Models of Hierarchically Constrained Dynamics for Glassy Relaxation

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A class of models for relaxation in strongly interacting glassy materials is suggested. Degrees of freedom are divided into a sequence of levels such that those in level $n+1$ are locked except when some of those in level n find the right combination to release them, this representing the hierarchy of constraints in real systems. The Kohlrausch anomalous relaxation law, $\exp[-(t/\tau)^{\beta}]$, emerges naturally, and a maximum time scale is found which exhibits a Vogel-Fulcher–type temperature dependence.

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Since Kohlrausch[1] it has gradually become clear that the relaxation in complex, slowly relaxing, strongly interacting materials often follows the stretched exponential form

$$q(t)=q_0\exp[-(t/\tau)^{\beta}], \quad 0<\beta<1. \tag{1}$$

This "anomalous" relaxation appears to be far more common than the "conventional" Debye exponential form ($\beta=1$). Kohlrausch[1] first suggested Eq. (1) as a description of viscoelasticity. Williams and Watts[2] postulated the same function for dielectric relaxation. Jonscher,[3] and most recently Ngai,[4] have collected many examples, the latter proposing that it occurs in a very wide range of phenomena and materials. It has also been reported recently for the relaxation of remanent magnetization in spin glasses,[5] and appears to provide a reasonable fit to spin relaxation in spin-glass alloys above T_f.[6]

We propose a class of models that we believe captures the essential physics of relaxation in complex strongly interacting materials. In contrast to earlier attempts[4,7,8] at explaining Eq. (1), our models are based on *hierarchically constrained dynamics,* from which the Kohlrausch law arises naturally.

Conventional Debye relaxation,

$$q(t)=q_0\exp(-t/\tau),$$

is characterized by a single relevant relaxation time τ—there are no appreciable dynamic correlations on a time scale longer than τ. The simplest way to obtain a different result for $q(t)$ is to postulate a statistical distribution of relaxation 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

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

Any reasonable $q(t)$ can thus be "explained" by a suitable choice of the weight distribution $w(\tau)$. However, this approach is microscopically arbitrary, and does not explain the universality of Kohlrausch's law. It is also normally associated with a picture of *parallel* relaxation, in which each degree of freedom x_i relaxes independently with characteristic time τ_i. We believe instead that a *series* interpretation is more appropriate, with the path to equilibrium involving many sequential correlated activation steps. The same equation (2) may be used, but the $w(\tau)$ distribution must have a microscopic source in the correlations—or constraints—between different degrees of freedom.

In our view, a successful theory of glassy relaxation must satisfy three requirements:

(1) The theory must be based on *dynamics,* not

just statistics. Glassy systems clearly break ergodicity,[9,10] so that equilibrium distributions in configuration space are of little use. The free-energy barriers dominating relaxation will in general depend on the time scale of observation, which determines which processes are (i) effectively frozen, (ii) so fast as to be included in the entropy, or (iii) in an intermediate "active" class. The free-energy surface should therefore be renormalized as time progresses by integrating fast degrees of freedom out into entropy. We proceed instead with a directly dynamical approach, and make connections with this quasistatistical view later.

(2) The theory must involve *constraints.* We cannot diagonalize any reasonable nonlinear system into independent modes, so we expect to be left with interactions among any chosen set of coordinates. In the strongly interacting systems under study these interactions are primarily constraints in which, for example, atom (or cluster) A cannot move until atom (or cluster) B moves out of the way. Indeed, the dominance of constraints persists over a very wide range of time scales; $\tau_0 < t < \tau_{\max}$, say where τ_0 is a microscopic time (e.g., 10^{-14} s) and $\tau_{\max}$ is many orders of magnitude longer. The ergodic time $\tau_{\max}$ grows larger than experimental times as temperature T is reduced through the glass transition temperature T_g.[10] For $T > T_g$ we speculate that $\tau_{\max}$ follows a Vogel-Fulcher–type law which is experimentally observed for characteristic times τ such as appear in Eq. (1).[11] That is, we expect

$$\tau_{\max} \sim \exp[A/(T - T_0)]. \tag{3}$$

The strong constraints discussed here must not be identified with frustration, though it is possible to see static frustration over many length scales as the underlying cause of dynamical constraints over many time scales.

(3) The theory should involve a *hierarchy* of degrees of freedom, from fast to slow. The fastest degrees of freedom might involve single-atom motion. Other atoms, or groups of atoms, might only be able to move appreciably when several of the fastest happen to move in just the right way, leaving a hole or weakening a bond, perhaps. Such a hierarchical scheme, with faster degrees of freedom successively constraining slower ones, seems to us the only reasonably natural way of generating a wide range of relaxation times. The scheme also exhibits a series, rather than parallel, approach to equilibrium, as suggested above. In a real system there will be reverse constraints too, in which the state of the slower degrees of freedom determines the detailed dynamics of the faster ones.

We propose the simplest possible model that embodies these three principles. We supply no detailed microscopic connection, hoping only to find a model in the right dynamical universality class. We consider a discrete series of levels, $n = 0, 1, 2, \ldots$, with the degrees of freedom in level n represented by N_n Ising spins (or pseudospins) S_i. Each spin in level $n+1$ is only free to change its state if a condition on some spins in level n is satisfied; for definiteness we take the condition to be that μ_n spins in level n ($\mu_n \leq N_n$) attain one particular state of their 2^{μ_n} possible ones. Ignoring all intralevel correlations, the average relaxation times τ_n will be related by

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

giving

$$\tau_n = \tau_0 \exp\left(\sum_{k=0}^{n-1} \tilde{\mu}_k\right) \tag{5}$$

where $\tilde{\mu}_k = \mu_k \ln 2$. If $\mu_n > N_n/N_{n+1}$ there will be overlap in level n, with some spins involved in the constraint of more than one level-$(n+1)$ spin. This induces some intralevel correlations, which should not, however, be important at long times. The relaxation function $q(t)$ may be computed as

$$q(t) = N^{-1} \sum_{i=1}^{N} \langle S_i(0) S_i(t) \rangle, \tag{6}$$

where $N = \sum_{n=0}^{\infty} N_n$, which gives on average

$$q(t) = \sum_{n=0}^{\infty} w_n \exp(-t/\tau_n), \tag{7}$$

with $w_n = N_n/N$. To avoid factors of 2 in Eq. (7) the probability per unit time of flipping a level-n spin is taken as $2/\tau_n$.

Thus far the theory contains two unspecified functions, μ_n and w_n (or N_n). The physical picture of constrained atomic motion suggests that μ_n should be at most 5 or 10, but could be less than 1 to represent a weak constraint. For $T > T_g$ we expect a large but finite value of $\tau_{\max} = \lim_{n \to \infty} \tau_n$ if the model considered is to be relevant for glassy relaxation. Thus μ_n should decrease with n rapidly enough to make $\sum \mu_n$ convergent, but barely so. We therefore expect our model to be relevant to glassy liquids when

$$\tau_0 << < \tau_{\max} < \infty. \tag{8}$$

For $t >> \tau_{\max}$, Eq (8) will necessarily give pure exponential relaxation.

We have examined three simple postulates for μ_n: (a) *Constant,* $\mu_n = \mu_0$; (b) *exponential,* $\mu_n = \mu_0 \times \exp(-\gamma n)$; and (c) *power law,* $\mu_n = \mu_0 n^{-p}$. Postulate (a), and postulate (c) for $p \leq 1$, do *not* give a

finite τ_{max}, but may be interesting for the region $T < T_g$. In (b) we need $\gamma << 1$ to get a large τ_{max}, while in (c) we need $p - 1 << 1$.

The weights $w_n = N_n/N$ must also decrease to make $N = \sum_{n=0}^{\infty} N_n$ convergent. We have considered three postulates for N_n: (d) $N_{n+1} = N_n/\lambda$; (e) $N_n = \mu_n/\alpha (\alpha \leq 1)$; (f) $N_{n+1} = (N_n/\alpha)\mu_n$. The geometric choice (d) is the simplest satisfactory guess. Choice (e) seems at first reasonable—a fixed fraction α of the spins level n constrain each one in level $n+1$—but takes no natural account of the locality of constraints ($\mu_n \lesssim 5$), particularly in the thermodynamic limit $N_n \rightarrow \infty$. Choice (f) relates the ratio of spins in successive levels to the constraint condition operating between the levels.

Detailed results for each case of interest will be reported elsewhere.[12] Here we mention certain interesting cases. Case (a),(d) is exactly soluble in terms of an incomplete gamma function, and gives power-law relaxation, $q(t) \sim t^{-(\ln\lambda)/\tilde{\mu}}$, at long times. Case (b),(d) gives a crossover from power-law behavior $q(t) \sim t^{-(\ln\lambda)/\gamma}$ for $t < \tau_{max}$ to pure exponential, $q(t) \sim \exp(-t/\tau_{max})$ for $t >> \tau_{max}$. Case (c),(d) gives $q(t) \sim \exp[-(lnt)^{1/(1-p)}]$ for $0 < p < 1$, a form also found by Palmer, Sethna, and Langer[13] as a lower bound for spin-glass relaxation. Identification with their result gives $p = 1 - 1/d$, where d is the dimensionality of the spin glass. The case $p = 1$, which signals the onset of the Kohlrausch law (see below), corresponds to $d \rightarrow \infty$ in their model.

Most interesting is the case (c),(d) with $p \geq 1$, which corresponds to the condition Eq. (8) and gives the Kohlrausch law. Replacing Eq. (8) by an integral, we find

$$q(t) = w_0 \int_0^{\infty} dn\, \lambda^{-n} \exp\{-t/\tau_0 \exp[\tilde{\mu}_0 \zeta(p;n)]\}, \tag{9}$$

where for large n

$$\zeta(p;n) = \sum_{k=1}^{n} k^{-p} \simeq (p-1)^{-1} + \gamma_0 + \gamma_1 (p-1) \ldots - n^{1-p}/(p-1), \tag{10}$$

with γ_r known constants.

We first examine the case $p = 1$, which corresponds to the weakest divergence of τ_{max} within this class of models. In this case Eq. (9) becomes

$$q(t) = w_0 \int_0^{\infty} dn\, \lambda^{-n} \exp\left\{-\frac{t}{\tau_0 \exp(\tilde{\mu}_0 \gamma_0)} n^{-\tilde{\mu}_0}\right\}. \tag{11}$$

This integral is adequately treated by saddle-point integration for large t. The saddle-point condition is $n \propto t^{\beta}$, with

$$\beta = 1/(1 + \tilde{\mu}_0). \tag{12}$$

This leads finally to

$$q(t) \sim w_0 e^{-(t/\tau)^{\beta}}, \tag{13}$$

with

$$\tau = \tau_0 \exp(\tilde{\mu}_0 \gamma_0) \left[\frac{\ln\lambda}{\mu_0}\right]^{-\tilde{\mu}_0} \{1 + \tilde{\mu}_0\}^{-\beta}. \tag{14}$$

The next order correction that appears in the exponent is of order $\ln(t/\tau)$ which is negligible for large t.

Our previous discussion indicates that the case $p = 1 + \epsilon$ ($\epsilon << 1$), which satisfies Eq. (8), is relevant to glassy relaxation. For $t >> \tau_{max}$, relaxation is simple exponential. The interesting region is $\tau_0 << t < \tau_{max}$. Expanding in the small parameter $\epsilon \ln t$, we find for this region

$$q(t) \sim w_0 \exp(-At^{\beta + C\epsilon \ln t}) \tag{15}$$

where

$$t = [\tilde{\mu}_0/(\ln\lambda)\exp(\tilde{\mu}_0\gamma_0 - \epsilon\gamma_1)](t/\tau_0),$$

$$A = (1 + \tilde{\mu}_0^{-1})\ln\lambda,$$

and $C = \tilde{\mu}_0/[2(1+\tilde{\mu}_0)^3]$. This equation holds when $\epsilon \ln t << 1$, and is barely distinguishable from the exact Kohlrausch form Eq. (13).

We expect p to be a monotonically increasing function of T, since as temperature increases more correlations get broken on a given time scale. At some temperature T_0, $p = 1$ and $\tau_{max} \rightarrow \infty$. We assume that nothing spectacular or pathological occurs at this or any other temperature, but rather that p remains a smooth function throughout, with a value of unity at T_0. For $p = 1$, Eq. (13) holds for all $t >> \tau_0$, while for $p > 1$ there is a crossover back to pure exponential behavior for $t > \tau_{max}$, where

$$\tau_{max} = \tau_0 \exp[\tilde{\mu}_0/(p-1)], \tag{16}$$

for p close to 1. Linearizing the temperature dependence of p near T_0, we immediately obtain a Vogel-Fulcher law (3) for τ_{max}, with T_0 defined by $p(T_0) = 1$. We should note, however, that the characteristic time τ (essentially a renormalized τ_0)

of relaxation in the Kohlrausch regime [Eqs. (13) and (14)] remains finite, so the connection to experiment is still unclear.

Finally, the more complex case (c),(f) gives only logarithmic corrections to the (c),(d) Kohlrausch-law result, replacing t by $t \ln t$ in Eq. (13). Indeed the Kohlrausch-law result, or a form barely distinguishable from it experimentally, seems to emerge from a wide range of assumptions for N_n.

The following picture therefore emerges: At a fixed temperature slightly above T_g, relaxation over time scales between τ_0 and $\tau_{\max}$ is of the Kohlrausch form (with a small correction), crossing over to pure exponential behavior ($e^{-t/\tau_{\max}}$) for $t \gg \tau_{\max}$, when the system becomes ergodic. As the temperature is lowered, $\tau_{\max}$ diverges in the Vogel manner, leaving behind a larger region of Kohlrausch relaxation (which becomes increasingly exact) as it does so.

In conclusion, an extremely simple class of models of hierarchically constrained dynamics has been defined and found to give Kohlrausch time dependence rather naturally. In addition, the maximum time scale $\tau_{\max}$ for Kohlrausch behavior exhibits a Vogel-Fulcher–type behavior. Many extensions are possible, including *energy* barriers, reverse constraints, and other μ_n or N_n postulates. While we believe the essential physics behind the models to be correct, they are intended to be phenomenological and illustrative. A complete connection to microscopic dynamics and geometrical constraints in real glassy systems has not yet been built.

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[1]R. Kohlrausch, Ann. Phys. (Leipzig) **12**, 393 (1847).

[2]G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[3]A. K. Jonscher, Nature **267**, 673 (1977).

[4]K. L. Ngai, Comments Solid State Phys. **9**, 127 (1979), and **9**, 141 (1980).

[5]R. V. Chamberlin, G. Mozurkewich, and R. Orbach, Phys. Rev. Lett. **52**, 867 (1984).

[6]F. Mezei and A. P. Murani, J. Magn. Magn. Mater. **14**, 211 (1979).

[7]M. H. Cohen and G. S. Grest, Phys. Rev. B **24**, 4091 (1981).

[8]M. F. Schlesinger and E. W. Montroll, Proc. Natl. Acad. Sci. U.S.A. **81**, 1280 (1984).

[9]R. G. Palmer, Adv. Phys. **31**, 669 (1982).

[10]R. G. Palmer and D. L. Stein, *Proceedings of Workshop on Relaxation Effects in Disordered Systems,* Blacksburg, VA, 1983 (U. S. GPO, Washington, D. C., 1984).

[11]H. Vogel, Phys. Z. **22**, 645 (1921); G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1925).

[12]D. L. Stein, R. G. Palmer, E. Abrahams, and P. W. Anderson, to be published.

[13]R. G. Palmer, J. P. Sethna, and J. S. Langer, Bull. Am. Phys. Soc. **29**, 423 (1984), and to be published.