

Single parameter aging and density scaling

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ABSTRACT

In a recent paper, Di Lisio *et al.* [J. Chem. Phys. 159, 064505 (2023)] analyzed a series of temperature down-jumps using the single-parameter aging (SPA) ansatz combined with a specific assumption about density scaling in the out-of-equilibrium system and did not find a good prediction for the largest down-jumps. In this paper, we show that SPA in its original form does work for all their data, including large jumps of $\Delta T > 20$ K. Furthermore, we discuss different approaches to the extension of the density scaling concept to out-of-equilibrium systems.

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I. INTRODUCTION

Physical aging is the gradual change in the physical properties of glass over time, typically at temperatures around or just below its glass transition temperature, T_g . These changes in properties over time happen because the glass is out of equilibrium and spontaneously and irreversibly evolves toward the equilibrium state.

Physical aging of glasses is an old topic dating back to at least Tool and Eichlin in 1931¹ rationalizing cooling and heating curves for oxide glasses. Nevertheless, the topic is far from understood, and research in the area is active to this day, with important new work and methods appearing in the last couple of years.^{2–20}

Experimental protocols for studying physical aging typically involve either temperature ramps or temperature jumps. The aging response to a given temperature input can be monitored by any experimental observable that can be acquired fast enough that the glass does not significantly change its properties during the measurement. Traditionally, quantities such as refractive index,^{21,22} volume,^{23–25} enthalpy,^{26,27} mechanical creep, or modulus^{28–30} have been used to quantify the out-of-equilibrium state of an aging glass. More recently, gas permeability,³¹ dielectric susceptibility,^{3,32–34} and dynamic light scattering¹⁹ have been added to the list.

Physical aging has obvious implications for the performance and properties of glassy materials used in applications, such as precision molding,^{35–38} oxide glasses used for optical fibers³⁹ and displays,⁴⁰ plastics,⁴¹ polymers used for membranes,^{31,42} bioactive glasses,⁴³ etc., but aging also poses interesting questions for fundamental research. An intrinsic feature of aging is that it is non-linear,

and a central fundamental question is whether this non-linear out-of-equilibrium relaxation is governed by the same slow degrees of freedom that are responsible for the linear structural relaxation in the equilibrium state. This has been the prevailing conception,^{27,44–48} but it is possible that the physical aging mechanism could be governed by other processes. In particular, there are indications that for large up-jumps, aging proceeds in a heterogeneous way, resembling nucleation and growth rather than a gradual homogeneous softening.^{7,8,13} Furthermore, there is evidence that for large down-jumps, a faster aging mechanism sets in at short aging times,^{2,49,50} while the long time aging (i.e., close to equilibrium) remains dominated by the slow structural relaxation.⁵¹

Altogether, these results suggest that other mechanisms could be playing a role in aging, at least far from equilibrium. However, the classical models that connect aging directly to equilibrium linear relaxation are still widely used in applied glass-science, e.g., Refs. 31, 35–38, and 41. Moreover, we and our colleagues have recently demonstrated with direct tests that this view can be confirmed experimentally³ and in simulations⁵²—at least for small temperature jumps.

If (or when) the structural relaxation governs physical aging, then the out-of-equilibrium situation must be strongly connected to the properties that govern the equilibrium structural relaxation. In general, there is no consensus as to what controls the structural relaxation time, but it has been established that many organic systems obey so-called density scaling.^{53–56} This means that the relaxation rate depends on a scaling parameter Γ , which in most cases is given by $\Gamma = \rho^v/T$. For the systems where density scaling applies in equilibrium, it is natural to attempt to generalize the

concept to out of equilibrium. One of us has earlier suggested how to do this,^{57,58} and recently Di Lisio *et al.*⁹ suggested an alternative generalization.

Single parameter aging (SPA)⁵⁹ is a framework for describing and predicting aging within the class of models that directly connect aging to equilibrium relaxation. Di Lisio *et al.*⁹ analyzed a series of temperature down-jumps using the SPA ansatz combined with assuming that density scaling as found in equilibrium for some systems generalizes directly to the out-of-equilibrium system. They conclude that SPA does not provide a good description for the largest down-jumps and use this result to argue that aging in those cases must proceed via a different—faster—mechanism than the alpha relaxation. In this paper, we show that SPA in its original form does work for all their data and argue that the reason for their finding could well be that their extension of the density scaling concept to out-of-equilibrium systems is not valid.

This paper is structured as follows: Sec. II gives a short introduction to the concepts of material time and single parameter aging (SPA). Section III focuses on a comparison of simple linear SPA analysis and the version of SPA suggested by Di Lisio *et al.*⁹ applied to their temperature jump data. Section IV compares the density scaling for out-of-equilibrium systems suggested by Di Lisio *et al.* with the expansion of density scaling proposed by Niss.^{58,60} Our main points and results are summarized and discussed in Sec. V.

II. MATERIAL TIME AND SINGLE PARAMETER AGING

Aging is, as mentioned, a non-linear phenomenon in the sense that the response to a temperature step input depends on both the magnitude and the sign of the jump. A temperature up- and down-jump of the same magnitude to the same target temperature will thus differ in shape: the down-jump will be stretched, while the up-jump is more compressed. This is called the asymmetry of approach^{44,61} and can be readily understood as a consequence of the change in relaxation time from the initial state to the final state of the sample. In the up-jump, the material comes from a state of long relaxation time and adjusts gradually to a shorter relaxation time—the dynamics in the material is “auto-accelerated.” The opposite is true for the down-jump, where the dynamics of the material gradually becomes slower—it is “auto-retarded.”^{62,63}

The Narayanaswamy model⁴⁵ proposes that linearity of aging is restored when measured with respect to the “internal clock” of the material, the so-called material time ξ , meaning that the evolution of a measured property X as a function of a temperature input $T(t)$ can be obtained by a linear convolution integral in the material time,

$$X(\xi) - X_{\text{eq}}(T) = -\alpha_X \int_{-\infty}^{\xi} M(\xi - \xi') \dot{T} d\xi, \quad (1)$$

where \dot{T} is the (material) time derivative of temperature, α_X is the thermal coefficient of the measured property (assumed to be constant), and M is the memory kernel. In his model, material time is related to the laboratory time through the instantaneous out-of-equilibrium relaxation time $\tau(t)$,

$$d\xi = \frac{dt}{\tau(t)}. \quad (2)$$

In equilibrium, τ is the structural relaxation time given by the temperature and does not vary as a function of time. Out of equilibrium, it is assumed that one extra parameter, the fictive temperature T_f , is sufficient to describe the state of the system. This approach is often referred to as the Tool–Narayanaswamy–Moynihan (TNM) formalism.^{44,45,64}

In general, making predictions with the TNM formalism thus requires analytical expressions for the memory kernel, M , and for the out-of-equilibrium relaxation time, $\tau(T, T_f)$. Traditionally, non-exponential fitting functions have been proposed (such as the stretched exponential) for M and various empirical expressions for the out-of-equilibrium relaxation time, the most used being Moynihan's.⁶⁴ However, even *in equilibrium*, we do not know the exact shape of M or how τ behaves as a function of temperature (in fact, these are the two big questions in glass science), so this introduces as a minimum four different fitting parameters depending on the choice of fitting functions.

Single parameter aging (SPA)⁵⁹ is a strategy to avoid fitting functions in the description of temperature jump experiments, but in its essence, it is not different from the TNM formalism. The fundamental idea of SPA is that all properties of the aging material are governed by a single non-equilibrium parameter. It follows that there is a one-to-one connection between any two aging properties, including the instantaneous relaxation time itself and some measured property, X . The simplest assumption for this relation is linearity, i.e., that the logarithm of the out-of-equilibrium relaxation time and the measured property are linearly connected: $\ln \tau(t) - \ln \tau_{\text{eq}} = a(X(t) - X_{\text{eq}}) = a\Delta X(t)$. Assuming furthermore that the total change in the measured property is linear with changes in temperature, $\Delta X(0) = b\Delta T$, i.e., the difference between the equilibrium value at the initial temperature before the jump and the equilibrium value at the new temperature, leads to the following expression for the out-of-equilibrium relaxation time:

$$\ln \tau(t) = \ln \tau_{\text{eq}} + g(R), \quad (3)$$

with

$$g(R) = c\Delta TR(t), \quad (4)$$

where $c = ab$ and $R(t) = \frac{\Delta X(t)}{\Delta X(0)}$ is the normalized relaxation function. Thus, the out-of-equilibrium relaxation time, $\ln \tau(t)$, is given by the equilibrium relaxation time at the annealing temperature, $\ln \tau_{\text{eq}}$, plus a function of the normalized relaxation, $g(R) = c\Delta TR$.

If TNM formalism applies, the relaxation curves from all jumps collapse when plotted as a function of material time by a transformation of the time axis according to Eq. (2). The transformation can also be reversed such that—if the material time and the out-of-equilibrium relaxation time $\tau(t)$ corresponding to a given temperature jump are known—we can obtain the laboratory time corresponding to that jump. In this sense, one can think of R as the independent variable and time as the dependent variable. This is true for any temperature jump, and consequently, we can transform the time axis from one non-linear jump to another. In condensed form, the above can be written as

$$\frac{dt_1(R)}{\tau_1} = d\xi(R) = \frac{dt_2(R)}{\tau_2} \Rightarrow dt_2(R) = \frac{\tau_2}{\tau_1} dt_1(R), \quad (5)$$

where the subscripts 1 and 2 refer to the two different temperature jumps, 1 and 2.

SPA gives a relation between the out-of-equilibrium relaxation time and the measured quantity [Eq. (3)], which inserted in Eq. (5) leads to the time axis for temperature jump 2,

$$t_2(R) = \frac{\tau_{\text{eq},2}}{\tau_{\text{eq},1}} \int_0^{t_1} \exp\{c(\Delta T_2 - \Delta T_1)R\} dt_1(R). \quad (6)$$

Thus, given c and the equilibrium relaxation times, $\tau_{\text{eq},n}$, SPA provides a recipe for obtaining any temperature-jump relaxation curve from a given measured temperature jump.

The linearity assumptions in the SPA approach reduce the number of fitting parameters to one (c) but are not strictly required for single parameter aging to hold.

III. SPA ANALYSIS OF TEMPERATURE JUMPS

SPA in its simplest form, described above, has been demonstrated to work for small temperature jumps.^{3,59,65,66} For large temperature jumps, neither of the two linearity assumptions necessarily hold, and this simplest formulation of SPA may well break

down and/or other aging mechanisms may set in. Indeed, there are indications that SPA breaks down for larger jumps, in particular larger up-jumps.^{3,65}

Di Lisio *et al.*⁹ measured a series of temperature down-jumps of sizes up to 22.5 K using fast scanning calorimetry for five different organic liquids: phenolphthalein dimethyl ether (PDE), o-cresolphthalein dimethyl ether (KDE), o-terphenyl (OTP), bisphenol-C-dimethylether (BMPC), and 1,1-bis (4-methoxyphenyl)cyclohexane (BMMPC). They used the enthalpy overshoot in heating to extract the fictive temperature, T_f , after different waiting times at the annealing temperature, T_a . In this way, they constructed curves for the temporal evolution of T_f during aging. Subsequently, these curves were analyzed in the SPA framework combined with a density scaling assumption.

It is by no means surprising if SPA did not work for the large temperature down-jumps presented by Di Lisio *et al.* However, applying the SPA in this simplest form, i.e., with linearity assumptions and c as the sole fitting parameter for all curves, we demonstrate below that the SPA does capture all of the measured data, even the largest down-jumps reported by Di Lisio *et al.*

Figures 1(a)–1(e) show the resulting SPA analysis (see the [supplementary material](#) for details of the analysis). For each liquid,

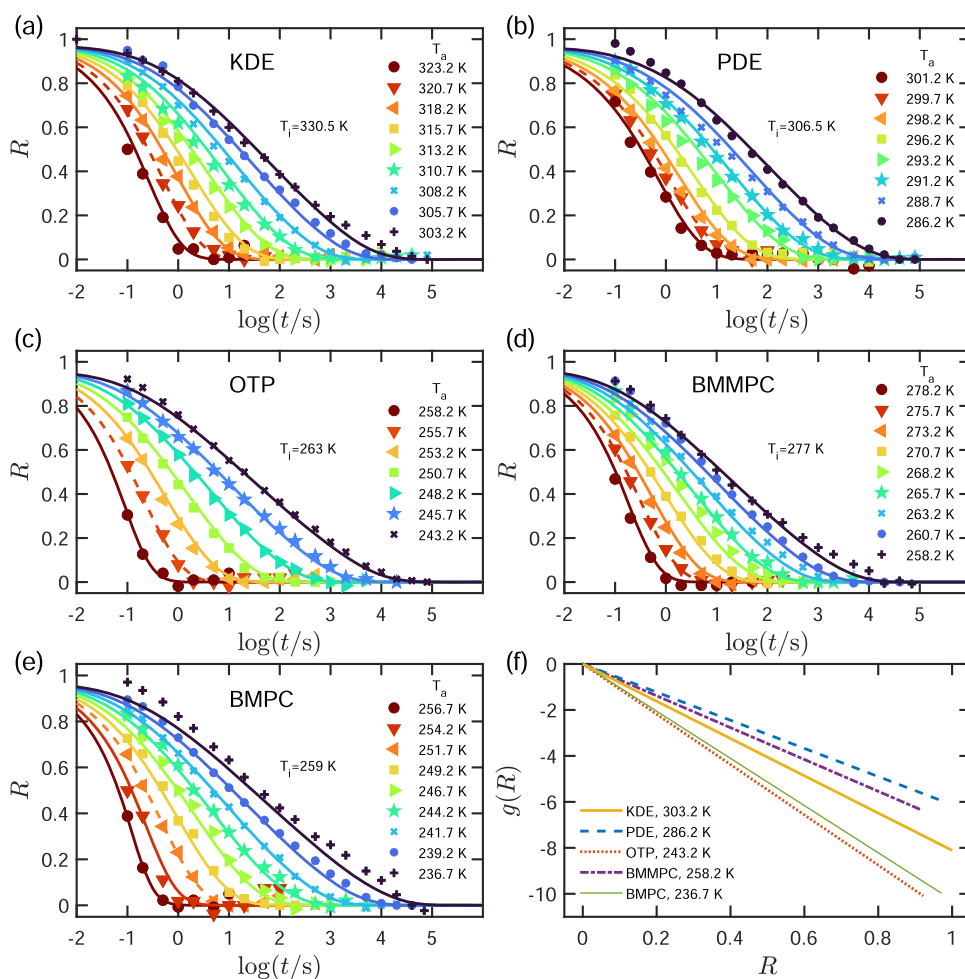


FIG. 1. Simple SPA analysis performed on the data from Di Lisio⁹ for (a) KDE, (b) PDE, (c) OTP, (d) BMMPC, and (e) BMPC. Symbols are the measured data points and full lines are the predicted aging curves. The curves predicted from SPA are based on the dashed line, which is a stretched exponential fit to the same-colored data points (see also the [supplementary material](#)). (f) Simple SPA expression for $g(R) = c\Delta TR$ as a function of R for the largest temperature jump for each of the liquids.

TABLE I. Fitted values for c of Eq. (6).

Liquid	c (K^{-1})
KDE	0.30
PDE	0.30
OTP	0.55
BMMPC	0.37
BMPC	0.46

one jump was selected as the predictor of the rest. Since the data are sparse, we fitted the selected jump with a stretched exponential to serve as an interpolation between data points. The curve fitted to the chosen jump is shown as a dashed line. This curve is then used to generate the other temperature jumps from Eq. (6), and the results are shown as full lines. For all datasets and all temperatures, there is a decent agreement between the predicted curve and the measured data points. The fitted values for c are given in Table I.

There are small deviations from the predictions for the largest temperature jumps for KDE, BMMPC, and BMPC at long times. For BMPC, the predicted curve for the largest temperature jump is consistently below the data points. However, this is a simple scaling

and can be explained by uncertainty in determining the equilibrium relaxation time from the data (see the [supplementary material](#) for more details). Overall, SPA works to a remarkably good degree, even for the largest temperature jumps of $\Delta T > 20$ K, when conducted in its original and simplest form. Figure 1(f) shows $g(R)$ as a function of R for the largest jumps for each liquid. The simple SPA $g(R)$ is linear by definition.

The analysis by Di Lisio *et al.*⁹ is shown in Fig. 2 for comparison. Their predicted model curves deviate significantly from the data, especially for the larger down-jumps. These model curves are based on a SPA analysis similar to Eq. (3); however, using a different expression for $g(R)$,

$$g(R) = \frac{C}{T_f V_0^\gamma} \left(\frac{1}{(1 - \Delta T_f (\alpha_l - \Delta \alpha R(t)))^\gamma} - \frac{1}{(1 - \alpha_l \Delta T_f)^\gamma} \right), \quad (7)$$

where C is a constant and γ is the density scaling exponent (both determined by equilibrium measurements), α_l is the thermal expansivity of the liquid, $\Delta \alpha$ is the difference in thermal expansivity between liquid and glass, and V_0 is the initial specific volume.

Their expression is based on the following three assumptions: (1) volume and fictive temperature relax in the same way so that the instantaneous volume can be calculated as

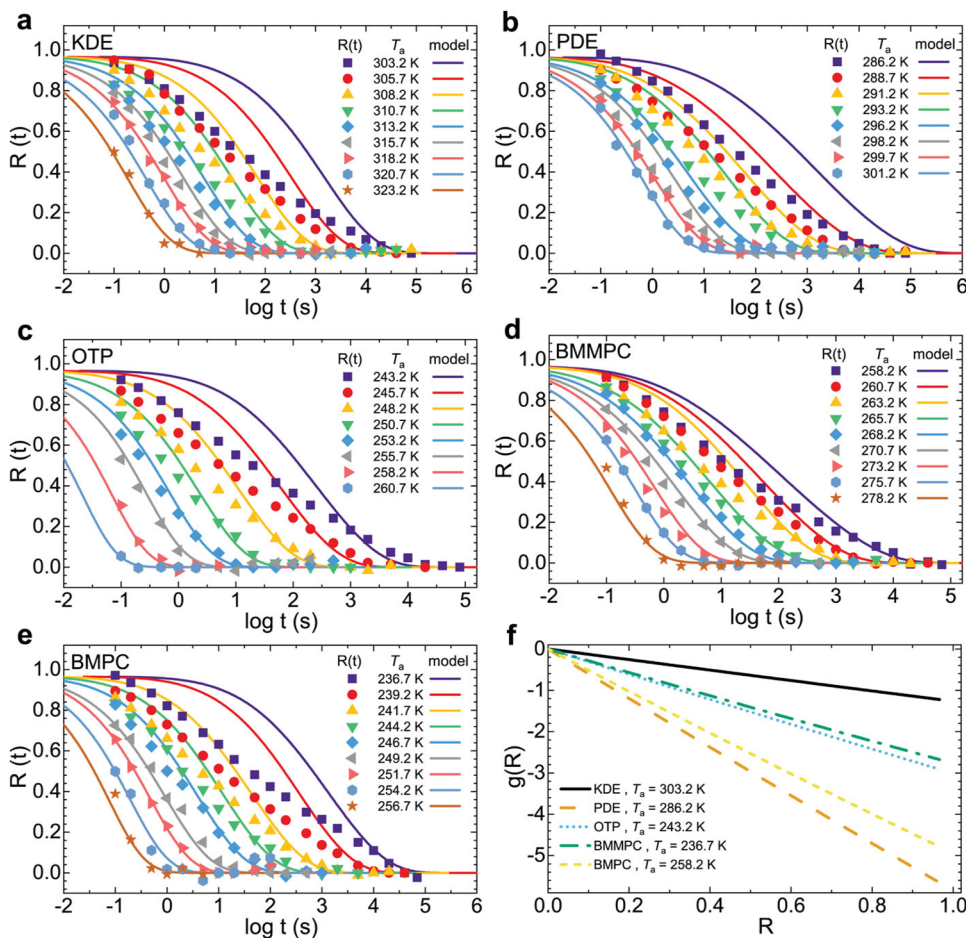


FIG. 2. Data and model curves for the same data as in Fig. 1. The model curves are based on a density scaling assumption for the out-of-equilibrium system. Reproduced with permission from Di Lisio *et al.*, J. Chem. Phys. **159**, 064505 (2023) with the permission of AIP Publishing.

$V(T_a, t) = V_0[1 - \alpha_l(T_f(0) - T_f(t)) - \alpha_g(T_f(t) - T_a)]$, where α_l and α_g are the thermal expansion coefficients of the liquid and the glass; (2) the instantaneous relaxation time is given by a direct use of density scaling for equilibrium to the out-of-equilibrium situation $\tau(T_a, t) = F\left(\frac{C}{T_a V(T_a, t)^{\gamma}}\right)$; and (3) the function F is an exponential.

Figure 2(f) shows that the $g(R)$ from Eq. (7) with the inserted parameters is virtually linear in R in the relevant range despite the complexity of the expression. This means that, effectively, Di Lisio *et al.* have fixed c in the simple SPA analysis (instead of keeping it as a fitting parameter) by introducing a series of assumptions for the out-of-equilibrium relaxation time. Thus, the approach of Di Lisio *et al.* does not directly test SPA because it requires additional assumptions for the out-of-equilibrium relaxation time to hold. The linearity of Di Lisio's $g(R)$ and the fact that another linear $g(R) = c\Delta TR$ (given by the simplest SPA with a single value of c) does accurately capture the aging curves suggest that one (or more) of the assumptions made by Di Lisio *et al.* for the out-of-equilibrium relaxation time is the reason for the failure of their SPA analysis. Below we will discuss their density scaling assumption and compare it to the generalized density scaling suggested in Ref. 58.

IV. COMBINING SINGLE PARAMETER AGING WITH DENSITY SCALING

While the mechanism and functional forms are unknown, the relaxation time in equilibrium is of course given by the equilibrium thermodynamic state of the system. Generally, the state of an equilibrium system is uniquely given by two thermodynamic state variables. It is most common to describe the system by pressure and temperature or density and temperature, but it could just as well be, for example, pressure and density or density and entropy. The point is that there are only two independent state variables and that the relaxation time as well as all other properties of the equilibrium liquid depend on these. However, for an out-of-equilibrium system, this is not the case; at least one parameter has to be added to account for the departure from equilibrium. Single parameter aging refers to a situation where the out-of-equilibrium relaxation time during aging is controlled by two thermodynamic variables plus a single additional parameter.

In the classical TNM-model, the parameter is, as mentioned in Sec. II, the fictive temperature, T_f . The state of the system is then given by T_f and the actual temperature T . In this classical work, it is implicitly understood that the sample is kept under ambient isobaric conditions, which means that, in this case, two state variables plus a parameter describe the system. Another way of describing the out-of-equilibrium state by three parameters is to acknowledge that temperature, density, and pressure are three independent variables, and if single parameter aging holds, then these can be used to fully characterize the system state, as developed in Ref. 66.

In equilibrium, it has been established that many systems obey density scaling, which means that the relaxation depends on a scaling parameter Γ , which is given by $\Gamma = e(\rho)/T$. In many cases, power law density scaling works well, which means that $e(\rho) = \rho^{\nu}$ and $\Gamma = \rho^{\nu}/T$. This means that the relaxation time depends on one thermodynamic state variable rather than two: $\tau_{\text{eq}} = f(\Gamma)$.

The density scaling ansatz by Di Lisio *et al.* is a direct use of power-law density scaling out of equilibrium. Thus they assume that $\Gamma = \rho^{\nu}/T$ controls the aging rate out of equilibrium exactly as it does

in equilibrium. In other words, only one thermodynamic parameter describes the system even when it is out of equilibrium, while there is no out-of-equilibrium parameter. If this ansatz holds, τ cannot age under isochoric isothermic conditions (e.g., after a temperature jump at constant volume), and aging of other properties would be linear. However, it is very well established from computer simulations that τ does change under isochoric conditions^{52,67} and that isochoric aging is nonlinear.^{13,68–70} It is theoretically possible that Di Lisio's ansatz could hold under isobaric conditions, meaning that it should be understood that the rate is governed by $\Gamma = \rho^{\nu}/T$ and the pressure. However, it is a bit counter-intuitive to generalize density scaling to something that only works at ambient pressure. Moreover, the finding of Di Lisio *et al.* that they cannot describe the aging curves with their model, while the original SPA does describe the aging curves, suggests that it may be the density scaling ansatz, which does not hold.

In 2022, one of us proposed another way to generalize density scaling to aging systems.⁵⁸ Here, the idea is that for systems with density scaling in equilibrium, one thermodynamic variable plus an out-of-equilibrium parameter are needed to describe the system during aging. The suggestion is that the relevant thermodynamic variable is Γ defined as in equilibrium and given uniquely by density and temperature ($\Gamma = e(\rho)/T$). The departure from equilibrium is proposed to be described by the parameter Γ_{fic} , which is defined to approach Γ as the system approaches equilibrium.

To get an expression of the relaxation time during aging in this framework, the starting point is the equilibrium density scaling in the original version of Alba-Simionesco, Tarjus, and Kivelson,^{53,54} where Γ is defined as $\Gamma = e(\rho)/T$ with $e(\rho)$ interpreted as an energy scale that only depends on density while the topology of the energy landscape depends on both temperature and density through Γ . This leads to the following expression for the activation energy in equilibrium:

$$\Delta E_{\text{eq}} = e(\rho)F\left(\frac{e(\rho)}{T}\right) = e(\rho)F(\Gamma), \quad (8)$$

and the expression for the relaxation time becomes

$$\tau_{\text{eq}} = \tau_0 \exp\left(\frac{e(\rho)}{T}F\left(\frac{e(\rho)}{T}\right)\right) = \tau_0 \exp(\Gamma F(\Gamma)). \quad (9)$$

When generalizing to the out-of-equilibrium, we assume that the energy scale $e(\rho)$ is controlled by density while the topology of the energy landscape is controlled by the non-equilibrium structural state of the system, described by the parameter Γ_{fic} . This parameter can be expressed as $\Gamma_{\text{fic}} = e(\rho)/T_{\Gamma f}$, where $e(\rho)$ is defined as in equilibrium and $T_{\Gamma f}$ is the Γ_{fic} -temperature (Gamma-fictive temperature), which is conceptually similar to the classical fictive temperature, although it has quite different behavior.⁵⁸

In this framework, the activation energy during aging becomes

$$\Delta E_{\text{aging}} = e(\rho)F(\Gamma_{\text{fic}}), \quad (10)$$

and it follows that the relaxation time during aging should be given by

$$\tau_{\text{aging}} = \tau_0 \exp(\Gamma F(\Gamma_{\text{fic}})), \quad (11)$$

where the functional form of F is the same as in equilibrium.

The ansatz in this framework is that Γ_{fic} , which is connected to the microscopic structure, needs time to change. Right after a temperature jump, it will therefore be equal to the value it had before the jump was performed. Thus, Eq. (11) predicts that the relaxation time is further from equilibrium at short times than predicted by Di Lisio *et al.* In the case of down-jumps in temperature, it means that the curves predicted by Eq. (11) will be more stretched than those predicted by Di Lisio *et al.*—consistent with the data in Fig. 2 being more stretched than the prediction. Hénot *et al.*¹⁶ earlier this year made a similar qualitative comparison and similarly found that Eq. (11) has a better chance of representing their data. Hénot *et al.* consider up-jumps, and in this case Eq. (11) predicts longer relaxation times right after the temperature jump is performed, than predicted by the Di Lisio expression, leading to a more compressed curve.

The downside of the expression in Eq. (11) is that actual quantitative tests are difficult and have not yet been performed. In order to do that, it is necessary to carry out dedicated high pressure aging experiments as proposed in Ref. 58 and preferably to have samples where the functional forms of $F(\Gamma)$ and $e(\rho)$ are known from equilibrium in addition to knowing both density and relaxation time during aging.

V. SUMMARY AND CONCLUDING REMARKS

We have shown that the temperature jump data of Di Lisio *et al.*⁹ can be described fully by the single parameter ansatz with one free fitting parameter for each sample. Di Lisio *et al.* arrived at the opposite conclusion. However, their conclusion is based on the SPA ansatz and assumptions for density scaling in the out-of-equilibrium system. At this point, it is not known if density scaling can be generalized to aging nor how to do it, but we argue that the following logic should apply: In general, two variables determine the equilibrium state of a liquid (for example, density and temperature). During aging, at least one extra parameter is added to account for the departure from equilibrium. In other words, three variables determine the non-equilibrium state if single parameter aging holds (the word *single* refers to the fact that only one parameter describes the departure from equilibrium). For the class of liquids where density scaling holds, one thermodynamic variable determines the relaxation time in equilibrium. As for the general state, a single additional parameter is needed to describe the departure from equilibrium during aging. The generalization of density scaling to aging is thus expected to give an expression where the relaxation time is given by two variables.

We cannot rule out that the assumptions for out-of-equilibrium density scaling of Di Lisio *et al.* are correct and that SPA does not work for large temperature jumps. In fact, the latter is very likely true, in particular for large up-jumps. We make the point that it is not trivial how to generalize density scaling, so when testing both SPA and out-of-equilibrium density scaling *at the same time*, it is not possible to determine which of the two is wrong if the test fails. A generalization of density scaling to the out-of-equilibrium situation is intriguing and possibly a fruitful path; however, more quantitative studies are necessary before we know which generalization scenario is correct.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) contains details on the data treatment behind Fig. 1 and the linear aging curves (i.e., the memory kernels) extracted from this data.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tina Hecksher: Conceptualization (equal); Data curation (lead); Formal analysis (equal); Methodology (equal); Visualization (lead); Writing – original draft (equal); Writing – review & editing (equal).
Kristine Niss: Conceptualization (equal); Formal analysis (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article, as no new data were created or analyzed in this study. Data presented in the paper are from Ref. 9.

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