

Long-time structural relaxation of glass-forming liquids: Simple or stretched exponential?

Cite as: J. Chem. Phys. 152, 041103 (2020); doi: 10.1063/1.5142189

Submitted: 10 December 2019 • Accepted: 8 January 2020 •

Published Online: 27 January 2020



View Online



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Kristine Niss,^{a)}  Jeppe C. Dyre,  and Tina Hecksher 

AFFILIATIONS

Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark

^{a)} Author to whom correspondence should be addressed: kniss@ruc.dk

ABSTRACT

This paper presents data for the physical aging of the density of squalane upon both non-linear and nearly linear temperature jumps from states of thermal equilibrium. Invoking the single-parameter-aging scenario [Hecksher *et al.*, J. Chem. Phys. **142**, 241103 (2015); Proc. Natl. Acad. Sci. U. S. A. **116**, 16736–16741 (2019)], the linear-response aging relaxation function is extracted from the data. Based on this, it is shown that the relaxation toward equilibrium follows a simple exponential function at long times; a stretched-exponential function provides a poor fit. This demonstrates the existence of a terminal relaxation rate for the physical aging of squalane, corresponding to an effective long-time cutoff in the spectrum of structural relaxation times.

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In condensed matter, relaxation toward equilibrium is often described by the stretched-exponential function of time t defined^{1–4} by

$$R(t) = e^{-(t/\tau)^\beta}. \quad (1)$$

Here, $R(t)$ is a relaxation function normalized to go from unity at $t = 0$ to zero at long times, τ is a characteristic time, and $0 < \beta < 1$ is the so-called stretching exponent. In many cases, this function provides an excellent single-shape-parameter fit to data, involving both linear and non-linear responses to a step perturbation.^{1–5} The mathematical function [Eq. (1)] is occasionally used in the “compressed” version with $\beta > 1$, for instance, in connection with the description of ballistic particles in soft colloids.⁶ We limit the discussion below to the standard stretched-exponential function with $\beta < 1$, though, which is by far the most common case.

In the context of viscous liquids and the glass transition, the stretched-exponential function has been, for years, the standard function used to describe data because it usually provides a better fit than other single-shape-parameter functions. For instance, in the last 30 years, numerous papers have reported dielectric spectra for glass-forming liquids fitted to the Laplace transform of the stretched exponential. The Laplace transform of the stretched exponential displays the characteristic asymmetric loss peak with

an approximate power-law decay above the loss-peak frequency but a Debye-like, i.e., asymptotic slope unity (in a log-log plot) increase in the loss below the loss-peak frequency.^{2,7,8} A Debye-like low-frequency behavior corresponds to a fairly sharp cutoff in the relaxation-time spectrum at long times; indeed, if Eq. (1) is written as a sum of exponentials, there is a rapid decay of the relaxation-time distribution at long times.⁹ This is the region in focus below where we address the following question: Does the relaxation-time distribution decay continuously to zero at long times or is there an effective cutoff at a “terminal” (longest) relaxation time? The latter situation yields exponential relaxation at long times. From a pragmatic, experimental point of view, it can be hard to distinguish between relaxations described by a stretched exponential and those described by a sum of exponentials with a cutoff at long relaxation times.^{10–13} This distinction is conceptually important, however, because many theories for glass-forming liquids predict a stretched-exponential relaxation function with focus on this function’s long-time behavior.² Classical examples include the mode-coupling theory,^{14,15} models based on many-body interactions,¹⁶ trapping models and models based on defect motion,^{2,17,18} and models involving a random walk on a hypercubic percolative network.^{19,20}

For any relaxation function $R(t)$, the Kovacs–McKenna (KM) relaxation rate $\Gamma(t)$ is defined^{10,21} by

$$\Gamma(t) = -\frac{d \ln R(t)}{dt} = -\frac{1}{R} \frac{dR}{dt}. \quad (2)$$

Note that the relaxation function does not have to be normalized for calculating $\Gamma(t)$. Substituting Eq. (1) into Eq. (2) leads to

$$\Gamma(t) = \beta \left(\frac{t}{\tau} \right)^{\beta-1} \frac{1}{\tau}. \quad (3)$$

The stretched-exponential function has a time-scale-invariant KM relaxation rate, i.e., one that decreases from infinity at $t = 0$ to zero at $t = \infty$ according to an inverse power law in time. This characteristic feature has been suggested by Ngai to give the physical justification of the stretched-exponential relaxation function.⁵ The special case $\beta = 1$ corresponds to a simple exponential relaxation function; in fact, this is the only function for which the KM relaxation rate is constant ($\Gamma = 1/\tau$).

Both the stretched-exponential function and the KM relaxation rate are concepts often encountered in the field of physical aging of glasses.^{10,22–28} Here, the temperature is perturbed while the quantity monitored as the response may be any material property that can be measured fast enough that the sample does not relax appreciably during the acquisition time.

This paper presents such physical aging data for the density of supercooled squalane following small temperature jumps from states of thermal equilibrium. Squalane has previously been studied with mechanical and dielectric spectroscopy^{29–32} and is a well-characterized sample known to be a good glass-former. The purpose of the present study is to investigate to which extent data are

well described by the stretched-exponential relaxation function in the long-time limit for which $\Gamma(t)$ goes to zero for this function [compare Eq. (3)].

Studying the long-time limit is experimentally challenging because it requires both accurate temperature control and accurate measurements of the quantity that ages. The first issue is addressed by the use of a Peltier element that keeps the temperature constant within 100 μK ; our setup has the additional advantage of establishing uniform temperature throughout the sample within a few seconds.^{33,34} The second challenge is addressed by measuring the real part of the dielectric loss at 10 kHz using an Andeen-Hagerling high-precision capacitance bridge. Details regarding the setup have been described elsewhere.^{33,34,36} Squalane has a very small dielectric loss and, for this reason, the real part of the high-frequency capacitance is a linear function of sample density.^{35–37} This means that the experiment monitors density changes following a temperature jump. This feature is not crucial, however, for the arguments given below in which we use capacitance simply as a quantity that can be measured fast and accurately.

Figure 1(a) shows the applied temperature protocol. The colored temperature jumps (all of which go to the same temperature, 167.73 K) were selected for further analysis. The smallest temperature jumps are of magnitude 0.12 K. This is small enough to result in a virtually linear response, i.e., a relaxation function that is independent of sign and size of the temperature jump. Figure 1(b) shows the measured real part of the capacitance at 10 kHz. The capacitance varies by less than 0.4% throughout the experiment. After each temperature step, before jumping to a new temperature, we

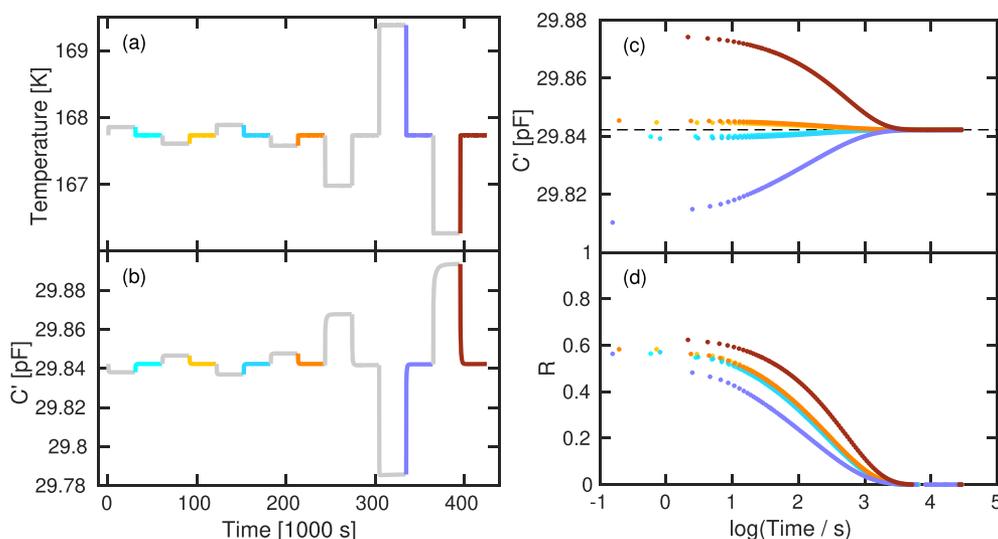


FIG. 1. (a) Temperature protocol applied for monitoring small density changes of squalane. The largest temperature jumps are 1.65 K and the smallest are 0.12 K. The colored temperature jumps are used in the subsequent data analysis; they all go to the temperature 167.73 K. (b) Real part of the capacitance at 10 kHz. This quantity is proportional to the density for small density changes.^{35–37} (c) The data of (b) plotted as a function of the logarithm of the time since each jump was initiated. The data have been corrected for a minor drift linear in time, as described in the text. The horizontal black dashed line marks the equilibrium capacitance at 167.73 K. (d) Normalized relaxation functions $R(t)$ calculated from the data in (c) using the difference between the equilibrium value before and after the jump as the normalization factor. The curves do not start at one in this plot because there is a sizable density change at times shorter than those monitored. The small jumps nearly collapse in this normalized plot, demonstrating that these are small enough to be almost linear.

annealed for enough time that the system was equilibrated within the experimental resolution. The data have been corrected for a minor drift arising from a very slow flow in the sample cell. The drift is a geometric effect due to the sample cell diameter being much larger than the sample gap, which hinders the contraction of the liquid when the viscosity becomes high. The temperature dependence of the flow time follows the structural relaxation time, but the flow time is several orders of magnitude larger. The drift is a small but unavoidable effect when temperature is changed repeatedly, and with our resolution, it is necessary to correct for. It is complicated to account for the drift in detail; since it is a minor effect, we did a simple linear correction as also described in Ref. 36. For the first series of small (linear) jumps, we used a correction of 2.5×10^{-21} F/s, while for the larger jumps, the correction was 5.2×10^{-21} F/s. We speculate that the reason for the larger correction in the latter case is the fact that the sample was heated to a state with a significantly smaller relaxation time, thus speeding up the drift.

For each temperature jump, Fig. 1(c) shows the measured capacitance as a function of the time that has passed after the jump was initiated. This figure shows more clearly the asymmetry already visible in Fig. 1(b) between temperature up jumps (red) and down jumps (purple), with down jumps resulting in a faster and more “stretched” approach to equilibrium than up jumps. This asymmetry, which illustrates that even a temperature jump of magnitude less than 1% may result in a highly nonlinear response, is even more evident from Fig. 1(d), which shows the relaxation functions normalized to unity at $t = 0$, $R(t)$, calculated from the data in Fig. 1(c). In this plot, the small temperature jumps almost collapse, showing that these jumps are small enough that the response is nearly linear.

Figure 2(a) is a classical Kovacs plot¹⁰ showing the KM relaxation rate Γ as a function of the variation of the capacitance relative to its equilibrium value at 167.73 K denoted by $\delta C/C$. As equilibrium is approached, $\delta C \rightarrow 0$. In this limit, all curves converge to the same KM relaxation rate, marked by the horizontal dashed line. The

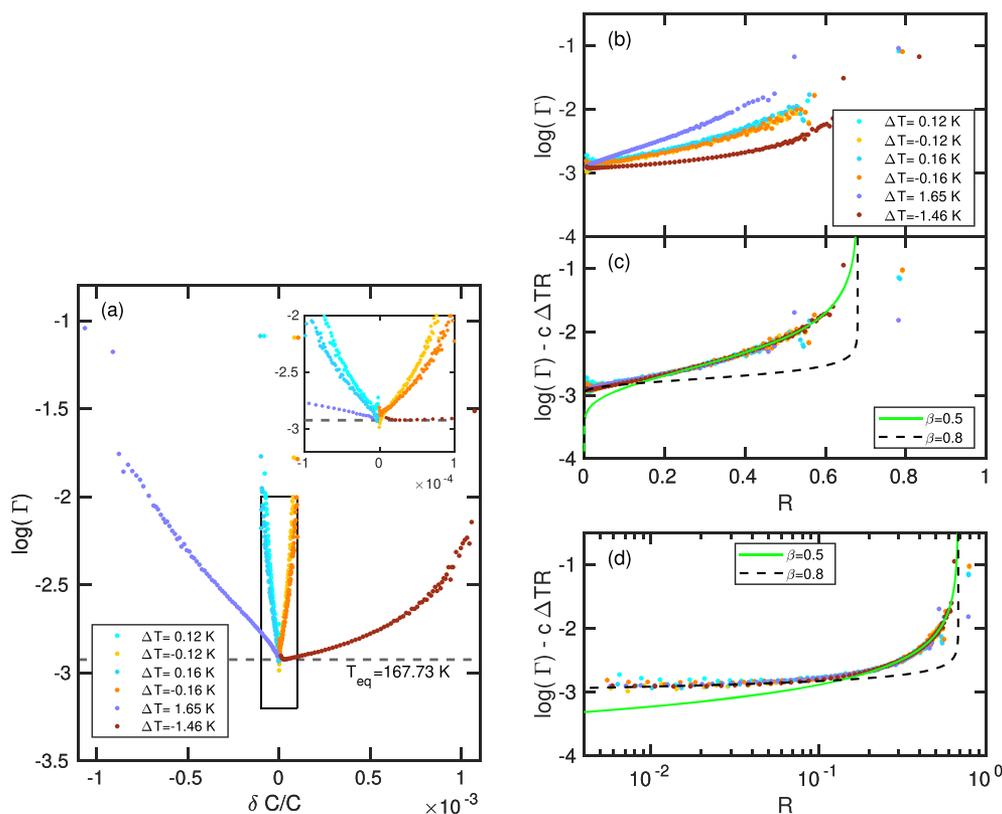


FIG. 2. (a) Logarithm of the Kovacs–McKenna (KM) relaxation rate Γ defined in Eq. (2) plotted as a function of the relative deviation of the capacitance from its equilibrium limit denoted by $\delta C/C$. The long-time limit corresponds to the middle part of the figure at which $\delta C/C = 0$. For all jumps, the KM relaxation rates converge to the same number (horizontal dashed line). The inset magnifies the long-time behavior. (b) Logarithm of Γ vs the normalized relaxation function R . The long-time limit corresponds to $R \rightarrow 0$. (c) Logarithm of the KM relaxation rate after being linearized as described in the text plotted vs R . All data superpose. This demonstrates that the physical aging of squalane density is described by the single-parameter-aging scenario.^{40,41} The full green and black dashed curves are stretched-exponential functions with β equal to 0.5 and 0.8, respectively. These functions represent the relaxing part of $R(t)$ [Eq. (5)], i.e., the relaxation taking place after the “instantaneous” jump that cannot be time resolved in the setup used. The green curve was optimized to fit the short-time data, and the black dashed curve was fitted to the long-time data. (d) Same as in (c) plotted vs the logarithm of R allowing for a focus on the long-time behavior.

inset magnifies the data close to equilibrium, focusing on the long-time behavior. Note that even very close to equilibrium, where $\delta C/C$ is just 0.1 per mille from its equilibrium value, there is an order of magnitude difference in the KM relaxation rate between the larger (non-linear) jumps and the small jumps; even the small nearly linear jumps do not superpose. The latter is a consequence of the non-exponential nature of the relaxation, while the former results both from the non-linearity and the non-exponentiality of the relaxation. If one did not have access to accurate long-time data, an extrapolation of the KM relaxation rate curves would appear to show the existence of a so-called expansion gap.¹⁰ This point has been discussed in detail by Simon and collaborators, concluding that there is no genuine expansion gap, merely an apparent one.^{38,39} This is confirmed in Fig. 2(a). Figure 2(b) shows the KM relaxation rate plotted as a function of the normalized relaxation function R ; here, long times correspond to $R \rightarrow 0$. In this plot, the small-jump curves nearly collapse, which reflects that these are close to being linear. The apparent expansion gap is only seen in the non-linear jumps.

We now apply the single-parameter aging scenario.^{40,41} It is assumed that physical aging is linear when described in terms of the so-called material time, even when the curves show strong non-linearities. The material time is the time measured with reference to the system's "internal clock," which becomes gradually slower for a temperature down jump and gradually faster for a temperature up jump. If one has access to the clock rate (relaxation rate) during aging, the material time is its time integral. The single-parameter aging scenario assumes that the quantity monitored during aging and the material-time clock-rate activation energy are both controlled by the same parameter Q ,⁴⁰ which may be thought of as the fictive temperature traditionally used in physical-aging studies,^{22,26,27} although the actual nature of Q is irrelevant. The result is that the KM relaxation rate is a function of R , which is the same for all jumps, times an exponential function of the product of R and the jump magnitude ΔT .⁴¹ Thus, the single-parameter assumption leads to the prediction

$$\Gamma(R) = \psi(R) e^{k\Delta TR}. \quad (4)$$

We here follow the tradition in physical-aging studies of considering jumps going from temperature $T_0 + \Delta T$ to temperature T_0 .

Equation (4) linearizes data in the sense that $\log(\Gamma) - c\Delta TR$ (where $c = k/\ln 10$) is the same function of R for all jumps.⁴¹ This gives the truly linear-response limit of physical aging corresponding to $\Delta T \rightarrow 0$. The small jumps in the present study are nearly linear, and similarly to the procedure applied in Ref. 37, they almost directly provide $\psi(R)$. Figure 2(c) shows that all curves, indeed, collapse when plotted as suggested by Eq. (4) ($c = 0.6 \text{ K}^{-1}$); the collapse gives the linear curve. This demonstrates single-parameter aging for squalane and that the applied procedure identifies the correct linear limit. The advantage of deriving the linearized data from larger temperature jumps in this way is that the signal is higher, and thus, the long-time behavior is resolved better.

It is now possible to investigate more closely the shape of the linear-response limit of the physical-aging relaxation function, the limit in which the material time is proportional to the actual time. Figure 2(c) shows the predictions of two different stretched-exponential functions for the relaxing part of the linear-response aging function, i.e., for the following ansatz:

$$R(t) = R_0 e^{-(t/\tau)^\beta}. \quad (5)$$

We here allow for an "instantaneous" change of $R(t)$ right after the temperature jump, reflected in $R_0 < 1$.⁴¹ The green curve in Fig. 2(c) is a $\beta = 0.5$ stretched-exponential function fitted to the short-time data with τ and R_0 as free parameters, and the black dashed curve is a $\beta = 0.8$ stretched exponential fit focusing on fitting the long-time data. Neither function fits well. The reason is that if the variation of Γ with R is to be fitted well, β cannot be close to unity. On the other hand, if β is not close to unity, the predicted long-time KM relaxation rate bends over and goes visibly to zero within the experimental window [recall that a stretched exponential predicts $\Gamma \rightarrow 0$ as $t \rightarrow \infty$, compare Eq. (3)]. Figure 2(d) is the same as Fig. 2(c) but with a logarithmic R axis, highlighting the long-time behavior. To be clear, the above data analysis is based on the Narayanaswamy aging formalism, and the conclusion relates to the nature of the kernel of the material-time convolution integral, i.e., it is the linear [or linearized through Eq. (4)] relaxation function that is shown to deviate from a stretched-exponential behavior at long times.

Data can be fitted by several different functions, but usually these would involve more than a single dimensionless shape parameter. An obvious question is whether a better function exists for fitting data, still involving just one shape parameter. Figure 3 compares the linearized aging data to the prediction of the product of a single exponential and a stretched exponential with $\beta = 0.5$, the "exponential \sqrt{t} relaxation function" introduced in Ref. 34,

$$R(t) = R_0 e^{-(t/\tau) - \alpha\sqrt{t}/\tau}. \quad (6)$$

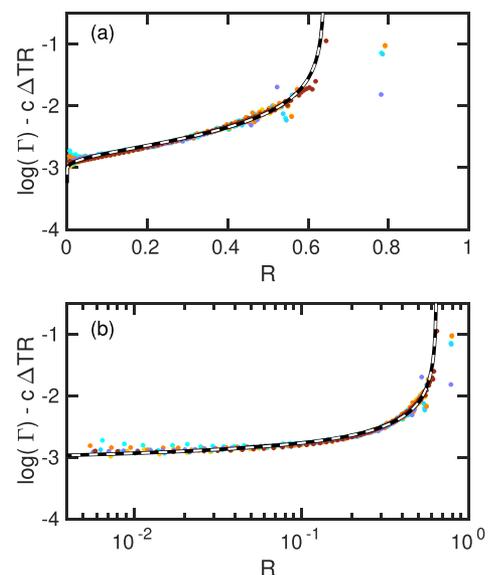


FIG. 3. (a) The data of Fig. 2(c) fitted to the exponential \sqrt{t} relaxation function of Eq. (6) with $\tau = 1800 \text{ s}$, $\alpha = 2.5$, and $R_0 = 0.64$. (b) shows the same data with a logarithmic R axis. The long-time limit of $\log(\Gamma)$ of the fit is $\log(1/1800) = -3.25$, which is seen in (a) but not in (b) because this limit is reached many decades below the scale of the logarithmic R axis.

The fit is significantly better than that of a stretched exponential. There is a small discrepancy between the fit and data at R values below a few percent. These data points are sensitive to the exact subtraction of drift discussed above; thus, the discrepancy may be due to a small systematic error in the data. The exponential \sqrt{t} relaxation function because the former has a terminal relaxation rate. Incidentally, the Laplace transform of Eq. (6) has the same asymptotic characteristics as the alpha relaxation part of the analytical function introduced in Ref. 32, which fits well with the dynamic shear modulus of squalane.

In summary, high-precision data demonstrate the existence of a terminal relaxation rate in squalane for the physical aging of density, implying that the long-time approach to equilibrium follows a simple exponential in time. While aging data for many years have been fitted by relaxation functions with more than a single shape parameter and a long-time cutoff,^{11,12} to the best of our knowledge, the data presented here provide the first direct experimental proof that long-time aging data cannot be fitted by a stretched exponential. The reason is that the stretched-exponential function does not have a terminal relaxation rate, i.e., a long-time cutoff in the relaxation time distribution. Mechanisms for such a cutoff have been discussed, e.g., in Refs. 42 and 43. More generally, one may speculate that the largest barriers for molecular motion are effectively cut off when the structure of a highly viscous liquid relaxes and, as a consequence, lowers these barriers. We conjecture that the existence of a terminal relaxation rate is a general feature of glass-forming liquids, which any reliable theory of viscous liquid dynamics must account for.^{34,42–47}

This work was supported by the VILLUM Foundation's *Matter* (Grant No. 16515). The authors thank Niels Boye Olsen for helpful comments on the manuscript.

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