1. Introduction

This chapter is concerned with the mechanical spectroscopy of glasses, and it will deal with this subject in two distinct parts. The first part will be devoted to the study of systems responding to mechanical stresses at the borderline between the supercooled liquid (or ergodic state) and the glassy (or non-ergodic state). Depending on the particular type of spectroscopy applied, the time scale on which ergodicity is restored, after a perturbation, may range from hours to as little as picoseconds [1-3]. In the first part of this chapter, we will concern ourselves only with the longer time scales since picosecond mechanical spectroscopy, which is carried out using light scattering techniques, is more correctly thought of as exploring the high fluidity liquid state responses. Although there is no real distinction (since in each case all that is being observed is the manner in which molecular motion allows the system to fully explore its configuration space), the term "glasses" in the title of this chapter obliges us to focus our attention on the behavior of systems where they are essentially in the solid state. Thus the spectroscopic tools we will be using will be either responses to low frequency oscillating mechanical stresses or strains in the range 1-100Hz or time domain stress relaxation measurements in the seconds to hours time range. In effect, in this section we will be examining the mechanical relaxation aspects of the glass transition phenomenon, which is determined by the so-called primary, or \( \alpha \)-, relaxation of the liquid state [1-3].

In the second part of the chapter, we will instead focus attention on processes which occur within the glassy state. These may have a number of origins, but the ones with which we will be exclusively concerned are those which arise due to the jumping of mobile ions, i.e. ions which are mobile relative to the majority of ions which make up the rigid glassy matrix. This type of relaxation process, which is the glassy state analog of internal friction phenomena in crystalline materials due to defect motion, has been
known for a very long time in glass science, but has recently achieved additional prominence because of the growing interest in glasses as solid state electrolytes for a variety of electrochemical devices [4]. It is a particular type of secondary, or $\beta\text{-}$, relaxation of the amorphous state, and is distinguished from other secondary relaxations by involving long range (diffusive) motions of a subset of the system's particles.

These modes arise in glasses because of structural changes which occur within the liquid during the cooling of the liquid toward the glassy state. As the structure becomes better defined the modes of motion of a subset of the particles, which are usually ions with low charge and small radius, become less constrained, and decouple from the modes of motion of those species which, by virtue of their strong interconnections, provide the matrix of the material. As the latter modes approach relaxation times typical of the glassy state, the matrix becomes a solid medium within which the decoupled motions of the mobile ions continue to occur. We may expect to see that some aspects of their motion will depend on the conditions (pressure and cooling rate) under which they have become decoupled from the host particles.

While there are a number of additional mechanisms by which mechanical energy may be dissipated in glasses, and while some of these may be extremely important in polymers, we will give them scant attention here in order to keep the chapter to manageable proportions. These other secondary processes, which involve local rearrangements of small numbers of bound particles or groups, have been discussed separately in the chapter on polymers, and repetition here is unnecessary. However, their relevance will be pointed out in relation to low loss vitreous materials, and appropriate references will be given.

The properties of relaxing systems in these two regimes will be illustrated by reference to a limited number of model systems. These are systems which, for one reason or another, have been adopted by the glass science community for intensive investigation because they are of particularly simple constitution or because they illustrate a particular type of bonding interaction – usually both. Two model systems will be used for the illustration of relaxation near the glass transition in the first part of this chapter.

The first of these is one composed of three simple ions, two of which, Ca$^{2+}$ and K$^+$, have the electronic structure of argon while the third, NO$_3^-$, is a simple, planar-triangular molecule-ion. Remarkably enough, there is a considerable composition range within this simple system in which the liquids are very slow to crystallize, and the glassy state is therefore easily achieved. Within this range, the composition [Ca(NO$_3$)$_2$]$_{0.4}$[KNO$_3$]$_{0.6}$ has been frequently selected for the study of different physical properties and has become known simply as CKN$^1$ in glass science circles.

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1 The fact that such a simple system can form glasses argues strongly for the relevance of the glass transition and all associated phenomena to the understanding of the simple liquid state. It is because of the existence of such systems that many theoretical physicists have, in the last decade, focussed attention on viscous liquids and the glass transition in the endeavor to formulate more complete theories of the liquid state.
Figure 1. Phase diagrams for model systems on which many of the data utilized in the chapter are obtained. (a) The system KNO₃-Ca(NO₃)₂: the composition range used in most studies is indicated by an arrow. (b) The system germanium-arsenic-selenium showing the glassforming composition domain and the line of compositions satisfying the ideal average coordination number condition, \( < r > = 2.4 \).

The glassforming region and glass transition temperatures in this system are shown in Fig. 1a.

The second system, which illustrates the case of glasses held together by rather homogeneous covalent bonds, is the system Ge-As-Se, a large part of which is very resistant to crystallization, and yields black semiconducting glasses on cooling to room temperature. Since these atoms are all neighbors on the periodic table, the glass is of particularly simple constitution but has the interesting property that the bond density can be changed by changing the relative proportions of the components. This is because Ge always forms four bond to other atoms, As always forms three bonds, and Se always two. The usefulness of this situation will be dealt with later. The glassforming region in this system is shown in Fig. 1b.

Also, we will see in the early development of our subject, reference will be made to what has become a classical, if not prototypical, glassforming system, namely the molecular liquid glycerol in which the molecules are tightly bound to one another by hydrogen bonds between -OH groups on the short (three-carbon) framework.

In the second part of the chapter, in which we are dealing with fast ion motion within the glassy state, we will utilize data on two systems which have been extensively studied, in each of which it is Ag⁺ which is the mobile species. The systems in question are mixtures of silver iodide with silver metaphosphate AgPO₃ on the one hand, and with silver diborate Ag₂O·2B₂O₃ on the other.
2. The Glass Transition

To understand the process which is being illuminated by mechanical spectroscopy in the first part of this chapter, it is necessary to briefly review what is meant by the term "glass transition," in order that we can define the moduli whose relaxation is being investigated. This is best achieved by consideration of the behavior of the volume $V$ of the liquid as it cools from above its melting point to successively lower temperatures.

It is well known that liquids shrink more rapidly on cooling than do crystals but if the cooling liquid fails to crystallize, the high rate of contraction does not continue indefinitely, see Fig. 2a. There comes a point in temperature where there is a rather abrupt change in the expansion coefficient, and this "point", to be discussed below, is known as the glass transition temperature $T_g$. Below $T_g$, the expansion coefficient is effectively the same as that of the crystal of the same composition, implying that now the liquid has available to it only the anharmonic vibration mechanism for changing its
volume. At the same temperature, if we consider the derivative of the volume, i.e. the expansion coefficient, we see something which looks rather much like a second order phase transition, Fig. 2b, except that it has associated with it a hysteresis, implying that kinetic effects are dominant in this process [1-3, 6]. It is these kinetic processes, of course, with which mechanical spectroscopy must be concerned.

The other, most common, phenomenon associated with the glass transition is an equally abrupt drop in the heat capacity from liquid-like values to crystal-like values. In the case of the model (chalcogenide) glasses which we will discuss below in some detail, the heat capacity below the transition is essentially the classical vibrational value of 3R per mole of atoms. Since we are concerned here with mechanical moduli and their relaxation, it is worthwhile to point out that the heat capacity is a susceptibility, and its inverse, which we could call the thermal modulus, see Fig. 2c, insert, is the property which is analogous to the mechanical moduli whose relaxation we will be studying in the following sections.

It is not surprising then that the relaxation of the thermal modulus can be studied by a cyclic stress technique which is the thermal analog of the mechanical spectroscopy which is the subject of this volume. Indeed the comparison of thermal modulus relaxation and mechanical modulus relaxation in recent studies [7] has proven very helpful in improving our understanding of the glass transition as a relaxation phenomenon.

The glass transition is actually somewhat more complex than a simple relaxation since it involves both the linear relaxation process, and a non-linear aspect of the process which enters as the system increasingly falls out of equilibrium during cooling. For further information on this problem, the reader is referred to the excellent text of Brawer [1].

To those seeking crystalline phase analogs of what is happening at the glass transition, the best comparison to be made is one with a crystal losing equilibrium with respect to its intrinsic defect population during cooling. It is useful to recognize that most crystals at room temperature are non-ergodic systems like glasses. The difference is that, as liquids pass into the non-ergodic state during cooling, the changes in moduli are very much more dramatic than those associated with the freezing of a defect population in a crystal.

It remains to comment on the time scale on which these events are occurring. While this depends on the actual cooling rate, for a standard rate of change of temperature of 10K/min, it turns out that the relaxation time for the material at Tg is about 200s [1] implying an equivalent frequency, \( f = (2\pi\tau)^{-1} \) of about 1 mHz. Let us stress that whenever reference is made to the glass transition, the conditions under which it is observed should always be clearly stated in order that one set of observations can be related to another set acquired using different thermal schedules.

We must discuss at the outset the different types of moduli which can be observed relaxing near the glass transition, and the relationships between them [8, 9]. The simplest to understand, but not the simplest to interpret, is the shear modulus G which measures the resistance of the system to a shearing strain. This is usually obtained by
measurements using a torsion pendulum with frequency <1Hz. The measurement yields the real and imaginary components of the shear modulus at (almost) fixed frequency during temperature change. It is found that the low-frequency shear modulus changes from a value characteristic of the solid glassy state to the vanishingly small value characteristic of a liquid in the temperature interval known as the glass transformation range, and some data for the case of Na$_2$O•3SiO$_2$ will be shown later. It is found that the modulus only reaches zero at a temperature significantly above the $T_g$ defined by DSC scans (see Fig. 2). This is because $T_g$ is defined by the onset of excitation of the configurational degrees of freedom which were frozen below $T_g$, and it is only near the point where the system achieves internal equilibrium (becomes fully ergodic) that the shear modulus (real part) reaches zero. Like the calorimetric glass transition, this temperature will depend on scan rate. However it will also depend on the frequency of the measurement, hence, in the torsion pendulum method, will depend on the sample size and experimental set-up since these fix the natural frequency of the measurements. In fact, a vanishing shear modulus cannot be measured with the torsion pendulum technique because of sample deformation.

A second modulus, which is relatively easily measured in the glass and liquid states, is the longitudinal modulus, $M_L$. This can be obtained by either ultrasonic [8a] or light scattering (hypersonic) [8b] measurements though there is some controversy in the latter case [8c]. The longitudinal modulus is somewhat more interesting since it has a finite value in the liquid state as well as in the glassy solid. The longitudinal modulus is composed of two components, one the bulk modulus $K$, and the other, $4/3$ of the shear modulus, according to

\[ M_L = K + \frac{4}{3}G \] (1)
above the relaxation region, the modulus measured is the pure bulk modulus since the shear modulus has vanished. In glasses, and in liquids near $T_g$, $K$ is typically larger than $G$ by a factor of three. The other commonly studied mechanical modulus is the tensile modulus (Young's modulus), $E$. This is a combination of shear and bulk components, with value below $T_g$ close to that of the bulk modulus

$$E = \frac{9KG}{G+3K} = 0.9K.$$ 

However, like the shear modulus, $E$ must vanish in the liquid state. These relationships [8] are represented schematically in Fig. 3. In the temperature range where the rapid changes are occurring, all moduli should be written as complex quantities $G^*$, $K^*$, etc., and will be time- and frequency-dependent quantities.

From the measured shear and longitudinal moduli we may extract the real and imaginary parts of the bulk modulus $K$ which is in some ways more fundamental than either of the easily measured quantities.\(^2\) The bulk modulus, we remember, is the in-

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\(^2\) We should note here the recent report by T. Christensen and N.B. Olsen on a method of measuring the frequency-dependent bulk modulus directly. The technique involves use of a piezoelectric spherical shell which converts cyclic mechanical signals in the frequency range 15 Hz to 15 kHz to dielectric signals.
verse of the isothermal compressibility which, in turn, is proportional to the second pressure derivative of the Gibbs free energy $G$. In statistical thermodynamics [9], the compressibility is directly related to the mean square fluctuation in volume by the relationship

$$\kappa T = -V^{-1}\partial^2 G/\partial p^2 = \langle \Delta V^2 \rangle/(VkB).$$  \hspace{1cm} (3)

If these volume (density) fluctuations arise and decay with a single characteristic time, then the imaginary part of the compressibility will be a Lorentzian function of log (frequency). It is almost universal among substances approaching the glass transition, however, that a single time constant (exponential relaxation, exp(-t/\tau)) is insufficient to describe the relaxation. The variation with frequency of the imaginary part of the bulk modulus $K''$ (i.e. the susceptibility relaxation spectrum) is broadened (see Fig. 4) and the broadening gives information on the distribution of relaxation times, or, alternatively, on the departure from exponential relaxation. We would note here a second statistical thermodynamic relationship [9]

$$C_p = T\partial^2 G/\partial T^2 = \langle \Delta S^2 \rangle / kB$$  \hspace{1cm} (4)

from which we see that the imaginary part of the thermal susceptibility (molar heat capacity) gives information on the spectrum of decay times for the entropy fluctuation.3 The characteristic time scale for the fluctuations may be obtained from the peak frequency of the glass spectrum by using the approximate relationship $\omega \tau = 1$, the maximum damping condition, as shown in Fig. 4b. Since $\omega$ is controlled by the experimentalist, the intrinsic relaxation time for the temperature at which the spectrum was determined is immediately obtained. $\tau$ can also be obtained from an experiment in which the maximum loss is observed during temperature scan at almost constant frequency (see Fig. 4) indeed this has been the common practice, for better or worse, because of the limited frequency range. (In some cases, e.g. Brillouin scattering the frequency will change slowly with changing temperature, and the relaxation time must be obtained from the frequency at the loss maximum.)

One of our interests in mechanical spectroscopy of the glass-liquid transition must be the question of difference between time scales and relaxation functions for relaxation under different stresses. Early work on the relaxation spectrum for density fluctuations was done by Litovitz and co-workers [10-11] using ultrasonic absorption methods, and it was shown there that for measurements made on glycerol by scanning temperature at a single frequency, that the relaxation spectrum for density fluctuations and for polarization fluctuations (obtained by dielectric spectroscopy) were essentially identical, see Fig. 5. More recently it has been shown [7, 12a], for the case of glycerol that this dielectric relaxation spectrum is essentially identical to that for the entropy

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3 There are corresponding relations for $C_v$, the constant volume heat capacity, $C_v = kT^2/\langle \Delta T^2 \rangle$ and $\alpha_p$, the isobaric expansion coefficient, $\alpha_p = \langle \Delta S \Delta V \rangle/(VkT)$. 

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fluctuations as judged from the frequency dependent heat capacity, and also shear compliance, insofar as the latter can be gauged from ultrasonic spectroscopy. However, this is not always the case [12]. Furthermore, in order to begin making useful comparisons, it is necessary to take account of the manner in which different analyses of the same set of data can lead to a determination of different relaxation times. We consider this problem in the following section.

3. Modulus vs. Susceptibility Comparisons

Because of the interest of relaxation spectroscopists in the comparison of the time scales for different responses in the same system, it is necessary to deal with the problem raised by the use of different formalisms in data analyses. There is a tendency to indiscriminately compare the results of measurements in which the relaxation of the modulus is observed, with the results of experiments in which the relaxation of the susceptibility is being measured. The danger is that these relaxation times cannot be the same even for measurements made on the same systems under the same conditions. The formalism used in the analysis of the data can, by itself, change the apparent characteristic time. The relationship is a simple one and is illustrated in Fig. 6 by

Figure 5. (a) Temperature dependences of high and low frequency limiting compressibilities, $\kappa_\infty$ and $\kappa_0$, for glycerol, and the dispersion of $\kappa'$ at 31 MHz. (b) Temperature dependence of the configurational contribution $\kappa_0 - \kappa_\infty$ to the total compressibility of glycerol between 20 and -30 C and a comparison of the reduced dielectric loss $\varepsilon''/\Delta\varepsilon$ with the reduced compressibility loss $\kappa''/\Delta\kappa''$. (Data from Ref. 11.)
dielectric data for the simple molecular liquid propanol [13]. The peak frequencies for data analyzed in susceptibility and modulus formalisms are seen to lie more than an order of magnitude apart. The reason is that the ratio of frequencies at the maximum of the loss spectrum is equal to the ratio of low frequency and "infinite" frequency susceptibilities [14],

$$\frac{\tau_{\text{(susceptibility formalism)}}}{\tau_{\text{(modulus formalism)}}} = \frac{\varepsilon_0}{\varepsilon_\infty} = \frac{M_\infty}{M_0}$$

(5)

The discrepancy in characteristic times can be very large for dielectric measurements because of the possibility of very large low frequency susceptibilities, e.g. 44 for propanol.
Fortunately, this is not such a serious problem for mechanical spectroscopy. This is because there is no mechanism for obtaining large susceptibilities in the liquid state such as is provided, in the dielectric susceptibility case, by the large hydrogen bond-driven correlation of molecular dipoles typical of liquid alcohols and amides. For mechanical purposes, the largest difference between susceptibility relaxation times and modulus relaxation times will be of the order of two. Nevertheless, some significance has been attached to the apparent two-fold differences in relaxation times in the past, ignoring the fact that the difference comes simply from the mixing of formalisms. Thus we make here the recommendation that any comparisons of time scales be made using the same formalism for each data set and, furthermore, ensuring that when possible this formalism is the susceptibility formalism.

For the relaxation spectrum of glycerol mentioned above [7, 12] the susceptibilities were studied [7] and it was found [7, 12] that for mechanical, dielectric, and thermal relaxations, not only the characteristic time is the same, but so also is the shape of the spectrum [15, 16]. This similarity is a tribute to the effectiveness of the multilateral hydrogen bonding scheme in insuring that all stresses are relaxed in a similar manner. Such uniformity is certainly not the general case.

Before passing to the analysis of mechanical responses of our model systems, we need to point out some problems associated with mechanical spectroscopy, parts of which involve the relation between modulus vs. susceptibility spectroscopy.

The first problem is that the frequency-dependent bulk modulus, $K$, which is the fundamental fluctuation-based quantity, is very difficult to measure near, and in, the glassy state. The modulus which is most easily measured, is the shear modulus $G^*$ but, as already mentioned, $G'$ unfortunately does not have a finite value in the liquid state above $T_g$ unless measured at very high frequencies.

This creates a second problem because the imaginary part of the susceptibility (in this case designated $J''$) increases continuously with decreasing frequency (according to $J''=\eta\omega^{-1}$ where $\eta$ is the shear viscosity), hence shows no peak value as in Fig. 4 for the isothermal compressibility. There are two ways of handling this problem. One is to treat the increasing compliance at low frequency as a simple consequence of an exponentially relaxing viscosity (Maxwell element) and subtract off the Maxwell $J''$ from the observed $J''$. What is then left exhibits a peak, the relaxation time from which can be used in comparisons with other susceptibility relaxation processes. This procedure is much used by rheologists [14], but has the problem that the characteristic spectral response is very sensitive to the accuracy of the viscosity measurements. Plazek [16] has pointed out, however, that the subtraction procedure can be avoided using Leaderman's technique which yields the "recoverable" compliance, $J_r(t)$, directly. He argues that this characterization of the response has advantages over the alternative widely used data treatment, in which the inverse of the complex susceptibility is

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4 This situation is changing due to the new technique for direct determination of $\kappa^*$ developed since this article was written, and referred to in an earlier footnote (footnote 2).
analyzed, i.e. the modulus formalism. In the latter formalism, the increasing loss occurring with decreasing frequency is suppressed and a peak in the $G''$ spectrum is therefore always obtained [8].

A third problem with mechanical spectroscopy is that, in comparison with dielectric and heat capacity spectroscopies, the range of frequencies available to most mechanical measurement techniques is very limited. Dielectric spectroscopy covers some 12 orders of magnitude in frequency with relative ease, requiring only three characteristically different experimental measuring devices [17]. Even better, a time domain method has now been developed [R.V. Chamberlin, (private communication)] in which a single instrument covers 12 decades. By contrast, mechanical spectrometers rarely cover more than three decades of frequency and the ultrasonic technique is limited to some two decades. A convenient apparatus is the high sensitivity mechanical spectrometer invented by Woigard [18] and developed by Etienne, et al. [18] which works with high accuracy and sensitivity at low frequencies covering some four decades under normal conditions.

The widest range techniques for mechanical spectroscopy operate in the time domain. Foremost is probably the digital photon correlation spectroscopy technique [8b, 19], which many believe measures the longitudinal modulus $M$ (but see ref 8c.). It is a short-to-medium time scale ($10^{-6} - 10^2s$) technique which requires sophisticated light scattering equipment as well as ultraclean samples. Among longer time scale methods currently in use are the creep technique of Plazek and McGill [20] and a transient elastometer technique which is operated in the authors' laboratory [21]. The latter method uses an automated Rheovibron instrument to impose a sudden step strain on a suitably mounted sample, and the resultant stress is monitored as it decays with time. It is possible to cover some five decades of time with each of these techniques. Typical stress relaxation curves for the latter are shown in Fig. 7. The solid lines passing through the curves are plots of the stretched exponential (Kohlrausch or KWW) function,

$$\theta(t) = \exp\left[-(t/\tau)^\beta\right]$$

(6)

(where $\tau$ is the characteristic time, and $\beta$ is the stretching exponent, $0 < \beta < 1$) and it may be seen that the data are fitted almost within the experimental noise over some three decades of time. These decay functions can also be Fourier transformed to obtain real and imaginary parts of the elastic modulus, but it is generally more profitable to analyze them directly, as demonstrated in Fig. 7, to obtain the spectral quantities of interest, $\tau$, and $\beta$. We note that this transient elastometer is equivalent to a frequency domain spectrometer with a frequency range of five decades, hence is a very useful device.
4. Mechanical Spectroscopy of Liquids Near the Glass Transition

With the above background material, we can now proceed to apply mechanical spectroscopy to the problem of elucidating the relaxation mechanisms which operate near and below the glass transition in vitreous materials. We proceed by asking a series of questions about mechanical responses, and then discussing the answers provided by the experimental investigations.

The questions are in general fairly obvious and it is the answers which are interesting for the case of glass-forming systems. For instance, an initial question we must ask is, is the liquid response an activated process as it is in crystals (and indeed in the majority of substances for which mechanical data have been reported). This can be rephrased by asking, does the temperature dependence of the mechanical relaxation time follow an Arrhenius law \( \tau = \tau_0 \exp \left( \frac{E_a}{RT} \right) \) with a phonon-like pre-exponent, \( \tau_0 \)?

The second question concerns the relaxation function. Is it Debye-like, and if not (as already seen in Fig. 7), is there a correlation between departures from Debye behavior and departures from Arrhenius behavior?

The third question asks whether all liquids behave in the same manner. For instance, it was thought for a long time that chain-polymers obeyed a universal law and there were frequent references to the "universal" WLF (Williams-Landel-Ferry) parameters. We will see later that in fact there is no universal behavior, indeed there are striking differences between different liquids.
Fourthly, we need to ask whether the mechanical relaxation time and the relaxation function is the same as that observed in response to other types of stresses.

A fifth question asks whether or not the response observed depends on the thermodynamic state of the relaxing system. Near the glass transition, this becomes very important because the time scale on which the equilibrium structure of the liquid is achieved becomes very long. We note here that when internal friction measurements are performed on conventional (crystalline) solids, those solids are very rarely in the ergodic state. Rather, they contain a number of defects which depends strongly on the thermal history, and the question might be asked whether this number of defects has an important effect on the mechanical response functions. We are asking the same question about glassy systems.

The first of the above questions can be answered by referring to either mechanical relaxation data obtained by the time domain technique mentioned above, or by any of a number of mechanical relaxation studies performed using the photon correlation spectroscopy technique referred to earlier. The latter have the advantage of extending the range of measurement well into the viscous liquid state, where the answer to the question becomes more obvious by virtue of the very strong departures from the Arrhenius law which may be observed.

A set of viscosity data [22] is displayed in Fig. 8 using a reduced inverse temperature scale in which the time scale characteristic of the glass transition (10² sec) is used as a scaling parameter. This procedure reveals a pattern of behavior which is characteristic of liquids, and which was first obtained using conventional shear viscosity

![Figure 8](image.png)

**Figure 8.** Variation of mechanical (i.e. viscosity) relaxation times obtained by various short-time and long-time techniques, for a variety of molecular liquids showing the strong/fragile pattern discussed in the text, (from ref 72, reproduced by permission).
data plotted on a comparable $T_g$-reduced Arrhenius plot. The pattern of behavior has been used [23] as the basis for a classification of liquids about which only the briefest comments will be included here. The pattern observed (though not the exact temperature dependence in many cases) can be reproduced by the variation of a single parameter $D$ in the Vogel-Tammann-Fulcher (VTF) equation,

$$\eta = \eta_0 \exp(DT_0/[T-T_0])$$

(7)

where $\eta_0$, $D$, and $T_0$ are constants. This behavior is more generally represented by plotting relaxation times $\tau$ rather than viscosities, using the Maxwell relation $\eta = G_\infty \tau$.

Eq. (7) implies that the mechanical relaxation time will diverge at a temperature $T_0$, and that $T_0$ is close to the glass transition temperature $T_g$ in proportion to how small the parameter $D$ is. It is simply shown that there is a linear relationship between $D$ and the ratio $T_g/T_0$,

$$T_g/T_0 = 1 + D/(17 \ln 10).$$

(8a)

in the case of viscosity data, or

$$T_g/T_0 = 1 + D/(16 \ln 10)$$

(8b)

in the case of relaxation data. The numerical factor expresses the number of orders of magnitude change in the variable $\eta$ or $\tau$ between $T = T_g$ and $T = \infty$. The difference between the values of this factor in Eq. 8(a) and 8(b) is due to the temperature dependence of $G_\infty$ [5].

Those systems which are characterized by small values of $D$, i.e. those whose relaxation times change extremely rapidly with temperature on the scaled Arrhenius plots, are described as fragile because their behavior can be explained in terms of the rapid breakdown of the packing order in the liquid with change of temperature. By contrast, those with large $D$ values are described as "strong" as an indication of the resistance of their intermediate range order to increase in temperature.

Since mechanical measurements using such devices as our time domain transient elastometer are easily obtained only near $T_g$, and since the range of temperatures which cause $\tau$ to traverse the instrumental time scale is usually quite small, it is not easy to detect the intrinsic non-Arrhenius character of the relaxation function. However, it is easily seen in most cases that the behavior must be non-Arrhenius in principle, since the pre-exponents of the best fit Arrhenius equations are quite unphysical. In this case the characteristic parameter $D$ of the system can be obtained by relating the Arrhenius slope at the glass transition temperature $T_g$ to the parameter $D$ utilizing the following expressions [24, 25].
where $\tau_g$ is the relaxation time at the glass transition temperature. This is usually about $\tau_g = 200\text{s}$ at the calorimetric $T_g$ when the latter is measured at a scan rate of $10\text{K/min}$.

Alternatively, the behavior of the systems can be discussed directly in terms of the slope of the $T_g$-scaled Arrhenius plot at $T_g$. This has been called [25] the fragility, $m$, [Eq. (9)] and also the "steepness index" [24]. The relation between $m$ and $D$ is an inverse one and is shown graphically in Ref. 26.

Much information on the behavior of vitreous systems within this scheme can be obtained from the study of a model mixed atomic system Ge-As-Se referred to in the Introduction, in which the bonds between the particles are all covalent. Since the bonds which form have approximately equal bond energy, this system provides an interesting test case for models of random bonding and mechanical strain optimization, which have been advanced by such authors as Phillips [27], and Thorpe [28]. These authors have developed the concept of "rigidity percolation" which occurs when there is an optimum distribution of bonds in the system, which in turn occurs when the average coordination number is 2.4. For the arguments leading to this conclusion, the reader is referred to references 27 and 28. We are interested here in observing the behavior in response to mechanical stresses on compositions in this system, and will naturally pay special attention to the compositions which satisfy the above condition. We recall, Fig. 1(b), that in such a ternary system, a number of compositions can give the same average coordination number (see the line traversing the diagram marked $<r> = 2.4$).

Fig. 9a shows the Fig. 7 type results of stress relaxation measurements, in Arrhenius form, for a number of compositions falling on the line $Y = 0.5$ in the ternary diagram Fig. 1(b). The relation of the limited temperature range data obtained with the mechanical technique to the bigger picture described earlier is shown in the insert to Fig. 9. We see immediately that the range of behavior displayed by this simple ternary system covers almost the entire range of fragilities observable with the whole available range of liquid types. Of special importance is the observation that the strongest liquid in our system is that with the "magic" coordination number $<r> = 2.4$.

The Fig. 9 data, and the comparable data for polymers [24, 28], makes clear that the answer to the first question we asked is that there are very pronounced and non-universal deviations from the Arrhenius law for relaxation time as indeed was to be anticipated from the viscosity patterns. The wide range of behavior seen in Fig. 9 will be taken to advantage in examining the relation of the other features of relaxation (which were the subjects of the other questions) to this primary departure from the Arrhenius law, i.e. to the characteristic fragility of the relaxing system.
Figure 9. Upper frame: Average equilibrium relaxation times $\tau$ obtained from stress relaxation measurements (by transient elastometry) as an Arrhenius function of temperature for various compositions along the line $Y = 0.5$ in the system Ge-As-Se, for various values of $<r>$. The $T_g$ used in the scaling is the calorimetric value. This plot is an extension, at the long relaxation time end, of the larger pattern shown in Fig. 8. Lower frame: Temperature dependence of the stretching exponents $\beta$ of Eq. (6) normalized to their respective values of $T_g$. Note that the deviations from thermorheologically simply behavior (corresponding to temperature independent stretching) are smallest in the least fragile liquid. Solid lines are guides to the eye.

Turning to the second question, we display in Fig. 10 the values of the KWW stretching exponent $\beta$ at $T_g$ observed in the relaxation measurements which provided the data for relaxation times displayed in Fig. 9. The temperature $T_g$ must be specified since $\beta$ is systematically temperature-dependent as shown in Fig. 9b. Fig. 10 shows the values of $\beta$ again as a function of mean coordination number, $<r>$ and displays them against the comparable variations in the fragility parameter $m$ obtained from the Arrhenius slopes of Fig. 9. It is seen immediately that, as long anticipated by Ngai from his coupling model [30], there is a close correlation between the two aspects of the relaxation process. Those compositions which have the highest fragilities have the largest departures from exponential relaxation. The variation in this stretching parameter, like the variation in the fragility parameter, seems to saturate at a composition close to the coordination number 2.4, and thereafter remain approximately constant with composition.

The question arises immediately as to whether this correlation of fragility with nonexponentiality is of general significance. We answer this question by plotting in Fig. 11 the data obtained in the present study along with data obtained for amorphous
Figure 10. Dependence of (a) the activation energy and (b) the fragility ($E_a/2.303 \, R \, T_g$), on the average coordination number $<r>$ in the system Ge-As-Se at the composition $y = 0.5$ [see Fig. 1 (b)]. (c) Variation of the fractional exponent $\beta$ of Eq. (6) with $<r>$. (From ref. 34, reproduced by permission).

polymers from mechanical relaxation studies of a different type by Plazek [16] and analyzed in the present terms by Plazek and Ngai [24]. The correspondence between the inorganic covalent glass behavior and the organic chain polymer glass behavior is striking. We note that a simple theory by Vilgis [31], which interprets the fragility in terms of the mean fluctuation in coordination number, predicts a curvilinear relationship for the variation of fragility with nonexponentiality, and this is included in Fig. 11. In work currently being reported [26], this correlation has been examined in more detail, employing results for some 70 different systems, and a broad band correlation is defined within which there are subgroups separated according to the degree of connectivity between the particles. The chalcogenides and polymers of Fig. 11, in this extended
correlation, are found to lie on the left-hand edge of the broad band, while systems which have only simple molecules interacting by van der Waals forces lie at the right-hand edge.

To respond to the fourth question concerning the relation of mechanical relaxation times to the response times for other stresses, we can cite at least the comparison of the temperature dependences. The viscosity activation energies which are seen in Fig. 10(a) to coincide with those for the stress relaxation time, have been compared elsewhere [32] with those for enthalpy relaxation obtained from a simple differential scanning calorimetry study of the same system. They showed a similar composition dependence, but the enthalpy relaxation values were fractionally lower. On the other hand viscosity and enthalpy relaxation activation energies have frequently been found to be very similar [33] in earlier studies and differences, if present, tend to be the inverse of the above in association with a decoupling of viscosity from structure. Thus the detailed relationship between different response functions is unclear and probably depends on the system under study. It provides a subject for future work. There are, however, some well-studied cases where the response to electrical stresses are extremely different from responses to other stresses and we deal with these in the second part of this chapter.

Turning to the fifth question, we examine the relationship between the relaxation functions obtained in the equilibrium state with those obtained when the system is far
from equilibrium. Some relevant data [34-35] are shown in Fig. 12. These are characteristic of the phenomenon of physical ageing for which a large literature exists, particularly for the case of polymers. For details the reader is referred to the book by Struik [36], and the recent studies in the Proceedings of the Heraklion Relaxation Conference [37]. To obtain the data in Fig. 12 (a), samples were rapidly cooled from a temperature above the glass transition temperature to a new temperature significantly below it, and a stress relaxation run was immediately performed. Successive repeat measurements were then made after longer and longer times at the same temperature, and the sequences of curves shown in Fig. 12 were obtained. The important observation is that after a sufficient period, the stress relaxation functions become reproducible, and this period corresponds to the time necessary for the system to achieve its true internally equilibrated state. The relaxation times for each of these annealing periods can themselves be used to get an approximate idea of the function which describes the relaxation of the structure to its equilibrium value, see Fig. 12 (a).

Figure 12. Part (a) Stress relaxation functions in the region below $T_g$ for various waiting times after an initial temperature equilibration following step down from above $T_g$. Diagram shows the effect on the approach to the equilibrium state of the form of the relaxation and the characteristic time $\tau$. Note that the effective relaxation time for the structure is some ten times longer than the values of $\tau$ themselves. The lower panel shows how the distinction between curves 1-5 of the upper panel are related to the change of configurational entropy during annealing.
For the Se system illustrated in Fig. 12, this function has a characteristic time almost ten times longer than that of the stress relaxation function. A similar relation was found earlier for CKN [35]. However, this is not always the case. Indeed we find, as far as the measurements have gone to date, that there is some systematic relationship between these two time scales and the mean coordination number \(<r>\) [34]. However, until more quantitative data are obtained, this question will not be pursued.

The existence of a state dependence of the relaxation function can be understood in terms of the influence of the state of disorder on the relaxation rates of the system, as measured by its total entropy. Fig. 12(b) shows how the arrival at the equilibrium state (represented by the equilibrium variation of the entropy/temperature relationship) determines that the stress relaxation function becomes reproducible.

Note that this type of measurement can only be carried out as long as the condition that the stress relaxation time is shorter than the structural equilibration time, is met. While this seems to be generally the case for fragile liquids, it is evidently not the case for the more highly connected, stronger "alloys" in the Ge-As-Se system [34]. This aspect of the problem requires further investigation. We suspect that a comparable phenomenology may be found in the case of highly defective crystals, but we do not know of any actual examples. The expectation is that, in crystalline systems which are highly defective obtained by quenching from high temperatures, the internal friction response will be more rapid than for the same system slowly cooled from the same temperature and studied at the same lower temperature. The condition for expecting comparable behavior under different quenching conditions must be that the defect population is large enough for defects to interact with each other, as well as with the lattice in which they occur. To support this contention we could quote the example of rotator phase crystals (the so-called "plastic" crystals) in which it is already well established that phenomenology essentially the same as that described above for supercooled liquids is found [23b]. However, it would be more interesting to observe it in more conventional crystalline materials in which structural state-dependent relaxation, like the non-exponential relaxation we have described, is normally not observed.

The foregoing observations of the behavior of mechanical relaxation in liquid systems (and, by inference, also plastic crystal systems) as they enter the glassy state, may be summarized as follows:

1. Mechanical relaxation processes are not Arrhenius and instead follow the strong/fragile pattern established from other measurements.
2. Mechanical relaxation processes are usually, but not always, faster than the primary structural relaxation.
3. Mechanical relaxation processes for systems in equilibrium are nonexponential in character, and their deviation from exponential behavior correlates well with the deviation from Arrhenius behavior, i.e. with the fragility of the relaxing system.
4. Mechanical relaxation processes for systems out of equilibrium are nonlinear, in the sense that the most probable time of the distribution depends on the state which is relaxing, and on how far from equilibrium that state happens to be.
5. MECHANICAL SPECTROSCOPY OF THE GLASSY STATE OF IONIC SYSTEMS

To simple inspection, a glassy material is rigid and macroscopically isotropic, and it therefore appears unlikely that there are significant relaxational degrees of freedom remaining to be characterized. On the other hand, it is well known that glasses are imperfect insulators, and that there are serious sources of loss from electrical fields, which the glass technologist must work hard to minimize. It is now generally recognized that these sources of loss are primarily due to the presence of mobile ions within the apparently rigid structure. This section of the chapter will deal with the phenomenology of mechanical loss which arises as a consequence of these "fast ion" motions.

In the last section we observed that, while there are some differences detectable, the response of the system to mechanical stress is usually very similar to its response to a thermal stress. The latter relaxation can be thought of as a relaxation of the "thermal modulus" (which is measured as the reciprocal of the heat capacity).

In Fig. 13 we repeat the Fig. 3 schematic of the changes in the different moduli in the vicinity of the glass transition temperature, and then add a plot to show how the electrical modulus $M_\sigma$ might be expected to behave in the same temperature regime. For an insulating system, the electrical modulus indeed behaves just like the others, and this has been seen in the comparison of mechanical, thermal, and electrical responses for various molecular liquids, e.g. Fig. 5, and the more recent cases described by Nagel and colleagues [15, 17]. However, for an inorganic system in which a fraction of the particles are ionic, and are capable of wandering from site to site within the quasi-lattice set up by the complex anionic host structure, the electrical modulus is very much lower. Indeed, in the majority of cases, it remains effectively zero at the glass transition, and only commences to rise at a much lower temperature when the ionic jump time becomes of the order of minutes. This is illustrated in Fig. 13 by the curve marked $M_\sigma'$.

Figure 13. Comparison of the electrical modulus for an ionically conducting glass with the various mechanical moduli. Note that the electrical modulus remains zero to temperatures well below the glass transition temperature.
In the following pages, we will examine what, if any, mechanical equivalent of the $M_\sigma$ relaxation there may be as a result of the ion motions within the frozen (vitreous) quasi-lattice.

To set the stage, we show the relationship between the relaxation time of the primary mechanical relaxation process discussed in the previous section and the relaxation time for the process which we will be following in the glassy state. Fig. 14 shows the primary relaxation time originating at the vibrational (phonon) relaxation time at infinite temperature and follows its non-Arrhenius course down to values longer than can be measured, below the glass transition. The electrical relaxation, which can hardly have a shorter time scale at infinite temperature, follows a different course with temperature increasingly deviating from the primary structural relaxation time as the glass transition temperature is approached. At $T_g$ where the overall structure becomes frozen, there is a change in the temperature dependence of the electrical relaxation time, due to the freezing of the matrix structure to which it remains weakly coupled. The electrical relaxation time itself, however, remains relatively short depending on how decoupled the electrical modes are from the mechanical modes. The question of decoupling of modes with decreasing temperature is a complex one which will not be entered into detail here. Suffice it to say that the field of Solid State Ionics, which is particularly interested in solid materials with high electrical conductivities, has focussed much attention on those systems in which this mode decoupling is very pronounced. We note that there is a possible decoupling of some 14 orders of magnitude at the glass transition [5, 38].

The electrical relaxation process we are describing is the primary relaxation for electrical stresses since, through it, the electrical modulus with increasing temperature falls to zero, precluding any others. Since the mechanical modulus is already finite and

![Figure 14](image)

*Figure 14.* Schematic representation of the variations with temperature of the primary ($\alpha$-relaxation) relaxation time and that of the secondary relaxation due to the mobile ions in an ion-conducting glass. Note the break in the temperature-dependence of the secondary relaxation at the glass transition temperature and the establishment of an Arrhenius behavior at lower temperatures.
large at temperatures below the glass transition, it is reasonable to ask what if any 
mechanical response will be seen on the time scale of the primary electrical response. The electrical relaxation is due to long-range ionic motion. Since long-range motion of 
the particles constituting the host structure is forbidden below $T_g$, it is not necessarily 
expected that a mechanical response to a sudden stress or strain will be observed. On 
the other hand, since the ionic motion occurs by jumps over barriers, it seems quite 
reasonable that the same ions can be stimulated to jump over the same barriers by the 
application of a mechanical stress. Clearly it is for experiment to decide.

The data for a sodium silicate glass system, gathered [39] from disparate sources [40, 41], (and involving some extrapolations to ensure equivalence of probe time scales) are shown in Fig. 15. The shear modulus [measured by the torsion pendulum technique 
at a frequency of 0.4 Hz (40)] shows a 15% decrease at the temperature where the 
electrical modulus measured on the same time scale (by short extrapolation of higher 
frequency data) shows its rapid increase from zero to a finite value. Evidently the 
mechanical probe can indeed be sensitive to the same motions responsible for the loss of 
the electrical modulus, and it therefore becomes necessary to address questions of detail.

We note here that the jump in the shear modulus is some sort of measure of a "glass transition for the mobile ions," i.e. a temperature below which long range motion of the mobile ions gets frozen out. This is best seen by inverting the plot so as to cast the data in the form of a susceptibility and then comparing the behavior observed with that familiar in the glass transition seen in Fig. 1 (where the increases in the volume

![Figure 15](image-url)
susceptibility and the thermal susceptibility at $T_g$ were displayed). Whether or not a thermal manifestation of the "glass transition for the mobile ions" can be observed is a matter currently under investigation. Preliminary reports from the calorimetric studies of Oguni [42] suggest that the freezing out of the mobile ion modes at a temperature where their relaxation time is of the order of 100 sec. can indeed be observed calorimetrically but is a very weak effect.

The degree of decoupling of the secondary modes from the primary modes can differ greatly from system to system. As observed in the Introduction, the systems with very high degrees of decoupling are currently of considerable interest because of their potential as solid state ionic conductors [4] and ionic rubbers [43]. The degree of decoupling which is possible is illustrated in Fig. 16 which shows the electrical conductivity of a selection of different glass-forming systems presented on a $T_g$-reduced temperature scale in order to put the data in a transparent relation to one another [44]. It is seen that in the case of the model nitrate system, CKN, the degree of decoupling is relatively small -- eight orders of magnitude smaller than for sodium trisilicate -- and, in fact, CKN is a rather good insulator at room temperature. By contrast, some of the glasses containing silver iodide are extremely conducting at their glass transition temperatures and, indeed, these are excellent solid state electrolytes.

To form some impression of the microscopic nature of the modes of motion responsible for the electrical conductivity and mechanical loss in the glassy state of these substances, we may turn to molecular dynamics computer simulations [45-48]. This interesting research area will be mentioned (only briefly) here in order that a microscopic picture of the processes to be probed by mechanical relaxation can be held in mind. Figure 17 [49] shows the projections on a plane of the motions of lithium ions in a

![Figure 16. Tg-scaled Arrhenius plot of conductance of systems with widely differing degrees of decoupling of conductivity from structural modes. Dashed line shows behavior for fully coupled system. (After ref. 44, reproduced with permission.)](image-url)
simulated lithium thiosilicate glass, which was chosen for its combination of relevance and ease of computation. The mobility of the lithium ions in this structure [49] is comparable with that in the best superionic glasses [50, 51]. The empty areas on the projection are where the silicon and sulfide ions are located, but these are not shown for clarity. During the course of the simulation presented in Fig. 17, the Si$^{4+}$ and S$^{2-}$ ions mostly execute small anharmonic oscillations about fixed sites, rather like the lithium ion seen in the lower left side of Fig. 17. This particular ion, because of its location in the glass, was unable to move out of its initial site during the 1500 steps of the simulation. The other Li$^+$ ions, however, are rather mobile as indicated by the channels of motion marked out by the overlap of their trajectories. It is the existence of continuous channels like these which permits the long range electrical conduction to occur. (One should caution that a continuous "percolation path" seen in a projection like this could be misleading since disconnected channels in the three dimensional box could project as continuous channels.)

Fig. 17 clearly indicates that we are dealing with a "rattle and drift" type of motion and we must therefore expect that at least one component, the short-time component, of our motion will have a phonon-like frequency (as incorporated in Fig. 14). Furthermore, at the low temperatures at which the mechanical relaxation studies are carried out, this rattling component will be far the dominant aspect of the motion. We should emphasize that the observations depicted in Fig. 17 cover an extremely short period of time, of order of picoseconds, but nevertheless probably contain the essential features of the motion that we will study in the laboratory on very much longer time scales.
With this background, we proceed to pose a number of questions of interest concerning these fast relaxation modes, which we may hope to answer by mechanical spectroscopic studies. The first three questions are essentially those we asked of the primary relaxation:
1. Is the process following an Arrhenius law or otherwise?
2. Is the relaxation exponential in character or otherwise?
3. Are there strong similarities between different systems or otherwise? We have already partly answered this latter question by drawing attention in Fig. 16 to the wide range of decouplings which are possible.
4. What is the relation of the mechanical response to the electrical response? We must note here that the electrical response is a primary relaxation in the sense that on cooling it is the first mechanism which gives rise to a finite electrical modulus (see Fig. 15.) The primary mechanical response shows up near $T_g$ hence the mechanical response of interest here is a secondary one. We must therefore expect some differences on this account alone.
5. What is the relation of the secondary mechanical response to the degree of decoupling of these modes of motion from those of the primary relaxation?
6. What is the relation of the (secondary) mechanical response to the fragility of the primary relaxation?
7. What is the dependence of the mechanical relaxation on the structural state of the glass, and how is any structural state dependence which may exist related to the degree of decoupling from the primary relaxation of the fast modes under study?
8. What is the background mechanical loss upon which the loss due to these fast modes is superimposed? In asking this question, we have in mind the better known case of background loss in electrical relaxation which has been quite well studied [2, 44, 52-57], but so far not properly explained.

In responding to these questions, we will be presenting a mixture of electrical and mechanical data on a restricted number of well-studied chosen systems. The system on which most data are available is the very highly decoupled system AgI0.6 • (Ag2O.2B2O3)0.4, which has now been studied by a variety of techniques of very different characteristic time scales [58-60]. In Fig. 18 we show the electrical relaxation data for this system [61] in the form of real and imaginary parts of the electrical modulus $M^\ast$. As is immediately clear, the range of electrical data is much greater than can be obtained by mechanical spectroscopy and the noise level is much lower. This is very convenient because it makes it possible to test the time-temperature-superposition (constant spectral shape) characteristics of these systems. To show that the electrical relaxation spectra have shapes which are essentially independent of temperature in this case (and many others), we superimpose the real and imaginary parts to yield the master plots shown in part c of Fig. 18. All data are seen to be collapsed to single curves. The relaxation is quite non-exponential, with $\beta$ of Eq. (4) being 0.48.
The mechanical relaxation data available on this system have been obtained by scanning in temperature at constant frequency and a data set analogous to the electrical data in Fig. 18 is not available. Before looking at the mechanical data, therefore, we will make one or two observations on the basis of the data in Fig. 18. While the KWW fitting function describes well the M" behavior in the vicinity of the M" maximum with a parameter $\beta = 0.48$, it does not do a very good job of accounting for the data at higher frequencies. Two decades above the peak frequency, the loss observed is almost twice the predicted value. This is typical for superionic glasses. Before we can say whether a similar discrepancy applies to the mechanical data, however, we must give some time to considering how the more limited mechanical data can be analyzed to advantage.

From the experience with primary relaxations in the first part of this chapter, the very large departures from exponential relaxation we observe for the fast ion relaxation might be expected to be associated with large deviations from the Arrhenius law. This, however, proves not to be the case. Mechanical relaxation time data for this system, extracted from the peak values of mechanical loss vs. temperature at constant frequency, are presented in Fig. 19 along with data in very different time scale ranges obtained by
ultrasonic absorption studies by Carini and co-workers [58] and hypersonic relaxation data from Börjesson and Torell [59].

It may be seen immediately from Fig. 19 that the process obeys the Arrhenius law over most of this range, though it appears that at the highest temperatures some deviation is occurring such that the infinite temperature time scale coincides with the observed far infrared absorption time scale. This is appropriate since it is unphysical to imagine a relaxation process which can occur any faster than the time scale for reversal of the ionic motion in its vibrational mode ("rattling"). For convenience, the peak of the far infrared absorption spectrum (115 cm\(^{-1}\)) is included as an insert in Fig. 19. Figure 19 also shows the electrical relaxation times [61] for the same system as extracted from the spectra presented in Fig. 18. It may be observed that the two time scales, which are separated by almost an order of magnitude at low temperatures, are merging in the high temperature (but still below \(T_g\)) regime.

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6 The fact that a hypersonic absorption can be seen below the glass transition temperature is a clear indication of how decoupled the mobile ion modes in the glass can be from the structural relaxation since the hypersonic study (performed using the Brillouin scattering method) probes processes of time constant of order of 10 ps. Note that, in this system, the mechanical relaxation process has been probed over more than ten orders of magnitude in time.
Included in Fig. 19 are data for one composition in the system AgI + AgPO₃. This latter system has been studied in some detail over a range of compositions and it is appropriate to examine its behavior as a (general) model for mechanical relaxation in this type of system. To this end, we present in Fig. 20, data obtained at constant frequency during temperature scans [62]. The data, obtained from the Rheovibron as the loss tangent, E''/E', (tan δ) and the tensile modulus, |E*|, have been decomposed to provide the real and imaginary parts, E' and E'', of the tensile modulus E*.* The values are displayed for compositions in the binary systems ranging from 0 to 60% AgI. One observes that as the silver iodide content increases, the loss, E'', increases in intensity and the temperature of maximum loss moves to lower values (implying faster process at higher silver iodide contents when compared at the same temperature).

The dispersion in the tensile modulus increases to about 15% in the highest silver iodide content glass studied. We note that the mechanical response is effectively unchanged between 50 and 60% AgI content. This is probably to be associated with a separation of these higher AgI content glasses on a microscopic level into two liquid phases which is suggested by the opaque yellow color of some of these glasses, and by photomicrographic studies [63].

Our next step is to see how data obtained during temperature scans at constant frequency can be used to compare with the electrical data obtained isothermally by varying the frequency. Fig. 21 [44] demonstrates the fact that, provided the relaxation process under study has an Arrhenius form of temperature dependence, and provided the shape of the relaxation spectrum is either a Lorentzian (as for a single relaxation time) or has a temperature independent shape and dispersion strength (as in Fig. 18),

![Figure 20. Real (E') and imaginary (E'') parts of the tensile modulus for (AgI)ₓ-(AgPO₃)₁₋ₓ glasses of different AgI contents as marked. The dispersion in E'' due to the mobile cation relaxation is shown at the midpoint of the relaxation for the case of XₐgI = 0.4 (from ref. 62 reproduced by permission).]
Figure 21. (a) Real parts of the electrical modulus for the superionic glass $0.6\text{Agl}\cdot 0.4\text{Ag}_2\text{B}_2\text{O}_7$ measured at -110 and -125°C. (b) Imaginary part of the electrical modulus for the same system measured at -110°C. Note maximum loss at $10^4$ Hz for $T = -110°C$. (c) Real and imaginary parts of the electrical modulus for the same system at a constant frequency of $10^4$ Hz measured as a function of temperature. (d) Real and imaginary parts of the electrical modulus for the same system plotted vs reciprocal temperature. Note identical shape of $M''$ in parts b and d. The scale factor converting $1/T$ units to log $\omega$ units is $E_a/2.30R$, where $E_a$ is the activation energy for the relaxation process. (After ref. 44, reproduced with permission.)

then the plot of data obtained at a constant frequency, using an inverse temperature axis, is the same as the plot of the loss measured isothermally as a function of the logarithm of frequency. The transposition from one form to another is obtained by the use of a scaling factor which is $E_a/(2.303R)$, where $E_a$ is the Arrhenius activation energy.

We now use this principle to compare, in Fig. 22, the mechanical and electrical relaxation spectra for the composition $(\text{Agl})_{0.6} (\text{Ag}_2\text{O}_2\text{B}_2\text{O}_3)_{0.4}$ in the frequency range centered around 100Hz. Extended frequency range measurements discussed below, (Fig. 23) show a noticeable effect of temperature of the spectral width, but not enough at low temperatures to invalidate the data reduction. The dashed lines show the electrical relaxation spectra taken from Fig. 18 at two different temperatures while the solid line shows the 110 Hz mechanical spectrum obtained by plotting the imaginary plot of the modulus against reciprocal temperature. The corresponding log $\omega$ scale is included as a second X-axis.
Two facts related to question 4 above can be taken from Fig. 22. Firstly, the time scale for the mechanical relaxation is somewhat longer at the same temperature than the time scale for the electrical response. A factor of 4 is suggested by comparison of the peak frequencies on the transposed frequency scale. Secondly, the mechanical relaxation is considerably broader than the electrical relaxation.

A similar situation is found in the case of silver iodide-silver metaphosphate glasses [62]. In this case, the two time scales are somewhat closer and if one turns to the case of anion-conducting glasses, such as those in the system PbF$_2$-MnF$_2$-Al(PO$_3$)$_3$ system one finds that the relaxation time relationship has reversed [64]. In all cases, however, the mechanical relaxation spectrum is much broader than the electrical relaxation time spectrum.

One way to account qualitatively, at least, for the difference in spectral width is to recognize the primary nature of the electrical relaxation. Associated with this observation is the fact that, due to conductivity, the system cannot reach a thermodynamic state of polarization in the electrically conducting case. This distinguishes it from the mechanical relaxation case. While we have obtained the narrow electrical spectrum by simply forming the electrical modulus from the raw data, it can be argued that a more appropriate procedure would yield a broader spectrum. The more appropriate procedure being advocated by a number of workers in the field [54, 65-67] would be to subtract out the loss due to a DC electrical conductivity and analyze the remaining component as a pure dielectric relaxation. The inevitable result will be a more asymmetric loss spectrum with a higher characteristic frequency for the residual (dielectric)
part of the total electrical response. The latter aspect would increase the peak frequency mismatch of Fig. 22.

Let us now look at the mechanical relaxation in the very different frequency regions for which data are available. This comparison is performed [61] by normalizing the losses by their maximum values to avoid distortions due to the different types of experiments under comparison and presenting the data at different temperatures using a reciprocal temperature representation to display the spectral shapes, see Fig. 23. We note that the shape obtained in the 100 Hz domain is very similar to that obtained in the ultrasonic domain, but a marked change occurs on passage to the gigahertz domain. Here it appears that an abrupt narrowing of the spectrum, almost to exponential relaxation half-width, has occurred. In a theoretical analysis Ngai [68] points out that this narrowing reflects the imminence of the cross-over from cooperative relaxation to the primitive relaxation process and may be associated with the beginning of the deviation from Arrhenius behavior which was seen in Fig. 19 at the highest temperatures.

We now turn briefly to the question of whether or not a relationship between the secondary relaxation mechanical spectrum and the degree of decoupling of the secondary modes from the primary mechanical modes, can be observed. In the case of electrical conductivity a correlation has been observed between the stretching parameter data of Eq. (1) and the decoupling index $R_{\tau^*}$ defined by the ratio of the structural relaxation time to the electrical relaxation time measured at the glass transition.

![Comparison of normalized moduli for mechanical relaxation over wide temperature/frequency regimes using a 1/T representation of the spectra form.](image)

*Figure 23.* Comparison of normalized moduli for mechanical relaxation over wide temperature/frequency regimes using a 1/T representation of the spectra form. Note that the spectra at 5 MHz [from ref. 58] and at 11 Hz are approximately the same in shape (approximately justifying the inclusion of an equivalent frequency scale discussed earlier under Fig. 20, while the high-temperature high-frequency spectrum is narrow. Dotted lines show predicted shapes at gigahertz and low frequencies according to the Gaussian activation energy distribution model of ref. 58. The frequency scales attached to the 5-MHz and 110-Hz plots are based on the equivalence of $1/T$ and $\log f$ discussed earlier under Figure 20. Each scale has its origin fixed such that the peak of the modulus plot falls at the appropriate fixed frequency, 5 MHz or 110 Hz. (From Ref. 61, reproduced by permission).
temperature [44]. The relationship is shown in Fig. 24 and implies that the more completely decoupled the fast modes are from the slow modes, the broader is the distribution of relaxation times, i.e. the smaller the value of the stretching parameter. While there are many more data available for electrical relaxation than for mechanical, a tentative extension of this correlation can be made to the mechanical case using data on a fluoride glass determined by the Lyons group [69], which shows a relatively narrow spectrum, and the data from the mobile silver ion glasses such as the AgI.AgPO3 glasses [62] and the iodoborate glass seen in Fig 23. While the correlation is crude at this time, it seems real, hence worthy of further examination.

It remains to discuss the matter of background absorption since this is a matter which has given rise to considerable interest in the electrical relaxation case [53-57]. To summarize the position in the latter case, we present a representation of the electrical energy absorption data (the absorptivity being proportional to the conductivity) as a function of frequency on a log-log scale. We note that the absorptivity $\alpha$ is the energy loss per unit length, and is the quantity obtained directly in ultrasonic absorption and hypersonic absorption studies [58-59]. In the electrical response case it is related to the frequency-dependent electrical conductivity $\sigma(\omega)$ by the simple expression [due to Moss (70)]

$$\alpha(\omega) = \frac{\sigma(\omega)}{cn(\omega)e_0}$$

where $c$ is the speed of light, $n(\omega)$ the refraction index, and $e_0$, the permittivity of free space.

![Figure 24.](image)

Correlation of non-exponentiality parameter $\beta$ of Kohlrausch function with decoupling index $R_{\tau}$ for a variety of ionic glasses. Squares are for conductivity relaxation and circles are for mechanical relaxation. Points at the same $R_{\tau}$ values are for the same glasses.
Fig. 25 shows the electrical absorptivities for the case of a sodium silicate glass determined at different temperatures below and above the glass transition temperature. The point of interest to this discussion is that at low temperatures, where the DC conductivity is low, the frequency-independent-regime is restricted to very low frequencies, and in most of the frequency range there is a linear relationship between absorptivity and frequency with a slope of unity on the log-log plot. This implies that there is a constant loss at the higher frequencies. The existence of this constant loss, which has been under discussion for a long time, is presumably related to the excess loss over that predicted by the stretched exponential relationship on which a comment was made in the discussion of Fig. 18. It can be seen from Fig. 25 that the background loss is such that the absorption spectra connects smoothly to the infrared absorption spectrum at the limit of high frequencies. The origin of this loss, which is also seen in dipolar molecular liquid systems, has been controversial though Ngai and colleagues [55] have argued plausibly that it is linked to the constant spin lattice relaxation time observed in glasses at low temperatures and has its origin in the heavy atom tunnelling (HAT) processes which are ubiquitous in glasses. Their argument is supported by reference to similar behavior in other disordered systems like $\beta$-$\text{Al}_2\text{O}_3$ [56] which also show the heavy atom tunnelling (i.e. Two Level Systems TLS) effects. An overview is given by Ngai in ref. 71.

Figure 25. Variation of the absorptivity $\alpha$ with frequency, in the form originally proposed by Wong and Angell (ref. 2, Ch. 11, Fig. 14), but containing additional data from the recent work of Burns et al. [53] and Cole and Tombari [54]. (From ref. 54, reproduced by permission)
The question which arises now is whether there is a comparable phenomenology for the case of absorption of mechanical energy as indeed the HAT interpretation would imply. The data available to answer this question are very limited, but sufficient to suggest that the situation is very similar to that for electrical relaxation. We turn to the data on the silver iodide-silver diborate system and present the ultrasonic data of Carini and co-workers [58] and the hypersonic data of Börjesson and Torell [59, 60] at several different temperatures shown in Fig. 22. In the mechanical absorption case we do not have the equivalent of the infrared absorption measurement, but an estimate of the mechanical absorptivity at the limit of phonon frequencies has been given elsewhere [44], and the point, with which a considerable error bar is associated, is shown in Fig. 25. A value in roughly the same domain is indicated by the Arrhenius extrapolation of the absorption maxima shown in part b of Fig. 25. This aspect of mechanical spectroscopy in glasses has received scant attention to date and deserves more. To the extent that tunnelling phenomena are involved, these effects should not be present in the behavior of glasses simulated by classical molecular dynamics methods. The time scales of the excitations involved are within range of current computational possibilities, and comparisons of classical simulations with quantum simulations could play an important clarifying role in future discussions.

Analog of Figure 25 for absorption of mechanical energy in the same system, based on limited ultrasonic [11] and Brillouin scattering [60] data. The mechanical process seems to have an $\alpha \sim f^{1.0}$ background over the major part of the frequency range, similar to that in dielectrically relaxing systems, and both backgrounds are probably due to heavy atom tunnelling as discussed in refs. 55 and 56. An Arrhenius temperature dependence for the acoustic absorption coefficient (at the frequency of the loss maximum, as shown on the right hand part of the figure) has not been discussed previously to the best of our knowledge, and the present discussion makes its origin apparent.
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63. Johari, G. P. (private communication).
Figure Captions

Figure 1. Phase diagrams for model systems on which many of the data utilized in the chapter are obtained. (a) The system KNO₃-Ca(NO₃)₂: the composition range used in most studies is indicated by an arrow. (b) The system germanium-arsenic-selenium showing the glass-forming composition domain and the line of compositions satisfying the ideal average coordination number condition, < r > = 2.4.

Figure 2. Temperature-dependence of state properties and derivatives at the glass transition. (a) Volume. (b) Thermal expansivity, showing hysteresis for measurements made on heating and cooling. (c) Behavior of the heat capacity at constant pressure showing hysteresis in the transformation range. Insert shows the variation of the "thermal modulus", defined by the reciprocal of the heat capacity, for comparison with later mechanical measurements.

Figure 3. Variation with temperature of the various mechanical moduli: shear modulus G', bulk modulus K', longitudinal modulus M', and tensile modulus E'. Note that the shear and tensile moduli have vanishing values in the liquid state.

Figure 4. Variations of the (a) real and (b) the imaginary parts of the complex isothermal compressibility κ'. The variation of κ' with T at constant frequency, is shown as a dashed line.

Figure 5. (a) Temperature dependences of high and low frequency limiting compressibilities, κ∞ and κ₀, for glycerol, and the dispersion of κ' at 31 MHz. (b) Temperature dependence of the configurational contribution κ₀ - κ∞ to the total compressibility of glycerol between 20 and -30°C and a comparison of the reduced dielectric loss ε''/Δε with the reduced compressibility loss κ''/Δκ''. (Data from Ref. 11.)

Figure 6. Real and imaginary parts of (a) the dielectric susceptibility and (b) the dielectric modulus (b) for a dilute solution of lithium perchlorate in propanol. Note the displacement of peak maximum to higher frequencies in the modulus representation of the data and the appearance of the low-frequency conductivity relaxation peak. Dielectric peak frequencies are related by the ratio of high-frequency to low-frequency dielectric constants (Eq. 5). Both differ by the factor 11 in this case. (From ref. 13, reproduced with permission.)

Figure 7. Examples of stress relaxation functions obtained using the transient elastometry technique. Data are obtained on the model system composition noted in the figure, and correspond to different temperatures from left to right of 433.4, 422.6, 413.3, 403.7, 394.5, and 385.3 K. The solid lines are fits using Eq. (6). The dashed line illustrates single exponential behavior. (Adapted from Ref. 21, reproduced by permission.)

Figure 8. Variation of mechanical (i.e. viscosity) relaxation times obtained by various short-time and long-time techniques, for a variety of molecular liquids showing the strong/fragile pattern discussed in the text, (from ref 72, reproduced by permission).

Figure 9. Upper frame: Average equilibrium relaxation times τ obtained from stress relaxation measurements (by transient elastometry) as an Arrhenius function of temperature for various compositions along the line Y = 0.5 in the system Ge-As-Se, for various values of < r >. The T_g used in the scaling is the calorimetric value. This plot is an extension, at the long relaxation time end, of the larger pattern shown in Fig. 8. Lower frame: Temperature dependence of the stretching exponents β of Eq. (6) normalized to their respective values of T_g. Note that the deviations from thermorheologically simply behavior (corresponding to temperature independent stretching) are smallest in the least fragile liquid. Solid lines are guides to the eye.

Figure 10. Dependence of (a) the activation energy and (b) the fragility (E_a/2.303 RT_g), on the average coordination number < r > in the system Ge-As-Se at the composition y = 0.5 [see Fig. 1 (b)]. (c) Variation of the fractional exponent β of Eq. (6) with < r >. (From ref.34, reproduced by permission).

Figure 11. Relationship between the fragility m and the fractional exponent β measured at T_g for the chalcogenide alloys of Fig. 10 and the linear chain polymers of Ref. 29, showing a common pattern of behavior. Solid line shows theoretical result of Vilgis (ref. 31).
Figure 12. Part (a) Stress relaxation functions in the region below $T_g$ for various waiting times after an initial temperature equilibration following step down from above $T_g$. Diagram shows the effect on the approach to the equilibrium state of the form of the relaxation and the characteristic time $\tau$. Note that the effective relaxation time for the structure is some ten times longer than the values of $\tau$ themselves. The lower panel shows how the distinction between curves 1-5 of the upper panel are related to the change of configurational entropy during annealing.

Figure 13. Comparison of the electrical modulus for an ionically conducting glass with the various mechanical moduli. Note that the electrical modulus remains zero to temperatures well below the glass transition temperature.

Figure 14. Schematic representation of the variations with temperature of the primary ($\alpha$-relaxation) relaxation time and that of the secondary relaxation due to the mobile ions in an ion-conducting glass. Note the break in the temperature-dependence of the secondary relaxation at the glass transition temperature and the establishment of an Arrhenius behavior at lower temperatures.

Figure 15. Variation of mechanical shear modulus of Na$_2$O•3SiO$_2$ (measured at 0.4 Hz) through fast and slow relaxation domains compared with that of the electrical modulus (measured at the same frequency). Note how the electrical modulus vanishes above the fast relaxation. [Data from refs 40 and 41 (solid lines) and from their extrapolations (dashed lines)]. (After ref. 39, reproduced with permission.)

Figure 16. $T_g$-scaled Arrhenius plot of conductance of systems with widely differing degrees of decoupling of conductivity from structural modes. Dashed line shows behavior for fully coupled system. (After ref. 44, reproduced with permission.)

Figure 17. Projection on a plane of the motions of lithium ions in a simulated lithium thiosilicate glass, showing examples of oscillatory, and drift motions believed characteristic of the mobile ions in superionic glasses and their relation to experimentally observed quantities (a.c. conductivity and far IR spectra). (From ref. 49 reproduced by permission.)

Figure 18. (a) Real $M'$, (b) imaginary $M''$ parts of electrical modulus for 60AgI•40(Ag$_2$O•2B$_2$O$_3$) at various temperatures, (c) Master plots for $M'$ and $M''$ obtained by shifts along frequency axis to superimpose peak maxima. Lines through most points are from the Fourier transform of the time derivative of $\theta(t) = \exp(-t/\tau)$. 

Figure 19. Arrhenius plot of relaxation times for mechanical and electrical mobile ion controlled processes in three different fast ion conducting glass systems, one containing only halide anions. Note that the latter, which was fully annealed, shows Arrhenius behavior over the whole temperature range with direct extrapolation to the quasi-lattice vibration time. Plot contains results of high-frequency study of Figure 23. (After ref. 49, reproduced with permission.)

Figure 20. Real (E') and imaginary (E'') parts of the tensile modulus for (AgI)$_x$-(AgPO$_3$)$_{1-x}$ glasses of different AgI contents as marked. The dispersion in E'' due to the mobile cation relaxation is shown at the midpoint of the relaxation for the case of X$_{AgI}$ = 0.4 (from ref. 62 reproduced by permission).

Figure 21. (a) Real parts of the electrical modulus for the superionic glass 0.6AgI•0.4Ag$_2$B$_4$O$_7$ measured at -110 and -125°C. (b) Imaginary part of the electrical modulus for the same system measured at -110°C. Note maximum loss at $10^4$ Hz for T = -110°C. (c) Real and imaginary parts of the electrical modulus for the same system at a constant frequency of $10^4$ Hz measured as a function of temperature. (d) Real and imaginary parts of the electrical modulus for the same system plotted vs reciprocal temperature. Note identical shape of $M''$ in parts b and d. The scale factor converting 1/T units to log f units is $E_a/2.30R$, where $E_a$ is the activation energy for the relaxation process. (After ref. 44, reproduced with permission.)

Figure 22. Reciprocal temperature display of imaginary parts of the electrical and mechanical relaxation for the case of 0.6AgI•0.4Ag$_2$B$_4$O$_7$, showing displacement of the temperature of maximum
loss for the two different stresses in the presence of similarity of spectral form. Solid curve through points for mechanical relaxation is the KWW function with $\beta = 0.29$. Electrical relaxations are well described by the same form with $\beta = 0.48$. An equivalent frequency scale is displayed for the mechanical relaxation centered at the peak frequency. The same scale size applies to the electrical relaxations since the activation energies for each process are essentially the same. (After ref. 61, reproduced with permission.)

**Figure 23.** Comparison of normalized moduli for mechanical relaxation over wide temperature/frequency regimes using a $1/T$ representation of the spectra form. Note that the spectra at 5 MHz (from ref. 58) and at 11 Hz are approximately the same in shape (approximately justifying the inclusion of an equivalent frequency scale discussed earlier under Fig. 20, while the high-temperature high-frequency spectrum is narrow. Dotted lines show predicted shapes at gigahertz and low frequencies according to the Gaussian activation energy distribution model of ref. 58. The frequency scales attached to the 5-MHz and 110-Hz plots are based on the equivalence of $1/T$ and log $f$ discussed earlier under Figure 20. Each scale has its origin fixed such that the peak of the modulus plot falls at the appropriate fixed frequency, 5 MHz or 110 Hz. (From Ref. 61, reproduced by permission).

**Figure 24.** Correlation of non-exponentiality parameter $\beta$ of Kohlrausch function with decoupling index $R_\tau$ for a variety of ionic glasses. Squares are for conductivity relaxation and circles are for mechanical relaxation. Points at the same $R_\tau$ values are for the same glasses.

**Figure 25.** Variation of the absorptivity $\alpha$ with frequency, in the form originally proposed by Wong and Angell (ref. 2, Ch. 11, Fig. 14), but containing additional data from the recent work of Burns et al. [53] and Cole and Tombart [54]. (From ref. 54, reproduced by permission)

**Figure 26.** Analog of Figure 25 for absorption of mechanical energy in the same system, based on limited ultrasonic [11] and Brillouin scattering [60] data. The mechanical process seems to have an $\alpha \sim f^{1.0}$ background over the major part of the frequency range, similar to that in dielectrically relaxing systems, and both backgrounds are probably due to heavy atom tunnelling as discussed in refs. 55 and 56. An Arrhenius temperature dependence for the acoustic absorption coefficient (at the frequency of the loss maximum, as shown on the right hand part of the figure) has not been discussed previously to the best of our knowledge, and the present discussion makes its origin apparent.
### Table of Symbols Used

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>c</td>
<td>- velocity of light</td>
</tr>
<tr>
<td>C_p</td>
<td>- constant pressure heat capacity</td>
</tr>
<tr>
<td>D</td>
<td>- strength parameter of Vogel Tamman Fulcher (VTF) equation</td>
</tr>
<tr>
<td>E</td>
<td>- tensile (Young's) modulus</td>
</tr>
<tr>
<td>E_a</td>
<td>- Arrhenius activation energy</td>
</tr>
<tr>
<td>G</td>
<td>- shear mechanical modulus (G* if modulus is time-dependent)</td>
</tr>
<tr>
<td>G</td>
<td>- Gibbs Free energy</td>
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<tr>
<td>J</td>
<td>- shear compliance</td>
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<tr>
<td>K</td>
<td>- bulk mechanical modulus</td>
</tr>
<tr>
<td>k_B</td>
<td>- Boltzmann constant</td>
</tr>
<tr>
<td>m</td>
<td>- fragility parameter = Ea/2.303RT_g</td>
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<tr>
<td>M</td>
<td>- longitudinal mechanical modulus (M*...)</td>
</tr>
<tr>
<td>M'</td>
<td>- real part of M*</td>
</tr>
<tr>
<td>M''</td>
<td>- imaginary part of M*</td>
</tr>
<tr>
<td>M_\infty</td>
<td>- value of M at frequencies high above relaxation frequency.</td>
</tr>
<tr>
<td>M_0</td>
<td>- value of M at zero frequency</td>
</tr>
<tr>
<td>M_\sigma</td>
<td>- electrical modulus</td>
</tr>
<tr>
<td>N</td>
<td>- normalized modulus (normalized to unity at peak value)</td>
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<tr>
<td>n(\omega)</td>
<td>- refractive index at frequency \omega</td>
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<tr>
<td>R_\tau</td>
<td>- decoupling index defined by the ratio of mechanical relaxation time to electrical conductivity relaxation time.</td>
</tr>
<tr>
<td>&lt;r&gt;</td>
<td>- average coordination number</td>
</tr>
<tr>
<td>S</td>
<td>- entropy</td>
</tr>
<tr>
<td>T_o</td>
<td>- ideal glass transition temperature or temperature of viscosity or relaxation time divergence</td>
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<tr>
<td>\alpha</td>
<td>- primary relaxation designator when used with &quot;relaxation&quot; or &quot;process&quot;</td>
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<tr>
<td>\alpha</td>
<td>- volumetric expansivity</td>
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<tr>
<td>\alpha(\omega)</td>
<td>- optical absorbivity or mechanical absorptivity at frequency \omega</td>
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<tr>
<td>\beta</td>
<td>- stretched exponential relaxation parameter</td>
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<tr>
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<td>\omega</td>
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