Relaxation Time Spectrum in Glassy States

Pik-Yin Lai

Institute of Physics, National Central University,
Chung-Li, Taiwan 320, R.O.C.

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The spectrum for the distribution of the relaxation times that leads to the universally observed Kohlraush law, or stretched exponential relaxation $\exp\left(-(t/\tau_o)^\alpha\right)$ $(0 < \alpha < 1)$, for the time correlation function in glassy systems, is calculated. For $a = \frac{1}{2}$, we obtain explicitly the distribution of the relaxation spectrum. For general values of a, all the moments of the distribution are computed explicitly. We find that for $\alpha < 1$ the distribution has a broad spectrum with the width of the distribution and the average relaxation time diverges over tens of orders of magnitude as α becomes close to 0. The plausible connections with the Vogel-Fulcher and Arrhenius laws are also discussed.

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I. INTRODUCTION

Many complex, strongly interacting, glassy materials show extremely slow relaxing behaviors, rather than simple Debye exponential relaxation. More than a century ago, Kohlraush [1] observed that the relaxation in connection with viscoelasticity has the anomalous stretched exponential form. The stretched exponential in time correlation function is often observed in a wide class of condensed matter systems [2,3] such as super-cooled liquids near the liquid-glass transition [4,5], dielectrics [6], metallic glasses, spin-glass alloys [7], dense polymeric materials [8] etc. The Kohlraush law is often associated with the huge divergence of relaxation time or viscosity below the glass transition temperature, and often manifested in the form of Vogel-Fulcher law [9] or Arrhenius law. Very recently, the Kohlraush law has also been observed in the adsorption of a long polymer chain in solution on an attractive surface [10]. To a certain degree, the low temperature dynamics of the adsorbed polymer layer resembles the super-cooled liquid-glass and other glassy systems, as is manifested by the fact that the Vogel-Fulcher law are also observed in these systems. There

is no detail theoretical account or direct microscopic derivation for the stretched exponential relaxation behavior and the Vogel-Fulcher law in glassy systems though there were models such as hierarchically constrained dynamics [11], hierarchically distributed energy barriers [12] that can lead to the Kohlraush relaxation law. There has been some calculations on a very special model of dense rods which suggested that the essential singular Vogel-Fulcher behavior can be derived if the movement of one rod is correlated in a circuit with itself [13]. However, these models are somehow artificial and we are still far from a detail microscopic understanding that leads to the Kohlraush law. In view of the universal occurrence of the Kohlraush law in glassy systems, it is worth to investigate the spectrum of relaxation times that leads to the stretched exponential behavior in the time correlation function. The stretched exponential form of correlation function can be interpreted as a sum of exponential decays with a board distribution of relaxation times. In this paper, we derive the distribution of the relaxation times that leads to the stretched exponential for the first time. The plausible connections with the Vogel-Fulcher and Arrhenius behaviors are also explored.

II. THE RELAXATION TIME SPECTRUM

The Kohlraush law for some relaxation function C(t), with the normalization C(0) = 1, reads

$$C(t) = \exp\left(-(t/\tau_o)^\alpha\right), \qquad 0 < \alpha \leq 1, \tag{1}$$

where τ_o is a characteristic time scale in the system and α is some parameter which is usually temperature dependent. It is easy to see that the Kohlraush law can be derived from the equation

$$\frac{dC(t)}{dt} = -\lambda(t)C(t), \tag{2}$$

with the time dependent relaxation rate

$$\lambda(t) = \frac{\alpha}{\tau_o}\left(\frac{t}{\tau_o}\right)^{\alpha-1}. \tag{3}$$

In contrast to the conventional Debye simple exponential decay (corresponds to $\alpha = 1$) with a constant relaxation rate, $\lambda = 1/\tau_o$, the relaxation rate $\lambda(t)$ decreases with time and therefore the relaxation becomes slower and slower in the long time limit. While simple Debye relaxation is characterized by a single relevant relaxation time τ_o with no appreciable dynamic correlation for time scale greater than τ_o, the stretched exponential relaxation indicates a statistical distribution of relaxation times across different time scales. It is natural to write

$$C(t) = \int_0^\infty g(\tau)\exp(-t/\tau)d\tau . \qquad (4)$$

The behavior of $C(t)$ can be accounted for by a suitable choice of the distribution of relaxation times g(r). g(r) is the spectrum of relaxation times characterized by the system. We shall see, by explicit calculations, that the slow relaxation in the Kohlraush law is due to a wide spectrum of g(r). The $g(\tau)$ must have a microscopic source in the correlations and its derivation from the microscopic relaxation mechanism will of course depends, to a certain extend, on the details of the system. The purpose of this work is not on the derivation of g(r) from the microscopic dynamical relaxation mechanism, but rather to obtain results on the general form of $g(\tau)$ corresponding to the Kohlraush law which has not been calculated explicitly before. Changing variables in Eq.(4), one can write

$$C(s) = \int_0^\infty u^{-2}g\left(\frac{1}{u}\right)\exp(-us)du \equiv \mathcal{L}\left[u^{-2}g\left(\frac{1}{u}\right)\right], \qquad (5)$$

where $\mathcal{L}$ is the Laplace transform with $\mathcal{L}[f(u)] \equiv \int_0^\infty f(u)\exp(-su)du$ for some function j(u). Hence the distribution function of the relaxation times can be obtained via the inverse Laplace transform

$$g\left(\frac{1}{u}\right) = u^2\mathcal{L}^{-1}[C(s)] = u^2\mathcal{L}^{-1}\left[\exp(-(s/\tau_o)^\alpha)\right]. \qquad (6)$$

For $\alpha = 1$, Eq. (6) gives $g(r) = \delta(\tau - \tau_o)$ agreeing with the conventional Debye relaxation with a single time scale. Unfortunately, the inverse Laplace transform in Eq. (6) is not easy to calculate analytically for general values of α. For $\alpha = 1/2$, we manage to compute the inverse Laplace transform and obtain

$$g(\tau) = \frac{1}{2\sqrt{\pi\tau\tau_o}} \exp\left(\frac{}{-4\tau_o}\right), \qquad \alpha = \frac{1}{2} . \qquad (7)$$

Fig. 1 shows the spectrum of relaxation g(r), in unit of τ_o, for $\alpha = 1/2$. g(r) is a continuous function with a finite width signifying a wide and continuous spectrum of relaxation times in contrast to the δ- function for Debye relaxation. Though it is difficult to compute the inverse Laplace transform in Eq. (6) for general values of α analytically, all the information about g(r) can still be obtained from its moments

$$\langle \tau^n \rangle = \int_0^\infty \tau^n g(\tau)d\tau , \qquad n = 0,1,2\cdots \qquad (8)$$

which can be calculated exactly as follows. The zero-th moment follows directly from Eq. (4) and the normalization of $C(t)$. By putting $t = 0$, one gets
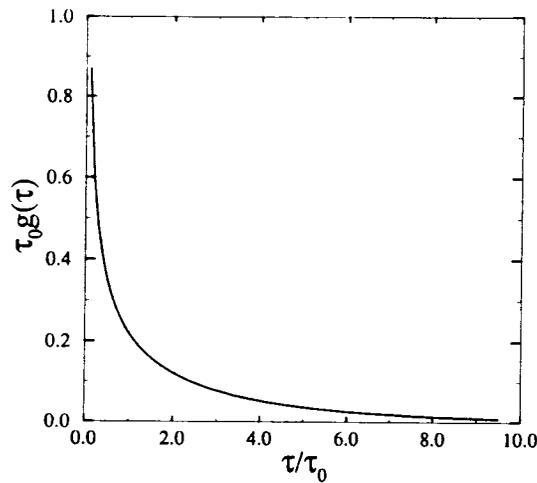
$$\langle \tau^0 \rangle = 1. \qquad (9)$$

FIG. 1. Relaxation time spectrum $g(\tau)$ for $\alpha = \frac{1}{2}$.

For higher moments, multiply Eq. (4) with t^{n-1} to both sides and integrate from 0 to ∞, one gets

$$\langle \tau^n \rangle = \frac{1}{(n-1)!} \int_0^\infty t^{n-1} \exp\left(\left(\frac{t}{\tau_o}\right)^\alpha\right). \tag{10}$$

The integral on the R.H.S. can be integrated upon transforming the variable $(t/\tau_o)^\alpha \to x$ and one finally gets

$$\langle \tau^n \rangle = \frac{\tau_o^n}{\alpha(n-1)!} \Gamma\left(\frac{n}{\alpha}\right), \qquad n = 1, 2 \cdots. \tag{11}$$

Thus all the properties of the spectrum $g(\tau)$ is known in the sense that explicit formulas for all its moments are obtained. The usual definition of the relaxation time corresponds to the first moment, with

$$\tau = \int_0^\infty C(t)dt \equiv \langle \tau \rangle = \frac{\tau_o}{\alpha} \Gamma\left(\frac{1}{\alpha}\right). \tag{12}$$

The relaxation time τ, in unit of τ_o, has a huge divergence as $\alpha \to 0$ even on logarithmic scale [Fig. 2]. τ increases by about fifteen orders of magnitude as α changes from 0.15 to 0.5! Such enormous growth in relaxation time is familiar in glassy systems in which the Vogel-Fulcher law [9]

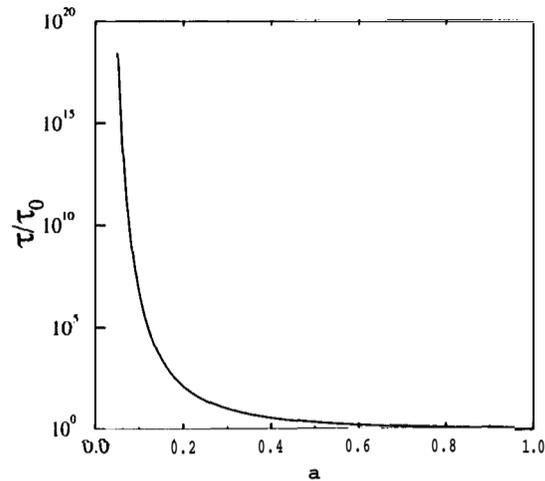$$\tau \sim \exp\left(\frac{A}{T - T_{VF}}\right) \tag{13}$$

FIG. 2. Average relaxation time τ, in unit of τ_o, as a function of α.

and Arrhenius law

$$\tau \sim \exp\left(\frac{A}{T}\right), \tag{14}$$

(where the A' s *are* some constants independent of T and T_{VF} is some temperature below the glass transition) are often observed. The width of the relaxation spectrum W_g can be measured by the second cumulant of g(r),

$$W_g = \sqrt{\langle \tau^2 \rangle - \langle \tau \rangle^2}. \tag{15}$$

Using Eq. (1 1), one gets

$$W_g = \frac{\tau_o}{\sqrt{\alpha}} \sqrt{\Gamma\left(\frac{2}{\alpha}\right) - \frac{1}{\alpha}\Gamma^2\left(\frac{1}{\alpha}\right)}. \tag{16}$$

For $\alpha = 1$, the width of the spectrum is zero corresponding to a single relaxation time of Debye exponential relaxation. For $\alpha < 1$, W_g is finite and increases as α becomes smaller. The variation of W_g, in unit of τ_o as a function of α is shown in Fig. 3. Below $\alpha \simeq 0.2$, W_g explodes over twenty orders of magnitude as α approaches 0.05. Therefore for smaller values of α, the relaxation has an extremely wide spectrum with time scales cover many orders of magnitude.

It is of interest to look at the small α behavior for the relaxation spectrum. Using the asymptotic form of the Γ function, one gets from Eq. (11)
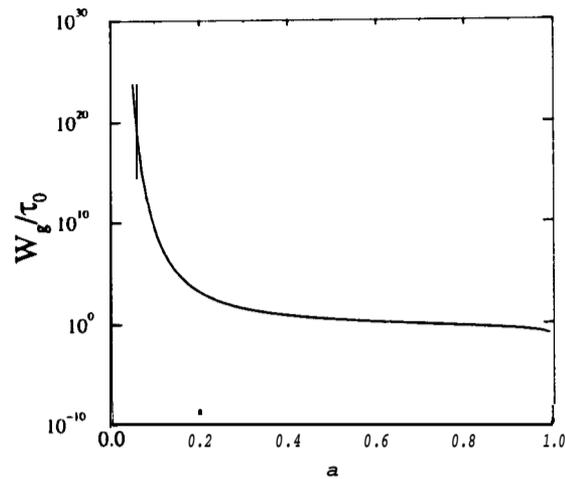
FIG. 3. Width of the relaxation time spectrum, in unit of τ_o, as a function of α.

$$\langle \tau^n \rangle \approx \frac{\sqrt{2\pi}\,\tau_o^n}{\alpha(n-1)!} \exp\left(\frac{n}{\alpha} \ell n \frac{n}{\alpha} \right), \qquad \alpha \to 0 \qquad n = 1, 2 \cdots . \tag{17}$$

Thus the relaxation time scales as

$$\tau = \langle \tau \rangle \sim \exp\left(\frac{1}{\alpha} \ell n \frac{1}{\alpha} \right), \qquad \alpha \to 0. \tag{18}$$

The huge growth in the relaxation time as $\alpha \to 0$ implies that the system is completely frozen, this phenomena is very similar to $T \to T_{VF}$ in the Vogel-Fulcher law. Hence it is tempting to identify $a \simeq (T - T_{VF})/T_{VF}$, then from Eq. (18), one has

$$\tau \sim \exp\left(\frac{\text{-constant x } \ell n(T - T_{VF})}{T - T_{VF}} \right) . \tag{19}$$

Eq. (19) differs from the empirical Vogel-Fulcher law in (13) which only holds for a limited temperature range. If $T - T_{VF}$ does not cover a wide temperature range, as in the range of validity of the Vogel-Fulcher law, $-\ell n(T - T_{VF})/(T - T_{VF}) \sim 1/(T - T_{VF})$ and hence it is plausible that Eq. (19) and the empirical form in Eq. (13) are not experimentally distinguishable within the limited temperature range. A similar plausibility also holds for the Arrhenius law in Eq. (14) with the identification of $\alpha \sim T$.

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