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LETTER TO THE EDITOR

Subensembles and Kohlrausch relaxation in electronic and molecular glasses

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Abstract. A new theory of glassy relaxation has recently identified *two* intrinsic stretched exponential relaxation channels associated with charge and density fluctuations characterized by *two* magic stretching fractions, $\beta_c = \beta_K = \frac{3}{7}$ and $\beta_d = \beta_{sr} = \frac{3}{5}$. The theory is revised here to describe structural relaxation in the presence of defects such as kinks in polymers. The revised theory explains recent NMR multiple-spin-echo experiments which exhibit *two* corresponding relaxation modes ('slow' and 'fast'). A remarkable byproduct of the theory is an explanation of the origin of the Vogel–Fulcher 'singularity' in the viscosity of fragile glass formers near the glass transition as the result of *two*-stage structural arrest.

Both electronic and molecular relaxation have been studied extensively in the 150 years that have elapsed since Kohlrausch measured the discharge of a Leiden jar capacitor and found that after an initial exponential transient the residual relaxation was described by a stretched exponential, $I(t) \propto \exp[-(t/\tau)^\beta]$, with $0 < \beta < 1$. It has turned out that $I(t)$ is ubiquitous and in hundreds (or even thousands) of experiments on not only electronic but also molecular relaxation this function fits the data even better than it did for Kohlrausch [1]. This success is far more surprising than one might suspect given its convenient two-parameter algebraic form, for $I(t)$ is only an asymptotic approximation, and of course it is not analytic. In a way this is not surprising, for residual relaxation in non-equilibrium disordered systems such as glasses should not be describable by power series expansions, for example. For a long time it was thought that $I(t)$ was only useful for fitting curves, and that β was no more than a felicitous curve-fitting parameter with no microscopic meaning. About twenty years ago, however, it was discovered (first in one dimension [2] and later more generally [3–5]) that the Kohlrausch function provided the asymptotic solution to a natural physical problem, that of dispersive current transport in a material with a high trap density as measured either with pulsed currents or through non-radiative exciton decay. In this model the origin of the stretched exponential is easy to understand. As the traps or sinks absorb excitations the density of excitations near the traps is depleted, resulting in a decreasing rate of relaxation as particles must diffuse increasingly large distances before being absorbed at the traps or sinks. Once this had been demonstrated there was a tendency to declare the problem *solved* (at least among some theorists [6]), even while experimentalists still regarded it as one of the major *unsolved* problems of physics [7].

This divergence of viewpoints arose because the theory seemed to be incapable of predicting the values of β observed in experiments on different materials with different pumps and probes. When the relaxation takes place entirely through short-range interactions at randomly distributed static traps in a configuration space of restricted dimensionality d^* , the theory [8] unambiguously predicts $\beta = d^*/(d^* + 2)$, and with the unrestricted

value $d^* = 3$ this gives $\beta = \beta_{sr} = 0.6$. However, in structural relaxation experiments a wide range of values of β between 0.9 and 0.1 is observed, corresponding to apparently arbitrary fractal configuration space dimensionalities d^* , even at low temperatures where β has become temperature independent. The natural explanation for this is that residual relaxation depends on the impurity structure in some way. However, if this is the case, then there is no reason for the observed invariance of the stretched exponential functional form either, and we are left no better off than Kohlrausch, whose value for β was 0.426 [1].

While the problem of connecting the theory of dispersive transport, with depletive effects near traps, to residual relaxation experiments quantitatively has long been deemed insoluble, a recent lengthy survey of conceptual and mathematical models, computer simulations and a very wide range of experimental data [8] has shown that the situation can be greatly clarified by combining fundamental understanding of the mathematical problems involved in defining d^* with a detailed analysis of material properties. One of the key steps was the realization that the randomly distributed sinks which are traps in the electronic case can become relaxation centres in the molecular case. These relaxation centres act as 'black holes' for the non-ergodic dissipation of structural excitations. The local nature of the electronic traps is irrelevant to the value of β ; all that is required is that the diffusion coefficient of these centres be small compared to that of medium excitations, and similarly for their decay rate. In this way it becomes possible to separate extrinsic and intrinsic effects, and to recognize that for dispersive electronic transport the dimensionality of configuration space d^* is the physical dimensionality d when relaxation occurs through density fluctuations, while $d^* = d/2$, corresponding to fractal dispersive transport (FDT), when the relaxation occurs through charge fluctuations. FDT was explained by an Ewald-like construction which assumed that collective plasma fluctuations are ineffective in linearly relaxing individual particles, much as only phonons, and not phasons, contribute to linear diffusion and relaxation in quasicrystals [9].

The analogy between quasicrystal structural relaxation and electronic relaxation is a natural one because in both cases the diffusional anomalies occur in the context of a translationally invariant medium. Because the two values of β which are widely observed in accurate studies of relaxation are $\beta = \frac{3}{5}$, corresponding to $d = d^* = 3$, and $\beta = \frac{3}{7}$, corresponding to $d^* = \frac{3}{2}$, it was natural to assume that the effective medium model which gave $d^* = \frac{3}{2}$ for electronic relaxation could also be used to explain the value of $\beta = \frac{3}{7}$ observed in many structural relaxation experiments, as the consequence of long-range forces. Certainly long-range Coulomb forces are present in all structural relaxation experiments. For example, one of the materials which exhibits $\beta = \frac{3}{7}$ is a-Se. This nominally non-polar material consists of ~ 300 -atom chains and it is known to exhibit strong infrared absorption bands which arise from internal distortions of its spiral symmetry. The induced effective charges could then introduce long-range interactions between kinks which would account for the observed value of β . However, there are some cases where these arguments appear to fail, notably in explaining results obtained in some very elegant molecular dynamics simulations of relaxation in fused salts. Also many scientists have expressed reservations about the overall soundness of using Coulomb forces to explain relaxation in non-polar hydrocarbons, regardless of geometry.

To resolve these questions this letter re-examines the basic electronic trap or sink model and suggests alternative molecular models based on subspace or subensemble relaxation. In the electronic case the excitations are injected into the bulk, either by electrodes or by light, and diffuse to point sinks. Depletion of excitations near the sinks is described by the diffusion equation, with logarithmic length scales on each side of the equation proportional

to d^* and $d^* + 2$. However, in structural relaxation experiments the nature of the relaxation is strongly affected by the various structural elements of the glass. Short-time relaxation of density fluctuations, which occurs at higher temperatures but still close to the glass transition, may be representative of the glassy medium as a whole. However, long-time relaxation may be associated with characteristic defects in the medium-range structure of the glass, as at long times only excitations localized at such defects have survived earlier thermalization. The nature of the configuration space in which the diffusion takes place may itself depend on the temperature at which the relaxation is studied and on the character of the pump used to produce that excitation and the probe used to detect its decay.

This model, in which bulk excitation is replaced by selective excitation of subspace subensembles, has the advantage for structural relaxation that the nature of the dissipation is clarified. However, in comparison with the bulk excitation model, we no longer have a nearly universal mechanism for a nearly universal observation. Instead we must find a new mechanism for structural relaxation which gives $d^* = d/2$ for each case of selective or defect-localized excitation, and this mechanism must be sufficiently general as to apply to many different materials in which one would expect the selected sources to behave quite differently. In other words, it is necessary to justify the model separately and in detail for each case, even though many cases lead to almost identical behaviour. At first it may appear that in trying to escape from the difficulties of 'universal' Coulomb fractal relaxation we have only jumped 'from the frying pan into the fire', but it turns out that the subspace or subensemble model contains some hidden simplifications which produce most of the desired results. In any case, with an alternative model the reader may choose for herself or himself the approach that seems better suited to a given situation.

The general idea that leads to fractal Kohlrausch relaxation is simple. Although the dimensionality of laboratory space is d , the effective dimensionality d^* of the configuration space, in which glassy relaxation takes place, is severely altered by the constraints imposed on particle motion by structural arrest. Thus $d^* = df_p$, where f_p is the partition or projection fraction of degrees of freedom available for relaxation, which is determined by analysing product vector spaces; the easiest way to understand f_p is through examples. With normal bulk density fluctuations $f_p = 1$. With bulk charge fluctuations $f_p = \frac{1}{2}$ because plasmons do not contribute to relaxation of individual charges [8]. In a three-dimensional quasicrystal $f_p = \frac{1}{2}$ because only phonons, not plasmons, contribute to diffusion. However, in an axial quasicrystal $f_p = \frac{3}{5}$ because there is normal periodicity along the axis [9].

As an example of subensemble relaxation, let us consider long-chain polymers without bulky side groups, such as a-Se or polybutadiene [8]. Here experimental probes have generally given $f_p = \frac{1}{2}$. This was previously explained [8] in the context of Coulomb-mediated long-range interactions involving chain ends. However, it is generally believed that polymer chains are composed of segments separated by kinks. It is quite possible that for many experimental pump/probes the studied excitations are concentrated at the kinks. How will these relax? At very long times and long distances relaxation occurs by reptation as the chain segments first adjust laterally within the reptation tube, and then longitudinally along this tube [10, 11]. However, within the Kohlrausch time frame associated with relaxation of the first structure factor peak, individual kink relaxation takes place within a local product vector subspace in which the kink can either rotate or move radially in the cylindrical coordinates defined by the chain axis. (At low temperatures longitudinal kink motion along the chain will require related kink motions in adjacent chains; these lie outside the subspace of individual kink motion.) Motion in the angular factor space is effective, while that in the radial factor space is ineffective. This is analogous to an unusual combination lock in which the dial can move both radially and angularly, but the tumblers are affected only by

angular motion. This suggests that $f_p = d_e/(d_e + d_i)$. With $d_e = d_i = 1$, this gives $f_p = \frac{1}{2}$, in agreement with experiment.

This simple but very important example shows how restricted subspace or subensemble relaxation at low temperatures can often yield $f_p = \frac{1}{2}$. One possible general mechanism for structural arrest can be dimensional regression of the defect configuration space; in effect, the dominant defect (here a kink) relaxes within a subspace of dimensionality $d - 1 = 2$, and in that subspace there is an effective principal axis and an ineffective one. Molecular dynamic simulations [12] provide another such example; although these calculations are relatively 'old' by now, they show how the mechanism just discussed for the simple cylindrical geometry applies equally well to an apparently much more complex geometry.

The example studied in [12] is a fused salt mixture, KCN $((K_2, Ca)(NO_3)_2)$, at a composition $Ca_{0.4}$ which maximizes the glass-forming tendency. To understand the local structure of this glass one should study the crystal structures of the components to see how they are affected by the presence of the triangular planar unit NO_3 . With K the NO_3 unit dominates and the crystal structure is rhombohedrally distorted (along the threefold body diagonals). With Ca the structure has the usual fluorite cubic form, with each NO_3 unit tetrahedrally coordinated and oriented normal to a threefold tetrahedral axis. In the glass there will be a mixture of NO_3 coordination configurations, dominated by complexes with one or two Ca ions in the first coordination shell. Molecular dynamics [12] showed that density relaxation, as measured by the height of the first structure factor peak, exhibits Kohlrausch relaxation with $\beta_d = 0.61$, corresponding to $d = 3$ and $f_p = 1$. They also found that of the three relaxation times, NO_3 translation along the planar normal (I) and NO_3 rotation around the twofold axis accompanied by a tilt of the molecular planar by π (IIA) or by $\pi/2$ (IIB) or around the threefold axis (III), at high temperatures I, IIA and IIB were almost equal, while III was rare. However, below $T_g + 50$ K, while the relaxation times of I and IIA remained nearly equal, that of IIB became almost a factor of 100 larger near T_g . Both IIA and IIB exhibited Kohlrausch relaxation, with $\beta_{IIA} = 0.61$, corresponding to density fluctuations with $f_p = 1$, and $\beta_{IIB} = 0.42$, corresponding to fractal relaxation with $f_p = \frac{1}{2}$. Thus as the density fluctuations freeze out planar tilt up to $\pi/2$ is almost always followed by continued tilting to π , with normal relaxation. The increasingly unlikely cases where the $\pi/2$ tilt is reversed to zero are described by fractal relaxation.

The microscopic interpretation of these results is that above $T_c \sim 450$ K $\sim T_g + 50$ K density fluctuations dominate and the Ca mobility is such that these ions enter and leave nitrate coordination spheres more rapidly than the rotational relaxation times, so that one cannot speak of a fixed number of Ca ions in a nitrate coordination sphere. Below T_c the latter becomes well defined and there are several subensembles. With two coordinated Ca ions both translational normal and twofold rotational motion are partially arrested, the former more than the latter. Thus the twofold rotation becomes the easy motion for this subensemble, while the translational motion becomes the hard one. In general a density fluctuation involves tandem or correlated translation-rotation, and this is the case for the tilt by π . However, to obtain angular motion involving a tilt jump by $\pi/2$ which is then reversed, one must project from translation-tilt product space directly into pure tilt factor space. The partition fraction for this projection is exactly $f_p = \frac{1}{2}$, which explains the simulated value $\beta_{IIB} = 0.42$. Previously [8] this was identified with β_K , the charge-fluctuation value, which also has $f_p = \frac{1}{2}$. However, this explanation is unsatisfactory, because both IIA and IIB are subject to the same long-range Coulomb forces.

To apply these ideas to the new NMR relaxation experiments [13] we review the results obtained on *ortho*-terphenyl (OTP) by deuterium NMR at $T = T_g + 10$ K. OTP is a crescent-shaped planar monomer, and one of the few which can be prepared with very

high purity and supercooled to a glass without crystallization. At $T_c = T_g + 50$ K its density fluctuations are arrested; measurements of β above T_c give $f_p = 1$, as expected. Below T_c we have a novel relaxation regime in which the relaxation time measured through the viscosity becomes 100 times shorter than that measured by NMR [14]. (Compare the divergence of the two relaxation times in KCN discussed above.) To explore the origins of this divergence the new NMR experiments employed suitably phased and oriented double and quadrupole echoes (pulse and reversing pulse configurations). The pulse spacing t_p for an echo is small compared to the relaxation times t_i between echoes, and $t_2 \sim 10^3 t_1 \sim 10^6 t_p$. The various pulse configurations are illustrated schematically in figure 1, as reproduced here for the reader's convenience from [13]. These pulse configurations determine the double-correlation function

$$F_2(t_1) = \langle \cos[(\omega_1 - \omega_2)t_p] \rangle \quad (1)$$

which acts as a filter for the spin orientational motion, and the quadruple-correlation function

$$F_4(t_1, t_2) = \langle \cos[(\omega_1 - \omega_2)t_p] \cos[(\omega_1 - \omega_2)t_p] \rangle \quad (2)$$

which acts as a double filter for the two widely different times t_1 and t_2 . Kohlrausch relaxation is found for both F functions, and the double echo is described by the relaxation time $\tau_2 = 17$ ms with $\beta_2 = 0.42$ and $f_p = \frac{1}{2}$. The two echoes are separated by a time t_1 , while the four-echo spacings are t_1 , t_2 and again t_1 . Thus in the quadruple-echo configuration the two t_1 pairs act as preparative pump and selective probe, respectively, while the t_2 pair measures the τ_4 , β_4 relaxation of the subensemble prepared or probed by the double echoes. This nested echo structure, with $t_1 t_2 \sim \tau^2$, is ideal not only for separating long and short relaxation processes, but also for exploring the intrinsically hierarchical nature of glasses. Again the prepared and selected subensemble quadruple F_4 relaxation has the Kohlrausch form, but the measured values of τ_4 and β_4 depend on the dynamic extent of subensemble preparation $x_1 = t_1/\tau_2$, as one would expect. The subensemble relaxation time τ_4 (denoted by κ^{-1} in [13]) increases with x_1 and is already $\sim 3\tau_2$ for $t_1 \sim 1$ ms $\sim 40t_p$; this increase reflects slower relaxation of the subensemble. This could be due to reduced relaxation within the subensemble itself (several microscopic models of this type are discussed in [13], all yielding similar results), or it could be caused by slowing of subensemble diffusion to traps.

The most decisive results of this experiment concern the magnitudes of β_2 and β_4 , which describe relaxation processes on differently prepared subensembles: the latter increased from 0.59 at $x_1 = 0.06$ at first parabolically, reaching 0.7 for $x_1 \sim 3$. It is striking that the initial values of β_2 and β_4 correspond so well to $f_p = \frac{1}{2}$ and 1, respectively. To identify the relevant subensembles we need a structural model for OTP below T_c .

Given the planar crescent shape of the molecule we suppose that the molecules are locally layered, with domains of chiral symmetry; that is, orienting the crescents from top to bottom, there are two possible conformations, right or left handed. The domains of opposite chiral symmetry are separated by chiral edges, which are segments with kinks. The nuclear spins within a domain are assumed to interact strongly enough so that they do not contribute to the echoes. The subensemble selected by the short-time filter pair t_1 is assumed to be localized on the chiral edge segments. These spins can diffuse either along the edge (effective direction) or normal to it (ineffective direction). When the excited spins diffuse into the pool of domain spins, no true relaxation occurs, and the excited spins eventually return to the chiral edge. True relaxation occurs only for diffusion of excited spins along the edge, giving $f_p = \frac{1}{2}$. After times of order $10\tau_2$ most of these spins have decayed, with many of them reaching chiral kinks. These kinks may involve vacancies and the local environment may have little or no layered character. Thus these point defects or

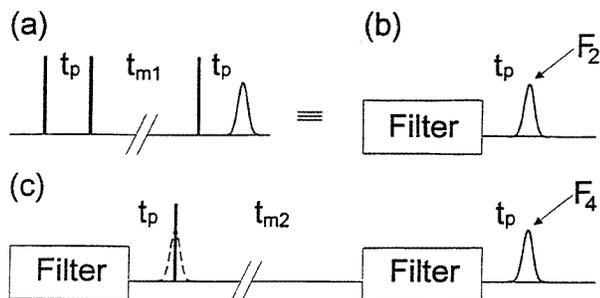


Figure 1. This figure, taken from [13], illustrates how a series of spin echo pulses can measure the correlation functions F_n ($n = 2, 4$) described by (1) and (2). In (a) and (b) the filter effect for F_2 is explained, while the double-filter effect for F_4 is illustrated in (c). The full information contained in these correlation functions is extracted by combining pulses of different polarizations, as explained in detail in [13]. For our present purposes it is enough that the reader appreciate that these correlation functions measure much more than the average relaxation properties, as determined in traditional relaxation experiments, described here by $\beta_2(t_1)$, because they also measure $\beta_4(t_1, t_2)$, where $t_2/t_1 \sim 10^3$ in the data of [13]. The hierarchical nature of the double filter is ideal for probing different relaxation regimes and for identifying the properties and even formation of relaxation centres. The nested data explore an entirely new regime of relaxation and they contain the many surprises discussed in the text.

traps have no constraints and spins neighbouring such defects may have $f_p = 1$. This is an unusual situation, as normally the relaxation hierarchy goes from larger values of β at shorter times and higher T to smaller values at longer times and lower T . Here however the subensembles studied are severely selected and the long time is ~ 1 s. It seems that the combined $t_1, t_2 \sim 10^3 t_1$ relaxation has taken us to the ultimate sink. Indeed as t_1 increases β_4 increases toward unity, which means that the remaining spins are sampling a local region which has not undergone full structural arrest.

The key question that will concern experimentalists is why these intrinsic results are specific to OTP. In the case of polyvinylacetate (PVAc) studied at $T = T_g + 20$ K by ^{13}C -NMR [15, 16] it was found that $\beta_2 = 0.52$, which is intermediate between β_K and β_{sr} . There are many differences between the experiments of [15, 16] and [13]. The ^{13}C substitution was made not at a backbone site but at the bulky polar carbonyl side group site (see figure 19 of [8]) of PVAc, a site which may see a complex mixture of long-range polar and short-range nonpolar forces respectively parallel and perpendicular to the backbone. It is worth noting that other polymers with bulky side groups, such as polyisobutylene (PIB) and polyisoprene (PI), also exhibit intermediate values of β , and that the chemical trends of β in these polymers correlate with the side group density [8]. What this also means is that in the presence of bulky side groups angular and radial kink motions no longer decouple from longitudinal chain translation.

The microstructural model discussed above, where it was applied to polymers, fused salts and complex glass-forming monomers, is helpful in understanding some of the qualitative aspects of glass formation widely discussed phenomenologically in terms of fragility [17–19]. Strong glass formers (such as network glasses) exhibit a viscosity $\eta(y)$, with $y = T_g/T$, with typical exponential (Arrhenius) behaviour with activation energies E_a of the order of E_{vap} , the heat of vaporization. ‘Fragile’ glass formers, such as OTP, characteristically exhibit a knee in $\log \eta(y)$, and above the knee near $y = 1$ typically $E_a \sim 5E_{vap}$. (This behaviour is sometimes fitted with the Vogel–Fulcher expression $\log \eta \sim (T - T_g)^{-1}$.) We

can explain this two-stage behaviour (including its correlation with β in the second stage near T_g [17]) microscopically by observing that the knee occurs at the crossover region from density to fractal relaxation. The abnormally large value of E_a/E_{vap} in the fractal region simply reflects the collective nature of fractal structural arrest, which involves the formation of ordered microdomains at fixed density. This also explains the origin of the Vogel–Fulcher fit, which now appears to be artificial. It is worth noting that single-stage singular behaviour has been widely discussed in the literature (for references see [19]).

In the first stage of relaxation involving density fluctuations, structural arrest can be observed directly as a pseudo-second-order transition in the radial Debye–Waller factor width of the first peak in the structure function, which takes place at the knee in $\log \eta(y)$ [20]. At temperatures below this density glass transition the only possible second-stage relaxation involves the development of locally ordered domains, presumably as a similar pseudo-transition takes place in the medium-range orientational order of anisotropic molecules with small electric dipole moments such as OTP. This is fully consistent with our above analysis of β_2 for OTP [13], and it shows that the subensemble observed in the short-time window is in some ways representative of the macroscopic supercooled liquid. Under high pressure such medium-range ordering might be enhanced by an incidental pseudo-first-order change in short-range order (for example, coordination numbers), and at times it has been suggested that such a change might be the primary mechanism responsible in general for two-stage behaviour [19]. The present discussion of OTP shows, to the contrary, that in many fragile molecular liquids the knee is related to medium-range order.

The two-stage fragility model [18, 19] also helps us to understand the behaviour of $\beta_4(x_1)$ in greater detail. The reversal of the magnetization by the echo pulses is always incomplete, and the dissipative loss increases as x_1 increases. This dissipative loss need not be entirely structureless. Just as the thermal quenching process produces metastable primary relaxation centres [8], so the magnetic echo dissipation can be accompanied by spin diffusion which rearranges the subensembles and concentrates them at secondary relaxation centres. It may seem that the energy dissipated is too small to produce such concentrations, but we must remember that the entire system is not far from equilibrium, and that the energy associated with medium-range order in a fragile liquid such as OTP is itself very small; in fact, in NMR spin echo experiments all preparation (rearrangement) energies are small and comparable. These secondary centres themselves can be associated with density fluctuations, so for small x_1 they give $\beta_4 = \beta_{sr}$. As x_1 increases, diffusion can continue from secondary centres to tertiary centres. The natural variable for thermally activated magnetic relaxation is $\ln t$ [21], and if the secondary centres originally are in metastable positions, there β_4 relaxation should develop not as $\ln t$ but rather as $(\ln t)^2$, as observed [13]. This point is very subtle; it illustrates the power of subensemble selection and preparation.

In conclusion, we have revised our earlier analysis [8] of molecular relaxation of glasses to distinguish the effects of specific structural elements, such as kinks in polymers, as sources of fractal relaxation. It appears that there are many mechanisms which can give rise to fractal relaxation with partition fractions $f_p = \frac{1}{2}$, and that these are generally based on local product subspaces in the non-polar molecular case, in contrast to the global product superspaces which produce fractal electronic and ionic charge, as well as orientational glass and quasicrystal, relaxation [8]. Our analysis has clarified the origin of normal and fractal Kohlrausch relaxation as calculated in MDS for the prototypical ionic glass KCN. We have proposed a new structural model for OTP for $T_g < T < T_c$ with which we have analysed new double- and quadruple-echo NMR data on OTP [13] which contain very accurate values of the Kohlrausch stretching fraction β . The analysis shows that when accurate values of β are combined with normal and fractal double-channel dispersive transport theory a remarkably

rich description of relaxation processes in glasses and deeply supercooled liquids emerges. From earlier experiments on a wide variety of materials with different pumps and probes it was already clear (see table 7 of [8]) that the intrinsic values of β are dominated by $d^* = d$ or $d/2$, but that the choice between these two cases is often surprising. The present analysis of NMR nested and hierarchical multiple echoes in OTP has brought fresh surprises. It appears that the complexity of relaxation processes in glasses and supercooled liquids is so great that many more surprises await us. Nevertheless, the present analysis has unexpectedly led us to a new picture of the two-stage nature of the relaxation that takes place in a deeply supercooled fragile liquid. Radial density fluctuations are arrested in the first stage in OTP near $T_g + 50$ K, while in the second stage an entirely different kind of relaxation develops as internal medium-range orientational (locally ferroelastic) order develops. Identification of the second channel, which is responsible for the second relaxation stage as a fractal chiral edge channel, resolves a number of paradoxes in the interpretation of other experiments.

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- [21] Marchand A, Sampaio L C and Barbara B 1995 *J. Magn. Magn. Mater.* **140–144** 1863. The spatially homogeneous model of [13] makes β_4 linear in $\ln t_1$. With spatial depletion near moving traps β_4 will be linear in $d(t_1)$, where $d(t_1)$ is the distance travelled by the trap away from the centre of the depletion region. Thus for initially metastable secondary traps, where $d(t_1)$ itself is linear in $(\ln t_1)^2$, $\beta_4(\ln t_1)$ will be flat for small t_1 , as shown in the lower panel of figure 4 of [13].