

NON-DEBYE RELAXATION IN CONDENSED MATTER

Proceedings of a Discussion Meeting, Bangalore

Editors: **T V Ramakrishnan**
M Raj Lakshmi

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Introduction

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This book consists mainly of lectures given at a discussion meeting on non-Debye relaxation in condensed matter. The meeting was aimed at focussing attention on a pattern of behaviour common to very different classes of systems. This similarity is beginning to be recognized phenomenologically, but is fundamentally not understood. For example, dielectric relaxation in supercooled liquids, plastic crystals and glasses, spin relaxation in spin glasses and superionic conductors, electron transport in amorphous semiconductors, stress relaxation in glasses, volume relaxation in polymers, all seem to exhibit very similar features. The relaxation spectra are broad, and are not described by a single relaxation time (hence the name non-Debye relaxation). The time scales extended over several orders of magnitude; these glassy systems are relaxing on all time scales. It seems probable (see Ngai, these proceedings) that a single simple phenomenological form fits a great variety of data and successfully relates different properties of a particular system. This form is obviously connected with (the poorly known) low energy excitations in such systems. Considering the wealth of phenomena, the manner in which physically related processes have been studied in isolation and its prevalence as well as fundamental importance for the physics of disordered systems, a discussion meeting was felt to be opportune. This introduction is an interested outsider's impression of the meeting and of the field.

The first talk, expanded out here into a detailed overview of the field, was by Ngai. The overview starts with a rather bewildering list of systems and processes with non-Debye relaxation. From the idea that the basic microscopic transition rate W_0 is muted in a singular way with time i.e. that $W(t) \sim W_0 (t/\tau)^{-n}$, several results follow. One consequence is non-exponential relaxation with time, the form being $p(t) \sim p(0) \exp[-(t/\tau)^{1-n}]$ with $0 < n < 1$. Another is that if the microscopic relaxation is due to an activated process with energy

E_A the effective activation energy $E_A^* = E_A/(1-n)$. These and related conclusions have been checked against the large amount of data existing. For example, E_A^* depends on n which varies with temperature near the glass transition. Since n can be determined independently, and E_A is expected to be a constant for a particular system, the E_A^* equation can be verified separately.

Considering that the fit is to a phenomenological form, there has been surprisingly little assessment of the quality of data and of the statistical content of the fit to the universal form. The data base is more than large enough for a fairly stringent analysis of the best form which fits the data. For example, Jonscher and coworkers believe that two independent indices (say for a.c. dielectric absorption) are needed to fit low and high frequencies, whereas in the Ngai non-exponential form, these two are related. There is no serious comparison yet of their relative statistical accuracy.

Amorphous semiconductors, polymers and systems near glass transition have been investigated extensively by Ngai in regard to their relaxation behaviour which seems again to be of the 'standard' non-Debye form. It is interesting that electronic relaxation (which is basically quantum mechanical) and classical configurational changes both have the same behaviour. A point made is that it is unnatural to separate conductivity into a.c. and d.c. parts with the tacit assumption of different physical origin for the two. This separation is conventional in the field of dielectric relaxation. The a.c. conductivity is ascribed to polarizable bound charge units or to permanent dipoles and the d.c. conductivity to the motion of 'free' charges. Clearly such a separation makes little sense for amorphous semiconductors where electrons are 'bound' to local potential fluctuations, but thermally hop from site to site so that the d.c. conductivity is non-zero.

An interesting aspect of the analysis of stress relaxation in supercooled liquids and glasses is the temperature dependence of the non-Debye parameter n . It increases as the liquid is supercooled and becomes independent of temperature at and below the glass transition T_g . There is an obvious suggestion of some kind of clustering, consequent slowing down of relaxation and freezing around T_g .

Condensed matter physicists became acquainted with wide distribution of relaxation times through the surprising behaviour of glasses at low temperatures ($T \lesssim 1^\circ\text{K}$). The linear specific heat, amplitude and temperature-dependent anomalies in ultrasonic propagation and attenuation etc are common to all glasses. A model for low energy excitations in a glass, the tunnelling or two-level systems model, was first proposed by Anderson, Halperin and Varma. This model ties together a number of cryogenic anomalies, and many novel experiments verify its predictions. A wide distribution of relaxation times and a non-zero density of low energy states can be naturally built into the model. The distribution experimentally is very wide, with time scales ranging from 10^{-8} sec to 10^4 or so seconds. Raychaudhuri, in his review here of low temperature anomalies, shows in detail how these and relaxation spectra of internal friction peaks at intermediate temperatures imply a distribution of relaxation times. The physical nature of these configurationally bistable, weakly connected entities is not known yet. It has been shown recently by Raychaudhuri and Pohl and by Reynolds that their low energy density of states depends inversely on T_g .

A survey of internal friction i.e. attenuation of vibrations in metallic glasses is presented by Purniah. The data clearly exhibit non-Debye relaxation, though in one case, a bizarre form e.g. a combination of split Gaussians is used to fit the data. Ngai, in his review in this volume, has analyzed some of the internal friction data and shows how they fit well into the 'standard' non-Debye scheme.

The density fluctuation excitation spectrum at intermediate energies $\lesssim \hbar\omega_D$ and relatively large wavevectors is probed by inelastic neutron scattering. Experiments on metallic glasses reviewed in this volume by Dasannacharya, strongly suggest that the spectral density of low energy excitations goes as $\omega^{1.5}$ or so, in contrast to ω^2 for phonons in crystalline solids. There is an excess of low energy excitations, the measurements being in the range $(\hbar\omega/k_B) \lesssim 100^\circ\text{K}$ or so. Another interesting observation is of shear modes. Because of the well-developed medium range order in metallic glasses represented by the rather sharp peak in the structure factor $S(q)$, the peak wave vector acts like a reciprocal lattice vector. This leads to umklapp-like scattering

because of which relatively short time scale shear excitations can be probed by neutron scattering. This point needs more careful analysis; so far, one-phonon scattering ideas used in crystals have been applied in their entirety here.

Non-Debye dispersion (in dielectric absorption $\epsilon''(\omega)$) was observed in a class of systems. Mansingh, in this volume, provides background information on the quantities actually measured, assumptions and difficulties involved in extracting dispersion information from this, as well as some models commonly used to interpret results. These models appear artificial and too specific. A brief review of a.c. conductivity of amorphous semiconductors is presented by Narasimhan who details some of the behaviour observed in amorphous elemental and III-V semiconductors.

Spin glass dynamics is discussed here by Dasgupta and by Deepak Kumar. In the last few years, it is being realized that dynamics is the key to the spin glass problem. For the Sherrington-Kirkpatrick model (infinite range interaction between Ising spins), the dynamics seems well understood, from computer simulation (Young and coworkers) as well as analytical work (Sompolinsky and others) as described by Dasgupta. The general picture is of many ground states or minima in configuration space. For a finite N spin system, and with the Gaussian random exchange interaction (centred around $J=0$) it is easy to see that statistically, $N^{1/2}$ spin configurations change and an energy barrier of order $N^{1/4}$ is overcome to go from one minimum to the other. Turning over all N spins takes one to another set of local minima. One is thus led to a spectrum of relaxation times growing as $\exp(CN^{1/4})$. This is generally discussed by Deepak Kumar. Dasgupta also reviews some computer simulation work suggesting that low-lying excitations in S-K spin glasses are spin reversals in small spin clusters (two-level systems). Among the questions not discussed are the relevance of S-K model (with its infinite range interactions and purely statistical origin of barrier heights etc) to other spin glasses, i.e. vector spin glasses with short range interactions. Though it has been speculated that spin glasses and glasses are dynamically similar, there is no serious theoretical or experimental effort to explore this similarity. For example, glassy systems have a ground state (crystal), evolution towards which is kinetically frustrated. However, in spin glasses, the exchange interactions are random and there is no ordered ground state.

Two rather unusual systems that exhibit non-Debye response are briefly described here by Ananthakrishna and Krishan. The former discusses time-dependent large deformation behaviour of solids. The kinetic equations governing the population and effectiveness of strength-determining defects are seen to be nonlinear. The spectral consequences of this for the repeated yield drop phenomenon and for creep have not been yet explored experimentally or theoretically. Krishan discusses the effect of irradiation on metals, where voids grow and coalesce. Here again, the system is far from equilibrium, and the rate equations are nonlinear.

Non-Debye relaxation is fundamentally not understood. A number of models and approaches have been proposed; some are discussed here. One common theme is that of distribution of relaxation times, the idea being that in a random system, relaxation times which depend on local conditions, are random variables. An early and detailed development of this idea is due to Majumdar (this volume) who developed a theory of stress relaxation of glasses in 1970. Assuming stress relaxation to be diffusive, so that the rate depends on the wavevector q as Dq^2 and making different kinds of short range order-dependent assumptions about the effectiveness of relaxational modes of wavelength $\lambda \sim 2\pi/q$, Majumdar found non-exponential relaxation in time, with the exponent taking definite values e.g. $n=2/3$, $1/2$, $2/5$ depending on the nature of short range order. It is an interesting detailed model in which the distribution of relaxation times is introduced at a microscopic level, but several of the basic assumptions, e.g. that basic stress relaxation is purely diffusive, are questionable. A microscopic model in which the distribution of relaxation times is due directly to a spread in intersite coupling, has been described by Dattagupta in this volume. Another common point of view is that the dipole in a disordered dielectric is relaxed instantaneously by a diffusing defect (Glarum model). Kumar has discussed this model here in his theoretical survey. While approximate treatments of defect diffusion lead to non-Debye relaxation, a more exact analysis by Bordewijk shows that the long time relaxation in this model is Debye-like. This conclusion seems relatively unknown, and the model enjoys wide currency. An interesting proposal for the origin of non-Debye relaxation has been made by Dhar (this volume). In a random system, there

are spatially localized eigenstates. For low energies E , their density goes as $\exp(-(E^{1/d})$ where d is the system dimensionality. Dhar suggests that these localized states control the long time-scale relaxation of the random system. The general idea, namely that some localized states determine relaxation, is quite attractive; most likely the long time relaxation is influenced crucially by the states near the mobility edge. These are large in extent and fluctuate strongly in amplitude, and have logarithmic anomalies associated with their diffusion.

The idea of infrared divergent response in a disordered system, introduced by Ngai, is discussed here at some length by Ngai and Rajagopal. The relaxing dipole (for example) is coupled to low-lying excitations of the disordered system or of the bath. The density of these states is assumed to be proportional to energy. Further, these excitations are assumed boson-like, so that multiple configurational excitations are possible and have the standard Bose probability factor. Under these assumptions, none of which is clear, a nonexponential relaxation form results. A new derivation, given by Ngai and Rajagopal, considers a relaxing two-level species coupled to the bath degrees of freedom. As the former relaxes the entropy ΔS of the bath decreases. If it decreases logarithmically with time, the nonexponential relaxation form follows. Ngai and Rajagopal show that a specific form of bath density of states and of the relaxation process leads to such a logarithmic decrease in ΔS . The physical nature of the 'bath' states, and the reason why this kind of picture is relevant for glassy systems but not, say, for crystals, are not clear.

It is clear that some very interesting physics is to be understood here. The phenomena unmistakably point to a deep similarity of relaxation processes in glassy systems. We do not know what these processes are and the nature of this similarity.

It is more than three years since the discussion meeting took place. In this time the problem of slow or glassy relaxation has moved to centre stage in condensed matter physics, thus making this survey of experimental facts and theoretical speculations relevant and timely. A number of interesting scenarios for glassy dynamics have been proposed recently; we mention some of these below for completeness.

Randeria et al (1985), considering spin glasses, point out that in the temperature range between T_{SG} (the spin glass transition temperature) and T_C (the ferromagnetic transition temperature the system would have had for a purely ferromagnetic interaction), there are always ferromagnetic spin clusters (Griffiths clusters). These are the most slowly relaxing species, and control the long term relaxation which has the form $\exp\{-c(\ln t)^{d/(d-1)}\}$ where d is the dimensionality of the system. The idea that such Lifshitz states determine the long term dynamics was first proposed by Dhar in this conference (see Dhar, these proceedings). Below the spin glass transition temperature, the low-lying excitations in short range Ising spin glasses are argued by Fisher and Huse (1986) to be flips (by reversal of all constituent spins) of spin clusters. Assuming that the density of zero energy excitations as well as the activation barrier energies scale with powers of the droplet or cluster size L , they find essentially logarithmically slow decay of the spin-spin auto-correlation function. A detailed microscopic picture of spin glass dynamics in terms of barely localized random J_{ij} eigenstates (the relevant slow interacting modes) has been presented by Ioffe and Feigelman (1985).

An interesting geometrical picture of relaxation in terms of proliferation and accessibility of states of the system (in state space) has been described by Mezard et al (1984) for spin glasses. The system is initially in state 0, one of a large number of configurational states 0, 1, ..., $N-1$ with nearly equal energy. The relaxation is sequential or hierarchical, a one-step relaxation is from 0 to 1 and the activation energy is ϵ_1 , a two-step relaxation is from 0 to 2 or 3 and the activation energy is ϵ_2 , a three-step relaxation can be to one of 2^{3-1} states, with energy barrier ϵ_3 and so on. Identical relaxation scenarios govern relaxation from any starting state to its surroundings. This describes an ultrametric topology in the space of states. The dependence of ϵ_m on m determines the long term relaxation behaviour. Ogielski and Stein (1985) have exactly solved a model of this sort, and find a Kohlrausch or fractional (stretched) exponential relaxation form for $\epsilon_m \sim \ln m$, a marginal case.

A related abstract scenario was proposed by Palmer et al (1984). They suggest that the key to slow relaxation is hierarchically constrained dynamics

or series relaxation. At the n th relaxation step, where the states of system are described by N_n two-level states or Ising spins, the system relaxes only if μ_n of these spins attain one of their 2^{μ_n} equally possible values; relaxation requires a particular configuration to be attained. Depending on the n dependence of N_n and μ_n various kinds of long time relaxation are possible.

Recently, a number of kinetic theory models of shear relaxation in super-cooled liquids near the glass transition regime have appeared (Das et al 1984 and references therein). They use the idea of coupled relaxing shear and density fluctuation modes. Since the theory involves an uncontrolled expansion, the results cannot be considered firm, but are very suggestive of an incipient glass transition and non-Debye relaxation.

The entire field of non-Debye relaxation is thus in a state of active evolution, and the next few years should see our understanding becoming much clearer.

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We thank the contributors for their great patience and apologize for the unconscionable delay in bringing out these proceedings. Obviously very slow relaxation processes have been at work. At a less rhetorical level, it is our belief that while a few papers are undeniably dated, a large number continue to be relevant and may serve as sources of information and insight.

We are very thankful to Mr G. Madhavan and his group at the Indian Academy of Sciences. Without his advice and active help, the typescript would not have been possible, and would look much worse. We apologize for the many imperfections which have escaped our attention.

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Mechanisms for non-Debye relaxation in condensed matter and possibility of universal dielectric response

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Earlier this morning Dr Ngai gave us overwhelming empirical evidence for the occurrence of 'universal' non-Debye relaxation - dielectric as well as mechanical in condensed matter. This universal non-Debye behaviour is perhaps best expressed, for the case of dielectrics, as the Curie-von Schweidler law, namely the algebraic rather than exponential long-time decay of the depolarization current $i_d \sim t^{-n}$ following the removal of the polarizing field. Here $0 < n < 1$. This time-domain spectroscopic result translates into the low frequency power-law behaviour of the dielectric susceptibility $\chi(\omega) \sim \omega^{n-1}$ obeyed over several decades of frequency, from ~ 1 Hz to $\sim 10^9$ Hz i.e., from sub-audio to the microwave frequencies. In point of fact there seem to exist classes of universality parametrized by narrow ranges of the values of the exponent n that may be somewhat temperature-dependent. Thus, e.g. for dipolar systems without freely hopping charge carriers one may find at lower ω a peak in the dielectric loss $\chi''(\omega)$, the so called α or β peak, while for systems with hopping charge carriers one has yet another universal (power-law) behaviour with a small value of $n \lesssim 0.3$ of the exponent. The different ranges of n seem to correspond to certain identifiable class characteristics, e.g. post-peak dispersion in dipolar systems has $n \sim 0.3-0.5$ for liquid like materials and $n > 0.6$ for solid-like materials. For systems with hopping charges, $n \gtrsim 0.6$ at higher frequencies but $n \lesssim 0.3$ for lower frequencies. This evidence for universality is based on almost half-a-century of data, mostly on dielectrics, compiled and reanalysed by Jonscher (1977) and Ngai (1986) in a search for universality. The data analysis covers polar and non-polar liquids, polymers, liquid crystals, amorphous semiconductors and semiconducting glasses, fast-ion conductors, ceramics, MOS and other solid-state interfaces. While it relates mostly to the dielectric data, the study also applies to stress relaxation in supercooled liquids and glasses,

internal friction and ultrasonic attenuation, and magnetic viscosity. It has been extended to phenomena like flicker and $1/f$ noise in conducting materials, DLTS in p-n and Schottky junctions, dispersive transport in chalcogenide glasses and NMR relaxation (Ngai 1980).

This material evidence, taken with an occasional absence of evidence which is not evidence of absence (Jonscher 1977) gives us a compelling reason to look for a possible underlying universal mechanism. And this brings me to the terms of reference of my talk i.e. to acquaint ourselves in about an hour with the known mechanisms that are consistent with the suspected universality of non-Debye behaviour. Let me hasten to add that completeness of any kind is out of the question. None is intended. Basic ideas will be our primary concern. I will thus discuss the three plausible mechanisms involving respectively: (i) distribution of relaxation times, (ii) defect-diffusion controlled relaxation, and (iii) infrared divergent response due to coupling to certain gapless excitations. I will also touch upon the question of the inevitability of non-Debye relaxation.

But first let us begin by asking some elementary questions about non-Debye relaxation. What is it? Well, I could say that it is relaxation against the 'will' of Peter Debye. As to what was his will I could say in the same vein - thou shalt relax exponentially! That is $\psi(t) \sim \exp(-t/\tau)$ where ψ is the response function and the relaxation time. This implies a single relaxation time. Now most systems relax algebraically or sub-exponentially at long times i.e. $\psi(t) \sim t^{-n}$ or $\exp(-t/\tau)^n$ implying a distribution of relaxation times. Hence the problem! It is exponential versus algebraic or sub-exponential. Exponential relaxation is a Debye paradigm and this is being questioned. (It is intimately related to the Markovian-Gaussian assumption made in the stochastic theory of relaxation processes).

Before we proceed further, let us fix our ideas about relaxation. The discussion is implicitly within the linear response theory. Since under most experimental conditions $k_B T \sim 25 \text{ meV} \gg \hbar\omega \leq 10^{-5} \text{ meV}$ we are in the classical regime. Thus the quantum-mechanical (impulse) response function