Justifying Narayanaswamy’s 1971 aging theory from statistical mechanics

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This paper shows how one may use the Bochkov-Kuzovlev nonlinear fluctuation-dissipation theorem to arrive at Narayanaswamy’s phenomenological theory of physical aging, in which this highly nonlinear phenomenon is described by a linear material-time convolution integral. We define the material time as the squared distance in configuration space to a system configuration of the distant past. Two other ingredients of the proposed formalism, which both apply rigorously in thermal equilibrium, are: 1) A geometric view in which a time-autocorrelation function is regarded as a spatial autocorrelation function in configuration space evaluated at the distance corresponding to the system’s displacement over the relevant time interval; 2) An assumption that the aging system obeys a “unique-triangles property” according to which any three points on the system’s configuration-space path form a triangle such that two side lengths determine the third. The paper concludes by suggesting computer simulations that may test the ideas put forward.

I. INTRODUCTION

Physical aging is the slow change of material properties observed for some solids, e.g., polymers and glasses close to their glass-transition temperature [1]. In contrast to the aging of most real-life materials resulting from chemical reactions, physical aging is exclusively due to adjustments of molecular positions. During the last 25 years there has been considerable progress in the description and understanding of aging in model systems. In particular, the study of spin glass aging has led to the concept of an “effective” temperature that quantifies violations of the fluctuation-dissipation theorem [2, 3]. There is still no good theoretical justification for Narayanaswamy’s remarkably successful phenomenological physical-aging theory [4], however, which for decades has been used routinely in industry [1]. The present paper is an attempt to derive central parts of the Narayanaswamy theory from basic principles.

We present below no new experimental or simulation data, but the paper concludes with proposals for computer simulations that can be carried out to check the assumptions involved in the framework proposed. The motivation is to understand the microscopic origin of Narayanaswamy’s aging theory according to which physical aging, which is strongly non-linear in the temperature history, is described by a linear convolution integral if one replaces the time variable by the so-called material time. In the words of Narayanaswamy’s seminal 1971 paper [4]: “The intrinsic relation between force and flow (or cause and effect) is assumed to be linear, i.e., it is assumed that the only cause of nonlinearity in glass transition phenomena is the changing viscosity of the glass as the structure (or fictive temperature) changes”. This led to the introduction of a “material time” quantifying how fast processes take place in an aging system.

The Narayanaswamy theory, which is known to work well for relatively small temperature variations [1], raises a number of questions:

1. How and why can the highly non-linear phenomenon of physical aging be reduced to a linear convolution integral?
2. What is the material time? Can it be defined rigorously in terms of the system’s microscopic variables?
3. Are all aging quantities subject to the same material time?
4. Which physical quantity controls the clock rate defining the material time?

This paper addresses the first three questions. In order to understand how Narayanaswamy’s formally linear description of aging may arise, we first need to define a material time in terms of microscopic variables. The idea below is the following: Any time-autocorrelation function \( \langle q(0)q(t) \rangle \) decays to zero as \( t \to \infty \) if \( \langle q \rangle = 0 \), because the two involved molecular configurations move apart and eventually become uncorrelated (it is assumed here and henceforth

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that all physical quantities are functions of the configuration-space coordinates, not involving any momentum coordinates). At short times, on the other hand, \( q(0)q(t) \) is non-zero simply because \( q \) is a continuous function of the configuration vector. Thus if a time-autocorrelation function is thought of as deriving from a spatial autocorrelation function in the high-dimensional configuration space, the relevant time measure must be the distance travelled over the given time interval. This “geometric” picture of time-autocorrelation functions can always be made to work in thermal equilibrium \( \mathbb{R} \); below we identify the condition for it to apply also for aging systems. This is done by defining the material time as the squared distance to a configuration of the system’s distant past. We proceed to use the Bochkov-Kuzovlev 1981 exact nonlinear fluctuation-dissipation theorem \( [2] \) to arrive at an approximate description of the nonlinear response in terms of a linear material-time convolution integral valid for small temperature variations (but much beyond the linear aging regime).

Section II gives the background needed to understand the paper, Sec. III defines the material time by first considering the thermal-equilibrium case. Section IV identifies the “unique-triangles property”, a geometric condition for the system’s path in configuration space that is trivially obeyed in equilibrium and which, if it applies also for the aging system, ensures consistency of the material-time definition. Section V derives the Narayanaswamy linear convolution integral from the nonlinear fluctuation-dissipation theorem, and Sec. VI suggests numerical tests of the theory. Finally, Sec. VII gives a few concluding remarks.

II. BACKGROUND

This section summarizes the necessary background.

A. Time-temperature superposition in thermal equilibrium

In supercooled liquids the average relaxation time is extremely temperature dependent. In some case it may increase by a factor of ten when temperature is lowered by merely 1% \( R, S \). This is reflected in the fact that loss peaks of linear-response functions such as the frequency-dependent dielectric constant \( R \) or shear modulus \( T \) move quickly to lower frequencies when the liquid is cooled. Many frequency-dependent linear-response functions keep their shape to a good approximation when plotted in a log-log plot, at least for limited temperature variations. This is referred to as “time-temperature superposition” (TTS). Physically, it is as if the same processes take place in the system upon cooling, just much slower – pictorially, the same movie of the molecular motion is being played in slow-motion.

If \( \chi(\omega, T) \) is a linear-response function where \( \omega \) is the angular frequency and \( T \) the temperature, TTS may be expressed mathematically as \( \chi(\omega, T) = \phi(\omega \tau(T)) \) \( [11] \) (for simplicity we ignore that the overall normalization factor may vary with temperature). Here \( \tau(T) \) is the response function’s average (alpha) relaxation time. Different response functions usually have average relaxation times that are proportional in their temperature variation \( [12] \); this is consistent with the above picture that when temperature is changed the same physics takes place, merely with a different rate.

B. The “inner clock” material-time concept and Narayanaswamy’s phenomenological aging theory

There is a huge literature on physical aging \( [1, 13–20] \), and the interest in this field is continuously stimulated by the practical importance of being able to predict aging quantitatively. An excellent introduction to the phenomenology of aging is given in Scherer’s book from 1986 \( [1] \). Experiments have studied aging by probing, e.g., density \( [13, 21] \), enthalpy \( [14] \), Young’s modulus \( [22] \), gas permeability \( [23] \), high-frequency mechanical moduli \( [24, 25] \), dc conductivity \( [15] \), frequency-dependent dielectric constant \( [26, 27] \), XPCS-probed structure \( [28] \), non-linear dielectric susceptibility \( [29] \), etc. Often one monitors aging upon a temperature jump, but more complicated temperature histories have also been studied.

To be specific we shall assume that the property \( X \) is monitored and that the experiment ends in equilibrium at the temperature \( T_0 \). The deviation of \( X \) from its equilibrium value at \( T_0 \) is denoted by \( \Delta X(t) \); thus \( \Delta X(t) \to 0 \) as \( t \to \infty \). Narayanaswamy’s novel idea, which was inspired by rheological models, was to introduce a so-called material time \( \xi \). This quantity is to be thought of as the time measured on a clock with a clock rate that itself ages \( R \), reflecting the fact that processes in an aging system proceed with a speed that changes as the structure changes during aging. Following a down jump in temperature, for instance, the clock rate decreases and eventually becomes constant when equilibrium is reached. The material time is analogous to the proper time of relativity theory, the time measured on a clock moving with the observer.

If the clock rate is denoted by \( \gamma(t) \), the material time is defined by
\[ d\xi = \gamma(t) \, dt. \] (1)

The clock rate is generally a complicated function of the system’s thermal history after it fell out of equilibrium. Narayanaswamy suggested that for the temperature variation \( T_0 + \Delta T(t) \), if rewritten as a function of \( \xi \), the variation \( \Delta X(t) \) can be written as an “instantaneous” contribution, \( C \Delta T(t) \), plus a relaxing contribution given by a linear material-time convolution integral [1, 4]:

\[ \Delta X(\xi_1) = C \Delta T(\xi_1) - \int_{-\infty}^{\xi_1} M(\xi_1 - \xi_2) \frac{d\Delta T}{d\xi_2}(\xi_2) \, d\xi_2. \] (2)

In particular, after a temperature jump at \( t = 0 \) from equilibrium at temperature \( T_0 + \Delta T \) to temperature \( T_0 \) one has \( \Delta X(t) = \Delta T(C + M(\xi)) \) in which \( \xi = \xi(t) \) is found by integrating Eq. (1). The point is that the function \( M(\xi) \) is the same for all temperature jumps whereas \( \xi(t) \) depends on \( \Delta T \) (often strongly).

For infinitesimal temperature variations around an equilibrium temperature the structure is virtually constant and the material time is proportional to the laboratory time, \( \xi \propto t \). According to Eq. (2) the same convolution kernel appears for infinitesimal temperature variations around different temperatures. Thus the Narayanswamy formalism implies TTS for the response of \( X \) to linear temperature variations. This fact is important for the reasoning below; it may explain why the Narayanswamy formalism works best for relatively small temperature changes [1] since TTS deviations are often observed for large temperature variations.

In the Narayanswamy formalism the rate of the aging system’s “inner clock” is a global variable in the sense that the material time increases at the same rate everywhere in the system. An interesting extension due to Castillo and co-workers [30–32] is to assume that aging is controlled by a space-dependent clock rate. This idea, which is consistent with the existence of dynamical heterogeneities in the non-equilibrium dynamics glassy systems, has been verified numerically in studies of various model systems [30–32]. Below we do not follow this interesting line of research, but focus on the simpler case of “global” clock.

C. Simplifications in the thermodynamic limit

A system of \( N \) particles is considered. If the particle positions are denoted by \( r_i \) \( (i = 1, ..., N) \), the system’s configuration vector is defined by \( R \equiv (r_1, ..., r_N) \). The dynamics may be Newtonian or Brownian (Langevin). The system’s path in configuration space as a function of time is denoted by \( R(t) \). We define the distance \( R_{12} \) between two configurations \( R(t_1) \) and \( R(t_2) \) as follows

\[ R_{12} \equiv \left( \frac{(R(t_1) - R(t_2))^2}{N} \right)^{1/2}. \] (3)

The normalization factor \( \sqrt{N} \) is introduced to get a well-defined thermodynamic limit. Fluctuations become insignificant in this limit, and consequently the distance between the system’s configurations at two times is a unique number. This simplification applies in equilibrium as well as for an aging system.

In thermal equilibrium the displacement of the system during time \( t \) is denoted by \( R_{eq}(t) \). In terms of the mean-square displacement in time \( t \), \( \langle \Delta R^2(t) \rangle \), \( R_{eq}(t) \) is given by

\[ R_{eq}(t) \equiv \left( \frac{\langle \Delta R^2(t) \rangle}{N} \right)^{1/2}. \] (4)

As discussed, the averaging is superfluous. Note that \( R_{eq}(t) \) is experimentally accessible via the incoherent intermediate scattering function.

D. Geometric ansatz for equilibrium time-autocorrelation functions

Some time ago I proposed a geometric view of thermal-equilibrium time-autocorrelation functions [5]. The background was the above-mentioned facts that TTS often applies and that, while the average relaxation time \( \tau(T) \) in
glass-forming liquids is strongly temperature dependent, for different linear-response functions $\tau(T)$ usually varies with temperature in the same way \[\tau\].

A simple way to understand these facts for the case of thermal equilibrium is that there is a geometric autocorrelation function, a quantity that in a somewhat sloppy notation will be denoted by $\langle q(0)q(R) \rangle$. By this we mean the quantity defined by averaging over all pairs of points along the system’s path in time $R(t)$ separated the distance $R = R_{eq}(t)$, corresponding to the time interval $t = t_1 - t_2$ between two path configurations, $R(t_1)$ and $R(t_2)$. Recall that this distance is unique for given $t$. $R_{eq}(t)$ is an increasing function of $t$ and thus in a one-to-one correspondence with $t$. In terms of the geometric autocorrelation function the equilibrium time-autocorrelation function is given \[2\] by

$$\langle q(0)q(t) \rangle = \langle q(0)q(R) \rangle |_{R = R_{eq}(t)} .$$

In Ref. \[3\] we proposed an ansatz for calculating the geometric autocorrelation function $\langle q(0)q(R) \rangle$ via a “double-canoncial” statistical-mechanical-averaging. The theory was validated by simulations of a one-dimensional double-potential model. A simple example of Eq. \[3\] also discussed in Ref. \[3\] is the case of a Gaussian geometric autocorrelation function, $\langle q(0)q(R) \rangle \propto \exp\left(-R^2/2R^2_{eq}\right)$, and linear diffusion, $R^2_{eq}(t) = 6Dt$ where $D$ is the diffusion constant. This leads to an exponentially decaying time-autocorrelation function, the so-called Debye relaxation that is the simplest possible linear-response situation. A more realistic case also assumes a Gaussian geometric autocorrelation function, but combines this with a short-time subdiffusive mean-square displacement. This leads to a high-frequency (short-time) non-Debye behavior. In experiments the relaxation is often Debye-like on the low-frequency side of the loss peak \[33\], which implies a Gaussian decay of the geometric autocorrelation function at long distances.

As it stands, Eq. \[3\] is a tautology because the geometric average $\langle q(0)q(R) \rangle$ is defined to make Eq. \[3\] apply at the thermodynamic state point in question. One of the consequences of Ref. \[3\] is that TTS finds a natural explanation if what happens when temperature is changed is simply the following: $\langle q(0)q(R) \rangle$ is unchanged, and $R_{eq}(t)$ is also unchanged except for a scaling of time. This geometric “explanation” of TTS admittedly presupposes TTS for the fact that the rate of motion has changed \[31\]. Below we assume this is the case and that consequently the geometric autocorrelation function of equilibrium, $\langle q(0)q(R) \rangle$, applies also for an aging system. These assumptions are consistent if TTS applies over the range of temperatures involved in the aging experiment.

E. The triangular relation

More than 20 years ago the study of aging in spin glasses and related systems resulted in a deep understanding of the nature of aging in these systems \[2\]. For spin glass aging there is time-scale separation, just as for aging in ordinary glasses. Thus on short time scales an analog of vibrational thermal equilibrium exists, whereas aging of the “structural” degrees of freedom – those of real importance – takes place on much longer time scales. This led to the introduction of the concept of an effective temperature \[2,3,52\], which is conceptually similar to Tool’s intuitive fictive temperature concept from 1946 \[37\], but founded in rigorous statistical-mechanical theory. These works led to the important insight that “the proper measure of time is the correlation itself, not the laboratory clock” \[36\].

The above insight into what is the proper time measure was formalized into the triangular relation which, if $t_1 > t_2 > t_3$ and $C(t,t')$ is a time-autocorrelation function, i.e., an average for the aging system of the form $C(t,t') \equiv \langle q(t)q(t') \rangle$, is the following interdependence equation \[2\]

$$C(t_1,t_3) = f[C(t_1,t_2),C(t_2,t_3)] .$$

It is understood that this only applies on long time scales. The above-mentioned idea that time is measured via the autocorrelation function itself \[2\] implies “time-reparametrization invariance”, see, e.g., Refs. \[32,38,39\], as well as earlier works \[10,11\].

A few notes relating to the triangular relation:

1. Equation \[10\] applies in thermal equilibrium for any “relaxing” time-autocorrelation function, i.e., a sum of positive, decaying exponentials. In that case the value of the time autocorrelation function $C(t_1,t_3)$ uniquely determines the time difference $t_1 - t_3$, and if one knows $t_1 - t_2$ and $t_2 - t_3$, one of course also knows $t_1 - t_3$.

2. For the case of equilibrium, if TTS applies the function $f$ is the same when temperature is changed.
3. The triangular relation applies for an aging system that has an “inner clock” and corresponding material time \( \xi \) in the Narayanaswamy sense. In that case one can write \( C(t_1, t_2) = F(\xi(t_1) - \xi(t_2)) \), and if the function \( F(\xi) \) goes monotonically to zero as \( \xi \) goes to infinity, \( C(t_1, t_2) \) determines the difference \( \xi(t_1) - \xi(t_2) \) and \( C(t_2, t_3) \) determines the difference \( \xi(t_2) - \xi(t_3) \). Thus \( C(t_1, t_2) \) and \( C(t_2, t_3) \) determine \( C(t_1, t_3) \).

4. The triangular relation applies whenever the system in question obeys so-called dynamic ultrametricity, i.e., \( C(t_1, t_3) = \min(C(t_1, t_2), C(t_2, t_3)) \), which is believed to be the case for spin glasses [42].

III. DEFINING THE MATERIAL TIME FROM THE DISTANCE TRAVELLED IN CONFIGURATION SPACE

The above discussed geometric view of autocorrelation functions is based on the fact that autocorrelation functions decay to zero at long times because the two configurations involved move further and further apart. This suggests measuring time via distance. We start by considering a system in thermal equilibrium before proceeding to investigate how to generalize to an aging system.

A. The case of thermal equilibrium

We first consider a simple diffusive system in thermal equilibrium, i.e., one for which \( R_{eq}^2(t) = 6D t \) at all times \( t > 0 \), where \( R_{eq}^2(t) \) is the distance of Eq. (3) between two configurations on the system’s path separated by the time interval \( t \). Choose a reference configuration \( R(t_0) \) corresponding to the system’s configuration at a distant time \( t_0 \), and consider two later times \( t_1 > t_2 \). Then one has for the distances from \( R(t_1) \) and \( R(t_2) \) to \( R(t_0) \): \( R_{01}^2 = 6D(t_1 - t_0) \) and \( R_{02}^2 = 6D(t_2 - t_0) \). Obviously, the time difference \( t_1 - t_2 \) can be found by subtracting the two squared distances,

\[
t_1 - t_2 = \left( R_{01}^2 - R_{02}^2 \right) / (6D).
\]

Thus the square of the distance travelled from a reference configuration may be used as a clock. Crucially, when defined in this way the time difference between two points on the system’s path is independent of the choice of reference configuration.

Consider next the general thermal-equilibrium case in which the (mean) squared displacement is not necessarily linear in time at all times. The generic behavior is that \( R_{eq}^2(t) \) is sublinear at short times (e.g., \( R_{eq}^2(t) \sim t^x \) with \( 0 < x < 1 \)) and linear in time at long times [34, 35, 43].

\[
R_{eq}^2(t) = 6D t \ (t \to \infty).
\]

The transition between the two regimes takes place around the average relaxation time \( \tau \), but we are not here interested in the details of \( R_{eq}^2(t) \) [44]. The important thing is to note that because of Eq. (5), one can still use the squared distance to a far-away reference configuration as a clock. Indeed, Eq. (5) implies Eq. (7). Just as in the purely diffusive case, the time difference between two events on the system’s path measured by this “geometric” clock is independent of the choice of reference configuration, as long as it is selected from one of the system configurations far back in time.

B. Defining the material time for an aging system

Can the above be generalized? Suppose that we for an aging system define a material time \( \xi \) as the squared distance from \( R(t) \) to a far-back-in-time reference configuration \( R(t_0) \):

\[
\xi(t) \equiv R_{0t}^2.
\]

If a dimensionless material time is wanted, one may multiply this with the particle number density to the power 2/3, but for simplicity we stick to the above definition. For it to make sense the difference in material time between two events on the aging system’s path in configuration space, \( \xi(t_1) - \xi(t_2) \), must be independent of the choice of reference configuration. To investigate whether this is the case we compare \( R_{01}^2 - R_{02}^2 \) with the analogous quantity using a
different reference configuration, $\mathbf{R}(t_0')$. Since $\mathbf{R}(t_1) - \mathbf{R}(t_0') = \mathbf{R}(t_1) - \mathbf{R}(t_0) + \Delta \mathbf{R}$ where $\Delta \mathbf{R} = \mathbf{R}(t_0) - \mathbf{R}(t_0')$, one has

$$R_{01}^2 = R_{01}^2 + \Delta \mathbf{R}^2/N + 2(\mathbf{R}(t_1) - \mathbf{R}(t_0)) \cdot \Delta \mathbf{R}/N.$$  \hspace{1cm} (10)

Likewise

$$R_{02}^2 = R_{02}^2 + \Delta \mathbf{R}^2/N + 2(\mathbf{R}(t_2) - \mathbf{R}(t_0)) \cdot \Delta \mathbf{R}/N.$$  \hspace{1cm} (11)

Subtracting these equations leads to

$$R_{01}^2 - R_{02}^2 = R_{01}^2 - R_{02}^2 + 2(\mathbf{R}(t_1) - \mathbf{R}(t_2)) \cdot \Delta \mathbf{R}/N.$$  \hspace{1cm} (12)

When $t_0$ and $t_0'$ are both far back in time, $\mathbf{R}(t_1) - \mathbf{R}(t_2)$ is uncorrelated with $\Delta \mathbf{R}$, because in terms of the velocity $\mathbf{V} \equiv \dot{\mathbf{R}}$ one has $[\mathbf{R}(t_1) - \mathbf{R}(t_2)] \cdot \Delta \mathbf{R} = \int_{t_1}^{t_2} ds_1 \int_{t_0}^{t_0'} ds_2 \mathbf{V}(s_1) \cdot \mathbf{V}(s_2)$, which goes to zero in the limits $t_0 \to -\infty$ and $t_0' \to -\infty$ since velocities far apart in time are uncorrelated. Thus the last term of Eq. (12) vanishes, which ensures consistency of the material time definition for an aging system Eq. 9.

IV. THE UNIQUE-TRIANGLES PROPERTY

The configuration-space path of a system in thermal equilibrium has an interesting geometric property. Consider three times, $t_1 > t_2 > t_3$. The corresponding distances between the configurations on the system’s path, $\mathbf{R}(t_1)$, $\mathbf{R}(t_2)$, and $\mathbf{R}(t_3)$, are denoted by $R_{21}$, $R_{31}$, and $R_{32}$. These quantities only depend on the time differences involved, $R_{21} = R_{eq}(t_1 - t_2)$, $R_{31} = R_{eq}(t_1 - t_3)$, and $R_{32} = R_{eq}(t_2 - t_3)$. Since $R_{eq}(t)$ is an increasing function of $t$, the triangle formed by the points $\mathbf{R}(t_1)$, $\mathbf{R}(t_2)$, and $\mathbf{R}(t_3)$ is unique in the following sense: If two of the triangle’s side lengths are known, the third one is also known. For instance, if $R_{21}$ and $R_{32}$ are known, $R_{31}$ is uniquely determined since $R_{21}$ determines $t_1 - t_2$ and $R_{32}$ determines $t_2 - t_3$, from which $t_1 - t_3$ and thus $R_{31}$ may be deduced. A system for which any three points on its trajectory determine a unique triangle in the above sense will be referred to as having the “unique-triangles property”.

In the next section we apply the geometric ansatz for time-autocorrelation functions of Sec. III D and the material-time definition of Sec. III B to an aging system. For this to work the unique-triangles property will be assumed to apply also for the aging system. This ensures that the difference of two material times, $\xi(t_1) - \xi(t_2)$, determines the distance $R_{21}$ between the corresponding configurations $\mathbf{R}(t_1)$ and $\mathbf{R}(t_2)$ and thus, via the geometric ansatz Eq. 5, generalized to the the aging system, the relevant time-autocorrelation $\langle q(\xi_1)q(\xi_2) \rangle$ (see the next section) as follows

$$\langle q(\xi_1)q(\xi_2) \rangle = F(\xi_1 - \xi_2).$$  \hspace{1cm} (13)

In effect, the unique-triangles property expresses the triangular relation Eq. 5 for systems obeying the geometric ansatz for time-autocorrelation functions Eq. 5.

V. DERIVING NARYANASWAMY’S FORMALLY LINEAR DESCRIPTION OF AGING

In order to finally arrive at our suggestion for how to justify Narayananswamy’s aging theory from basic principles, four ingredients will be combined. The first one is the definition of the material time given in Eq. 9. The second ingredient is the unique-triangles property, which as shown in Sec. IV ensures that the difference between two material times $\xi_1 = \xi(t_1)$ and $\xi_2 = \xi(t_2)$ determines the distance between the corresponding system configurations $\mathbf{R}(t_1)$ and $\mathbf{R}(t_2)$. Via the geometric ansatz for time-autocorrelation functions Eq. 5, which is the third ingredient, the difference $\xi_1 - \xi_2$ determines the autocorrelation function $\langle q(t_1)q(t_2) \rangle$ needed below (Eq. 13). But we still haven’t addressed the fundamental puzzle: How is a theory that is linear in the material time to be arrived at? To do this we apply Bochkov’s and Kuzovlev’s non-linear fluctuation-dissipation theorem from 1981. This is the fourth ingredient.

It is convenient to adopt the language of the energy-bond formalism according to which any system interacts with its surroundings via one or more so-called energy bonds 14–18. Each energy bond is characterized by two variables, an effort and a flow variable, the product of which gives the energy per unit time transferred into the system from its
surroundings. Effort could be, e.g., voltage drop or force, in which cases the corresponding flow variables are electrical current and velocity, respectively. The formalism is quite general, and even a heat flow may be modelled in this way—in that case energy is generalized into free energy, the effort is the temperature deviation from a reference temperature \( T_0 \), and the flow is the entropy current \[1, 5\]. Emphasizing further the general nature of the energy-bond formalism is the fact that for any physical quantity \( q \) one may define a flow by \( f \equiv dq/dt \) and let \( e \) be a fictitious field coupling linearly to \( q \) in the Hamiltonian.

We consider the case of a single energy bond in which \( e(t) \) is the effort and \( f(t) \) the flow. If the effort is externally controlled, the standard linear fluctuation-dissipation (FD) theorem is the following expression for the average flow at time \( t_1 \) in the (infinitesimal) time-dependent external field \( e(t) \)

\[
\langle f(t_1) \rangle = \beta_0 \int_{-\infty}^{t_1} \langle f(t_1)f(t_2) \rangle_0 e(t_2) \, dt_2 .
\]  

(14)

Here \( \beta_0 \equiv 1/k_B T_0 \) where \( T_0 \) is the system’s temperature and \( \langle f(t_1)f(t_2) \rangle_0 \) is the thermal equilibrium time-autocorrelation function, which by time-translational invariance is a function of the difference \( t_1 - t_2 \). There is complete symmetry between \( e \) and \( f \), so if the flow \( f \) is externally controlled, the FD theorem is

\[
\langle e(t_1) \rangle = \beta_0 \int_{-\infty}^{t_1} \langle e(t_1)e(t_2) \rangle_0 f(t_2) \, dt_2 .
\]  

(15)

In 1981 Bochkov and Kuzovlev derived a general, non-linear response theory \[6\]. It is assumed that the system was in equilibrium at the temperature \( T_0 \) far back in time and ends up in equilibrium at the same temperature in the distant future. If the non-equilibrium cumulant averages are denoted by \( \langle \langle \ldots \rangle \rangle \), the following exact relation applies (Eq. (2.18) in Ref. \[4\] in the above energy-bond notation):

\[
\langle f(t_1) \rangle = \sum_{k=2}^{\infty} (-1)^k \frac{\beta_0^{k-1}}{(k-1)!} \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_1} dt_k \langle \langle f(t_1)f(t_2)\ldots f(t_k) \rangle \rangle e(t_2) \ldots e(t_k) .
\]  

(16)

To first order in \( e \) all but the first term on the right-hand side may be ignored, and since \( \langle f(t) \rangle_0 = 0 \) the two-point cumulant average may be replaced by the equilibrium product average \( \langle f(t_1)f(t_2) \rangle_0 \), reducing Eq. (16) to the standard FD theorem Eq. (14).

The derivation of Eq. (16) is based on Bochkov and Kuzovlev’s fluctuation theorem \[6\] according to which the ratio of probabilities of a given path in time \( R(t) \) and the corresponding time-reversed path \( R(-t) \) is the ratio of the Boltzmann probabilities of the starting and ending points. During the 1990s this result became known as the fluctuation theorem \[5, 6, 7\], but to the best of my knowledge the first general derivation of it was given in Refs. \[2, 5\] covering both the classical Hamiltonian, stochastic, and quantum-mechanical cases.

Note that Eq. (16) is not the trivial higher-order generalization of the linear FD theorem in which the right-hand-side averages are equilibrium averages. In fact, as shown some time ago by Stratonovich \[54\] (see also Ref. \[3\]), there is no general non-linear FD theorem determining the response from equilibrium averages. The occurrence of non-equilibrium averages on the right-hand side makes Eq. (16) appear to be of little use. We proceed to show how—in conjunction with the above material-time definition and geometric ansatz for time-autocorrelation functions—one can in fact use Eq. (16) to arrive at a Naryanaswamy-type expression that is linear in the material time.

The starting point is the already mentioned fact that Naryanaswamy’s theory works best for small temperature changes \[1\]. Thus there is an aging regime in which the temperature change involved is fairly small (typically a few percent), but large enough that aging is still strongly non-linear, e.g., with changes of a factor of ten or more in characteristic relaxation time between up and down jumps to the same temperature. Since the effort \( e \) is the temperature difference to a reference temperature \( T_0 \), for the regime of relatively small temperature variations it makes good sense to ignore the higher-order terms on the right-hand side of Eq. (16), leading to

\[
\langle f(t_1) \rangle \approx \beta_0 \int_{-\infty}^{t_1} \langle \langle f(t_1)f(t_2) \rangle \rangle e(t_2) \, dt_2 .
\]  

(17)

To consistently ignore higher-order terms, however, one must also ignore the difference between the cumulant average \( \langle \langle f(t_1)f(t_2) \rangle \rangle \) and the product average \( \langle f(t_1)f(t_2) \rangle \), because this difference is \( \langle f(t_1) \rangle \langle f(t_2) \rangle \) and thus of second order in \( e \) (assuming \( \langle f(t) \rangle_0 = 0 \)). This leads to

\[
\langle f(t_1) \rangle \equiv \beta_0 \int_{-\infty}^{t_1} \langle \langle f(t_1)f(t_2) \rangle \rangle e(t_2) \, dt_2 .
\]  

(18)
\[ \langle f(t_1) \rangle \equiv \beta_0 \int_{-\infty}^{t_1} \langle f(t_1) f(t_2) \rangle e(t_2) dt_2. \tag{18} \]

Equation (18) has the appearance of the standard linear FD theorem Eq. (14), but since \( \langle f(t_1) f(t_2) \rangle \) is evaluated along the actual system path, this quantity is generally a complicated, highly nonlinear function of the external field history \( e(t) \).

We now combine Eq. (18) with the geometric ansatz for time-autocorrelation functions, Eq. (5). First, one writes the flow variable as a time derivative of a generalized “charge” \( q \),

\[ f = \frac{dq}{dt}. \tag{19} \]

and changes the integration variable in Eq. (18) from the time \( t \) to the material time \( \xi = \xi(t) \). This leads to

\[ \left\langle \frac{dq}{d\xi_1}(\xi_1) \frac{dq}{d\xi_2}(\xi_2) \right\rangle \cong -\beta_0 \int_{-\infty}^{\xi_1} F''(\xi_1 - \xi_2) e(\xi_2) d\xi_2. \tag{20} \]

By the geometric ansatz Eq. (5) and the unique-triangles property the autocorrelation function \( \langle q(\xi_1) q(\xi_2) \rangle \) is a function of \( \xi_1 - \xi_2 \). This is expressed in Eq. (13), which implies that

\[ \left\langle \frac{dq}{d\xi_1}(\xi_1) \frac{dq}{d\xi_2}(\xi_2) \right\rangle = -F''(\xi_1 - \xi_2). \tag{21} \]

Equation (20) thus becomes

\[ \frac{d}{d\xi_1} \langle q(\xi_1) \rangle \cong -\beta_0 \int_{-\infty}^{\xi_1} F''(\xi_1 - \xi_2) e(\xi_2) d\xi_2. \tag{22} \]

Replacing \( \xi_1 \) with \( \xi \) and integrating from \( -\infty \) to \( \xi_1 \) leads to (with \( \Delta q(\xi_1) \equiv q(\xi_1) - q_{eq}(T_0) \))

\[ \langle \Delta q(\xi_1) \rangle \cong -\beta_0 \int_{-\infty}^{\xi_1} d\xi_2 \int_{-\infty}^{\xi} d\xi F''(\xi - \xi_2) e(\xi_2). \tag{23} \]

Interchanging the order of integration we get since \( -\infty < \xi_2 < \xi < \xi_1 \)

\[ \langle \Delta q(\xi_1) \rangle \cong -\beta_0 \int_{-\infty}^{\xi_1} d\xi_2 e(\xi_2) \int_{\xi_2}^{\xi_1} d\xi F''(\xi - \xi_2). \tag{24} \]

Utilizing that \( F'(0) = 0 \), which follows from the fact that \( F(\xi) \) also describes the equilibrium linear response for which \( (d/dt) \langle q(0) q(t) \rangle_{t=0} = 0 \) because of time-reversal invariance, we get

\[ \langle \Delta q(\xi_1) \rangle \cong -\beta_0 \int_{-\infty}^{\xi_1} F'(\xi_1 - \xi_2) e(\xi_2) d\xi_2 = \beta_0 \int_{-\infty}^{\xi_1} \left( \frac{d}{d\xi_2} F(\xi_1 - \xi_2) \right) e(\xi_2) d\xi_2. \tag{25} \]

When integrated partially with respect to \( \xi_2 \), since \( F(\xi) \to 0 \) for \( \xi \to \infty \) this leads to

\[ \langle \Delta q(\xi_1) \rangle \cong \beta_0 \left( F(0)e(\xi_1) - \int_{-\infty}^{\xi_1} F(\xi_1 - \xi_2) \frac{de}{d\xi_2}(\xi_2) d\xi_2 \right). \tag{26} \]

This is the sum of an “instantaneous” and a “relaxing” contribution. If the identifications \( q = X \) and \( e = \Delta T \) are made, Eq. (26) is the Narayanaswamy expression Eq. (1). This one cannot do, however, because these variables generally below to different energy bonds. The solution is straightforward as we now proceed to show.
If the effort $e$ is the temperature variation $\Delta T$, which is the usual aging situation, the corresponding flow variable is the entropy current that is basically the heat current into the system [49]. The Narayanaswamy theory deals with aging of other quantities than enthalpy, however. These cases are easily taken into account since Eq. (16) generalizes straightaway to any number of energy bonds [6]. The resulting equation involves a sum over all combinations of energy-bond indices, $j_2, \ldots, j_k$, such that for $i = 2, \ldots, k$ each flow variable $f_j(t_i)$ in the right-hand-side cumulant of Eq. (16)’s generalization is paired to a same-index effort variable $e_j(t_i)$. If there are $n$ energy bonds, the leading term is the following sum generalizing Eq. (18):

\[ \langle f(t_1) \rangle \cong \beta_0 \sum_{j=1}^{n} \int_{-\infty}^{t_1} \langle f(t_1) f_j(t_2) \rangle e_j(t_2) dt_2. \] (27)

In particular, if one is interested in how the quantity $X$ responds to a temperature variation, only one term in the above sum is of interest, namely that coupling the $X$ energy bond to the thermal energy bond whose generalized charge – the time-integrated entropy current – will be denoted by $q_S$. In this way one arrives at an expression of the form Eq. (26) with a different function $F(\xi)$, but the same material time. In this general case the function $F(\xi)$ is given as $F(\xi_1 - \xi_2) = \langle X(\xi_1)q_S(\xi_2) \rangle$. Note that the above used identity $F'(0) = 0$ applies also in the general case because it follows from the time reversibility valid in equilibrium, $\langle X(t_1)q_S(t_2) \rangle_0 = \langle q_S(t_1)X(t_2) \rangle_0$.

\section{VI. POSSIBLE NUMERICAL TESTS OF THE PROPOSED FRAMEWORK}

The assumptions made in order to justify the phenomenological Narayanaswamy aging theory from basic principles can be checked by computer simulations. To do this it is first necessary to identify a system and some variable $X$ that obey the Narayanaswamy formalism. This may be challenging because computers are not yet able to simulate realistic aging situations so temperature jumps larger than a few percent may be needed in simulations.

Once a suitable model system has been identified, the following tests can be performed:

1. The geometric ansatz for time-autocorrelation functions of an aging system. Equation (3) applies by definition in thermal equilibrium. To check it for an aging system one could proceed as follows. First evaluate the equilibrium geometric autocorrelation function $\langle q(0)q(R) \rangle_0$. This may be done by tracing out and storing the system’s path in configuration space $\mathbf{R}(t)$. For many pairs of configurations on this path, $\mathbf{R}_1$ and $\mathbf{R}_2$, the distance $R_{12}$ and product $q(\mathbf{R}_1)q(\mathbf{R}_2)$ is then evaluated and $\langle q(0)q(R) \rangle_0$ is the average of these products with $R = R_{12}$. After this, the same procedure is performed for an aging system to see whether the same geometric autocorrelation function applies in this case. An equivalent test is to investigate whether $\Delta q \equiv q(\mathbf{R}_1) - q(\mathbf{R}_2)$ is the same function of the distance $R(t)$ in equilibrium and during aging, which can be done by plotting $\Delta q$ versus $R$ and comparing the two plots.

2. The unique-triangles property for an aging system. This can be investigated in a way similar to how the triangular relation has been checked [36]: First the system’s path in configuration space $\mathbf{R}(t)$ is traced out and stored. Different triplets of configurations, $\mathbf{R}(t_1)$, $\mathbf{R}(t_2)$, and $\mathbf{R}(t_3)$, are then picked out and the corresponding distances $R_{21}$, $R_{31}$, and $R_{32}$ evaluated. The system obeys the unique-triangles property if for a given value of $R_{21}$ there is a one-to-one correspondence between $R_{31}$ and $R_{32}$. This may be checked by plotting $R_{31}$ versus $R_{32}$ for a narrow range of $R_{21}$ values.

3. Predicting nonlinear aging from linear aging The ultimate test of Eq. (2) is to investigate whether information from very small temperature-jump simulations, i.e., in the linear regime, is enough to predict the aging following larger temperature jumps when the material time is defined by Eq. (9).

If simulations have also identified a model in which the Narayanaswamy theory does not apply, it would be interesting to see whether this system also violates the unique-triangles property. This may clarify whether that property is a good “thermometer” for which systems obey the Narayanaswamy theory and which do not.

\section{VII. CONCLUDING REMARKS}

This paper has addressed the challenge of justifying from basic principles the phenomenological, but indisputably successful, 44 years old Narayanaswamy description of aging. Most likely, there are other ways to do this, and therefore the above should not be regarded as an attempt to formulate a compelling theory for physical aging. One may
regard the Narayanaswamy expression Eq. (2) as the simplest description of aging consistent with time-temperature superposition (TTS). Indeed, TTS motivates the geometric ansatz for equilibrium time-autocorrelation functions Eq. (5), which is a central ingredient in the proposed formalism.

The above ideas are geometric, but they refer to the multidimensional configuration space, not to ordinary 3d space. The main assumption is that during aging the system’s path \( R(t) \) is very similar to that of an equilibrium system, the only substantial difference being that the rate of motion changes significantly during aging. In particular, our material-time definition presupposes the unique-triangles property. This configuration-space geometric assumption is the present paper’s version of the well-established triangular identity [32, 36].

In the Introduction we listed four questions relating to the Narayanaswamy formalism. The above developments address the first three of these. Thus we have shown how, by use of the Bochkov-Kuzovlev exact nonlinear fluctuation-dissipation theorem, the highly nonlinear aging phenomenon may be reduced to a linear material-time convolution integral. In the process, the material time was identified as the distance to a reference configuration far away. The third question, whether all quantities age following the same material time, is implicitly answered with a yes since the material-time definition of Eq. (9) is unique.

A most important remaining question is: what controls the material time? The traditional answer to this is: the fictive temperature \( T_f \) [4, 37], which by definition quantifies the structure in such a way that in \( T_f = T \) in equilibrium.

The fictive temperature concept is hand waving, however, and it would be nice to have a microscopic understanding of what controls the material time’s clock rate \( \gamma(t) \) of Eq. (1) [1, 24, 57].

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