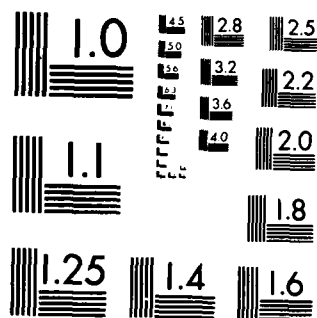END

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An Entropy Maximum Principle and Relaxation Phenomena

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A Shannon (epoch) entropy is defined in terms of an integral over the full temporal epoch of relaxation. A maximum entropy principle yields a linear exponential as a fundamental form for relaxation to equilibrium. It is observed that the time scale of measurements does not in general coincide with the time scale on which the fundamental form is described. Time scale transformations are considered. The maximum entropy density is taken to be form-invariant independent of the time scale used in its description, and the resulting epoch entropy is itself taken to be an invariant. This latter invariance leads to a relation between the time unit on a transformed time scale and the time unit on the fundamental time scale. An appropriate choice for the form of a time scale of measurements for relaxation phenomena is rationalized. The results of the complete formalism are a fractional exponential for relaxation decay, and renormalization relations for scaling parameters and activation energies. These results have been consistently verified in a wide range of relaxation measurements for many kinds of condensed matter.

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CONTENTS

AN ENTROPY MAXIMUM PRINCIPLE AND RELAXATION PHENOMENA

I. Introduction

In this paper we consider a general approach to the description of the relaxation of an open system based on a maximum Shannon entropy principle.[1] The definition of the Shannon entropy involves an integral over the full temporal epoch of the relaxation and will be designated the epoch entropy. The definition of the epoch entropy is based on a dimensionless quantity termed the incremental relaxation density (IRD). The dimensionless character of the IRD is maintained by the introduction of a unit of time, and the integral of the IRD over the full epoch is unity so it is normalized. The IRD itself is defined in terms of the approach to equilibrium of the singlet probability for a particular state in a discrete state space used to describe the system of interest. The singlet probability for this state is assumed to approach its equilibrium value monotonically, and at a rate that is equal to the slowest among all states. When such a state exists, it clearly controls the ultimate approach of the system to equilibrium, and the relaxation is said to be simple. We deal only with simple relaxation in this paper.

The IRD is defined in such a way that it is positive with negative slope throughout the epoch of relaxation. It therefore has the properties of a Lyapounov function,[2] and provides a measure of the status of the relaxation process. Furthermore the IRD is normalized so that it also has the mathematical properties of a probability density. It is therefore an appropriate quantity to be used in the definition of a Shannon (epoch) entropy which provides a measure of information about the relaxation process throughout the epoch for the system of interest.

We maximize the epoch entropy subject to minimal constraints for a relaxation process, namely, that the IRD is normalized, and that there is a mean

1

time of relaxation that corresponds to the first moment of the IRD. The resulting form for the IRD that assures maximum epoch entropy is a linear exponential. Since it is derived directly from a maximum entropy principle subject only to the minimum constraints necessary to specify a relaxation process, we consider the linear exponential to be the fundamental form for the IRD. With this IRD in hand, we can find a general expression for maximum epoch entropy. However, we note that the time scale on which the IRD takes a linear exponential form is not in general the time scale on which measurements are made. We argue that the value of maximum epoch entropy should not depend on the time scale that is used to describe it. We are led thereby to enunciate a principle of invariance of maximum epoch entropy in which the maximum epoch entropy evaluated in terms of the transformed IRD is equal to the maximum epoch entropy evaluated in terms of the fundamental IRD. This principle leads to an invariance relation between units of time on the fundamental time scale and a transformed time scale.

We then use some general arguments to rationalize the use of a monomial (with positive fractional power) time scale transformation in the description of relaxation phenomena in an open system. The fundamental form corresponds to the case when the monomial is at the linear limit. However the general monomial transformation leads to an empirically well-established[3] description of relaxation phenomena that also coincides with a description based on an existing microscopic model of relaxation.[4,5] Furthermore the invariance relation between units of time that is derived from the principle of invariance of maximum epoch entropy leads to renormalization relations for scaling parameters and activation energies that enter into the physical manifestations of these units. Similar renormalization relations also arise in the aforementioned microscopic model,[4,5] and have been repeatedly verified empirically.[3]

2

II. The Incremental Relaxation Density (IRD) and Maximum Temporal Epoch Entropy

We considered a perturbed open system that is relaxing to equilibrium with order parameter (time) $\theta = \tilde{\theta} - \tilde{\theta}_0$, where $\tilde{\theta}_0$ denotes the time when the relaxation begins. The system is taken to be characterized by a singlet probability $P_s(\theta)$ over a discrete state space with states labelled by s. $P_s(\infty)$ are the equilibrium values of $P_s(\theta)$ so a state retains its identity throughout the relaxation process. Since $P_s(\theta)$ are state probabilities, we have for all θ

$$\sum_s P_s(\theta) = 1 \tag{1}$$

Among the states s, there is a subset consisting of at least two states for which the relaxation is slowest. These will be called the slowest relaxing states. The evolution of the probabilities associated with such states therefore control the ultimate approach to equilibrium. We say that a relaxation is <u>simple</u> if for at least one of the slowest relaxing states, the state probability approaches its equilibrium value monotonically. Let us designate that state (or a chosen one of a number of such states) to be the rth state with probability $P_r(\theta)$ and equilibrium probability $P_r(\infty)$. We now make a weak assumption (to be strengthened below) that because of the nature of a relaxation process, $P_r(\theta)$ approaches $P_r(\infty)$ sufficiently rapidly that the integral of $P_r(\theta) - P_r(\infty)$ over the full epoch of the relaxation process is finite.

$$N_r = \int_0^\infty [P_r(\theta) - P_r(\infty)] d\theta / \tau_\theta \tag{2}$$

Here N_r has the unchanging sign of the difference $P_r(\theta) - P_r(\infty)$, and τ_θ is a (for the moment arbitrary) constant unit of time on the θ-scale so that the integral is dimensionless.

We now observe that for simple relaxation, we may define a dimensionless incremental relaxation density (IRD) to be

$$f(\theta) = N_r^{-1}[P_r(\theta) - P_r(\infty)] \tag{3}$$

3

The IRD is a positive semi-definite function of θ with negative slope that has its maximum at θ=0 and which vanishes as θ→∞. Therefore by its positivity and negative slope for θ≧0, the IRD has the properties of a Lyapounov function. In addition the integral of the IRD over the epoch is just unity. Thus the IRD also has the properties of a dimensionless probability density. Its accumulation integral

$$F(\theta) = \int_0^\theta f(\theta')d\theta'/\tau_\theta, \quad F(\infty) = 1 \tag{4}$$

is positive with positive slope for all θ≧0. Now the properties of $F(\theta)$ could also arise from an epoch integral over a density function which is positive but with a slope whose sign changes during the epoch. It is interesting to speculate that the conditions on a Lyapounov function may be similarly weakened so that the requirement of negative slope is replaced by a condition that the accumulation integral of a generalized Lyapounov function over the epoch is finite. Of course, then the relaxation would not be simple so we leave this point for further consideration elsewhere.

We have already observed that the slowest relaxing states and hence also the IRD describe the status of the ultimate relaxation of the system to equilibrium. Further as also previously noted, the IRD has the mathematical properties of a dimensionless probability density. Thus we are led in analogy with procedures used by Shannon[1] to define a Shannon temporal epoch entropy S_θ as a measure of information about the relaxation process over its full epoch.

$$S_\theta = -\int_0^\infty f(\theta)\ln[f(\theta)]d\theta/\tau_\theta \tag{5}$$

It should be noted that S_θ is an implicit function of $\tilde{\theta}_o$.

We now require that there is a minimum of information about the relaxation process subject only to those constraints appropriate for specifying the process to be a relaxation process. Equivalently, this means the epoch entropy is a maximum subject to appropriate constraints. We already have the

4

condition that the IRD is normalized, by its definition Eq. (3). In addition, a relaxation process is typically characterized by a relaxation time. We specify the relaxation time to be represented by the first moment of the IRD, namely

$$<\theta> = \int_0^\infty \theta f(\theta) d\theta / \tau_\theta \qquad (6)$$

This provides a somewhat more stringent condition on the rapidity with which $P_r(\theta)$ approaches $P_r(\infty)$ than required for Eq. 2.

Now introducing two Lagrange multipliers λ_1 and λ_2 in the usual way, we obtain from the variation of S_θ that the maximum epoch entropy occurs for

$$f^M(\theta) = \exp[-(\lambda_1 + \lambda_2 \theta)] \qquad (7)$$

Consistency with Eqs. (3) and (6) allows us to determine λ_1 and λ_2.

$$\exp(-\lambda_1) = \tau_\theta / <\theta> \quad , \quad \lambda_2 = <\theta>^{-1} \qquad (8)$$

Then the IRD consistent with the maximum epoch entropy has the form

$$f^M(\theta) = [\tau_\theta / <\theta>] \exp[-(\theta / <\theta>)] \qquad (9)$$

The maximum epoch entropy can itself be determined to be

$$S_\theta^M = 1 + \ln<\theta> - \ln\tau_\theta \qquad (10)$$

so the specific value of S_θ^M is determined modulo a choice for τ_θ.

There are several important observations that should be made concerning Eqs. (9) and (10). First from Eq. (9) we note that the linear exponential form is consistent with the Lyapounov function properties of the IRD. Also the linear exponential form for the IRD represents a fundamental form in the sense that it arises from the maximum epoch entropy principle subject only to the minimum constraints necessary to characterize the (simple) relaxation process. However, it has long been recognized[6] that an exponential form is

5

not completely appropriate for the description of the dynamics of decay at the shortest times (or at the highest frequencies). Therefore the point $\theta=0$ is physically singular. Here, we understand this to mean that there must be a pre-relaxation regime, before simple relaxation begins, that may be characterized by a high frequency cutoff ω_c. Thus the present discussion is valid only for long times corresponding to frequencies lower than ω_c. Empirical evidence[3] indicates that for many cases ω_c may be in the range 10^8-10^{11} Hz for relaxation phenomena in condensed matter.

It is also useful to note that although $f^M(\theta)d\theta/\tau_\theta$ is independent of the time unit, $f^M(\theta)$ alone takes on a particularly simple form when τ_θ is taken to equal to $<\theta>$. Namely $f^M(\theta)$ is then equal to unity at $\theta=0$ and homogeneous in $\theta/<\theta>$. Thus $<\theta>$ is a natural time unit for the θ time scale. A similar simplification occurs for S_θ^M which just becomes unity when $\tau_\theta=<\theta>$. However for any particular choice of τ_θ, S_θ^M is an epoch integral whose value should be independent of the time scale on which it is described. This condition of invariance serves to place a stringent condition on the relationship between τ_θ and the unit of time on the new time scale. This is probably obvious for a linear time scale transformation but we are interested here in a wider class of time scale transformations. We are motivated here by the fact that there is no reason to believe that the time scales on which measurements are made coincide with the time scale on which the IRD, $f^M(\theta)$, appears in its fundamental linear exponential form.

III. An Invariance Relation for Time Scale Units

A time or order parameter is just a positive cumulative function that increases monotonically from an origin. We have already introduced the $\tilde{\theta}$ time scale, its corresponding difference time scale $\tilde{\theta}=\tilde{\theta}-\tilde{\theta}_0$ and its constant unit

6

of time τ_θ. In a similar way, we introduce another time scale $\tilde{t}$ with difference time scale $t=\tilde{t}-\tilde{t}_o$, and constant unit of time τ_t. From the context of application, it is clear that we should align the respective origins $\tilde{\theta}_o$ and $\tilde{t}_o$ since both represent the time when the (simple) relaxation process begins (after a pre-relaxation time regime). Thus if

$$\theta=\theta(t) \quad , \quad \theta(t=0) = 0 \quad . \tag{11}$$

We specify further that $d\theta/dt$ is positive and finite everywhere except possibly at isolated points. For example, such an isolated point might be expected at the end of the pre-relaxation regime which corresponds to the origin for the time regime of simple relaxation.

We can now describe the incremental relaxation de ɔʏ (IRD) and maximum epoch entropy in terms of t. Namely, we obtain a tra ʋormed IRD $g^M(t)$ by a direct transformation from $f^M(\theta)d\theta/\tau_\theta$ to $g^M(t)dt/\tau_t$. ʍ ɟind using Eq. (9)

$$g^M(t) = \exp\{-[\theta(t)/\langle\theta\rangle]\}[\tau_t/\langle\theta\rangle][d\theta(t)/dt] \quad . \tag{12}$$

The maximum epoch entropy is now taken to be form-invariant so that it is written in terms of $g^M(t)$ and an integral over the total epoch on the t-scale.

$$S^M_t = \int_o^\infty g^M(t)\ln g^M(t)dt/\tau_t = 1+\ln(\langle\theta\rangle)$$
$$- \int_o^\infty \exp[- \frac{\theta}{\langle\theta\rangle}]\ln(\tau_t \frac{d\theta}{dt}) \frac{d\theta}{\langle\theta\rangle} \tag{13}$$

Within the integral on the right hand side, $d\theta/dt$ is expressed as a function of $\langle\theta\rangle$ and $\theta/\langle\theta\rangle$. We now use the requirement that S^M is invariant independent of the time scale used in its evaluation together with Eqs. (10) and (13) to obtain a general invariance condition.

$$\ln(\tau_\theta/\tau_t) = \int_o^\infty \exp[-(\theta/\langle\theta\rangle)]\ln[d\theta/dt]d\theta/\langle\theta\rangle \tag{14}$$

7

To understand the ramifications of this relationship we should consider a specific time scale transformation. The immediate problem then is to choose a time scale that is meaningful for measurements of relaxation phenomena.

IV.   A Measurement Time Scale for Relaxation

We observe that even after a time scale transformation, $\exp[-\theta(t)/\langle\theta\rangle]$ is positive for all $\theta(t)$, $t>0$, has value unity at $\theta(0)$ because of Eq. (11), and vanishes as $\theta(t)\to\theta(\infty)$. It was previously argued[7] that such a decay in an open system can be described in terms of the squared magnitude $|c(t)|^2$ of the antocorrelation amplitude of a decaying state $|R\rangle$. That argument may be sharpened as follows. A density matrix representing the system at any time is a Hermitian trace-class operator with eigenvalues that are positive, real, and nonvanishing, and which lie between 0 and 1. The eigenvalues belong to the complete set of the eigenstates of the density matrix which includes both non-stationary decaying and stationary states. In equilibrium the decaying states no longer have non-vanishing eigenvalues so that the residual eigenvalues of the density matrix belong only to its stationary eigenstates. The decaying states are therefore not relevant for the description of equilibrium. Hence the approach of the incremental relaxation density (IRD) to zero matches the vanishing of the autocorrelation of a decaying state. In such a case

$$\exp[-\theta(t)/\langle\theta\rangle] = |c(t)|^2 \tag{15}$$

where

$$c(t) = \langle R|\exp(-(iDt)|R\rangle \quad , \quad t \geqq 0 \tag{16}$$

The state $|R\rangle$ is associated with the continuous spectrum of the development operator D and is orthogonal to all the stationary eigen-states of the density matrix operator. It is assumed that the development operator has a non-singular continuous spectrum. If μ_ε denotes the spectral projection of D,

8

$$D = \int \varepsilon \, d\mu_\varepsilon = \int \varepsilon |\varepsilon\rangle\langle\varepsilon| \, d\varepsilon \quad , \tag{17}$$

then the function $\langle R|\mu_\varepsilon|R\rangle$ is absolutely continuous. Its derivative

$$\rho(\varepsilon) = \frac{d}{d\varepsilon} \langle R|\mu_\varepsilon|R\rangle = \langle R|\varepsilon\rangle\langle\varepsilon|R\rangle \tag{18}$$

can be interpreted as the spectral distribution of the state $|R\rangle$. In other words, the integral $\int_E^{E+\Delta E} \rho(\varepsilon) d\varepsilon$ is the probability that the eigenvalue of the state $|R\rangle$ lies in the interval $(E, E+\Delta E)$. The function $\rho(\varepsilon)$ has the following properties.

i) $\rho(\varepsilon) \geqq 0$

ii) $\int \rho(\varepsilon) d\varepsilon = 1$, since $\langle R|R\rangle = 1$ $\tag{19}$

iii) $\rho(\varepsilon) = 0$, $\varepsilon \notin \mu_\varepsilon$

Thus $\rho(\varepsilon)$ is a probability density. Now it follows that $c(t)=\langle R|\exp(-iDt)|R\rangle$, $t \geqq 0$, can be expressed as

$$c(t) = \int \exp(-i\varepsilon t) \, \rho(\varepsilon) d\varepsilon \tag{20}$$

Thus $c(t)$ is a characteristic function for the spectral probability density of the decaying state.

We now note that there is some arbitrariness in the specification of $|R\rangle$ and its spectrum. In general we consider $|R\rangle$ to represent a decaying state for a complex many-body system. Then the description of the decay should not depend on an exact specification of the number of components in the system. In other words we should obtain the same form of decay respectively for one portion, or several portions of the system. Mathematically this means that $\rho(\varepsilon)$ must be superposable probability density, as discussed by Rajagopal et al.[8] so that $\rho(\varepsilon)$ must be a stable distribution. Recently Weron et al.[9] have considered the application of the mathematical theory of stable distributions for systems with semibounded spectra to problems of interest in physics. Of

9

pertinence to present considerations is the result that for a semibounded

stable distribution, the appropriate characteristic function for causal time,

$t \geq 0$, has squared magnitude

$$|c(t)|^2 = \exp(-\tilde{a}t^b), \quad \tilde{a}>0, \quad 0<b<1, \quad t \geq 0 \quad . \tag{21}$$

A comparison with Eq. (15) then provides a time scale transformation appropri-

ate for the description of relaxation phenomena. Namely the fundamental time

scale is related to the time scale of measurement by

$$\theta = at^b, \quad a>0, \quad 0<b<1, \quad t \geq 0 \tag{22}$$

where $a = \tilde{a}<\theta>$. We shall apply this time scale transformation in a discussion

of the invariance relation, Eq. (14), in the next section. Before that,

however, some remarks concerning Eq. (21) are appropriate.

We note first the form of $|c(t)|^2$ in Eq. (21) is consistent with the

Paley-Wiener theorem in fourier transform theory.[7,10] The Paley-Wiener

theorem states that a necessary and sufficient condition for the existence of

a semibounded $\rho(\varepsilon)$ (with properties given in Eq. (19)) which is the fourier

transform of a square integrable $c(t)$ is that

$$\int_{-\infty}^{\infty} \frac{\ln|c(t)|}{1+t^2} \, dt < \infty \tag{23}$$

This condition is guaranteed if for $t \to \infty$, $|c(t)|^2$ is greater than or equal to

the right hand side of Eq. (21). The important point is that for the stable

distribution argument used here, Eq. (21) is an equality and valid throughout

the full epoch.

It should also be noted that although the limit $b=1$ can never be reached,

b may approach arbitrarily close to 1. It is that latter limit that corre-

sponds to the fundamental form. The deviation of b from unity is a manifesta-

tion of the complex nature of the system as it appears on the time scale of

measurement.

10

V. Parameter Renormalization

We now consider the effect of the time scale transformation Eq. (22) as applied in Eq. (14). We obtain

$$\ln\left\{ \frac{\tau_\theta}{\tau_t} \frac{1}{b\langle\theta\rangle} [\langle\theta\rangle/a]^{1/b} \right\} = -(1 - \frac{1}{b})\gamma \qquad (24)$$

where $\gamma = 0.577215 \ldots$ is the Euler constant. If we now choose τ_θ to coincide with the natural unit on the θ-scale, namely $\langle\theta\rangle$, we obtain the relationship

$$\langle\theta\rangle = ab^b \exp[(1-b)\gamma]\tau_t^b \qquad (25)$$

It is convenient to define a new time unit on the t-scale, namely

$$\bar{\tau}_t = b \exp[(1-b)\gamma/b]\tau_t \qquad (26)$$

so that

$$\langle\theta\rangle = a \bar{\tau}_t^b \qquad (27)$$

Then using Eq. (12), we obtain for $g^M(t)dt/\tau_t$

$$g^M(t)dt/\tau_t = \exp[-(t/\bar{\tau}_t)^b] b(t/\bar{\tau}_t)^{b-1} dt/\bar{\tau}_t$$

$$\equiv \bar{g}^M(t)dt/\bar{\tau}_t \qquad (28)$$

The function $\bar{g}^M(t)$ is just the incremental relaxation density (IRD) on the t-scale with time unit $\bar{\tau}_t$.

It is useful to relate this IRD to a relaxation rate W(t) to facilitate comparison with the usual description of relaxation phenomena. Note that the unrelaxed portion at any time t is just

$$1 - \int_o^t \bar{g}^M(t)dt/\bar{\tau}_t = \exp[-(t/\bar{\tau})^b] \qquad (29)$$

The relaxation rate in a particular time interval is just the ratio of $\bar{g}^M(t)/\bar{\tau}_t$ to the remaining unrelaxed portion, namely

11

$$W(t) = b(t/\bar{\tau}_t)^{b-1}(\bar{\tau}_t)^{-1} \quad , \; 0<b<1 \tag{30}$$

We have previously discussed[11] such time dependent relaxation rates, and used a phenomenlogical introduction of a monomial time scale transformation for their application in the description of relaxation phenomena. On the t-scale, the relaxation rate decreases with time. Hence for measurements made on a t-scale, the relaxation will appear to have a long tail.

The decay represented by Eq. (21) and the relaxation rate in Eq. (30) are the prototypical forms observed in many types of relaxation experiments in a wide range of condensed matter samples. Even more remarkable are the applications of Eq. (27). Its significance resides in the fact that the t-scale is only the time scale of measurement and not the fundamental time scale for the maximization of epoch entropy subject to the minimum constraints necessary to specify a simple relaxation process. Thus parameter dependences determined for $\bar{\tau}_t$ are only apparent. The actual dependencies are those that enter into $\langle\theta\rangle$. The two dependencies are related by Eq. (27).

For example, consider a material made of polymer with a relaxation time dependent on the molecular weight, M, of its chemical building blocks. On the fundamental scale, we take the relaxation time, for specificity, to have a simple monomial dependence on M.

$$\langle\theta\rangle = kM^{\beta} \tag{31}$$

Then on the time scale of measurement, the relaxation time $\bar{\tau}_t$ has the dependence

$$\bar{\tau}_t \propto M^{\beta/b} \tag{32}$$

$\bar{\tau}_t$ therefore has a power dependence that appears greater than it actually is since $0<b<1$. If now we consider polymer samples with different values of M, relaxation measurements will typically provide different values of the frac-

tional exponent b. The prediction of the invariance relation is that the M-dependence of $\bar{\tau}_t$ will vary in such a way that β is the same for the samples with different M. On the other hand, the measured β/b would appear anomalous without an understanding of the need for renormalization. Similarly it may also be possible to change the fractional exponent b by changing the environment in which relaxation measurements are made. Then the prediction is that the power of M that is measured for $\bar{\tau}_t$ changes with b in such a way that β again remains constant.

A more general application occurs in the case of the variation of $\langle\theta\rangle$ and $\bar{\tau}_t$ with temperature. In the usual way we assume an Arrhenius dependence so that

$$\langle\theta\rangle = \langle\theta_\infty\rangle \exp(E_A/kT) \tag{33}$$

Here E_A is an activation energy and $\langle\theta_\infty\rangle$ is the relaxation time on the fundamental scale at (nominally) infinite temperature. For simplicity sufficient for our present expository purposes, we consider that the fractional exponent b to be independent of temperature. On the time scale of measurement, we find

$$\bar{\tau}_t = (\bar{\tau}_t)_\infty \exp(E_A^*/kT) \tag{34}$$

Here E_A^* is an effective activation energy. It is clear that for the invariance relation Eq. (27) to hold, E_A^* must be related to the actual activation energy E_A by the renormalization relation

$$E_A^* = E_A/b \tag{35}$$

Thus measured activation energies invariably seem to be greater than they actually are.

The remarkable feature of results like Eqs. (21), (30), (32) and (35) is that they and their mutual dependencies are consistently verified by experi-

13

ment on many kinds of condensed matter for a wide range of relaxation phenomena.[3] This verification lends credibility to the ideas that have been invoked in the present development. These include: the concept of incremental relaxation density for simple relaxation; the principle of maximum epoch entropy; the existence of a fundamental time scale for simple relaxation; the need for a time scale transformation to obtain the time scale of measurement; the invariance of the value of the maximum epoch entropy when evaluated on different time scales; and the procedure presented in Sec. IV to justify the choice of time scale to correspond to the time scale of measurement for relaxation phenomena.

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