Chapter 11

RELAXATION SPECTROSCOPY

11.1 Introduction

11.2 Relaxation Spectroscopy in the Linear Response Regime
(A) Polarizing Systems: Electrical and Mechanical Relaxations
(B) Nonpolarizing Systems: Electrical and Mechanical Relaxations
(C) Light Scattering Studies of Relaxation by Digital Photon Correlation Techniques
(D) NMR Relaxation Studies
(E) Pressure and Temperature Jump Relaxation Studies

11.3 Relaxation Spectroscopy Outside the Linear Response Regime. Temperature or Pressure Step, and Temperature or Pressure Ramping Studies
(A) Enthalpy and Volume Studies
(B) Electrical Conductivity Studies
(C) Spectroscopically Selected Structural Group Relaxation Studies

11.4 Summary

References

11.1 INTRODUCTION*

Throughout this book we have been observing and interpreting the relation between the atomic level structure of glassy materials and the characteristic frequencies at which energy from an external field
of some sort is dissipated within them. Up to this point the energy-dissipating processes have always had a common basis, viz., a resonance transfer of energy from the field to nuclear, electronic, vibrational, or Zeeman quantum levels of the ionic or molecular glass constituents, followed by decay of the excited state energy to the thermal bath (or in rare cases by reemission at some other frequency).

There exist, however, other processes whereby energy from an external source may be dissipated in the glass in characteristic frequency regions—frequencies which, at root, are also determined by the glass structure, and, therefore, properly deserve discussion in this book. These are the relaxation processes in which configurational rearrangements of atomic or molecular constituents of the glass are induced by the external stress. The characteristic relaxation frequencies are of particular interest because, in contrast with resonance frequencies, they are highly temperature-dependent, varying over some 13-15 orders of magnitude between the glass temperature and the normal melting temperature. A number of additional relaxation processes, e.g., those involving alkali cation motion in silicate glasses, side-group motions in polymers, and certain local rearrangements in molecular glasses, may also be studied at temperatures far below \( T_g \). The appearance of these new characteristic frequencies in amorphous phases reflects the progressive decoupling of the possible modes of motion of the particulate system which accompanies progressive decrease in the level of thermal excitation.

Energy dissipation in the most important and obvious of these cases is associated with long-range irreversible motion of particles, hence the relaxation spectra afford a means of studying the important mass transport and structural rearrangement mechanisms by means of which the glass structure is reached (continuously) from the liquid state. In the case of very mobile liquids, the frequencies associated with relaxation and resonance absorption processes may be observed to merge, under conditions in which the distinction between vibrational and diffusional motions becomes very blurred.

The merging occurs in the far infrared region and is of great significance in the understanding of the dynamics of "normal" liquids. A merging of resonance and relaxation frequencies can also be observed in the case of glassy materials in which constituent particles have very different mobilities, e.g., network oxide glasses containing alkali metal cations. In some such cases the time scale for alkali metal migration near the glass transition temperature may be of the order of \( 10^{-10} \) sec and the high frequency end of the relaxation loss spectrum (see below) then overlaps the low frequency tail of the resonance spectrum arising from anharmonic alkali metal cation vibrations within the oxide quasi-lattice. In principle, of course, there must always be some overlap if there is to be any conductivity at all, since a passage from anharmonic oscillator to relaxing migrator is intrinsic to the concept of activated transport. However, it is only when the probability of an oscillation becoming a migration begins to approach unity that the frequency overlap will be experimentally observable. As in the case of structural relaxation of a low viscosity liquid, the distinction between migration and vibration becomes rather meaningless under these conditions since both modes of motion are explored simultaneously and continuously.

Some poorly understood high frequency relaxational modes also exist in molecular and polymeric glasses in which they are known as \( \beta \)-relaxations. The elucidation of such apparently ubiquitous modes and of their coupling to the vibrational modes of the frozen superstructure is of major concern in understanding the nature of the glassy state. In the latter aspect and in many others relaxation spectroscopy is a very inadequately researched area. This is particularly true for relaxation spectroscopy studies in which the resonance spectroscopy of earlier chapters is utilized as a specific and, as will be seen, very incisive research tool. The inclusion of relaxation spectroscopy in this book alongside the more familiar branches of vitreous state spectroscopy is, therefore, very appropriate.
With the exception of the rather specialized areas of neutron and electron inelastic scattering, resonance spectroscopy is based entirely on the inelastic interaction of matter with electromagnetic radiation fields. Relaxation spectroscopy, in this respect, is a more versatile field. A system of interest can be perturbed from its equilibrium state by a variety of mechanical and thermal as well as electrical and magnetic field stresses for each of which the system will exhibit a characteristic frequency-dependent response. While these responses will frequently have features in common, no two will be identical. Thus relaxation spectroscopy is potentially a powerful means of probing the glass and viscous liquid properties. Applied stresses to which glassy and liquid system responses have so far been studied have included electric field, magnetic field, mechanical shear, compression, and uniaxial tension. In addition, system responses to uniform displacements from thermodynamic equilibrium caused by sudden changes of temperature or by continuous displacements caused by ramping the temperature, have been studied. The responses to such displacements may be monitored in different ways, some of which (measurement of volume or enthalpy) are determined by the whole system, while others (conductivity or optical density at frequencies characteristic of specific subunits of the glass structure) follow the relaxation of particular parts of the system. From the correlations and contrasts of these many different types of experiment, much can be inferred about the dynamic relationship amongst the different elements of the glass structure and among the different energy and volume-changing processes which occur within that structure. Indirectly, therefore, new insights into otherwise obscure aspects of the structure itself are obtainable. A striking finding of these studies is that more variety can be observed within a single system by monitoring different relaxing elements than can be discerned between entirely different systems responding to quite different perturbing stresses when monitored with respect to the total system response.

A great many different measurement techniques may be applied in the study of the system responses to each of the stresses referred to above, and the choice of technique will usually depend on the frequency range being investigated. It will not be feasible in this chapter to enter into any detailed discussion of measurement techniques. For detailed information on the techniques of relaxation spectroscopy the reader is referred to various excellent specialized monographs [2,6] and to the original literature.

Because of the many ways of perturbing an equilibrium state, and of the great variety of liquid and glassy systems whose responses have been investigated, some restrictions in coverage must be imposed to keep this chapter in proportion. For instance, more research has probably been done on stress relaxation in polymers than in all the other subject areas of this book combined. At the same time, to devote the chapter to the inorganic glasses which have provided the subject materials for the majority of electronic and vibrational spectroscopy studies on glasses would be to ignore some of the best-developed aspects of the subject. We will resolve this dilemma by departing from the format used in preceding chapters and dividing the chapter into subject areas within the general relaxation spectroscopy field. Within each of these we will review findings on those viscous liquid and glassy materials whose study has contributed most to the development of understanding. To restrict the scope of the chapter and at the same time to provide links between the sections, certain systems representative of inorganic network glasses, simple ionic glasses, hydrogen bonded liquids, and van der Waals liquids, will be used selectively in preference to extensive reviews of all the important systems studied. Enough examples will be provided within the sections to establish that the response functions within a class of systems tend to be rather uniform. In fact, the general lack of spectral variety in this field turns out to be one of its most puzzling and significant features.

11.2 LINEAR RESPONSES IN TIME AND FREQUENCY DOMAINS

We will concern ourselves principally with the study of systems near equilibrium. In practice this means that the stresses applied to the system must be small compared with, e.g., the electrical forces
11.2 LINEAR RESPONSE REGIME

(A) Polarizing Systems: Electrical and Mechanical Relaxations

The only cases where nonlinear responses are a problem are those in which perturbation from equilibrium is brought about by changes in one of the thermodynamic variables, temperature or pressure, particularly the former. Relaxation after temperature change perturbation is of enormous practical importance, however, and Sec. 11.3 is devoted to a discussion of its study and analysis. It is fortunate that very recently an effective method of dealing with the nonlinearity problem for such cases has been developed.

(i) PRINCIPLES

Even though the inorganic glasses which dominate earlier chapters do not qualify for discussion in the major part of this section, there are conceptual advantages in discussing first the cases of (1) the response to an electric field stress of a nonconducting dielectric fluid, and (2) the response to an isotropic compression of a compressible fluid. In each of these cases, unlike those of the conducting or shearing fluids, a steady stress will not lead to a continuous dissipation of energy, and an instantaneous stress will not decay to zero over a period of time. Rather, in the case of steady stresses there will be (1) a flow of charge which decreases to zero with time as the polar molecules of the dielectric fluid progress towards some limiting state of reorientation in the imposed electric field, and (2) a "flow" of molecules with respect to one another which decreases with time as the molecules reach some limiting state of compaction linearly related to the magnitude of the compressive forces imposed.

In each of these cases, as before, there will be a characteristic time taken by the system to respond to the imposed force, and for observations made on a time scale short with respect to the response time, only an elastic, reversible response (displacement polarization and elastic compression, respectively) will be observed.

These response functions (sometimes called "decay", "relaxation", or "time correlation" functions) are illustrated in Fig. 1 where changes in polarization P and volume V induced by sudden...
11.2 LINEAR RESPONSE REGIME

Application of a stress are plotted as a function of time. Corresponding responses may, of course, be observed when an applied stress is suddenly removed from a polarized dielectric or a compressed liquid. In fact, this course is the more frequently adopted in experimental measurements.

In some cases, perhaps to be described as "simple" or "ideal" cases, the transition from elastic to dissipative response shown in Fig. 1 can be described in terms of a single "relaxation time" constant \( \tau \). In such cases, the response is such that the polarization or volume varies exponentially with passing time in accord with the simple expressions:

\[
P = P_1 + (P_2 - P_1)(1 - e^{-t/\tau}) = P_1 + (P_2 - P_1)(1 - \phi(t))
\]

\[
V = V_1 + (V_2 - V_1)(1 - e^{-t/\tau}) = V_1 + (V_2 - V_1)(1 - \phi(t))
\]

(1)

where \( \phi(t) \) is the normalized response function* \( \phi(0) = 1, \phi(\infty) = 0 \).

Clearly, elastic responses \( (P_0 \to P_1, V_0 \to V_1) \) to the imposed stress will only be observed if measurements are made on a time scale which is short with respect to the "relaxation time", \( \tau \), the time taken for \( P \) or \( V \) to decay to 1/e of its initial value.

In viscous liquid and glassy systems single relaxation time behavior is rarely found, and it is in the departures from single relaxation time behavior that much of the interest in relaxation spectroscopy in viscous liquids and glasses resides. The departures which are observed and the manner in which they are interpreted will be discussed further below. Phenomenologically, nonexponential decay functions can be described with complete generality by writing

\[
\phi(t) = \int_0^\infty g(\tau)e^{-t/\tau}d\tau
\]

(2)

*It is common to represent the decay of an initial system stress or strain, or any other system property whose value may be correlated in time with its initial value, in a normalized form, e.g., \( (V = V_2)/(V_1 - V_2) \), such that the ordinate value is unity at \( t = 0 \).
where \( \phi(t) \) is the normalized response and \( g(\tau) \) is a probability density or distribution function for relaxation times. Empirically it is found that the experimental function can often be well reproduced by the simple nonexponential function \( \phi(t) = e^{-t/\tau} \beta \), where \( \beta \) usually turns out to be 0.5 or a value close to it.

The system constant, \( \tau \), (or an average \( \tau \) in the general case) in most cases increases with decreasing temperature in an exponential or greater-than-exponential manner and, at temperatures which are high with respect to the glass temperature, only dissipative responses are observed unless very specialized short time observation techniques are applied. Although these are available in some cases (e.g. time domain reflectometry for electric field responses), it is more common to study fast-responding (short relaxation time) processes using cyclic stresses.

An exact equivalence exists between experiments in which the decay of strain response to a constant imposed stress is followed as a function of time, and those in which the continuous dissipation of energy by a system acted on by a sinusoidally time-varying stress of the same type is measured [1-3]. The relationship is found by one-sided Fourier transformation of the time derivative \( \dot{\phi}(t) \) of the decay or time correlation function of Eq. (1) into the frequency domain [4] to obtain the permittivity of the system \( \varepsilon^* \). \( \varepsilon^* \) is necessarily a complex quantity

\[
\varepsilon^* = \varepsilon' - i\varepsilon''
\]

Thus,

\[
\varepsilon^*(\omega) = \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty) \int_0^\infty \phi(t) \exp(-i \omega t) dt
\]

(3)

\[
\varepsilon'(\omega) = (\varepsilon_0 - \varepsilon_\infty) \int_0^\infty \phi(t) \cos \omega t dt
\]

(4)

\[
\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \int_0^\infty \phi(t) \sin \omega t dt
\]

(5)

where \( \phi(t) \) is the normalized response function given for the single relaxation time case by Eq. (1), \( \varepsilon_\infty \) is the limiting high frequency "elastic" dielectric constant, and \( \varepsilon_0 \) is the static dielectric constant. \( \varepsilon'' \) measures the out-of-phase or dissipative response to the fluctuating stress and is termed the "loss" (whether dielectric or mechanical in nature). The energy dissipated per unit of time per unit of volume of sample from an applied field \( E_0 \sin \omega t \) is given by [2,4]

\[
W(J s^{-1} cm^{-3}) = E_0^2 \varepsilon'' \omega
\]

(6)

In fact it is possible to study the time-dependent properties of a relaxing dielectric by making the dielectric cell one arm of a differential thermal analysis couple and monitoring the temperature rise in the sample (\( \Delta T = E/C_p \)) as a function of the frequency of an applied field. Some results for glycerol and the supercooled plastic crystal cyclohexanol have been described by Matsuo et al. [4].

The loss \( \varepsilon'' \) is related to the absorbance \( \alpha \), with which we have been dealing in earlier chapters, by the relation [5]

\[
\alpha(\omega) = \frac{\omega \varepsilon''(\omega)}{cn(\omega)}
\]

(7)

where \( c \) is the velocity of light and \( n(\omega) \) the (frequency-dependent) refractive index. The dispersion in \( n \) is very small in most liquids, hence the energy dissipation rate is directly related to the absorption coefficient. We can observe that \( \alpha \) gives a measure of the characteristic energy dissipation per unit length (cm) while \( \varepsilon'' \) measures the energy dissipation per unit wavelength or cycle [2,6].

\( \varepsilon'' \) is also related to the conductivity \( \sigma \) of the medium which would be measured by a conventional admittance bridge, according to

\[
\varepsilon''(\omega) = \sigma(\omega)/\varepsilon_0 \omega
\]

(8)

where \( \varepsilon_0 \) is the permittivity of free space (8.854 x 10^{-12} F/cm). In a pure polar liquid \( \varepsilon'' \) will vanish as \( \omega \to 0 \). If an ionic impurity which provides a source of d.c. conductance is present, then the contribution \( \varepsilon(\omega) = \sigma/\varepsilon_0 \) of this conductance to the measured
loss must be subtracted out before the spectroscopic characteristics of the dielectric relaxation can be correctly assessed. From Eqs. (8) and (9) it is seen that the a.c. conductance and the absorption coefficient are directly proportional to one another,

\[ a(\omega) = \sigma(\omega)/cn(\omega) \epsilon_0 \]  \hspace{1cm} (9)

In this sense a standard a.c. conductance bridge can be viewed as an ultra-low frequency, ultrasensitive spectrometer, which can measure absorption coefficients, on the order of \( 10^{-10} \) Nernst cm\(^{-1}\) (see Fig. 3 below).

\( \epsilon' \) and \( \epsilon'' \) are not independent quantities. They are connected by the Kramers-Kronig relationship referred to in earlier chapters, and one may be determined from the other if data over a sufficiently wide range of frequencies are available. Although such conversions provide very important ways of determining absorption parameters in difficult areas of spectroscopy (Chap. 5 and Chap. 7), they are rarely utilized in relaxation spectroscopy since it is usually a simple matter to measure both.

When the decay function is a simple exponential as in Eq. (1), Eq. (2) yields

\[ \epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega \tau} \]  \hspace{1cm} (10)

Separating the real and imaginary parts yields

\[ \epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2} \]  \hspace{1cm} (11)

and

\[ \epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega \tau}{1 + \omega^2 \tau^2} \]  \hspace{1cm} (12)

\( \epsilon' \) is usually referred to simply as the dielectric constant.

The equation for the loss, Eq. (12), is a simple Lorentzian with \( \epsilon'' \max = \frac{\epsilon_0 - \epsilon_\infty}{2} \) at \( \omega = 1/\tau \), as illustrated in Fig. 1c. In the usual case, where the decay function is not a simple exponential,
The quantity $\Delta\kappa$, which depends on the ability of the liquid structure to change in response to a change of external conditions, has been discussed before in Chap. 1 where relations amongst thermodynamic quantities measured above and below the glass temperature were considered. For thermodynamic purposes the separation of $\kappa$ (measured) into $\Delta\kappa$ and $\kappa_0$ terms can be achieved by freezing out the $\Delta\kappa$ term altogether by sufficient change of temperature. Equations (15)-(17) show that it is quite practical to determine $\Delta\kappa$ at temperatures well above the glass temperature by means of cyclic stress techniques using ultrasonic pressure waves, and much work done in the past on viscous liquids and glasses used these techniques [6]. Recently such measurements have been increasingly abandoned in favor of the less time-consuming light-scattering measurements which yield equivalent information [7].

11.2 EXPERIMENTAL FINDINGS

Because of their natural connection to the resonance absorption studies of earlier chapters, we consider the dielectric relaxation findings before those for mechanical relaxation.

Experimental data for relaxing liquids are presented most usefully in the form of plots of $\varepsilon''$ vs. f at various temperatures approaching $T_g$. It has, however, been very common to report the loss $\varepsilon''$ or the loss tangent $\varepsilon''/\varepsilon'$ as a function of temperature at various fixed frequencies. Typical are the early data of Morgan [8] for the much-studied glass-forming polar liquid, glycerol (propanetriol $\text{C}_3\text{H}_5\text{(OH)}_3$), shown in Fig. 2. The glass transition temperature for glycerol determined at $10^6$ min$^{-1}$ heating rates is $-89^\circ\text{C}$. The corresponding isothermal loss curves, which are consistent with more recent studies by Davidson and Cole [9] at low temperatures and by McDuffie and Litovitz [10] at high temperatures, are shown in Fig. 3a. The frequency of maximum loss is seen to move rapidly to high frequencies with increasing temperature, although at 40$^\circ\text{C}$ the dielectric loss maximum has still not reached the frequencies characteristic of FIR resonance absorption, 10-200 cm$^{-1}$ ($3 \times 10^{11}$ - $6 \times 10^{12}$ Hz). At temperatures above $\sim$100$^\circ\text{C}$ (or $\sim$2T$_g$) it would no longer be possible

![Fig. 2. Dependence of the real and imaginary parts of the permittivity on temperature at various frequencies (in Hz) for glycerol. (From Morgan [8]. Reproduced with permission of Am. Electrochem. Soc.)](image)

to distinguish clearly the energy dissipation due to resonance absorption from that due to relaxation.

Data in the frequency region $10^9$ - $10^{11}$ Hz are inaccessible to bridge techniques but have been obtained, with much difficulty, using microwave methods. A simpler and more rapid measuring technique, time domain reflectometry (TDR), has recently been developed by Felner-Feldegg [11] and others [12], and the present data gap for liquid dielectric processes between the upper bridge limit and the FIR region should soon be closed. Our present interest, however, is more in the low temperature region near and below the glass transition. It should be pointed out before leaving discussion of the high temperature region that because of the relationship between $\varepsilon''$ and $\omega$ embodied in Eq. (8), the impressive $\varepsilon''$ maxima of Fig. 3a become completely insignificant shoulders on an exponentially increasing background when plotted on the normal linear absorbance scale. The background is made up of contributions from widely distributed
11.2 LINEAR RESPONSE REGIME

Fig. 3. (a) Dielectric loss as a function of frequency at various temperatures for glycerol. (b) Data of Fig. 3a converted to absorptivity units using Eq. (7) with $n = 1.6$, and combined with far IR data to show relation of dielectric losses to resonance absorption at the high frequency limit for collective intermolecular motions. The broadening of the far IR-IR libration-vibration band with increasing temperature while qualitatively correct is not drawn to scale.

*The large positive slope for this plot is due to the existence of high frequency processes whose nature is imperfectly understood but which cause almost constant loss in the frequency region between the primary relaxation range and the FIR absorption region. The reversal of the temperature dependence of $\alpha$ in the far IR region is due both to a smearing of the liquid structure with increasing temperature, and to a decrease with increasing temperature in ground state phonon population. (This is seen particularly clearly in the temperature dependence of low frequency Raman intensities: data for glycerol have been reported by C. H. Wang and R. B. Wright, J. Chem. Phys. 55, 3300 (1971) and are consistent with the harmonic oscillator theory for the region 5-100 cm$^{-1}$.)
intermediate situation exists, which can be illustrated and elucidated by the findings of Williams and co-workers [16] on solutions in o-terphenyl of various dipolar molecules. These workers chose as solutes dipolar molecular species very different in structure from o-terphenyl and which, in their pure states, have glass temperatures both above and below that of o-terphenyl. The frequencies of maximum loss in each case moved with composition in the direction expected from the change in viscosity or glass temperature and extrapolated at infinite dilution in every case to the value found for the (very weak) loss peak for o-terphenyl itself. This shows that the dipole reorientation process in liquids approaching their glass transition temperatures is a highly cooperative one depending more on solvent rearrangement kinetics than on the independent motion of the individual dipolar solute molecules. Consistent with this observation, the "activation energy" of the frequency of maximum loss is the same for all dilute solutions and coincides with that for viscosity of o-terphenyl. Similar observations, though with some important provisos, will be made subsequently for relaxation processes in ionic liquids near their glass transitions.

The other impressive feature of Williams' findings is the similarity of the relaxation spectra for the different solutions. Almost without regard to the dipolar molecule shape, the solutions exhibit the same spectral form, viz., a form broader than for a single relaxation time, and skewed to the high frequency side. For instance, Fig. 4a shows data for several temperatures for two anthrone solutions of different concentration, the individual temperature curves being first collapsed onto master curves by plotting \( \varepsilon'' \) vs. \( f/f_{\text{max}} \), where \( f_{\text{max}} \) is the frequency of maximum loss. Clearly the frequency-dependence of the loss in these systems conforms to some rather general principle. Williams and Hains [16a] showed, in fact, that a master curve for all the anthrone solutions could be closely reproduced by assuming that the normalized response function \( \gamma(t) \) has the "fractional exponential" form [16f]

\[
\gamma(t) = \exp \left[ (-t/\tau_0)^\beta\right] \quad 0 < \beta \leq 1
\]

(18)

FIG. 4. (a) Master dielectric loss curves for solutions of anthrone in o-terphenyl at two concentrations, 4.2 and 8.5 mol\%, demonstrating the constancy of spectral form in the interval 250-270K despite ~200-fold increases in \( f_{\text{max}} \). (b) Superposition of master curves of Fig. 4a, and comparison with Williams-Watts function for \( \beta = 0.55 \). Also shown is the loss curve for an exponential decay process. (From Williams and Hains [16a]. Reproduced with permission of the Chem. Soc.)

with \( \beta = 0.55 \). The fit is shown in Fig. 4b, where the spectrum is compared with that for a single relaxation time process, \( \beta = 1.0 \).

It will be seen below that decay functions of the form of Eq. (18) are generally very successful in describing relaxation processes of mechanical as well as electrical origin in supercooled...
Equation (18) transforms tend to underestimate the loss at high frequencies in the cases quoted, and this discrepancy is quite important in other liquids, e.g. the binary solutions in decalin solvent studied by Johari and Smyth (15) which yielded very broad spectra. Another widely used loss function which gives more weight to the high frequency end of the spectrum is that due to Davidson and Cole [9].

\[
e^* = \varepsilon' + i\varepsilon'' = \varepsilon_m + \frac{(\varepsilon_0 - \varepsilon_m)}{(1 + i\omega_0\gamma)} , \quad 0 < \gamma \leq 1
\]  

(19a)

from which

\[
\varepsilon' = (\varepsilon_0 - \varepsilon_m)(\cos \phi)^\gamma \cos \gamma \phi
\]  

(19b)

\[
\varepsilon'' = (\varepsilon_0 - \varepsilon_m)(\cos \phi)^\gamma \sin \gamma \phi
\]  

(19c)

Like Eq. (18) this function reduces to that for a single relaxation time when the width parameter \( \gamma \) is unity. Equation (19) implies a distribution of relaxation times, \( g(\tau) \), which rises sharply to a cutoff value at \( \tau_0 \). It has been used by numerous authors to describe the typically skewed distributions encountered in practice and its usefulness will be further illustrated in Sec. 11.3.

Even Eq. (19) fails to account for the highest frequency end of the loss spectra in many cases, particularly at low temperatures [15], suggesting that a distinct set of high frequency cooperative motions remains to be accounted for. In isolated cases, e.g. a toluene-pyridine solution [25], distinct subsidiary loss peaks with maxima located some four decades of frequency above the main loss maximum have been identified in the liquid. Subsidiary relaxations in fact emerge clearly in almost all substances studied, when temperatures below \( T_g \) are investigated. These secondary or \( \beta \)-relaxations are considered in more detail in a following section.

For glycerol at -71°C (\( T_g = -89°C \)) the parameter \( \gamma \) of Eq. (19) is 0.56 [9]. At high temperatures, after a plateau at 0.61, it increases to 0.71 [7]. The effect of pressure on \( \gamma \) for glycerol,
RELAXATION SPECTROSCOPY

determined recently to 56 kbar by Johari and Whalley [18], is to
decrease its value linearly, i.e. to broaden the spectra. At 14 kbar
γ has fallen to 0.43 (values at higher pressures were not quoted and
there was evidence that subsidiary higher frequency relaxation pro-
cesses were determining the high frequency band shape). Pressure
also affects the frequency of maximum loss in a manner directly re-
tated to that of decreasing temperature (see below).

Information on the microscopic aspects of the relaxation pro-
cess is probably (though not necessarily) contained in the param-
eters β and γ of Eqs. (18)-(19). This is suggested by data on the
relaxation of large ion dipoles in o-terphenyl by Davis et al. [16d]
and by the results of equivalent experiments on electrical relaxa-
tion and optical probe relaxation studies referred to below (Secs.
11.2(B) and 11.3(C)). These authors observed that, in o-terphenyl
solutions containing the massive ion-pairs tri-n-butylammonium pic-
rate and tri-n-butylammonium iodide in o-terphenyl, instead of the
like-size or smaller molecule solutes of earlier studies, the die-
лектric relaxation times are ~50 times larger than for the smaller
solutes, and the spectra are narrow, approaching the 1.14 decade
half-width for a single relaxation time. This and the parallel
examples quoted later for other types of relaxation can be under-
stood if it is recognized that during the particular relaxation be-
ing monitored, the solute molecules have themselves undergone so
many rearrangements that all local environmental effects on the probe
relaxation have been averaged out. This would leave a Brownian pro-
cess which is intrinsically exponential [1].

Interestingly enough all three cases, the Cole-Davidson, the
Williams-Watts, and the single exponential functions, can be inter-
preted using a model in which the relaxation of the dipole depends
on diffusion to the dipole site of a suitable defect or defects.
The initial model due to Glarum [19] was based on relaxation of the
dipole by the first-arriving defect and led to the Cole-Davidson
function. A development of the model by Phillips, Barlow, and Lamb
[20] to include the effects of the second-nearest neighbor defects
leads to the Williams-Watts function with β = 0.51. When the dipole

11.2 LINEAR RESPONSE REGIME

only relaxes under the combined influence of a great many defects,
exponential functions must be obtained. If these models were com-
pletely adequate, the amount of structural insight issuing from re-
lexation spectroscopy would be restricted to that derived from the
temperature dependence of the processes. However, the existence
of temperature- and pressure-dependent β and γ parameters, and the
emergence, at sufficiently low temperatures, of well-defined sec-
dondary loss spectra, suggests that much of structural interest remains
to be interpreted.

Behavior rather similar to the above is found for a variety of
supercooled plastic crystals which exhibit a glass-like transition
in which a state of orientational disorder is kinetically frozen in
the presence of positional order. Dielectric and NMR relaxation
studies which have been carried out on these phases [21-23] show
solvent-controlled solute relaxations [21] as in Williams' liquid
solution studies, and essentially single relaxation time spectra
with Arrhenius temperature-dependences in the case of alcohols
Equation (20) type behavior has not yet been clearly identified in
the plastic crystals. There is very little additional entropy pro-
duced by the positional disordering of these crystal phases on melt-
ing and on the basis of entropy theories of the viscous liquid phase
(Chap. 1) one might expect to find little distinction between the
viscous liquid and plastic crystal phenomenologies.

Less detailed information is available on the characteristics
of the mechanical equivalent of ε". Until recently the complex com-
pressibility κ" = κ' + iε" could only be determined at short times
by ultrasonic methods [6] which are rather limited (~2 decades) in
frequency range. These measurements are also complicated by the
fact that both shear and compressional relaxation processes contrib-
ute to the observed longitudinal sound wave energy absorption. The
development of light scattering techniques [7] which, through the
frequency and line shape of the Brillouin peaks in the spectrum,
allow the characteristics of propagating shear and compressional
waves to be studied to much higher frequencies, has greatly increased
the potential of mechanical relaxation studies. Photon correlation techniques developed very recently extend the range of frequencies investigable by light scattering methods to very low frequencies. These techniques are discussed in a separate section. For long time measurements pressure step techniques may be employed though the problem of nonlinear responses will then have to be dealt with (Sec. 11.3) unless the pressure step can be kept rather small.

We will limit ourselves here to a few observations on the relation between mechanical (compressional) and dielectric loss spectra for selected molecular liquids based mainly on early work by Litovitz and co-workers for molecular liquids [24], and a brief discussion of the characteristics of some representative inorganic glass-forming systems.

For glycerol, in which the constituent molecules are interconnected by many "net" (25% H₂O) range of ultrasonic spectrum, Fig. 5b suggests that the most probable relaxation times are evidently very similar. If the loss behavior of glycerol conformed to the Cole-Davidson dispersion equations, Eqs. (19a-19c), and if the width parameter γ were constant with changing temperature, the γ for each process could be obtained from a plot of k''/Δk vs. k'/Δk (the Cole-Cole plot [2]) for which the graphical forms for

![Image](image-url)

Fig. 5. (a) Temperature dependences of high and low frequency limiting compressibilities, κ₀ and κ_∞, for glycerol and the dispersion of κ' at 31 MHz. (b) Temperature dependence of the configurational contribution κ_0 - κ_∞ to the total compressibility of glycerol between 20 and -30°C and a comparison of the reduced dielectric loss e''/Δε with k''/Δk. (Data from Ref. 24.b.)

different γ parameters are known. Unfortunately, unlike the case of the o-terphenyl solutions discussed earlier, the γ parameter of the relaxation is not temperature-independent for glycerol [9,10]. The failure of the Cole-Cole plot for the acoustic data to match any single theoretical curve [24b] suggests the same is probably true for the compressional behavior. γ values of 0.5-0.7, perhaps higher at high temperatures, are indicated for the compressional process.

For n-propanol, which exhibits a simple single relaxation time dielectric loss spectrum [9] a very broad mechanical loss spectrum is found [24c]. A superposition of the low frequency elements of the isothermal loss spectra for this liquid could be achieved by proper choice of an f_max value for each temperature. However, the
the potential of mechanical relaxation studies. Photon correlation techniques developed very recently extend the range of frequencies investigable by light scattering methods to very low frequencies. These techniques are discussed in a separate section. For long time measurements pressure step techniques may be employed though the problem of nonlinear responses will then have to be dealt with (Sec. 11.3) unless the pressure step can be kept rather small.

We will limit ourselves here to a few observations on the relation between mechanical (compressional) and dielectric loss spectra for selected molecular liquids based mainly on early work by Litovitz and co-workers for molecular liquids [24], and a brief discussion of the characteristics of some representative inorganic glass-forming systems.

For glycerol, in which the constituent molecules are interconnected by many hydrogen bonds, there is apparently much similarity between the two relaxation processes. Some comparative data for "wet" (5% H₂O) glycerol [24b] are shown in Fig. 5. A sufficient range of ultrasonic data is not available to make a useful isothermal comparison, but the reduced loss vs. temperature plots of Fig. 5(b) suggest that the mechanical process has a somewhat narrower spectrum than the dielectric process. This is supported by limited loss vs. frequency data at -28°C. The most probable relaxation times are evidently very similar. If the loss behavior of glycerol conformed to the Cole-Davidson dispersion equations, Eqs. (19a-19c), and if the width parameter γ were constant with changing temperature, the γ for each process could be obtained from a plot of κ''/Δκ vs. κ'/Δκ (the Cole-Cole plot [2]) for which the graphical forms for

*The configurational part Δκ of the liquid compressibility used in the above κ' and κ'' reductions is a quantity of much interest in connection with thermodynamic aspects of the glass transition [Chap. 1]. The fact that Δκ is almost independent of temperature for glycerol (Fig. 5b) but rapidly decreasing with decreasing temperature for other molecular liquids (e.g. acrochlor [24a]) while increasing for the inorganic nitrate glasses discussed below demonstrates that a great deal of variety exists for this thermodynamic property among liquids of different constitution. (As for ΔCp, see Chap. 1, Fig. 5.)

**Fig. 5.** (a) Temperature dependences of high and low frequency limiting compressibilities, κ₀ and κₐ, for glycerol and the dispersion of κ' at 31 MHz. (b) Temperature dependence of the configurational contribution κ₀ - κₐ 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. 24b.)

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For n-propanol, which exhibits a simple single relaxation time dielectric loss spectrum [9] a very broad mechanical loss spectrum is found [24c]. A superposition of the low frequency elements of the isothermal loss spectra for this liquid could be achieved by proper choice of an f_max value for each temperature. However, the
high frequency ends of the master spectrum so formed did not super-
pose, the high frequency skew becoming greater at low temperatures.
The emergence of a secondary high frequency loss mechanism similar
to those observed in dielectric studies seems a probable explanation.

Very similar behavior has been observed in two simple molecular
liquids by Dexter and Matheson [25a] and in the polymeric materials
studies by Mason et al. [25b]. For these the loss becomes essen-
tially constant at high frequencies and a distinct secondary loss
band was found in a loss vs. temperature plot in the former case.
Mason et al. suggested that a hysteresis phenomenon causing a con-
stant loss per cycle is present in these systems, though Dexter and
Matheson think nonlinear elasticity effects are important. The
great variety of behavior exhibited by polymeric materials under
compressional stresses has been discussed in review by Marvin and
McKinney [26]. They describe some cases in which the reduced loss
spectrum (at 5-1000 Hz) is so broad at high frequencies that a half-
width can only be defined for frequencies below \( f_{\text{max}} \). In poly(vinyl
acetate) on the other hand the halfwidth is only of the order of two
decades and high frequency losses are absent within experimental
scatter. Generally, \( f_{\text{max}} \) for compression and shear stresses in both
polymeric [26] and molecular liquids [24a] are the same though there
are cases (e.g. the methacrylates) in which \( f_{\text{max}} \) for compression is
lower than for shear. Loss spectra shapes for both polymeric [26]
and molecular liquids [24a] are also different, the shear losses be-
ing more broadly distributed. For polymers this is interpreted [26]
as a consequence of the longer range molecular motions which occur
under shear (systems are nonpolarizing to shear stresses), and the
extra molecular entanglement couplings which then come into play.

According to Litovitz [24a] the loss spectra for compressional
and shear relaxation have different shapes although the average re-

taxation times are usually the same. It would seem from our intro-
ductory discussion that dielectric loss spectra are most appropri-
ately correlated with compressional rather than shear relaxation
spectra. It should be noted, nevertheless, that Williams et al. [27]
have recently compared dielectric loss and shear compliance

spectra for some nonhydrogen bonded molecular liquids and have
shown that they are very similar (though high frequency losses are
more pronounced for the shear process). On the other hand, major
differences between shear and compressional (bulk) modulus spectra,
including the presence of secondary maxima in the latter, have been
implied for some molecular liquids in Ref. 25a. Some clarification
of these relationships would seem desirable.

A simple ionic glass \( 60\text{KNO}_3 \cdot 40\text{Ca(NO}_3\text{)}_2 \) has been studied by
Macedo et al. [28] who, according to common practice, reported their
results as components of the complex longitudinal modulus \( M^* \), rather
than complex compliance or compressibility \( K^* = 1/M^* \). \( M^* \) is a com-
posite of the complex compressional and shear moduli \( M^* = K^* +
(4/3)G^* \) [6]. Although the temperature range studied was only 24°C
(between 102° and 126°, \( T_G = 70°C \)) they were able to observe very
pronounced changes in the spectra, a rapid broadening occurring as
the temperature decreased. Interestingly enough, this simple glass
(only argon core cations and a small planar anion) also proves to
have an unusually broad spectrum for the enthalpy relaxation deter-
mined near \( T_G \) by differential scanning calorimetry studies (see
Sec. 11.3(A)). An explanation of the unusual breadth (more similar
to polymers than to oxide glasses or molecular liquids) is not ob-
vious at this time. A temperature-dependent spectral width of the
opposite sense is found for the conductivity relaxation (next sec-
tion).

For pure B\(_2\)O\(_3\), one of the most thoroughly studied oxide glasses,
the dispersion in the longitudinal modulus fits a single relaxation
time curve within experimental error over the 200° temperature range
800-1000°C [29]. At lower temperatures it becomes necessary to in-
troduce a broadening distribution of relaxation times, and it was
shown that the assumption of a Gaussian distribution of times with
temperature-dependent width could provide a good account of the loss
spectra. Recent studies [30] on B\(_2\)O\(_3\) using light-scattering digital
correlation techniques in a later section have indicated that this broadening continues down to \( \sim \)300° but then ceases. Using an Eq. (18) form to describe the experimental correlation functions,
these authors report $\beta$ parameters of 0.8 at 470°C falling to 0.6 at 300°C.

For GeO$_2$ and ZnCl$_2$ [31,32] the losses can also be described by a single time over almost the whole accessible liquid range; some broadening appears at the lowest temperatures accessible to the technique and, according to volume relaxation studies near $T_g$, continues to increase down to $T_g$. In glasses subject to phase separation a temperature-dependent spectral width can be associated with the growth of composition fluctuations. Such fluctuations can, therefore, be investigated using relaxation spectroscopy, but it is recommended [33] to study only the shear wave absorption because of its relative simplicity (no compressional component, no interaction with volume or energy-sensitive equilibria). A theory for spectral broadening has been given by Macedo et al. [33].

(b) Temperature Dependence of the Characteristic Relaxation Frequency. The further manner in which relaxation spectra reflect the influence of glass or liquid structure is through the temperature dependence of their characteristic frequencies. The more compact or rigid the structure the lower this frequency is expected to be for a given temperature. In practice, separate and distinguishable dependences of relaxation frequencies on the structure alone and on temperature alone may be demonstrated.

Again choosing glycerol as an example, we show, in Fig. 6, how the characteristic relaxation frequency $f_{\text{max}}$ of Fig. 3a (or the characteristic relaxation time $\tau_{\text{o}}$ of the Davidson-Cole analysis or the average relaxation time $\tau_{\text{o}} \propto (2\pi f_{\text{max}})^{-1}$) varies with temperature. As Davidson and Cole pointed out, the temperature dependence in this case is greater than exponential, conforming well to the VTF (or Fulcher) equation

$$f_{\text{max}} = A \exp \left[ -B/(T - T_o) \right]$$

(20)

the relation of which to the thermodynamic state of the liquid was discussed in Chap. 1 and will not be further dealt with here. Equation (20) holds for most liquids in the relaxation time region $10^{-9}$ to $10^{-9}$ sec. but only in a few cases (some polyalcohols and inorganic glasses) when $\tau = 10^3 - 10^6$ sec., i.e. close to or below the ordinary DTA-determined $T_g$. In the latter region, Arrhenius behavior with a very large activation energy, 100-300 kJ mol$^{-1}$ is usually encountered. All the spectra of Fig. 4, for instance, are characterized by $f_{\text{max}}$ activation energies of 260-275 kJ mol$^{-1}$ [16], although it is known that at higher temperatures the transport properties of o-terphenyl follow Eq. (20). Some data for the lowest concentration anthrone solution of Fig. 4 are included in Fig. 6.

It should be emphasized here, however, that while the characteristic frequency for relaxation exhibits this very pronounced
temperature dependence, the characteristic frequency for resonance absorption in the FIR remains essentially constant. The increasing separation of these characteristic frequencies with decreasing temperature reflects the progressive uncoupling of the modes of motion responsible for them.

A further uncoupling of the characteristic modes of motion occurs at temperatures near and below $T_g^*$, giving rise to the so-called "secondary" or "β" relaxations to which scattered references have been made above.

(c) Secondary Relaxations. Secondary relaxations which occur at temperatures well below the glass transition are very familiar in polymer science, just as the existence of frequency-dependent dielectric and mechanical losses in the glassy state is well recognized in oxide glass science. In each of these cases a natural explanation for the phenomena - side-group as distinct from main chain motion in the first, and relatively free alkali cation motion in the second - seemed at hand. What has created new interest in sub-glass temperature relaxations is the demonstration [34] that they also occur, and almost universally so, in simple molecular and nonnetwork ionic liquids without free or flexible sub-units. This finding, predicted by Goldstein [35], implies that such subsidiary relaxations may be a fundamental feature of the dynamics of random close-packed systems, or at least of their somewhat less regular molecular counterparts. In the majority of cases the β-processes are most clearly identified by Fig. 2-type loss $e''$ (or loss tangent $e''/e'$) vs. temperature plots in which $T$ passes through $T_g^*$. Examples are shown in Fig. 7a for dielectric loss in some decalin + chlorobenzene solutions and in Ref. 25a for mechanical loss in sec-butylbenzene. The reason such plots are preferred is that secondary relaxations are usually weaker by about an order of magnitude than the main α-relaxations. They are also decades broader in frequency and, since in constant temperature plots of loss vs. frequency they would fall on the high frequency side of the α-relaxation loss maximum, it is difficult to discern them even for $T < T_g^*$. For $T > T_g^*$ the problem is compounded since it appears from several sources [34,36,37] that spectral broadening culminating in the appearance of a distinct β-relaxation only occurs in the temperature region slightly above $T_g^*$, i.e. it appears that the motions responsible for the phenomenon do not persist as an identifiable sub-class far above $T_g^*$. Consistent with this idea is the fact that the resolution of the secondary peak becomes weaker with increasing scan frequency and all peak positions move to higher temperature (see Fig. 7a). In a few cases [23,24] such as 5-ethyl-3-heptanol (Fig. 7) for which $T_g^* = -114^\circ C$, the β-relaxation remains resolved for $T > T_g^*$ (see the -107.4° isotherm). At $T < T_g^*$ the strength of the relaxation increases with increasing cooling rate, i.e. with the glass fictive temperature [23,24], consistent with the idea that the phenomenon is connected with loosenesses in the structure.

The resolution below $T_g^*$ seems to be somewhat sharper for the equivalent phenomenon in supercooled plastic crystals [23].

The merging of α- and β-processes at $T > T_g^*$ is directly implied by the relatively small temperature dependence of the process, as pointed out by Johari and Goldstein. Figure 8 shows an Arrhenius plot for $f_{\text{max}}$ for several alcohols which indicates total merging (identical $f_{\text{max}}$) at about 1.2 $T_g^*$. The breadth of β-spectrum, however, implies extensive coupling of the α and β modes of motion at much lower temperatures. In isolated cases (e.g. isobutanol, propylene carbonate [34]) the separation of a distinct β-spectrum fails to occur at all.

Johari [23] has pointed out that in many instances the β-process has essentially the same temperature dependence as the α-process in the high temperature region, and in fact appears as a low temperature extension of it in an extended Arrhenius plot. This observation is combined in Fig. 9 with our earlier comments on the merging of the dielectric loss with the approximately temperature-independent librational and vibrational modes, to show the relationship in temperature of the characteristic frequencies for the three major electrically active modes of motion of the amorphous phase. There exist, as further documented below, mechanically active counterparts for all
FIG. 7. (a) Dielectric loss factor tan δ (log scale) as a function of temperature for binary mixtures of rigid molecules at temperatures above and below T_g, showing secondary relaxation losses at low temperatures. Note improving resolution with decreasing frequency (♦ 100 kHz, Ô 1 kHz, 0 0.1 kHz). Curves are identified as follows: 1--pure cis-decalin; 2--11.5 mol% chlorobenzene + 88.5 mol% cis-decalin; 3--16.5 mol% chlorobenzene + 83.5% cis-decalin. (b) Product of dielectric loss and cell capacitance for α- and β-relaxations in 5-methyl-3-heptanol vs. frequency at various temperatures showing resolution of secondary relaxation above T_g (T_g = -114°C). (Data from Johari and Goldstein [34]. Reproduced with permission of the Am. Inst. Phys.)

FIG. 8. Arrhenius plots of the frequency of maximum dielectric loss in the α- and β-relaxation regions for 0, 5-methyl-3-heptanol; ©, 4-methyl-3-heptanol; ●, 3-methyl-3-heptanol; □, n-butanol; △, iso-butanol; and ■, 3-methylpentane. (From Ref. 34.)

three. It should be pointed out that due to the rapidly increasing breadth of the β-spectrum with decreasing temperature (Fig. 8) this branch of Fig. 9 may essentially fade away at sufficiently low temperatures. A relationship to the low frequency modes responsible for the cryogenic range heat capacity anomalies in amorphous phases, which are currently receiving great attention [38,39], perhaps remains to be established. It is not known whether any perceptible changes in the far IR vibrational spectrum occur in the temperature region in which the β-relaxation separates out. Signal-to-noise ratios are so poor in this spectral region with presently available techniques that subtle changes in band shape are not easily detected.

The study of β-processes in polymers by dielectric, mechanical, and NMR spectroscopic methods has a rather extensive literature of which no review will be attempted here. We note, however, that there is usually good agreement among the different measurements on the frequency domains of secondary losses. An excellent coverage of this
subject area is contained in Ref. 40. Some discussion of mechanical losses in inorganic glasses is given in a following section.

(B) Nonpolarizing Systems: Electrical and Mechanical Relaxations

(1) PRINCIPLES

In ionic liquids, and in glasses containing mobile ions, a step voltage will be completely relaxed by a flow of charge across the sample, and steady voltage $V$ will cause a steady dissipation of energy $W = Vi J s^{-1} \text{ cm}^{-3}$ where $i$ is the current density in amperes per cm$^2$. This is similar to the response of any liquid to a shear stress. An instantaneous shear is relaxed completely by a small irreversible flow, while a steady shear stress causes a continual dissipation of mechanical energy via a steady flow of material. Because of the phenomenological similarity of the conductance and flow processes it seems logical to analyze the time dependence of the processes using the same formalism. Until recently, unfortunately, this had not been done. The results of shear relaxation studies in the frequency domain (by ultrasonic shear wave velocity and absorption measurements) have usually been analyzed in terms of a complex shear modulus

$$G^* = G' + iG''$$

rather than of a shear compliance. The results of a.c. electrical measurements on the other hand have mostly been analyzed by treating the conductor as a dielectric fluid with a large d.c. conductivity, i.e. by analyzing the losses in terms of an electrical modulus

$$M^* = \varepsilon' - i\varepsilon''$$

in which a large part, $\varepsilon''$, of the measured loss arises from the d.c. conductivity, and $\varepsilon'$ subtracted out before any curve fitting or parameterization is attempted. If there were in fact a large source of dielectric loss which was not dependent on the same mechanism as the d.c. electrical conductance, this procedure could be