RELAXATION IN RANDOM BINARY COMPOSITES

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Abstract : Relaxation behaviour in a two-component carbon-wax composite subjected to a voltage greater than onset voltage (V_o) is presented. Relaxation from nonlinear states (between V_o and V_S) is marked by a single stretched exponential ($\beta \sim 0.4$) whereas that from higher voltages ($>V_S$) is characterised by two exponentials (non-Debye type) with $\beta \sim 0.4$ (stretched or sub-exponential) and ~ 1.4 (super exponential) in the early and later time respectively.

Keywords : Composites, nonlinear, dynamical conductance, sub- and super exponential relaxation, onset voltage, saturation voltage.

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1. Introduction

If a dynamical system in equilibrium is perturbed or disturbed by external parameter like voltage (V), temperature (T), external magnetic field (H) etc, it takes variable length of time depending on the dynamics of the system and the magnitude of these external parameters to relax back to the equilibrium state. The cooperative interaction between the constituent microscopic elements drives the systems towards equilibrium. The time taken by the system to come to the equilibrium state from the disturbed state is characterised by the relaxation time (τ). This relaxation time is found to depend on the dynamics of the system. The concept of τ can be easily understood in an *LCR* circuit by solving the first order differential equation for the decay of charge in a fully charged capacitor.

The time evolution of the small departure Δ from equilibrium determines the decay rates and the relaxation behaviour in these systems. The linear relation connecting Δ is given by

$$\frac{d\Delta}{dt} \cdot \frac{\Delta}{\tau} \tag{1}$$

where τ^{-1} is the rate at which the system is driven towards equilibrium from perturbed state. This relation does not take into account the detailed microscopic mechanism [1]. The relaxation time (τ) in a percolative systems shows a critical slowing down near percolation threshold (p_c) and diverges at p_c [2] as:

$$\tau \sim \xi^z \sim (p - p_c)^{-\nu z} \tag{2}$$

where z is the dynamic exponent and ξ is the correlation length with an exponent ν defined by $\xi \sim (\Delta p)^{-\nu}$ where $\Delta p = p - p_c$ [3,4]. But in the glass systems, τ shows a completely different behaviour described by the Vogel-Fulcher law [5,6]:

$$\tau \sim exp[1/(T - T_0)] \tag{3}$$

where T_0 is a fitting parameter and the relaxation time diverges usually at a temperature T_0 different from T_g, the glass transition temperature $(T_0 < T_g)$. The response function $\Delta(t)$ is of the conventional Debye form for a single value of τ. However, a distribution of τ values and its time dependence may lead to non-Debye type relaxation of the form

$$\Delta(t) \sim exp[-(t/\tau)^\beta]. \tag{4}$$

$\beta = 1$ corresponds to the standard Debye form of relaxation and $\beta \neq 1$ gives the stretched or super exponential relaxation behaviour and holds for dielectric, optical, recombination, mechanical, volume, enthalpy, conductivity relaxation etc., independent of whether the relaxation species is an electron, ion, dipole, polymer segment or polymer chain. Recently, this stretched exponential relaxation has been observed in various types of systems like amorphous hydrogenated silicon [1], neural networks [2], spin glasses [7], charge density wave [8], supercooled liquids [9,10] and percolating systems [11-13]. This non-Debye-like relaxation behaviour is generally explained in terms of two scenarios. In the disordered structure, there are a large number of channels for the response function to propagate through the system. Each channel acts as an independent relaxational (Debye-like) process with a particular relaxation time. The overall response of these independent parallel processes with a distribution of relaxation times, $n(\tau)$ is the non-Debye like behaviour. In the

other model, these parallel independent processes are assumed to be strongly coupled so that the dynamics is severely constrained, one needing to relax before another can do so; even if each relaxation site has the same value of τ, the coupling between them ensures that the time domain is effectively stretched, thereby ensuring a non-Debye response. Recognizing the strong similarities of relaxation processes in different random systems like glasses, spin-glasses, polymers, viscous fluids, disordered dielectrics, Ngai et al. [7] found that the common origin of such stretched exponential relaxation behaviour is due to the strong coupling of the relaxing modes to low-energy excitation showing infrared divergence. In these studies the focus was on the parameter τ as a function of magnetic field (H), temperature (T) or conducting fraction (p).

A composite system consists of conductors and insulators and is characterised by the conductor fraction (p). For low value of p, the composite shows insulating behaviour. If the value of p is increased from low, at a certain value of p known as percolation threshold (p_c), the composite starts conducting for the first time. At p_c, a sample spanning cluster (an incipient infinite cluster) is formed. This percolation cluster is known to be fractal [3, 4]. Near p_c various quantities like correlation length (ξ), macroscopic resistance (R), percolation probability ($P(p)$) and noise power $S_v(f)$ at a frequency (f) diverge with their own critical exponents. Resistance tends to diverge as p_c is approached from above: $R \sim (\Delta p)^{-t}$, where t is the conductivity exponent in the limit of $V \to 0$. Measurements of these quatities near p_c reveal that the response is very sluggish and the system takes several hours to relax back from nonlinear state to linear state. To materialise this observation, the relaxation time τ is experimentally measured as a function of voltage in a carbon-wax composite.

2. Experimental

Relaxation measurements were carried out on the disc-shaped (10 mm in diameter, 2 mm in height) carbon-wax samples under dc excitation by sending constant currents at the room temperature. The samples used for studying the relaxation behaviour are similar to the ones as in ref. [14, 15] where further details can be found. This system has a low value of p_c of 0.76% by volume and the transport exponent t equal to 2.1. Resistances of the samples chosen in the present study ranged from few tens of kΩ to MΩ. All measurements were performed using pressed circular brass electrode contacts in the two probe configuration. A programmable constant current source (Keithley, Model 224) was used to send a constant current through the sample and the sample was allowed to stabilise for almost one hour at this current. The voltage across the sample was recorded by using a digital multimeter with an integral time

of 16.66 msec and typically 500 data were stored in a personal computer at
an interval of 250 msec. These data were then averaged to get the average
voltage across the sample. The current was then adjusted to a low value such
that sample is expected to relax back to the linear regime. As soon as the
current was set at this value, the corresponding voltage recording was started
and the data were stored in a file at an interval of 250 msec. The interval
was then changed at some other value and the data were stored. The voltages
were recorded at four such intervals for fixed value of current. The length of
such intervals were chosen according to the resistance of the sample and the
voltage from which the sample was allowed to relax. The intervals were larger
for the larger resistances and the large voltages. Then the current was set at
an another value and the same procedure was repeated.

3. Results and discussions

Fig. 1 shows schematically the behaviour of dynamical conductance (dI/dV)
as a function of the dc bias (V)
at a fixed T and p close to
the percolation threshold. At
very low bias we have the lin-
ear regime ('a') where the con-
ductance is practically constant.
Relaxation in this regime is too
fast to be measured. As V is in-
creased there is a crossover from
linear to nonlinear regime at a
bias V_o called the 'onset' bias
or voltage and the correspond-
ing current is called onset cur-
rent I_o. This onset current I_o

Fig. 1: A schematic diagram showing behaviour
of dynamical conductance dI/dV as a function
of dc bias. The regions are marked as follow:
(a) onset of nonlinearity; (b) saturation; (c) joule
heating and breakdown regime.

scales with the linear conductance Σ_0 [14, 16] as

$$\Sigma_0^x \qquad\qquad (5)$$

where x is the onset exponent. The value of this onset exponent in composite
systems is 1.4 [14, 17]. As the bias increases to V_S the conductance still keeps
on increasing but at a lesser rate. With further increase in the bias, dI/dV
approaches asymtotically a constant value, corresponding to the saturated
state ('b') [15]. The saturated state is fairly wide in the voltage scale. The
nonlinear regime as shown in the figure may be also called 'tunneling' regime.
When a sample relaxes from this region, it takes about few minutes to relax
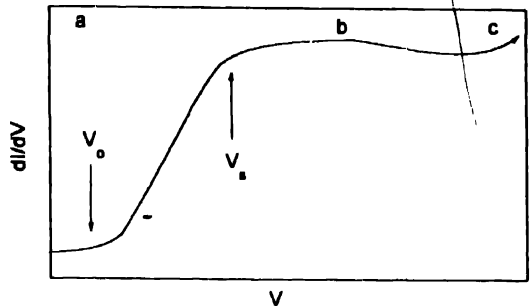
back to the linear region (marked by 'a') and a single value of β is observed. On the other hand, for relaxation from the saturated state, the time to come back to the linear regime is of the order of several hours. Two values of β are observed (~ 0.4 and ~ 1.4). The region marked 'c' is actually the Joule or irreversible regime where the large sample current may causes Σ to decrease a little before leading to irreversible state of breakdown or destruction. This regime is of no interest in the present work.

The sample is initially biased at a voltage $V(= IR(I))$ by sending a current I through it where $R(I)$ is the resistance of the sample at a current I. When the value of the current is set to a lower value I' the voltage across the sample should be $V' = I'R(I)$, if it could be measured. But the system undergoes a very rapid relaxation to a resistance $R(t = 0) > R(I)$ so that the experimentally measured voltage V_{meas} is somewhat greater than the voltage $V'(t = 0)$. With time, $R(I)$ increases towards its linear value R_0 and hence V_{meas} also increases. V_{meas} is normalized by its maximum value and is denoted
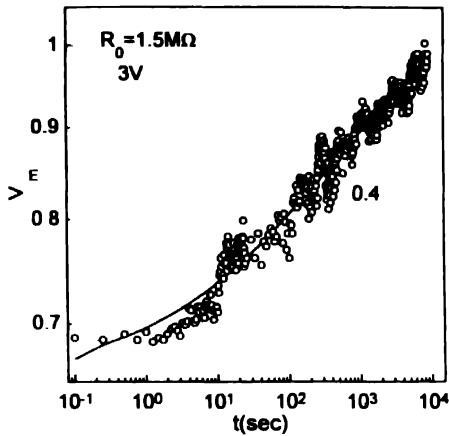

Fig. 2: Log-log plot of normalized voltage V_m vs time t for a sample of linear resistance R_0=1.5MΩ at 3V. The value of β is indicated in the figure.
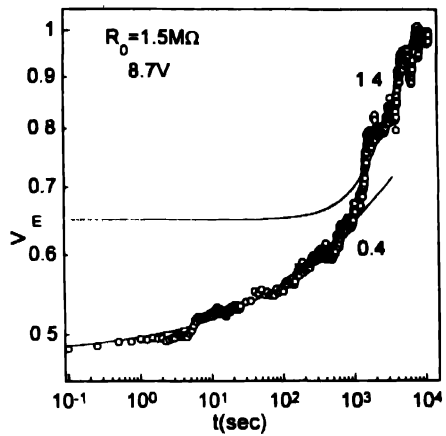
Fig. 3: Log-log plot of normalized voltage V_m vs time t for the same sample as shown in Fig. 2 at 8.7V. The two values of β are indicated in the figure.

by V_m. Fig. 2 shows the typical plot of V_m vs time (t) for a sample of linear resistance R_0=1.5 MΩ at 3 V.The solid line is a fit to the data by the function:

$$V_m(t) = A_0 exp[-(t/\tau)^\beta] \qquad (6)$$

where A_0 is a prefactor. The value of $\ddot{\beta}$ is found to be ≈ 0.4 as indicated in the figure. By measuring the total charge sweeping out from the band-tail states, Kakalios et al. [1] found almost the same value of $\beta(=.45)$ in hydrogenated amorphous silicon at the room temperature. The exponent β

was found to depend on the temperature and increase linearly with it. They explained the stretched exponential behaviour from time dependent relaxation rate. Kriza et al. [8] measured the decay of polarization current as a function of time t in a charge-density-wave compound $K_{0.3}MoO_3$ well below the Peierls transition temperature $(T_p = 180 \ K)$ and found β=0.7, higher than the value observed in the present study. This result was explained by assuming the strong coupling between the different relaxation rates. Recently, Lamaignere et al. [13] experimentally observed the dynamical rupture in a heterogeneous composite of insulating epoxy resin and conducting carbon microbeads. At a current greater than a certain value which leads to irreversible electrical breakdown, the resistance of the composite increases with time and follows a power law behaviour with a exponent $\approx.65$. It may be noted that the samples were in the breakdown regime. So one cannot be sure whether the system reaches equilibrium state or not. A qualitative physical picture for this observation was rationalised by assuming the coupling between the Joule heating due the large current or voltage and postive temperature coefficient of the system resistance. All the works cited above including the present one deal with the relaxation in the reversible regime but this work is done in the irreversible regime. This does not allow comparison with this work

V_m vs t data at 8.7 V has been shown in a log-log plot in Fig. 3 for the same sample as in Fig. 2. Here the sample is allowed to relax from the saturated state i.e from a voltage higher than the saturation voltage V_S. The data could not be fitted to a single function as in eqn. (6). It was found that the data can be divided into two sets and separately fitted by the above mentioned function as in Fig. 2. We get two values of β as indicated in the figure. Thus the relaxation measure-ment in the high voltage $(>V_S)$ confirms that there are two rates by which the system relaxes to the state of zero-voltage resis-tance. The early time exponent

Fig. 4: Semi-log plot of β vs voltage V for two samples. One is the same as shown in Fig. 2 and 3 and other sample is of linear resistance 65kΩ. The solid lines are guides to the eye.

agrees well with the reported value but the later time exponent (~ 1.4) is observed for the first time in a real experiment. Ghosh et al. [2] also found the value of β greater than unity ($\beta \sim 1.3$) in a computer experiment by using
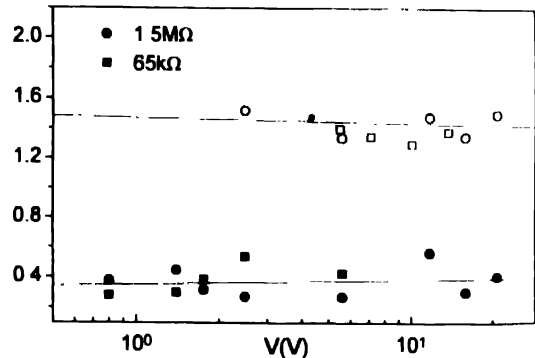
antiferromagnetic interaction with the high value ($\sim$ 15) of the ratio of two exchange interaction in opposite sign.

In Fig. 4 the β values for two carbon-wax samples of linear resistances as shown in the figure have been plotted against the voltage V. This figure clearly indicates the existence of two β values and that these values are pratically independent of V. The dependence of τ on the conducting fraction p will be discussed elsewhere [18].

4. Conclusion

In conclusion, we measured the voltage-dependent relaxation time in a metal-insulator composite in the nonlinear regime and found both sub- and super-exponential behaviour in relaxation.

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