Slow Relaxation in Hierarchically Constrained Glassy Models

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Palmer, Stein, Abraham, and Anderson (PSAA) models of hierarchically constrained dynamics for glassy relaxation are revisited. The relaxation distribution and standard deviation for the Kohlrausch (or stretched) relaxation function ($\exp(-(t/\tau_e)^\beta)$) are derived in large t region. We also introduce the temperature dependence of the stretched exponent β and the effective relaxation time τ_e which exhibits the Vogel-Fulcher-like divergence at low temperature through the constrained variable μ_0.

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I. Introduction

Many systems (for example glasses, polymers, proteins and dielectrics $\cdots$) show at low temperature a slow relaxation to equilibrium [1]. The most commonly used empirical decay function for handling relaxation data affected by disorder is the Kohlrausch [2] (or stretched exponential) decay function

$$q(t) \sim q_0 \exp\left[-\left(\frac{t}{\tau_e}\right)^\beta\right], \qquad 0 < \beta < 1, \tag{1}$$

which is slower than the conventional Debye exponential form ($\beta = 1$) but faster than power law or logarithmic decay. The stretching exponent β and effective relaxation time τ_e are, in general, temperature dependent. Though particular experimental results may be better fitted by other empirical functions, Eq. (1) is the best two-parameter fit known across wide class of glassy materials and properties.

The simplest way to obtain a different result for $q(t)$ is to postulate a statistical distribution of relaxing times τ across different atoms, clusters, or degrees of freedom. Then, with the assumption of additive contributions to the relaxing quantity $q(t)$, it is natural to write

$$q(t) = \int_0^\infty \omega(\tau)\exp(-t/\tau)d\tau\,, \tag{2}$$

here $\omega(\tau)$ is so called relaxation distribution or weight function which satisfies $\omega(\tau) \geq 0$ and $\int_0^\infty \omega(\tau)d\tau = 1$. Different aspect of $\omega(\tau)$ will give different $q(t)$. However such aspects are specious unless reasons for a particular form for $\omega(\tau)$ are advanced. Eq.(2) tell us that $\omega(\tau)$ needs to be very broad, often having appreciable weight over many decades of τ. That is a wide distribution of times τ is essential for slow relaxation.

On the other hand, the temperature dependence of the effective relaxation time in Eq.(1) is well fitted by the Vogel-Fulcher (VF) [3] law

$$\tau_e = \tau_0 \exp\left(\frac{A}{T - T_0}\right), \tag{3}$$

where τ_0 is a microscopic time (e.g, 10^{-14} s), A is an apparent activation temperature, and T_0 is called Vogel-Fulcher temperature where the effective characteristic time becomes diverge. Typically, T_0 is several tens of degrees below the glass transition T_g. The physical meaning of this temperature where the singularity occurs is not known and it is often believed that Eq.(3) has no physical background and is just a fit function. However, we will show that the VF law will emerge in some cases as a limit of approximation.

In general, $\omega(\tau)$ is not easy to calculate analytically via the inverse Laplace transformation for general stretching exponent β, except $\beta = 1/2$ [5]. However, if we don't insist that Eq.(1) should hold for all time but only for large t, then we may have some models to calculate the relaxation distribution $\omega(\tau)$. Especially, Palmer, Stein, Abrahams, and Anderson (PSAA) [4] proposed a class of models that have been believed to capture the essential physics of relaxation in complex strongly interacting systems. Therefore, we would have a starting point to study slow relaxation. The organization of this letter is as follows: In sec. 2 we summarize the PSAA hierarchically constrained model. In Sec. 3 we derive the relaxation distribution $\omega(\tau)$ and higher moments which reveal the broadness of the distribution in PSAA model. We also proposed a temperature dependence of the effective relaxation time τ_e which reveals the Vogel-Fulcher-like divergence. Conclusion and discussion are given in Sec. 4.

II. PSAA hierarchically constrained models

PSAA chose a hierarchical arrangement of constraints in order to model sequential relaxation, in which each level must relax to release the next. They consider a discrete series of levels, $n = 0, 1, 2, \ldots$, with the degree of level n represented by N_n spins. Each spin in level $n+1$ is only free to change its state if $\mu_n(\leq N_n)$ spins in level n attain one particular state of their 2^{μ_n} possible ones. Thus the relaxation times can be expressed recursively as follows

$$\tau_{n+1} = 2^{\mu_n}\tau_n, \qquad n \geq 0. \tag{4}$$

They supposed the spin autocorrelation function $q(t)$ may be computed as a discrete sum

$$q(t) = \frac{1}{N}\sum_{i=1}^{N}\langle S_i(0)S_i(t)\rangle = \sum_{n=0}^{\infty}\omega_n \exp(-t/\tau_n), \tag{5}$$

where $\sum_0^\infty N_n = N$ and $\omega_n = N_n/N$. The specific ω_n and μ_n used by PSAA are

$$\omega_n = \frac{\omega_0}{\lambda^n}, \qquad n \geq 0, \tag{6}$$

$$\mu_n = \frac{\mu_0}{(n+1)^p}, \qquad n \geq 0, \quad p \geq 1, \tag{7}$$

where ω_0, λ, τ_0, and μ_0 are parameters which will determinate the stretching exponent β and the effective relaxation time τ_e (see below). For $p = 1$, on converting the sum in Eq.(1) to an integral and then evaluating the integral by saddle-point approximation (in large t region), Eq.(5) leads finally to

$$q(t) \sim \omega_0 e^{\left(\frac{t}{\tau_e}\right)^\beta} \tag{8}$$

with

$$\beta = \frac{1}{1+\overline{\mu_0}}, \qquad \tau_e = \tau_0 e^{\overline{\mu_0}\gamma} \left(\frac{\ln\lambda}{\overline{\mu_0}}\right)^{-\overline{\mu_0}} (1+\overline{\mu_0})^{-(1+\overline{\mu_0})}, \tag{9}$$

where γ is the Euler constant (≈ 0.577) and $\overline{\mu_0} \equiv \mu_0 \ln 2$. For $p = 1+\varepsilon$, Eq.(8) got a small correction (which is barely distinguishable from the exact Kohlrausch form) and they also obtained a Vogel-Fulcher law for $\tau_{\max} \equiv \lim_{n\to\infty} \tau_n = \tau_0 \exp(\overline{\mu_0}/\varepsilon)$ by linearizing the temperature dependence of ε near T_0 defined by $\varepsilon(T_0) = 0$. Therefore, at high temperature, relaxation over time scales between τ_0 and $\tau_{\max}$ is of the Kohlrausch form and crossing over to pure exponential behavior ($\exp(-t/\tau_{\max})$) for $t \gg \tau_{\max}$. As the temperature is lowered, $\tau_{\max}$ diverges in the Vogel-Fulcher manner, leaving behind a large region of Kohlrausch relaxation.

III. Relaxation distribution of the PSAA model

Under PSAA's construction, $\overline{\mu_0}$ was assumed to be a constant. Thus, the stretching exponent β and effective relaxation time τ_e are all temperature independent. However, experiments show that this is not the case [6]. If we plot the Kohlrausch relaxation function $q(t)$ against a logarithmic time scale (six decades) for the cases $\overline{\mu_0} = 0.1$, 1, and 5 respectively (see Fig. 1), then we find that at large $\overline{\mu_0}$, $q(t)$ crosses over more time scales than the case of small $\overline{\mu_0}$. To demonstrate this point more transparently, let us calculate the relaxation distribution $\omega(\tau)$ of the hierarchically constrained model as described above. Eqs.(4), (7) show that, for $p = 1$ and large n, we have

$$n = \left(\frac{\tau_n}{\hat{\tau}_0}\right)^{\frac{1}{\overline{\mu_0}}}, \tag{10}$$

where $\hat{\tau}_0 \equiv \tau_0 e^{\overline{\mu_0}\gamma}$. Then ω_n can be written in terms of τ_n as

$$\omega_n = \omega_0 \exp\left[-\ln\lambda \left(\frac{\tau_n}{\hat{\tau}_0}\right)^{\frac{1}{\overline{\mu_0}}}\right], \tag{11}$$

and $q(t)$ can be rewritten as

$$q(t) = \int_0^\infty d\tau \left[\frac{\omega_0}{\hat{\tau}_0 \overline{\mu_0}} \left(\frac{\tau}{\hat{\tau}_0}\right)^{\frac{1}{\mu_0 - 1}} e^{-\ln\lambda\left(\frac{\tau}{\hat{\tau}_0}\right)^{\frac{1}{\mu_0}}} \right] e^{-\frac{t}{\tau}} . \tag{12}$$

Comparing with Eq.(2), the weight function is easily read out to be

$$\omega(\tau) = \frac{\omega_0}{\hat{\tau}_0 \overline{\mu_0}} \left(\frac{\tau}{\hat{\tau}_0}\right)^{\frac{1}{\mu_0 - 1}} \exp\left[-\ln\lambda(\tau/\hat{\tau}_0)^{\frac{1}{\mu_0}} \right] . \tag{13}$$

Moreover, the normalization condition set $\omega_0 = \ln\lambda$, and $\omega(\tau)$ turns out to be a total derivative

$$\omega(\tau) = -\frac{\partial}{\partial\tau} \exp\left[-\omega_0(\tau/\hat{\tau}_0)^{\frac{1}{\mu_0}} \right] . \tag{14}$$

Substituting the spectrum function $\omega(\tau)$ into the integral representation of $q(t)$, we get

$$\begin{aligned} q(t) &= -\int_0^\infty d\tau \left\{ \frac{\partial}{\partial\tau} \exp\left[-\omega_0(\tau/\hat{\tau}_0)^{\frac{1}{\mu_0}} \right] \right\} \exp\left(-\frac{t}{\tau}\right) \\ &= \int_0^\infty d\tau (t/\tau^2) \exp\left[-\omega_0(\tau/\hat{\tau}_0)^{\frac{1}{\mu_0}} \right] \exp\left(-\frac{t}{\tau}\right) . \end{aligned} \tag{15}$$

Now changing the variable $\mu = t/\tau$, we have

$$q(t) = \int_0^\infty du \exp\left[-\omega_0 \left(\frac{\tau}{u\hat{\tau}_0}\right)^{\frac{1}{\mu_0}} \right] e^{-u} . \tag{16}$$

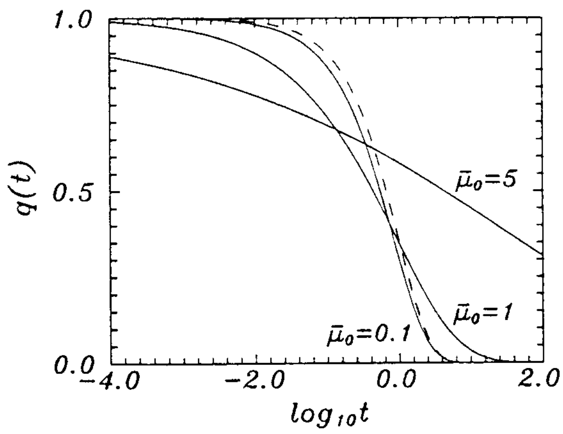
For large t, the saddle-point approximation give

$$q(t) \sim \exp\left[-\omega_0 \left(1 + \frac{1}{\overline{\mu_0}}\right) \left(\frac{t\overline{\mu_0}}{\hat{\tau}_0 \omega_0}\right)^{\frac{1}{1+\mu_0}} \right] , \tag{17}$$

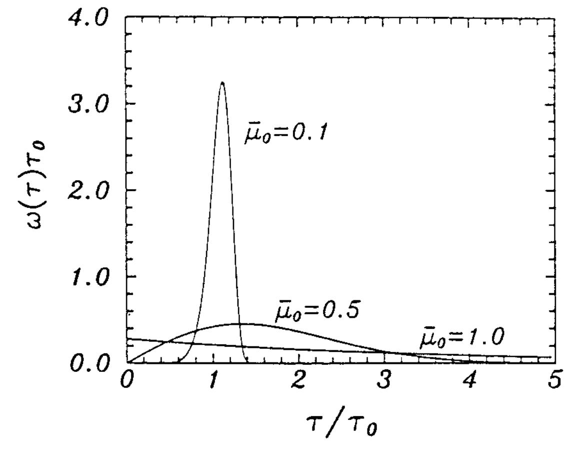
this leads to

$$q(t) \sim \exp\left[-\left(\frac{t}{\tau_e}\right)^\beta \right] ,$$

with β and τ_e, as expected, coincide with Eq.(9). Fig. 2 shows the distribution of the relaxation spectrum $\omega(\tau)$ for $\overline{\mu_0} = 0.1$, 0.5, and 1.0 respectively. We see that as $\overline{\mu_0}$ goes to zero, $\omega(\tau)$ will concentrate at τ_0. While $\overline{\mu_0}$ deviates from zero, the relaxation distribution will become more broader. This is not hard to aspect through the constrained dynamics point of view. According to Eq.(7), when $\overline{\mu_0} \to 0 (\beta \to 1)$, all levels are decoupled (because $\overline{\mu_0} \to 0$ for all n) and the system is characterized by a single relevant relaxation time τ_0,



(Fig. 1)



(Fig. 2)

FIG. 1. The relaxation function $q(t)$ plotted against a logarithmic time scale (six decades) for $\omega_O = 0.5$ and $\overline{\mu_0} = 0.1$, 1 and 5 respectively. The dashed line stands for the limiting case $\overline{\mu_0} \to 0$.

FIG. 2. Relaxation distribution $\omega(\tau)$ vs τ for $\omega_0 = 0.5$ and $\overline{\mu_0} = 0.1$, 0.5 and 1.0 respectively.

this gives $\omega(\tau) = \delta(\tau - \tau_0)$. On the other hand, when $\overline{\mu_0}$ increases, the correlations between levels become more and more stronger, leading to a very wide range of time scales.

Futhermore, with $\omega(\tau)$, the moments $\langle\tau^m\rangle_\omega \equiv \int_0^\infty d\tau\tau^m\omega(\tau)$ can be calculated as follows

$$\langle\tau^m\rangle_\omega = \left(\frac{\hat{\tau_0}}{\omega_0^{\overline{\mu_0}}}\right)^m \Gamma(1 + m\overline{\mu_0}), \qquad m = 0, 1, 2\cdots \tag{18}$$

The most important quantity which characterizes the width of the distribution is the standard deviation, defined by

$$\Delta\tau \equiv \sqrt{\langle\tau^2\rangle_\omega - \langle\tau\rangle_\omega^2}, \tag{19}$$

and can be expressed as

$$\Delta\tau = \tau_0 e^{\overline{\mu_0}\gamma}\omega_0^{-\overline{\mu_0}}\sqrt{\Gamma(1 + 2\overline{\mu_0}) - \Delta(1 + \overline{\mu_0})^2}. \tag{20}$$

The $\overline{\mu_0}$ dependence of $\Delta\tau$ is shown in Fig.3. Where we see that $\Delta\tau$ approaches to zero as $\overline{\mu_0} \to 0$ and goes up very fast as $\overline{\mu_0}$ increases. In fact, this behavior is intimated with another important phenomena called freezing that is frequently associated with slow relaxation [7]. Therefore, decreasing temperature or increasing $\overline{\mu_0}$ (in fact μ_0), the constrained spins in level 0 will cause the system to fall out of equilibrium. Moreover, the effective relaxation time τ_e is also divergent with $\overline{\mu_0}$. Eq.(9) shows that for large $\overline{\mu_0}$, $\ln(\tau_e/\tau_0)$ behaves linear in $\overline{\mu_0}$ (see Fig. 4). Based on these observations, we may assume that

$$\overline{\mu_0} \simeq \frac{T_0}{T - T_0}, \tag{21}$$

here T_0 is the temperature where $\overline{\mu_0}$ diverges. Therefore, as T approaches to T_0 the effective relaxation time diverges as

$$\tau_e \sim \tau_0 \omega_0^{-\overline{\mu_0}} e^{\overline{\mu_0}\gamma} = \tau_0 \exp\left[\frac{A}{T - T_0}\right], \tag{22}$$

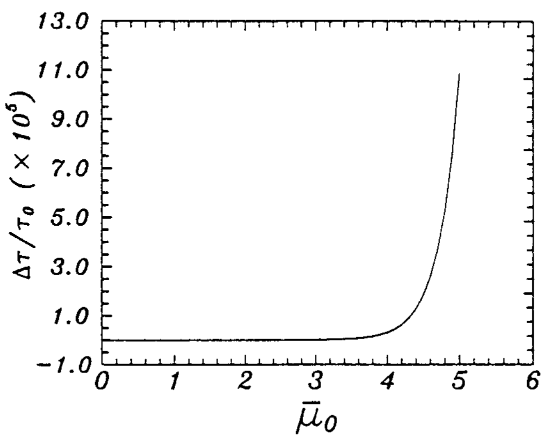
which is nothing but Vogel-Fulcher law with

$$A = (\gamma - \ln \omega_0) T_0 , \tag{23}$$

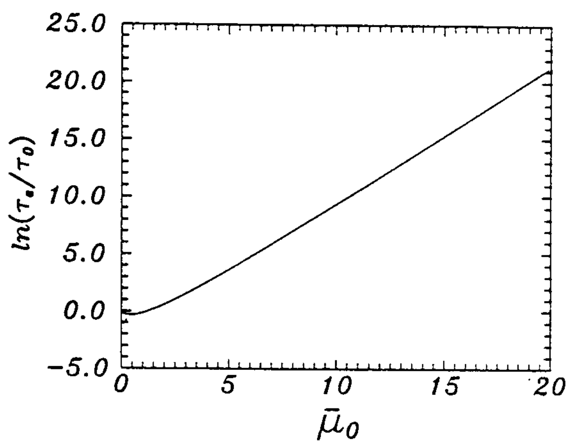
and T_0 should correspond to the Vogel-Fulcher temperature.

To get some feeling about these parameters, we can fit some data from experiments. For example, the slow relaxational component of the colloidal polystyrene micronetwork spheres gives $A = 2.01$ and $T_0 = 1.45° K$ [8]. Then from Eq.(23), we have $\omega_0 \simeq 0.445$ for the model discussed above. Finally, using Eq.(9), we also obtain the temperature dependence of the stretching exponent

$$\beta \simeq 1 - \frac{T_0}{T} . \tag{24}$$



(Fig. 3)



(Fig. 4)

FIG. 3. Standard deviation $\Delta\tau$ vs $\overline{\mu_0}$ for $\omega_0 = 0.5$.

FIG. 4. Logarithm of τ_e/τ_0 vs $\overline{\mu_0}$ for $\omega_0 = 0.5$.

IV. Conclusion and discussion

Let us summarize our results as follows:

a) Based on PSAA model, we have derived the relaxation distribution $\omega(\tau)$ which turns out to be a total derivative. The distribution involves more and more time scales as the constraints ($\overline{\mu_0}$) of the system becomes stronger.

b) We must stress that in our approach, the Vogel-Fulcher law is coming from τ_e rather than $\tau_{\max}$. Therefore, as T goes down to T_0, $\overline{\mu_0} \to \infty$, τ_e for Kohlrausch law exhibits a Vogel-Fulcher-type behavior. At the same time, $\beta \to 0$ which makes the tail of the relaxation longer. On the other hand, as T goes away above T_0, we have $\overline{\mu_0} \to 0$, $\tau_e \to \tau_0$, $\beta \to 1$, and the conventional Debye relaxation will be recovered.

c) Eq.(21) is crucial for obtaining the Vogel-Fulcher-like divergence of the effective relaxation time. However, it seems that this assumption is closely related to the divergence of the energy barriers between the metastable states in configuration space. To demonstrate this, let us consider the diffusion models in ultrametric space [9]. As temperature approaches to T_0 we can relate $\overline{\mu_0}$ to the energy barrier as follows

$$\overline{\mu_0} = \frac{\Delta \ln 2}{T},$$

where Δ is the unit of the energy barriers in configuration space. Then Eq.(21) implies that Δ diverges at T_0 as

$$\Delta \simeq \frac{DTT_0}{T - T_0},$$

and this type of divergence has been observed in experiments [10].

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