Topological derivation of shape exponents for stretched exponential relaxation

J. R. Macdonald
*Department of Physics and Astronomy, University of North Carolina, Chapel Hill,
North Carolina 27599-3255*

J. C. Phillips
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019

In homogeneous (ideal) glasses, the important dimensionless stretched-exponential shape parameter β is described by magic (not adjusted) simple fractions derived from fractal configuration spaces of effective dimension d^* determined by different topological axioms (rules) in the presence (absence) of a forcing electric field. The rules are based on a new central principle for defining glassy states: equal *a priori* distributions of fractal residual configurational entropy. Our approach and its β estimates are fully supported by the results of relaxation measurements involving many different glassy materials and probe methods. The present unique topological predictions for β typically agree with observed values to ~1% and indicate that for field-forced conditions β should be constant for appreciable ranges of such exogenous variables as temperature and ionic concentration, as indeed observed using appropriate frequency-domain data analysis. The present approach can also be inverted and used to test sample homogeneity and quality. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850901]

I. BACKGROUND

Among nature's nearly infinitely many materials one finds only a few good glass formers. The rarity of such materials is not widely appreciated, because the attention of science has focused on the few that do exist (such as window glass) because of their immense technological value. Almost all materials are "normal," in the sense that when they are cooled slowly their viscosity increases linearly with temperature, until the freezing point is reached, where they crystallize. Good glass formers, by contrast, encounter configurational barriers to crystallization on laboratory time scales. As a result, they can be cooled far below their equilibrium freezing points into metastable states characterized by an exponentially increasing viscosity η described[1] by ubiquitous functions of the Vogel–Fulcher form $\eta \sim \exp([T^*/(T-T_g)]^\alpha)$ with $\alpha \sim 1$ [or 1.5 (Ref. 1)].

At present there is no consensus regarding the nature of the configurational barriers to crystallization that characterize good glass-forming liquids. There are many families of good glass formers (network glasses, such as window glass; molecular glasses, such as glycerol; polymeric glasses, such as synthetic rubber, fused salts, …, and even electronic glasses) Ref. 2, and it seems likely that each family utilizes different kinds of configurational barriers to avoid crystallization. There is one practical observation that can be made: whatever these barriers are, it seems likely that they can be studied more easily, more accurately, and more completely in the glass than in the supercooled liquid. However, as implied by the Vogel–Fulcher relation, the viscosity itself is so large in glasses as to be nonmeasurable.

Fortunately, experiment has shown that in ideal glasses (ones that are microscopically homogeneous) there is a second ubiquitous relation that describes relaxation of any probe pulse of intensity I as a function of time: $I(t) \sim \exp[-(t/\tau)^\beta]$, where conventional exponential relaxation with a relaxation time τ is obtained when the dimensionless fraction $\beta=1$. In fact, this function [called stretched exponential relaxation (SER)] also describes relaxation in metastable glass-forming liquids with $\beta<1$. As T decreases towards T_g, β decreases, sometimes reaching a plateau near or somewhat above T_g, depending on the probe. This glassy plateau value $\beta(T_g)$ is discussed in great detail in a lengthy review;[2] it is also an important subject of this paper. Unlike the Vogel–Fulcher α, which is subject to 50% uncertainties,[1] the SER β has been determined with high precision (~1%),[2] rendering it an object of greatest theoretical importance in the study of glasses and their microscopic properties.

One can "explain" SER by noting that it corresponds merely to a particular distribution of relaxation times, and one would expect the relaxation times of glasses and supercooled liquids to be broadly distributed, because of the exponential complexity of the Vogel–Fulcher relation. This explanation, however, begs the question of why in microscopically homogeneous (ideal) glasses and supercooled liquids the distribution of relaxation times *always* has the stretched exponential form, after artifacts (associated, for example, with sample boundaries such as electrodes) have been removed. Moreover, this explanation does not indicate a path towards understanding the microscopic significance of the *dimensionless* shape fraction β.

Broadly speaking, at present one can distinguish two different ways of approaching descriptions of the glassy state. One can start with the picture of a normal liquid with inde-

pendent gaslike particles, and add correlations through polynomial interactions from presumed collective modes {as in mode-coupling theory [Ref. 2 (Sec. 3.1) and Ref. 3]}. These hydrodynamic mode-coupling models are useful, for example, in weather forecasting, and they can be used to fit some properties of the supercooled liquid, especially after three-mode interactions are added[3] which include adjustable parameters to fit T_g (poorly predicted by the two-mode model). Although this polynomial approach is useful for curve fitting some kinds of experimental data (especially scattering data taken by the very powerful spin-polarized neutron method[2,3]), it still leaves unanswered the central question discussed here, namely, the meaning of β.

In this paper and in the lengthy review,[2] which provides the foundation necessary to understand our axiomatic model, one takes a different approach. One argues that the appearance of the singular (or stretched) exponential functions in supercooled liquids (or glasses) shows that no polynomial, perturbative, or hydrodynamic approach based on ideas appropriate to normal gases and liquids is appropriate for glasses. Instead, one utilizes axiomatic topological models that are qualitatively different from geometrical models of normal liquids. These models plausibly assume that glasses, which differ from normal liquids because they are "frozen" into configurations with exponentially large (effectively infinite) viscosities, correspondingly occupy exponentially small fractions of free particle configuration space. Thus all geometrical real-space models, especially those that depend on parametrized polynomial assumptions, are exposed to the risk that the configurations they describe are not, in fact, *consistently* glassy (exponentially entangled). As an aside, one should note that this kind of problem has been familiar to mathematicians, especially set theorists and topologists, for more than 100 years; they refer to such problems as "non-polynomial (NP) complete" or exponentially complex. The prototypical exponentially complex problem is the traveling salesman, who should visit randomly placed cities along the shortest path. Mathematicians frequently emphasize that such problems cannot be solved by brute-force polynomial methods, not even with the largest computers.

One of the most obvious weaknesses of many theoretical papers is that they are connected to only one (more often, no) experiment. Moreover, older SER experiments (say, before 1980) were often made with samples that were not ideal (microscopically homogeneous); in addition, relaxation measurements require large databases, and before the widespread use of digital data acquisition and processing, these older databases, many incorporated in the broad collection of Ref. 4, contained many errors. More recent digital data have been of much higher quality, and these were identified and emphasized in the lengthy review.[2] Moreover, that review predicted certain "magic" values of β, and these predictions have been confirmed (with accuracies of order a few or even one percent), often without the authors being aware of the predictions, in *almost all* subsequent experiments that involved samples close enough to ideal to exhibit SER over many (>3) decades. The *predictive success* of the present approach in analyzing field-free experimental data could be taken as paradigmatic for quality control of analysis of a large, broad range of experimental data from multiple sources using many different methods. Several new examples of ideal SER are discussed below.

Although the topological approach has been reviewed in depth (Ref. 2, Sec. 3.2), it is summarized here for the reader's convenience. All glassy relaxation is supposed to take place in an exponentially restricted configuration space that is drastically different from conventional free particle configuration space. There are many ways that could be used to describe this abstract space, but happily it has turned out that the simplest way is by far the most successful, as verified by comparison with many experiments (Ref. 2, Secs. 6–9), and subsequent amazingly successful predictions (described here). The simplest way is topological: one imagines that relaxation paths are obtained by diffusion to relaxation sinks or defects[1,2] in a space of restricted dimensionality $d^* < d = 3$. There are a very few simple axiomatic rules for determining d^*, which turns out to be of the form fd, with $f = m/n$, where m and n are *integers* (not irrational numbers!) and $m \leq n < 10$. In other words, the configuration space is fractal, but it is a very simple fractal space. The integers m and n arise in obvious physical ways and they are not adjustable; there are only a few possibilities, and once determined for a given material, process, and probe, they are fixed and unique for the given situation.

There are two kinds of data on glass SER: temporal data, where the relaxation time τ and β can be obtained simply by fitting the residual $[t > 100\tau$ (Ref. 2)] field-free relaxation regime, and dispersive frequency-response data, usually obtained by measuring steady-state dielectric (field-forced) responses over limited, but often broad, frequency ranges.[2,4–6] Because glassy states occupy only exponentially small fractions of phase space, one should not assume (as is usually done) that the values of the dimensionless stretching fraction β are the same when measured in steady-state dielectric and in field-free relaxation experiments. Standard procedures exist for obtaining τ and β in the field-forced case by fitting to accurate numerical frequency-response models, but these must be handled with exceptional care to obtain reliable results, especially for β.[5,6] The kind of SER that is observed also depends sensitively on the excitation and measuring probes used, and it is much more sensitive to the nature and scale of sample inhomogeneities (static or dynamic). Usually there is independent evidence of the existence of static inhomogeneities. Such evidence is increasingly plentiful, or may be well known to experts in specific materials,[2] but this evidence is often overlooked in global geometrical models that claim to explain the microscopic origin of SER.

To establish the *intrinsic* behavior of field-free SER in homogeneous glasses we have critically reviewed and augmented (Ref. 2, Secs. 6–9) the very large (but old) database[4] of temporal SER structural relaxation experiments, ones that cover a wide range of undifferentiated homogeneous and statically inhomogeneous materials, probes, and detectors. We have also critically deconvoluted field-forced conductive-system dispersion data, being careful to separate the dispersive (ionic or dopant) part from the nondispersive host electronic and dipolar parts, and adequately accounting for the effects of charging at electrode interfaces.[5–7]

Our results may be summarized as follows: there exist a surprisingly large number of microscopically homogeneous glasses, including the most important ones technologically, whose properties, including the dimensionless stretching factor β, have been established with great accuracy ($\sim 1\%$ in β in many cases), through careful analysis. The data exhibit simple magic β fractions that can be explained *entirely topologically*, that is, in terms of only the connectivity and dimensionality of relaxation paths in configuration space. Geometrical factors, such as filling factors[8] or ranges of interactions[9] become important only in inhomogeneous glasses. Moreover, the topological dependence of the magic β fractions on the effective dimensionality d^* is different in the presence of a forcing electric field involving mobile charge carriers [conductive-system relaxation, β_f (Refs. 5 and 6)] than it is for field-free structural relaxation (β_0); the differences, though small, are systematic, independent of microscopic geometry, and fully explicable. The validity of the present topological approach is confirmed by the many successful predictions discussed below and in Refs. 5 and 6.

II. FIELD-FREE RELAXATION EXAMPLES

While much has been said rather generally about glass inhomogeneities, one can appreciate their significance most easily through examples. Silica, $(Na_2O)(SiO_2)_4$, and $(Na_2O)_{16}(CaO)_{10}(SiO_2)_{74}$ (window glass) are all homogeneous network glasses, but GeO_2 is not [in addition to the host fourfold coordinated Ge, it contains inclusions of fivefold or sixfold coordinated Ge in the form of deformed nanocrystallites with the much denser rutile structure (Ref. 2, Sec. 6.3)]. Thus β_0 [silica, $(Na_2O)(SiO_2)_4$]=0.60 (the theoretical magic fraction 3/5), while $\beta_0(GeO_2)=0.9$; the former value is intrinsic, while the latter is not.[2] Similarly, polybutadiene (synthetic rubber) is a prototypical polymer; properly prepared samples studied as a function of vinyl (cis-trans) sidegroup fraction gave a nearly constant $\beta_0=0.41-0.43$, in agreement with the predicted topological magic fraction 3/7 (Ref. 2, Sec. 7.2), whereas varying the vinyl fraction in samples stabilized by peroxide addition gave the much wider range 0.50–0.26; the former nearly constant values are nearly intrinsic and independent of geometrical factors, while the latter widely varying ones are not (see Fig. 20 of the lengthy review[2]). The "worst case" polymer, polyvinyl chloride (PVC), is partially crystallized.[2]

One of the most accurate ways of measuring β is through stress relaxation, which can take place at temperatures low compared to the glass transition temperature, and over very long times [see Fig. 15 of the lengthy review (Ref. 2, Sec. 6.1)]. This method has been used for several chalcogenide network alloy glasses, including pure Se itself (chain structure, few octet rings, unlike S, and very nearly ideally homogeneous), with results in excellent agreement with theoretical predictions.[2] The stress results for Se, measured on a time scale of 10^3 s, concur exactly with those obtained by neutron spin-echo studies with a time scale of 10^{-9} s, and they also agree with the predicted theoretical value of β $=3/7 \simeq 0.43$. Exact concurrence may be fortuitous, but as

theory and the two experiments all appeared concurrently and independently, it is not easy to dismiss such concurrence as the result of "data selection."

More recently the relaxation of polystyrene (PS) has been studied with stress relaxation.[10] PS consists of the usual hydrocarbon main chain with a phenyl side group. Pure PS is atactic (shapeless, presumably because of buckling stresses caused by the bulky side group).[2] Commercially PS is stabilized, and presumably rendered microscopically homogeneous, by the addition of a suitable volume fraction of acrylonitrile. How can one test this picture of the commercial product, an exponentially unlikely "straw" found as the result of a searching through a very large "haystack" by trial and error? It turns out that analysis of the birefringence of commercial poly(styrene-*co*-acrylonitrile) films[10] led to the identification of two relaxation processes, the fast one of the main chain and the 10^3 slower one of the phenyl side group. The main chain shows the same value of $\beta=3/7=0.43$ as Se chains did in both experiments described above, while the phenyl side group gave $\beta=0.32$. The interpretation of the side group result will be given below, after discussion of the microscopic axiomatic model, but it strains one's credulity to believe that all these concurrences are merely the result of data selection.

Among nonpolar molecular glass formers, orthoterphenyl (OTP) is the most studied, because it is available commercially in high purity. Relaxation in OTP has been studied by very accurate multidimensional (spin echo) nuclear magnetic resonance (NMR) methods,[11] yielding two values of β_0 for long and short preparation times, 0.59 and 0.42, compared to the topologically predicted fractions[2] 3/5 and 3/7, respectively. Brillouin scattering experiments also involve both long- and short-range forces, and these also give β_0 $=0.43$ for OTP.[12] Relaxation of propylene glycol (PG) molecules and polymers (PPG), where relaxation is driven by OH groups, vicinal in PG, but separated in PPG by 70 nondipolar monomers,[13] shows $\beta_0=0.43$ (PPG) and 0.6 (PG), agreeing *exactly* with topological *predicted fractions*.[2] Similarly good agreement ($\sim 1\%$) with *prediction* is obtained for orientational glasses, both dipolar[2] and quadrupolar.[14] The doped (conductive-system) field-forced dielectric relaxation examples listed in Table I show virtually identical values of β_f:[5] this similar behavior is also explained below topologically, *without the use of adjustable geometrical parameters*.

III. TEMPORAL TRAP MODELS

By now we expect that most readers will have been impressed enough with the examples above of spectacular agreement between theory and experiment to want to know briefly how the field-free theory (described in detail in the lengthy review[2]) actually works. Many derivations of structural SER begin with an axiomatic trap model similar to that introduced in the seminal context of dispersive transport;[15] the simplest and most physical derivations are summarized in Ref. 2, Sec. 3.2. In the field-free case, excitations are supposed to diffuse to immobile and randomly distributed traps, which act as sinks. At short times the initial $\beta=\beta_{0i}$ $=1$, while at longer times, scaling of the diffusion equation

TABLE I. Complex nonlinear least squares frequency-response fitting results using $K1$ (proper high-frequency limit) and $K0$ (uncorrected high-frequency limit) models (Refs. 5 and 6). We deal here with β_F quantities, but designate them by β_k, with the subscript k specifying the model used for fitting. The $\beta_1 = 1/3$ values listed below were held constant during fitting. Here $100S_F$ is the percentage relative standard deviation of a fit. The high-frequency limiting slope of the real part of the conductivity is $(1-\beta_1)$ for a $K1$ model and is the same in the limit when the $K0$ model is used to fit very-wide-range $K1$ synthetic data, so then $\beta_0 = 1-\beta_1$.

Material	T (K)	Fit models	$100S_F$	β_k	High-frequency limiting slope
$0.88ZrO_2 \cdot 0.12Y_2O_3$	503	$K1$	0.49	1/3	2/3
(single crystal)		$K1$	0.43	0.32	0.68
		$K0$	0.76	0.49	0.49
$0.03Na_2O \cdot 0.97GeO_2$	571	$K1$	1.4	1/3	2/3
		$K1$	1.3	0.36	0.64
		$K0$	2.3	0.55	0.55
$Na_2O \cdot 3SiO_2$	303	$K1$	0.55	1/3	2/3
		$K1$	0.56	0.33	0.67
		$K0$	0.67	0.56	0.56
$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	297	$K1$	2.2	1/3	2/3
		$K1$	2.2	0.34	0.66
		$K0$	3.0	0.56	0.56

(Ref. 2, Sec. 3.2) gives for residual relaxation (SER) in a configuration space of effective dimensionality d^*

$$\beta_0 = d^*/(d^* + 2) \quad \text{(field free)}, \tag{1}$$

yielding $\beta_0 = \beta_{0s} = 3/5$ for $d^* = d = 3$, often observed in field-free relaxation involving only density fluctuations. Because SER involving the β_0 of Eq. (1) is only asymptotic, one must utilize the results of some quite successful numerical simulations (Ref. 2, Sec. 2) to discuss the crossover to the residual regime.

One notes that in later data, especially for polymers and molecular glasses,[2] many values of β_0 are clustered near $\beta_{0l} = 0.43 \simeq 3/7$, which suggested a fractal interpretation of d^* as

$$d^* = fd \quad \text{(fractal)} \tag{2}$$

with $f = 1/2$ and thus $\beta = d/(d+4)$. Diffusion can take place equally in two channels, only one of which is relaxational, while the other is cyclical or ineffective. The two channels could depend on short- and long-range forces, as in PG and PPG,[11] with the long-range (ineffective) forces being either electrostatic (OH groups) or strain (polymers, whose chain structure generates strong, long-range, H-bond mediated strain fields). (Note that relaxation of a space-filling structure by long-range forces cannot occur by diffusive exchange; it can occur only via tunneling, which is exponentially unlikely.)

The two channels that give $f = 1/2$ are nearly always weighted *equally*, a characteristic of fractal models, and the result of microscopically equal residual configurational entropies. The assumption of the latter in describing exponentially restricted glass phase space is analogous to the *a priori* equal weighting of unrestricted phase space in statistical theories of gases. It appears to be the central unifying principle that describes glassy states, whether formed experimentally by slow quenching or in numerical simulations.[2] This

assumption is implicit in writing Eq. (2) for the fractal factor f that compresses the dimensionality of configuration space. [Note that such a compression, as it applies to *all* the N particles in the system, amounts to an exponential reduction of the combinatorially available phase space by a factor $(N!)^{1-f}$, where $N \gg 1$.] It can be justified in much the same way that one justifies *a priori* equal weighting of unrestricted phase space in statistical theories of gases, namely, in the absence of some other identifiable factor (such as the long-range potential associated with an externally applied electric field), equal weighting is the only choice available. In fact, as we shall see, Eq. (2) is not correct for ionic relaxation in the presence of an applied field; it is correct only for field-free relaxation. Of course, Eq. (2) is valid only for microscopically homogeneous samples. In the presence of microscopic inhomogeneities, anything is possible, but usually the distribution of relaxation times is broadened and β_0 is reduced. This explains the very small values of $\beta_0 (<0.2)$ that are sometimes reported for partially crystallized polymers, such as PVC.

At this point readers may be skeptical if they have a mental picture of glasses as extremely complex systems subject to a multitude of unspecified (and therefore uncontrolled) relaxation mechanisms. This picture is completely general and therefore it seems to be quite appealing. In fact, however, it is fatally flawed because it does not explain the ubiquitous occurrence of stretched-exponential relaxation, with its unique distribution of relaxation times. Of course, since such pictures cannot predict SER, they are completely unable to match the amazing predictive success of the relaxation channel model with only a few discrete channels. Glasses are, in fact, able to fill space yet avoid crystallization only because they are stabilized by self-organization of internal stress fields. Self-organization defines the available relaxation channels; the way in which glassy networks self-organize has been studied in several numerical simulations,

the most recent one involving 40 000 atoms.[16] Of course, we do not know from our axiomatic model the details of how this occurs, but we do not need to know such details because there are only a few possibilities for f to be considered. Similarly, in equilibrium thermodynamics many systems that differ from each other in detail still obey the law of corresponding states. The relaxation channel model is the glassy analog of the law of corresponding states. Much more detailed discussion of these methodological matters has already been given in the lengthy review.[2]

We can now return to the analysis of the birefringence data on relaxation of commercial poly(styrene-*co*-acrylonitrile) films.[10] There were two relaxation processes with relaxation rates separated by a factor of 10^3. The authors identified these two relaxation processes as belonging to (fast I) the main chain and (slow II) the phenyl side group, with $\beta_I = 0.43$ and $\beta_{II} = 0.32$. As we saw above, the value of $\beta_I = 0.43$ is just what we can expect from main chain relaxation with two channels and $f_I = 1/2$, only one of which is relaxational, while the other is cyclical or ineffective. Obviously $\beta_{II} = 0.32$ corresponds to $f_{II} = 1/3$, that is, relaxation with three channels, only one of which is relaxational, while the other two are cyclical or ineffective. What is the origin of the extra ineffective channel for the slow relaxation of the phenyl side group? It is probably the long-range interactions of the phenyl side group with the acrylonitrile copolymer, added commercially to stabilize the film and assure microscopic homogeneity. This hypothesis suggests a series of further experiments, studying the slow relaxation as a function of added fraction of acrylonitrile. It seems likely that $f_{II} = 1/3$ only for a narrow range of compositions near the commercial value, where the macroscopic properties of the film are optimized. This theoretical prediction, if confirmed, would provide additional positive support for the channel model. However, it has been our experience that no amount of predictive success will satisfy all the skeptics of such a simple, yet deep, model as that discussed herein.

IV. DYNAMICAL DIELECTRIC RELAXATION

In the past, analysis of frequency-dependent field-forced dielectric relaxation has tended to rely on awkward and inaccurate analytic approximations for converting estimated values of β to the time-domain values (Ref. 2, Sec. 5). More fundamentally, these transformations also assume that the presence of an applied field does not alter mobile charge relaxation kinetics. More recent analyses[5,6] of ionic conductive-system (doped dielectric) dispersive relaxation, measured in plane-parallel capacitor configurations, have revealed a universal frequency dependence associated with β_f that is not merely directly transformed from the time-dependent SER characterized by β_0. A bulk response model, called the Kohlrausch $K1$, involving only two free parameters with a fixed shape parameter, $\beta_1 = \beta_f$, has been found to fit frequency-response data for a wide variety of homogeneous materials with β_f equal to the unique value of $1/3$ for mobile charge carriers of a single type. This model is indirectly derived from a correlation function of exact SE form with the fixed value $\beta_1 = 1/3$. Its associated temporal response is not, however, of SE character with a constant value of β_1. Instead, separate approximate fits of the SE model to the full $K1$ response over limited temporal ranges show that the effective β approaches unity in the high frequency limit, is of the order of 0.5 for midrange times, and reaches $1/3$ only in the long-time limit.

A $K1$ composite model with $\beta_1 = 1/3$, one which includes dispersive electrode effects when significant, generally fits wide-frequency-range data sets appreciably better than do other models with more free parameters. The $K1$ part of the total response model fits the bulk part of the data exceptionally well over the entire frequency span; at high frequencies it leads to a limiting power-law log-log slope of the real part of the conductivity of $n_1 = 2/3$. In contrast to the $K1$ model, the $K0$ one is derived directly, rather than indirectly, from a correlation function of SE form with a fixed shape parameter of β_0, and its temporal response is therefore of exact SE form with a constant value of β_0 over the entire time domain. When the $K0$ model is used to fit the high-frequency part of $K1$ response, it leads in the high-frequency limit to the power-law exponent $n_0 = 2/3$ and to $\beta_0 = 2/3$ as well, in accordance with the well-established relation $\beta_0 + \beta_1 = 1$.[5,6]

These apparently universal shape parameter values may be explained as follows. At sufficiently low frequencies or long times, capacitor plane-parallel boundary conditions require that the current flows in one-dimensional "streams" normal to the plates, but at high frequencies the current is locally random, as expected for a fully glassy medium. Our model, as discussed below in detail, explains these two limiting fractions in terms of pinning of the current by the electric field, either globally at low frequencies, or locally at high frequencies. In addition, an entirely different theoretical model leads to the same unique values of the two limiting β parameters, thus providing additional support for their validity and universality.[6]

Results of fits of appropriate models to some experimental data sets are shown in Table I; many others are included in Refs. 5–7. Note that while the estimated β_0 values in the table, obtained from fitting experimental data with the $K0$ model, are the same as the high-frequency slopes of synthetic data derived using the $K0$ parameters estimated from the experimental data fitting (i.e., $n_0 = \beta_0$), they do not reach the value of $2/3$ because of the limited range of the available data. The more appropriate $K1$-model fits of the same experimental data, do, however, yield high-frequency slope estimates very close to $2/3$, as shown in the table. For comparison, Table I includes results for the $K1$ model with β_1 fixed at $1/3$ during fitting as well as taken as a free fitting parameter.

Even when the experimental data involve high-frequency limiting power-law slopes near or even exceeding unity, fitting using a composite model that includes the $K1$ one (representing bulk charge-carrier response) as well as other dispersive contributions, such as that associated with partial blocking of mobile charge carriers at the electrodes,[7] leads to bulk response best represented by the $K1$ with its fixed β_1 shape parameter of $1/3$ and its associated high-frequency-limiting power-law slope of $2/3$.

Seemingly, both ionic and electronic transport may have ranges that depend on r^s with $0 < s < 1$.[9] The resulting s dependence of β may be removed in a random-walk lattice model with long waiting times,[17] leading to an interesting relation involving $\beta_f(d)$, namely, $\beta_f(1) = \beta_f(3)/2$, first applied to frequency-domain results in Ref. 6. This relation appears to be satisfied only for conductive dielectric dispersive relaxation data that give $\beta_{fl}(1) = 1/3$ and $\beta_{fh}(3) = 2/3$,[5,6] where the subscripts indicate low- and high-frequency regions. The lattice model predictions agree with those of the diffusion model for $d^* = 1$, but disagree by ~10% for $d^* = 3$, while it is not immediately clear what role the forcing electric field plays in distinguishing the two models at low and at high frequencies.

V. FRACTAL DYNAMICAL MODEL

One can derive $\beta_{fh}(3) = 2/3$ topologically in a fractal model by postulating that in the presence of a forcing electric field, the carriers relax exponentially with respect to randomly oriented local polar coordinates. This assumption of maximally disordered local polar coordinates, compatible with space filling,[18] has also been made in analyzing three-body forces in a space-filling glassy network.[19] Constraint theory has also been very successful in predicting and describing the phase diagrams of network glasses, including the glass-forming (noncrystallizing) ability and other remarkable glass properties, such as the reversibility and nonaging compositional windows centered on average valence $12/5$;[20,21] these properties directly reflect the exponentially small phase space occupied by homogeneous glasses.

Within a local polar coordinate frame one has a radial coordinate and $(d-1)$ angular coordinates. *A priori* in the glassy state the residual entropies associated with these coordinates should be equal, and contribute equally to exponential relaxation, represented topologically by a harmonic product

$$\exp - ([t/\tau]^{1/d})^d = \exp[-t/\tau] \quad \text{(fractal exponential)}. \quad (3)$$

However, the d configurational coordinates are not all equally effective in relaxing currents in the presence of a forcing applied electric field at a polar angle θ. The field induces a uniaxially anisotropic local dynamical metric. In a general $d=3$ geometry, motion with respect to the azimuthal coordinate φ is irrelevant for homogeneous materials. Although there can be transient relaxation involving φ, in the steady state relaxation occurs with respect to only r and θ. The effective dimensionality for relaxation is thus $d^* = 2$, while the embedding dimensionality is $d = 3$, so Eq. (3) becomes

$$\exp - ([t/\tau]^{1/d})^{d^*} = \exp - [t/\tau]^{d^*/d}$$

$$\text{(fractal effective stretched exponential)}$$

$$(4)$$

and $\beta_{fh} = f = d^*/d = 2/3$. When currents "stream" normal to capacitor plates, transverse motion parallel to the plates is irrelevant (cyclical) giving $d^* = 1$. Now we forget about traps completely and simply assume that the residual dispersive

currents are those pinned to the forcing field. In that case, the fractal or topological value of β can only be

$$\beta_f = d^*/d = f \quad \text{(field forced)}. \quad (5)$$

This gives both $\beta_{fl}(1) = 1/3$ and $\beta_{fh}(3) = 2/3$, as found experimentally. This derivation has the advantage of incorporating the forcing character of the applied field explicitly in distinguishing between low and high frequencies. Note that it applies to $K1$ temporal response for the low-frequency limit and to $K0$ and power-law response for the high-frequency limit.

One can now easily see why the hopping range power-law exponent s does not appear in β_f, although it does appear in explicit algebraic models;[9] similar adjustable parameters appear in geometrical models with variable filling factors for trapping sites.[8] The algebraic models include the hopping range of the carriers, but they do not include the dynamically correlated polarization of the medium. The latter, however, arises from virtual hopping processes that have the *same* range dependence as the carrier motion; the local field corrections to the forcing field can then be screened in exactly the same way as the hopping length. But, one can ask, is the cancellation of the two factors perfect? The answer is yes, because motion in the glass is exponentially hindered, implying exponentially exact cancellation of power-law range hopping factors by power-law polarization hopping factors: after this cancellation all that can remain is the exponentially small fraction of phase space that is relaxationally effective. Therefore, we expect, as found previously for dispersive charge transport,[5,6] that the $1/3$ value of β_{fl} and the $2/3$ value of $\beta_0 = \beta_{fh}$ (obtained from the limiting slope of the conductivity) must be both temperature and ionic-concentration *independent*, contrary to the predictions of most geometrical models. Finally, in contrast to Ref. 17, which used a lattice model and derived only $\beta f(1) = \beta_f(3)/2$, the present model leads to unique values for both quantities.[6] For the reader's convenience field-free and field-forced values of β are summarized in Table II.

As we have seen, the $K1$ fractal dynamical model, with the fixed value $\beta_1 = 1/3$, fits field-forced dispersive frequency response data for an extremely wide variety of homogeneous ion-conducting materials. One may well ask, however, to what degree is it only an empirical, phenomenological data-fitting model of unknown physical significance? The model involves three distinct components. First is its form, second is the ion-ion correlation function that it involves, and third is the value of any shape parameter appearing in the correlation function. It turns out that the form of the model is the only conductive-system dispersive one that has been derived from both a macroscopic relaxation approach[22] and from the detailed and deservedly famous continuous-time-random-walk hopping model of Sher and Lax.[15,23] This model involves a general but specifiable correlation function. Next, when this function is taken to be of the popular stretched-exponential form, one that has itself been derived from microscopic analyses in various ways, one obtains the $K1$ model with a stretched-exponential shape parameter β_1 satisfying $0 < \beta_1 \leqslant 1$. Finally, the justification for the virtually

TABLE II. Values for β predicted for molecular and ionic relaxation depend on the range of forces (short or both long and short) for the former, and on whether or not one includes the correct high-frequency limiting slope behavior (entered here as $*$) in transforming the frequency data of the latter to the temporal regime. When the latter is included, β_{fl} is given as $1/3$, but when it is omitted values close to $1/2$ are found (Table I) for usual limited-range data.

Excitation	Notation	Internal	External	d	f	β	References	Year
Molecular	β_0	Short	None	3	1	3/5	13	1973
Molecular	β_0	Long	None	3	1/2	3/7	14	1994
Ionic	β_{fl}	None	Low	3	1/3	1/3 ($\sim$1/2)	5 and 6	2004
Ionic	β_{fh}	None	High	3	$2/3^*$	2/3	5 and 6	2004

universal applicability of the full model follows from the joint topological and analytic derivations of the uniquely economical $\beta_1 = 1/3$ value.

The distinctions made here between field-free β_0 and field-forced β_f relaxation produce differences in β that are sometimes numerically small (2/3 compared to 3/5), but they nevertheless imply that the two cases represent thermodynamically different phases. New low-field longitudinal magnetoconductance oscillations have been discovered in two-dimensional electron glasses in a forcing microwave field;[24] these oscillations are qualitatively different from high-field de Haas–Shubnikov oscillations and are described topologically as a new synergistic phase.[25] One can also note that dielectric hole burning in glycerol[26] is described by a dynamically heterogeneous SER model with $\beta = 0.65$, very close to our expected (field-forced) value of $\beta_f = 2/3$. Partitioning or coarse graining is a physically appealing way to reduce phase space in nonequilibrium disordered systems;[27] however, it does not distinguish between static and dynamic inhomogeneities, fractal dimensionalities, or forcing effects.

VI. ANISOTROPY OF CUPRATE PHOTOINDUCED (SUPER)CONDUCTIVITY

While there are many examples of intrinsic topological relaxation, the most demanding application is probably to photoinduced (super)conductivity in the cuprates [specifically the very well-studied $YBa_2Cu_3O_x$ at the metal-insulator transition, $x = 6.4$, where ideal (microscopically homogeneous) electronic networks are formed].[2,28] Here the laser field clearly is forcing the development of a field-pinned internal filamentary structure upon a precursive percolative structure, so both field-free and field-forced mechanisms are contributors to this remarkable effect: which makes the greater contribution? The superconductive cuprates are layered pseudoperovskites, with in-plane conductivities 10–100 times larger than perpendicular conductivities. The phenomena exhibit SER, so we can use the anisotropy of observed values of β, shown in Table III, to answer this question. The in-plane low-temperature limit agrees well with $\beta_0 = 3/5$, suggesting that the internal structure develops mainly through atomic density relaxation. The systematic difference $\delta\beta \sim 0.05$ between in-plane and out-of-plane β values suggests that the in-plane rearrangement is more nearly completed (with applied fields shorted out by the large planar conductivity), while the plane-normal relaxation still retains some memory of the insulating state and resembles the high-

frequency limit $\beta_{fh} = 2/3$ of field-forced relaxation. Thus this small difference in β appears to be significant quantitatively, and it is in accord with our intuitive expectations regarding the photoinduced formation of weak, low-conductivity interplanar links (traps are present in the insulating layers).

VII. CONCLUSIONS

The dynamic and thermodynamic properties of glasses are rich and diverse; they appear in at least twelve different categories and all seem to be related through β.[29] In our experience in fitting one category, dispersive transport,[5–7] we have found that β_f (which describes the shape of the relaxation-time distribution) is much more stable than is the SE characteristic relaxation time τ itself (which is discussed more often, especially in the context of percolative models), and thus β_f can be used to test power-law assumptions regarding frequency or time ranges outside those studied experimentally. For statically homogeneous samples one can have much more confidence in data fits that yield magic fractions for β, and therefore more confidence in chemical trends of other less stable parameters (such as τ) that depend implicitly on β as well as other "hidden" parameters. In emerging fields of materials science (such as cuprates), the materials that yield magic fractions for β_0 are consistently of higher quality.[2] By explaining the topological origins of β without the use of adjustable parameters, the present theory may provide useful guides to more consistent theories of all the properties of glasses.

Postscript. A complex geometrical (hyperspherical) fractal model of random walks on percolation clusters[30] yields SER exactly, showing that SER is the result of phase-space compression. However, the values of β range from ~ 0.7 ($d = 2$) to $1/3$ ($d \rightarrow \infty$), in disagreement with our results and experiment. Note that the percolation clusters, although exponentially unlikely, are still *static* geometrical constructs,

TABLE III. SER parameters for photoexcitation of resistivities in layered YBCO (Ref. 20). The theory, discussed in the text, refers to an ideal sample without ferroelastic fluctuations, which may reduce both β's by 5%–10%.

T (K)	β (in plane)	β (out of plane)
275	0.54	0.57
200	0.55	0.59
125	0.56	0.61
50	0.58	(Noisy)
Theory	0.60	0.67

and that these constructs need not be fully consistent with glassy relaxation *dynamics*.

After Ref. 2 was published, skeptics who picture glasses as extremely complex systems subject to a multitude of unspecified (and therefore uncontrolled) relaxation mechanisms suggested privately that the relaxation channel model provides only an incomplete description of glassy relaxation at the microscopic level. The theory had been found to fit relaxation of the intermediate scattering function $S(Q,t)$ only at $Q=Q_1$, where Q_1 is the position of the largest peak. A more complete description, they said, would include a function $\beta(Q)$, which would oscillate, much as $S(Q,0)$ does. This conjecture has recently been tested[31] with spin polarized neutron scattering studies of $S(Q,t)$ in polybutadiene and polyisobutylene in the temperature range above the glass transition dominated by segmental relaxation. Even in this range in both cases the result was that β is fixed and independent of Q. These results provide further validation of the relaxation channel model and greatly enhance the significance of data obtained by spin polarized neutron scattering as measures of intrinsic relaxation dynamics that are independent of the probe neutron momentum.

While it is obvious that ideal properties, such as microscopic homogeneity, are of great importance for commercial quality control of synthetic materials, it is also possible to prove that evolutionarily designed networks living materials, such as neuronal networks also benefit from a high level of microscopic homogeneity.[32]

[1] J. T. Bendler, J. J. Fontanella, and M. F. Shlesinger, Chem. Phys. **284**, 311 (2002).

[2] J. C. Phillips, Rep. Prog. Phys. **59**, 1133 (1996); Physica C **340**, 292 (2000).

[3] V. Krakoviack and C. Alba-Simionesco, J. Chem. Phys. **117**, 2161 (2002).

[4] R. Bohmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).

[5] J. R. Macdonald, J. Appl. Phys. **90**, 153 (2001); J. Chem. Phys. **116**, 3401 (2002); J. Appl. Phys. **95**, 1849 (2004).

[6] J. R. Macdonald, Phys. Rev. B (submitted).

[7] J. R. Macdonald, J. Non-Cryst. Solids **307–310**, 913 (2002).

[8] B. Sturman, E. Podivilov, and M. Gorkunov, Phys. Rev. Lett. **91**, 176602 (2003).

[9] J. Klafter and M. F. Shlesinger, Proc. Natl. Acad. Sci. U.S.A. **83**, 848 (1986).

[10] S. Takahashi and H. Saito, Macromolecules **37**, 1062 (2004).

[11] R. Bohmer, G. Hinze, G. Diezemann, B. Geil, and H. Sillescu, Europhys. Lett. **36**, 55 (1996).

[12] G. Monaco, D. Fioretto, L. Comez, and G. Ruocco, Phys. Rev. E **63**, 061502 (2001).

[13] R. Bergman, C. Svanberg, D. Andersson, A. Brodin, and L. M. Torell, J. Non-Cryst. Solids **235**, 225 (1998).

[14] M. Winterlich, G. Diezemann, H. Zimmermann, and R. Böhmer, Phys. Rev. Lett. **91**, 235504 (2003).

[15] H. Scher and M. Lax, Phys. Rev. B **7**, 4491 (1973).

[16] J. Barre, A. R. Bishop, T. Lookman, and A. Saxena, Phys. Rev. Lett. (in press).

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

[18] J. C. Phillips, cond-mat/0402111.

[19] J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).

[20] Y. Wang, J. Wells, D. G. Georgiev, P. Boolchand, K. Jackson, and M. Micoulaut, Phys. Rev. Lett. **87**, 185503 (2001).

[21] S. Chakravarty, D. G. Georgiev, P. Boolchand, and M. Micoulaut, cond-mat/0312481.

[22] C. T. Moynihan, L. P. Boesch, and N. L. Laberge, Phys. Chem. Glasses **13**, 171 (1973).

[23] J. R. Macdonald, Solid State Ionics **150**, 263 (2002).

[24] R. G. Mani, J. H. Smet, K. Von Klitzing, V. Narayanamurthi, W. B. Johnson, and V. Umansky, Nature (London) **420**, 646 (2002).

[25] J. C. Phillips, cond-mat/0402112.

[26] K. R. Jeffrey, R. Richert, and K. Duvvuri, J. Chem. Phys. **119**, 6150 (2003).

[27] R. V. Chamberlin, Phys. Rev. Lett. **82**, 2520 (1999).

[28] W. Markowitsch, C. Stockinger, W. Lang, R. Rossler, J. D. Pedarnig, and D. Bauerle, Physica C **366**, 277 (2002); (private communication).

[29] K. L. Ngai, J. Non-Cryst. Solids **275**, 7 (2000).

[30] P. Jund, R. Julien, and I. Campbell, Phys. Rev. E **63**, 036131 (2001).

[31] B. Frick, G. Dosseh, A. Cailliaux, and C. Alba-Simionesco, Chem. Phys. **292**, 311 (2003).

[32] T. Nishikawa, A. E. Motter, Y. C. Lai, and F. C. Hoppensteadt, Phys. Rev. Lett. **91**, 014101 (2003).