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Nonexponential Decay in Relaxation Phenomena

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A variety of considerations from different points of view including non-Markoffian stochastic processes, basic quantum mechanics and a mechanism based on condensed matter physics, all lead to the fractional exponential decay at long times in relaxation processes. Implications of this decay law and its verifiable predictions in a broad range of phenomena in condensed matter physics are pointed out.

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I. Introduction

Experimental data on relaxation phenomena in diverse areas of condensed matter physics are quite generally found to exhibit slower than exponential decay for long times in the form (see ref. 1 and references therein)

$$\exp[-at^b],\ a>0,\ 0<b<1. \tag{1}$$

The physical origin of this behavior will be discussed here from several points of view. These include the necessity of time dependent transition rates (TDTR) in relaxation theory and their treatment via a time scale transformation, the constraints on the form of the TDTR from quantum mechanical considerations and a theorem in Fourier transforms, the requirements on microscopic distributions in frequency of the underlying relaxing entities such as dipoles or charge carriers from basic probability theory of limit distributions for sums of independent random variables, and consideration of the generalized master equation (GME) with an underlying nonMarkoffian stochastic process with TDTR, all leading to long time nonexponential relaxation given by Eq. (1). We also discuss the relationship of Eq. (1) with the mathematical framework of the continuous time random walk (CTRW), GME, and the H-theorem of statistical mechanics. A quantum mechanical model is described which leads to Eq. (1) and in addition predicts a relaxation time renormalization which alters activation energies, and temperature and molecular weight dependences. These predictions have been verified experimentally in electronic materials, ionic conductors, glasses, polymer melts, and other materials. The calculational ease of the time scale transformation method is demonstrated for an important physical example. The general applicability of Eq. (1) to elucidate the vast array of experimental results in relaxation phenomenon in condensed matter is briefly described. Thus TDTR leading to Eq. (1) is found to be essential in describing relaxation phenomena.

II. Time Scale Transformation

The traditional phenomenological description of relaxation is based on stochastic processes with time independent transition rates (TITR) leading to the usual exponential decay. In view of the experimentally observed nonexponential behavior, given by Eq. (1), it is necessary to consider TDTR in the stochastic theory. We have shown[2] that a special class of TDTR given by, t^{b-1}, can be related to TITR by means of a time scale transformation, for which the relaxation function is of the form Eq. (1) and the time scale transformation is the monomial, $\theta(t) = at^b$. This comes about by the requirement that the TDTR be such that the relaxation function associated with it depend only on the ratio t/τ where τ is a constant characteristic time and in the time transformed frame this process becomes one with TITR with corresponding relaxation function $\exp(-\theta/\tau_s)$ where τ_s is another constant. The only time transformation that has the property $\theta(\tau) = \tau_s$ which converts a TDTR to a TIDR as above is the monomial.

III. The Paley-Wiener Theorem and TDTR

The transition rate can be calculated quantum mechanically and the use of the golden rule leads to TITR. However the golden rule is an approximation and this breaks down whenever the energy difference of the two states between which transitions are taking place goes to zero. In the relaxation regime, typically in the range of 10^{10} Hz and below, such characteristic energy differences may approach zero and a more careful calculation leads to TDTR. A general bound on TDTR is provided by the Paley-Wiener theorem[4] in Fourier transform theory, which is found to lead to a lower bound on the relaxation function in the form Eq. (1). The requirements of the Paley-Wiener theorem in our context are semiboundedness of the energy spectrum of the Hamiltonian and

the quadratic integrability of the relaxing states, both of which are physically acceptable.

The relaxing system is a complex many-body system whose low energy excitations below approximately 10^{10} Hz determine TDTR. A detailed knowledge of the many-body excitations is not available at present. However, the many-body density of states of a random matrix Hamiltonian has been deduced by Wigner sometime ago and this can be used here to obtain TDTR. Interestingly, this also leads to Eq. (1). More details of this dynamical model are given in Sec. VIII.

IV. Limit Distributions of Low Energy Excitations

Given the universal form of the macroscopic relaxation function in Eq. (1), one is led to consider a microscopic mechanism underlying relaxation phenomenon in general. We may think of the relaxing body as being composed of some species of relaxing entities such as electric dipoles in a dielectric, charge carriers in a semiconductor, etc., each of which has identically distributed energy variables with the same energy distribution. The macroscopic energy distribution function $\rho(\varepsilon)$ associated with the relaxing body for low energies is the limit distribution of normalized sums of the microscopic energy variables. A similar procedure is involved in statistical mechanics for deriving equilibrium ensemble distributions. The resulting macroscopic density distribution $\rho(\varepsilon)$ necessarily obeys the relationship[5]

$$\rho(a\varepsilon+b) = (a_1a_2/a)\int_{-\infty}^{\infty}d\varepsilon'\rho(a_1(\varepsilon-\varepsilon')+b)\rho(a_2\varepsilon'+b_2) \tag{2}$$

for every set of parameters $a_i > 0$, b_i with the corresponding $a > 0$, b related to the parameters a_i, b_i. The relaxation function is proportional to the modulus square of the Fourier transform, $|c(t)|^2$, of the energy distribution function $\rho(\varepsilon)$. For distributions obeying Eq. (2) this is necessarily of the form[5]

$$|c(t)|^2 = e^{-a|t|^b}, \quad a>0, \quad 0<b\leq 2 \tag{3}$$

If in addition, the spectrum of the Hamiltonian is semibounded as in Sec. III, then the Paley-Wiener theorem applies and the values of b have to be in the smaller range $0<b<1$, leading us again to Eq. (1). For such microscopic models, we see that the Paley-Wiener bound becomes exact.

V. An Oscillator Relaxation Model

A chain of coupled oscillators can serve as a model of a Brownian particle in contact with a heat bath.[6] For arbitrary oscillator interactions, the Brownian particle obeys a generalized Langevin equation with a time dependent friction coefficient, and a Gaussian random force determined solely by the Hamiltonian of the coupled oscillators and the canonical distribution of the initial coordinates and momenta. The Paley-Wiener theorem[4] can be applied to this problem if the normalized frequency spectrum of the oscillator assembly is bounded from below. The Fourier transform of the spectrum is the momentum autocorrelation function of the single Brownian oscillator and this is then bounded by a function of the form Eq. (1). If the bound is assumed, a time scale transformation can be used to convert the generalized Langevin equation into the classical Langevin equation with a time-independent friction coefficient and a Gaussian white noise random force. Transforming back to the t-frame, we find that the covariance of the external random force takes the form of white noise modulated by a monomial friction coefficient, t^{b-1}. It can be noted that a covariance of the same form is obtained in the long time limit from fractional Brownian motion.[7] However, this connection to fractional Brownian motion is rather tenuous because the form of the noise does not uniquely specify the stochastic equation of motion.

VI. Continuous Time Random Walk and Generalized Master Equation

There exists a mathematical framework of the continuous time random walk (CTRW)[8] and the associated generalized master equation (GME)[9] for studying time-dependent problems. The basic quantity entering the formalism is the waiting time distribution function $\psi(t)$, which is the probability density function for the time between the arrival of a walker at a given lattice point and the initiation of the next step to another site. If the waiting time distribution function is taken as minus the derivative of Eq. (1), then the CTRW framework can be applied to relaxation problems in condensed matter. When the moments μ_m of the waiting time distribution functions are all finite, the Markoffian master equation is an appropriate description for times which are large compared with $t^*=\sup(\mu_m/m!)^{1/m}$. For $\psi(t)$ given by minus the derivative of Eq. (1) it is found that t^* is finite for $1\leq b\leq 2$ and infinite for $0<b<1$.[10] Thus a non-Markoffian description is always required for relaxation functions of the form Eq. (1).

In most applications of CTRW, in order to have a $\psi(t)$ which is universal for all sites, one has to perform an average over all possible configurations of the walkers. This physical picture is inappropriate for materials where short range order exists, which is the common situation in condensed matter. A model, described in Sec. VIII, in which a relaxation function of the form Eq. (1) arises from a fundamental mechanism that is operative at every hop of the walker from any lattice site, produces a $\psi(t)$ universal for all sites without averaging.

VII. CTRW, GME, and the H-Theorem

In CTRW, the weighting time distribution function is related to the memory function of the GME.[9] If the GME is to describe a time-dependent statistical mechanical phenomenon, it must obey the H-theorem, which is a

statement of the second law of thermodynamics. The H-theorem cannot accommodate arbitrary memory functions and therefore also arbitrary waiting time distribution functions. The choice of minus the derivative of Eq. (1) for the waiting time distribution in the CTRW along with the time scale transformation of Sec. II enables us to demonstrate the validity of the H-theorem for this choice.[10]

VIII. Model for Low-Energy Excitations

A model[1] in which a relaxing primary species, such as a reorienting electric dipole, a hopping charge carrier or a flexing polymer chain, interacts with a new class of very low energy states (correlated states or CS) produces a relaxation function of the form Eq. (1) as well as correlates the dispersion with shifts in activation energies, molecular weight dependence, temperature dependence, and other quantities. A random matrix formulation of energy level distributions can be used to study the properties of the CS. It is found that for materials having short-range spatial order, the effect of such CS excitations is to alter a constant TITR τ_o^{-1} to a TDTR given by τ_o^{-1} $\exp(-n\gamma)$ $(\omega_c t)^{-n}$ for times greater than approximately ω_c^{-1}. Here n is a measure of the coupling strength of the CS and is restricted to $0<n<1$. The cutoff frequency ω_c depends on material structure but is typically of the order 10^{10} Hz for glasses, polymers, and amorphous metals and semiconductors, and $\gamma \cong 0.577$.

The above TDTR results in a relaxation function of the form Eq. (1) with $b=1-n$ and a shifted relaxation time $\tau_p \equiv a^{-1/b}$ given by

$$\tau_p = [(1-n)e^{n\gamma}\, \omega_c^n\, \tau_o]^{1/1-n} \tag{4}$$

The CS model is therefore able to identify the physical meaning of the parameters in Eq. (1) and is able to make predictions other than dispersion.

The implications of Eq. (4) are widespread. For example if τ_o is temperature activated with activation energy E_A, then the relaxation process will appear to be activated with energy $E_A^* = E_A/(1-n)$. This prediction has been verified in detail for transient current in chalcogenide glasses.[11] The correct value of E_A^* is predicted from the measured value of E_A and the value of n obtained from the dispersion of the current. In addition, the values of E_A^* correlate correctly with changes in the dispersion as the value of n is changed by doping.

Another result of Eq. (4) is the prediction of molecular weight dependences of viscoelastic quantities for polymer melts.[12] Low molecular weight polymer chains move essentially independently and the relaxation times of these chains scale as M^2. As the molecular weight increases, entanglements with neighboring chains are more frequent and large scale cooperative motions couple via the entanglement junctions to the CS of the polymer system. The longest relaxation times of the chain then scale, by Eq. (4), as $M^{2/(1-n)}$. If, in addition, spatial entanglements are imposed by confining the chain within a tube-like region, quantitatively accurate predictions are obtained concerning the viscosity η (where $\eta \alpha M^{\mu}$), the recoverable compliance J_e^o, the plateau modulus G_N^o and other quantities in the terminal regime for both linear and branched polymers. For linear polymers, n is typically between 0.4 and 0.5, and this results in $3.3 \leq \mu \leq 4$ and $2 \leq J_e^o G_N^o \leq 3$. For branched polymers, as determined from dispersion, n typically has larger values which implies larger μ and $J_e^o G_N^o$. These quantities can simultaneously be correlated with changes in the temperature dependence by the flow activation energy. All these features are in remarkable agreement with data. The ability of this model to describe polymer melt dynamics is far superior to the reptation model.[13] Details of the polymer melt model are presented elsewhere.[12]

Other implications of Eq. (4) include dielectric and structural relaxations near T_g for polymers and small molecule glasses,[14] γ relaxation of bulk polycarbonate,[15] and volume recovery[16] of PVAC. Thus the dispersion given by Eq. (1) and the shifted relaxation times given by Eq. (4) play important roles in a large number of materials and relaxation phenomena.

IX. Calculations Using Time Scale Transformations

Within the model of CS excitations of Sec. VIII, the time scale transformation of Sec. II becomes $\theta(t)=A_n t^{1-n}$ where $A_n=(1-n)^{-1}e^{-n\gamma}\omega_c^{-n}$. The use of this technique considerably simplifies calculations of relaxation phenomena. This is illustrated here by considering hole transport across a biased chalcognide glass sample of thickness L. In the θ-frame, hopping relaxation at any site will have the same time independent transition rate W_s. The current in the θ-frame, $I(\theta)$, is easily determined and the transient current in the laboratory t-frame can be calculated by $I(t)=I(\theta)(d\theta/dt)$. With $\theta(t)$ given as above, it is found that $I(t)\alpha t^{-n}$ for $t<<t_T$ and a more rapid drop-off for $t>>t_T$. The transit time $t_T\alpha(E/LW_s)^{1/1-n}$ exhibits superlinear thickness and electric field dependences and is thermally activated with energy $E_A^*=E_A/(1-n)$ if W_s is thermally activated with energy E_A.[1]

X. Applicability of Fractional Exponential Relaxation

The fractional exponential relaxation function given by Eq. (1) along with the shifted relaxation times of Eq. (4) lead to unifying predictions in many fields and materials. These include dielectric relaxation, viscoelastic relaxation, nuclear spin relaxation, flicker 1/f noise, generation-recombination noise, transient electrical transport, transient capacitance, photoluminescence, volume and enthalpy recovery, physical aging, plasticity and yielding, and polymer melt dynamics. Further study can be expected both

to yield deeper insight into the nature of low frequency fluctuation, dissipation and relaxation phenomena in condensed matter, and to result in predictions for many other materials and applications.

XI. Summary and Conclusions

The dominance of fractional time exponential relaxation of the form Eq. (1) in diverse phenomena has been emphasized here. Such relaxation functions require that the accompanying transition rates have power law time dependences. These dependences can be physically motivated in several different ways. However the dispersion of the relaxation predicted b q. (1) is observed to correlate with several physical quantities includin tivation energies, and temperature and molecular weight dependences. A ph model in which a relaxing species interacts with a set of low energy states is able to predict such correlations. It is important to stress that a proper description of relaxation requires not only fractional powers of time in the dispersion as in Eq. (1), but also relaxation times which shift with changes in dispersion as in Eq. (4).

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