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Characterization of mechanical relaxation processes

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The experimental observation of power-law behaviour in the spectral response of dielectric relaxation has been extended to other relaxation processes, particularly mechanical loss. Examples of the power-law behaviour are given and summarized diagrammatically. It is shown that there is an essential difference between the magnitudes of the power-law exponents for mechanical and dielectric relaxation. A relationship between the two is proposed and shown to be experimentally valid.

1. Introduction

The presence of power-law behaviour in the frequency response of the dielectric susceptibility of solids as a universal phenomenon was first proposed by Jonscher [1] and has since found to be the case [2, 3]. In general the susceptibility can be expressed in the form

$$\chi(\omega) = \chi(0)F(m, n, \omega/\omega_p), \tag{1}$$

where $\chi(0)$ is the susceptibility increment of the relaxation process being observed and $F(,,)$ is a spectral shape function in which the frequency, ω, is normalized to the frequency of maximum loss, ω_p. The shape parameters m and n are related to the indices of the power-law behaviour at low and high frequencies, with respect to ω_p. The detailed form of $F(,,)$ depends on the model of relaxation being considered, for example the spectral shape function derived by Dissado and Hill [4, 5] can be written as

$$F(m, n, x) = (1 + ix)^{-(1-n)} \times {}_2F_1\left(1-n, 1-m; 2-n; \frac{1}{1+ix}\right) \tag{2}$$

where x is the normalized frequency, ω/ω_p, and ${}_2F_1(,;;)$ is the gaussian hypergeometric function [6].

Equation 1 is the basis of the data normalization technique developed by Jonscher [1] and by Hill [2], and also of the reduced variable technique developed by Ferry [7] for use with mechanical loss data. It has been shown [8] that Equation 2 gives a generalization of the empirical distribution function responses used to characterize susceptibility behaviour and includes these as special cases. The power laws in the frequency response are obtained in the limits of x being greater and less than unity as

$$x > 1 \quad \chi'(\omega) \propto \chi''(\omega) \propto \omega^{-(1-n)} \tag{3a}$$

$$x < 1 \quad \chi(0) - \chi'(\omega) \propto \chi''(\omega) \propto \omega^m, \tag{3b}$$

where $\chi'(\omega)$ and $\chi''(\omega)$ are the real and imaginary parts of the susceptibility, respectively, and n and m are fractional. Equation 3a is of the form originally proposed by Jonscher [1] who determined the constant of proportionality as

$$\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2) \tag{4}$$

and pointed out that this implies a constant ratio of energy lost to energy stored in the medium over the frequency range in which Equation 4 applies.

The equivalence between dielectric relaxation and other relaxation processes such as mechanical relaxation and internal friction [9–11] and acoustic absorption suggests that Equations 1 to 4 might describe the spectral responses of these processes as well as that of dielectric relaxation. It is the intention here to examine this proposition in terms of the relevant spectral response functions and, where possible, to compare the responses obtained from different methods of investigation on the same materials.

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The amount of experimental information that is available in the published literature for the frequency characterization of mechanical loss and internal friction relaxation is much more limited than that for dielectric relaxation. This is a consequence of the difficulties encountered in carrying out mechanical measurements over a wide frequency range. Usually a particular technique of measurement can only be applied over a 10 to 1 or 100 to 1 range. Much more common is the alternative method in which measurements are made at a single frequency over a range of temperatures. In principle, exactly the same information is contained in the two sets of data but in the temperature case assumptions about the temperature dependencies of ω_p and $\chi(0)$ require to be made. Elsewhere it has been shown [12] that the general assumption of activated behaviour in relaxation processes, without confirmatory evidence, can be inapplicable. For this reason the temperature technique will not be greatly used here.

In the original derivation of the co-operative theory of relaxation which leads to Equation 2 the characteristic indices *m* and *n* were defined to be the fractional correlation indices for two different dipolar processes that occur in the dielectrically active material [4, 5]. The latter, *n*, was shown to be the correlation index for single dipolar flips whereas the former, *m*, was determined as the correlation index for synchronous exchange flip-flops. In the present context it is more useful to consider the identically equivalent descriptions in which *n* is the fraction of energy stored in the material by a flip process that can be recovered by the dipoles together with a similar description for *m* in which the storage and recovery is now due to synchronous flip-flop exchanges. These alternative descriptions lead directly to the equivalent definitions for other methods of energy storage.

2. The spectral response

The mechanical equivalence of the dielectric susceptibility is the compliance, which is the complex inverse of the mechanical modulus [7]. Fig. 1 presents four compliance plots, as functions of frequency, in double logarithmic scales. In these diagrams use has been made of the normalization technique [2] in which measurements taken over a range of an external variable, typically temperature, are fitted together without prior assumptions as to the spectral shape function or the temperature dependencies of either ω_p or $\chi(0)$. When a datum point marked on the original plot is carried through each fitting it gives a trace of the inverse shifts used in both frequency and magnitude of response. Such datum traces are given together with the master curves of the data in the figure. In two of the cases both the real and imaginary parts of the compliance were available and the normalization has been carried out in terms of both. In all cases the plots show the type of power-law behaviour characterized by Equation 3 and from the real and complex plots in Fig. 1a and b Equation 4 was verified.

The information presented in Fig. 1 has been chosen from the limited range available in the literature on the basis of two criteria. Firstly that the measured frequency range was of reasonable magnitude and secondly that a representative spectrum of types of materials should be presented. In each of the cases given in the figure the continuous curves through the master plots was calculated using Equation 2 together with the values of *m* and *n* determined from the power-law regions at low and high, relative, frequencies. The agreement between the theoretical spectral response function and the experimental data is good and indicates that the co-operative model is capable of being applied to relaxation processes generally.

A similar investigation of electrically active materials has been made [2, 3, 8] and the characteristic exponents *m* and $(1-n)$ of one hundred dielectric loss processes have been reported [3]. Since that time the survey has been extended to almost double that number without significant change in the general pattern of behaviour observed. The plot of the power-law exponents obtained earlier is again presented in Fig. 2a and can be compared with a similar plot of mechanical and internal friction and acoustic loss processes which is shown in Fig. 2b. In the latter diagram the acoustic indices are shown by the hexagonal markers. The key to Fig. 2b is given in Table I and the key to Fig. 2a in an earlier paper [3]. The unexpected feature of Fig. 2 is that whereas in the dielectric plot the majority of the markers lie above the diagonal $m = (1-n)$, shown dotted in Fig. 2b, in the mechanical case the converse is true. The observation that for mechanical data *m* is generally less than $(1-n)$ can also be seen in Fig. 1. Insufficient acoustic data is contained in the plot to make any significant comment about the relative magnitudes of the shape indices for

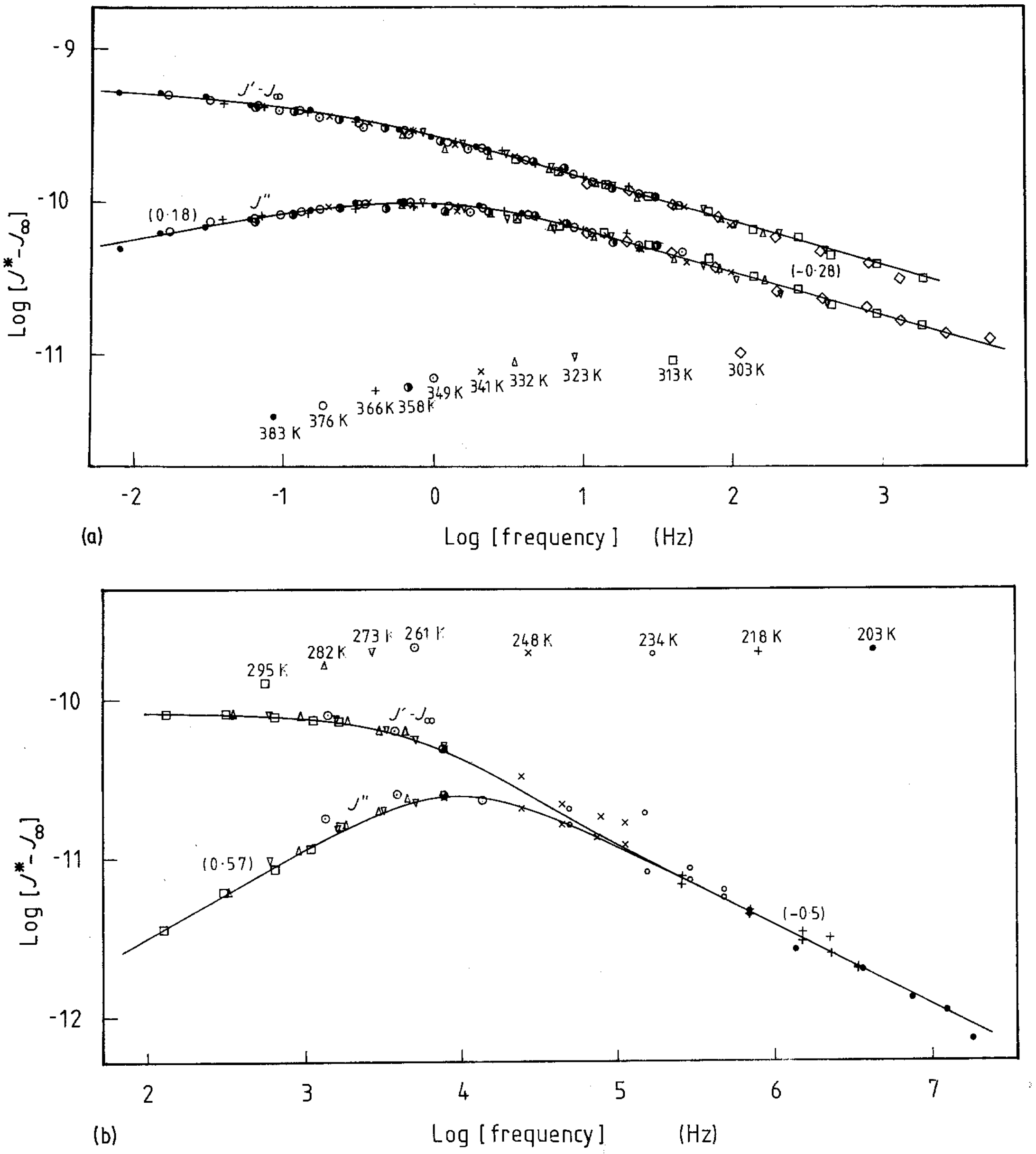
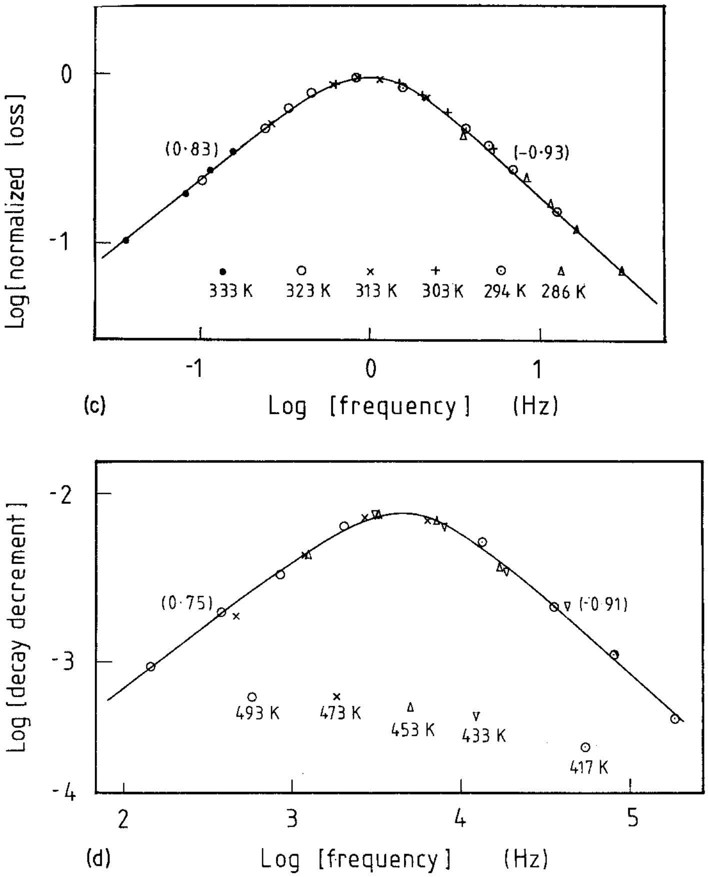


Figure 1 Normalized plots of (a) compliance of chlorocyclohexylacrylate from the measurements of Heijboer [14]. The plot is scaled at 383 K, $m = 0.18$ and $n = 0.72$; (b) the compliance of polyethylene from the measurements of Kyu *et al.* [21] sample (MD). The plot is scaled at 295 K, $m = 0.57$ and $n = 0.5$; (c) the mechanical loss from measurements of the internal friction in an iron–carbon alloy by Wert and Zener [23]. The plot is scaled at 313 K, $m = 0.83$ and $n = 0.07$. (d) the mechanical loss in doped silicon from measurements of the decay decrement by Berry [22]. The loss peak is due to the boron and lithium doping and its magnitude decreases with doping concentration. The plot is scaled at 453 K, $m = 0.75$ and $n = 0.09$. In all the diagrams the function given by the curves was calculated from Equation 2 using the values of m and n determined from the power-law indices and fitted to the peak loss point.

this technique but the evidence for power-law behaviour in the shape functions was clear.

From the limited set of data points contained in Fig. 2b some interesting points arise. All the poly-methacrylate samples have large values for $(1 - n)$ and the specific materials have low values of m. Similarly, the butadienes and the butadiene copolymer have large values of $(1 - n)$ and a wide range in the values of m, indeed it appears that the response of the copolymer is dominated by that of 1,2 polybutadiene. Samples 9 and 10 give the results of two sets of measurements made on the

Figure 1 continued



same sample of polyethylene. One set of measurements (MD) were made parallel to the direction in which the material was mechanically drawn and the other set normal to that direction (TD). The differences between the indices is small but measureable but what is more significant is that the frequencies of maximum loss at the same temperatures differed significantly, i.e.

$$\omega_p(\text{TD}, 110\,\text{K}) = 0.15\,\text{Hz};$$

$$\omega_p(\text{MD}, 110\,\text{K}) = 0.9\,\text{Hz},$$

which implies that the shape parameters measure a different property, or properties, to that giving the relaxation rate constant.

The closest to Debye behaviour [13], for which $m = 1$ and $n = 0$, observed here is for the sample of α brass measured by Berry. The earlier measurements on α brass give a similar high value for m but a very low value for $(1 - n)$. There is no obvious reason for this wide discrepancy but it does show that the indices measured are pertinent to that particular sample and should not be taken as totally representative of the material. In particular it should be noted that the response from the silicon sample was directly due to the high doping with boron and lithium for it was noted that the magnitude of the loss decreased on temperature cycling as lithium was lost. Similarly the measurements on the calcium fluoride are probably dominated by the sodium fluoride dopant.

3. Discussion

Fig. 2 suggests a possible interdependence between the spectral shape indices for mechanical and dielectric relaxation. If we consider a system comprising, say, electric dipoles embedded in a coherent structure in which the only means of storing energy are electrical, by re-alignment of the dipoles, and mechanical, by adjustment of the structure, then the total energy stored will be divided between these two contributions, that is

$$E_{\text{stored}} = E_{\text{mech.}} + E_{\text{diel.}}. \qquad (5)$$

Consider now a mechanical investigation. Mechanical distortion of the structure stores energy within the structure but the electrically active part of that

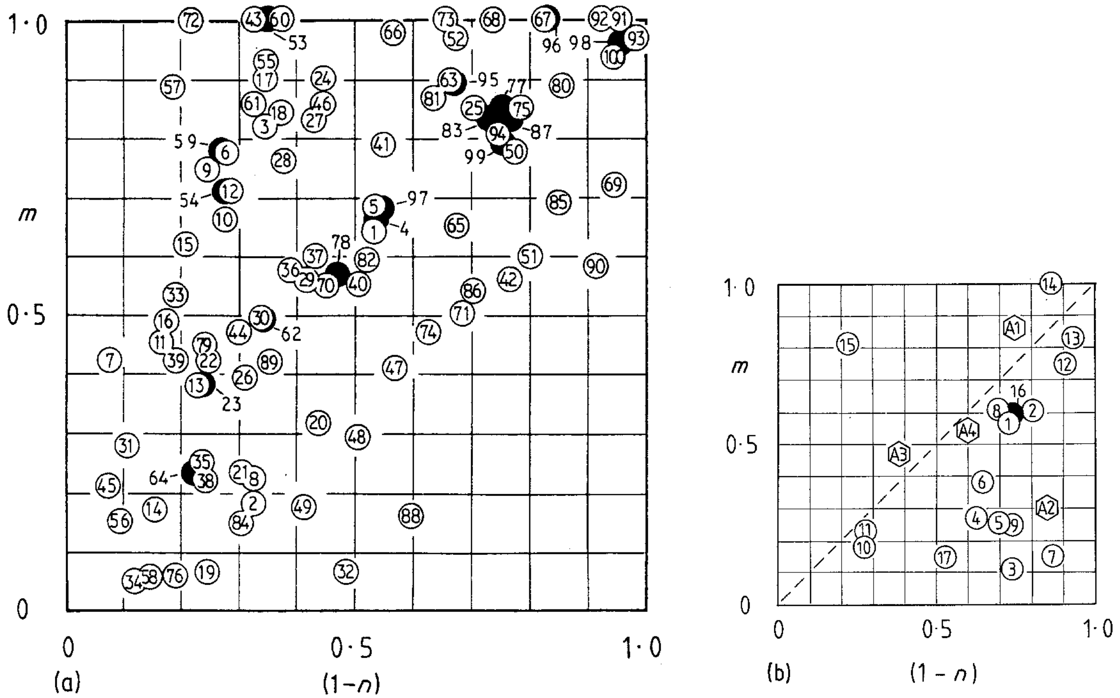


Figure 2 Diagrammatic representation of the values of power-law indices m and $(1-n)$ observed in a range of materials: (a) from dielectric susceptibility measurements. The key to the points is given in [3]; (b) from mechanical and acoustic loss measurements. The key to the points is given in Table I. ○ mechanical, ⬡ acoustic.

TABLE I Key to Fig. 2b. Plain numbers indicate mechanical measurements, numbers pre-fixed with A indicate acoustic loss

Number in figure	Material	m	$(1-n)$	Reference
1	Chlorocyclohexylacrylate	0.57	0.28	[14]
2	Polymethylacrylate	0.61	0.8	[15]
3	Poly-*n*-octyl methacrylate	0.11	0.73	[16]
4	Poly-*n*-hexyl methacrylate	0.28	0.62	[17]
5	Poly-*n*-butyl methacrylate	0.25	0.7	[18]
6	Polyisobutylene	0.38	0.63	[19]
7	1,2-Polybutadiene	0.16	0.86	[20]
8	1,4-Polybutadiene	0.68	0.73	[20]
9	Styrene–butadiene copolymer	0.25	0.72	[20]
10	Polyethylene (MD)	0.18	0.28	[21]
11	Polyethylene (TD)	0.22	0.28	[21]
12	Silicon (doped)	0.75	0.91	[22]
13	Iron–carbon alloy	0.83	0.93	[23]
14	Brass	1.0	0.86	[24]
15	Brass	0.80	0.21	[25]
16	CaF_2 + 1% NaF	0.60	0.74	[26]
17	Gel of 20% dimethyl phthallate in cellulose tributyrate	0.15	0.51	[27]
A1	*n*-Propyl alcohol	0.85	0.26	[28]
A2	M.B.B.A.	0.3	0.85	[29]
A3	Naphthalene	0.46	0.38	[30]
A4	Benzene (*a*-axis)	0.54	0.6	[31]

TABLE II Relationships between the dielectrical and mechanical spectral shape indices

Material	Index	Mechanical	Dielectrical	Sum	Reference
Chlorocyclohexylacrylate	m	0.57	0.42	0.99	[14]
	n	0.28	0.75	1.03	
Poly-*n*-octyl methacrylate	m	0.11	0.84	0.95	[16, 32]
	n	0.27	0.62	0.89	
Poly-*n*-hexyl methacrylate	m	0.28	0.9	1.18	[17, 32]
	n	0.38	0.65	1.03	
Poly-*n*-butyl methacrylate	m	0.25	0.71	0.96	[18, 33]
	n	0.3	0.71	1.01	
Tri-*o*-tolyl phosphate	n	0.55	0.4	0.95	[34, 35]
Di-*n*-butyl phthallate	n	0.5	0.45	0.95	[34, 35]

structure stores its component by electrical interactions. The fraction of the total energy that can be recovered, however, is only the mechanical part. Hence this fraction is

$$E_{\text{mech.}}/E_{\text{stored}} = n_{\text{mech.}}, \qquad (6)$$

from the definition of the correlation index. Similarly for an electrical investigation we would obtain

$$E_{\text{diel.}}/E_{\text{stored}} = n_{\text{diel.}}. \qquad (7)$$

From Equations 5 to 7 we have that

$$n_{\text{mech.}} + n_{\text{diel.}} = 1. \qquad (8)$$

The equivalent m processes arise from a different type of interaction within the material and in exactly the same way we can obtain

$$m_{\text{mech.}} + m_{\text{diel.}} = 1. \qquad (9)$$

In broad terms, Equations 8 and 9 can be seen to be satisfied by the observation in Fig. 2 that the mechanical and dielectric exponents are mirrored in the diagonal. However, the model used to derive Equations 8 and 9 is seriously limited in that real materials would be expected to have other means of storing energy such as magnetic or other non-elastic processes. These considerations suggest that the equalities in these equations should be replaced, in general, by "less than".

In order to carry out an experimental appraisal of the relationships given in Equations 8 and 9 it is essential, as has already been indicated, that the samples used in the mechanical and dielectric investigations should be identical, or as near to identical as possible. A number of the materials listed in Table I have been measured both mechanically and dielectrically. Table II lists the indices obtained from each of these experiments, together with the summation of the relevant values. Considering the accuracy with which some of the gradients could be determined the results strongly support the applicability of the proposed interrelationships. In two of the cases reported it was not possible to obtain the low-frequency indices but all the cases of equivalent measurements that have been found in the literature are reported in the table.

4. Conclusions

Although only a limited survey of the frequency response of mechanical and acoustic relaxation has been carried out, a number of specific conclusions can be established. It has been observed that power-law behaviour of the form given by Equations 1 to 4 is universal and that the Dissado–Hill spectral-shape function describes the frequency dependence of the compliance. The characteristic shape indices of the spectral response have been determined for a range of materials and it has been observed that for the mechanical response, in general, $m < (1 - n)$ in contrast to the dielectric case where the opposite condition applies. It has been proposed that for materials in which energy storage is only by electrical and mechanical means there is a specific pair of relationships between the dielectric and mechanical spectral shape parameters which has been observed in a number of polymeric materials.

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