10. Dielectric Response

Nearly all materials are dielectrics, and the measurement of their dielectric response is a very common technique for their characterisation. This chapter is intended to guide scientists and engineers through the subject to the point where they can interpret their data in terms of the microscopic and atomistic dynamics responsible for the dielectric response, and hence derive useful information appropriate to their particular needs. The focus is on the physical concepts underlying the observed behaviour and is developed from material understandable by an undergraduate student. Emphasis is placed on the information content in the data, and the limits to be placed on its interpretation are clearly identified.

Generic forms of behaviour are identified using examples typical of different classes of material, rather than an exhaustive review of the literature. Limited-range charge transport is included as a special item. The theoretical concepts are developed from a basic level up to the ideas current in the field, and the points where these are controversial have been noted so that the readers can choose for themselves how far to rely on them.

Nearly all materials are dielectrics, that is they do not exhibit a direct-current (DC) conductivity on the macroscopic scale, but instead act as an electrical capacitance i. e. they store charge. The measurement of the dielectric response is noninvasive and has been used for material characterisation throughout most of the 20th century, and consequently a number of books already exist that cover the technique from various points of view. Those that have stood the test of time are *Debye* [10.1], *Smyth* [10.2], *McCrum* et al. [10.3], *Daniels* [10.4], *Bordewijk* and *Bottcher* [10.5], and *Jonscher* [10.6]. These texts cover the subject in terms of the basic physics [10.1, 5], the material properties [10.2–4], and the electrical features [10.6]. An introduction to the wide range of dielectric response measurements that are undertaken can be obtained by referring to the proceedings publication of the International Discussion Meeting on Relaxations in Complex Systems [10.7]. In view of the enormous range of properties and materials covered by the topic it is not feasible or desirable to attempt to review the whole field in a chapter such as this. Instead the topic is approached from the viewpoint of a researcher who, having measured the dielectric *spectrum* (i. e. frequency-dependent complex permittivity) of a material sample, wishes to know what information can be taken from the measurements. Along the way the limits on the information content and the problems (and controversies) associated with the microscopic and molecular-scale interpretation will be identified. Emphasis will be placed on the physical concepts involved, but inevitably there will be some mathematical expressions whose features I aim to place in as simple a physical context as possible.

10.1 Definition of Dielectric Response

10.1.1 Relationship to Capacitance

Stated simply the dielectric response of a material is its response to an electric field within it. Let us start in the simplest way with some basic macroscopic definitions. Imagine that we have a flat slab of our material of thickness d with electrodes of area A on each opposing surface, and we apply a potential difference between opposing sides (Fig. 10.1). Since the material is a dielectric our system is a capacitor and electric charges $\pm Q$ will be stored on the surfaces between which the potential difference V is applied with Q given by

$$Q = CV \,, \tag{10.1}$$

where C is the capacitance of the system. For the sample geometry considered C is given by the expression

$$C = (\varepsilon_0 \varepsilon_r A)/d \,. \tag{10.2}$$

Here the factor ε_0 is a fundamental constant termed the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}}$) and ε_r is the permittivity of the material relative to that of free space and hence is termed the relative permittivity. Of course it is a pure number, which is a material property that contains information about the way the material responds to the application of the potential difference. Since however, the replacement of our sample by a vacuum yields a capacitance given by

$$C = (\varepsilon_0 A)/d \,, \tag{10.3}$$

i.e. $\varepsilon_r = 1$, the information about the response of the material to the electric field is contained in a factor χ, which is called the susceptibility of the material and is given by

$$\chi = \varepsilon_0(\varepsilon_r - 1) \,. \tag{10.4}$$

Noting that the electric field for the parallel electrode geometry described is given by $E = V/d$ and that the electrostatic flux density (electric displacement field) D within the material is $D = Q/A$, allows (10.1) and (10.2) to be transformed into the familiar constitutive relationship,

$$\boldsymbol{D} = \varepsilon_0 \varepsilon_r \boldsymbol{E} = \varepsilon_o \boldsymbol{E} + \chi \boldsymbol{E} \tag{10.5}$$

which is valid irrespective of the geometry. Here the response of the material has been explicitly separated out in the form of an additive term that is called the electric polarisation $\boldsymbol{P}$, which has dimensions of charge/area or more familiarly electric dipole moment density (electric dipole moment/volume), and is given by

$$\boldsymbol{P} = \chi \boldsymbol{E} \,. \tag{10.6}$$

An electric dipole occurs when electric charges of opposite polarity are separated in space and the magnitude of the dipole moment is given by $\mu = \delta \boldsymbol{r}$, where δ is the magnitude of the charge and $\boldsymbol{r}$ is the separation vector. The connection between $\boldsymbol{P}$ as defined above and the dipole moment density can be easily seen once it is recognised that the separation of the charges $\pm Q$ by the inter-electrode separation d constitutes a macroscopic dipole moment of magnitude Qd contained within the volume Ad. The definition of the polarisation as the dipole moment density makes it clear that the dielectric response to an electric field relates to the generation of a net dipole per unit volume in the material. In most cases the dielectric has a zero net dipole moment in the absence of an applied electric field and the action of the electric field is to produce one. Some materials such as electrets [10.9] and ferroelectrics lack a centre of symmetry, however, and possess a nonzero polarisation in the absence of an electric field. Therefore the definition of the polarisation P in (10.6) that is applicable to all cases is that P is the *change in net dipole moment density* produced by the applied field.

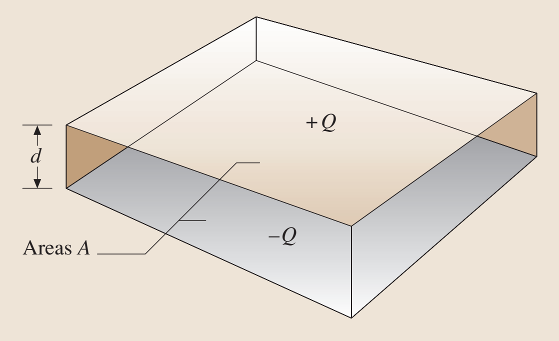

Fig. 10.1 A schematic representation of a dielectric in the form of a parallel-sided slab of surface area A and thickness d that has acquired surface charges $+Q$ and $-Q$ as a result of a potential difference applied across it. After [10.8]

10.1.2 Frequency-Dependent Susceptibility

The outline given above has been written as if the electric field within the material was a static field ($f = 0$)

but (10.6) is equally valid if the field oscillates with a circular frequency ω ($\omega = 2\pi f$, where f is the frequency in Hertz). In this case (10.6) becomes

$$\boldsymbol{P}(\omega) = \chi(\omega)\boldsymbol{E}(\omega)\,, \tag{10.7}$$

where $\boldsymbol{E}(\omega) = \boldsymbol{E}_0 \exp(\mathrm{i}\omega t)$.

The fundamental reason for the dependence of $\boldsymbol{P}(\omega)$ upon the frequency of the alternating-current (AC) field, as in (10.7), can be envisaged by constructing a general picture of the way that a material responds to an electric field. Let us imagine that we have our material in thermal equilibrium in the absence of an electric field and we switch on a constant field at a specified time. The presence of the electric field causes the generation of a net dipole moment density (or change in one already existing). This alteration in the internal arrangement of positive and negative charges will not be instantaneous. Instead it will develop according to some equation of motion appropriate to the type of charges and dipole moments that are present. Consequently some time will be required before the system can come into equilibrium with the applied field. Formally this time will be infinity (equivalent to an AC frequency of zero), but to all intents and purposes we can regard the system as coming into equilibrium fairly rapidly after some relevant time scale, τ, with the polarisation approaching the static value $\boldsymbol{P} = \boldsymbol{P}(0)$ for $t \gg \tau$. If now we think of the electric field as reversing sign before equilibrium is reached, as is the case for an AC field at a time $t = 1/4f$ after it is switched on, it is clear that the polarisation will not have reached its equilibrium value before the field is reversed and hence that $\boldsymbol{P}(\omega) \lesssim \boldsymbol{P}(0)$, and $\chi(\omega) \lesssim \chi(0)$. The frequency dependence of the dielectric susceptibility $\chi(\omega)$ is therefore determined by the equation of motion governing the evolution of the ensemble of electric dipole moments.

In general $\chi(\omega)$ will be a complex function with a real component $\chi'(\omega)$ defining the component of $\boldsymbol{P}(\omega)$ that is in phase with the applied AC field $\boldsymbol{E}(\omega) = \mathrm{Re}[\boldsymbol{E}_0 \exp(\omega t)] = \boldsymbol{E}_0 \cos(\omega t)$, and $\chi''(\omega)$ defining the component that is 90° out of phase. The conventional form is given by

$$\chi(\omega) = \chi'(\omega) - \mathrm{i}\,\chi''(\omega)\,, \left[\mathrm{i} = \sqrt{-1}\right]\,. \tag{10.8}$$

It is easy to see that $\chi'(\omega)$ determines the net separation of charge with the dielectric in the form of a macroscopic capacitor, but the nature of $\chi''(\omega)$ is not so obvious. The answer lies in considering the *rate of change of polarisation*, $\mathrm{d}[\boldsymbol{P}(\omega)]/\mathrm{d}t$. This has the dimensions of a current density (current/area), is sometimes termed the polarisation current density, and is given by,

$$\begin{aligned}\mathrm{d}[\boldsymbol{P}(\omega)]/\mathrm{d}t &= \left[\chi'(\omega) - \mathrm{i}\,\chi''(\omega)\right]\mathrm{d}[\boldsymbol{E}(\omega)]/\mathrm{d}t \\ &= \left[\chi'(\omega) - \mathrm{i}\,\chi''(\omega)\right]\mathrm{i}\,\omega[\cos(\omega t) \\ &\quad + \mathrm{i}\,\sin(\omega t)]\boldsymbol{E}_0\,.\end{aligned} \tag{10.9}$$

Thus $\chi''(\omega)$ determines the real component of the polarisation current density that is in phase with the electric field, i. e. $\boldsymbol{J}_{\mathrm{pol}}(\omega)$ given by

$$\boldsymbol{J}_{\mathrm{pol}}(\omega) = \chi''(\omega)\omega\boldsymbol{E}_0\cos(\omega t) = \sigma_{\mathrm{AC}}(\omega)\boldsymbol{E}_0\cos(\omega t)\,. \tag{10.10}$$

Here $\chi''(\omega)\omega = \sigma_{\mathrm{AC}}(\omega)$ is the contribution to the AC conductivity due to the polarisation response to the electric field. If we remember Joule's Law for the power dissipated thermally by an electric current, i. e. power lost $= IV$, then we can see that $\chi''(\omega)\omega(\boldsymbol{E}_0)^2$ is the power dissipated per unit volume resulting from the generation of a net polarisation by the electric field, i. e. the power dissipation density. The imaginary susceptibility $\chi''(\omega)$ is often termed the power dissipation component. It arises because the electric field has to carry out work on the dielectric in order to produce a net dipole moment density. Some of this energy is stored in the charge separations and is recoverable in an equivalent way to the elastic energy stored in a spring. The rest of the energy is used to overcome the friction opposing the establishment of the net dipole density. This energy is transferred to the dielectric in an unrecoverable way, i. e. it is dissipated within the dielectric. It can be seen that $\chi''(\omega)$ is dependent upon the form of the equations of motion governing the evolution of the net dipole moment density under the action of an electric field.

10.1.3 Relationship to Refractive Index

Equation (10.7) can be regarded as relating to the polarisation response purely to an oscillating electric field, but of course all electromagnetic waves contain such a field. In general the topic of dielectric response includes the response of the material to the electric field component of an electromagnetic field, i. e. the electromagnetic spectrum of a material is a form of dielectric response. This form of response is generally characterised by a complex frequency-dependent refractive index $n^*(f)$, with

$$n^*(f) = n(f) - \mathrm{i}\kappa(f)\,, \tag{10.11}$$

where n is the real refractive index expressing the velocity of light in the material, v, as $v = c/n$, and κ is the absorption coefficient, which defines the reduction of intensity of light of frequency f as it passes through the medium due to absorption of the photons by the medium, i. e. it relates to energy dissipated from the electromagnetic wave. The absorption coefficient can be determined from the Beer–Lambert law,

$$I = I_0 \exp\left(-4\pi\kappa f z/c\right) . \tag{10.12}$$

For nonmagnetic materials an equivalence can be established between n^* and the relative permittivity (see [10.10] for example). If we think of two slabs of dielectric material placed in contact with an electromagnetic wave passing through them, the component of the field $\boldsymbol{D}$ perpendicular to the boundary is unchanged as the wave passes from one medium to another. Essentially the same electrostatic flux passes through the same perpendicular area. Equation (10.5) gives the ratio of the electric fields in the two dielectric media to the inverse of the ratio of their relative permittivities. A comparison with Snell's law [10.10, 11] then yields

$$\varepsilon_{\mathrm{r}} = [n^*(f)]^2 . \tag{10.13}$$

Measurement of the dielectric response of a material involves the determination of the polarisation and its frequency dependence in some form or other. This can be carried out in a large number of ways such as the absorption spectra of electromagnetic radiation as has been described above as well as the application of an AC electric field across a sample of defined dimensions. Those readers interested in the technical details of the measurement systems are referred to the general literature, which has an enormous number of works on these experimental techniques (see for example [10.12] for bridge techniques and [10.13] for recent microwave techniques). This chapter will have a different focus. It will in essence be a discussion of the microscopic origins of the polarisation $\boldsymbol{P}(\omega)$ and the physical reasons for its variation in frequency so that data obtained from such measurements can be used to gain information relevant to the nature of the material to be studied.

10.2 Frequency-Dependent Linear Responses

In this context a linear response is one in which $\boldsymbol{P}(\omega)$ is only dependent upon the first power of the electric field, i. e. $\chi(\omega)$ is independent of the electric field. The general form of frequency dependence expected for $\varepsilon(\omega) = [\varepsilon_0 + \chi(\omega)]$ is shown schematically in (Fig. 10.2), where it can be seen that two basic types of response can be distinguished: a resonance response at high frequencies in the quantum region, and what is termed a relaxation response at lower frequencies.

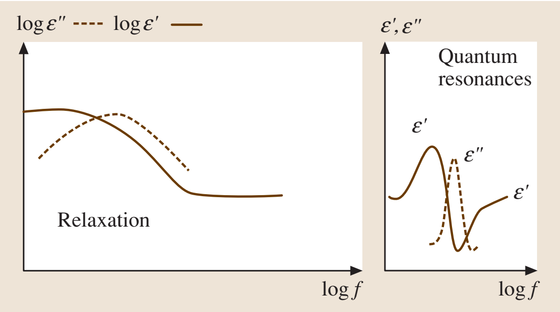

Fig. 10.2 Schematic representation of the frequency dependence of relaxation and resonance responses

10.2.1 Resonance Response

Although our main topic in this chapter will be the relaxation behaviour I will start with the resonance response as this has been dealt with extensively [10.14] from the spectroscopic viewpoint. Here we shall approach it from the perspective of its identity as a dielectric response with the intention of identifying basic features that also occur in relaxation responses. The equation of motion is familiar: this form of response relates to a *net* electric dipole moment, ϕ, that undergoes damped simple harmonic oscillation at a natural oscillation frequency $\Omega = 2\pi\nu$ in the absence of an electric field,

$$\mathrm{d}^2\phi/\mathrm{d}t^2 + \gamma\,\mathrm{d}\phi/\mathrm{d}t + \Omega^2\phi = 0 . \tag{10.14}$$

The interpretation of (10.14) is not as obvious as it seems. We have to remember that we are always dealing with a sample of material that contains an enormous number of molecules or molecular moieties. Two types of situation may lead to this form of equation of motion. In one case a fluctuation in the positions of *groups* of positive and negative charges may form an oscillating net dipole moment. Plasma oscillations, found in metals [10.15], are an example of this type of behaviour. In the other case, individual molecules may possess identical dipoles oscillating independently at a frequency Ω.

Equation (10.14) then describes the behaviour of a *net* dipole moment produced by a fluctuation in the system of molecules independent of an applied electric field. Such fluctuations are deviations from the average equilibrium state produced by random impulses that act only for an infinitesimal time at $t = 0$, and (10.14) describes the subsequent evolution of the fluctuation. In both cases the damping (friction) term $\gamma\,\mathrm{d}\phi/\mathrm{d}t$, where γ is the damping factor, expresses the way in which the fluctuation dies away in the absence of an applied electric field and the net dipole moment density of the system returns to zero.

The situation applying in the case of most spectroscopic responses relates to dipole density fluctuations in which individual molecules contribute oscillating dipoles, and it is this form of behaviour that will be used to illustrate the resonance form of response. The first thing we have to do is to ask what kinds of dipole moments oscillate in our material at frequencies in the range $\nu \gtrsim 5\times10^{10}$ Hz where most resonance responses are found. The answer to this question lies in the electronic structure of the atoms, ions and molecules that make up our material. The uncertainty principle states the energy of a system cannot be specified at any precise instant of time. This means that the electronic structure of atoms and molecules is allowed to continuously fluctuate between quantum states as long as the average energy over a period of time remains constant. The averaging time is determined by the uncertainty relationship between energy and time. The molecule is thus continuously moving back and forth between ground state and its excited states. These quantum fluctuations (between ground and excited states) displace the negative charge of the electron cloud with respect to the positive charge of the nucleus, and produce oscillating dipoles, termed transition dipoles (Fig. 10.3a). Their oscillation frequencies have specific values depending upon the energy difference between excited and ground quantum states of the species concerned, typically in the range $\nu \gtrsim 4\times10^{14}$ Hz [10.14, 16]. These oscillating dipolar fluctuations give no net contribution to the dipole moment of the molecule or atom. The uncertainty principle similarly allows the nuclei of molecules, and the molecules themselves to vibrate and fluctuate between different vibration states. In many cases these nuclear fluctuations produce dipole moments [10.10, 16, 17] (Fig. 10.3b), which typically oscillate in the frequency range $4\times10^{14}\,\mathrm{Hz} \gtrsim \nu \gtrsim 5\times10^{10}$ Hz. As with the electronic transition dipoles, these vibration fluctuations do not contribute to the dipole moment of the molecule or system of molecules.

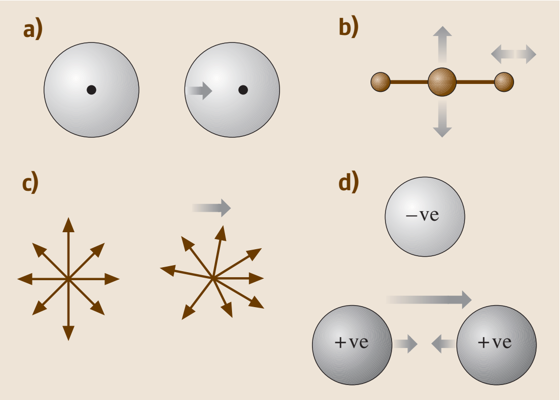

Fig. 10.3a–d Schematic representation of the various forms of dipole fluctuations: **(a)** atomic dipole, **(b)** dipoles formed by bending and stretching motion of a tri-atomic molecule of the form A–B–A, **(c)** net dipole fluctuation produced in a system of permanent dipoles, **(d)** reorienting dipole formed by transfer of an ion between two different centres of vibration. In all cases the *light arrow* shows the net dipole

When an AC electric field, such as that provided by an electromagnetic wave, is applied to the material, it couples to the transition dipoles to give a force that drives the system. As a result the population of dipoles is altered such that there is now a *net* average density of transition dipole moments. This oscillates with the frequency of the *field*, i. e. the system is polarised as defined by (10.7). Since transition dipoles do not contribute to a permanent dipole moment of a molecule, the net dipole moment density produced by the electric field is referred to as an induced dipole moment density. The response of the system to an electric field oscillating at a frequency ω is essentially obtained by adding the driving force to (10.14) and determining the solution for ϕ that oscillates with the same frequency, i. e. $\phi(t) \propto \mathrm{e}^{\mathrm{i}\omega t}$. The components of the frequency-dependent relative susceptibility, $\chi_\mathrm{r}(\omega) = \chi(\omega)/\varepsilon_0$, then take the form

$$\chi_\mathrm{r}'(\omega) = \frac{\chi_0\Omega^2(\Omega^2-\omega^2)}{(\Omega^2-\omega^2)^2+\omega^2\gamma^2}\,, \tag{10.15}$$

$$\chi_\mathrm{r}''(\omega) = \frac{\chi_0\Omega^2\omega\gamma}{(\Omega^2-\omega^2)^2+\omega^2\gamma^2}\,. \tag{10.16}$$

These equations exhibit the typical signature of a resonance response such as shown in Fig. 10.2. The imaginary component $\chi_\mathrm{r}''(\omega)$ goes through a peak at $\omega = \Omega$ (the resonance frequency). The real component $\chi_\mathrm{r}'(\omega)$ exhibits a rise in positive value as the driving frequency ω approaches the natural frequency Ω from below, passes through zero when ω and Ω are equal, and rises towards zero from a negative value when $\omega \gg \Omega$. In some cases the exact frequency dependence of the relative susceptibility can be slightly different from that given above. Typically the peak in $\chi_r''(\omega)$ is broadened due to the possibility that either the resonance frequencies of different transitions of the same molecule can be close together and their responses can overlap, or that local electrical interactions between molecules cause the transition energies of individual molecules to be slightly shifted in energy.

As long as the transition energies are sufficiently far apart to be resolved experimental data of the resonance type will yield three pieces of information, which can be related to the electronic (or vibration) structure of the molecules. These are: (a) the natural oscillation frequency Ω, (b) the damping constant γ, and (c) the amplitude factor χ_0. The natural frequency ν is equal to the energy difference of the electronic states between which the fluctuation occurs, ξ, divided by Planck's constant i. e. $\nu = \xi/h$, and so provides information about the different quantum states in relation to one another. The amplitude factor χ_0 is proportional to the square of the transition dipole and therefore yields information on the relative rearrangement of positive and negative charges within the molecule by the transition fluctuation. Damping in these types of systems arises from the sharing of the transition energy between many energy states of the molecule and its vibrations. It removes energy from the specific oscillating dipoles for which the field produces a net dipole moment density. It may act through a delay in returning energy to the electromagnetic wave, i. e. incoherent reradiation, or by transferring it to other energy states where it cannot be reradiated. The damping therefore expresses the way that the energy transferred from the electromagnetic field to the molecule is absorbed and dissipated in the system. The damping factor γ often will have a complicated form. There is of course one other piece of information that is implied by data that fit (10.15, 16) and that is that the equation of motion for the natural oscillating dipole moments is given by (10.14). In some cases, however, the damping factor may be frequency dependent as a result of changes in the interaction between different energy states of the system that occur on the same time scale as the relaxation time, $1/\gamma$. The equation of motion will now have a different and more complicated form than that of (10.14).

The above outline of spectroscopic responses is of necessity very sketchy as it is not the main theme of this chapter, and is dealt with in detail in many standard textbooks (e.g. *Heitler* [10.14]). There are however, a number of general features that can be used as a guide to what happens in the *linear* relaxation response. In the first place the dipoles involved are a property of natural fluctuations of the system, in this case quantum fluctuations in molecules. They are not produced by the electric field. In the absence of an electric field the fluctuating dipoles do not contribute to the net dipole moment of the system, in this case individual molecules. The action of the electric field in linear responses is solely to alter the population of the fluctuations such that a net dipole moment density is produced. This is achieved in the resonance cases considered above by the production of a net density of molecules in an excited state proportional to $\chi_0 E_0$. The irreversible transfer of energy from the electric field to the system relates to the sharing of this energy between the oscillating dipoles coupled to the electric field, and many equi-energetic states of the system that do not couple directly to the electric field. The energy shared in this way is dissipated among the many connected states. Dissipation is an essential consequence of natural fluctuations in an ensemble [10.18] and expresses the requirement that the fluctuation die away to zero at long times. The function $\phi(t)$ must therefore approach zero as t tends to infinity. In the absence of an electric field dipole density fluctuations utilise energy gained transiently from the ensemble and return that energy via the dissipation mechanism. When however an electric field is present, the relative number of fluctuations with dipole moments in different directions is altered and the dissipation term irreversibly transfers energy from the electric field to the ensemble.

10.2.2 Relaxation Response

We turn now to the relaxation response. The simplest way to view this behaviour is as an overdamped oscillation of the net dipole moment density, i. e. one for which $\gamma^2 > 4\Omega^2$. There are a number of ways of addressing this situation and below I shall develop the description starting from the simplest model whose behaviour is rarely found in condensed matter.

The Debye Response

In this case we can neglect the force constant term in (10.14), i. e. the term $\Omega^2\phi$. This leads to an equation of motion with the form

$$\mathrm{d}\phi/\mathrm{d}t + \gamma\phi = 0\,. \tag{10.17}$$

The solution to this equation is the very familiar exponential form, $\phi(t) \propto \mathrm{e}^{-t/\tau}$. Equation (10.17) can be interpreted by taking on board the lessons from the resonance response. As before we have to view it as describing the behaviour of a natural fluctuation in our system that produces a net dipole moment density as the result of a random impulse at $t = 0$. Now however, there is no evidence for dipole oscillation, so we are not looking at the quantum fluctuations of electronic charge clouds and nuclei positions of molecules. In this case the response originates with the permanent dipoles that many molecules possess due to the asymmetry of their atomic construction. We should also remember that, though atoms do not possess a permanent dipole moment, ion pairs in a material will act as dipoles. Such systems contain a large number (ensemble) of permanent dipoles and this ensemble will obey the laws of thermodynamics. Therefore, with the exception of such materials as electrets and ferroelectrics the orientation of the permanent dipoles will be random in the absence of an electric field, i. e. the *average* net dipole moment of the system will be zero. Thermodynamic ensembles are however described by distributions that allow for fluctuations about the defined average values, thus for example canonical ensembles allow for fluctuations in energy about a defined average energy content, and grand canonical ensembles allow for fluctuations in the number of effective units (e.g. net dipole moments) as well. In the case of dipole responses we are looking at fluctuations that involve the orientations of the permanent dipoles and hence create a net dipole density (Fig. 10.3c,d). Such fluctuations are natural to the ensemble, but are transient, i. e. as in Sect. 10.2.1 $\phi(t) \to 0$ as $t \to \infty$. Equation (10.17) describes the way in which such a local fluctuation in the dipole moment density decays (regresses) to zero, i. e. the ensemble relaxes. An applied electric field couples with the permanent dipoles to produce a torque that attempts to line the dipole with the electric field vector where its energy is lowest. Consequently the linear response of the system to the application of an electric field is an increase in the population of the permanent dipole fluctuations with a component oriented in the field direction as compared to those which have components oriented in the reverse direction. This relative change in the populations of the natural fluctuations of the system gives a net dipole moment density that is driven at the frequency of the electric field as in (10.7) [10.19].

As in the resonance case the polarisation can be obtained by adding the AC driving force oscillating at frequency ω to (10.17) and determining the solution for ϕ oscillating with the same frequency. The corresponding relative susceptibility components have the form

$$\chi_r'(\omega) = \frac{\chi_0}{1+\omega^2/\gamma^2}\,, \tag{10.18}$$

$$\chi_r''(\omega) = \frac{\chi_0\omega/\gamma}{1+\omega^2/\gamma^2}\,. \tag{10.19}$$

These functions show a peak in the imaginary susceptibility component, $\chi_r''(\omega)$, at a frequency $\Omega = \gamma$, which is sometimes called the loss peak frequency since $\chi_r''(\omega)$ is associated with the dissipation of energy, or equivalently the loss of energy from the driving electric field. The real component of the susceptibility, $\chi_r'(\omega)$, changes monotonically from zero at high frequencies to a limiting low-frequency value of χ_0. This is termed the dielectric dispersion.

Equations (10.17–10.19) define what has come to be known as the Debye response after *P. Debye* who first addressed the nature of relaxation dielectric responses [10.1]. It is characterised by two pieces of information: the magnitude of the dispersion χ_0 and the damping factor γ, more usually defined via the relaxation time $\tau = 1/\gamma$ of the dipole density fluctuations. The dispersion magnitude χ_0 is a measure of the net change in dipole density fluctuations that can be produced by a unit field (i. e. $E_0 = 1\,\mathrm{V\,m^{-1}}$), and is proportional to the square of the individual permanent dipole moments. As with the resonance response an exact fit between the relaxation response data and (10.18), (10.19) implies a specific form for the equation of motion of the dipole density fluctuations of the permanent dipole ensemble, i. e. that of (10.17).

Frequency-Dependent Dielectric Response in Condensed Matter

In practice the Debye response is rarely observed outside of the gas phase. Instead the experimental data can usually be characterised through fractional power laws in the frequency dependence of $\chi_r''(\omega)$ [10.6, 8, 20] in the regions away from the peak (see Fig. 10.4), i. e. for $\omega \gg \gamma$, and $\omega \ll \gamma$, giving

$$\chi_r'(\omega) \propto \chi_r''(\omega) \propto \omega^{n-1}\,,\ \omega \gg \gamma\,, \tag{10.20}$$

$$\chi_r'(0) - \chi_r'(\omega) \propto \chi_r''(\omega) \propto \omega^{m}\,,\ \omega \ll \gamma\,. \tag{10.21}$$

Here n, and m are fractional exponents, i. e. $0 < n,\ m < 1$. This general form was first defined empirically as the Havriliak–Negami function [10.21, 22]. A number of special cases have been identified [10.5, 8]. Thus for example the Cole–Cole function is given by $n + m = 1$. When $m = 1$, and $0 < n < 1$, the Cole–Davidson form is produced, which obeys (10.20) and

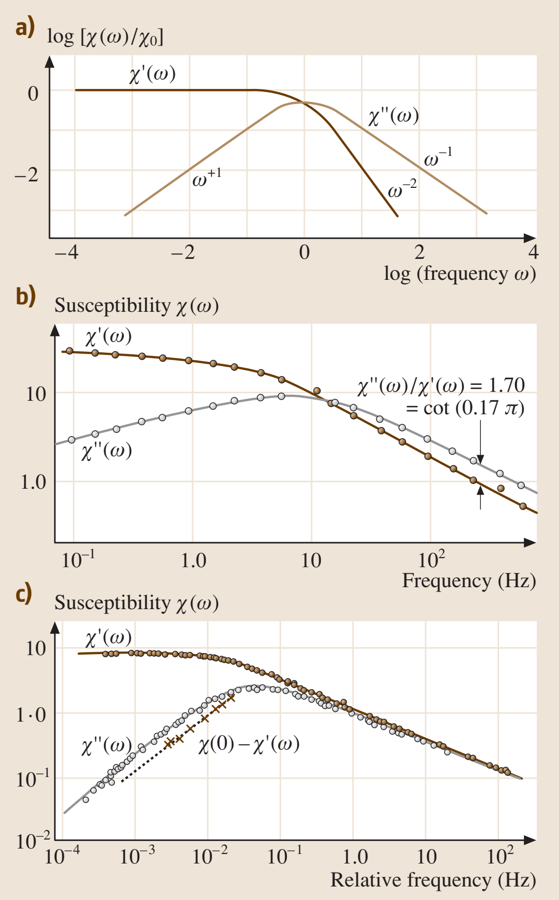

Fig. 10.4 **(a)** Schematic drawing of the Debye response. **(b)**, **(c)**Examples of measured data fitted to the response function $\chi(\omega)/\chi(0) \propto [(1+\mathrm{i}\,\omega\tau)^{n-1}\;{}_2F_1(1-n;\,1-m;\,2-n;\,(1+\mathrm{i}\,\omega\tau)^{-1})]$ resulting from the response function $\phi(t)$ of (10.22). The function ${}_2F_1(,\,;\,;)$ is the Gaussian hypergeometric function [10.25]. *Plot* **(b)** data from irradiated tri-glycine sulphate (TGS) ; *Plot* **(c)** data from polyvinylacetate. After [10.26]

follows $\chi_\mathrm{r}''(\omega) \propto \omega^m$ $(m=1)$ for $\omega \ll \gamma$ but without $\chi_\mathrm{r}''(\omega)$ being proportional to $\chi_\mathrm{r}'(0)-\chi_\mathrm{r}'(\omega)$ as in (10.21).

The physical theory of *Dissado* and *Hill* [10.23, 24] yields analytical expressions for $\chi_\mathrm{r}'(\omega)$ and $\chi_\mathrm{r}''(\omega)$ that contain both the Debye and Cole–Davidson functions as *exact* limiting cases, and the Cole–Cole and Havriliak–Negami functions as approximations with only minor differences in the curvature in the region of the peak in $\chi_\mathrm{r}''(\omega)$. The frequency-dependent susceptibility given by this theory has come to be known as the Dissado–Hill function and is defined in terms of a hypergeometric function [10.25], which is an infinite series with similarities to that of the exponential function. The reader is referred to [10.23, 24] for details. Unlike the empirical functions the Dissado–Hill dielectric response function has a clearly defined equation of motion for $\phi(t)$ [10.24],

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}t^2}+\frac{[2+n+(t/\tau)]}{t}\frac{\mathrm{d}\phi}{\mathrm{d}t}+\frac{[n+(t/\tau)(1+m)]}{t^2}\phi=0\,. \tag{10.22}$$

This equation has an analytical solution for $\phi(t)$ in terms of a confluent hypergeometric function [10.25], which has the limiting behaviour $\phi(t) \propto t^{-n}$ at times $t < \tau = 1/\gamma$ and $\phi(t) \propto t^{-(1+m)}$ when $t > \tau = 1/\gamma$. When $m = 1$ the solution is $\phi(t) \propto t^{-n}\exp(-t/\tau)$ giving the Cole–Davidson susceptibility function, and the Debye response function $\phi(t) \propto \exp(-t/\tau)$ is obtained when $n = 0$ and $m = 1$. The general analytical function for $\phi(t)$ was first derived in [10.27] and later re-derived and its equation of motion discussed in [10.23, 24] to which the reader is referred for details. The form of (10.22) illustrates clearly the development of the relaxation response from short-time high-frequency damped harmonic oscillations, characterised by (10.14), as a consequence of time-dependent damping functions and oscillation frequencies. More specifically the damping function approaches a constant value $1/\tau$ (equivalent to γ) at long times, while the oscillation frequency approaches zero. In contrast the Debye model assumes that the dipole motions are overdamped motions with no time-dependent transition from the damped oscillations occurring at short times. Of course there are many ways that time-dependent damping functions and oscillation frequencies may be introduced, most of which involve making similar approximations to that of Debye as regards the ensemble forces that control these factors, but only the specific forms of (10.22) give the power-law frequency dependencies observed in the susceptibility (10.20), (10.21). These forms are produced because the dipole density fluctuations retain some memory of the restoring and damping forces that act on it over very long periods of time, i. e. these forces are not random impulses. The reader is referred to [10.24] for more detail.

The Response Function

A different approach may be taken to deriving the frequency-dependent susceptibility of linear responses. Returning to (10.14), (10.17), and (10.20) it can be seen that the solutions for $\phi(t)$ in the absence of a driving field give the time evolution of the dipole density fluctuation caused by a dipole generating impulse at $t = 0$, i.e. the natural motions of the system. The resulting expression for $\phi(t)$ is called the response function [10.19], and the complex susceptibility is obtained through (10.23).

$$\chi_r(\omega) = \chi_r'(\omega) - \mathrm{i}\,\chi_r''(\omega) = \underset{\varepsilon\to\infty}{\mathrm{Lt}}\left[\int_0^\infty \phi(t)\,\mathrm{e}^{-\mathrm{i}\omega t-\varepsilon t}\,\mathrm{d}t\right] . \tag{10.23}$$

Here ε is an infinitesimal quantity that is taken to zero after the integral has been carried out. This equation is valid for all linear dielectric responses. The requirement that $\phi(t) \to 0$ as $t \to \infty$ for natural fluctuations ensures that $\chi_r'(\omega)$ and $\chi_r''(\omega)$ remain finite. The equations of motion, (10.14), (10.17), and (10.22) have solutions for $\phi(t)$ that can be transformed in this way to yield analytical expressions for the frequency-dependent susceptibility. An important consequence of (10.23) is that the frequency dependencies of $\chi_r'(\omega)$ and $\chi_r''(\omega)$ contain the same information since they are Laplace transforms of the same time-dependent function. This also means that a frequency-dependent conductivity $\sigma(\omega) \equiv [\omega\chi_r''(\omega)]$ contains no more information than the equivalent dielectric dispersion $\chi_r'(\omega)$. In fact the linear susceptibility components $\chi_r'(\omega)$ and $\chi_r''(\omega)$ are related to one another through the Kramers–Kronig relationships [10.5, 6]

$$\chi_r'(\omega) = \frac{2}{\pi}\int_0^\infty \frac{x\chi_r''(x)}{x^2-\omega^2}\,\mathrm{d}x , \tag{10.24}$$

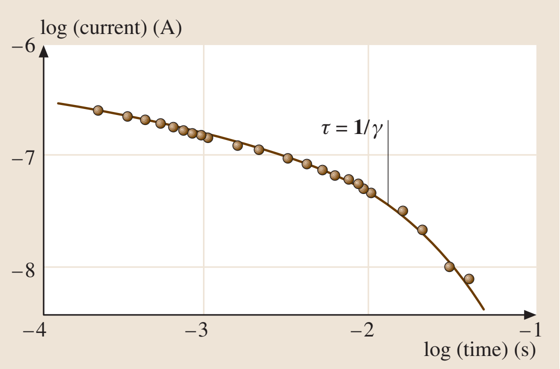

Fig. 10.5 The fit between the response function $\phi(t)/\phi(0) \propto (t/\tau)^{-n}\,\mathrm{e}^{-t/\tau}\;{}_1F_1(1-m;\,2-n;\,t/\tau)$ from (10.22) (where ${}_1F_1(;\,;)$ is the confluent hypergeometric function [10.25]), and experimental data for amorphous gallium arsenide. After [10.24]

$$\chi_r''(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\chi_r'(x)}{x^2-\omega^2}\,\mathrm{d}x . \tag{10.25}$$

The imaginary contribution from the pole at $x = \omega$ is excluded from these integrals. Although formally values of $\chi_r'(\omega)$ and $\chi_r''(\omega)$ are required over the frequency range from zero to infinity, the reciprocal relationships are adequately reproduced as long as the major part of the dispersion from any specific relaxation process is used.

Equation (10.23) means that linear dielectric responses are characterised through the time dependence of $\phi(t)$. This led *Williams* and *Watts* [10.28] to approach the description of the frequency dependence commonly observed by proposing that the exponential behaviour of

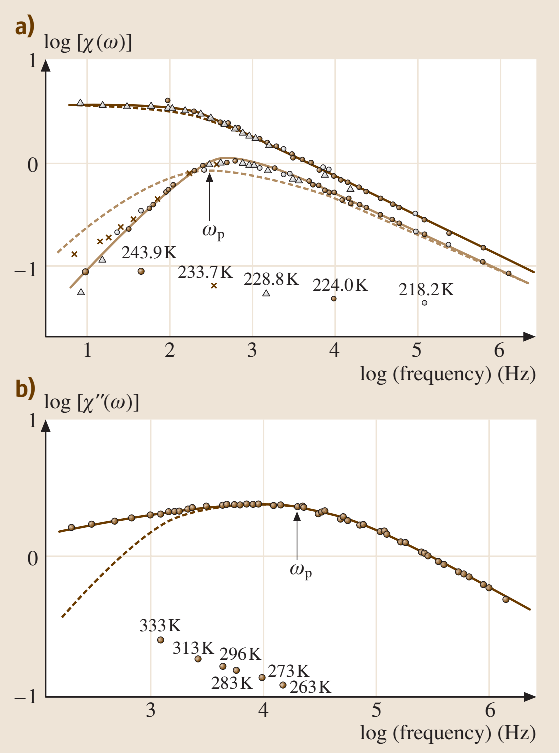

Fig. 10.6a,b Two examples of the fit between the susceptibility functions resulting from the response function $\phi(t)$ of (10.22) (*continuous line*) and (10.26) (*broken line*) and experimental master curves: **(a)** Nematic form of N–(2–hydroxy–4–methoxybenzylidene)–pn–butylaniline (OHMBBA), and **(b)** Polyallylbenzene. The shift of the representative point required to construct the master curve is marked on the plot. After [10.24]

$\phi(t)$ resulting from the Debye model, (10.17), should be generalised to the form

$$\phi(t) \propto (t/\tau)^{-n} \exp\left[-(t/\tau)^{1-n}\right] . \tag{10.26}$$

This expression is sometimes called the expanded exponential function or the Kohlrausch–Williams–Watt function, as it was later found that it was first proposed in [10.29] for mechanical responses. It is not known to possess a simple equation of motion such as (10.14), (10.17), and (10.22) but its relaxation function $\Phi(t)$, defined by $\Phi(t) = \int_t^\infty \phi(t)\,\mathrm{d}t$ [10.19] obeys a relaxation equation of the form of (10.17) with a time-dependent damping factor $\gamma(t) \propto t^{-n}$. The corresponding frequency-dependent susceptibility has the same power-law form as (10.20) for $\omega \gg \gamma = 1/\tau$, but exhibits a slowly varying decrease of slope as the frequency γ is approached from below that, with suitable choices for the value n, can approximate a power law for $\chi_\mathrm{r}''(\omega)$ such as is defined in (10.21). The relationship between experimental data for $\phi(t)$ and that derived in the Dissado–Hill cluster model, i. e. the solution to (10.22), is shown in Fig. 10.5. It can be seen that the data and the function for $\phi(t)$ approaches zero as t tends to infinity, with the time power law $t^{-(1+m)}$, but accurate experimental data for times several decades beyond τ is required if this behaviour is to be distinguished from that of (10.26). A better means of distinguishing the two results can often be had by recourse to their appropriate frequency-dependent susceptibilities, see Fig. 10.6.

10.3 Information Contained in the Relaxation Response

As described in Sect. 10.2.2 relaxation responses contain three pieces of information. The strength of the coupling of dipole density fluctuations to the electric field characterised by χ_0, a characteristic relaxation frequency $\gamma = 1/\tau$, where τ is the characteristic relaxation time, and the relaxation dynamics characterised by the frequency dependence of $\chi_\mathrm{r}'(\omega)$ and $\chi_\mathrm{r}''(\omega)$. This latter feature is open to different interpretations, as will be discussed later.

10.3.1 The Dielectric Increment for a Linear Response χ_0

The dielectric increment is proportional to the square of the permanent dipole moments that give rise to the dipole density fluctuation. It is a feature of the dielectric response that does not usually receive the most attention, mainly because a quantitative relationship to the molecular physics of the relaxation process is often difficult to achieve. Nevertheless it has been used to determine the dipole moments of polar molecules using measurement in the gas phase or if necessary dilute solutions in a nonpolar solvent. In these cases the permanent molecular dipoles, μ, can be assumed to be independent of one another and to be able to adopt all orientations with equal probability in the absence of an electric field, i. e. all dipole moment orientations are at the same energy. This section starts by outlining the derivation of χ_0 for this situation even though this is not the topic area of this book and chapter. The aim is to demonstrate the procedure and bring out the assumptions involved so that the more complicated nature of dipole density fluctuations in condensed-state materials can be better appreciated.

Independent Free Dipoles

In an electric field a dipole that is at an angle θ to the field direction is at the energy $-\mu E \cos\theta$. Those molecules aligned with the electric field are therefore at the lowest energy. The thermal motions of the molecules will however tend to randomise the dipole orientations and the probability of finding a dipole with an orientation angle θ becomes $\exp(\mu E \cos\theta / k_\mathrm{B} T)$. The average value of $\mu \cos\theta$ is given by

$$M = \langle \mu \cos\theta \rangle = \frac{\int_0^\pi \mu \cos\theta \exp(\mu E \cos\theta / k_\mathrm{B} T) \sin\theta \,\mathrm{d}\theta}{\int_0^\pi \exp(\mu E \cos\theta / k_\mathrm{B} T) \sin\theta \,\mathrm{d}\theta} \tag{10.27}$$

and the contribution to the static polarisation is given by $N\langle \mu \cos\theta \rangle$, where N is the number of permanent dipoles per unit volume. The term independent of the electric field is zero because all orientations are equally probable in the absence of the field. Equation (10.27) results in a nonlinear function in the electric field E for M, which is called the Langevin function, $L(\mu E / k_\mathrm{B} T)$, with,

$$L(\mu E / k_\mathrm{B} T) = \coth(\mu E / k_\mathrm{B} T) - (k_\mathrm{B} T / \mu E) . \tag{10.28}$$

This function saturates at unity for very high values of $\mu E/k_\mathrm{B}T$, reflecting the total alignment of all the permanent dipoles in the electric field. At low fields defined by $\mu E/k_\mathrm{B}T \ll 1$, $L(\mu E/k_\mathrm{B}T)$ is a linear function of E and gives the linear dielectric increment as

$$\chi_0 = \mu^2/3k_\mathrm{B}T \ . \tag{10.29}$$

Dipoles in Condensed Matter

In condensed-phase systems, particularly solids, the approximations that lead to the Langevin function and (10.29) no longer apply, and hence these expressions no longer hold. In the first place the dipoles are constrained by the local structure and in general will not be able to assume all orientations with equal probability in the absence of an electric field. In the second place we cannot assume that the dipoles are independent of one another. This dependence may arise in more than one way. For example there may be electrostatic interactions between the dipoles, such as would be responsible for the formation of ferroelectric and anti-ferroelectric states. However when the dipoles concerned are of a low concentration such as those that originate with impurities, lattice defects, interstitial ions etc., these dipole–dipole interactions may be weak. The dipoles concerned may also be arranged in such a way that even though they can adopt one or more alternative orientations their dipole–dipole interactions essentially cancel, such as might be expected in dipole glasses [10.30]. The common way to deal with this situation is to assume that a dipole representative of the average dipole in the ensemble experiences the average electric field of all the other dipoles. This is called the *mean-field* approach [10.31]. Since the mean field will be a function of the average dipole moment due to the applied electric field it is usually possible to construct an equation that can be solved to yield M and hence χ_0. Another way in which the dipoles can interact arises because permanent dipoles are part of the lattice structure of the material. Those permanent dipoles that lead to a polarisation in the presence of an electric field must have two or more local orientations available to them, i. e. they must be able to adopt a different orientation that in the presence of an electric field has a lower energy. Any such change will inevitably alter the local atomic and molecular interactions around the dipole that has moved. This effect will travel through the structure and influence other permanent dipoles through changes in atomic and molecular positions in its environment [10.32]. The strength of such interactions will vary depending of the type of dipole and the way that it is connected to the structure. For example reorientable dipoles formed by small interstitial (or substitution) ions may not interact very strongly with the surrounding lattice, whereas polar groups attached to a polymer chain will in many cases interact very strongly when they adopt a different orientation. Similarly the reorientation of polar molecules in liquids may be expected to distort their surrounding solvent cage and create a disturbance that will be transmitted to other polar molecules. The special feature of this form of interaction is that it is transmitted along specific directions depending upon the lattice structure and hence is nonisotropic.

Order–Disorder Ferroelectrics

These are materials in which the permanent dipoles possess two or a limited number of possible orientations. At high temperatures the dipoles are randomly distributed between the alternative orientations in the absence of an electric field. As the temperature is lowered the electrostatic field of the dipoles acts on any one dipole to make one of the orientations more preferable than the others. This causes the permanent dipole system to adopt a specific orientation at the Curie temperature T_c. The mean-field approach results in an expression for χ_0 that diverges at T_c, i. e.

$$\chi_0 \propto \mu^2/|(T-T_\mathrm{c})| \ . \tag{10.30}$$

This expression is so common to us that it is easy to overlook the physical meaning that it contains, which is much better expressed in the renormalisation group approach [10.33]. Essentially the interactions between the dipoles cause their orientation and dynamics to become correlated to some extent. As T_c is approached from above, the dipole fluctuations in the system are correlated over increasingly long distances and involve increasingly larger groups of individual dipole moments μ. The dielectric increment increases in proportion to a power of the correlation length $\xi \propto |(T-T_\mathrm{c})^{-\delta}|$ and a more exact form for χ_0 is

$$\chi_0 \propto \mu^2/|(T-T_\mathrm{c})|^\alpha \ . \tag{10.31}$$

At temperatures below T_c the material will possess domains in which all the dipoles are aligned together. Dipole fluctuations in this state have the opposite orientation to that of the polarity of the domain dipole that is they are *changes in net dipole moment density*, see Sect. 10.1.1. These dipole fluctuations also produce an electrostatic field that causes them to be correlated. As the temperature reduces their correlation length reduces and hence so does χ_0. These materials show that the responding dipole in condensed-phase materials will not always be that of individual molecular or ionic components of the system, they may in fact be groups of individual dipoles that respond as a single unit. In fact the susceptibility increment may be written in terms of an effective dipole moment that is also a power of the correlation length, i. e. $\mu_{\text{eff}} \propto (\xi)^{\alpha/2\delta}$.

Kirkwood Correlation Factor

The particular feature of the ferroelectric order–disorder transition is that the correlation between dipoles in the dipole fluctuations is temperature dependent. In general this will not be the case; instead we can expect the correlation to be dependent upon the lattice structure of the material, and hence independent of temperature except for discrete step changes when the material undergoes a phase transition. One way of allowing for these correlations is to introduce a factor g, termed the Kirkwood factor [10.10, 34], into the expression for χ_0 such that it becomes

$$\chi_0 \propto Ng\mu^2 \,. \tag{10.32}$$

Here a value of $g = 1$ defines a system in which the dipoles are uncorrelated, i. e. they are independent of one another. Values of $g > 1$ indicate positive correlation i. e. the dipoles align in the same direction as in the ferroelectric case where g diverges as discussed. Values of $g < 1$ indicate dipoles that are anticorrelated i. e. pairs of dipoles tend to align in opposite directions. Both kinds of behaviour are known to occur.

General Features of the Temperature Dependence of the Dielectric Increment

Section 10.3.1 gives examples of behaviour in which an electric field imposes order, in terms of the polarity of the net dipole density fluctuations, upon an ensemble where the temperature acts as a disordering factor. In the case of independent free dipoles it is the applied field that attempts to align dipoles and for order–disorder ferroelectrics it is the electrostatic field of the other dipoles. It might therefore be expected that the temperature is always a factor that attempts to oppose the field and that the dielectric increment will decrease at high temperatures, but this is not always the case. For example, in situations where the dipole can adopt one of two orientations one of which is favoured by the local lattice structure, the equilibrium population will be heavily weighted towards the favoured orientation. The equilibrium value of M in such a region can be expressed as,

$$M = \mu \tanh[(\Delta_\chi / k_{\text{B}} T)] \,, \tag{10.33}$$

where $2\Delta_\chi$ is the energy difference between the alternative orientations produced by the local structure. Here μ is the reorientable component of the dipole moment, see Fig. 10.7. An applied electric field that will favour the one orientation over the other will change the energy difference between alternative orientations from $2\Delta_\chi$ to $2(\Delta_\chi - \mu E)$. Differentiation with respect to E then gives the susceptibility increment as $\chi_0 \propto (\mu^2/k_{\text{B}}T)\cosh^{-2}(\Delta_\chi/k_{\text{B}}T)$, with the approximately activated form

$$\chi_0 \propto (\mu^2/k_{\text{B}}T)\exp(-2\Delta_\chi/k_{\text{B}}T) \tag{10.34}$$

holding when $\Delta_\chi/k_{\text{B}}T \gg 1$. Although (10.33) implies that regions exist where dipoles are aligned by the structure this does not necessarily mean that the material has a net dipole in the absence of an electric field. Such regions may be local and with dipole vectors randomly arranged by the structure. This behaviour has been found in ferroelectric ceramics [10.35, 36] in both the ferroelectric and paraelectric phases outside the transition region where T approaches T_{c}. Expression (10.34) indicates that in the appropriate temperature range the effect of the thermal fluctuations is effectively to increase the density of dipoles that can respond to the electric field, and that this overcomes any randomising behaviour. In contrast, at high temperatures ($\Delta_\chi/k_{\text{B}}T \ll 1$) the distribution of dipoles between the alternative orienta-

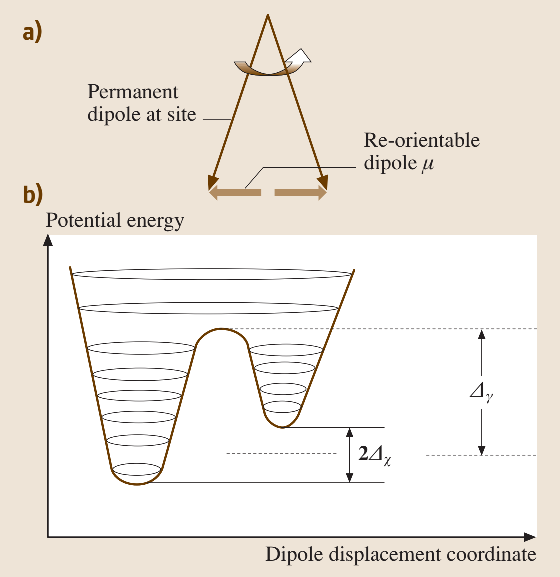

Fig. 10.7a,b Dipole reorientation between two potential wells: **(a)** shows the reorientable component of the dipole, **(b)** shows the potential-energy surface

tions becomes almost random and χ_0 approaches the free-dipole result (10.29).

In many experimental situations the value of the dielectric increment is essentially independent of temperature. It is difficult to see how this can occur in an ensemble where the dipole density fluctuations are produced by fluctuations in thermal energy about the average value, which couple to the electric field via changes in the heat content as in (10.27). However it may be possible to conceive of this behaviour as due to fluctuations in the configuration entropy of the molecular system, of which the dipole is a part, that take place without any change in the heat content. The effect of the field would be to change the configuration entropy S rather than the heat content H. As a result the susceptibility would be independent of temperature. This picture implies that we must think of the dipoles in this case not as local elements embedded within the material matrix moving in a fixed local potential, but as an integral part of the matrix whose dynamics is described by fluctuations in the Gibbs free energy $G = H - TS$ of the whole ensemble. In this case correlations between dipoles would be expected to occur mainly via the indirect route through their interaction with their local environment, rather than their direct electrostatic interactions.

Equation (10.31) describes the behaviour of a system undergoing an order–disorder transition *among the permanent dipole orientations*. A similar behaviour will be found for the relaxation response of a first-order ferroelectric or dipole alignment transition [10.37]. In general phase transitions will not give rise to a divergence in χ_0, which occurs because the phase transition in these cases is defined through the dipole, i. e. the dipole orientation is the order parameter. In other types of phase transition the dipoles are not the primary cause and what can be expected is an abrupt change of χ_0 as the dipoles find themselves embedded into a different lattice structure with different local potentials and orientation positions, different ensemble energies, and different correlations with one another and the material matrix.

The Information Content of the Dielectric Increment

As is clear from the above discussion it is not easy to make definite quantitative statements about the dipole system based on the dielectric increment. The basic reason for this situation is that the measurements are made on a macroscopic sample that contains an ensemble of an enormous number of dipoles, up to $\approx 10^{28}\ \mathrm{m}^{-3}$. The description of such systems can be carried through if the elements, here electric dipoles, are independent and their orientation is defined by a static local potential; as discussed above this will not be the case in general. More typically the dipoles will be correlated with the matrix in which they are embedded and/or one another. This means that the dipoles that are involved in the dipole density fluctuations are not site dipoles but groups of molecules/ions including dipoles, i. e. the responding features have a size intermediate between that of the molecule/unit cell and that of the sample. Determination of the temperature dependence will give some clues as to how to regard the dipole system through the definition of an effective dipole. The way the effective dipole changes with temperature will allow some interpretation of the kind of system that is present. Variation with other control parameters will produce more information, and systematic variation of the structure, for example replacement of side groups in polymers by longer or different side groups, or substitution of impurity ions by similar ions of different oxidation state or ionic radius, will help to identify the local dipole moment contributing the dielectric increment. However, even if the form of the site dipole is known, the quantitative evaluation of a factor such as the Kirkwood factor g (10.32) is not trivial. In condensed matter, as can be seen from Fig. 10.7, only a component of the site dipole is likely to be involved in reorientation. Unless the local structure is very well known it will not be possible to determine the actual value of the reorientable component in order to obtain a quantitative estimate of g. What can be achieved is a fingerprint of the dipole fluctuations in the material that can be used to characterise it. However at best this will be a partial picture of the dipole fluctuations in the material and information gained from the relaxation time and the relaxation dynamics should be used to enhance it further. In this way a holistic view of the dipole fluctuation can be attempted. It is important to realise that the picture obtained from these three features must be complementary. It is not acceptable to regard them as three independent features, as in fact they just yield different facets of the same process.

10.3.2 The Characteristic Relaxation Time (Frequency)

Equation (10.14), (10.17), (10.22), and (10.23) define a characteristic relaxation rate γ or relaxation time $\tau = 1/\gamma$ for the dipole density fluctuations. In the case of the Debye response, whose susceptibility functions are given by (10.18) and (10.19), γ is the frequency at which the imaginary (dielectric loss) component $\chi_r''(\omega)$

exhibits a peak. It has therefore become customary to determine the dependence of the relaxation time (rate) upon the control parameters (e.g. temperature, pressure, etc.) that are varied via that of the loss peak frequency. As long as the frequency dependence of $\chi_r''(\omega)$ (i. e. the loss peak shape) remains unchanged this procedure is valid because essentially the dielectric response investigated can be treated as a single composite process, even though it has a wider frequency dependence than that predicted for the independent free dipoles. Both the theoretical equation of motion (10.22) and response function (10.26) do in fact describe the response as a single composite process with a characteristic relaxation rate (time). However the frequency of the peak in $\chi_r''(\omega)$ (loss peak frequency) predicted from (10.22) is not γ but γ multiplied by a numerical factor depending upon the power-law exponents, n and m. In many cases the loss peak is very broad ($n \to 1, m \to 0$) and it is difficult to locate the peak precisely and to be sure that the point located is at the same position with respect to the functional dependence of $\chi_r''(\omega)$ upon ω. Under these circumstances a better procedure is to construct a master curve, which is done by plotting $\chi_r''(\omega)$ as a function of ω in log–log coordinates. Translation of the data along the $\log(\omega)$ and $\log[\chi_r''(\omega)]$ axes will bring the data into coincidence if the susceptibility frequency dependence is unchanged. The translation required to achieve coincidence gives the dependence of the susceptibility increment [$\log(\chi'')$-axis] and characteristic relaxation frequency [$\log(\omega)$-axis] on the controlled variable. For example it gives the ratios $\gamma(T_1)/\gamma(T_2)$ [or $\chi_0(T_1)/\chi_0(T_2)$] for the temperature change T_1 to T_2. This technique also has the advantage of illustrating clearly whether or not the frequency dependence is independent of the variation in temperature (or other parameter), i. e. whether or not the different sets of data can be brought into coincidence. It can also be used to determine any relationship between χ_0 and γ. This is done by selecting a reference point (e.g. the point $\chi_0 = A, \omega = B$) and marking the position on the master curve of this point from each data set after it has been translated to achieve coincidence. A trace is formed giving the dependence of $\log[(\chi_0)^{-1}]$ as a function of $\log(\gamma^{-1})$.

The relaxation rate is the dielectric response feature that shows most dependence upon the variation in the control parameters and so is the feature that is most often studied. In the following sections I will outline some of the most common types of behaviour and discuss their implications for the physics of the relaxation process.

Site Dipole Reorientation

The simplest form of relaxation rate is that described by Debye for independent molecular dipoles suspended in a viscous continuum. As described in Sect. 10.3.1 these dipoles are regarded as free to adopt any orientation in the absence of an electric field. Relaxation of a dipole density fluctuation involves the rotation of the molecular dipoles in the fluctuation to a state in which the net dipole density is zero. In such a situation the rotation of each individual dipole occurs at the same speed determined by the viscosity, η, of the medium, and the relaxation time ($\tau = 1/\gamma$) of the dipole density fluctuation is governed by that speed. For a molecular dipole whose effective length is a the relaxation time has the form [10.10],

$$\tau \propto \eta a^3 / k_B T \,. \tag{10.35}$$

The more viscous the medium, or the bigger the molecular dipole, the slower it rotates and the slower will be the relaxation of a fluctuation, giving a net dipole moment to the ensemble.

Of course the conditions for this behaviour to be exactly applicable cannot be met except in a gaseous medium. Condensed-phase materials are not continua. Even liquids possess a local structure and molecular dipoles will either be part of that structure if they are contributed by the medium, or will be surrounded by a solvent shell if they are dissolved in the medium. In solids the molecular (or ionic) dipole is of necessity part of the structural matrix, and even though this must be irregular enough to permit rotational displacement to at least one other orientation the matrix can be expected to maintain some structural correlation to distances well away from the site of a reorientable dipole. These are the conditions that must be included in any description of the relaxation frequency (time).

The first point of departure from the picture of a free dipole in a continuum is that the dipole will possess only a limited number of orientations that it can adopt. Consequently there will be a potential barrier between these alternative equilibrium orientations. The rate of transition between alternative orientations and hence the relaxation frequency will be determined by the rate at which a dipole or, to be more specific, the atoms or ions that form the local dipole can pass over the potential barrier to switch orientation, as shown for example in Fig. 10.7. In this case the relaxation frequency will possess an activated (Arrhenius) form where the activation energy Δ_γ is the mean potential barrier height between the alternative orientations, i. e.

$$\gamma = 1/\tau = A \exp\left(-\Delta_\gamma / k_B T\right) . \tag{10.36}$$

The expression to be used for the pre-exponential factor A depends on the way in which the atoms/ions comprising the local dipole pass through the transition region at the top of the barrier [10.38, 39]. In the schematic drawing of Fig. 10.7 the dipole is described as having an atom (ion) at its head that performs quantum oscillations in one of two potential wells. As long as it can be assumed that there is a thermal equilibrium between all the vibration states and that the dipole head passes into the alternative well in a single transit of the barrier region, then $A = \nu$, where ν is the frequency of the quantum vibrations at the bottom of the wells. This result continues to hold even if thermal equilibrium is established only for the states at the bottom of the well as long as the effective friction acting on the dipole head in the barrier region is weak. The type of potential surface with these properties is one that remains essentially rigid during the actual transit of the barrier region, which takes place in a time typically of $\approx 10^{-14}$ s. The activated factor in (10.36) expresses the thermal probability of finding a dipole in a quantum state at the top of the barrier. The other extreme situation occurs when the friction ς_{d} in the barrier region is high, for which $A \propto (1/\varsigma_{\mathrm{d}})$. This occurs when the transit of the barrier region is slow enough to allow interactions with neighbouring vibrating atoms to overdamp the motion. In this case the potential surface distorts during the transit of the barrier. Such situations can be expected when the barrier is broad and ill-defined, and correspond to local structures that are flexible, such as may be expected in viscoelastic materials. A general expression $A = \lambda_{\mathrm{r}}(\nu/\nu_{\mathrm{b}})$ has been developed by *Grote* and *Hynes* [10.39] where λ_{r} is a function that describes the change from low to high friction and ν_{b} is the quantum frequency in the barrier region.

An interesting consequence of this type of potential surface is that, regardless of the magnitude of the barrier energy Δ_γ, a temperature should exist below which reorientation over the barrier would take so long that any dipole fluctuation would essentially remain unrelaxed, i. e. the dipole system becomes frozen. However when the moving atom in the permanent dipole is a hydrogen atom this is not the case; relaxation can occur by the tunnelling of the hydrogen atom through the barrier [10.40]. This has been demonstrated by experiments on deuterated oxidised polyethylene molecules at millikelvin temperatures [10.41, 42]. In this case the relaxation frequency is determined by the tunnelling probability of the deuterium/hydrogen atom through the barrier, which is dependent upon the atomic mass, the barrier width and height, but *not the temperature*, i. e. the relaxation frequency becomes temperature independent at temperatures below ≈ 100 mK.

Relaxation on a Free Energy Surface

The situation described in the previous section is one in which the dipole moves on a potential surface provided by the surrounding structural matrix. The only dynamic effect of the matrix is via elastic and inelastic interaction between the quantum vibrations of the dipole and the matrix. In many cases however, the atoms (ions) comprising the dipole will cause the displacement of the centres of motion of the surrounding atoms during its transit between alternative orientations. In this case the expression for the relaxation frequency has to refer to the group of atoms affected as a unit, and an appropriate form is that derived by *Eyring* [10.43] for chemical reactions

$$\gamma = (k_{\mathrm{B}}T/h)\exp\left(-G^{\#}/k_{\mathrm{B}}T\right) . \tag{10.37}$$

Here $G^{\#}$ is the change in Gibbs free energy on passing from the ground state to the transition state in the process of reorientation. The barrier is now a free energy rather than a potential barrier and reflects the need for the involvement of displacements in a number of atoms, ions or molecules in order to achieve the dipole reorientation. If we refer again to Fig. 10.7 the difference is that the normal coordinate of the quantum vibrations in the barrier region is a mixture of several different normal coordinates of the surrounding matrix as well as that of the dipole in the well. In general $G^{\#}$ will be composed of an activation entropy contribution $S^{\#}$ as well as an activation enthalpy contribution $H^{\#}$ with $G^{\#} = H^{\#} - TS^{\#}$, and both will be properties of the group of atoms/molecules involved and their structural relationship. The expression for γ therefore takes a form similar to that of (10.36):

$$\begin{aligned}\gamma &= \left[(k_{\mathrm{B}}T/h)\exp\left(S^{\#}/k\right)\right]\exp\left(-H^{\#}/k_{\mathrm{B}}T\right)\\ &= A_{\mathrm{eff}}\exp\left(-H^{\#}/k_{\mathrm{B}}T\right) .\end{aligned} \tag{10.38}$$

The activation entropy $S^{\#}$ will reflect the configuration rearrangement required for the dipole to reorient. Thus for example, when reorientation requires the surrounding matrix to adopt a more irregular (disordered) arrangement so as to remove a steric hindrance to reorientation the transition region entropy will be greater than that of the dipole in the bottom of the well and $S^{\#}$ will be positive. Alternatively the transition region may require specific local arrangements in order that the dipole can avoid such hindrances. In this case the entropy of the transition state will be less than that of the dipole in the bottom of the well and $S^{\#}$ will be negative. A nonzero value of $S^{\#}$ will therefore lead to a relaxation frequency with an effective pre-exponential factor, A_{eff}, that is either greater or less than $k_B T/h$.

An interesting variation on this behaviour has been suggested by *Hill* and *Dissado* [10.44] who showed that several experimental relaxation frequencies could be described via what they termed an activated tunnelling expression. Here they allowed the possibility that the transfer between alternative orientations could take place by thermal activation to an energy state for which the tunnelling of hydrogen atoms through the barrier was feasible. An expression for the relaxation frequency was obtained by determining the optimum transfer rate, with all processes considered from that of an unactivated quantum tunnelling to activation over the top of the barrier. If the energy difference between the alternative orientations is zero the resulting relaxation frequency had the form

$$\gamma \propto \exp(BT) \tag{10.39}$$

over a considerable temperature range, where B is a temperature-independent factor dependent upon the tunnelling distance, the barrier height and shape, and the mass of the tunnelling particle. If the *barrier* in this work is taken to be a free-energy barrier rather than a potential barrier, the analysis can be seen to be equivalent to a situation whereby the dipole relaxes by finding a route between the alternative orientations that allows for lower values of $H^{\#}$ at the expense of ordering the surrounding molecules/atoms, i. e. a negative $S^{\#}$. Routes with higher values of $H^{\#}$ require values of $S^{\#}$ that are less negative. In this case the optimum relaxation frequency will take a form such as (10.39) and only at very high temperatures will γ become purely activated with $S^{\#} \approx 0$. The picture of dielectric relaxation provided by this interpretation is consistent with the *defect diffusion* mechanism [10.45], in which defects diffusing in the structural matrix, such as a kink in a polymer chain or a dislocation in a crystal, lower or remove barriers when they reach a dipole, allowing it to take an alternative orientation of equal energy. When the defect moves on, the dipole is locked into the new position until another defect arrives.

The Glass Transition

A glass is essentially a material that has become macroscopically rigid without attaining its thermodynamically favoured crystalline state. The manner in which this occurs for a liquid or viscoelastic (rubbery) material that has been rapidly cooled has been the subject of intense investigation over a large number of years (see *Angell* [10.46]). A simple, some would say oversimple, view of the situation is to regard it as a concatenation of two effects. In the first place supercooling the liquid phase will at some temperature result in a situation where the liquid no longer possesses a heat content in excess of the crystal state at that temperature [10.47]. The liquid will be unstable with respect to a disordered solid possessing only local crystalline order. In the second place the lowering of the temperature during the supercooling will cause the lattice to contract thereby introducing and increasing barriers to local molecular/atomic motions. At some temperature the thermal fluctuations [described by the Boltzman factor in (10.36), (10.37)] that are responsible for raising the site energy to that of the barrier become so rare that the time required for rearrangement becomes enormously long. At this temperature, termed T_g, the structure is essentially locked into a macroscopically rigid state, termed a glass. The glass transition cannot be regarded as a thermodynamic transition of state (unlike a melting/crystallisation temperature for example) and there are different ways of defining and determining T_g (see [10.46]).

During the approach to the glass state the rate of reorientation of permanent dipoles will become slower and eventually reach zero as shown in Fig. 10.8. It is common to denote the response due to a set of dipoles that are frozen during glass formation as the α-response. A second response can be seen in the figure: termed the β-response. This is provided by dipoles that are able to reorient without requiring any substantial rearrange-

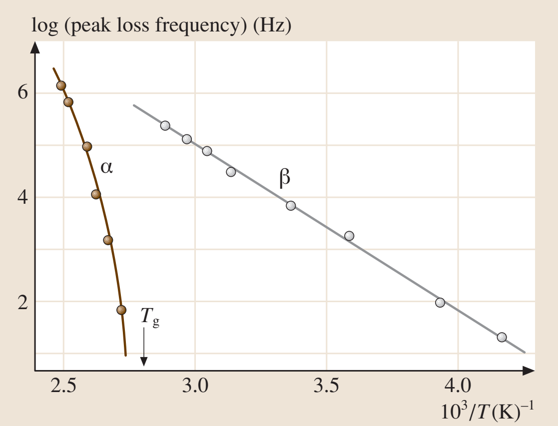

Fig. 10.8 The Arrhenius plot of the glass-forming polyvinylchloride system showing the slowing down of the α-response ($T > T_g$) as T_g is approached and the activated β-response. After [10.8]

ment of the surrounding structural matrix. It should not be expected however that this response is due just to a dipole reorientation with respect to the molecule it is attached to. In many cases the β-response involves the displacement of the molecule or part thereof as a whole [10.48]. In polymers this is a local *inter*-chain motion and either the free-energy expression (10.38) or the potential-energy expression (10.36) will apply, depending on whether the surrounding chains remain rigid during the relaxation or rearrange locally. These dipoles are active in the glass state and can be expected to have a relaxation rate of the form of (10.36), i. e. reorientation over a potential barrier. In the case of the α-response it is clear that the relaxations must involve displacements in a number of molecules/atoms other than just those comprising the permanent dipole, and hence it is instructive to discuss the behaviour in terms of the rate expression (10.37). What can be seen is that, as the temperature at which the system becomes rigid is approached, the gradient in the Arrhenius plot gets steeper, and $H^{\#}$ therefore becomes larger. The non-thermally-activated pre-exponential factor, A_{eff}, in (10.36) is greater than $k_{\mathrm{B}}T/h$ and hence $S^{\#} > 0$. As the temperature approaches T_{g} there is an increase in A_{eff}, by many decades in frequency, which must be due to an increase in $S^{\#}$. These changes in $H^{\#}$ and $S^{\#}$ indicate that, as T_{g} is approached, dipole-orientation relaxation not only requires an increased amount of energy in order to enter the transition (barrier) region but also a larger amount of configuration disordering in the surrounding structure that makes up the molecular/atom group involved in relaxation. Although it is possible that such a situation may come about because reducing the temperature produces a local increase in density that increases steric hindrances for the same group of atoms and molecules, it is more likely that the number of molecules that are displaced in order to allow the dipole to pass through the transition region has increased. These considerations are consistent with a structure that is becoming either tangled or interlocked as the temperature decreases. Detailed expressions based on these concepts but involving macroscopic parameters have been attempted (see for example [10.46, 49–52]).

The glass formation discussed above has a structural basis and dipole–dipole interactions will play at most a minimal role. In some situations however, the glass is a disordered array of dipole orientations [10.30]. This sort of state is most likely to occur at very low temperatures in materials that possess dipoles occupying the sites of a regular lattice. At high temperatures the dipole orientations will be disordered but, as the temperature is reduced to low values, each individual dipole would be expected to adopt their lowest-energy orientation, resulting in a state of ordered dipole orientation. A *dipole glass* will result instead when the dipole–dipole interactions produce forces that generate barriers to the local reorientation and frustrate the ordering process at temperatures low enough that the barriers generated cannot be overcome in any conceivable time.

Ferroelectric Transition

The dielectric response of ferroelectrics at temperatures in the vicinity of their Curie (critical) temperature also exhibit relaxation frequencies that approach zero, just as their dielectric increment approaches infinity (Fig. 10.9a,b) as discussed in Sect. 10.3.1. In this case both the dielectric increment and the relaxation frequency are functions of a hidden variable that characterises the system, the correlation length ξ of the dipole fluctuations. Just as the dielectric increment increases with a power of the correlation length, the relaxation frequency will decrease. Put simply the more dipoles are correlated in the fluctuation the longer the time that is required for its relaxation. Scaling theory [10.33] describes the system by a hierarchy of self-similar correlations. The strongest correlations are between the dipole and its nearest neighbours. This gives a local geometrical arrangement of correlations. The next-strongest correlations are between the same geometrical arrangement of groups of nearest neighbours, and the next strongest is between the same geometry of groups of groups. Eventually the whole system up to the correlation length is constructed in this way. Because the geometrical arrangement is preserved at each stage the properties for each stage have to be proportional to a power of the size. This gives

$$\gamma \propto |(T - T_{\mathrm{c}})|^{\beta} \propto \xi^{-\beta/\delta} \tag{10.40}$$

and using (10.31) the relationship

$$\chi_0 \propto (\gamma)^{-\alpha/\beta} \tag{10.41}$$

follows. But the theory can go further and predict the frequency dependence of $\chi_{\mathrm{r}}''(\omega)$ and $\chi_{\mathrm{r}}'(\omega)$ for $\omega > \gamma$. This follows because we can think of the response of the system to a field of frequency ω as being due to the correlation scale that can relax at the frequency ω, i. e. $\xi_\omega \propto \omega^{-\delta/\beta}$. The dielectric increment appropriate to this length scale can be obtained from (10.31) as $(\xi_\omega)^{\alpha/\delta}$ and hence,

$$\chi_{\mathrm{r}}''(\omega) \propto \chi_{\mathrm{r}}'(\omega) \propto (\xi_\omega)^{\alpha/\delta} \propto \omega^{-\alpha/\beta} = \omega^{n-1} \tag{10.42}$$

with $n = 1-\alpha/\beta$. These relationships describe what is called dynamic scaling. A detailed description of the derivation of the frequency dependence in (10.42) is given in [10.33] and the relationship of the power-law frequency dependence to self-similar relaxations is shown explicitly using scaled electrical circuits in [10.53]. Because of the small range of temperatures around T_c over which the power-law relationships (10.40, 10.41) are expected to hold it is difficult to determine the exponents α and β with any accuracy, however the dynamic scaling law can be easily demonstrated by using the master-curve technique and determining the locus of the representative point (see the beginning of Sect. 10.3.2). An example is shown in Fig. 10.9c where it can be seen that the representative-point locus of χ_0 as a function of γ is a power law with the same exponent as that of the frequency dependence of $\chi_r''(\omega)$ and $\chi_r'(\omega)$ for $\omega > \gamma$.

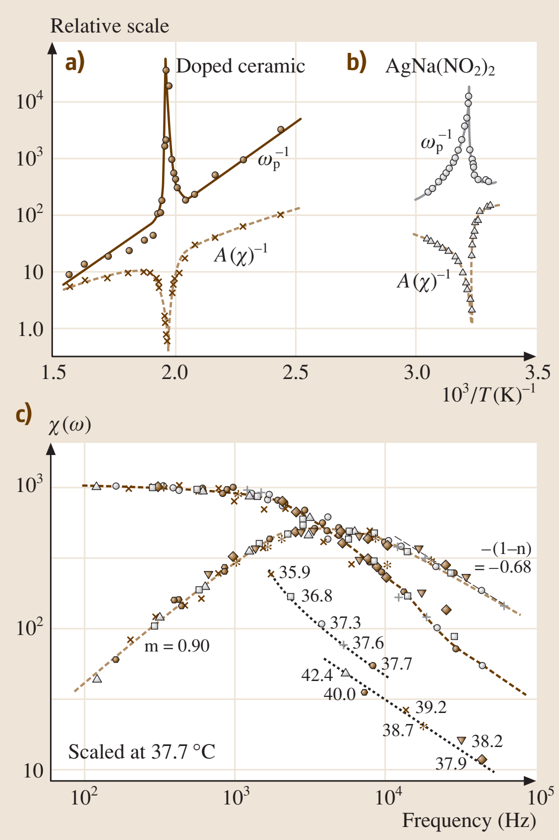

Fig. 10.9a–c An Arrhenius plot of the inverse of the susceptibility increment $A(\chi)(\equiv \chi_o)$ and loss peak frequency $\omega_p(\equiv \gamma)$ is shown for **(a)** a ceramic and **(b)** AgNa(NO$_2$)$_2$. The frequency-dependent susceptibility of AgNa(NO$_2$)$_2$ is shown in **(c)** together with the locus of the representative point as $T_c = 37.8\,°\text{C}$ is approached from above and below. Note the power-law relationship between the dielectric increment and the relaxation frequency, and the parallelism between this locus and the frequency dependence at $\omega > \gamma$, demonstrating an identical power-law behaviour. After [10.35]

The Information Content of the Relaxation Frequency (Time)

The typical starting point in investigating the relaxation frequency (time) is to make an Arrhenius plot, i. e. $\log(\gamma)$ is plotted as a function of $1/T$. A straight line is taken to indicate an activated process of the form of (10.36), with the gradient yielding the activation energy Δ_γ. However in most cases data is only available from a restricted temperature range and so the variation of $k_B T/h$ with temperature will be small. In this case the free energy expression (10.38) would give an equally good straight line. Since there are many situations in which the pre-exponential factor in (10.36) will be less than a quantum vibration frequency $10^{12}\,\text{Hz} \le \nu \le 3\times10^{13}\,\text{Hz}$, it is difficult to discriminate between the potential-barrier situation and the free-energy barrier in which $S^\# < 0$. Only when $A \gg 3\times10^{13}\,\text{Hz}$ will identification with relaxation via a free-energy barrier be certain. As can be seen from the foregoing it is difficult to obtain any definite information from the pre-exponential factor in an activated relaxation, except for the latter case where an evaluation of $S^\#$ is possible. Where $S^\#$ can be determined it gives us a qualitative picture of a relaxing dipole centre which has to be structurally distorted in order for the dipole to adopt a different orientation. The corresponding value of $H^\#$ gives the amount of energy that has to be supplied to the group in order for the reorientation to occur even allowing for the distortion. What cannot be determined from this information is the size of the group that is involved, though the behaviour and magnitude of χ_0 may give an idea as to the dipole magnitude and density. To give an idea of the difficulty of a molecular interpretation let us take the case of cyclo-hexanol [10.54]. This molecule forms a plastic crystal, i. e. the molecular centres are located on a crystal lattice but their orientations are disordered. The dipole moment is associated with the only strong polar feature, the alcohol (−OH) group, which can take one of two orientations with respect to the molecule. It would therefore be expected that the measured activation energy of ≈ 0.5 eV would be the potential barrier to the transfer of the alcohol group between the two positions, with its contributions from the neighbouring molecular cage as well as the molecular energy change. However, the molecular structure of the cyclohexanol can itself exist in two conformations, the chair and the boat, and can rearrange its orientation in a lattice by passing through the alternative conformation as an intermediate. The free-energy barrier to this interconversion is also ≈ 0.5 eV. So we cannot decide from the relaxation frequency whether the relaxation involves just $-$OH group transfer or transfer via a boat-to-chair transition or a mixture of both. In this case the pre-exponential frequency $A_{\text{eff}} \approx 6 \times 10^{16}$ Hz, so relaxation has to have a positive $S^{\#}$ and involve a number of atoms rather than a dipole reorienting on a rigid potential surface.

In the case of near-crystalline materials where the dipole is associated with defect centres we would expect the potential-barrier approach to be the best, but even here the fact that local reorientation is possible implies some sort of interaction between the surroundings and the moving dipole head. Calculations based on a rigid cage should (see for example [10.55]) however be possible, and comparison with experiment can be expected to determine how well this represents the situation and to what extent the transit of the barrier is affected by the barrier friction. Information provided by the dielectric increment should be of help here. The calculation ought to be able to yield an estimate of the reorientable component of the dipole, and if as seems likely the alternative orientations are at different energies, the temperature dependence of χ_0 should follow (10.34).

Although it is conceptually simple to think of dipoles relaxing upon a potential surface that remains unchanged during the relaxation, this is likely to be only an approximation to reality. The fact that alternative orientations exist indicates that in most cases the surrounding structure must be modified to some extent to accommodate the change; at the very least we can expect the dipole to polarise its surroundings differently according to its orientation. The expressions in Sect. 10.3.2 for the relaxation frequency of dipoles relaxing on a free-energy surface and dipoles in ferroelectrics reflect this fact in different ways. The ferroelectric behaviour described in Sect. 10.3.2 shows that when the *dipoles* become extensively correlated the relaxation frequency reduces as an inverse power of the correlation length and the dielectric increment increases as a power of the relaxation length. The self-similar scaling relates this behaviour to the frequency dependence of the susceptibility. The behaviour of the α-response of a glass-forming system involves dipole–structure interaction in a different way. The relaxation frequency approaches zero as T approaches T_{g} from above. Whatever the details of the process this behaviour has to indicate an increased difficulty for the dipole to reorient, which here is associated with structural ordering, densification, and atomic packing, rather than long-range correlations as in ferroelectrics. This response is also one for which the dielectric increment is often insensitive to temperature. If we put the two dielectric response features together we come to a picture in which the electric field effectively modifies the configuration entropy of the system in generating a net dipole density fluctuation. The net dipole density produced is essentially the same at different temperatures, so the change in configuration density generated by the electric field does not vary, but the relaxation time increases as the activation enthalpy $H^{\#}$ and entropy $S^{\#}$ increases. Put together with the fact that in structural glass formation small local regions are attempting to adopt a crystalline structure, this data indicates that there are *local* values of ground-state configuration entropy that reduce as T_{g} is approached, with a transition state involving a disordering of the local regions to free the dipole enough to let it adopt an alternative orientation in an equally ordered but different configuration. The dipole density fluctuations that couple to the electric field seem to involve reorganisations of the structure that can occur without a change in the value of the heat content H, i. e. they are essentially configuration entropy fluctuations rather than thermal fluctuations. In contrast to the ferroelectric situation the slowing down of the relaxation is not caused by longer-range correlations but by the increasingly larger numbers of molecular adjustments required to achieve a dipole reorientation.

The message of this section is that in most cases a detailed molecular description of the dipole motions is generally not accessible just from an analysis of the dielectric response. The reason is that, in general, dipole reorientations involve adjustments in the surrounding molecules/atoms that are not easy to define in molecular terms. However by putting together the behaviour of the dielectric increment and relaxation frequency it should be possible to obtain some general idea as to the extent of the connection of the reorientation to the molecular environment and the way in which it takes place.

10.3.3 The Relaxation Peak Shape

The explanation of the frequency dependence of the susceptibility is currently the most contentious of the features of the dielectric response. Many workers are content with just defining the shape by one or other of the empirical functions mentioned in Sect. 10.2.2, or through the power-law exponents of (10.20, 10.21). This gives a fingerprint of the dipole dynamics but no more. In particular it does not provide a description of the equation of motion of the dipole density fluctuation. Others determine what is termed a *distribution of relaxation times* for the loss peak in $\chi_r''(\omega)$. Essentially this approach is predicated on the assumption that the broadening of the loss peak compared to that of the Debye response (10.19) is the result of dipoles of the same type and dipole moment that each relax according to the Debye equation of motion (10.17) but possess different relaxation times with a distribution denoted by $g(\tau)$, which is defined via (10.43)

$$\chi_r''(\omega) = \int_0^\infty g(\tau) \frac{\chi_0 \omega \tau}{1+\omega^2\tau^2} \, d\tau \; . \tag{10.43}$$

This construction is still no more than a fingerprint unless a physical reason for the distribution $g(\tau)$ can be found. Usually this is ascribed to a distribution of local activation energies associated with dipoles that each exist in their own potential surface independent of one another. The system usually quoted as an example is that of the β-response in the rigid glassy phase, which typically has a very broad loss peak. In this case it is assumed that each dipole that can reorient to contribute to the β-response is essentially trapped in a local potential surface that is held rigid in the glass state. Of course the potential surface is not truly rigid, molecular/atomic vibrations must take place, but it is assumed that their effect on the potential averages out during the relaxation and their only effect is to raise the energy state of the reorienting dipole head to the state at the top of the barrier. One problem associated with this explanation of the origin of $g(\tau)$ is that, if the *function* $g(\tau)$ is independent of temperature the values of exponents n and m (10.20), (10.21) will be temperature dependent. This does not seem to be the case in general, with these exponents usually either constant or changing at the most slowly or discretely at a transition of state (see for example [10.8, 56]), but there is no real agreement on this point. Of course a temperature-dependent distribution function $g(\tau)$ may be assumed, but then the question arises as to why it *is* temperature dependent in a system that is presumed to be macroscopically rigid. Another facet of the problem associated with non-Debye loss peaks that does not seem to have received any consideration is the possibility that the magnitude of the reorientable dipole moment associated with each site of a given activation energy is also distributed. It is clear that this is highly likely even if the dipole moment that changes direction is the same everywhere, as illustrated in Fig. 10.7. Also, as described in Sects. 10.2 and 10.3, the local dipole may be correlated with other dipoles or its surroundings, and in this case we can expect the Debye rate equation not to hold. The ferroelectric result (Sect. 10.3.2) already shows that this is the case when the dipoles motions are correlated giving the system a scale relationship in its dynamics, and even correlation between the dipole and its surroundings, for which there is considerable evidence (Sects. 10.2 and 10.3) can be expected to alter the form of the equation of motion from (10.17), by for example anharmonic coupling between the various modes. Even if we assume that all the criteria for the application of (10.43) are met, the $g(\tau)$ that are required to fit the experimental form of response defined by (10.20), (10.21) [and its corresponding theoretical response function, (10.22)] have unique features that require a physical justification, i. e. there is a cusp or sharp peak at the value of τ corresponding to the characteristic frequency ($\tau_c = 1/\gamma$), and power-law wings to either side whose power exponents are $1-n[g(\tau) \propto \tau^{1-n}]$ for $\tau < \tau_c$, and $-m[g(\tau) \propto \tau^{-m}]$ for $\tau > \tau_c$. In the Debye case the distribution becomes a delta function at the characteristic relaxation time. Essentially the *distribution of relaxation times* approach is convenient but it is not as easy to justify as would seem at first sight.

The Williams and Watt response function [10.28] started life as a heuristic suggestion but has received some later theoretical support [10.57–62]. The dynamic scaling behaviour appropriate to ferroelectrics gives a clue as to the way in which a frequency-dependent susceptibility of the form of (10.20) can come about, which results from both the equation of motion (10.22) and the response function (10.26). Essentially there has to be a self-similarity (or scaling) between the relaxation frequency of subcomponents of the system and their contribution to the dielectric increment (as illustrated in the circuit model of [10.8]). The theory proposed by *Palmer* et al. [10.60] refers this scaling to the removal of a hierarchy of constraints, thus for example we may imagine that close neighbours move quickest and remove the constraints imposed on larger groups of molecules and so on. This picture would be appropriate to a system such as a glass-forming material. The assumption however is that the motions are overdamped at all levels of the hierarchy, and hence no bridge is provided to the oscillatory motions known to occur at times close to quantum vibrations. A rather different stochastic approach has been taken by *Weron* and *Jurlewicz* [10.61, 62] who assumed that the system relaxation followed a path in which the fastest dipoles out of a distribution relaxed first and then the fastest out of the residual distribution and so on. The key feature is that the relaxing dipole is the extreme fastest from the distribution existing at the time. It was argued that the extreme-value statistical distribution function then led automatically to the response function of (10.26). The choice of appropriate extreme-value distribution was made on the grounds that the relaxation time was a positive definite variable. However this is not a sufficient criterion [10.63]. In order for (10.26) to apply the continuous distribution density of relaxation times (i. e. the distribution the system would have if it were of infinite size) has to be stable to scale changes (see for example [10.64]) and thus has to approach the extreme of long times as an inverse power law, otherwise a different extreme value statistic or *none at all* applies. The required form of distribution from which an extreme selection has to be made is one that applies to the size distribution of scaling systems [10.65] such as percolation clusters [10.66] for example. So even with this stochastic approach we are led back to a system for which the dynamics scale in some way.

The Dissado–Hill function [10.23, 24] for which the response function obeys (10.22) also has scaling features as its basis, however unlike the other approaches it starts with the vibration dynamics of the system. It is assumed that a dipole that can reorient couples local vibration modes to itself. These are no longer extended normal modes but modes centred on the dipole that reduce in frequency according to the molecular mass involved. Their frequencies lie in the region between optical modes and the relaxation frequency and have a scaling relationship one to another. In the theory of *Nigmatullin* and *Le Mehaute* [10.67, 68], the modes are impulses that are involved in the dipole relaxation process whose time of action is scaled, i. e. the longer the time of action the more correlated they are to the dipole motion. In general these modes are local versions of coupled optical and acoustic modes and it is not surprising that they extend to such low frequencies as those involved in relaxation, as acoustic modes essentially extend to zero frequency. Their coupling with the dipole leads to the high-frequency power law of (10.20), where n expresses the extent to which the dipole reorientation couples to the surroundings, i. e. $n = 0$ corresponds to no coupling and the dipole moves independently of its surroundings, and $n = 1$ corresponds to full coupling in which the dipole motion is just part of the local mode. In a sense the short-time development of the response function of (10.22) is that of the changes in the configuration entropy as various amounts of different local modes are progressively coupled into the dipole motion [10.23]. In this case there is no necessity for n to be temperature dependent. At the characteristic relaxation frequency, the *characteristic* dipole group relaxes and transfers energy to the heat bath. The low-frequency behaviour of (10.21) is the result of a distribution in the ensemble of locally coupled dipole motions. This occurs because the motions of local dipole centres may be weakly coupled to one another. As a result the relaxation of the centres proceeds in a scaled or self-similar manner. First the dipole in a local centre relaxes with respect to its own environment, this leaves each dipole centre unrelaxed with respect to one another. Next groups of dipole centres, with some arrangement depending upon the specific structure involved, relax as a group. Then groups of groups relax and so on. Each level of inter-group complexity essentially has a time scale associated with its relaxation that cannot be reached until the preceding level has been completed. This is rather similar to the constraint relaxation concept of *Palmer* et al. [10.60]. The power-law exponent m expresses the way that this hierarchy of relaxing groups is scaled, by defining the power-law tail of the distribution of inter-group relaxation times in the ensemble [10.69]. A value of $m = 1$ corresponds to a sequence of inter-group relaxations with a relaxation time that is proportional to the number of groups involved in the sequence [10.69]. This implies that the sequential events are uncorrelated, i. e. the long-time relaxation is a white-noise (random) process [10.23]. When combined together with $n = 0$ the Debye response is recovered. On the other hand a value of m approaching zero corresponds to relaxation times that are a very high power of the number of groups involved [10.69] and indicates a very strong connection between groups at all levels of the hierarchy. This will spread the response to very low frequencies, as observed. Essentially m is a measure of the extent to which energy is transferred to the heat bath (dissipated) at each level of the hierarchy compared to being stored in the inter-group interactions of the next level. Again scaling is at the basis of the theory, but now with two different ways in which it can be involved. This theory is not generally accepted. The controversial parts of the theory are firstly the coupling of the dipole motions with vibration modes, which modifies the oscillator behaviour towards an over-damped form, and secondly the hierarchy of relaxations whereby energy is transferred to the heat bath. However it should be noted that the susceptibility function that results has a general form that agrees well with experiment. In addition the concepts are reasonable given the complexity that is likely to occur in the internal motions once an ideal crystalline regularity is ruled out by the possibility of dipole reorientation. Thus for example this concept would apply to the dipoles involved in the β-response of the glass state as well as correlated motions of dipoles over long distances, since even in a macroscopically rigid material local vibrations take place. In fact the limited regions of local order in a glass phase can be expected to favour such local modes and increase the coupling of the dipole motions with them, as observed.

The Information Content of the Loss Peak Shape

It is clear from the foregoing discussion that for all theoretical models of the loss peak shape the characteristic or loss peak frequency is but the culmination of a process in which subsections of the dipole and environment (with or without dipoles) are mixed into the motion of the dipole centre. In these models the dipole is not an independent entity, but rather an entity that is connected to some extent over a region that may be small or large. This implies that the dipole is not a particle that relaxes on a rigid potential surface independently of its environment. Only the *distribution of relaxation times* approach preserves the latter concept. If the theoretical models are correct they reflect the fact that we are looking at entities that are not truly of molecular scale but are of a mesoscopic nature. The correlations noted to occur in χ_0 and the need to use free energy rather than potential surfaces in describing the relaxation frequency support this view. The local entities involved are however not rigid features like permanent dipoles, and for this reason we should expect there to be weak connections between them that can be expected to relate to the way in which the relaxation of the whole system takes place. That is, not all entities relax at the characteristic time. As one entity relaxes its neighbours have to come into equilibrium with its new orientation and the system approaches equilibrium more slowly [i. e. as the time power law $t^{-(1+m)}$] than the exponential behaviour of the Debye response function or the expanded exponential function. The information contained in the loss peak shape indicates the way in which a dipole density fluctuation evolves from its state when initially created to an ensemble of mesoscopic dipole centres. The broadening of the peak from that of a Debye peak indicates the involvement of faster and slower processes as part of the overall mechanism, whatever their detailed origin, and in particular processes that have a scale relationship to one another. This must apply even to a distribution of relaxation times because of the unique form required for that distribution. Equation (10.22) implies an equivalent description that refers the overall relaxation process to a conversion of the vibration oscillation at short times to an overdamped motion as the dipole density fluctuation dissipates its energy irreversibly. In this sense evaluation of the shape parameters n and m give a means of describing this conversion process. At the very least they give a sense of the scaling involved in spreading the relaxation process around the characteristic relaxation frequency or equivalently the characteristic relaxation time.

10.4 Charge Transport

All dielectrics possess a constant (DC) conductivity (σ_{DC}), although usually it is very weak. Since $\chi''(\omega) = \sigma(\omega)/\omega$ as demonstrated in Sect. 10.1 (10.10), it would be expected that a dielectric response at low frequencies ($f \lesssim 10^{-2}$ Hz) would take a form in which $\chi''(\omega) = \sigma_{\mathrm{DC}}/\omega$ and χ' is independent of frequency. In many cases however the conduction process is blocked at the electrodes or internal interfaces. In this case the DC conduction charges the interface, which behaves as a capacitor, and the whole system behaves as a single dipole. As long as the interface does not possess relaxation dynamics of its own, the response that would be observed is that given by the Debye response of (10.18, 10.19), with $\tau = 1/\gamma = RC_{\mathrm{i}}$, where R is the resistance of the body of the material and C_{i} is the capacitance of the interface. The measured dielectric increment $\chi_0 = dC_{\mathrm{i}}/A$, where A is the electrode area and d is the sample thickness, and can be very large depending upon the ratio of the sample thickness to that of the interface. The situation where the interface has a frequency-dependent capacitance has been thoroughly discussed by *Jonscher* [10.6] who has shown that $\chi'_{\mathrm{r}}(\omega)$ is modified from $\chi'_{\mathrm{r}}(\omega) \propto \omega^{-2} (\omega > \gamma)$ to $\chi'_{\mathrm{r}}(\omega) \propto \omega^{-q}$, while $\chi''_{\mathrm{r}}(\omega) \propto (1/\omega)(\omega > \gamma)$ as in (10.19). The value of q lies in the range $1 < q < 2$ with its value depending upon the frequency dependence of the interface capacitance.

The bulk DC conductance arises from charged particles whose movements are not bound to a charge of the opposite polarity as in dipoles but are free to move independently of their countercharge, resulting in a net charge displacement in the same way that a liquid flows. However the transport of charged particles within the body of the sample can give rise to a very different form of response when their movement lies along defined paths such that the longer the displacement of the charge the lower the number of paths or equivalently the more difficult the transport becomes. This behaviour was called low-frequency dispersion by *Jonscher* [10.6, 20] and quasi-DC conduction (q-DC) in the theoretical model of *Dissado* and *Hill* [10.70] who wished to distinguish it from low-frequency dipole responses. At frequencies below some characteristic value ω_c this form of response takes the form,

$$\sigma(\omega) \propto \omega^{1-p}$$
$$\left[\text{i. e. } \chi_r''(\omega) \propto \chi_r'(\omega) \propto \omega^{-p}\right] , \quad \omega < \omega_c \qquad (10.44)$$

and at frequencies above ω_c,

$$\sigma(\omega) \propto \omega^{n}$$
$$\left[\text{i. e. } \chi_r''(\omega) \propto \chi_r'(\omega) \propto \omega^{n-1}\right] , \quad \omega > \omega_c . \qquad (10.45)$$

The power-law exponents p in (10.44) and n in (10.45) have positive fractional values near to unity. It is obviously difficult to identify a value of p close to unity from measurements of $\chi_r''(\omega)$ [or equivalently $\sigma(\omega)$] and in many cases it is assumed that the measured behaviour shows a static (DC) conductivity. It is then common to subtract its supposed value from the measured data for $\sigma(\omega)$ to obtain an expression for the dipole relaxation response supposedly responsible for the behaviour at $\omega > \omega_c$. The values obtained in this way for $\chi_r''(\omega)$ at frequencies $\omega < \omega_c$ will not be zero as $\sigma(\omega)$ is not in fact constant, instead they will reduce as the frequency is reduced. This procedure yields a spurious loss peak in $\chi_r''(\omega)$ if the response is actually due to the q-DC mechanism, for which the high-frequency behaviour is an essential component of the whole q-DC mechanism and can never be resolved as a separate peak in $\chi_r''(\omega)$. The way to be certain that the response is really of the q-DC form is to measure the frequency response for $\chi_r'(\omega)$ and show that it takes the same frequency dependence. A convenient check is to determine the ratio of $\chi_r''(\omega)$ to $\chi_r'(\omega)$ (i. e. $\tan\delta$) which will have a constant value [10.6, 20] given by

$$\chi_r''(\omega)/\chi_r'(\omega) = \tan\delta = \cot[(1-p)\pi/2] . \qquad (10.46)$$

Here $\tan\delta$ is called the loss tangent and δ is the phase angle between the real and imaginary components of the susceptibility. This relationship holds for pairs of values of $\chi_r'(\omega)$ and $\chi_r''(\omega)$ at the same frequency even if the measurements are noisy and so make it difficult to determine accurately the value of p from the frequency dependence. Another situation where it is difficult to detect the q-DC behaviour occurs in heterogeneous materials when one component has a low DC conductivity. This will add to the AC component, (10.44) and obscure the q-DC behaviour. In this case the DC conductivity can be eliminated from the data, if it is available over a large enough frequency range, by applying the Kramers–Kronig transform of (10.25) to obtain the function $\chi_r''(\omega)$ without the DC component (σ_{DC}/ω). The validity of the procedure can be checked by applying the inverse transform (10.24) to the measured data for $\chi_r''(\omega)$. This should yield the measured $\chi_r'(\omega)$ since the DC conductivity does not contribute to the real component of the susceptibility.

The q-DC behaviour, (Fig. 10.10a), is most often found in materials that are heterogeneous on a mesoscopic scale such as ceramics [10.71], rocks [10.72], porous structures [10.73], and biological systems [10.74]. In these materials charged particles are transported via structured paths over some finite range. The transported charge and its countercharge give rise to an effective dipole with a large dipole moment. However the q-DC behaviour rarely appears as an isolated response. Because of the heterogeneous nature of the materials it is usually found to be electrically in series with other dielectric response elements such as interface capacitances, and electrically in parallel with a capacitive circuit element. The origin of the q-DC behaviour lies in a hidden scale relationship, with the dipole contribution to the susceptibility increment and its relaxation time both being a power of the length over which the transport takes place. The circuit models of *Dissado* and *Hill* et al. [10.8, 75] show how this behaviour can be produced when the system is represented by a geometrically self-similar arrangement of transport paths and blocking capacitive regions. Such geometrical regularity is not essential however [10.76]; a random arrangement of conductors (transport paths) in a dielectric (i. e. residual set of capacitances) will also result in the q-DC behaviour. It is clear that this construction yields percolation clusters below the size necessary to span the material, and these sub-percolation clusters will of necessity possess scaling relationships dependent on their size and the number of paths within them, and between clusters of different sizes. Such percolation systems also show q-DC behaviour when below their critical limit [10.77]. The theory proposed in [10.70]

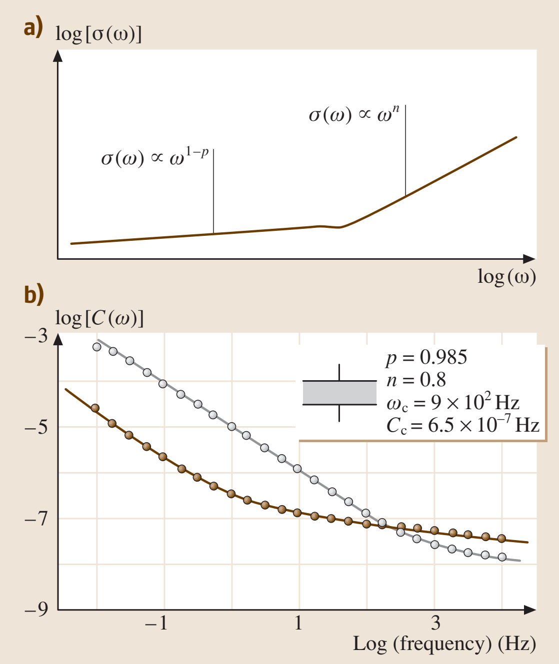

Fig. 10.10 **(a)** A schematic representation of the frequency dependence of $\sigma(\omega)$ for the q-DC process, **(b)** the equivalent q-DC susceptibility function $\chi(\omega)/\chi_c \propto (1+i\omega\tau)^{n-1}\,{}_2F_1[1-n;\, 1+p;\, 2-n;\, (1+i\omega\tau)^{-1}]$ derived from the response function of (10.47) fitted to data from the leaf of *Nicotania* (Solanaceae), the *inset* gives the fitting parameters, with $\omega_c \equiv 1/\tau$, and $C_c \equiv \chi_c$. This data was chosen as it exhibits an isolated q-DC process. As before ${}_2F_1(,;;)$ is the Gaussian hypergeometric function; see [10.25]. After [10.79]

described the q-DC mechanism in similar terms to that used in percolation theory. At high frequencies they assumed that the charged particles had a short range of motion restricted to local clusters in which they were bound to their countercharges. The power-law exponent n reflected the extent of binding of the motions of the charges in the cluster and the local motions in the same way as for the dipole motions. Its value close to one indicates that the binding is strong and that the polarisation of the local clusters increases only to a small extent as the frequency is lowered, i. e. the net displacement of positive and negative charge is local and small. At the characteristic frequency the charged particles become free of their locality and are able to move over much longer distances. The range allowed by the AC frequency increases as the frequency reduces, but the number of effective routes decreases as the distance becomes longer and hence the current becomes smaller. This leads to the weak dependence of the conductivity upon the AC frequency defined in (10.44). In the zero-frequency limit $\sigma(\omega) = 0$, which means that there are no paths across a system of infinite length, i. e. the system is formally below the percolation limit. Of course in reality the sample is of finite size and some routes may cross the sample, leading to a termination of the q-DC behaviour at low frequencies, either by a blocking capacitance at the electrodes or a weak DC current [10.78]. The theory leads to an analytical expression for the q-DC susceptibility in terms of a confluent hypergeometric function [10.25] (see [10.70] for the detailed expression), which is obtained from a response function that obeys an equation of motion similar to that of the permanent dipoles

$$\frac{d^2\phi}{dt^2} + \frac{(2+n+t/\tau)}{t}\frac{d\phi}{dt} + \frac{[n+(t/\tau)(1-p)]}{t^2}\phi = 0\,. \tag{10.47}$$

At times $t < \tau = 1/\omega_c$ the behaviour of the dipole density fluctuation is the same as that appropriate for permanent dipoles (10.22) with the same limiting solution, i. e. $\phi(t) \propto t^{-n}$ at $t < \tau$. At long times $t > \tau = 1/\omega_c$, however, it takes a different form in which the dipolar fluctuation relaxation has only a weak dependence on t, i. e. $\phi(t) \propto t^{p-1}$ at $t > \tau$. An example of the q-DC behaviour in frequency is given in Fig. 10.10b. The reader is referred to [10.74, 79, 80] for other examples.

In the limit of $p = 1[\sigma(\omega) = \text{constant};\, \omega < \omega_c]$, the last term of (10.47) is zero in the limit $t > \tau$ at which time the decay of ϕ is governed by the first two terms. The solution for $\phi(t)$ now takes the form

$$\begin{aligned} &\phi(t) \propto t^{-n}\,, \quad t < \tau\,, \\ &\phi(t) \propto \exp(-t/\tau)\,, \quad t > \tau\,. \end{aligned} \tag{10.48}$$

In this case we can see that the dipole density fluctuations are produced within the local clusters and that they relax by freeing the charges to move independently at $t = \tau$. At this time there is a density of completely free charged particles with charge and countercharge cancelling throughout the system giving a net dipole of zero as in a true DC-conduction process.

10.5 A Few Final Comments

The basic difficulty associated with the interpretation of dielectric responses is that they are of necessity macroscopic measurements made on samples that contain enormous numbers of atoms and molecules. In condensed-phase materials it is not possible to consider these systems as made up of local entities each moving independently of one another. All entities that contribute a permanent dipole are part of the condensed-phase structure, and even though they have a degree of freedom associated with the possibility of dipole reorientation, they will have motions that are correlated or connected to some extent to the molecules/atoms in their environment. This means that dipole reorientation is not that of a bare entity; instead it involves to some extent a local region. These regions will behave differently in different kinds of material and their definition and the way of describing their behaviour has not yet been established with any sort of rigour. Since we are dealing with a macroscopic measurement, there will of necessity be an ensemble of the local entities. This will result in a distribution of entities, but since these are part of the structure there will be some sort of connection between them unless the structure itself is disconnected dynamically. This means that fluctuations will take place among our entities, and perhaps even dissociation and amalgamation. These effects will also have an influence on the relaxation dynamics. In the foregoing I have tried to give some simple pictures as to what is happening and to do so in a holistic way by correlating information from different facets of the measurement. What is abundantly clear is that the dynamics of such systems are very complicated in detail, but I hope that I have done enough to convince you that there are some basic features of the relaxation process that are common to all systems of this type, even though a full understanding of their nature does not yet exist.

References

10.1 P. Debye: *Polar Molecules* (Dover, New York 1945)
10.2 C. P. Smyth: *Dielectric Behaviour and Structure* (McGraw–Hill, New York 1955)
10.3 N. G. McCrum, B. E. Read, G. Williams: *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York 1967)
10.4 V. V. Daniels: *Dielectric Relaxation* (Academic, New York 1967)
10.5 C. J. F. Bottcher, P. Bordewijk: *Theory of Electric Polarisation*, Vol. I,II (Elesvier, Amsterdam 1978)
10.6 A. K. Jonscher: *Dielectric Relaxation in Solids* (Chelsea Dielectric, London 1983)
10.7 K. L. Ngai, G. B. Wright (Eds.): Relaxations in Complex Systems. In: *Proc. The International Discussion Meeting on Relaxations in Complex Systems* (Elsevier, Amsterdam 1991)
10.8 R. M. Hill: Electronic Materials from Silicon to Organics. In: *Dielectric properties and materials*, ed. by L. S. Miller, J. B. Mullin (Plenum, New York 1991) pp. 253–285
10.9 T. Furukawa: IEEE Trans. E.I. **24**, 375 (1989)
10.10 C. J. F. Bottcher: *Theory of Electric Polarisation* (Elsevier, Amsterdam 1952) p. 206
10.11 M. Born, E. Wolf: *Principles of Optics* (Pergamon, Oxford 1965)
10.12 A. R. von Hippel (ed.): *Dielectric Materials and Applications* (Wiley, New York 1958)
10.13 R. N. Clarke, A. Gregory, D. Connell, M. Patrick, I. Youngs, G. Hill: Guide to the Characterisation of Dielectric Materials at RF and Microwave Frequencies. In: *NPL Good Practice Guide* (Pub. Inst. Measurement and Control, London 2003)
10.14 W. Heitler: *The Quantum Theory of Radiation*, 3rd edn. (Dover, London 1984)
10.15 D. Bohm, D. Pines: Phys. Rev. **82**, 625 (1951)
10.16 H. Eyring, J. Walter, G. E. Kimball: *Quantum Chemistry* (Wiley, New York 1960)
10.17 P. Wheatley: *The Determination of Molecular Structure* (Clarendon, Oxford 1959) Chap. XI
10.18 R. Kubo: Rep. Prog. Phys. **29**, 255–284 (1966)
10.19 R. Kubo: J. Phys. Soc. Jpn. **12**, 570 (1957)
10.20 A. K. Jonscher: J. Phys. D Appl. Phys. **32**, R57 (1999)
10.21 S. Havriliak, S. Negami: J. Polym. Sci. C **14**, 99 (1966)
10.22 S. Jr. Havriliak, S. J. Havriliak: *Dielectric and Mechanical Relaxation in Materials* (Hanser, New York 1997)
10.23 L. A. Dissado, R. M. Hill: Proc. R. Soc. London **390**(A), 131 (1983)
10.24 L. A. Dissado, R. R. Nigmatullin, R. M. Hill: Dynamical Processes in Condensed Matter. In: *Adv. Chem. Phys*, Vol. LXIII, ed. by R. Evans M. (Wiley, New York 1985) p. 253
10.25 M. Abramowitz, I. A. Stegun: *Handbook of Mathematical Functions* (Dover, New York 1965)
10.26 L. A. Dissado, R. M. Hill: Chem. Phys. **111**, 193 (1987)
10.27 L. A. Dissado, R. M. Hill: Nature (London) **279**, 685 (1979)
10.28 G. Williams, D. C. Watt: Trans. Farad. Soc. **66**, 80 (1970)
10.29 R. Kohlrausch: Pogg. Ann. Phys. **91**, 198 (1854)

10.30 A. K. Loidl, J. Knorr, R. Hessinger, I. Fehst, U. T. Hochli: J. Non-Cryst. Solids **269**, 131 (1991)

10.31 C. Kittel: *Introduction to Solid State Physics* (Wiley, New York 1966)

10.32 J. Joffrin, A. Levelut: J. Phys. (Paris) **36**, 811 (1975)

10.33 P. C. Hohenberg, B. I. Halperin: Rev. Mod. Phys. **49**, 435–479 (1977)

10.34 J. G. Kirkwood: J. Chem. Phys. **7**, 911 (1939)

10.35 L. A. Dissado, R. M. Hill: Phil. Mag. B **41**, 625–642 (1980)

10.36 L. A. Dissado, M. E. Brown, R. M. Hill: J. Phys. C **16**, 4041–4055 (1983)

10.37 L. A. Dissado, R. M. Hill: J. Phys. C **16**, 4023–4039 (1983)

10.38 H. A. Kramers: Physica **VII**(4), 284–304 (1940)

10.39 R. F. Grote, J. T. Hynes: J. Chem. Phys. **73**, 2715–2732 (1980)

10.40 W. A. Phillips: Proc. R. Soc. London A **319**, 535 (1970)

10.41 J. le G. Gilchrist: Cryogenics **19**, 281 (1979)

10.42 J. le G. Gilchrist: Private communication with R.M. Hill, reported in 10.44, (1978)

10.43 H. Eyring: J. Chem. Phys. **4**, 283 (1936)

10.44 R. M. Hill, L. A. Dissado: J. Phys. C **15**, 5171 (1982)

10.45 S. H. Glarum: J. Chem. Phys. **33**, 1371 (1960)

10.46 C. A. Angell: Encyclopedia of Materials. In: *Science and Technology*, Vol. 4, ed. by K. H. J. Buschow, R. W. Cahn, M. C. Fleming, B. Ilschner, E. J. Kramer, S. Mahajan (Elsevier, New York 2001) pp. 3565–3575

10.47 W. Kauzmann: Chem. Rev. **43**, 219 (1948)

10.48 G. P. Johari, M. Goldstein: J. Chem. Phys. **53**, 2372 (1970)

10.49 M. L. Williams, R. F. Landel, J. D. Ferry: J. Am. Chem. Soc. **77**, 3701 (1955)

10.50 M. Goldstein: J. Chem. Phys. **39**, 3369 (1963)

10.51 D. Turnbull, M. H. Cohen: J. Chem. Phys. **14**, 120 (1961)

10.52 R. R. Nigmatullin, S. I. Osokin, G. Smith: J. Phys. Cond. Matter **15**, 1 (2003)

10.53 R. M. Hill, L. A. Dissado, R. R. Nigmatullin: J. Phys. Cond. Matter **3**, 9773 (1991)

10.54 M. Shablakh, L. A. Dissado, R. M. Hill: J. Chem. Soc. Faraday Trans. 2 **79**, 369 (1983)

10.55 R. Pirc, B. Zeks, P. Goshar: Phys. Chem. Solids **27**, 1219 (1966)

10.56 K. Pathmanathan, L. A. Dissado, R. M. Hill: Mol. Cryst. Liq. Cryst. **135**, 65 (1986)

10.57 K. L. Ngai, A. K. Jonscher, C. T. White: Nature **277**, 185 (1979)

10.58 K. L. Ngai, A. K. Rajgopal, S. Tietler: J. Phys. C **17**, 6611 (1984)

10.59 K. L. Ngai, R. W. Rendell, A. K. Rajgopal, S. Tietler: Ann. Acad. Sci. NY **484**, 150 (1986)

10.60 R. G. Palmer, D. Stein, E. S. Abrahams, P. W. Anderson: Phys. Rev. Lett. **53**, 958 (1984)

10.61 K. Weron: J. Phys. Cond. Matter **4**, 10507 (1992)

10.62 K. Weron, A. Jurlewicz: J. Phys. A **26**, 395 (1993)

10.63 E. J. Gumbel: *Statistics of Extremes* (Columbia University Press, New York 1958)

10.64 J. T. Bendler: J. Stat. Phys. **36**, 625 (1984)

10.65 J. Klafter, M. F. Schlesinger: Proc. Natl. Acad. Sci. **83**, 848 (1986)

10.66 D. Stauffer: *Introduction to Percolation Theory* (Taylor Francis, London 1985)

10.67 R. R. Nigmatullin: Theor. Math. Phys. **90**, 354 (1992)

10.68 R. R. Nigmatullin, A. Le Mehaute: Int. J. Sci. Geores. **8**, 2 (2003)

10.69 L. A. Dissado, R. M. Hill: J. Appl. Phys. **66**, 2511 (1989)

10.70 L. A. Dissado, R. M. Hill: J. Chem. Soc. Faraday Trans. 1 **80**, 325 (1984)

10.71 T. Ramdeen, L. A. Dissado, R. M. Hill: J. Chem. Soc. Faraday Trans. 2 **80**, 325 (1984)

10.72 R. R. Nigmatullin, L. A. Dissado, N. N. Soutougin: J. Phys. D **25**, 113 (1992)

10.73 A. Puzenko, N. Kozlovich, A. Gutina, Yu. Feldman: Phys. Rev. B **60**, 14348 (1999)

10.74 L. A. Dissado: Phys. Med. Biol. **35**, 1487 (1990)

10.75 L. A. Dissado, R.M. Hill: Phys. Rev. B **37**, 3434 (1988)

10.76 D. P. Almond, C. R. Brown: Phys. Rev. Lett. **92**, 157601 (2004)

10.77 Yu. Feldman, N. Kozlovich, Yu. Alexandrov, R. Nigmatullin, Ya. Ryabov: Phys. Rev. E **54**, 20–28 (1996)

10.78 L. A. Dissado, R. M. Hill, C. Pickup, S. H. Zaidi: Appl. Phys. Commun. **5**, 13 (1985)

10.79 R. M. Hill, L. A. Dissado, K. Pathmanathan: J. Biol. Phys. **15**, 2 (1987)

10.80 M. Shablakh, L. A. Dissado, R. M. Hill: J. Biol. Phys. **12**, 63 (1984)