representation, in effect treating these data as results of a step displacement stress relaxation. Thus real and imaginary parts of a modulus are obtained, and a peak or spectrum is recovered because large low frequency components are suppressed by the inversion. The pros and cons of this treatment have been discussed in some detail in the literature, and strong opinions exist.⁸⁹ The best test may lie in finding which procedure permits the clearest correlation with other independent relaxation measurements; e.g., enthalpy. In this respect, the modulus analysis has performed well.⁹⁰

As far as the section heading topic is concerned, the important problem arises when the two types of measurements or data treatments are applied to liquids that polarize. Then it is clear that the spectral shapes must be different. If the stretched exponential function (Fourier transformed) fits one data presentation, it cannot fit the other. Even if it fits each equally badly, the values of β would not be the same.

A corollary of the above discussion is that, if relaxation functions for different types of stresses are to be compared, they should be compared in a consistent way; e.g., as susceptibilities, not as moduli in some cases and susceptibilities in others. It should be noted that, apart from the matter of spectral shape, the most probable relaxation time itself changes value when the data presentation mode changes. The shift is quite small, a factor of 2 or less, except for the di-

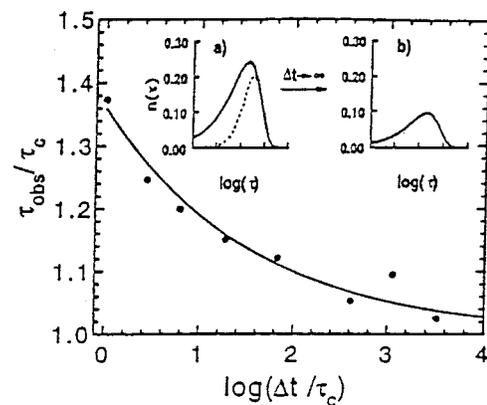


FIG. 12. Tests of the presence of microheterogeneous domains in viscous liquids by means of selective destruction probe techniques. Inset (a) schematically illustrates the initial distribution of relaxation times (full line) and the distribution of relaxation times after destruction of some mobile probes. 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 (from the work of Cicerone and Ediger, Ref. 92, as presented in Ref. 1. Reproduced by permission).

electric case where, because the zero frequency dielectric constant can be so large, it can exceed an order of magnitude. This is because the relationship is

$$\frac{\tau''_{\epsilon}}{\tau''_M} = \frac{\epsilon_0}{\epsilon_{\infty}}. \quad (12)$$

It is worth noting how this problem is resolved at high temperature when both times should approach the microscopic value of 10^{-14} s. This happens by ϵ_0 approaching ϵ_{∞} as two-step relaxation passes over to one-step relaxation in Fig. 10(a) and energy storage ceases.

A.2.6. Interpretation of stretching in terms of domain structure

(What is the relevance of domain structures and their temperature dependence to this problem? Are the inhomogeneities growing in length scale with decreasing temperature?)

Much attention has been given in the past decade to the idea that deviations from simple Debye behavior are best interpreted in terms of microheterogeneity of structure or, at least, of dynamics. The idea, which is actually quite old,^{31(c)–(e)} is that different relaxation times are associated with different exponentially relaxing regions or domains of different size or structure. The distribution of domains must be such as to yield a law close to that of Eq. (12). The classic illustration of the problem is that in Ref. 28(c), reproduced in Ref. 1. Direct evidence for microscopic regions of different relaxation time has been obtained by multidimensional nuclear magnetic resonance (NMR),⁹¹ photobleaching,⁹² excess light scattering near T_g ,⁹³ and dielectric hole burning.⁹⁴ Some findings from the photobleaching studies of Cicerone and Ediger⁹² are shown in Fig. 12. An analysis of probe dielectric relaxation results to prove that the individual domain relaxation is exponential has recently been offered.^{28(c)} A key question here concerns the temperature dependence of

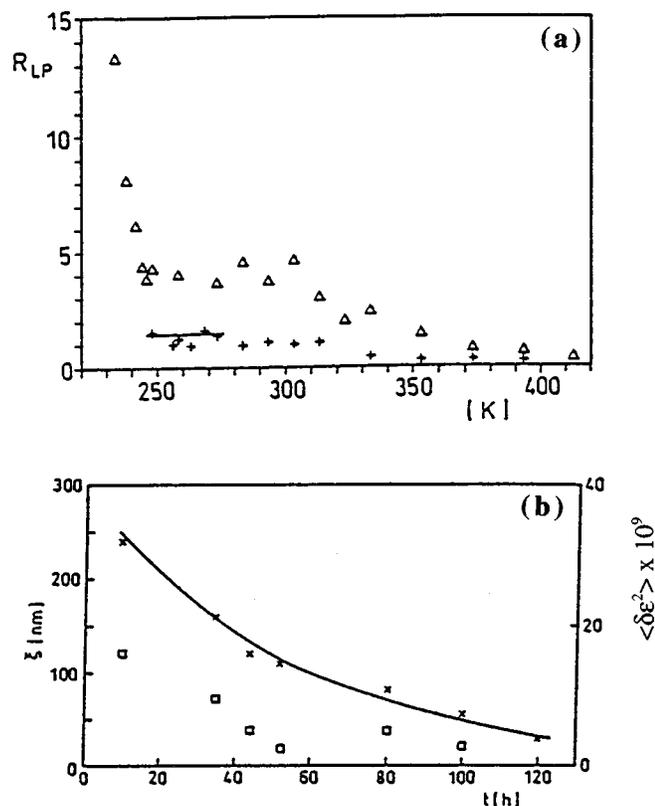


FIG. 13. (a) Variation of the Landau–Plazek ratio for *o*-terphenyl (OTP), with and without the clusters. The latter grow in with time on standing, particularly below 250 K. The solid line is predicted from the measured compressibility. (b) The values of the correlation length $\xi(x)$ and $\langle \delta \epsilon^2 \rangle$ obtained for OTP with clusters after different annealing times at 90 °C. The solid line represents an exponential fit to the correlation length (from Ref. 95 by permission of J. Non-Cryst. Solids).

this inhomogeneity and its relation to growing length scales in glassforming liquids. This is an area of great current activity both experimentally and computationally. Recent experimental work has been reviewed by Bohmer⁹⁵ and theoretical treatments have been reviewed by Sillescu.⁹⁶ A current statement on the findings for shorter time scales (above T_x) by molecular dynamics (MD) studies is to be found in Ref. 74(d).

Another kind of domain structure that has drawn some attention is the almost macroscopic (order of microns) clusters found in dynamic light scattering of some systems, both molecular and polymeric in nature. These structures have relaxation times several decades longer than the primary structural relaxation time.⁹⁷ The presence of these large clusters seems to be real and not an artifact of sample preparation. Under certain conditions, the clusters can be removed, and they then re-establish themselves with what appears to be nucleation and growth kinetics. The behavior of the Landau–Plazek ratio with temperature for samples, with and without developed clusters, is shown in Fig. 13(a). Figure 13(b) shows the exponential growth rate, with time, of the cluster correlation length in annealing OTP samples. While it is not clear that it is a related phenomenon, excess light scattering also occurs in tri-phenyl phosphate but in this case the clusters grow without limit to become a separate and

distinct amorphous or plastic crystal phase, the so-called “glacial” phase.⁹⁸

Recently it has been found in careful studies (including photon correlation spectroscopic measurement) on poly(methyl *para* tolyl siloxane) (PMpTS)⁹⁹ that the primary relaxation remains the same in samples with or without the clusters. Therefore, the clusters have no influence on the dynamics of the glass transition. Such clusters, however, would be an important consideration in optical applications of glassforming materials. At the moment, there is no accepted theoretical account of the origin of these clusters, although most workers seem satisfied that they are real.^{95–97}

A.2.7. Stretching and the Adam–Gibbs equation

(How can the Adams–Gibbs equation be consistent with stretched exponential relaxation?)

While assessments of rival theories is not an objective of this review we note the popularity, among molecular liquid phenomenologists^{47–49} of the configurational entropy model of Adam and Gibbs (AG) for the temperature dependence of molecular mobility. According to AG, relaxation is accomplished by rearrangements within cooperative regions (CRRs). The length scale of the CRRs increases with decreasing temperature, although very slowly until close to the Kauzmann temperature. However the polymer community, particularly workers in the field of viscoelasticity and rheology, have long shown a preference for employing the free volume theory to interpret the WLF equation. This may be due to the large influence of Ferry on the field of polymer viscoelasticity and his preference for the free volume picture of the temperature dependence of mobility.

A reasonable question to ask is whether AG theory is compatible with the existence of stretched exponential relaxation since it assumes that the CRRs are all equivalent. This would imply a single relaxation time. Even if we relax this simplifying assumption and admit a distribution of sizes of the independently relaxing CRRs, there is no guidance from the theory as to what the distribution should be and why it would be consistent with the experimentally observed approximately stretched exponential functions. This manner of generalizing the AG theory may in any case not be compatible with the findings of multidimensional NMR experiments⁹¹ for polymers such as poly(styrene), poly(methylmethacrylate), and poly(vinyl acetate) which show that molecules that relax initially fast will be switched rapidly thereafter to the slow relaxing population.^{100,101} Another possible shortcoming of the AG equation is the assumption that the individual CRRs can relax independently of each other without interaction or coupling. Efforts to correct this shortcoming have been carried out in the framework of the coupling model.¹⁰¹ The result is a stretched exponential relaxation within a modified VFTH equation for the most probable relaxation time. The generalized theory is not inconsistent with the multidimensional NMR data because the coupling model has averaged all fast and slowly relaxing molecules at all times.

Many theoretical efforts to validate the AG relations have been and are being made, including one by DiMarzio who finds finally a quite different relationship between vis-

cosity and temperature. A review of relaxation theory is needed to accompany this review of the phenomenology.

A.2.8. Single component nonexponentiality versus nonexponentiality due to composition fluctuations

(How can spectral broadening effects due to composition fluctuations be separated from that due to single component stretching?)

There is a distinction to be made between intrinsic nonexponentiality, nonexponentiality due to structural fluctuations, and nonexponentiality due to composition fluctuations. Intrinsic nonexponentiality is implicit in mode-coupling analysis of relaxation, and in the coupling model of relaxation. Structural fluctuations are a requirement of thermodynamic equilibrium, and the magnitude of pure volume fluctuations is dictated by the bulk compressibility. Volume fluctuations have been characterized by x-ray scattering¹⁰² and other methods,¹⁰³ and shown to accord with the thermodynamic quantities.¹⁰⁴ The decay of these fluctuations is related to the response functions observed in driven experiments (like those discussed in this review) by the fluctuation dissipation theorem.¹⁰⁵

Whether or not these fluctuations and their decay functions are sufficient to account for the observed heterogeneous dynamics is a matter for debate though several authors have argued that they are.^{92,93} However, a quite different source of broadening can arise in multicomponent systems from composition fluctuations. These fluctuations are also measurable by thermodynamic functions, in this case the activity coefficient, and by neutron scattering, through the concentration-concentration correlation function. Because these fluctuations involve interdiffusion of species, covering larger diffusion distances than single component structural relaxation, they are intrinsically slower, as has been demonstrated repeatedly.¹⁰⁴ However, the existence of a range of local compositions raises the possibility of a broadening of the structural relaxation function; e.g., near T_g where the system is effectively frozen with respect to composition fluctuations. If there is a strong composition dependence of the glass transition in the multicomponent system, then it must be expected that the frozen composition fluctuations will cause a broadened response in the structural relaxation.

Another example of the influence of composition fluctuations on relaxation time spectra concerns the secondary relaxations at temperatures below T_g when the density fluctuations become frozen in. The pioneering work done in glassy polymers with emphasis on *bis* phenyl-*A* polycarbonate (BPA-PC), with and without the presence of a diluent, was done by Fischer *et al.*¹⁰⁶ The density fluctuation does give rise to inhomogeneous broadening of the secondary relaxations. In BPA-PC, the secondary relaxation involves a π -flip of the phenyl rings located in the main chain. The possible additional spectral broadening of the secondary relaxation by intermolecular interaction in BPA-PC has also been considered.¹⁰⁷

Composition fluctuations exist also in blends or mixtures. Such composition fluctuations can be determined by neutron scattering and have been shown to exist in miscible

blends. In a miscible blend of two components A and B, compositional fluctuation leads to local regions richer in either the A or the B component. The mere existence of a distribution of compositionally different regions will contribute spectral broadening additional to the mechanism present already in a single component system. If the latter is well described by a stretched exponential function as found experimentally, then in a blend, there is no guarantee that the spectral broadening mechanisms when combined will give rise to a stretched exponential form for relaxation of either an individual component (when resolved) or both components together (unresolved). In fact, the dynamics of a component when resolved in experiments^{75,107} have been shown to depart dramatically from a stretched exponential form. For example, dielectric investigation of a 50%/50% poly(vinyl methylether)/poly(styrene) blend has shown the dielectric response of the poly(vinyl methyl ether) broadens towards the low frequency side as temperature is lowered to the extent that the dielectric loss peak has the opposite skew asymmetry from that obtained from the stretched exponential correlation function. It is an extremely difficult task to separate the spectral broadening effects due to composition fluctuations¹⁰⁷ from that due to intrinsic broadening because of several reasons including: (1) the distribution of the composition fluctuations is not exactly known; and (2) the need of a reliable theory of relaxation for a single component and the method of generalizing it to treat this more complicated situation.

So far there are only two theories, for the local segmental dynamics of polymer blends (one¹⁰⁸ based on the coupling model⁷⁵ and the other on the free volume model¹⁰⁹) that are applicable to polymer/solvent mixtures¹¹⁰ as well. In the theory based on the coupling model, the composition fluctuations modify the intrinsic stretching mechanism of the single component system, and thus the two effects are not additive in a simple way. The essential features of the component relaxation dynamics in the blends and mixtures have been reproduced and explained. Qualitatively, the effects of spectral broadening due to composition fluctuations have been explained by both theories. However, both theories have parameters that cannot be determined independently at this point.

To date the component dynamics have been studied experimentally in a few polymer blends. In all the blends studied, the component that has the higher glass transition temperature also has a smaller stretching exponent *in the neat side*. It would be interesting to find miscible blends in which the reverse is true; i.e., the higher T_g component have a larger β . Interesting new properties may show up in this case as seen already in a polymer/small molecule liquid mixture consisting of poly(methylphenylsiloxane) (PMPS) and 1,1-*bis* (*p*-methoxyphenyl)cyclohexane (BMC). In this mixture, the BMC relaxation is sped up by the presence of PMPS even though the latter has a higher T_g .¹¹¹ Such anomalous properties of component dynamics in blends will critically test proposed theories.

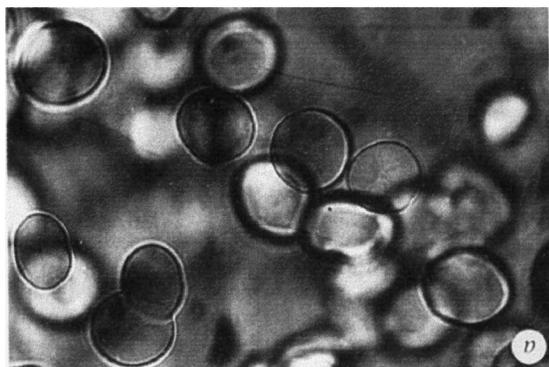


FIG. 14. Photomicrograph of the beads of glass II separated from the matrix of identical composition glass I during the cooling of the mixed oxide melt $Y_2O_3-Al_2O_3$ (from Ref. 120 by permission, copyright MacMillan).

A.3. Systems with complex behavior

(Are there systems which fall outside the pattern of behavior under which the “normal glassforming systems” are discussed? What is polyamorphism? Where does amorphous silicon fit in?)

It has long been recognized that some classes of liquids, including simple metals, inorganic polymers such as the chalcogens and iodine, and liquid carbon and group IV or III–V semiconductors, exhibit large structural changes (e.g., changes in coordination state or local bonding environment) as a function of temperature or pressure.^{112–115} To understand the effect on the liquid properties and phase relations, in particular, the occurrence of maxima in the melting curves, a two-state (states A and B) model with structural configurations based on those of the corresponding solids was postulated to describe the atomic configurations in the liquid.¹¹⁶

The mixing relations of the two states are usually treated within the formalism of regular solution theory. The configurational energy contains a term in the excess energy of mixing w . It was demonstrated early on¹¹⁶ that $w/kT=2$ represents a critical point, at which the liquid would separate into pure components A and B, which would have the same composition, but different density and configurational entropy.^{115,116} At this point, the two-state model has generated a two-phase system, which must have discontinuous molar thermodynamic properties at a particular temperature, which will itself depend on the pressure. It has been argued by various authors¹¹⁷ that a phase transition of this type in the liquid state is implied by the quasifirst-order phase changes (“polyamorphism”) observed in a number of glassy systems^{118,119} under pressure, in particular, the case of vitreous water.¹¹⁸ Whether or not the glacial phase of OTP discussed earlier⁹⁸ is an example of polyamorphism or something else of more familiar character (e.g., a plastic crystal of high disorder) is currently under discussion.

A.3.1. Polyamorphism originating in the liquid

(What is polyamorphism?)

The occurrence of liquid state polyamorphism as a function of pressure and temperature has been described for several systems, based on measurements of physical

properties.^{114,115} Recently, the occurrence of a first-order transition between two liquid phases has been verified by direct visual observation for liquids in the $Y_2O_3-Al_2O_3$ system,¹²⁰ see Fig. 14. The transition could be arrested by rapid quenching, and the resulting glasses were found to have the same chemical composition but different densities and degree of structural order. It has also been seen directly in MD computer simulation studies of liquid silicon,¹²¹ for which first order melting of the laboratory amorphous tetrahedral phase has also been reported.¹²²

Such liquid state polyamorphism, based on large differences in local structure or bonding environment between the two liquid or glassy states, has now been discussed for many classes of systems. These include simple metals and semiconductors, chalcogenides and halogens, the refractory aluminates mentioned above, framework oxides including SiO_2 , GeO_2 , and water (H_2O), and the liquid elements: carbon, silicon, and germanium.^{118–123} This list is obviously far from complete, and further work is required to determine how general this type of behavior is and in how many cases an actual boundary between two phases, the acid test of polyamorphism, can exist.

In the case of true two-phase equilibrium between phases of identical composition, the energy hypersurface of Fig. 7 characteristic of one density must, in certain cases, have a quite different topology at other densities. Such a system must have distinct megabasins in configuration space, separated at low temperatures by a density gap in which there are no low energy states available for the system. This provides an energy barrier which the system can only pass by a process of nucleation and growth. In the more common cases, such as SiO_2 , the different structural configurations are accessed gradually and continuously, and the behavior is that of a single liquid undergoing rapid changes in its physical properties. Such continuous transitions can be well described by simple two-state models.^{119(d)} The possibility of systems in which a liquid–liquid critical point exists is under active discussion.¹¹⁷

Further experimental and theoretical studies of this behavior are called for to investigate the generality of these phenomena and the nature of the liquid as the critical point is approached. Above the critical point, it is likely that the liquid would exhibit two-state behavior. It is certain that all of these liquids must exhibit large deviations from “normal” rheology as the two-state region is traversed.

In the cases of water and silicon at least, it seems that the high density liquid is also that with the larger configurational entropy, and it is certainly the more mobile phase. What is not so obvious, but apparently is true (at least far from the transition), is that it exhibits a larger deviation from Arrhenian behavior; i.e., is more fragile. The liquid–liquid transition can then be described as a crossover from “fragile” to “strong” behavior as the transition region is traversed.¹²¹ For a given cooling rate, the high density fragile liquid would show a much higher glass transition temperature if it did not transform to the strong liquid. In the case of the $Y_2O_3-Al_2O_3$ system these relations have been confirmed.^{120(c)} So far no detailed relaxation studies have been performed on the different phases.

The systems, Si and Ge, were used as test cases by Poyatovsky and Barkalov¹¹⁵ in their extension of Rappoport's¹¹⁶ arguments on two-state liquid behavior to the supercooled metastable two-phase regime. For Ge, they predict a first-order transition to a low T tetrahedral semiconducting liquid at $-900\text{ }^\circ\text{C}$, when the 1 atm, high temperature metallic (octahedral Ge) is supercooled. Recent EXAFS measurements of DiCicco and Filiponi^{122(b)} bear this out. Liquid Ge can be supercooled to $-900\text{ }^\circ\text{C}$, retaining the EXAFS oscillations of the metallic high-coordinated state. At this temperature, the system crystallizes "catastrophically," presumably assisted by the large density and entropy fluctuations in the vicinity of the $L-L$ transition. The tetrahedrally bonded amorphous phase can only be obtained by unconventional routes. Similar observations have been made even more recently for supercooled liquid Si.^{122(b)}

A.3.2. Amorphous silicon (and related substances)

(Where does amorphous silicon fit in?)

The field of amorphous silicon, which is the low temperature, tetrahedral, polyamorph of liquid silicon, is very large and important and will be considered in more detail in a later section. As implied above, tetrahedral a -Si cannot be studied in the liquid state because of the extremely high crystallization rates. Even in computer simulations, crystallization is rapid near the liquid-liquid transition temperature.^{121(b)} The amorphous tetrahedral phases of Si and Ge are only made by special routes such as vapor deposition, chemical vapor deposition, and irradiation. Their properties are discussed further in Sec. C, in which systems very far below T_g are dealt with. In the case of Ga-Sb, which exists in a tetrahedral semiconducting crystal state at normal pressure, vitrification from the liquid state can be observed under high pressure.¹¹⁵ This would seem to be a borderline case which merits much more attention.

B. GLASSFORMERS BELOW T_g : BEHAVIOR IN THE NONERGODIC REGIME (DOMAIN B)

B.1. Not far below T_g : Non-linear relaxation, annealing, aging

B.1.1. The present state of understanding: Principal models and key experiments

(What are the current approaches to the nonlinear relaxation problem?)

The kinetics of structural evolution in glassforming systems in the vicinity of T_g , but below, is well understood in the formulation of the Tool-Narayanaswamy-Moynihan and Kovacs-Aklonis-Hutchinson-Ramos (TNM-KAHR) frameworks.¹²³ The use of these frameworks has been extensively reviewed by Scherer¹²⁴ and Hodge.¹²⁵ The TNM-KAHR framework captures the preponderance of the phenomenology of the structural recovery event by including several important concepts in the proposed constitutive relationships:

(1) The principle of thermorheological and structural simplicity relates the molecular mobility to the structural departure from equilibrium through a simple shift factor a_{TF} or a_δ , where T_F is the fictive temperature measure of structure

and δ is the volume or enthalpy departure from equilibrium measure. Importantly, it is proposed in these models that all relaxation times depend in the same way on the global structure and temperature. We do note that, in the KAHR^{123(e)} model, it was recognized that this may not be true but, for computational purposes, the model was developed in this way.

(2) The retardation (sometimes referred to as the relaxation) response of the structural recovery needs to be represented with a nonexponential decay function. Kovacs *et al.*^{123(e)} chose to use a sum of exponentials while Moynihan *et al.*^{123(d)} chose the Kohlrausch-Williams-Watts (KWW) function of Eq. (11).

(3) The constitutive equation itself adds responses as one finds from Boltzmann superposition in linear viscoelasticity,¹²⁶ and all of the nonlinearity results from the structure dependence of the shift factor mentioned in Sec. A.1 above.

The implementation of the models is discussed in reviews by Scherer,¹²⁷ McKenna,¹²⁸ and Hodge.¹²⁹ Briefly, from the above considerations, we find that the TNM-KAHR frameworks are represented by the following set of equations:

$$\tau = \tau_0 \exp\left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f}\right], \quad (13a)$$

(x being the nonlinearity parameter), so that τ is more nonlinear the further T_f is from T , and the smaller x is, of

$$\tau = \tau_R a_T a_\delta, \quad (13b)$$

where

$$a_T = \exp[-\theta(T - T_R)]; \quad a_\delta = \exp\left[\frac{-(1-x)\theta\delta}{\Delta\alpha}\right], \quad (13c)$$

$$\theta = \exp\left[\frac{E_a}{RT_R^2}\right], \quad (13d)$$

where T is absolute temperature, ΔH and E_a are activation energies, the subscript R refers to a reference state and x is a parameter that separates the temperature dependence of the retardation time τ_R into pure temperature and structural temperature components, and is often referred to as the nonlinearity parameter. For the TNM model, when $x=1$, the response is purely temperature dependent, and when $x=0$, the response depends only on structure, hence it would be highly nonlinear. For the KAHR model, $x=0$ also defines pure structure dependence. Also note that a T_f dependence and S dependence define structure differently.

In discussing the concepts, it is important to note that Eq. (13a) defines the retardation response in terms of the fictive temperature T_F , and Eqs. (13b) and (13c) define it in terms of a departure of the structure from equilibrium. In this instance, the volume v is used, and δ is defined as $(v - v_\infty)/v_\infty$ and where the subscript ∞ denotes the equilibrium value. Finally, the $\Delta\alpha$ refers to the change in coefficient of thermal expansion at the glass transition. The two models are, however, mathematically equivalent.

Equations (13) define the retardation response for the structural recovery. The next step is to introduce a convolu-

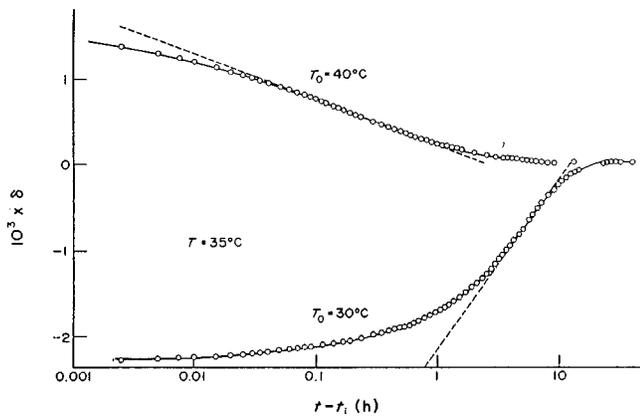


FIG. 15. Expansion and contraction isotherms for a poly(vinyl acetate) glass at $T=35\text{ }^{\circ}\text{C}$ after heating and cooling from $T_0=T\pm 5\text{ }^{\circ}\text{C}$. This plot shows the asymmetry of approach of the expansion and contraction isotherms [after A. J. Kovacs, *Fortschr.Hochpolym.Forsch.* **3**, 394 (1963)].

tion integral approach equivalent to that used in linear viscoelasticity to get the material response to different thermal histories. This is done by writing

$$\delta_v(z) = \Delta\alpha \int_0^z R(z'-z) \frac{dT}{dz'} dz', \quad (14)$$

where now one sees from the reduced time

$$z = \int_0^t \frac{d\xi}{a_T a_0} \quad (15)$$

and from Eq. (14) that the nonlinearity arises because δ depends upon itself through the a_δ structure shift factor.

There are several sorts of experiments that show the nonlinearity of the response and the exponentiality of the retardation function. In the first instance, it was Tool¹²³ who recognized that the mobility depends on the structure (fictive temperature or departure from equilibrium) in what are now referred to as asymmetry of approach experiments. Hence in dual experiments, if temperature jumps to a final temperature T , from initial temperature, T_0 , the nonlinearity of response

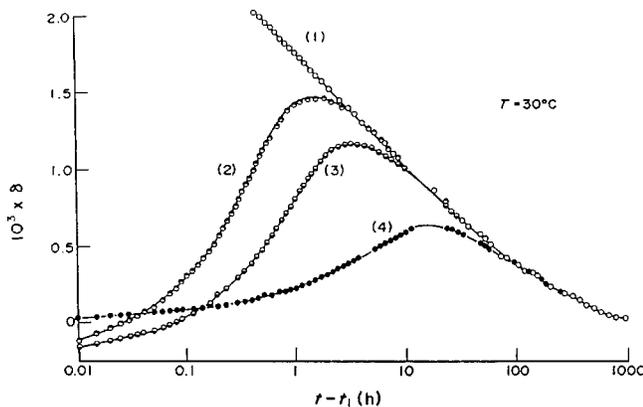


FIG. 16. Isothermal evolution at $T=30\text{ }^{\circ}\text{C}$ for poly(vinyl acetate) showing the memory effect: (1) quench from 40 to 30 °C; (2) quench from 40 to 10 °C for 160 h followed by rapid heating to 30 °C; (3) quench from 40 to 15 °C for 140 h followed by rapid heating to 30 °C; and (4) quench from 40 to 25 °C for 90 h followed by rapid heating to 30 °C [after A. J. Kovacs, *Fortschr.Hochpolym.Forsch.* **3**, 394 (1963)].

is observed. By jumping to the same temperature T from some T_0 that is ΔT above or below, one observes that the responses are not mirror images of each other, as depicted in Fig. 15. Hence, in the down jump, the volume evolves to equilibrium beginning at much smaller values than in the up-jump. Evidently the mobility in the jump from high volume (structure) is higher than in the jump from low volume. In the former, we see what Kovacs^{123(e)} referred to as an autoretarded event, and the latter looks autocatalytic on a logarithmic time scale.

The other important response is seen in Fig. 16 where the nonexponentiality of the decay is depicted. In the relevant experiments, the sample is annealed sufficiently that upon jumping up in temperature, the departure from equilibrium is near to zero (one jumps to a point where the fictive temperature is equal to the temperature), and the volume is seen to recover through (away from) equilibrium ($\delta=0$), go through a maximum, and return toward equilibrium. Such a response does not occur without a nonexponential retardation function.

Importantly, the TNM–KAHR models describe the major events of structural recovery as well as describing nonisothermal events such as the enthalpy overshoot seen in scanning calorimetry. The reviews of Scherer,¹²⁷ McKenna,¹²⁸ and Hodge¹²⁹ discuss various aspects of the models. However, the simple models do not fully capture the full range of experiments in several instances. These are the so-called τ -effective paradox^{130,131} discussed below and experiments in which large temperature excursions are used or when extremely long annealing (aging) times below the glass transition are explored. Hence while the models form an excellent resource for glass manufacturers to estimate residual stress calculations (in fact the original attempts by Narayanaswamy^{123(c)} addressed this problem), the lack of success in extreme conditions leads to several important fundamental questions;¹³¹ the possible problems are:

(1) The assumption of thermorheological–structural simplicity (TRSS) is simply only a good approximation and, in fact, β of Eq. (11) is a function of temperature and/or structure. Evidence was given in Sec. A.2.2 that this is the case for molecular liquids, but how much this contributes to the breakdown of the TNM–KAHR models has not been systematically explored.

(2) The viscoelastic constitutive model [Eq. (14)] is incorrect. This is a complex issue since there are several pieces to the model itself. For example, is the model correct, but TRSS needs to be modified? Is the origin of the nonlinearity actually different from that postulated in the model (i.e., could the mobility dependence on structure be only an apparent one-to-one correspondence)? There have been some recent developments of this in a new model from Caruthers' group at Purdue University. Here the Rational Mechanisms framework of Coleman and Noll, etc. is modified to include a reduced time (shift factor) that depends upon the configurational entropy. This model has been very successful in describing the asymmetry of approach and memory experiments as well as some mechanical viscoelasticity experiments. However, the model itself is new¹³² and the full range of successes are not included in the first article. It

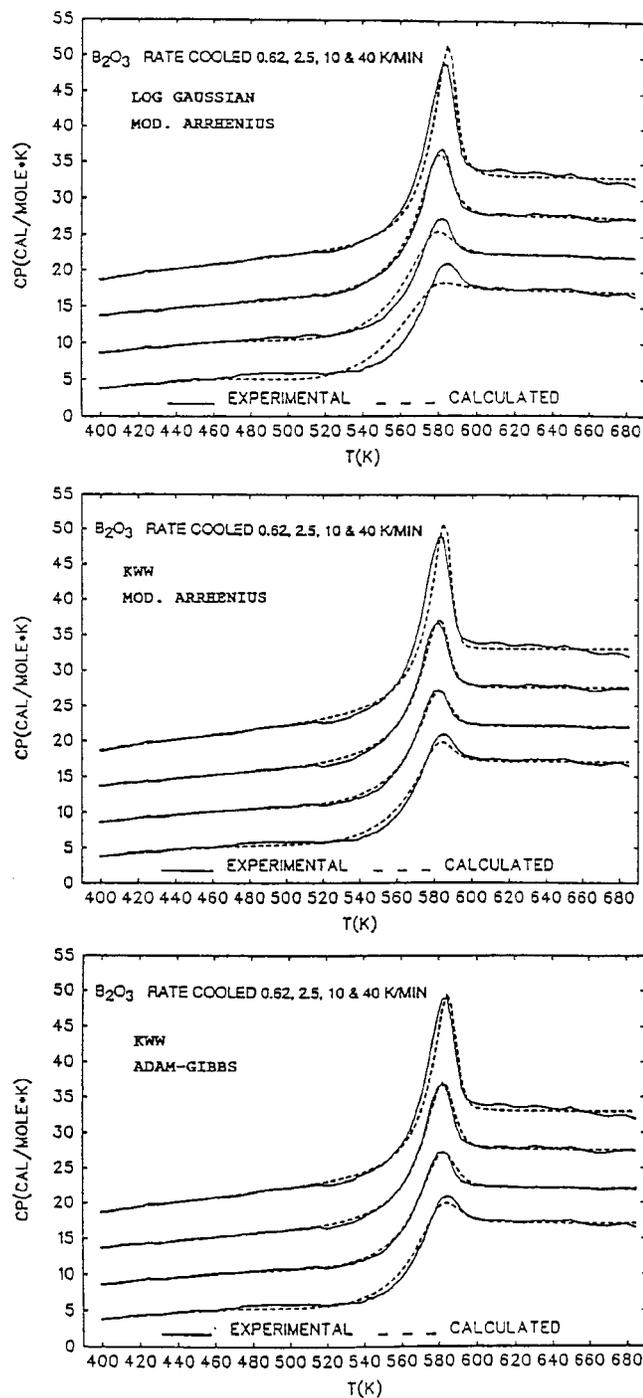


FIG. 17. Example of the ability of the TNM phenomenological model to reproduce the glass transition phenomenon observed in differential scanning calorimetry [after Moynihan *et al.*, Ref. 134, with permission from J. Non-Cryst. Solids].

remains to be seen how powerful this model will be. Also, the Ngai coupling model¹³³ has been extended to describe nonequilibrium structural recovery and initially showed some success in fitting the τ -effective paradox.¹³⁰ However, subsequently there were difficulties that arose for multiple step histories (such as the memory effect),¹³¹ and the model has been little explored subsequently for these phenomena.

Notwithstanding these latter problems, the phenomenological models have done rather well in reproducing the ex-

perimental findings for such fundamental phenomena as the glass transition itself as observed so commonly by differential scanning calorimetry. Examples are given in Fig. 17 for rate heating and cooling experiments.¹³⁴ Comparable success for quench, anneal and rate heat experiments by Hodge and Berens¹²⁹ are reviewed in Ref. 131. Readers are referred to the original articles for details.

B.1.2. The TTS assumption in modeling nonlinear relaxation

(How serious is it in each of the above to neglect the variation of β with T , when we know in some cases it is changing?)

If the constitutive equation is not working simply because the thermo-structural-rheological simplicity assumption is incorrect, this can be fixed by writing a different equation that includes variable β . One would then lose the simplicity of a reduced time equation and would need something more general (see Sec. B.1.1 above). Without an alternative framework, it is difficult to establish whether or not β is indeed a function of temperature (or structure/ T_F) below T_g .

B.1.3. TNM-KAHR versus Scherer-Hodge approach: Conceptual advantages

(Is there any conceptual or analytical advantage of TNM over Scherer-Hodge approach?)

Although TNM-KAHR and Scherer-Hodge phenomenological models give essentially equivalent results, since the parameters of one can be mapped onto those of the other with little approximation the Scherer-Hodge approach has certain conceptual advantages which lead to reality checks. For instance, the source of the nonlinearity is identified as the directly measurable excess entropy of glass over crystal and the fit to data should then provide parameters which should match known quantities: the τ_0 parameter should not be too far from a lattice vibration period 10^{-14} s, and T_K should be comparable with the value obtained from calorimetric studies.

B.1.4. Optimum conditions for comparison of models

(What are the best conditions under which to critically compare alternative models?)

The comparison of different models requires a single set of data on a single material that covers the range of important properties that need to be tested with each model. The Kovacs data on poly(vinyl acetate) certainly fits this mold, for the case of volumetric recovery. In fact, one can show that different models break down in different ways using these data. One problem is that often models show agreement with the data for one thermal history, and the agreement is published. Then, when the other thermal history is tested, it doesn't work, and the result may not be published. Hence, the question is never really how do we "critically" compare alternative models, but rather what is the range of applicability of each model. What are the strengths and weaknesses? A good example might be to take the TNM-KAHR model

and show that it works to within 20% over a range of $T_g - 30^\circ\text{C}$ to T_g and for annealing/aging times from 10^4 to 10^7 s with a single set of parameters. It may be that the Caruthers or Ngai models work to within 10%, but there are more parameters required for the model, and the computational complexity leads to a tenfold increase in calculation time for the analysis of interest. At this point, we do not have a demonstrably correct model, and the usefulness of each is determined by the use to which we want to put the model.

B.1.5. The “ τ -effective” paradox or expansion gap

(Is the “expansion gap” (τ -effective paradox) a consequence of incomplete modeling or merely inadequate data?)

The “ τ -effective paradox” is actually a misnomer. There is now no paradox, but there is an “expansion gap.” This is seen in many studies, that of Kovacs being the most obvious and well known. However, it was not suggested that the relaxation time at equilibrium differs depending on how one arrives at equilibrium. Rather the expansion gap was suggested by a simple extrapolation to equilibrium and as often happens (e.g., Kauzmann) this results in a “paradox.” In the model of Caruthers, the expansion gap arises because of the thermal history dependence of the reduced time and the coupling of two sets of integral equations. This is interesting and requires further investigation.

B.1.6. Relaxation far from equilibrium

(Is the description of relaxation far from equilibrium our biggest problem?)

In his early work, Kovacs¹³⁵ observed that the volume recovery kinetics in the asymmetry of the approach experiment (see Fig. 16) were not only nonlinear, but also gave rise to what he referred to as the τ -effective paradox. If one defines an apparent or effective retardation time [see Eqs. (13)–(15)] simply as

$$\tau_{\text{eff}}^{-1} = -\frac{1}{\delta} \frac{d\delta}{dt}, \quad (16)$$

then the response seen by Kovacs¹³⁵ looked as though the value of the retardation time t_{eff} as it approached zero departure from equilibrium varied with thermal history (i.e., magnitude of the up-jump to the same final temperature, up- vs down-jump to the same final temperature, etc.). Hence, the apparent paradox. This is shown in Fig. 18. Subsequently, in work in which the approach to equilibrium was made smaller (the values of δ were smaller than those of Kovacs), McKenna *et al.*¹³⁶ showed that the paradox went away, and all of the curves converged toward the same point. However, the gap seen in Kovacs data and seen so clearly in Fig. 18 remained. The TNM–KAHR models do not give that gap; hence, if it exists, it is not simply due to viscoelastic effects.

The importance of resolving the issue of the existence of the expansion gap is that it has become a benchmark for testing alternative models to the TNM–KAHR approach. Hence, some recent work by Struik,¹³⁷ which suggested that the expansion gap itself (as manifested in Fig. 18) is questionable, becomes important. For example, if a model looks better because it reproduces the gap, is it wrong if the gap

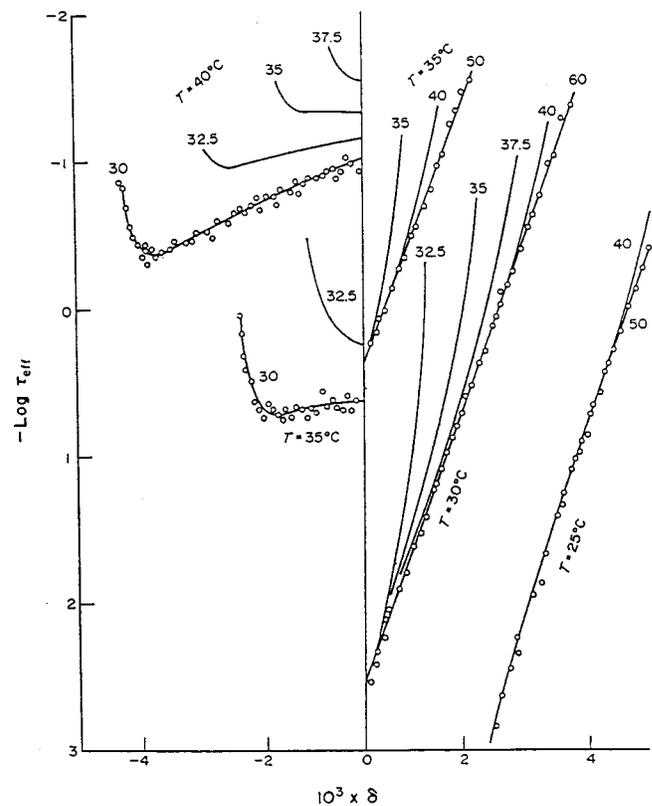


FIG. 18. $\text{Log } \tau_{\text{eff}}$ vs departure from equilibrium δ for expansion ($\delta < 0$) and contraction behaviors ($\delta > 0$) of a poly(vinyl acetate) glass. Experiments were conducted by equilibrating the samples at the temperatures indicated on each curve and jumping the temperature to that indicated with each family of curves. Thus, volume contraction experiments were carried out at $T = 30^\circ\text{C}$ after equilibrium at temperatures of 32.5, 35, 37.5, 40, and 60°C . Importantly note that while contraction curves merge at $\delta = 0$, the expansion curves do not. The latter is referred to as the “expansion gap” [after A. J. Kovacs, *Fortschr. Hochpolym. Forsch.* 3, 394 (1963)]. Note figure is corrected from the original, courtesy of A. J. Kovacs.

doesn't really exist with such strength? In the work of McKenna *et al.*,¹³⁸ the gap may or may not exist as the experiments took place so close to equilibrium that it may simply be a displacement of the curves due to viscoelastic effects, rather than the fanning of the data seen in Fig. 18. As a result, a collaborative effort took place between researchers at NIST and the Institut Charles Sadron¹³⁸ to reanalyze the original data of Kovacs,¹³⁷ including unpublished data from the original notebooks. The outcome is that the new analysis and that of Struik¹³⁷ disagree. This interesting problem needs to be resolved definitively.

B.1.7. Correlations of nonlinearity with other canonical features of relaxation

(How good is the correlation of nonlinearity with fragility?)

From his analysis of nonlinear enthalpy recovery experiments in many polymers and other materials, Hodge¹³⁹ has found empirically a strong correlation between the nonlinearity parameter x and the activation enthalpy ΔH (or $\Delta\mu$) in the TNM (or the Scherer–Hodge) model. $\Delta\mu$ itself is, in Hodge's view, the key determinant of the fragility. Subsequently, Ngai and Rendell¹⁴⁰ and Böhmer¹⁴¹ have further

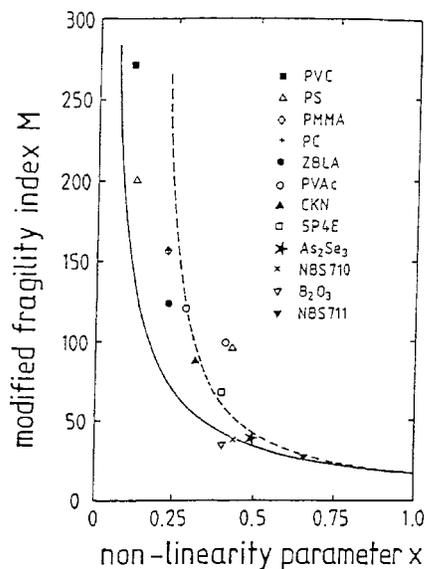


FIG. 19. Inverse correlation of the nonlinearity parameter x with the liquid or polymer fragility m . Equivalent correlations are shown in Ref. 131 (from Ref. 163 reproduced by permission).

shown that the stretching exponent β from linear relaxation data also correlates with x or ΔH from nonlinear enthalpy recovery data. The correlations obtained are quite good, indicating a connection between the characteristics of linear and nonlinear relaxation. The correlation of fragility with nonlinearity parameter x is shown in Fig. 19.

B.1.8. Fast relaxing versus slow relaxing perturbations

(Are there any systematic relations between fast relaxing and slowly relaxing perturbations?)

The nonequilibrium state of glasses is one that is difficult to define and describe simply because the tools of nonequilibrium thermodynamics are not as well developed (nor accepted) as are those of equilibrium systems. However, as is often found in dynamics of simple liquids, it might be expected that the kinetics of different processes will be different. Hence, it is of interest to note that there is a considerable amount of work currently exploring the issue of different time scales in materials. First, there is some evidence that the volume and enthalpy (nonequilibrium state variables) evolve toward equilibrium differently,^{142,143} either manifesting different times to attain equilibrium or different rates of approach to equilibrium. More recently though, the issue of different time scales has become more important due to the development of the field of “physical aging” that was greatly popularized by Struik.¹⁴⁴ Essentially, physical aging is the evolution of the dynamic variables such as viscoelastic or dielectric response of the material during the structural recovery (volume or enthalpy) that occur subsequent to temperature changes from above to below the glass transition. In addition, other histories have been examined, such as the asymmetry of approach and memory experiments.

Hence, in aging experiments, Roe and Millman¹⁴⁵ observed that enthalpy recovers into equilibrium faster than does the mechanical response. In more extensive studies, McKenna and co-workers^{138,146–150} have explored the rela-

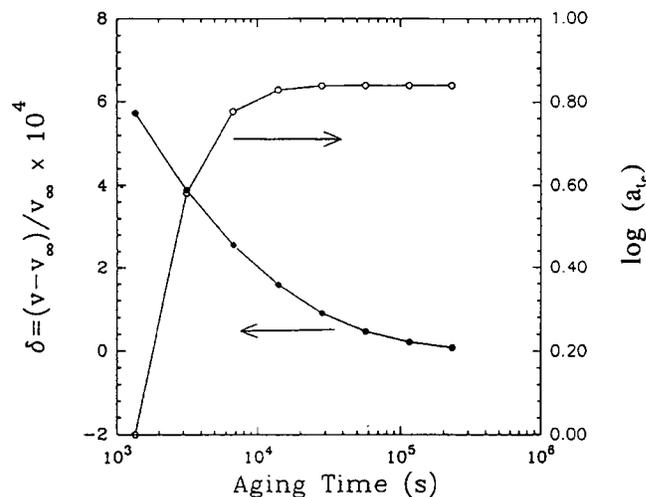


FIG. 20. Comparison of aging time shift factor ($\log a_{te}$) evolution towards equilibrium with that of volume departure δ . Plot provides evidence of differing time scales for different processes in glassy materials [after G. B. McKenna, *J. Res. NIST*, **99**, 169 (1994)].

tive time scales of what they referred to as “evolutionary properties” and found that both thermal history and the actual temperature affect the apparent result, suggesting different activation energies for different processes. Hence, they found that in down-jump thermal histories, the mechanical response evolves into equilibrium faster than does the volume in experiments using the NIST torsional dilatometer.¹⁵¹ Such a response is shown in Fig. 20. However, in up-jump experiments, the opposite was found to be true. There is also support for such behavior in the experiments by Delin and co-workers¹⁵² in which the mechanical response is found to evolve toward equilibrium faster than the volumetric response. On the other hand, in elegant work, Echeverria *et al.*^{153(a)} have found that the creep compliance and the enthalpy recover at the same time, and Simon *et al.*^{153(b)} report that while volume and enthalpy recover to equilibrium at the same time, the rate of approach is different. Evidently there is a nonuniversality to the behavior, and it is unclear at this juncture what the importance of the results is and how to treat them in the context of nonequilibrium processes. Some help may be available here from MD computer simulations because nonlinear relaxation has now been seen in simulations of ionic systems that are fragile in the domain accessible to simulation,^{154(a)} and aging has been studied in mixed LJ with interesting findings about and correlation lengths^{154(b)} and the nature of the T_c of mode coupling theory.^{154(c)}

In addition to the evolutionary processes described above, there is also the question of the rate of relaxation itself. In a paper by Santore *et al.*,¹⁴⁷ it was observed that the relaxation time scale (mechanical) was much more rapid than the thermal one. Hence, the relaxation of a mechanical stress in response to a mechanical deformation was observed to be one to two orders of magnitude more rapid than the structural recovery. Similar findings have been reported for ionic CKN^{6(a)} and covalent Ge–As–Se at high Se contents.¹⁴¹ The question that then arises is do mechanical perturbations relax differently than do thermal ones? The situation is similar to

that which makes it possible to obtain a viscosity in a structural glass below the glass transition where the structure has not attained equilibrium¹²⁹ (see also Sec. B2 below).

B.1.9. Shear relaxation versus bulk

(Is shear relaxation always faster than bulk relaxation in the nonlinear regime?)

The study of bulk relaxation has been made infrequently. Some examples include the measurement of the increase in compressibility of polystyrene with time after the application of a small hydrostatic pressure at temperatures between 90 and 96 °C by Rehage and Goldbach¹⁵⁵ and the complex dynamic compressibility of poly(vinylacetate) by McKinney and Belcher.¹⁵⁶ Both sets of results indicate that the associated measurable retardation spectrum is about 5 decades wide and that it reflects mechanisms seen in the retardation spectrum obtained from shear measurements¹⁵⁷ at relatively short times when the shear compliance is between 10^{-10} and 10^{-8} cm²/dyne. This comparison between shear and bulk compliances indicates that not only the local segmental motion but also the sub-Rouse modes have length scales inbetween the local segmental motion and the Rouse modes¹⁵⁸ contribute also to the bulk compliance. The relative contributions of the sub-Rouse modes and the local segmental mode to the compliance are drastically different for shear and bulk deformations. The fact that Rouse modes (which contribute to shear compliances approximately in the range $J_N^\circ > J > 10^{-8}$ cm²/dyne) do not contribute to bulk compliance is consistent with measurement of specific volume of polymers during cooling which show abrupt changes in thermal contraction coefficients similar to that of low molecular weight or small molecule glassforming materials. Thus, only fairly short range coordinated motions like the local segmental motion and the sub-Rouse modes must be involved in the liquid structure rearrangements that determine the volume; otherwise polymers would exhibit much less abrupt change in thermal contraction coefficients than low molecular weight substances, and they generally do not.

A comparison between shear and bulk retardation times of polymers has not been made based on the experimental data. If a comparison were to be made in the future, care must be exercised to ensure the samples can be assumed to be the same (i.e., for polyvinylacetate, the samples are thoroughly dry). It would be meaningful only if the local segmental retardation times of shear and bulk deformations are extracted from the data and compared. For nonpolymeric substances, there is practically no experimental data on the bulk relaxation or compliance to compare with the shear counterpart. The problem is of great interest and should be pursued further.

B.2. Glassformers at $T < T_g$, with structure almost constant

B.2.1. The temperature dependence of relaxation at constant structure

(What is the temperature dependence of relaxation at constant structure?)

At temperatures somewhat lower with respect to T_g than those considered in the previous section, responses to shear

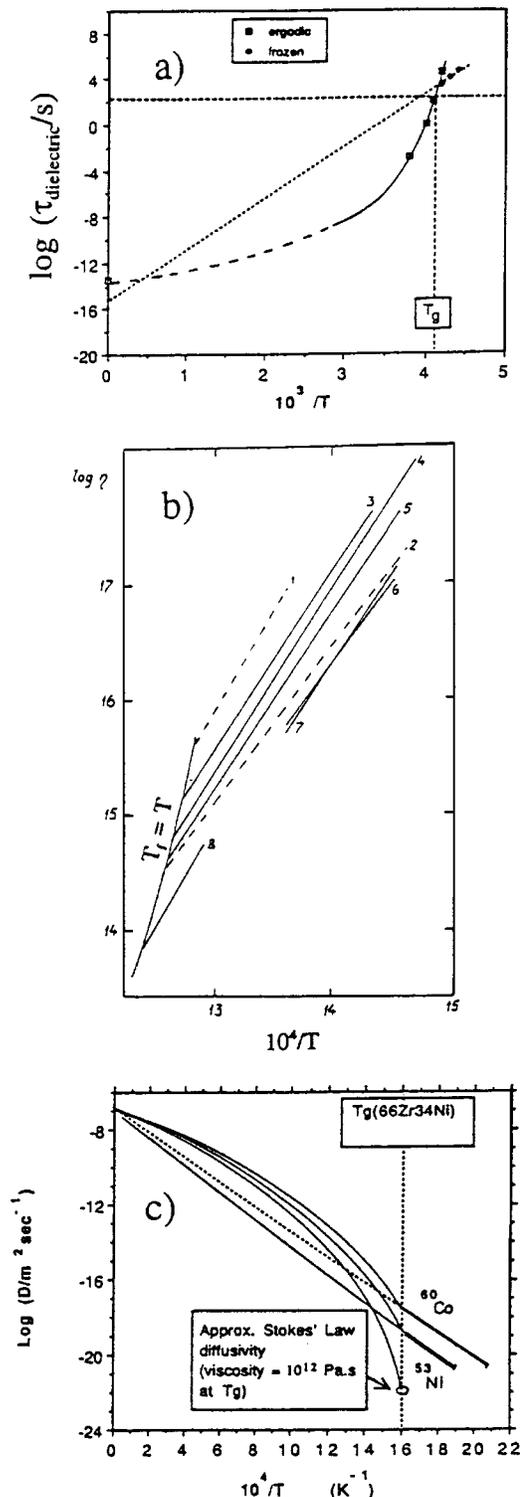


FIG. 21. Effect on relaxation and transport properties of freezing the structure at T_g . In each case, properties are well described by an Arrhenius temperature dependence below T_g . (a) Dielectric relaxation times in poly(vinyl methyl ether). Enthalpy relaxation data show similar behavior. (b) Shear viscosity in window glass ($\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$). The line labeled $T = T_f$ indicates the behavior of the equilibrium supercooled liquid. The numbers indicate glass preparations with different fictive temperatures. (c) Tracer diffusivities of ^{60}Co and ^{53}Ni in the metallic glass $\text{Zr}_{50}\text{-Ni}_{50}$. The value of T_g for this composition is uncertain; the value for $\text{Zr}_{66}\text{Ni}_{34}$ 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 (from Ref. 1 by permission of J. Phys. Chem.).

and electric stresses that are related to the α relaxation can still be observed. However, now they occur with essentially no change in the structure, hence take place at constant S_c . Thus, according to Eq. (9), the relaxation should follow the Arrhenius law. Furthermore, the slope should depend on the depth of previous annealing. Data generally supporting this expectation were obtained long ago by Russian workers making very sensitive viscosity measurements on silicate glasses¹⁵⁹ and are qualitatively confirmed by recent measurements of dielectric relaxation on polymers well below T_g ¹⁶⁰ [see Fig. 21(a)]. However, measurements on fragile systems are inevitably complicated by continuing structural relaxation, so there is much uncertainty in the Arrhenius plot slopes.

More convincing support can be provided from electrical conductivity measurements on nearly insulating glasses because here the conductivity is only weakly decoupled from the viscosity but the decoupling is sufficient that the relaxation can be studied sufficiently below T_g that no structural annealing occurs during the measurement. In such cases, the Arrhenius slope changes systematically with depth of annealing, and the pre-exponent is phonon-like in time scale. The case of conductivity is interesting because it is possible in principle to pass continuously from insulating glasses in which the conductivity must reflect the kinetics of the α relaxation to cases in which the process is at least as fully decoupled from the α process as are the β relaxations of molecular glasses (these cases are discussed in Sec. C).

B.2.2. Value of the stretching exponent in constant structure relaxations

(What is the relation of β , the stretching parameter under constant structure conditions far from equilibrium, to β measured when structure is equilibrated; i.e., is β simply an index of structure, hence of fictive temperature?)

According to the dielectric measurements of Algeria *et al.*,¹⁶⁰ the value of the stretching exponent β of Eq. (11) is independent of temperature and remains at the value characteristic of the temperature at which the structure became fixed. This is consistent with the trend observed during annealing to equilibrium of glasses quenched from higher temperatures. This behavior supports the notion that the value of β is determined by the structure per se, not the kinetic energy, and is best understood in terms of a fixed distribution of microheterogeneities (clusters) since relaxation of shear or electrical stress at constant structure is most easily understood via microheterogeneous models in which the mobile units permitting the relaxation reside in the intercluster component of the structure. It is important to know the relation between enthalpy or volume relaxation on the one hand, and shear and field relaxation on the other, at “constant structure” since this would help decide whether the α relaxation is controlled by the distribution of molecules between “cluster” and “tissue” material or by relaxation within clusters.¹⁶¹ Unless it is the latter, it is not easy to see how enthalpy could relax at constant structure, although some energy change could occur by morphology refinement.¹⁶²

B.2.3. Differences between relaxation at constant structure in fragile versus strong glassformers

(Is the relation between bulk and shear relaxation very different under “constant structure” conditions? Are there special differences between “strong” and “fragile” glassformers under these conditions? What are the best techniques for examining the kinetics of relaxation at constant structure?)

To date, there has not been any systematic study of the relation between constant structure relaxation in “strong” versus “fragile” glassformers. One study (on chalcogenide glasses of differing fragility^{141(b),163}) has suggested that the gap between shear relaxation time and structural relaxation time might decrease dramatically with decreasing fragility, and vanish before strong character is obtained. If this is the case, it would be expected to bear on conditions for observing structural inhomogeneities in viscous liquids near T_g (see Sec. A.2.6.). It is suggested by analysis of the AG predictions by Takahara *et al.*¹⁶⁴ that it is only for $T < 1.25T_0$ that any significant (i.e., measurable) increase in the size of the cooperatively rearranging regions occurs, and for intermediate liquids the system is already vitreous by $1.33T_g$. In the latter, therefore, no structural inhomogeneity would ever be observable.

The measurement of relaxation at constant structure demands very sensitive tools. Such have been described for viscous relaxation by Mazurin *et al.*¹⁵⁹ and for response to torsional stresses by McKenna *et al.* (Refs. 128 or 136). Algeria *et al.*¹⁶⁰ seem to have obtained the necessary sensitivity within the normal dielectric techniques.

C. DYNAMIC PROCESSES IN GLASSES (DOMAIN C)

[Behavior very far below T_g where only decoupled motion is possible]

C.1. The range of processes

(What types of processes remain active in the glass when the α relaxation has been completely frozen?)

While glasses are often thought of as rigid and completely immobile, it is well known that relaxation processes of one type or another continue to be measurable all the way down to the cryogenic range. In the latter range, the famous two-level systems (tunneling modes) are found, although we will not give much attention to these processes in this review. Hundreds of degrees below T_g , on the other hand, there is frequently an important source of dielectric loss in ordinary glass insulators. This is attributed to mobile alkali ions and, to a lesser extent, protons, in the anionic network. In many cases; e.g., the field of solid electrolytes, these quasifree modes of motion are the focus of special materials interest; e.g., in the search for advanced solid electrolytes based on freely mobile cations which is currently a major field of research. In between those two extremes lie the ill-understood β (Johari–Goldstein) relaxations and even more obscure lower activation energy modes known as γ and δ relaxations. These reflect the stepwise deactivation of various subtle degrees of freedom as thermal energy decreases and systems settle deeper and deeper into the substructures

of the individual energy minima of the Fig. 7 hypersurface in which they become trapped during the initial Domain B ergodicity-breaking process.

Since the residual motion of cations in glasses is at the core of a major branch of solid state electrochemistry, we give it considerable attention in the next section. We then consider more briefly, the comparable phenomena in metallic glasses, polymer glasses, bioglasses, and amorphous silicon.

C.2. Mobile ions in ionic glasses

(What is the source of ionic conductivity in some glasses?)

C.2.1. The maximum ionic conductivity concept

(What is the theoretical maximum conductivity?)

As suggested briefly in Sec. A.1.9., where the concept of decoupling was introduced in the context of liquid state relaxations, there are a number of factors that control the extent to which mobile ions in ionic glasses are decoupled from the viscoelastic relaxations of the host network glass. The question that we seek to answer here is, what is the maximum decoupling chemically and physically practical for these ionic motions? One can set a theoretical limit, the maximum ionic conductivity,¹⁶⁵ which is determined by the quasilattice rattling current (Boltzmann factor for barrier hopping=unity) which, for physical reasons, is close to the Mott minimum metallic conductivity.¹⁶⁶

For such a glass, the energy wells that trap and “solvate” the mobile ions in the glass should be as close as possible and as shallow as possible. Ideally, the structural-energetic topology that is sought would be one where the energy traps look more like “dimples” of minimal energy depth rather than deep wells capable of retaining the mobile ions for long periods compared to their hopping time. This requires minimizing both the energy barriers thought to be active in ion conducting glasses, the Coulomb energy, and strain energy barriers. In addition to minimizing these energy barriers, there are a number of less well understood, but equally important glass synthesis observations that are known to be important to increasing the ionic conductivity in glass. Our search for maximum conductivity, or maximum decoupling, in ion conducting glasses will therefore include well understood principles and less well understood glass synthesis and processing observations.

C.2.2. Composition and interaction factors which maximize the mobility of cations in glasses

(What are the physical and chemical factors which determine whether ions will migrate freely through the structure?)

To minimize the Coulomb energy barrier in glass, large anions and “soft” cations should be used at as high a mole fraction as possible. Hence, the well known increase in conductivity associated with additions of silver iodide to silver ionic glasses is associated with the decreased Coulombic interaction of the large and singly charged polarizable iodide anion with the polarizable and singly charged silver cation. Similar increases in the conductivity of sulfide glasses over that of oxide glasses is also a result of the decrease in Cou-

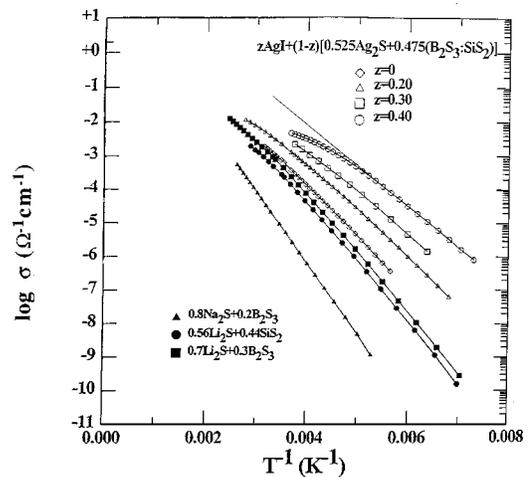


FIG. 22. Arrhenius plots of the ionic conductivity for $\text{Ag}_2\text{S}-\text{SiS}_2-\text{B}_2\text{S}_3$ glasses (Ref. 167) compared to those for other Li- and Na-conducting glasses. Notice that for the poorer conducting glasses, the Arrhenius plots are linear, whereas the optimized Ag conducting FIC glasses show strong deviations from linearity at the highest temperatures (from Ref. 167 by permission).

lomb interaction with the larger and more polarizable sulfide anions. The increase in conductivity in these optimized “chalcogenide” glasses, as described above, can be quite dramatic, as is shown for a typical lithium sulfide-based glass in Fig. 22. Such increases make these glasses attractive as solid electrolytes in a number of electrochemical devices, not the least of which is the solid state battery.

Less well understood, however, are the other factors that affect the conductivity of these glasses. One of the most important is the little understood “mixed glassformer effect,” so named after the equally little understood “mixed alkali effect.” These effects change the conductivity in opposite directions. The first increases it above the additive value; hence it is of special interest. An example is shown in Fig. 23, where the conductivity is seen to maximize at the

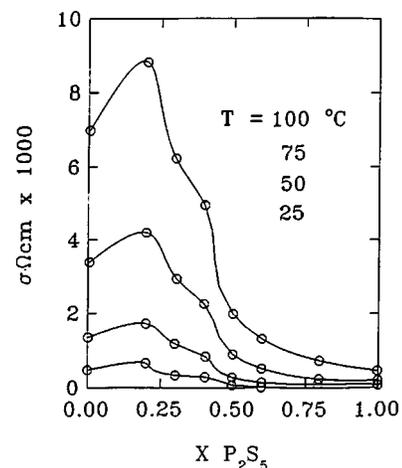


FIG. 23. Composition dependence of conductivity for ternary $\text{Li}_2\text{S}+\text{SiS}_2+\text{P}_2\text{S}_5$ glasses across the series $0.6\text{Li}_2\text{S}+0.4[(1-x)\text{SiS}_2-x\text{P}_2\text{S}_5]$, showing maximum in “mixed” glassformer effect at $x=0.25$ (after Ref. 167 by permission).

SiS₂ glassformer fraction of 0.20. Similar trends are observed in silver-based and chalcogenide-based glasses.

Seeking to maximize conductivity by combining the above principles, Martin and Kincs¹⁶⁷ synthesized and characterized glasses in the ternary mixed glass-former system Ag₂S+B₂S₃+SiS₂ and then doped them with AgI, up to 40 mol % AgI. The conductivities of glasses of different AgI fraction are shown in the Arrhenius plot, Fig. 22. As expected, the glasses exhibit exceptional conductivities which increase with the fraction of AgI in the glass. The room temperature conductivities of these glasses are among the highest reported to date. However, unexpectedly the best conducting glasses develop strongly non-Arrhenius behavior at the higher temperatures, which prevents them from reaching the unprecedented values promised by their low temperature Arrhenius trends.

Non-Arrhenius behavior in Ag-based fast ionic conducting glass has been observed before by Ingram *et al.*,¹⁶⁸ among others. In these cases, the glass compositions were the so-called “silver oxysalt” glasses of general composition AgI+Ag₃AsO₄. In such a glass, there is no network. The glass is a low temperature salt type glass that forms presumably because of a melting point lowering effect of the added AgI to the already low melting Ag₃AsO₄ salt. Ingram *et al.* argued that the non-Arrhenius behavior of the conductivity was associated with the restructuring or relaxation of the weakly bound *anions* in the glass as the glass temperature approached room temperature from above. To support their observations, these authors found that annealing the glass below T_g progressively decreased the extent of the non-Arrhenius behavior to the point that at the extreme of long time annealing, the temperature dependence of the conductivity returned to a simple Arrhenius behavior.

However comparable annealing treatment has no effect in the case of the network glasses. The observations suggest that the search for a maximally decoupled, highest conducting glass, may be compromised. To see if this behavior might be universal among optimally decoupled fast ion conducting glasses, Martin and Kincs¹⁶⁷ explored other highly conducting glasses, and found (Fig. 22) that even alkali metal glasses of high conductivity exhibit this behavior, though to a lesser extent. Note that the lower conducting sodium thioborate glass appears not to exhibit this behavior.

Attempts to interpret the decrease in “apparent” activation energy have been made by several authors.^{169,170} It will require the application of tools sensitive to cation–cation correlations and cation clustering effects¹⁷¹ to decide what the final limits will be on glassy conductivity. Particularly desirable are extensions of the Fig. 22 studies to higher temperatures, since T_g is quite high in these systems.

An old problem in this field has been that of deciding between the ionic equivalent of the electronic semiconductor problem, namely finding the relative importance of electron mobility vs. conduction band population effects in fixing the measured value of the conductivity. The ionic glass model which contains these elements is the “weak electrolyte model”,^{171(a)} which has been a source of contention in the field since its beginning. Many attempts have been made to determine an ionic Hall mobility, so far without success.

Some new light may be thrown on this problem by a method for determining the hopping rate of Li⁺ ions in lithium conducting glasses by Bohmer and co-workers.^{171(b)} They use a stimulated spin echo NMR technique to determine residence times in the ms range.

C.2.3. Frequency dependence of ionic conductivity in glasses

Much effort has gone into the study of frequency-dependent conductivity phenomenology and this has been the subject of a number of previous reviews^{71,172} which will not be repeated here. We only mention a new development in the understanding of the controversial regime lying between the attempt frequency set by ionic rattling and the relaxation frequency set by ionic jumping. There is now much evidence^{71,172} that, between these two characteristic frequencies, there is a regime in which the loss (component of the energy per cycle of applied field that is dissipated as opposed to stored) is independent of field frequency. What has been a mystery has been the difference in the magnitude of the loss in this regime for different glasses, and for the same glass at different temperatures.

Recently this phenomenology has been systematized by Ngai¹⁷³ from an exhaustive collection of dielectric relaxation data of glassy, crystalline, and molten ionic conductors. The data were analyzed to obtain the magnitudes of the constant losses and their dependence on temperature, ion density, ion mass, dc conductivity activation energy, dc conductivity level, the nonexponential conductivity relaxation parameter, the effect of mixed alkali, and the decoupling index R_τ . The results indicate that the ions are responsible for the loss. As a rule of thumb, the magnitude of the constant loss at the same temperature and its variation with temperature are greater in a glass or crystal that has higher ionic conductivity. Qualitatively speaking, the more loosely the ions are bound, the greater is the constant loss. The temperature dependence of the near constant loss of glassy and crystalline ionic conductors is well described by $\exp(T/T_a)$. T_a is typically of the order of 100 K and hence the change of the constant loss with temperature is very modest compared to the Arrhenius temperature dependence of the dc conductivity. For example, in the Na₂O–3SiO₂ glass the loss changes only by about a factor of 4 over the temperature range of 100 to 300 K, while the dc conductivity extrapolated using an activation energy of 62 kJ/mol is expected to change by twenty one orders of magnitude over the same temperature range.

For the glass-forming molten salt, 0.4 Ca(NO₃)₂–0.6KNO₃ (CKN), the loss has been determined below as well as above T_g . Like other glassy ionic conductors, the loss has the same mild temperature dependence at temperatures below T_g . However, above T_g , the increase of the loss with temperature is much more rapid. A distinct change in the temperature dependence observed near T_g indicates that the constant loss is also sensitive to the structural glass transition.¹⁷³ It has been found that the constant loss in CKN has approximately the same temperature dependence as the mean square displacement of the ions obtained by elastic neutron scattering measurement. The mechanism contributing to the loss at lower temperatures and all frequencies may

not be the same as the one responsible for the loss at high temperatures and high frequencies. The relation of the constant loss to the mean square displacement of the ions suggests the mechanism at lower temperatures arise from some forms of local displacement of the ions and at higher temperatures from relaxation of vibration of the ions caused by the anharmonic potential. The origin of the ubiquitous constant loss in ionic conductors remains a challenging problem.

C.3. Mobile ions or atoms in metallic glasses

(Is there a similar decoupling possible for nongaseous elements in metallic glasses?)

The existence of high mobility for cations (or the equivalent atoms) in metallic glasses has been demonstrated by many measurements such as those shown in Fig. 21(c). These show diffusivities^{174(a),(b)} far above the Stokes–Einstein value at the glass transition temperature of the system.^{1,174(c)} The decoupling index of Co in Zr₅₀Ni₅₀ may be taken as

$$R_{\tau} = D_{\text{Co}(T_g)} / D_{\text{Zr}(T_g)} = 10^{4.5}$$

although this is low compared to superionic species in ionic glasses. However, much more decoupled species have been observed.^{174(c)} Elements whose cores are highly polarizable, like Ag and Cu, seem to be particularly mobile, as in the case of ionic glasses and doubtless for the same reason. On the other hand, Au seems to be slow both in Zr-based alloys and in *a*-Si (see Sec. C.5.). The phenomenon should be susceptible to study by the same mechanical relaxation methods that have been used to study conductivity relaxation/mechanical relaxation relations in superionic glasses.^{172(c)} It would be interesting to know if the same relation between relaxation spectral width and decoupling index suggested for superionic glasses¹⁷⁴ would apply also to decoupled atom motion in metallic glasses.

C.4. Mobile atoms and molecules in polymer glasses

(What about gas molecules in glasses and polymers?)

A great deal of work has been done on gas molecule mobility in polymers above and below T_g and it is known, for instance, that mobility is much lower in nonfragile polyisobutylene than in other chain polymers (hence its use as an inner tube rubber in all pneumatic tires) and that it is much less in polymer glasses than in polymer liquids [hence the use of polycarbonate plastics ($T_g > \text{ambient}$) in plastic bottles for carbonated beverages].⁶⁶ However, the reviewers have little expertise in this area.

C.5. Mobile water molecules in biomaterials

(What about decoupling of water molecules in biopolymers?)

It is known that H₂O molecules are relatively mobile in certain hydrogel polymers and biopolymers near and below their T_g , but we have little quantitative information on the subject.¹⁷⁵ An interesting situation is found in aqueous sugar solutions in which rotational diffusion of water molecules becomes very free at high sugar concentrations (and seems

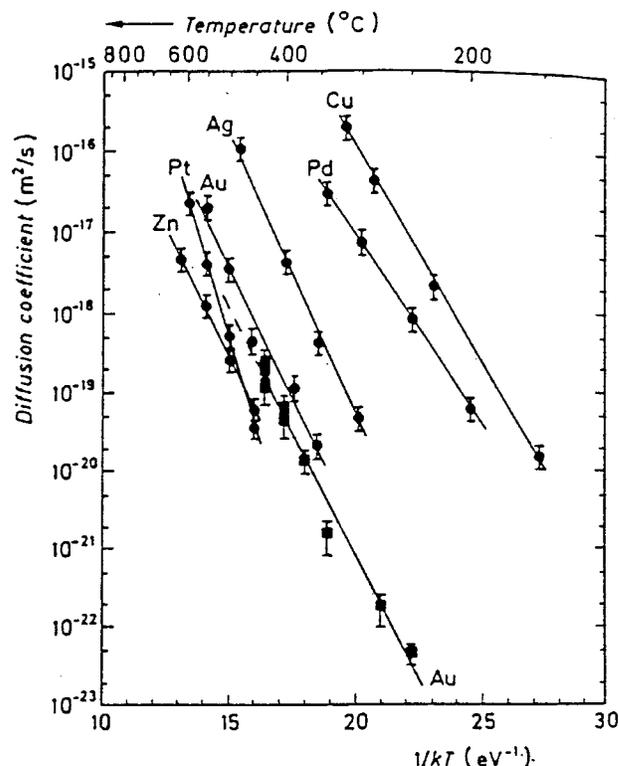


FIG. 24. Diffusivities of dopant species in *a*-Si by Rutherford backscattering and tracer diffusion (from Ref. 178, by permission).

as if it is unaware of the impending glass transition), while translational diffusion continues to be coupled to that of the sugar molecules.¹⁷⁶ These systems deserve much more study.

C.6. Mobile atoms in amorphous silicon

(What about mobility of dopant species in *a*-Si?)

The special interest of liquid silicon and its metallic liquid-tetrahedral semiconducting phase, was mentioned in Secs. A.3.1. and A.3.2. The amorphous solid obtained by vapor phase routes has been the subject of intense research, much of which is reviewed in Ref. 177.

Although *a*-Si is not normally formed by a liquid-quenching process, we find here that it shows most of the properties expected for the low temperature polyamorph of a strongly tetrahedral glassformer. The closest analog of *a*-Si among the liquid-formed glasses is that provided by the Zr-based metallic glasses discussed above. Just as transition metals diffuse rapidly in Zr–X (X=Cu, Co, etc., see Fig. 21) so do doped-in metals (and nonmetals also) rapidly diffused in *a*-Si.^{178,179} The most rapid diffusion is that of Cu, data for which are shown in Fig. 24.

To link this behavior into that of other glassy systems we should attempt to assign decoupling indices to the mobile elements. In previous work, this has been done¹⁸⁰ by comparing the mobility of the mobile species with that of the host at the glass transition temperature, defining the decoupling index by $\tau_{\text{host}}/\tau_{\text{mobile}}$ at $T_g = 100/\tau_{\text{mobile},(T_g)}$ since $\tau_{\text{host},(T_g)} = 100$ s. The problem in the case of *a*-Si is that the glass transition temperature is not known. To remedy this

defect we need to estimate the glass transition temperature that *a*-Si would have if it did not crystallize.

We can do this from available data in several ways. The most direct would be to use data on the diffusivity of Si in *c*-Si and *a*-Si to calculate the temperature at which it would have the value, $10^{-18} \text{ cm}^2/\text{s}$ characteristic of nonfragile liquids at their T_g . For *c*-Si, measurements have been made in the temperature range 1000–1400 °C.¹⁷⁹ Extrapolation to lower temperature shows that D_{Si} would reach $10^{-18} \text{ cm}^2 \text{ s}^{-1}$ at 920 °C.¹⁸¹ This must place an upper limit on the hypothetical T_g for *a*-Si since it is not easy to imagine an elemental glass in which the glassy state is *less* mobile than the crystal. Data for *a*-Si itself are, unfortunately, not available since *a*-Si usually recrystallizes above 550 °C. Pending data, we make the informed assumption that $T_g = 800$ °C, which is not far above the crystallization temperature observed in some of the diffusivity studies of trace elements in *a*-Si (see Fig. 24). It is consistent with the observation of large annealing enthalpy stabilizations in *a*-Si after initial preparation, observed in the work of Roorda *et al.*^{182(a)} and Donovan *et al.*^{182(b)} and even larger effects in *a*-Ge.^{182(c)}

A further way to estimate T_g for *a*-Si would be to use measurements of the Debye–Waller factor for *a*-Si to find the temperature at which $\langle r^2 \rangle$ would become $d_{\text{Si}}/3$, at which strong liquids undergo their glass transitions (due to some Lindemann-like critical displacement phenomenon (see Sec. D.2.)).

Using the estimate of 800 °C as T_g for *a*-Si we may obtain decoupling indices for the elements whose diffusion coefficients have been measured by extrapolating the data to 800 °C and then ratioing their values to the T_g characteristic value, $10^{-18} \text{ cm}^2 \text{ s}^{-1}$. Values thus obtained range from $10^{11.2}$ for Cu down to $10^{6.1}$ for Zn, (i.e., $R_\tau = 6.1$) which may be compared with that for Co in $\text{Zr}_{50}\text{Ni}_{50}$ met glass, viz. $10^{4.5}$.

The value for Cu is comparable to those found for superionic glasses;¹⁸⁰ e.g., the best Li^+ conducting glass has $\log R_\tau = 11$. It is interesting that the largest decoupling indices in ionic systems are also found in systems whose structures are of tetrahedral network character,¹⁸³ like *a*-Si.

In hydrogenated amorphous silicon, diffusivities of dopant species such as Pd are increased¹⁷⁹ by more than an order of magnitude. As in the case of ions in glasses, such an effect may be traced to either of two effects: (i) the process has become more decoupled from the host; (ii) the glass transition temperature of the host has decreased (as if the whole mobility landscape has been raised). Without diffusivity data on Si in *a*-Si:H, no decision between those two can be made though, based on the common experience that breaking networks lowers T_g , it seems likely that this is also the case with *a*-Si:H; i.e., option (ii) is correct. What is needed to complete this phenomenological connection of *a*-Si:H to other glassy systems is a study of D_{Si} as a function of H content.

C.7. Relation of mobile species relaxation in glasses to β relaxations

(What is the relation between secondary relaxation in glasses due to fast-translating species on the one hand, and nontranslating entities (e.g., side chains) on the other?)

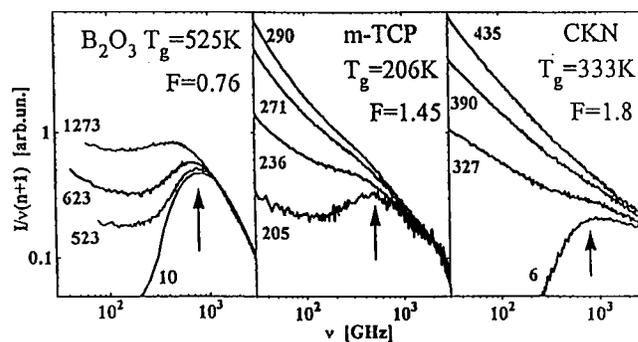


FIG. 25. Examples of the boson peak, based on low-frequency Raman spectra of different glass forming system peak $(n+1) = [1 - \exp(-h\nu/kT)]^{-1}$ is a temperature of Bose factor. TCP is tricesylphosphate and CKN is calcium potassium nitrate 40:60 (from Ref. 185, by permission).

Both secondary relaxations due to local rearrangements (of uncertain character) and secondary relaxations due to well-identified mobile species, have Arrhenius temperature dependences that seem, by extrapolation to high temperature, to result from bifurcation of the primary relaxation process. Thus it is natural to ask how closely the two types of secondary relaxations are related.

In the first place, secondary relaxation of nontranslating entities, like β relaxations in small molecule liquids and polymers, to the extent that they can be studied, generally remain Arrhenius *even above* T_g .¹⁸⁴ On the other hand, above T_g , the temperature dependences of the transport coefficients of the diffusing species generally deviate from Arrhenius behavior. Examples for which such observations have been made include the conductivity relaxation of ions in vitreous ionic conductors which do not have large decoupling indexes (e.g., CKN), and diffusing tracer molecules in small molecule liquids and polymers. A second difference is that these latter relaxations usually exhibit a stretched exponential relaxation function with almost temperature-independent stretching exponents; i.e., TTS applies. The Johari–Goldstein β relaxation, on the other hand, shows a very broad distribution of relaxation times, and one which has a very temperature-dependent width due to a Gaussian distribution of barrier heights.

C.8. Other questions

The other questions raised in Sec. C.7, of the introduction remain unaddressed, as challenges to future research workers.

D. SHORT TIME DYNAMICS

D.1. Boson peaks in Raman and neutron scattering

D.1.1. Empirical observations

(How good are the data?)

Data on the boson peaks have been collected by Raman scattering and neutron scattering in many different kinds of materials ranging from inorganic network, to small molecules, and polymeric glasses. It is seemingly ubiquitous and, at sufficiently low temperatures, is seen experimentally in all glassforming substances, strong or fragile except glassy

water and *a*-Si. Examples are shown in Fig. 25. At higher temperatures near T_g and above, the increasing quasielastic (relaxational) contribution to the scattered intensity (spreading out about zero frequency) tends to obscure the boson peak to a degree that seems to correlate with the fragility of the material. The relaxational contribution decreases with frequency, while the vibrational contribution increases with frequency up the maximum of the boson peak. Sokolov and co-workers¹⁸⁵ considered the ratio R_1 of the intensity at the minimum to the intensity of the boson peak maximum measured at T_g as a measure of the relatively contributions of relaxation and vibration to the normalized Raman spectrum. A correlation between R_1 and fragility was found. This correlation will be discussed immediately below.

D.1.2. Relation of Boson peaks to longer time behavior

(Is there a correlation with strong/fragile behavior in the longer-time properties?)

Sokolov and co-workers have established a correlation between the ratio R_1 of boson peak to relaxational contributions to the Raman spectra (normalized by the temperature factor $\omega[n(\omega)+1]$) and the fragility of the glassformer,¹⁸⁵ see also Ref. 186. The fragility of the substance was quantified by the ratio E_η/T_g , where E_η is the apparent activation energy of viscous flow at T_g . We note that this definition for fragility is inappropriate for polymers (which were included in the correlation) because the viscosity of a polymer depends on the chain length, and often has a different temperature dependence than the local segmental motion which is responsible for the glass transition in polymers.¹⁵⁸ The appropriate definition for fragility that applies also to local segmental motion in polymers has been given previously¹⁸⁷ although the more recent $F_{1/2}$ definition^{6(b)} may be obtained from data sets such as given in Ref. 187(c). Only two polymers, polystyrene and polybutadiene, were included in the original published works of Sokolov and co-workers. At that time, there were boson peak data only in polybutadiene. Hence the error turns out to be inconsequential. Since then, Raman and neutron data for boson peaks in several polymers including polystyrene, polycarbonate, and polyisobutylene have become available. The polyisobutylene experimental data are particularly significant because this polymer is the least fragile among amorphous polymers.^{141,187-189} When the appropriate fragility index is used, the correlation between R_1 and fragility is clearly valid for polymers also.¹⁸⁹

Raman scattering in the most fragile polymer poly(vinyl chloride) was studied by Viras and King.¹⁹⁰ Neutron scattering measurements on poly(vinyl chloride) were made by Colmenero and co-workers.¹⁹¹ From their published data, the boson peak is not observable, indicating $R_1 \geq 1$, consistent with the extremely fragile nature of this polymer, see also Sec. D.1.5. Recently Duval and co-workers¹⁹² have obtained the Raman spectra of poly(vinyl chloride) plasticized by the addition of 10% dioctylphthalate. They were able to observe the boson peak at room temperature and confirm that the strength of both the boson peak and the excess heat capacity are relatively weak in this plasticized fragile glassformer. However, at room temperature, the observation of the boson

peak in plasticized poly(vinyl chloride) and the lack of it in unplasticized samples remain to be explained. Duval *et al.*, although recognizing the fact that plasticization decreases the intermolecular interactions between the polymer chains, rationalize the difference of boson peak strength in plasticized and neat poly(vinyl chloride) by diminished quasielastic Raman scattering in plasticized samples permitting the boson peak to become more visible. The boson peak in plasticized samples has been interpreted as being due to surface vibrations of cohesive domains in a model of phonon localization in inhomogeneities.¹⁹³ However, there is a simpler alternative explanation¹⁹⁴ based on the decrease of fragility with plasticization of poly(vinyl chloride) which has been shown from dielectric relaxation data in an earlier publication.¹⁹⁵ The reduction of fragility with the addition of a diluent to a polymer naturally explains the appearance of the Boson peak at room temperature via the correlation between fragility and R_1 .

D.1.3. Relation of the Boson peak to the FSDP

(Is there a correlation with the structural features responsible for the first sharp diffraction peak?)

The original expectation of Novikov and Sokolov¹⁹⁶ was that the boson peak would be the dynamic corollary of an extra feature in the static structure factor of some of the more structured glasses, a feature known as the FSDP. The FSDP arises from some little understood and hotly debated aspect of the intermediate range order.^{192,193,197-199} That there should be a relation is certainly a corollary of the association of both the intermediate range order and strong boson peaks with diminished glassformer fragility. However, the relationship is evidently a subtle one¹⁹⁹ and cases of anticorrelation have even been suggested.²⁰⁰ Further references to this problem will be made in the next section.

D.1.4. Do boson peaks measure cluster dynamics or cage rattling dynamics, or "interstitial" resonance modes?

There are many points of view as to the origin of the boson peak. If it is assumed that excitations in disordered systems have no well-defined wave vector \mathbf{q} , then they can contribute to the light scattering spectra.²⁰¹ The first order Raman intensity $I(\omega)$ is written in the form

$$I(\omega) = C(\omega)g(\omega)[n(\omega)+1]/\omega, \quad (14)$$

where $g(\omega)$ is the density of states of these excitations, $n(\omega)+1$ is the Bose factor, and $C(\omega)$ is the coupling coefficient of light to these excitations. The boson peak has often been attributed to a maximum in $C(\omega)$, after the theory of Martin and Brenig.¹⁹⁷ However, a comparison with inelastic neutron scattering data indicated that the boson peak is related to an excess in the vibrational density of states.²⁰¹

Several models have been proposed to explain the boson peak. One model¹⁹³ assumed that the glass is composed of nanometric scale inhomogeneities, and $g(\omega)$ is the density of vibrational excitations localized in the inhomogeneities. Another model is based on phonon localization.²⁰² The soft-potential model²⁰³ assumes the main contribution to the low frequency Raman spectra comes from localized excitations

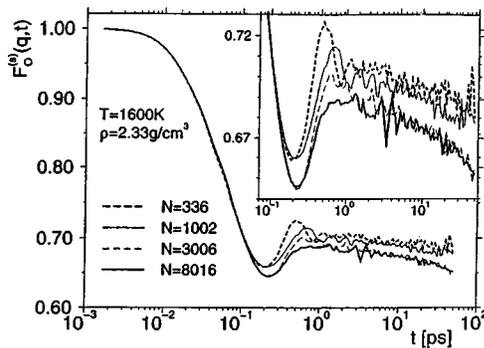


FIG. 26. System size dependence of the “boson bump” in the intermediate scattering function (from Ref. 207 by permission).

in soft potentials which may be relaxational or quasi-harmonic vibrational in character. The vibrational excitations give rise to the boson peak. On the other hand, Roe, on the basis of his MD simulations on models of polyethylene and polystyrene,²⁰⁴ has suggested that the boson peak originates in cage rattling of the monomers. Finally, Granato²⁰⁵ has argued that they are the glassy state equivalent of resonance modes associated with the interstitials of the defect crystal state. (See also Sec. D5 below.)

The boson peak intensity can depend strongly on structure and it almost disappears in *a*-GeO₂ on compression to 20 GPa during which changes of the Ge coordination number from 4 to 6 occur.²⁰⁵ While this may be just a reflection of decreasing Raman cross section with increasing coordination number, it would also be consistent with a proposed change for such networks from strong to fragile behavior under strong compression.²⁰⁶

At low temperatures where there is no relaxation within the time window of the computer experiment, the mean square displacement of the atoms increases monotonically with time and shows an overshoot before returning to the temperature dependent value defined by the Debye–Waller factor. The overshoot is related to the boson peak. This viewpoint is supported by molecular dynamics simulations of An-

gell and co-workers^{121(c)(d)} in SiO₂, B₂O₃, and BOF. However, caution must be exercised in interpreting these overshoots. In small systems of strongly bound particles with well-defined intermediate range order, like SiO₂, this overshoot, and a subsequent “ringing” which may also be observed with careful averaging, can be shown to be a consequence of small system size.²⁰⁷ These effects are illustrated in Fig. 26. The first bump in *S*(*q*,*t*), and the overshoot in $\langle r^2 \rangle$, survive in large systems. Their association with the boson peak has been confirmed by the investigation of their *q* dependence by Horbach *et al.*²⁰⁸ At higher temperatures when relaxation becomes important, the mean squared displacement continuously increases with time and the boson peak is obscured.

An important insight into the relation between the boson peak and the quasielastic contribution has been gained from a careful comparison of Raman and neutron scattering data of polystyrene, polybutadiene, and SiO₂ at different temperatures above and below *T_g*.²⁰⁹ The neutron and Raman spectra are found to be similar in the frequency range from low frequencies where the quasielastic or relaxational contribution dominates up to the vibrational boson peak frequency ω_{\max} . Thus the coupling coefficient of light to excitations, *C*(ω), is constant and independent of frequency for $\omega < \omega_{\max}$. This important result suggests that there is a connection between the quasielastic scattering and the boson peak at all temperatures. This connection is supported by the depolarization ratio $\rho(\omega)$, defined as the ratio of scattering intensity of depolarized to polarized light. Although this ratio varies widely; e.g., 0.24 for the fluorozirconate glass, 0.3 for SiO₂, and 0.75 for most of the organic glassformers (including the polymers polystyrene and polybutadiene); in all cases it was found that it has the same value for the boson peak, and the quasielastic scattering contribution found is consistent with the soft potential model, the cage rattling scenario, and a phenomenological model,²¹⁰ which assumes that the low frequency vibrations are damped due to some relaxation channel. As a consequence, a vibration mode has both vibrational and relaxational character.

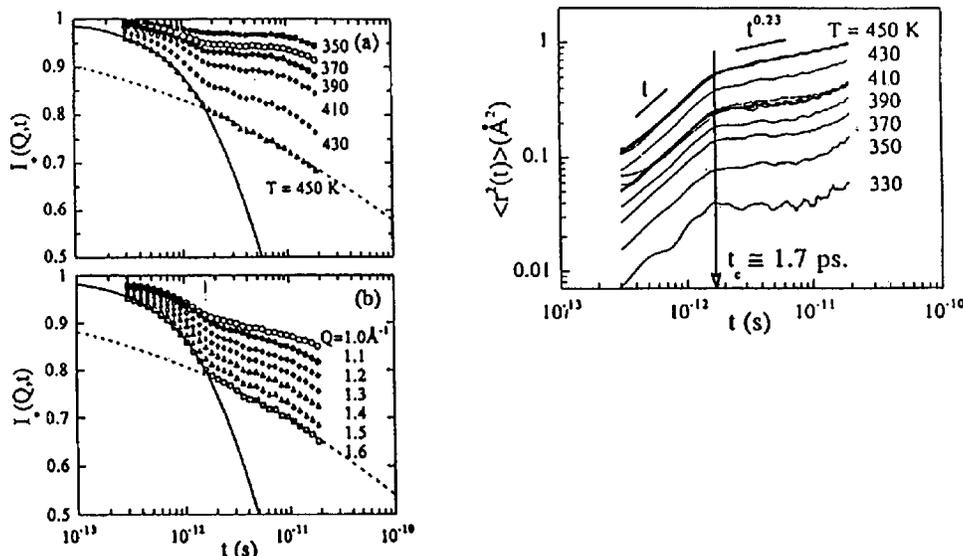


FIG. 27. Intermediate scattering function for polyvinyl chloride (a) at different temperatures for fixed (1.5 \AA^{-1}) and (b) for different values at fixed *T* (450 K) showing crossover to slow dynamics similar to the phenomenon seen in molecular dynamics (Fig. 26) but without the boson bump. (c) shows $\langle r^2 \rangle$ vs time behavior for same system, at different temperatures. The absence of boson bump or $\langle r^2 \rangle$ overshoot is a consequence of the very fragile character of PVC (from Ref. 211, by permission).

D.1.5. Are there relaxation dynamics before the boson peak?

The very short time component of the intermediate scattering function—that which precedes the dip associated with the boson peak—is also subject to different interpretations.

For very fragile systems like PVC, both the short time and relaxational components can be observed in time-of-flight neutron scattering experiments.²¹¹ In such fragile systems, the boson dip does not appear and, as seen in Fig. 27, the short time component has the aspect of an exponential relaxation, as is indeed observed to account for the whole of $S(k,t)$ at temperatures near and above the melting point. Thus a natural interpretation of the decay before the boson bump seen in less fragile liquids has been that of Ngai *et al.*,²¹² who interpret it as a “primitive relaxation”—a remnant of the high temperature exponential process which then gets slowed down by the crossover to cooperative dynamics. The “primitive process” is considered to involve rotation around the $C-C$ axis, because the characteristic time of the exponential decay obeys an Arrhenius law with an activation energy of ≈ 15 kJ/mole which corresponds with the known energy barrier to the *trans-gauche* rotation. Mode coupling theorists simply call this part of the decay “the microscopic process.” It is given little attention until it enters the plateau regime via the “fast β relaxation.”

For stronger liquids there is structure in this part of the decay^{206,213} and it seems clear that some sort of vibrational dephasing is involved. This is consistent with the existence of this component of $S(q,t)$ at low temperatures far below T_g in the harmonic dynamics regime where dephasing is the only mechanism for loss of correlation. In simple glassformers this decay component at low temperature remains exponential, consistent with the notion of “diffusion in a harmonic potential”—a description of the configuration space state point, when deep in one of potential minima of the “energy landscape.”

Whatever the detailed explanation may turn out to be, this part of the dynamics contains information on the manner in which a disordered system engineers the transition from vibrational to relaxational dynamics. Since, in stronger liquids, the dynamics of the boson peak is found entrenched at the crossover point,²⁰⁸ we consider it an area worthy of much more detailed investigation.

D.2. Vibrational amplitudes and the glass transition

(Breaks in the Debye–Waller factor—what do they signify?)

An alternative way of looking at the early time dynamics focuses attention on the postboson peak behavior below and about the glass transition temperature. Here concern is with the behavior of the Debye–Waller factor $\langle r^2 \rangle$, which is obtainable from Mössbauer spectroscopy, neutron scattering, and with less precision, x-ray scattering data. It can also be studied by MD computer simulations, from which much additional information can be obtained. Unlike the intermediate scattering function of Figs. 10(a), $\langle r^2 \rangle$ shows no q dependence [see Fig. 27(b)].

A provocative finding has been that of Buchenau and Zorn²¹⁴ for the elemental glass selenium. Using an instrument with time resolution in the ps range, these authors found that the vibrational amplitudes in the glass increase more rapidly than in the crystal. More significantly, at the same amplitude as that at which the crystal melted, the glass exhibited a fairly sharp change in $d\langle r^2 \rangle/dT$. The temperature of this event was the same as that of the glass transition. Recalling the Lindemann criterion for melting,²¹⁵ this suggests that the glass, confined to a single energy minimum on the Goldstein–Stillinger landscape, can only tolerate a certain critical mean vibrational amplitude before the crossing of energy barriers between configurational microstates becomes probable on the normal observation time scales of minutes. At T_g , evidently, 1 in 10^{15} oscillations result in diffusion; i.e., “basin hopping.” Above this temperature, configurational volume changes take over from anharmonicity-driven changes, and the vibrational expansivity remains constant at its value at T_g rather than accelerating. Comparable “breaks” in $\langle r^2 \rangle$ vs T have now been reported in many polymer systems,²¹⁶ biophysical systems,²¹⁷ and some molecular liquid systems,²¹⁸ although opinion as to where the “break” commences varies according to author. As for the early time part of the dynamic structure factor, opinions vary as to the physical significance of the two slopes.²¹²

A component of the increase in mean square displacement (MSD) seen in the experiment may be associated with the constant pressure increase in volume which occurs as $T > T_g$ (due to the increase in expansivity at T_g), however this is uncertain because the motions responsible for the increased MSD are not well understood. At T_g , the center of mass diffusional displacement in a ps, calculated from the known diffusivity, is completely negligible so the increase in $\langle r^2 \rangle$ comes from some nondiffusional source. Part of it at least is associated with the change in vibrational behavior accompanying structural excitation since the corresponding quasielastic light scattering shows an annealing effect.²¹⁹ This means that the intensity of quasielastically scattered light changes at constant temperature during relaxation, so it relates to *fictive* temperature rather than to actual temperature.

On the other hand is the fact that a change in $d\langle r^2 \rangle/dT$ can also be seen in constant volume computer simulations in the *absence* of any change in structure.^{121(c),(d)} This is because, on the MD time scale, diffusion (by which structure changes) can only be observed at a temperature far in excess of the normal glass transition temperature. The constant structure (i.e., prediffusion) $\langle r^2 \rangle$ behavior appears to show its change of slope around the temperature where the experimental substance shows a glass transition.^{121(d)} At this temperature the value of $\langle r^2 \rangle$ for the oxygen in oxide glasses of different dimensionalities^{121(d)} is 0.1 \AA^2 , the same as for Se at its T_g . The Se atom and the oxide ion are comparable in size, so it seems from the analysis that the glass transition occurs when the mean square vibrational amplitude is about 10% of the particle diameter. It is notable that in one relaxation time the average (viscosity-determining) particle in a nonfragile liquid moves a distance which is about one mo-

molecular diameter. [This is obtained by writing, after Einstein, $l = \sqrt{6D\tau}$, and using data for hot liquids in which D and τ are both known at the same temperature and in which no decouplings have occurred.] The sharper of the break in r^2 vs. T the greater the fragility of the liquid appears to be.^{121(c),(d)} This is confirmed by the most recent experimental result (for B_2O_3) by Engberg *et al.*^{188(a)} Roland and Ngai,^{188(b)} also considering the relation of r^2 to fragility, note a connection between the temperature dependence of r^2 and the “short time noncooperative relaxation” called by others the “microscopic process” (See also Sec. D.5).

An alternative but related viewpoint concerning the above type of data is presented in intermediate scattering function $F(k,t)$ form. The temperature dependence of the prediffusion plateau height is reported as the “nonergodicity parameter” $e^{(r^2k^2)}$. This parameter takes the place of the mean square displacement, and is predicted by mode coupling theory^{11(b)} to exhibit a quadratic form up to the temperature T_c , where the structure should precipitously “unfreeze.” This prediction of the theory has been roughly supported by data fits to the constant pressure Debye–Waller factors obtained in a number of experiments.^{220–222} Note that, in these experiments, the $\langle r^2 \rangle$ observations refer to different structures (average of a narrow range of “inherent structures”) at each temperature for which $T > T_g$ (T_g the laboratory glass transition temperature), as in the case of selenium referred to earlier. Again, however, a similar phenomenon can be observed at constant volume and structure using computer simulations.^{73,121(g)}

D.3. Localization of vibrational modes

(What is vibrational localization? What special dynamical characteristics are associated with localized modes? And how might it be related to relaxation?)

The criterion usually applied to classify a vibrational mode as localized or otherwise is the participation ratio.²²³ On examining the participation ratio as a function of frequency in the density of states it is found that, for simple systems, vibrational localization occurs at the two extremes. The presence of localization at the high frequency extreme has been documented many times and causes no surprise.²²³ Localization at the low frequency edge is more controversial.^{224,225}

The low frequency modes, which are localized by the above criterion, have been examined in some detail by such authors as Schober and Laird,²²⁴ and Van Ee *et al.*²²⁵ The eigenvectors have been characterized and found to involve a large number of atoms. Van Ee *et al.* probed their stabilities by driving them with a harmonic excitation of the same frequency and found that this provoked irreversible changes of atomic positions which did not occur when the same type of excitation was applied to nonlocalized modes. They therefore associated the localized modes with weak spots in the amorphous structures, like fault zones, which serve as the sites where atomic rearrangement occurs. However, the focus of attention in this work was on the modes which are involved in low temperature anomalies in glasses. How these

observations relate to structural relaxation near the glass transition is unclear.

Clouding the issue of low frequency mode localization are the studies of Ruocco and colleagues.²²⁶ These authors studied very large systems of Lennard Jones particles, and found that low frequency modes, despite low participation ratios, were still delocalized.

D.4. Slow modes in strong liquids

(What is the decay time for the FSDP in relation to the peak of the structure factor?)

The tenet of MCT is that relaxation in a dense liquid can be described adequately in terms of the decay of the fluctuations which are dominated by the modes in the vicinity of Q_0 , the peak of the structure factor. The temperature dependence of relaxation is then controlled by the temperature dependence of the structure factor. MCT has been found more applicable to fragile liquids than to the more structured “strong” and “intermediate” liquids. These more structured liquids are frequently distinguished by the presence of additional modes in the structure factor which correspond to distances larger than the nearest neighbor which determines Q_0 (Sec. D.1.3.). Madden and co-workers¹⁹⁹ have raised the possibility that these smaller Q modes, which originate in the special structural complexities of these liquids, might be the slow modes which dominate the dynamics, and have suggested that this could explain the difficulties encountered by MCT in dealing with these liquids. The validity of the first part of this conjecture has held up under study by molecular dynamics. Foley *et al.*¹⁹⁹ report that in stimulated $ZnCl_2$ the FSDP fluctuations decay much more slowly than do the Q_0 fluctuations. Experimental studies to confirm this observation are awaited with interest.

D.5. New developments

Since this review was submitted, some important gaps in our knowledge of the short time phenomenology have been filled, thanks to development of some new techniques and the careful application of others. We will give a brief review of two major advances and their significance.

Both make use of electromagnetic radiation, but use it in very different ways. One²²⁷ applies it directly, using developments in the generation and detection of electromagnetic waves at high frequencies (on the relaxation spectroscopy scale) to determine previously missing parts of the dielectric relaxation spectrum. These new results fall in the gigahertz and terahertz range at zero wave vector. The other²²⁸ uses extremely short wavelength radiation (x-rays) to probe wave vectors of atomic dimensions, and makes use of extraordinary technology to enable the study of inelastic scattering at angles so small that the energies probed are those of phonons ($\sim 10^{-8}$ of the incident radiation energy). Thus, this technique can equal and extend the domain of study formerly covered only by neutron scattering techniques. Of particular significance to this review is the way this development has made possible the study of viscoelasticity on the time scale of picoseconds cf. microseconds for ultrasonic studies and fractions of nanoseconds for Brillouin scattering.

Thus, the time range in which the slow modes of principal interest to this review merge with the “fast” (“microscopic” or “vibrational”) modes, has finally become accessible to detailed studies of both dielectric and mechanical character. Some details are given below.

At the same time as we mention this extension to extremely short times, and wavelengths, it is appropriate to emphasize the recent extension in the opposite direction made possible by the conscious use of electric modulus spectroscopy on systems of high dielectric constant. Wagner and Richert²²⁹ have made use of the relation between relaxation time (often called the modulus relaxation time) τ_M , and retardation time (the correct term for the usual “dielectric relaxation time” τ_D), and the high and low frequency dielectric constants, to obtain precise data on τ_D extending to some two orders of magnitude below the usual limit. The relation being exploited is Eq. (12) of Sec. A.2.5.

Using this approach and time domain measurements, values of τ_D out to $10^{7.5}$ s (\sim one year) for polyvinyl acetate have been obtained. It requires this extension to long times at high precision to be able to clarify whether or not a power law (with implications for percolation physics²³⁰) is a viable or superior description of the temperature dependence of the relaxation time in polyvinyl acetate near the glass transition. (Evidently it is not, see Ref. 231.)

D.5.1. Ultrahigh frequency dielectric spectroscopy

While a number of authors^{71,174,232–234} have attempted to connect the libration–vibration part of the far infrared spectrum to the lower frequency relaxation spectra for both molecular and ionic liquids and glasses, the systematic exposition of this vital crossover region of the spectrum has been left to Lunkenheimer, Loidl, and co-workers.^{227,235–238} In their recent extensive and detailed studies using both standard and newly developed equipment, these workers have systematically replaced the few data from earlier studies by a detailed mapping of the whole frequency range in which librations (or vibrations in the case of ions) become overdamped and finally evolve into the distinct and separate relaxation functions seen earlier in this review. The resolution is achieved by change of temperature, which shifts the relaxation time up with respect to the (more or less) unchanging libration (or vibration) time [Ref. 227, see also Ref. 71, Chap. 11, Fig. 9].

While they include work in familiar frequency ranges, Lunkenheimer and co-workers^{2(c),227,235–238} have used a battery of techniques to obtain the dielectric susceptibility of a selection of molecular and ionic liquids and glasses with unprecedented detail in the GHz–THz range. For this they combined use of coaxial transmission and reflection measurements with far IR absorption and reflection measurements, filling the gap between them with data from a novel quasi-optical spectrometry technique.²³⁹ They used a bank of ten “backward wave oscillators” to cover the range 40 GHz to 1.2 THz ($0.1\text{--}40\text{ cm}^{-1}$).

In this manner they were able to observe in detail the manner in which the gap between the “microscopic peak” (or libration band) and the relaxation (or loss) peak fills up as the high frequency edge of the loss peak moves up in fre-

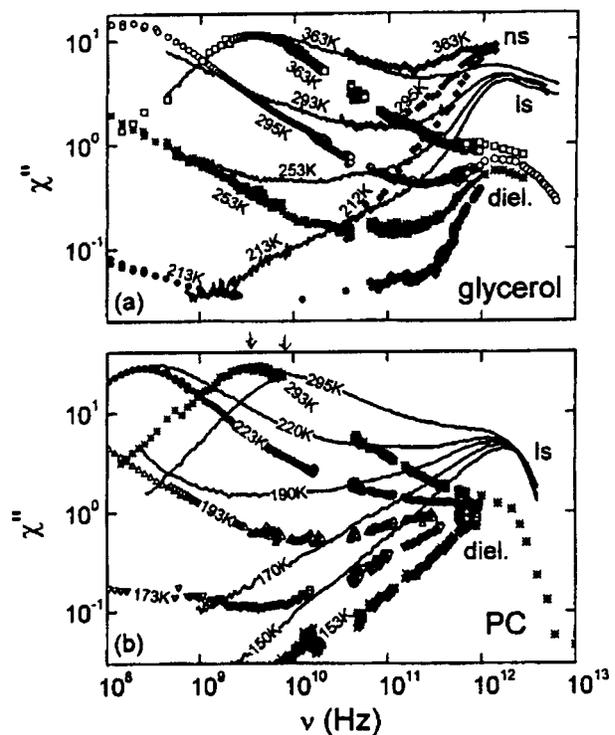


FIG. 28. Comparison of mechanical susceptibilities from light and neutron scattering with dielectric susceptibilities in the high frequency regime at different temperatures: (a) glycerol (intermediate) (b) propylene carbonate (fragile). Note that Fig. 2 and its relaxation time equivalent imply that the relaxation frequency can never be higher than the attempt frequency. The latter is suggested by this figure to be the boson peak frequency. On the other hand, Fig. 10(a) shows that at high temperatures $S(q,t)$ can decay to zero before the onset of caging can occur, yet it is at this caging onset time that the (system size dependent) “boson dip” is found^{207,208} in structured liquids. The implied dynamical crossover is associated, in MD studies^{60(c)} with the crossover from Arrhenius to super-Arrhenius transport temperature dependence as the system point moves over the edge of the landscape “high plains” onto the steep slope of the “excitation profile”—see Fig. 7(d). However, in propylene carbonate, the transport crosses over to Arrhenius behavior when the relaxation time is only $10^{-9.5}$ s, far longer than the boson peak time scale.^{227,238(b)} (Figure from Ref. 227, by permission.)

quency with increasing temperature. This is the merging of relaxation and oscillatory modes that is seen, in the time domain, as the elimination of the “caging plateau” see, e.g., Fig. 10(a). Above the merge temperature the appropriate description of the liquid is one of “itinerant oscillators.”

The observations of Lunkenheimer *et al.* are the dielectric equivalent of the relation between the “boson” peak of light and neutron scattering and the quasielastic scattering seen in each case at lower frequencies. This subject has been studied by Sokolov and colleagues for many years,^{185,196,201,209,211(b),219(b),240(c),241–243} and has been followed over wider frequency ranges by Cummins and co-workers using Fabry–Perot techniques.^{82(b),244–246} The latter work has revealed the full relaxation spectrum for the density–density correlation function which is essentially the same as that obtained from neutron scattering conducted over the same GHz–THz frequency range. Comparable behavior is of course expected in the phenomenologically equivalent “plastic crystal” (or “rotator,” “glassy crystal,” or “orientationally disordered crystal ODC”) phases^{6(a)} ex-

cept that in this case there is no translational component to the motion.

Comparison of light scattering and neutron scattering susceptibilities χ'' , with the new dielectric susceptibilities (or loss) ϵ'' , have been made and are presented in Fig. 28. Part (a) shows the comparison for an intermediate liquid, glycerol and part (b) makes the comparison for a fragile liquid, propylene carbonate PC. Note, in the case of propylene carbonate, the narrower, and lower frequency, dielectric loss peak²³⁸ relative to the mechanical loss peak^{82(b)} which was commented on in Sec. A.2.2.2.

The dielectric susceptibility data of CKN, glycerol and propylene carbonate^{227,235–238} taken at temperatures below the critical temperature, T_c , of the mode coupling theory no longer exhibit well-defined *minima* like those in Fig. 28. Instead, a broad and almost frequency independent trough or flat loss appears in the susceptibility spectrum. The flat loss in CKN extends over increasing numbers of decades at lower temperatures, which has been discussed as the constant loss of ionic conductors at the conclusion of Sec. C.2. The similarity of this peculiar feature in the dielectric spectra of CKN to features in recent light scattering and neutron scattering data of CKN, orthoterphenyl and other glass-formers performed at and below T_c ^{244(a)–244(c)} has been pointed out in Ref. 245(a). Such evidence of constant loss in the dielectric spectra of small molecule glass-formers as well as ionic systems suggests that it may be quite general (full spectra can be found in Refs. 227 and 235–238). In fact, Lunkenheimer and co-workers have obtained good fits to their dielectric spectra of CKN, glycerol, and propylene carbonate for all temperatures with expressions using the constant loss as the fast relaxation. A generalization of the constant loss analysis to light scattering and neutron scattering data of many glass-formers has revealed that the “almost constant” losses of different glass-formers exhibit a pattern that correlates with the stretch exponent, $\beta_\alpha(T_g)$, of the Kohlrausch–Williams–Watts function, Eq. (11), i.e., with the special time dependence of the structural α relaxation at T_g .^{245(b),245(c)} A spectacular demonstration that the constant loss is a potential candidate for fast relaxation in light scattering spectra can be found in the data of polyisobutylene (PIB) obtained by Sokolov and Kisluk.²⁴⁶ The flat loss of PIB in the light scattering susceptibility spectra is clearly seen at temperatures from $T_g=200$ K up to 290 K ($1.45T_g$).

In light scattering, a plot vs T of the scattered intensity at the frequency of the minimum seen at lower temperatures, shows a break at the glass transition temperature.²⁴⁰ This is of course where the structure begins to change with temperature and above which $T_{\text{fictive}}=T$. A similar break at T_g in ϵ'' vs T would presumably also be seen near the ϵ'' minimum if it could be measured. While this is unfortunately not possible, the same break could probably also be seen in the observable range closer to the peak frequency, since Sokolov^{240(c)} reports such a break in CKN at a frequency which only corresponds to that of a minimum at very high temperatures. The temperature variation of the constant loss of CKN¹⁷³ and of other glass-formers^{245(a)–245(c)} can be measured easily at low frequencies (e.g. below 1 MHz), and it also shows a break at T_g . Such breaks reflect the fact that no

part of the frequency spectrum is insensitive to changes in the liquid *structure*, not even the microscopic peak itself.

The effects of structure on the microscopic peak are revealed by annealing studies. Frozen-in components of the low frequency vibrational density of states DOS of fast-quenched glasses, components that lie in the boson peak frequency region, have been found to anneal out near T_g .²⁴⁷ In some cases the total DOS seems to narrow at both ends during annealing.^{247(a)} This implies that configurational excitations are associated with both lower and higher vibrational frequencies. However, the high frequency increases occur far from the boson peak frequency, indeed well above the Debye frequency (which typically corresponds²⁴⁸ to $5-7\nu_{\text{boson}}$). A frequency at which the DOS is independent of annealing is found at about 3–4 times the boson peak frequency in NiZr₂ glass.^{247(a)} Some of the broadening of the libron peak on the low frequency side observed with increasing temperature by Lunkenheimer *et al.*^{227,238} can therefore be associated with this effect of changing structure.

The terms “microscopic” peak, “boson” peak, and “librational” or “libron” peak all seem to address the same sort of anomaly in the density of states, though one is linked to an acoustic branch of the density of states while the other is optical in character. While the peak shapes are not identical, the similarity and near ubiquity of the excess DOS implies some generality for flat dispersion relations (ω vs Q) for both (transverse) optical and acoustic branches of the collective vibrational excitation spectra in this frequency range. Does this mean that avoided crossings of optical and acoustic dispersion curves are the rule for glassformers? Then the higher the Q value the more optical character the modes in the boson peak will have. Only more data on different systems, particularly studies using techniques which interrogate the system at high Q , will tell. Fortunately, such high Q techniques have recently become available.

D.5.2. Ultrahigh frequency and high Q measurements

One of the major instrumental/technique developments of the decade has undoubtedly been the development by Masciovecchio, Sette, Ruocco, and collaborators²⁴⁹ of inelastic x-ray scattering IXS. (Other synchrotron facilities have also developed IXS, but not applied it to liquid relaxation problems.) We will not attempt to describe details of the brilliant manner in which these workers have solved the problem of measuring meV excitations using incident radiation of x-ray energies, 21.7 keV,²⁴⁹ but will only deal with the findings.

The energy of acoustic modes excited at different wave vectors Q have been mapped out over a range of Q values from $1-10\text{ nm}^{-1}$ for both liquids and glasses, both fragile and strong. The first and striking finding is that it is possible to excite well-defined acoustic modes at frequencies well above that of the boson peak in both liquids and glasses. These modes are best defined in the case of fragile liquids^{250,251} (in which the boson peak is not very pronounced). The dispersion relation is linear through this frequency region for liquids that lack well-defined intermediate range order, again confirming the relation between fragility and degree of intermediate range order. Matic *et al.*²⁵² con-

trast the behavior of the glass of fragile CKN with that of the more structured B_2O_3 glass, for which there is a break in the dispersion relation at the boson peak frequency. Scattering becomes much stronger at higher frequencies in this case. This is described as a “crossover” by Matic *et al.*²⁵² and it takes place at a Q value of $2\text{--}3\text{ nm}^{-1}$ corresponding to a real space dimension of about 2.5 nm. These authors note that the first sharp diffraction peak in these two cases is similar and then make their interpretation in terms of the larger fluctuations in force constants associated with the 2D character of the B_2O_3 network. This is consistent with the viewpoint advanced by Sokolov, in his interpretation of the boson peak and the relation between strong and fragile glassformers.²⁵³ A challenge then is to relate this picture to (a) the energy landscape scenario in which the excitation profile is in focus, and its steepness, scaled by the Kauzmann temperature, is a measure of the fragility, and (b) the anharmonicity scenario²⁵⁴ in which the quasielastic scattering, and indirectly the whole of the relaxation time temperature dependence, is connected to the relation between 3rd and 4th order anharmonicity coefficients for the boson peak vibrations. It is here that we may understand, through the anharmonicity coupling of the vibrational and configurational energy manifolds, the reason that the T_g tends to scale with the Debye temperature in many simple glasses,²⁵⁵ but greatly to exceed it in stronger glassformers. The occurrence of the related umklapp processes (momentum conserving) in glasses and liquids²⁵⁵ is only now being recognized as a physical reality.²⁵⁶

Another accomplishment of the inelastic x-ray scattering technique is to observe the viscoelastic behavior of liquids on the picosecond time scale and to determine the structural relaxation from the $\omega\tau=1$ condition in this highly fluid regime. This extends the study of viscoelasticity orders of magnitude beyond the previous limit attained by the related Brillouin light scattering technique and into a regime previously only studied by computer simulations.²⁵⁷ A new and detailed paper²⁵⁸ presents the analysis for the case of water and shows that the relaxation times have the same Arrhenius slope as the earlier longitudinal relaxation times obtained by extrapolation of ultrasonic data on glycerol+water solutions.²⁵⁹ No one has yet paid attention to the fact that these measurements prove correct what had only been noted previously from data on deeply supercooled water.²⁶⁰ This is that water has in common with propanol and butanol a dielectric relaxation that is (i) Debye-like despite being super-Arrhenius (in fact, power law²⁶¹) in temperature dependence, and (ii) that is much slower (an order of magnitude) than the mechanical relaxation time. As in the normal alcohols, there now seems to be, in water, a weak high frequency component of the dielectric relaxation of water that is on the same time scale as the mechanical relaxation. It must mean that the Debye component is due to multimolecule clusters of four-bonded waters that carry the dielectric strength while rotating slowly, hence diffusively, in the matrix of faster molecules.

Another aspect of these ultrafast measurements of mechanical relaxation is that they offer some hope that the shear modulus, real part, may sometime become measurable at

temperatures very far above the glass temperature. This would permit the temperature dependence of the shear modulus to be determined with much less ambiguity than before.²⁶¹ In turn, this would permit the validity of relations like Eq. (10) for the relaxation time temperature dependence of the relaxation time to be tested properly. So far only the longitudinal modulus has been accessible.

CONCLUDING REMARKS

We see that in the past few years, major advances have been made (and continue to be made) in the liquid relaxation field and that the relaxation phenomenology gap between normal liquids and viscous liquids is steadily being removed. Controversy continues in many areas, particularly in the different crossover regions *within* region A of Fig. 1. These are highlighted as T_c in Fig. 6, and as the temperature where “caging” (the second step) disappears in Fig. 10(a). This corresponds to the temperature at which the system “hovers” around the “top of the excitation profile” seen in Fig. 7(d). At this temperature, which is approximately $2T_c$, or $2.4T_g$, the relaxation frequency is closely approaching the (almost temperature-independent) boson peak resonance frequency. Thus, there is a sort of vibration/relaxation crossover, above which the liquid is in the “simple liquid” regime. (This is best seen in the time domain using the intermediate scattering function, displayed in Fig. 10(a). In liquids stronger than mixed *LJ* the boson peak is manifested as a dip in $S(q,t)$ between the microscopic process and the caging plateau.) In this “simple liquid” regime every boson peak oscillation is overdamped, which means that all low frequency modes are highly anharmonic. A central role in relaxation spectroscopy for anharmonicity in the boson peak oscillations may emerge from future work of high precision in this area.

Another domain in which much remains to be clarified, in particular, the utility of the energy landscape paradigm, is that in which microheterogeneities in the relaxation dynamics are becoming prominent (Sec. A.2.6.). To the extent that these are connected to microheterogeneities in the structure, it needs to be asked how these are represented in the landscape scenario when the glass is conceived as a system which is trapped in a single energy minimum. Clearly, the landscape needs to be described with more sophistication than is depicted in Fig. 7(d), and this will no doubt happen in the near future.

Unfortunately, or otherwise, depending on one’s point of view, the deeply supercooled regime near and below the glass transition is out of reach to MD simulations as we know them for the foreseeable future. In this long time domain, there are sufficient puzzles remaining that, even if the short-time problems are fully resolved, the full understanding of relaxation processes in viscous liquids and glasses is likely to remain a challenge for many years to come.

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