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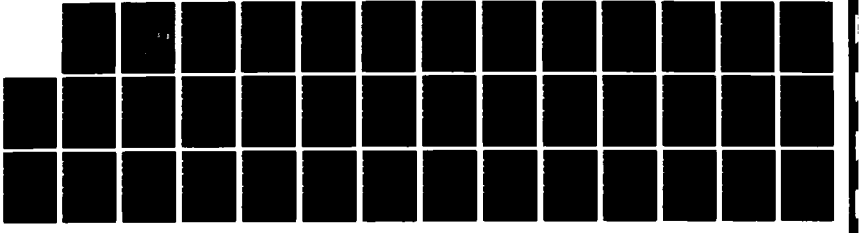

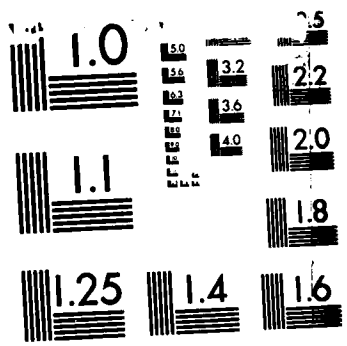

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An Examination of Models of Relaxation in Complex Systems
I. Continuous Time Random Walk (CTRW) Models

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Models of relaxation in complex systems based on the continuous time random walk (CTRW) formalism are examined on the basis of: (1) their robustness; (2) the nature of technical procedures employed; (3) the appropriateness of assumptions when subjected to physical tests; (4) the inclusion of a description of established experimental results; and (5) the consistency of predictions with experimental results. Inadequacies of the CTRW models are shown to exist for all these features. It is concluded that CTRW models, as they exist today, must be rejected as viable descriptions of the relaxation process in complex systems.

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CONTENTS

AN EXAMINATION OF MODELS OF RELAXATION IN COMPLEX SYSTEMS
I. Continuous Time Random Walk (CTRW) Models

A. Introduction

We initiate here a detailed examination of existing models of relaxation in glass-forming materials. In general, our considerations will include: (1) the robustness of the models; (2) technical procedures employed; (3) physical tests of assumptions; (4) predictability. A model is robust if it is insensitive to untestable or omitted details while being consistent with tests of premises and established facts. The predictability of a model is determined by its capability to generate new predictions that are actually verified empirically.

In this report we consider relaxation models [1,2] based on the continuous time random walk (CTRW) formalism [3]. In these models, mobile random walkers identified as defects move on a lattice in a sequence of steps and pauses, and cause relaxation of the entities of interest which are located at lattice points. The entities of interest will be designated the relaxors. The basic function entering into these models is the pausing time distribution $\psi(t)$ which must be specified either by assumption or by a further model within a model. Although the nature of the defects and the physical mechanism of defect-relaxor interaction is left unspecified, the models based on CTRW do include an assumption about whether N, the number of defects per relaxor, is large or not.

As will be discussed below, for a given $\psi(t)$, different relaxation functions are obtained depending on which of the above assumptions about N are made [4,5,6]. Since typically no information is provided on the identities of

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the defect and the relaxor, either assumption must be considered ad hoc physically. However, there are physical systems which are also glass-formers and have mobile entities which can be considered as random walkers in a CTRW framework. Such physical situations provide a useful testing ground for the validity of the assumptions used in relaxation models based on CTRW. Then the CTRW models can be evaluated according to the considerations mentioned above: (1) Their robustness can be tested on the basis of the sensitivity of the dependence of the calculated relaxation function on the assumption made for form of the pausing time distribution $\phi(t)$, and also on the assumption made for N, the number of defects per relaxor. (2) Their technical soundness can be assessed by careful evaluation of the assumptions used and modelling proposed for $\phi(t)$. (3) The general assumptions can be tested physically by their consistency with observed phenomena in physical situations that involve random walkers. (4) Predictability can be tested by either the comparison of predicted phenomena with observed results or the absence of descriptive power in dealing with established phenomena.

The relaxation model based on CTRW proposed by Shlesinger and Montroll (SM) [1] which is a generalization of earlier defect diffusion models of Glarum and others [7] is representative of the class of CTRW relaxation models. We will focus attention on the SM model. A representative example of modelling of $\phi(t)$ has been provided by Bendler and Shlesinger (BS) [2], and this work will also be reviewed in detail.

B. Robustness

As mentioned above, a model of dielectric relaxation based on CTRW has been promulgated by Shlesinger and Montroll (SM) [1]. This model is a generalization of the defect diffusion models of Glarum and others [7] which assume that the physical system contains two types of physical species: frozen

dipoles and mobile defects. On reaching the site of a frozen dipole, a mobile defect causes the dipole to relax. That is, a contact interaction between dipole and dipole is assumed but no physical mechanism is specified.

In the SM model, a frozen dipole is at the origin of a lattice and, at t=0, the defects lie with equal probability at any lattice point. Diffusion of the defects is executed as a continuous-time random walk [3] composed of a sequence of steps and pauses. The pausing time distribution function $\psi(t)$ is assumed to have a power law form at sufficiently long time

$$\psi(t) \sim At^{-1-\alpha}, \quad 0<\alpha<1, \quad t\to\infty \tag{1}$$

The complete distribution function must be normalizable

$$\int_0^\infty dt\psi(t) = 1. \tag{2}$$

Obviously, the form of Eq. (1) cannot be extrapolated back to short times and still satisfy the normalization requirement of Eq. (2). The form of $\psi(t)$ at short times has not been specified in the model. As will be detailed below, the model [1] then commits to the assumption that N, the number of defects per dipole, is large. The defects and the dipole are not assigned explicit physical identities. Therefore, any assumption concerning the relative number of defects (e.g. large, equal, etc.) to dipoles or relaxors does not have a direct physical basis. Sensitivity to the assumption about relative number of defects that will be shown to exist reveals one lack of robustness in CTRW models.

SM follow Tachiya [6] in the derivation of the equation for the survival probability of dipoles. Let N_d be the number of frozen dipoles in a polymeric system or a glass of volume Ω. The system is divided into N_d identical unit cells each of volume $\Omega_d=\Omega/N_d$, and each containing one frozen dipole and N defects. Each dipole is fixed at the origin of its unit cell and, excluding the origin, there are V lattice points for each unit cell. The N defects in

each unit cell are treated as independent and are totally randomly distributed on the V lattice sites. Periodic boundary conditions proposed by Shlesinger [5] are used in each unit cell such that if a defect leaves the cell, it is effectively replaced so that the proper defect number N in each unit cell is maintained. Let $f(\ell,t)$ be the probability density that a defect originally at a lattice point ℓ reaches the origin for the first time at time t. Then $[1-{}_0\int^t dt' f(\ell,t')]$ is the probability that this defect has not reached the origin in the time interval (o,t). The defects are treated as independent so so there is a tacit assumption that they are non-interacting and there are no correlations among the defects. The quantity $\prod_{i=1}^{N}[1-{}_0\int^t dt' f(\ell_i,t')]$ is the probability that none of the N defects has reached the origin in the time interval (o,t). Averaging over the initial uniform distribution of defect positions gives an expression for the survival probability of frozen dipoles (the relaxation function $\phi(t)$) as

$$\phi(t) = \Big[1-\frac{1}{V}\sum_{\ell}\int_o^t dt' f(\ell,t')\Big]^N = \Big[1-\frac{1}{V}\int_o^t dt' I(t')\Big]^N \qquad (3)$$

Here $I(t) \equiv \sum_{\ell\neq o} f(\ell,t)$ is the flux of defects into the dipole. This result has been derived as Equation (20) in Reference [5] and equation (3.5) in Reference [6], and written as Eq. (8) in the work by SM. Now we come to a step in which a critical assumption about the size of N has to be made.

If the number N is large, the right hand side of Eq. (3) can be approximated by an exponential function. With constant defect concentration c=N/V as $N\to\infty$, $V\to\infty$, the dipole relaxation becomes

$$\phi(t) = \exp\Big[-c\int_o^t dt' I(t')\Big] \qquad (4)$$

SM complete their dielectric decay model by relating the flux I(t) to the pausing time distribution $\psi(t)$ of the defects. The relation between the Laplace transforms of I(t) and $\psi(t)$, namely I(u) and $\psi^*(u)$, turns out to be

$$I(u) = \frac{1}{[1-\phi^*(u)]P(o,\phi^*(u))} - 1 \quad , \tag{5}$$

where the specific form of the function $P(o,z)$ depends on the type and dimension of the lattice. SM have only evaluated $I(u)$ for small u which corresponds to the long time regime. They cannot address the short time regime because only the long time behavior of $\phi(t)$ has been specified. For a simple cubic lattice in three dimensions, the SM method of evaluating $I(u)$ leads to $I(u)=0.659u^{-\alpha}/A$ for small u. This is given by Eq. (27) in [1]. This leads to

$$I(t)\sim t^{\alpha-1} \quad , \quad t\to\infty \tag{5SM}$$

However, in an earlier work on the electron scavenging problem, Shlesinger [5] used an expression which is completely equivalent to Eq. (3) and where $\phi(t)\sim t^{-1-\alpha}$ as $t\to\infty$. In this earlier work, the expression for $I(u)$ for small u was evaluated in a different way and Shlesinger obtained $I(u)=1-Bu^{\alpha}$ for small u. This is given by Eq. (17c) in [5] where $\tilde{F}(u)$ in [5] is proportional to $I(u)$ here. Shlesinger uses this to obtain the relation $\lim_{t\to\infty} I(t)\sim\lim_{t\to\infty}\phi(t)$, so that

$$I(t)\sim t^{-\alpha-1} \quad , \quad t\to\infty \tag{5S}$$

The result for $I(t)$ as $t\to\infty$ is quite different depending on whether $I(u)$ is evaluated at small u by the method of SM or by the earlier method of Shlesinger. Since both these asymptotic expressions begin from the same equations, it is incumbent upon these authors [1,5] to clarify which method for obtaining $I(u)$ for small u is appropriate.

If the SM expression Eq. (5SM), $I(t)\sim t^{\alpha-1}$ as $t\to\infty$, is used in Eq. (4), we find

$$\phi(t)\sim\exp(-c_1 t^{\alpha}) \quad , \quad t\to\infty \tag{6}$$

where $c_1 = 0.659c/[\Gamma(\alpha)\Gamma(1-\alpha)A]$. The SM model thus leads to the stretched exponential for ϕ <u>but</u> one that is only valid as $t\to\infty$, i.e. at the tail end of

the stretched exponential. Note that if the earlier Shlesinger expression Eq. (5S), $I(t)\sim t^{-\alpha-1}$ as $t\to\infty$, had been used in Eq. (4), we would have obtained

$$\phi(t)\sim\exp(-c_2t^{-\alpha}) \quad , \quad t\to\infty \tag{6S}$$

instead of the stretched exponential Eq. (6).

The stretched exponential Eq. (16) for <u>both</u> short and long times was first proposed by Kohlrausch [8] in 1847. This is now often referred to as the Kohlrausch-Williams and Watts (KWW) function [9]. Incidentally, the asymcotic large t behavior of $\phi(t)$ as given by relation (6) was actually derived earlier by Hamill and Funabashi [4] using the same tail for $\phi(t)$ as in Eq. (1) and the same conditions including $N>>1$ for the electron scavenging problem [10]. However, Tachiya [6] has shown that the Hamill-Funabashi model involving diffusion of either the trapped electron or the acceptor molecule is not relevant for explanation of the unusual kinetics of trapped electron decay. Tachiya maintained that a tunneling mechanism proposed earlier and which invokes direct electron *transfer from trap to acceptor* [6,10] is the correct one. In any event, such a mechanism can be used to explain the experimental data [10].

It is important to emphasize that the limited result of an asymptotic KWW function obtained by the SM model is even further weakened if N is finite and not actually taken to the limit $N\to\infty$ for fixed $c=N/V$. For finite N, we must return to Eq. (3). If the $t^{-1-\alpha}$ tail in Eq. (1) is valid for times greater than some time t^*, then we can use the previous result of SM, Eq. (5SM), that $I(t)\alpha t^{\alpha-1}$ for $t>t^*$ to express $\phi(t)$ in Eq. (3) as

$$\phi(t) = \left[1- \frac{z}{N} - \frac{c_1}{N}\, t^{\alpha}\right]^N \quad , \quad t^*<t<t^{**} \tag{7}$$

Here $z = c\int_0^{t^*}dt'I(t')-c_1t^{*\alpha}$. Recall that, according to the SM model, the quantity in the brackets $\left[1- \frac{z}{N} - \frac{c_1}{N}\, t^{\alpha}\right]$ represents the probability that the defect has not reached the dipole at time t. For $t>t^{**}\equiv\left[(N-z)/c_1\right]^{\frac{1}{\alpha}}$, this survival probability would become negative so that the formalism cannot be

applied. Therefore, when N is finite, Eq. (7) is restricted in its applicability by both a lower and an upper time limit: $t^* < t < t^{**}$. This is an inherent problem for the SM model with finite N. For sufficiently large but fixed N, it is possible for Eq. (7) to approximate a KWW function over some time regime between the limits t* and t**. Tachiya has pointed out [6] that, whatever the value of N, the approximation of $\left[1-\frac{x}{N}\right]^N$ to exp(-x) becomes increasingly worse as $x \to \infty$. Therefore, for fixed large N, the time interval over which Eq. (7) approximates a KWW function depends both on the value of N and the values of t* and t**. And when N is not sufficiently large, Eq. (7) will not approximate a KWW function at <u>any</u> time, even between the limits t* and t**.

An interesting special case of Eq. (7) occurs for N=1, i.e. when there is only one defect per relaxor. Then the relaxation function is given by

$$\phi(t) = [1-z-c_1 t^{\alpha}] \tag{7a}$$

Just as Eq. (7) this result follows from Eq. (5SM) (Eq. (28) of SM). An alternative procedure for evaluating I(t) was used earlier by Shlesinger [5] which leads to Eq. (5S) (Eq. (22) of Ref. [5]). Shlesinger rewrote Eq. (3) as $\phi(t) = \int_t^{\infty} F(\tau)d\tau$ which is Eq. (20) of Ref. [5] for N or M=1. This expression together with the asymptotic relation $\lim_{t\to\infty} F(t) = VW \lim_{t\to\infty} \phi(t)$ leads to

$$\phi(t) \propto t^{-\alpha} \quad , \quad t \to \infty \tag{7b}$$

(Eq. (30) of Ref. [5]), this result is reiterated by Shlesinger as Eq. (21) in a more recent Reference [1b]. Thus, we see from Eqs. (7a) and (7b) that two different expressions are obtained depending on which of the two computational procedures is used. Advocates of CTRW models then must make clear which procedure is actually appropriate. Shlesinger [1b] attempted to show the relevance of Eq. (7b) to actual experimental observations. He quoted a decay which has the form of Eq. (7b) with $\alpha \simeq 0.3$ due to electron-hole recombination in sputtered a-Si:H. It should be noted that Shlesinger's calculations [5] leading to Eq. (7b) as well as the other calculations quoted in Sec. 4 of Ref.

[1b] are based on the assumption of unimolecular reactions. On the other hand, the experimentalists in Ref. [25] of Ref. [1b] have explicitly stated that electron-hole recombination in a-Si:H is a bimolecular process. This conclusion is based on measurements of the laser intensity dependence. Comparison of bimolecular data with results of a unimolecular model surely cannot be used to resolve the dilemma posed by the two alternatives for computational procedure.

There is a drastic difference in the long time dependences of the relaxation function predicted by the SM model depending on the value of the number of defects per frozen dipole N. Thus the long time dependence of the relaxation function obtained in the SM model is not robust against the choice of N. Further, it does not seem possible for SM to make an estimate for the size of N in any real glass or polymer system because the identities of the defect and the frozen dipoles have not been specified for any system. Before the SM model can be accepted as a general explanation for KWW relaxation, validity of the condition of $N \gg 1$ must be checked for each glass and polymer system. In fact, there are many real glass systems in which the size of a dipole is comparable to that of the smallest molecular unit. In each of these cases, it would be difficult to visualize mobile defects which are far more numerous than dipoles, and it is not likely to have $N \gg 1$. The SM model would then lead to a relaxation function whose tail has the dependence (7) which is not KWW like.

In order to specify the time scale for the onset of the KWW behavior, the full $\phi(t)$ is needed and not just its long-time behavior. It also should be noted that the SM model does not derive the KWW function from fundamental properties of dynamical equations of motion. Within the model, the power law t^{α} in the KWW function Eq. (6) is related to an <u>assumed</u> power law $t^{-1-\alpha}$ in the

pausing distribution Eq. (1). One power law is simply traded for another. Even if the N>>1 hypothesis could be justified for some systems, physical insight into the KWW form would require physical insight into the $\psi(t)$ function. Further, KWW relaxation is observed in many other relaxation processes besides dipolar relaxations of amorphous polymers and glasses. For example, it has been accurately established for thermoremanent magnetization in spin glasses [11-13], where we can hardly think of defects and diffusion processes. There seems to be no basis for the introduction of a pausing time distribution $\psi(t)$ in this case.

The discussions of this section have revealed that the derived relaxation function depends sensitively on the assumption of the form of $\psi(t)$ and on whether the condition of N>>1 is satisfied. The choice of the pausing time distribution of the form $\psi(t)\sim t^{-1-\alpha}$ for long times will be shown in a later section to contradict direct experimental evidences in the closely related problem of hopping ions in glass systems. The picture of mobile diffusing defects is very specific but is immediately inapplicable in the closely related problem of spin glasses which has been experimentally observed to follow a full KWW form [11-13]. Therefore, we conclude that the SM model and other CTRW based models are not robust in their invocation of a specific ad hoc pausing time distribution, in their requirement for a very large ratio of defects to relaxors and in the absense of physical counterparts for the components of the models.

C. Technical Results

In this section, we shall follow the SM and Bendler-Shlesinger (BS) [2] models and work out some of their technical consequences. From these results we will show explicitly that these models can be used to derive a relaxation function which must depart from the KWW form except in the tail portion of the

relaxation function. The early and major part of the derived relaxation function will not have the KWW form in disagreement with experimental data.

In [1], SM motivate the asymptotic form of the pausing time distribution in Eq. (1) by referring to a similar hypothesis used earlier [14,15] in dispersive transport in semiconductors[16]. One of the models used to produce a $\psi(t)$ with a $t^{-1-\alpha}$ tail in dispersive tranpsort was a distribution of activated barriers [17]. The distribution of barriers leads to a distribution of rates $\rho(\lambda)$ which determines $\psi(t)$ as

$$\psi(t) = \int_{\lambda_1}^{\lambda_2} \lambda \exp(-\lambda t)\rho(\lambda)d\lambda \tag{8}$$

Recently, Bendler and Shlesinger (BS) [2] have advocated using this as a model within the SM model to provide a <u>normalizable</u> pausing time distribution function. A thermally activated jump rate in the presence of a single free energy barrier F_o, $\lambda_o=\lambda_\infty\exp(-F_o/kT)$, is modified by the entropy and energy fluctuations generated by local neighboring rearrangements: $\delta F = \delta E - T\delta S$. For simplicity the linear relation $\delta S = \sigma\delta E$ is assumed by BS. As a further assumption δE is taken to have exponential distribution. A generalization of the distribution used by BS can be written in the form

$$g(\delta E) = A \begin{cases} \exp(-q\delta E) & , \quad 0<\delta E\leq\delta E_2 \\ \exp(+q\delta E) & , \quad \delta E_1\leq\delta E<0 \\ 0 & , \quad \delta E>\delta E_2,\ \delta E<\delta E_1 \end{cases} \tag{9}$$

Here A is a normalization constant. The normalization of $g(\delta E)$ insures the normalization of $\psi(t)$ in Eq. (2). BS actually specialized Eq. (9) by assuming $\delta E_1=0$ and $\delta E_2=\infty$. In other words, they cut off the negative fluctuations without physical justification. More general distributions of the form Eq. (9) had been studied over twenty years earlier by MacDonald [18] in the context of modelling mechanical relaxations. Using $\rho(\lambda)=g(\delta E)|d\delta E/d\lambda|$ in Eq. (8) leads to

$$\psi(\tau)/\lambda_o = c_\alpha\left[\int_1^{u_1} du u^{-\alpha}\exp(-u\tau) + \int_{u_2}^{1} du u^{\alpha}\exp(-u\tau)\right] \tag{10}$$

where $\tau \equiv \lambda_o t$, $\alpha \equiv kTq/(1-\sigma T)$, $u_1 \equiv \exp[-q\delta E_1/\alpha]$, $u_2 \equiv \exp[-q\delta E_2/\alpha]$, and $c_\alpha \equiv \alpha/[2-u_1^{-\alpha}-u_2^{\alpha}]$.

Equation (10) provides an expression for $\phi(t)$ that allows examination of the properties of the SM model. The BS choice $\delta E_1=0$ and $\delta E_2=\infty$ corresponds to $u_1=1$ and $u_2=0$. With this choice, the asymptotic expansion of Eq. (9) at long times yields $\phi(\tau)/\lambda_o \to \alpha\Gamma(1+\alpha)\tau^{-1-\alpha}$, which is a power law tail as required by the SM model (as long as $\alpha=kTq/(1-\sigma T)<1$). As discussed in Section B, this leads only to the tail end of the KWW function of Eq. (6) with

$$c_1 = \left[0.659c/\alpha\Gamma(\alpha)\Gamma(1-\alpha)\Gamma(1+\alpha)\right]\lambda_o^{\alpha} \qquad (11)$$

To examine the timescale for the onset of the $\tau^{-1-\alpha}$ tail of the $\phi(\tau)$ given by Eq. (10) we have evaluated Eq. (10) numerically for several values of α. Fig. 1 shows the calculated $\phi(\tau)/\lambda_o$ for $\alpha=0.5$ with the BS choice $u_1=1$, $u_2=0$. The dashed curve shown is the asymptotic expression $\alpha\Gamma(1+\alpha)\tau^{-1-\alpha}$, which approaches the calculated $\phi(\tau)/\lambda_o$ values (solid curves) near $\tau\simeq 4$. As a measure of the meaning of this onset time, we have also computed the median time τ_m, defined by

$$\frac{1}{2} = \int_o^{\tau_m} d\tau\phi(\tau)/\lambda_o \qquad (12)$$

The median time divides the total weight of the $\phi(\tau)$ distribution, giving exactly half the weight for the short time region $\tau<\tau_m$ and half the weight for the long time region $\tau>\tau_m$. The curve in Fig. 2 is shaded for times up to τ_m. Notice that $\phi(\tau)$ assumes the $\tau^{-1-\alpha}$ form only beyond τ_m. Since the SM model with $\phi(\tau)$ modelled by BS can arrive at a KWW tail when $\phi(\tau)$ approaches the asymptotic $\tau^{-1-\alpha}$ long time tail, this means that over half of the relaxation will have decayed according to a function with time dependence which departs <u>strongly</u> from KWW. On the other hand in reality the KWW function gives a good description of the <u>entire</u> physically measured relaxation of a dipolar entity. Let us use the example of the primary relaxation in polyvinylacetate as quoted

by SM. The experimentally measured quantity is the frequency dependent dielectric function $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$. In the theory of dielectric relaxation:

$$\varepsilon^*(\omega)=\int_0^\infty dt\ e^{-i\omega t}[-d\phi/dt] \tag{13}$$

The polyvinylacetate experimental $\varepsilon^*(\omega)$ data is well fit by Eq. (13) with a KWW function ϕ of Eq. (6) having the (slightly temperature dependent) fractional exponent $\alpha\approx 0.56$ [19]. Moreover, the fit covers significant frequency ranges on both sides of the frequency ω_p of the dielectric loss peak. The experimental frequency range is wide enough to cover essentially the entire relaxation process from beginning to end. However, the SM model will not produce a KWW function for $\tau<\tau_m$ and therefore the model will not fit the dielectric $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ data at least for the high frequency side of ω_p. This can be understood from the fact that ω_p for the KWW function corresponds approximately to the time at which the decay has reached 1/e of its initial value. This disagreement of the SM result for the high frequency side of the dielectric relaxation function also occurs for the primary relaxations of supercooled liquids and polymers studied by Williams and Watts themselves [9,20].

Dielectric relaxation can be carried out in the time domain by measurement of discharge of the depolarization current for a wide range of dielectric materials. The current in the short time domain follows the power law of time dependence.

$$i(t)\ \alpha\ t^{-n} \tag{14}$$

This form of the dielectric response has been known since the turn of the nineteenth century under the name of the Curie-von Schweidler law [21,22]. At longer times, the time dependence of the current departs from Eq. (14). From the formalism of dielectric relaxation, $i(t)\ \alpha\ d\phi/dt$. The classic Curie-von Schweidler law is consistent with the KWW form Eq. (6), because $d\phi/dt=$

$-\alpha c_1 t^{\alpha-1}\exp(-c_1 t^{\alpha})$ and at short times the $t^{\alpha-1}$ factor dominates. This demonstrates how essential it is for any dielectric relaxation model to capture the entire KWW form over <u>both</u> the short and long time regions. Zwanzig [23] has emphasized this in his comment on another model.

It is interesting also to consider the effect of modifying the choice for $g(\delta E)$ in the BS model on the median time. We have calculated Eq. (10) numerically for the distributions Eq. (9) with $\delta E_2=\infty$ and various values of $\delta E_1<0$, which corresponds to $u_2=0$ and $u_1>1$. Including contributions with $\delta E_1<0$ further delays the onset of the $\tau^{-1-\alpha}$ tail beyond the median time. Fig. 2 shows the calculated $\psi(\tau)/\lambda_o$ corresponding to the case where the fraction of the weight of $g(\delta E)$ with $\delta E<0$ is $f_{-}=0.45$ (i.e. nearly symmetric in positive and negative fluctuations). The asymptotic power law tail is again shown by the dashed curve. The onset of $\psi(\tau)$ to the power law tail is delayed even further beyond the median time τ_m as compared to the $f_{-}=0.0$ case in Fig. 1. As shown in Fig. 3, the value of τ_m in fact decreases rapidly as the $\delta E<0$ contributions occupy more weight in the $g(\delta E)$ distribution, i.e. as f_{-} increases. However, they do not contribute to the $\tau^{-1-\alpha}$ tail except in the normalization prefactor: $\psi(\tau)\rightarrow\alpha\Gamma(1+\alpha)(2-f_{-})\tau^{-1-\alpha}$. This modified prefactor moves the onset of the power law tail to shorter times, but not as rapidly as the decrease ot τ_m. The result is that as the fluctuations δE in $g(\delta E)$ are allowed to become more symmetrical, the SM model produces a relaxation function that coincides with a KWW form over a steadily diminishing tail portion of the dielectric relaxation curve. This situation is further exacerbated if the positive fluctuations are truncated at a finite value of δE_2, and also if α is increased. Thus the SM model with $\psi(t)$ in turn modelled by BS, even aside from the status of its assumptions, can only lead to a relaxation function that coincides with the KWW form in a long time regime that cannot coincide with the full time regime in which the observable relaxation occurs.

As seen in Eqs. (6) and (11), the KWW relaxation time τ^*, defined by rewriting the KWW form as $\phi(t)=\exp[-(t/\tau^*)^\alpha]$ is calculated by BS to be $\tau^*\sim\lambda_o^{-1}$. BS state that $\phi(\tau)/\lambda_o$ goes to a constant, $\phi(o)/\lambda_o=\alpha/(1+\alpha)$, for $\tau<1$. If $\phi(t)=\alpha\lambda_o/(1+\alpha)$ at short times, then Eq. (5) leads to $I(u)=\alpha\lambda_o u^{-1}/(1+\alpha)$ at large u for any lattice. This produces a short time exponential decay as claimed by BS. In particular, $\phi(t)=\exp(-t/\tau_o)$ with $\tau_o=(1+\alpha)\lambda_o^{-1}/\alpha c$. This would lead to the prediction $\tau^* \propto \tau_o$, which disagrees with a wide range of experimental data [24-26]. Note from Fig. 1 that $\phi(\tau)/\lambda_o$ is really not constant for $\tau<1$ as stated by BS, but instead decays by almost 60% of its initial value during this interval. The initial decay of $\phi(\tau)/\lambda_o$ becomes even steeper if $\delta E<0$ is allowed as in Fig. 2. Therefore, the short time behavior predicted by BS model will not actually be an exponential decay for the $g(\delta E)$ distribution as chosen by them.

The unsatisfactory nature of the SM model with $\phi(t)$ as modelled by BS in deriving only a tail portion of the KWW form is not unique to the activated barrier model for $\phi(t)$. Any $\phi(t)$ with an asymptotic $\tau^{-1-\alpha}$ tail will produce the same problems as discussed above. For example, in an earlier discussion in the context of dispersive transport, Shlesinger [15] adopted a Levy stable function in time (see Appendix A of Ref. [15]) for $\phi(t)$. This has the property that the Laplace transform of $\phi(t)$ is a fractional exponential in the Laplace transform variable u: $L[\phi(t)]=\exp[-(u/\lambda_o)^\alpha]$. Here λ_o is a rate parameter that is distinct from that used in the barrier distribution model. For example, when $\alpha=0.5$, the corresponding form of $\phi(t)$ can be written analytically: $\phi(t) = \exp[-1/4\lambda_o t]/2\sqrt{\pi(\lambda_o t)^3}$. This is properly normalized and has a long-time $t^{-1-\alpha}$ tail. Indeed, the only physical rationale implied for the choice of the Lévy stable function is that it has the appropriate long-time tail. We have calculated this $\phi(t)$ with $\alpha=0.5$ and the results are shown in

Fig. 4. Again, the onset of the $\tau^{-1-\alpha}$ tail is found to be beyond the median time τ_m. Note that a Levy stable function in time for $\phi(t)$ is quite different from the use of stability for the frequency spectrum of $\phi(t)$ as discussed by us elsewhere [27]. Recall that we have shown that the relaxation functions derived by SM and BS cannot explain the short time regime of the KWW function which is observed so widely that it is called the Curie-von Schweidl$\acute{e}$r law. For the same reason one might question also the claims in Refs. [14,15] that the characteristic $t^{-1+\alpha}$ dependence of the transient current in dispersive transient transport in chalcogenide glasses [17] for $t<<t_T$, the transit time, can be explained by a $\phi(t)\sim t^{-1-\alpha}$ at long times in CTRW framework.

In this section, the technical results were carefully carried out and examined in detail. We found that the result of all the modelling of $\phi(t)$ [1,2] will produce relaxation functions which coincides with the KWW only over a tail portion at long times. This contradicts the dielectric relaxation data in the time domain (Curie-von Schweidler law) as well as the frequency dependence of the measured dielectric function $\varepsilon^*(\omega)$ first given by Williams and Watts themselves [9,20]. We conclude that the technical results of the SM and the BS or any of the presently proposed models for $\phi(t)$ do not produce the entire KWW form. Thus, CTRW models of relaxation do not provide a satisfactory basis for description of physical phenomena.

D. Physical Tests of Assumptions

One of the key assumptions of the SM model is that the pausing time distribution has a $t^{-1-\alpha}$ tail. The repeated advocation of the $t^{-1-\alpha}$ form [1,2, 14,15] gives the impression that it is generally applicable to different random walkers in many different systems. We have found physical systems which are glass-forming materials and have mobile random walkers. The pausing-time

distribution $\psi(t)$ applies directly [28,29] in these systems, if the experimental data is interpreted in a CTRW framework [3]. However, we must emphasize that a CTRW framework is not required to interpret the experimental data. Nonetheless, if a CTRW framework is used, it can be put to a clean test in such systems.

To do this we examine electrical relaxations due to ionic diffusion in glasses above and below the glass transition temperature. It was recognized by Moynihan, Macedo and co-workers [28,29] that for electrical relaxations in dielectrics containing a substantial concentration of mobile charges, the appropriate physical picture is the decay of the electric field $\underline{E}$ at constant displacement vector $\underline{D}$. In contrast, relaxation of permanent dipoles is characterized by the decay of $\underline{D}$ under the condition of constant $\underline{E}$. The decay of the electric field is due to diffusion or migration of the mobile ions and may be described by

$$E(t) = E(o)\gamma(t) \tag{15}$$

where $\gamma(t)$ is a decay function. If the mobile ions are described as random walkers in the continuous time random walk formalism, then $\psi(t)=-d\gamma(t)/dt$. That is, the rate of decay of the electric field is a measure of the pausing time distribution of the mobile ions. Experimentally, systems including alkali network oxide glasses, fused salts, and concentrated aqueous electrolyte solutions have been studied for electric field relaxation [27-32].

Let us focus our attention on the alkali silicate glasses. There are no permanent dipoles in these systems and dielectric relaxation is due to diffusion of the alkali ions. Since there are no frozen dipoles in an alkali silicate glass and only a diffusing species, we have a direct test of the $\psi(t) \alpha t^{-1-\alpha}$ hypothesis of the SM model. We need not worry about the validity of the subsidiary hypotheses of the model. If we take the SM model seriously,

in particular that the $t^{-1-\alpha}$ pausing-time distribution is very general, then the diffusion of the alkali ions should be well described by Eq. (1). However, experimentally it has been found repeatedly [28-32] that the decay function $-d\gamma(t)/dt$ in Eq. (14) is <u>not</u> $t^{-1-\alpha}$ but remarkably is itself the time derivative of a KWW fractional exponential function. Examples include alkali silicate and borate glasses, a glass-forming 40mol% $Ca(NO_3)_2$-60mol% KNO_3 melt, Na beta alumina, LiCl electrolyte solutions and others [28-32,24]. These are examples of KWW decay involving only diffusing species. This means that if we wish to use a pausing time distribution to describe these experiments, it must have the form $\psi(t)=-d\gamma(t)/dt=(\alpha t^{\alpha-1}/\tau^{*\alpha})\exp(-[t/\tau^*]^\alpha)$. This obviously does <u>not</u> have a $t^{-1-\alpha}$ long time tail. Thus the claim of generality of a $t^{-1-\alpha}$ tail in the pausing-time distribution is not supported by experimental data on electric field relaxations due to diffusing ions in glasses.

The failure of a $\psi(t)$ with a $t^{-1-\alpha}$ tail to describe experimentally the diffusing ions can also be seen explicitly by calculation of a corresponding frequency spectrum known as the electric modulus, $M^*(\omega)$. This is the inverse of the dielectric function, $M^*(\omega)\equiv 1/\varepsilon^*(\omega)$, and is related to $\psi(t)$ by

$$M^*(\omega) = M'(\omega)+iM''(\omega) = M_\infty[1-\int_0^\infty dt e^{-i\omega t}\psi(t)] \tag{16}$$

Experimentally [28-32], $M''(\omega)$ shows a characteristic asymmetric broad peak which is skewed toward high frequencies. The data can be fit very well if $\psi(t)$ is taken to be the derivative of a KWW function [28-32]. Now let us compare this with the results of the SM model with $\psi(t)$ as modelled by BS. Using the activated barrier distribution model for $\psi(t)$, Eq. (10), we find

$$M'(\omega)/M_\infty = 1-c_\alpha\left[\int_1^{u_1} du\ \frac{u^{1-\alpha}}{u^2+\Omega^2} + \int_{u_2}^1 du\ \frac{u^{1+\alpha}}{u^2+\Omega^2}\right] \tag{17}$$

$$M''(\omega)/M_\infty = c_\alpha\Omega\left[\int_1^{u_1} du\ \frac{u^{-\alpha}}{u^2+\Omega^2} + \int_{u_2}^1 du\ \frac{u^{\alpha}}{u^2+\Omega^2}\right] \tag{18}$$

where $\Omega\equiv\omega/\lambda_o$. We have evaluated Eqs. (17) and (18) numerically for different choices of the distribution Eq. (9). The calculated $M''(\omega)$ shows the peak near

$\omega \approx \lambda_o$ but the shape of the curve disagrees with experiment. If the fluctuations δE are symmetric in positive and negative contributions (i.e., $u_1 = u_2^{-1}$) the calculated $M''(\omega)$ curve is symmetric about its peak. This is shown in Fig. 5. On the other hand the experimental M" curves are skewed as shown in Fig. 7. If we follow BS and remove all negative fluctuations, emphasizing the power law tail as much as possible, then the calculated $M''(\omega)$ curve is asymmetric as shown in Fig. 6 but skewed in the opposite way from the experimental curves. Hence the BS model of $\phi(t)$ based on a distribution of barriers with only positive fluctuations as well as more physically reasonable models of $\phi(t)$ which have symmetric fluctuations all disagree with the experimental measurements. Therefore, diffusing species in glass forming systems are not generally described by a $t^{-1-\alpha}$ tail. The hypothesis of the SM model that $\phi(t)$ of a yet unspecified defect has a $t^{-1-\alpha}$ tail thus becomes questionable.

There is another difficulty in using a defect diffusion model for relaxation in realistic glass forming materials. In many glasses and amorphous polymers [33], several relaxations of different nature are present in the same system. It has been demonstrated that even small molecule glasses have both primary and secondary relaxations [34]. Often the different relaxations in the same system all have the KWW form, although each has its own own characteristic fractional exponent α [35]. This is known to proponents of the CTRW based relaxation models. In fact they [36] have fit the experimental data of a secondary relaxation of a small molecule glass to the KWW form and claimed good agreement. Consider, for example, glassy polycarbonate. There are at least three distinct relaxations traditionally labelled alpha, beta, and gamma [37,33]. The alpha and gamma relaxations have been extensively studied [33, 35,37,38], and they both have the KWW form but with quite different values for the fractional exponent: $\alpha \approx 0.4$ for the alpha relaxation [35] and

α=0.2 for the gamma relaxation [38]. Many other such examples can be cited. This type of example presents a difficulty for the SM model, because the value of α in the KWW tail derived is the same as that in the hypothesized $t^{-1-\alpha}$ tail of the pausing-time distribution of the diffusing defect, Eq. (1). In order to account for two different KWW exponents observed in the same physical system, the SM model would require two different types of diffusing defect, each with a different $t^{-1-\alpha}$ tail. Furthermore, defect 1 (2) must be required to interact only with dipoles of the alpha (gamma) relaxation but never with the gamma (alpha) relaxation. Such a requirement seems very difficult to justify on physical grounds.

E. Predictability

An important aspect of predictability is whether significant phenomena that occur empirically are predicted or at least included in the phenomenology of the model. We have seen the models of relaxation based on CTRW have not predicted an entire KWW function but rather a relaxation function that approaches a KWW form $\exp(-c_1 t^{\alpha})$ only at the tail end. Therefore, they [1,2] cannot even claim that their models predict a genuine KWW relaxation function. One of the assumptions that has to be made is the pausing time distribution $\psi(t)$ having a long time tail of $t^{-1-\alpha}$. Since the KWW relaxation function is generally observed, a fact subscribed by authors of these CTRW models, logically the key assumption of $\psi(t) \sim t^{-1-\alpha}$ must be at least or even more ubiquitous. The electrical relaxation data of many glass-forming systems (Section D) demonstrate that the latter is not true. Hence this key assumption is questionable. Thus, at the expense of at least one ad hoc assumption, the SM model has predicted only part of a KWW relaxation function. There are no other concrete predictions or further applications.

The BS model, with the assumption of a one-sided fluctuation of energy barrier heights with an exponential distribution does provide an additional prediction. There, the quantity α in the $t^{-1-\alpha}$ tail of $\phi(t)$ becomes temperature dependent and the exponent α of the predicted tail of the KWW function, $\exp(-c_1 t^{\alpha})$ will also be temperature dependent. Let us compare this prediction with experimental data. Actaully there is no completely consistent way of making such a comparison. The experimental data show that the relaxations are entire KWW functions, while the BS model predicts only relaxation functions whose tails are KWW like (see Section C). Even when we ignore this problem of the BS model, experimentally there are glass-forming materials such as $Si-O_2$ [39], polystyrene [40], polyethyl acrylate [41], etc. for which the fractional exponent α of the entire KWW relaxation function in each case remains constant over a sizeable experimental temperature range. The polyethyl acrylate data is particularly worth noting because it was obtained by Williams and Watts themselves. McDuffie, Quinn and Litovitz [42] have studied the dielectric properties of glycerol-water mixtures. They observed that the shape of the relaxation function is independent of the concentration and conclude this result is not in accord with the concept that the origin of the departure from exponential relaxation lies in the existence of a distribution of barrier heights in the liquid. Litovitz and McDuffie [42] compare the dielectric rotational time with structural break-up time and point out a difficulty of the Glarum's model [7] when applied to associated liquids. There are also many other systems whose relaxation behavior are of the KWW form, with temperature dependent fractional exponents α [43]. However, again in each of these cases, the relaxation can be described by an entire KWW function in disagreement with the predicted relaxation function of the BS model.

There are three empirical relations of relaxation in addition to the KWW function (which we call the first relation) that have been seen repeatedly in experimental data. The second relates the effective relaxation time τ^* that appears in the KWW form, now written as

$$\phi(t) = \exp\left(-(t/\tau^*)^{\alpha}\right) , \tag{19}$$

to a primitive relaxation time τ_o that has a microscopic and fundamental meaning as

$$\tau^* = (\omega_c^{1-\alpha}\tau_o)^{1/\alpha} \tag{20}$$

where ω_c is a characteristic frequency. It is important to emphasize that the fractional exponent α and τ^* appearing in Eq. (20) are the <u>same</u> as those in the KWW form (19). The third relation states that for the same relaxation process, the relaxation function is an entire KWW function (19) if $\omega_c\tau_o>>1$ but crosses over to an entire linear exponential

$$\phi(t) = \exp(-t/\tau_o) \tag{21}$$

if $\omega_c\tau_o<<1$. The quantity τ_o in Eq. (21) and ω_c in the conditions $\omega_c\tau_o<<1$ or $\omega_c\tau_o>>1$ are again the same as that appears in Eq. (20). The relaxation models based on CTRW predict neither of these two extra empirically verified relations [24,26,30,31,35,38,44,45] but at best, predicts $\tau^* \alpha \tau_o$ [25].

F. Summary and Conclusions

We have initiated an examination of existing models of relaxation by consideration of models [1,2] based on the continuous time random walk (CTRW) formalism [3]. CTRW is only a mathematical scheme. To address a physical problem such as relaxation in glass forming systems described by the Kohlrausch-Williams and Watts or KWW function, additional physical inputs are required. These include (1) the pausing time distribution $\psi(t)$, (2) the ratio of defects to relaxors, and (3) the contact nature of the defect-relaxor

interaction that causes relaxation. In order to obtain a physical model of relaxation based on CTRW, these inputs must be the consequences of or derivable from some general physical principles and fundamental laws. This level is not achieved in either of the two proposed models [1,2]. In the prototypical work by Shlesinger and Montroll (SM) [1], the choice made for the pausing time distribution function $\psi(t)$ has a $t^{-1-\alpha}$ tail ($o<\alpha<1$) at long times is made. The exact nature of $\psi(t)$ at earlier times before the $t^{-1-\alpha}$ tail takes over is left unspecified. An unspecified contact interaction between defect and relaxor is assumed. Another essential assumption is that the number of defects per relaxor is large. With these hypotheses, SM have shown us how to turn the crank of CTRW mathematics to derive a tail portion of the KWW relaxation function. This result depends on how I(u) in Eq. (5) is evaluated at small u. If an earlier method for this evaluation due to Shlesinger [5] is used, the result would be given by relation (6S), i.e. $\phi(t)\sim\exp(-c_2t^{-\alpha})$ for $t\to\infty$, and it would not be KWW anywhere. The CTRW workers [1,5] should clarify the methodology to be employed in evaluating I(u) for small u.

Even with the machinery used by SM, one only obtains a relaxation function that coincides with the KWW function in a limited long time regime. The shorter time regime in which the KWW form is empirically satisfied is not described adequately. Thus Eq. (29) of the SM paper is imprecise. It is an asymptotic equation for the behavior of $\phi(t)$ for large t and should not be interpreted as an equation valid for all times. To make sure that this distinction between an asymptotic relation and an equation is not splitting hairs, we examined the two pausing time distributions respectively modelled by Bendler and Shlesinger (BS) [2] and by Shlesinger above, [15]. Both of these are distributions which have a $t^{-1-\alpha}$ tail and normalized over all times. We found that the weight of the distribution for the short time regime where $\psi(t)$

departs strongly from the $t^{-1-\alpha}$ dependence has more than half of the total weight of the distribution. These calculations point to a serious problem common to all existing models of relaxation based on CTRW. They have not accomplished the primary objective of a derivation of an entire KWW relaxation function. Their relaxation function will approach a KWW form only at times after the quantity to be relaxed has been reduced by more than one-half or much more than half of its initial unrelaxed value. Experimentally this initial relaxation as well as its continuation to long times correspond throughout to a single KWW function. This initial part of the KWW relaxation is observed repeatedly in dielectric relaxation time domain measurements based on the technique of charging and discharging currents. The phenomenon has been referred to as the Curie-von Schweidler [21] law. In the frequency domain, the same phenomenon is observed by the wide occurrence of the ω^{n-1} frequency dependence ($o<n<1$) for the real and imaginary parts of the dielectric function $\varepsilon^*(\omega)$ on the high frequency side of the dielectric loss peak frequency ω_p. This feature has been emphasized by Jonscher [22,46]. It was pointed out [35] that this feature not only follows from the KWW function but also from other empirical dielectric relaxation functions such as those proposed by Cole-Cole, Cole-Davidson and by Havriliak-Nagami[45]. The relaxation functions predicted by models of relaxation [1,2] based on CTRW contradicts this well established phenomenology of dielectric relaxation.

After the assumption of $\phi(t)\sim t^{-1-\alpha}$ has been made, the relaxation function obtained by CTRW depends sensitively on whether number of defects N per relaxor is large. We have shown explicitly how the $\phi(t)$ deviates from the KWW form even in a long time regime when N is finite. (See discussions following Eq. (7)). Further, we have pointed out possible physical cases where the assumption of very large N is untenable. This lack of robustness of CTRW

models against choice of N is not appropriate for models designed to describe a very general phenomenon, namely KWW relaxation.

We have also given evidence to dispel the belief that the distribution with a $t^{-1-\alpha}$ tail have general applicability. The evidence comes directly from experimental measurements of electrical relaxation of diffusing ions in glass forming systems. The experimental data [28-32] clearly indicate that, if we insist on a CTRW approach, the pausing time distribution function is the derivative with respect to time of a KWW function, and this does not have a $t^{-1-\alpha}$ tail.

Furthermore, the CTRW models [1,2] lead to a physically untenable picture when applied to realistic glass forming materials which have primary and secondary relaxations and both are well described by KWW functions. The different fractional exponents now require two types of defects each with its own inverse power tail. One type of defect is responsible for only one type of relaxation process and not the other. The number of assumptions and hypotheses involved increases rapidly, making the applicability of the models [1,2] less likely.

All theoretical models in physics are ultimately judged by the capability to generate <u>new</u> testable predictions. The models [1,2] based on CTRW at the expense of an ad hoc assumption of the pausing time distribution function predicts a relaxation function that only approaches a KWW function at long times. At an initial but experimentally significant part of the relaxation, this predicted relaxation function fails repeatedly when compared with dielectric relaxation phenomena. There is no other sustainable prediction. In the model by Bendler and Shlesinger [2] for $\phi(t)$ there is one additional prediction. The extra prediction is that the fractional exponent α will necessarily be a function of temperature. However, there are a number of glass forming systems

in which the experimentally measured α is insensitive to temperature, in disagreement with this prediction.

In brief, we have examined the models of relaxation [1,2] based on CTRW. The conclusion we reach is that they must be rejected as relevant models for KWW relaxations in glass forming systems because they lack robustness, employ certain questionable technical procedures, introduce general assumptions that fail to meet specific physical tests, lead to unverified predictions, and fail to predict or describe verified properties of KWW relaxation.

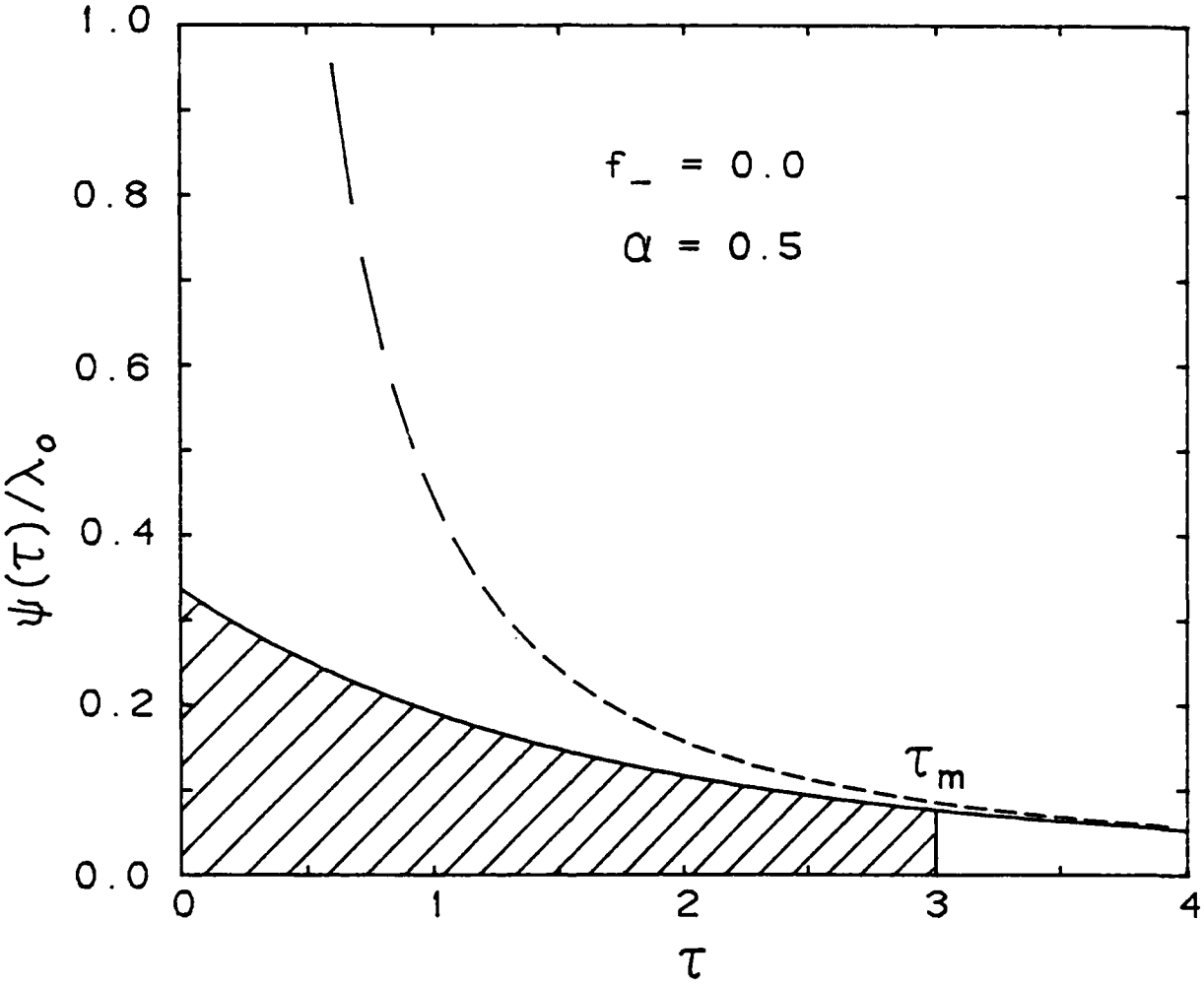

Fig. 1 Solid curve is calculated from Eq. (10) with α=0.5 corresponding to $g(\delta E)$ in Eq. (9) with $\delta E_2=\infty$ and only positive fluctuations: $f_-=0.0$. Dashed curve is the asymptotic power law tail. τ_m is the median time, Eq. (12). Here $\tau=\lambda_o t$.

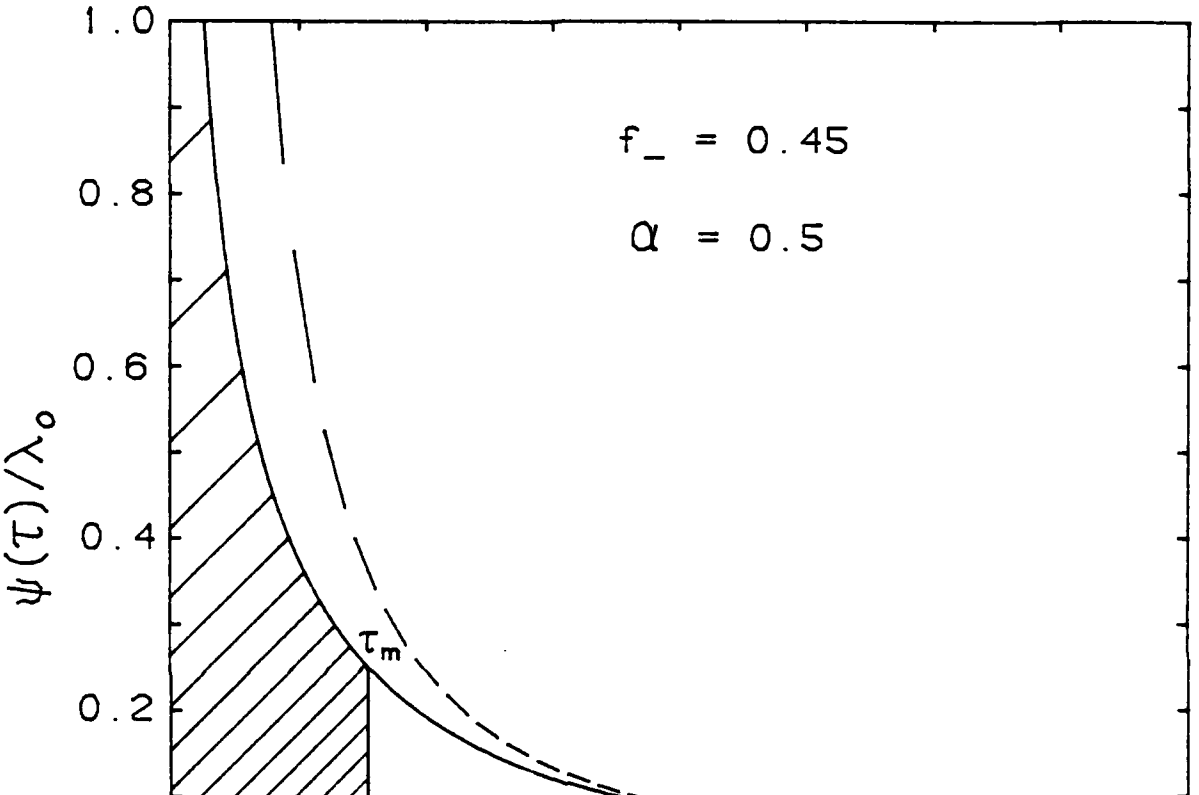

Fig. 2 Solid curve is calculated from Eq. (10) with α=0.5, corresponding to $g(\delta E)$ in Eq. (9) with $\delta E_2=\infty$ a fraction of negative fluctuations, f_-=0.45. Dashed curve is the asymptotic power law tail. τ_m is the median time, Eq. (12). Here $\tau=\lambda_o t$.

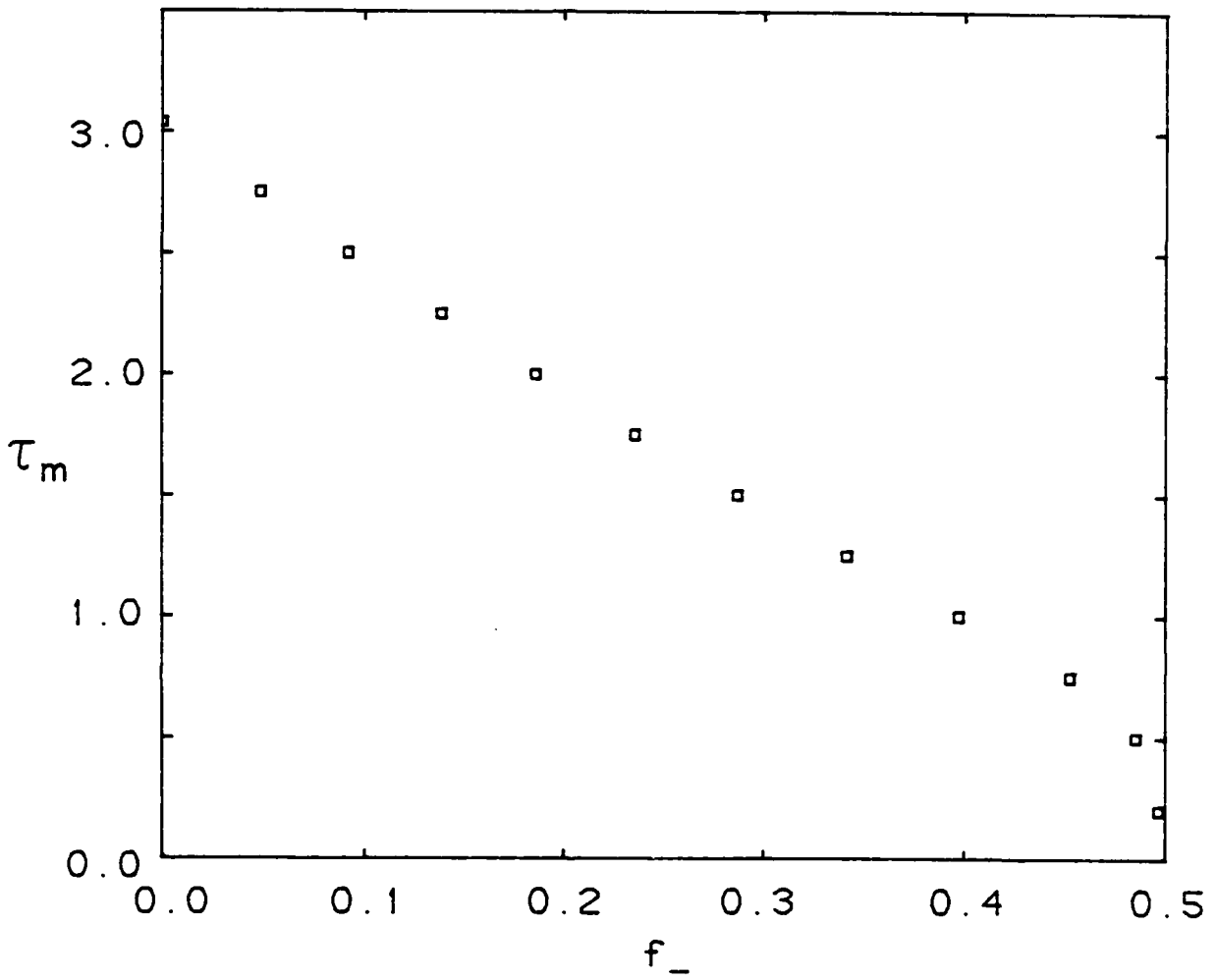

Fig. 3 Median time, Eq. (12), calculated from Eq. (10) with α=0.5 corresponding to $g(\delta E)$ in Eq. (9) with $\delta E_2=\infty$ and a fraction of negative fluctuations f_-.

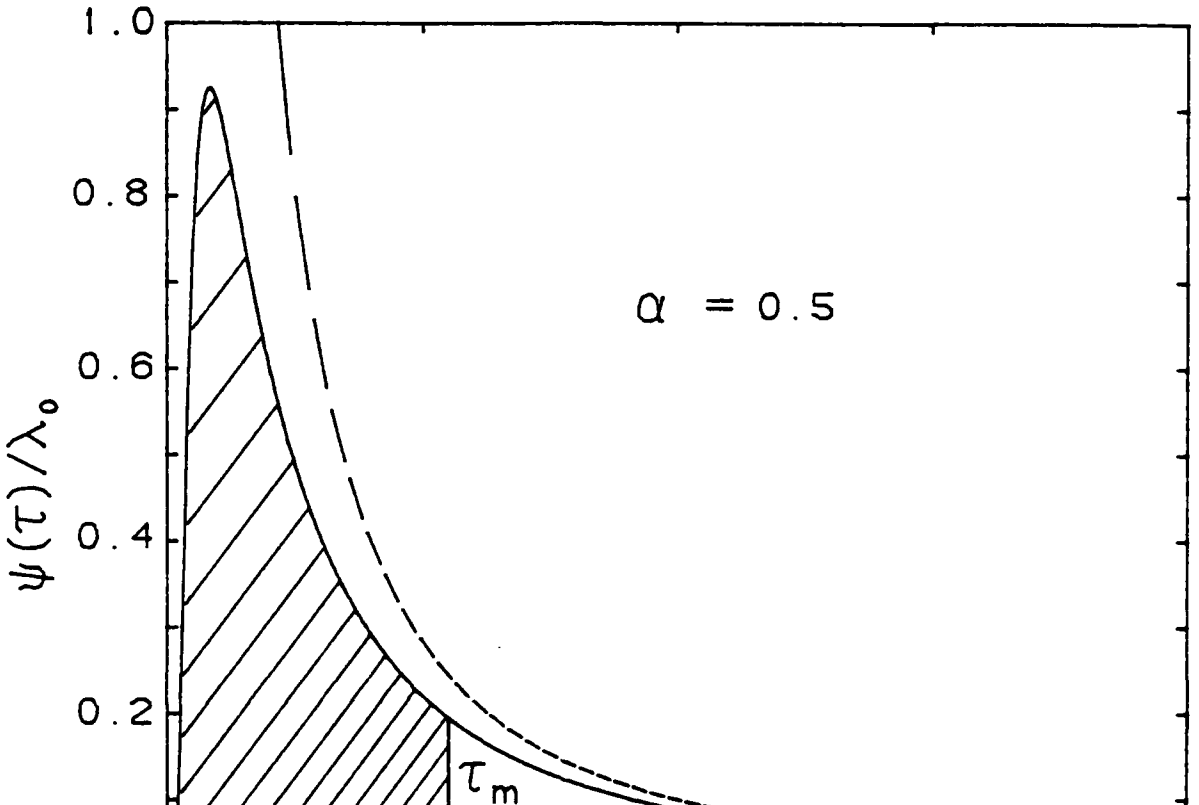

Fig. 4 Solid curve is $\psi(t)$ corresponding to a Levy stable distribution with α=0.5. Dashed curve is the asymptotic power law tail. τ_m is the median time, Eq. (12). Here $\tau=\lambda_o t$.

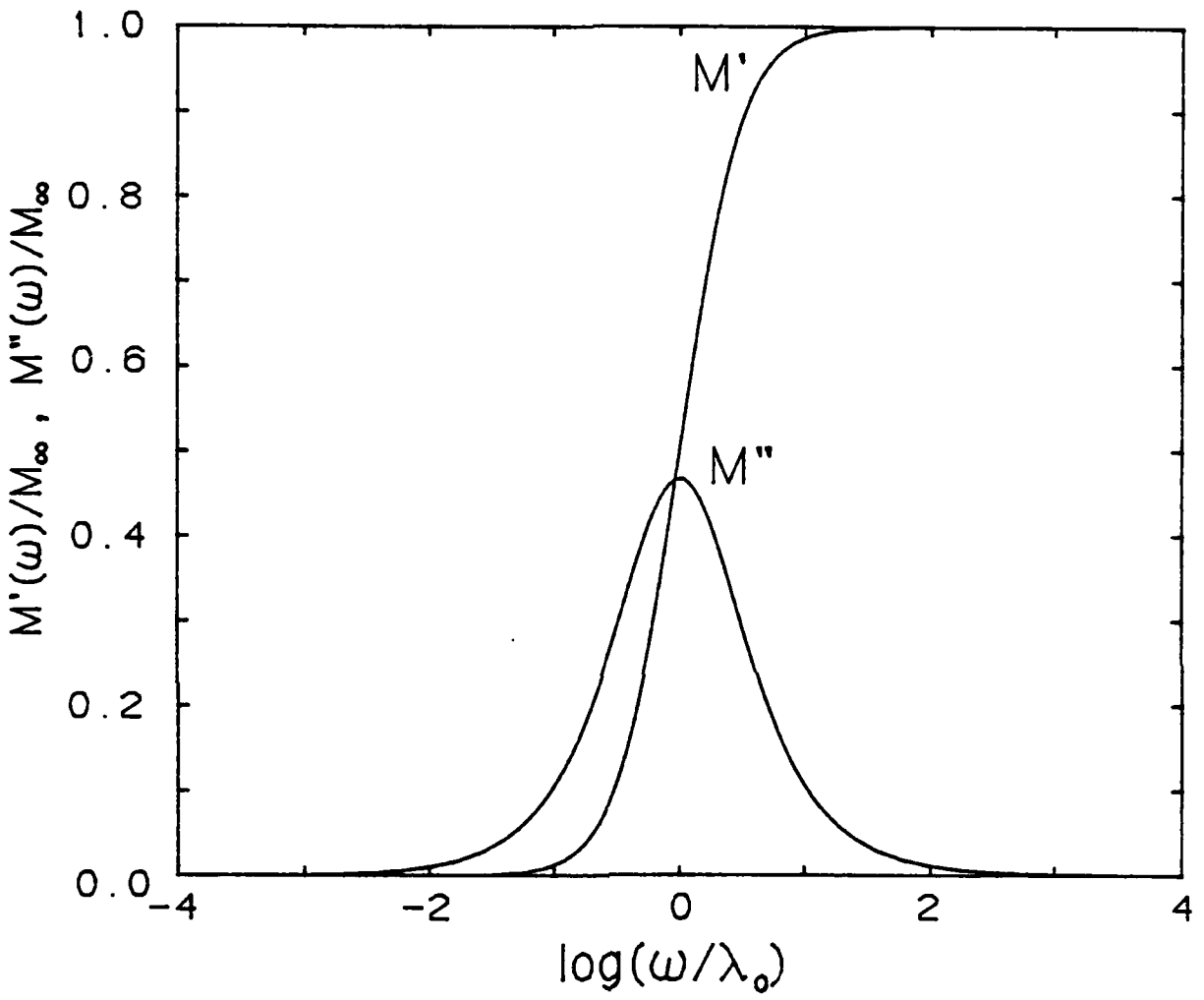

Fig. 5 Real and imaginary parts of the electric modulus, calculated from Eqs. (17) and (18) with α=0.5 corresponding to g(δE) in Eq. (9) with symmetric positive and negative fluctuations δE ($u_1=u_2^{-1}=2.0$).

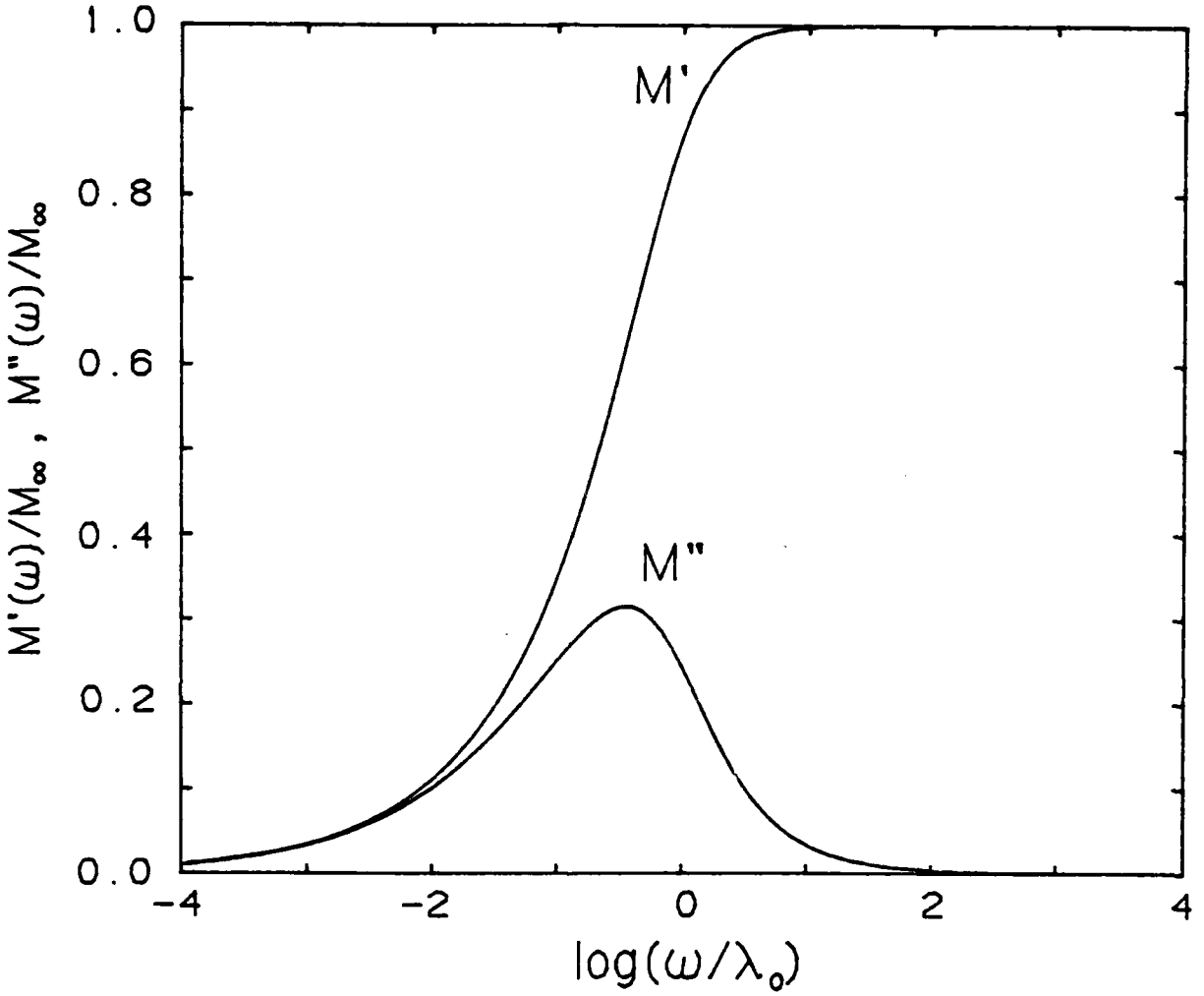

Fig. 6 Real and imaginary parts of the electric modulus, calculated from Eqs. (17) and (18) with α=0.5 corresponding to $g(\delta E)$ in Eq. (9) with $\delta E_2=\infty$ and only positive fluctuations: $f_- = 0.0$.

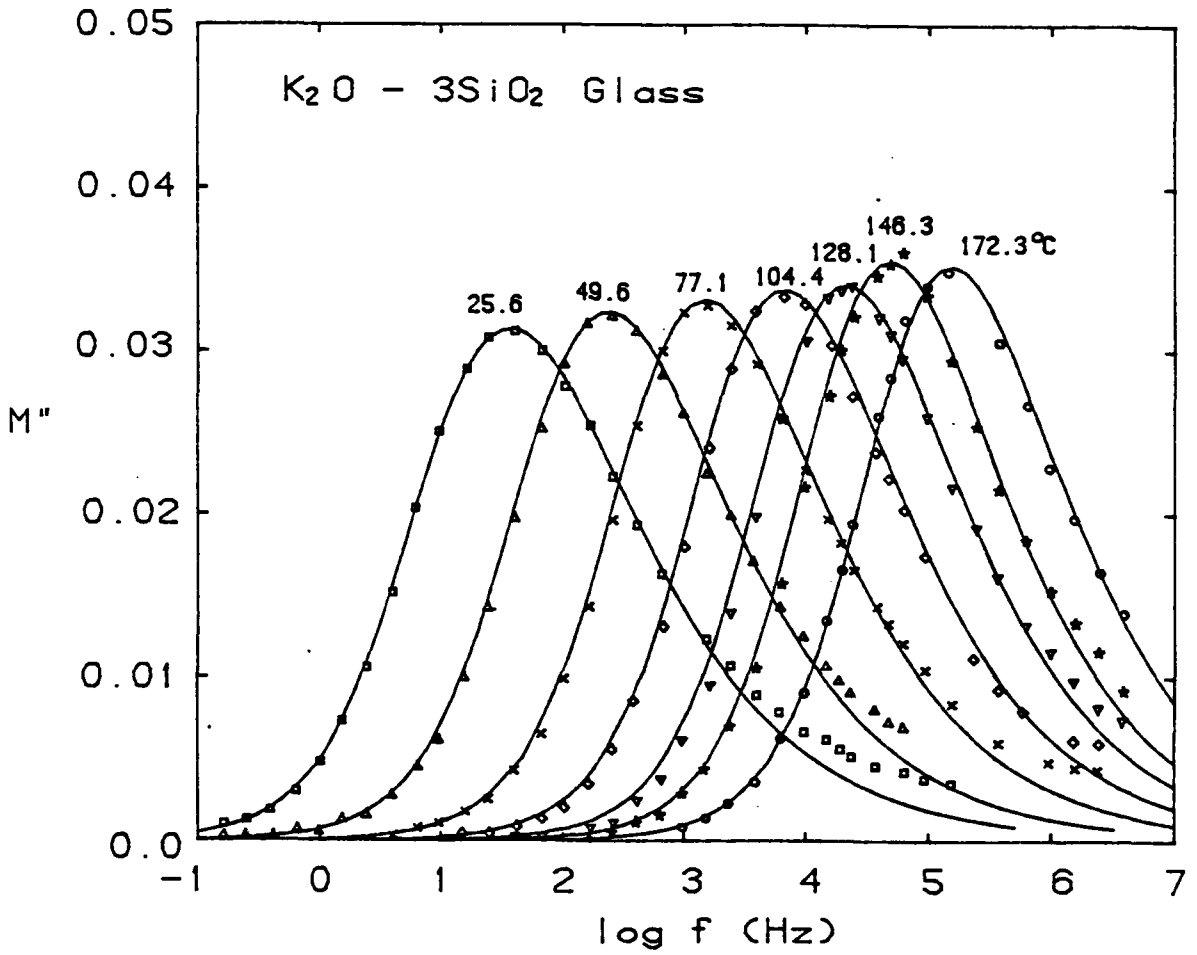

Fig. 7 M" vs log f data at several temperatures for K_2O-$3SiO_2$ glass annealed at 479°C and quenched. The points are experimental data and curves are recalculated by us using Eq. (16) and $\phi(t)=\exp[-(t/\tau)^{\alpha}]$ with the parameters α, M_∞ and τ given by Boesch and Moynihan (L.P. Boesch and C.T. Moynihan, J. Non. Cryst. Solids 17, 44 (1975)).

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