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ABSTRACT

The description of kinetics of physical aging, namely the slow evolution of a glass thermodynamic state toward equilibrium, generally relies on the exclusive role of the main α relaxation. Here, we study the kinetics of physical aging over a wide temperature range in five small molecules interacting via van der Waals forces monitoring the time evolution of the glass enthalpic state. To this aim, we employ fast scanning calorimetry, which permits exploring a wide range of aging times. To challenge the role of the α relaxation in the description of physical aging, we employ a model-independent approach, based on the time to reach equilibrium, and a modified version of the single parameter aging model. The latter accounts for the non-linearity of aging making use of the so-called density scaling approach to describe the dependence of the α relaxation time on the glass thermodynamic state. We show that the α relaxation is generally adequate to describe aging at temperatures close to the glass transition and, for lower temperatures, the latest stages of equilibration. In contrast, at low aging temperatures, it fails to catch a wide portion of the time-dependent evolution of the glass thermodynamic state, which is found to be much faster than predicted considering only the α relaxation. Hence, our results and analysis provide compelling arguments that the description of glass equilibration under a wide range of aging conditions is conveyed by different molecular mechanisms, beyond the mere role of the α relaxation.

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I. INTRODUCTION

Liquids can be supercooled below their melting temperature, provided that crystallization is avoided. On further cooling and depending on the applied rate of temperature decrease, the supercooled liquid transforms into a non-equilibrium glass, a phenomenon addressed as vitrification or glass transition.¹ The non-equilibrium glass exhibits a solid-like behavior and excess free energy with respect to the metastable supercooled liquid. The time-dependent reduction in the glass free energy toward equilibrium defined by the metastable supercooled liquid is known as physical aging^{2,3} or structural recovery.^{4,5}

The kinetic nature of vitrification and, once in the glassy state, of physical aging implies that both phenomena must be mediated by at least one molecular mechanism. Within the commonly accepted picture, in both vitrification and physical aging, the main α relaxation with super-Arrhenius temperature dependence has been regarded as the only relevant mechanism. Concerning vitrification

kinetics, this has been shown studying the cooling rate dependent glass transition temperature, T_g , and the temperature-dependent α relaxation time, τ_α . It was shown that, in both polymeric^{6–8} and low molecular weight glass formers,^{9,10} the cooling rate dependent glass transition exhibits the same super-Arrhenius temperature dependence as τ_α . Furthermore, several studies where physical aging after non-linear thermal^{11–14} and dielectric¹⁵ perturbations is monitored in a limited range in the proximity of T_g showed that the typical time scale of aging follows the same behavior as τ_α .

The paradigmatic picture addressing the role of the α relaxation has recently been challenged. Experiments where the vitrification kinetics was explored in a wide range of cooling rates for a metallic glass former showed that this takes place at lower temperatures than expected only accounting for the α relaxation.¹⁶ This behavior is exacerbated in polymeric¹⁷ and metallic glass formers¹⁸ subjected to geometrical confinement. Regarding physical aging, there exists increasing evidence that the simple scenario where the approach to equilibrium exclusively depends on the α relaxation must be deeply

revisited. When aged significantly below T_g , polymeric,^{19–21} chalcogenide,²² metallic,^{23,24} and simple molecule^{25,26} glasses exhibit at least two steps in the kinetics of equilibrium recovery. In polymeric glass formers, for which aging experiments at various aging temperatures and times were carried out,¹⁹ while the slow step can be associated with the α relaxation, the fast one exhibits mild temperature independent activation energy, underlying the existence of molecular mechanisms different from the α relaxation triggering physical aging at short aging times.

While the mentioned activity evidences the presence of multiple mechanisms of equilibration, a systematic study, above all in small molecule glasses, has so far remained elusive. The present study aims to provide a comprehensive characterization of physical aging, monitored following isothermal enthalpy relaxation, of five small molecule glasses, interacting via van der Waals forces, and challenges the role of the α relaxation in the kinetics of physical aging. To this aim, on the one hand, we consider a model-independent metric, based on the determination of the aging temperature-dependent time to reach equilibrium. On the other hand, we employ a modified version of the so-called single parameter aging (SPA) model, which has been shown to catch the entire phenomenology of physical aging after temperature jumps of a few Kelvin.^{27–29} To account for the thermodynamic state dependence of the α relaxation time, τ , our approach employs the density scaling relation,³⁰ where both temperature and volume contributions to τ are included. Based on these two complementary approaches, we show that the α relaxation is able to provide a complete description only in a limited temperature range in the proximity of the glass T_g . In contrast, when the aging temperature largely departs from T_g , accounting exclusively for the α relaxation generally fails to describe the kinetics of glass equilibration. The natural consequence of this finding is that mechanisms beyond the α relaxation contribute to glass equilibration significantly below T_g and must be accounted for in both theoretical modeling of aging and lifetime prediction of products made of glass,³¹ where modifications of properties may be detrimental to practical applications.

II. EXPERIMENTAL

o-Cresolphthalein dimethyl ether (KDE $\geq 98\%$ purity), phenolphthalein dimethyl ether (PDE $\geq 98\%$ purity), and 1,1-bis(4-methoxyphenyl)cyclohexane (BMPC $\geq 98\%$ purity) were provided by Polymer Source, while *o*-terphenyl (OTP, $\geq 99\%$ purity) was provided by Sigma-Aldrich. BMPC (also referred to as bisphenol-C-dimethylether) was obtained from the Max Planck Institute for Polymer Research, Mainz, Germany. All materials were used as received.

Fast Scanning Calorimetry (FSC) was performed using a Mettler-Toledo Flash Differential Scanning Calorimeter (DSC) 1 equipped with an intracooler and operating in a temperature range between 173 and 723 K. A Leica M60 optical microscope is integrated in the FSC system, and it is operating at a 400 $\times$ magnification, allowing the evaluation of the quality of the chip and the observation of the deposition of the sample on it. Furthermore, a Leica IC80 HD camera is connected, offering the possibility of acquiring micrographs of the chip. The sample chamber was purged with

dry nitrogen at a flow rate of 20 ml/min. The specimens were prepared by the direct deposition of the material (sample mass ≈ 100 ng) onto a Mettler-Toledo UFS 1 chip. The samples deposited on the chip exhibited an equivalent diameter of ≈ 200 μm , which, given the sample mass of ≈ 100 ng and densities of our materials between 1 and 1.3 g/cm³, resulted in samples' thickness of the order of 10 μm .

Standard Differential Scanning Calorimetry (DSC) was performed by means of a TA Instruments DSC Q2000, equipped with an intracooler and operating in a temperature range between 193 and 873 K. The oven was purged with dry nitrogen at a flow rate of 50 ml/min. Specimens have been prepared by weighing about 10 mg of sample in a 40 μl aluminum pan without lid.

Isothermal aging experiments at different times were performed for all samples, aiming to characterize the vitrification kinetics. The temperature program comprises heating and cooling scans at a rate of 1000 K/s in a temperature range between 173 K and $T_m + 10$ K, depending on the melting temperature of the compound. After cooling from the melt, the samples were kept at T_a for different aging times (t_a), ranging from 0.1 to 80 000 s. After each isotherm, the samples were immediately cooled down to 173 K and a heating scan was recorded. Prior to the evaluation of the time- and temperature-dependent fictive temperature $T_f(T_a, t_a)$ (see Sec. III), the glass and liquid heat flow rates of a given set of experiments were superposed on the unaged reference via the VITRIFAST method, recently introduced by Abate *et al.*,³² an optimization procedure based on the minimization of the mean squared error between aged and unaged scans in the glass and liquid.

For each specimen, the time scale of spontaneous fluctuations associated with the α relaxation was characterized in terms of frequency-dependent complex thermal susceptibility (i.e., the complex specific heat, c_p^*) by means of FSC and DSC step-response analyses.^{33–35} The step-response protocol, spanning the whole range of the glass transition, consists of a loop of down-jumps of $\Delta T = -2$ K at a nominal cooling rate (β), followed by an isotherm of duration t_{iso} . The base angular frequency ω_0 can be determined as

$$\omega_0 = 2\pi/t_p = 2\pi/(t_{\text{iso}} + \Delta T/\beta), \quad (1)$$

where the period of stimulation t_p is the cumulative time of the down-jump and the isotherm. The real (c_p') and imaginary (c_p'') contributions to the complex susceptibility c_p^* , as well as the reversing specific heat (c_p^{rev}), i.e., the modulus of the complex susceptibility, were calculated for ω_0 and higher-order harmonics $\omega = k\omega_0$ ($k = 2, 3, 4, \dots$) by using a Discrete Fast Fourier Transform (DFFT) relationship of the form

$$c_p^*(\omega) = c_p'(\omega) - ic_p''(\omega) = \frac{\sum_{t=0}^{t_p} HF(t) e^{-i\omega t} \Delta t}{\sum_{t=0}^{t_p} q_c(t) e^{-i\omega t} \Delta t}, \quad (2)$$

where $HF(t)$ and $q_c(t)$ are the instantaneous heat flow and the instantaneous cooling rate, respectively. The temperature dependence of $c_p^*(\omega, T)$ has been assessed by running the DFFT algorithm for each loop composing the step-response protocol. Finally, the temperature-dependent relaxation time, $\tau(T) = (2\pi\omega)^{-1}(T)$, has been determined at the inflection point of $c_p^{\text{rev}}(\omega, T)$, that is, the modulus of the complex specific heat, which approximately equals the real part of the complex specific heat, $c_p'(\omega, T)$, due to the fact

TABLE I. Experimental parameters of the step-response protocol.

Technique	β	Isotherm (s)	t_p (s)	ω_0 (rad s ⁻¹)
FSC	2000 K s ⁻¹	0.1014	0.1024	61.3
FSC	500	1.6344	1.6384	3.83
FSC	100	16.364	16.384	0.38
DSC	15 K min ⁻¹	120	128	0.049
DSC	1.875	960	1024	0.006 1
DSC	0.5	7956	8196	0.000 77

that c_p'' is at least one order of magnitude smaller than c_p' . The determination of the time scale of spontaneous fluctuations in a frequency range of about six orders of magnitude is achieved by performing six different step-response experiments for each specimen and combining the measurements of FSC and DSC. Table I reports the experimental parameters of the step-response protocols that have been adequately chosen to probe $c_p^*(\omega, T)$ in the largest frequency range available, while maintaining a good accuracy and low signal-to-noise ratio (Table I).

III. RESULTS

We begin presenting the calorimetric response underlying physical aging at one aging temperature for each investigated system as showcases. Similar results were obtained at the other aging temperatures. Figure 1 shows the heat flow rate scans, proportional to the specific heat, c_p , collected at 1000 K/s on samples cooled down at the same rate to the indicated temperature and aged isothermally in a wide range of times. The typical signature of glass equilibration resulting from physical aging—that is, the development of an endothermic overshoot with magnitude increasing with aging time^{5,36}—can be observed. The temperature interval where the overshoot is located depends on the aging time. Shortly after the beginning of aging, it grows on top of the specific heat step underlying the glass transition. At longer aging times, the endothermic overshoot shifts to higher temperatures, indicating that accessing low energy states delays devitrification when heating the aged samples.

From the connection between specific heat and enthalpy: $c_p = (\frac{\partial H}{\partial T})_p$, the area between the aged and unaged scans contains the amount of enthalpy relaxed during physical aging. The enthalpic state of the glass can be parameterized via the concept of fictive temperature, T_f , that is, the temperature at which the glass line drawn from the glass thermodynamic state crosses the supercooled liquid line.^{36,37} Hence, low T_f (s) are characteristic of low enthalpy glasses. The fictive temperature is obtained via the Moynihan method,³⁸

$$\int_{T_f}^{T_1} (c_{p,l} - c_{p,g}) dT = \int_{T_2}^{T_1} (c_p - c_{p,g}) dT, \quad (3)$$

where c_p is the specific heat of the sample, $c_{p,l}$ and $c_{p,g}$ are the liquid and glassy lines, respectively—fitted by linear equations (see the

dashed lines in Fig. 1)—and T_1 and T_2 are the temperatures well above and below T_g , respectively.

The aging time and temperature evolution of T_f is presented in Fig. 2 for all investigated systems. The T_f of OTP at zero aging time and after cooling at 1000 K/s, $T_f = 263$ K, agrees with previous reports.^{32,39} Data at such a high rate for the other glass formers are not available. However, as expected, the zero aging time T_f of these glass formers is systematically larger than T_g at rates of several K/min.⁴⁰ As a general rule, decreasing the aging temperature entails increasing times to reach equilibrium and lower T_f . In all cases, the values of T_f at the end of the aging process lie in close proximity to the aging temperature, apart from some minor deviations for aging temperatures significantly lower than T_g , likely resulting from the inaccurate extrapolation of $c_{p,l}$ below T_g .⁴¹

The aging time evolution of T_f allows obtaining insights into aging kinetics. A model-independent approach relies on the use of the time to reach equilibrium, τ_{eq} , indicated with open symbols in Fig. 2, which does not depend on the previous thermal history⁴² and is representative of the glass close to equilibrium.¹⁹ Here, τ_{eq} was determined considering that equilibrium was reached when T_f was less ± 1 K different from its average plateau value. Figure 3 depicts the aging temperature dependence of τ_{eq} for all investigated systems. In the same figure, the temperature dependence of the α relaxation time, τ , obtained from the step-response analysis in the linear regime delivering the frequency and temperature dependence of complex specific heat,^{34,35} is presented (see Sec. II for details). As a general feature, τ_{eq} follows the same temperature dependence of τ at large aging temperatures. In all cases, except for PDE, the same applies for lower aging temperatures. For PDE at low aging temperatures, τ_{eq} seemingly exhibits a slight deviation from τ toward a mildly activated temperature dependence.

A. Modeling the kinetics of physical aging

The time to reach equilibrium is representative of the kinetics of physical aging of the glass in the proximity of equilibrium and, therefore, only conveys information on molecular mechanisms active under these conditions. For a comprehensive description of the overall kinetics of physical aging, the entire aging time evolution of the glass thermodynamic state must be described. For this purpose, the unavoidable requirement stands on implementing a framework including the typical signature of physical aging, that is, its non-exponentiality and non-linearity.⁴ The former regards the intrinsic nature of the α relaxation, resulting in a response more stretched than a simple exponential.⁴³ The non-linearity of physical aging is due to the fact that the relaxation time of molecular mechanisms assisting equilibration changes with the glass thermodynamic state. In particular, in aging protocols where a reduction in T_f takes place—as is the case of the present study— τ progressively increases during aging, whereas the opposite holds for experiments entailing a T_f increase.

The non-linearity of aging can be quantified employing the concept of material time, ξ , related to the clock rate, that is, the inverse of the relaxation time, by^{27–29,44}

$$d\xi = \tau^{-1} dt. \quad (4)$$

Within the conventional description of physical aging, the relaxation time is identified with that of the α relaxation. In such

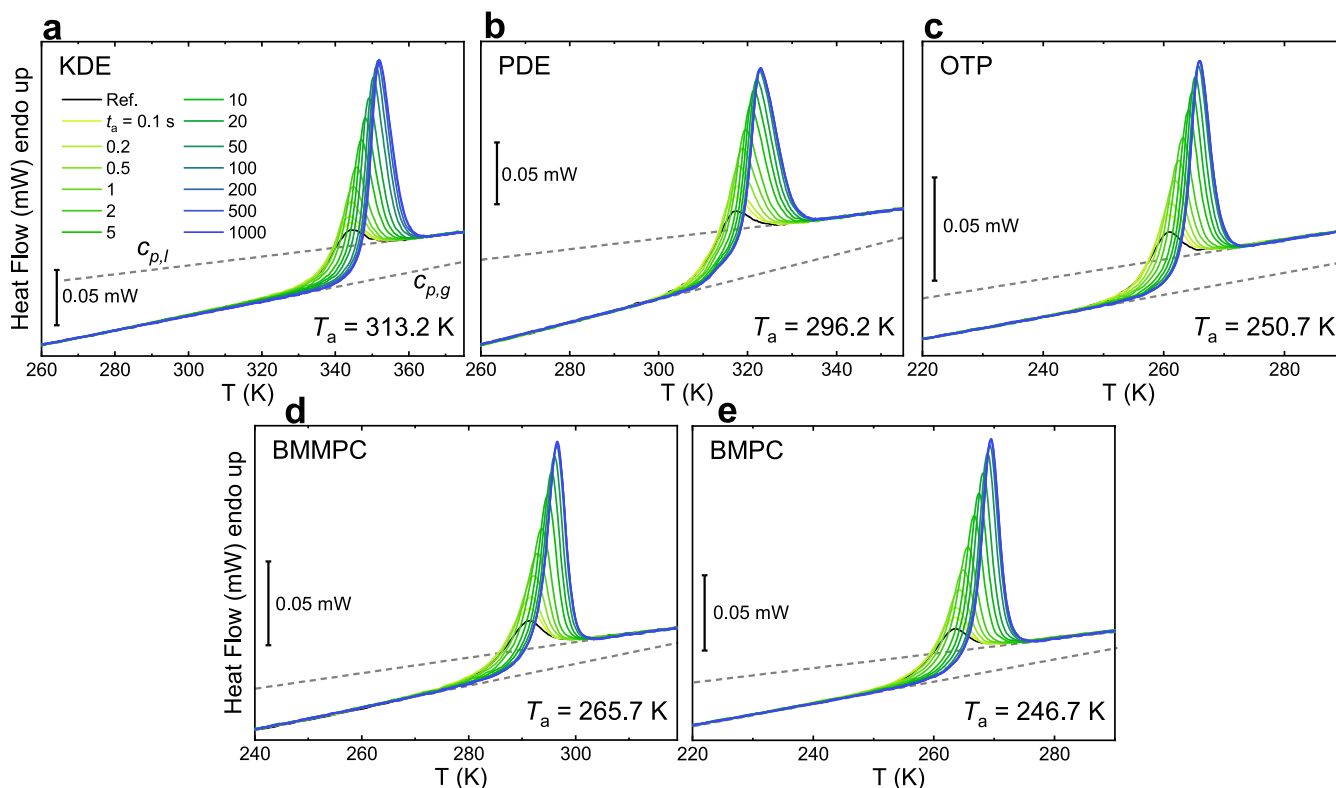


FIG. 1. Heat flow rate scans, proportional to the specific heat, for all glasses at the indicated aging temperatures and times.

a way, the non-linear response of physical aging can be reduced to the linear response at equilibrium by simply replacing the time, t , with the material time, ξ .²⁹ Popular phenomenological approaches, implementing the non-exponential and non-linear behavior of aging, are the Tool–Narayanaswamy–Moynihan (TNM)³⁸ and Kovacs–Aklonis–Hutchinson–Ramos (KAHR)⁴⁵ models, which share the common feature of requiring multi-parameter fitting. Furthermore, both models impose a temperature independent activation energy at equilibrium, which is at odds with the super-Arrhenius temperature dependence of the α relaxation time. Efforts to account for the increasing activation energy with decreasing temperature have recently been implemented.^{46–49}

Here, differently from TNM and KAHR approaches, we describe α relaxation driven aging without making an explicit assumption on the mathematical form of non-linearity. This approach, known as single parameter aging (SPA), has recently been shown to accurately describe aging of several glasses^{27,28} and, for the first time, to predict non-linear aging from linear response.²⁹ Given the relatively small temperature jumps explored in previous applications of SPA, the aging time dependence of $\ln \tau$ was assumed to be linear with the instantaneous thermodynamic state of the glass: $\ln \tau(t) = \ln \tau_\infty + \Lambda(T_f(t) - T_a)$, where Λ is the single fitting parameter and $\ln \tau_\infty$ is the equilibrium relaxation time, attained after aging completion, at the aging temperature, T_a . In this way,

higher order terms of the Taylor expansion are neglected. While this assumption is certainly acceptable for temperature jumps of a few Kelvin, our study entails changes of T_f with the aging time as large as more than 20 K (see Fig. 2), for which the linear assumption may be inadequate.

While keeping the overall philosophy, we implement the SPA model describing the dependence of τ on the aging temperature, T_a , and specific volume, $V(T_a, t)$, of the glass, namely its thermodynamic state, via the so-called density scaling approach,³⁰ which has recently been rationalized on the basis of free volume models.⁵⁰ The underlying idea is in the same spirit as the density scaling approach to non-equilibrium glasses recently proposed by Niss,⁵¹

$$\tau(T_a, t) = \tau_0 \exp \frac{C}{T_a V(T_a, t)^\gamma}, \quad (5)$$

where C and γ are material specific constants.

In Eq. (5), the dependence of both $\tau(T_a, t)$ and $V(T_a, t)$ are shown in Fig. 4 for OTP at equilibrium, just after cooling to T_a and at a given aging time at T_a . In our study, the relaxation time at equilibrium, τ_∞ , is obtained from calorimetric measurements in the linear regime (the same data as shown in Fig. 3). The specific volume at the beginning of aging, $V(0)$, and that at equilibrium, V_{eq} , can be calculated from the equilibrium volume, V_0 , at the initial fictive

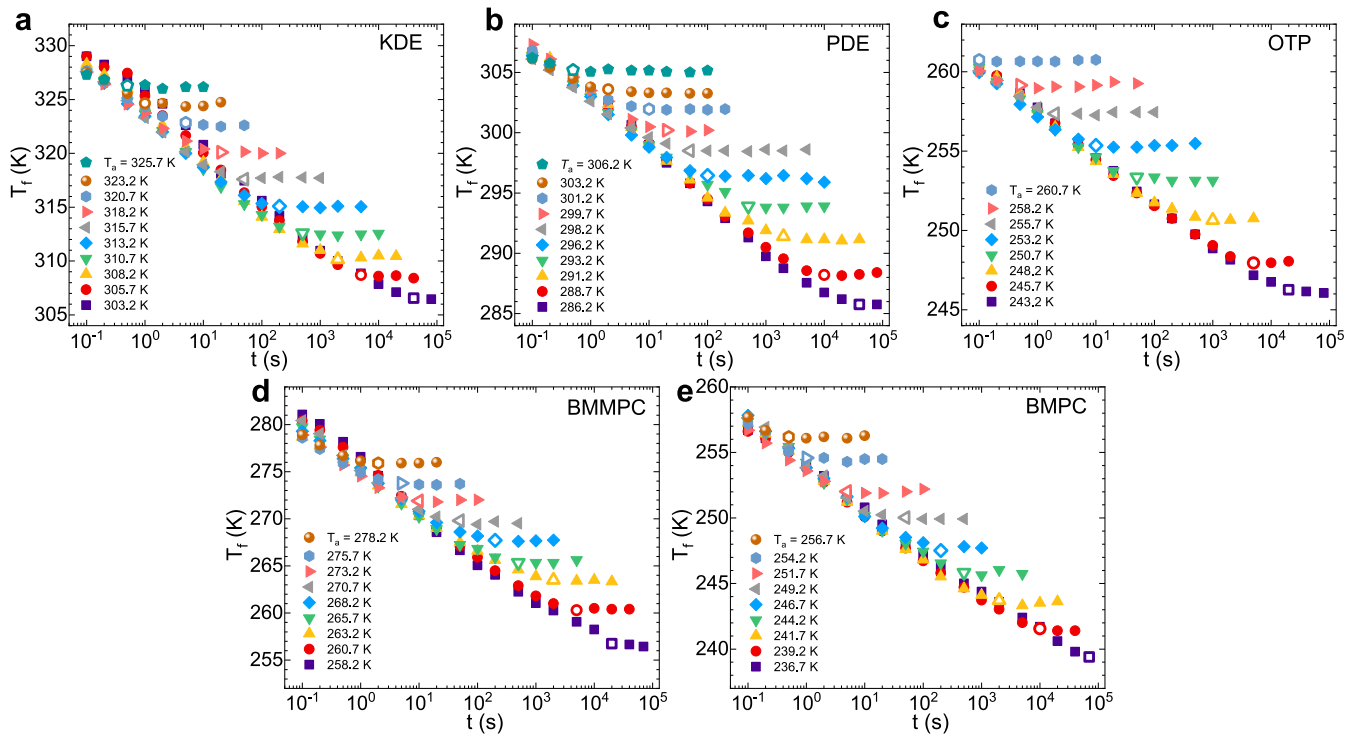


FIG. 2. Aging time evolution of the fictive temperature at different aging temperatures for all investigated glasses. The open symbols indicate the time to reach equilibrium τ_{eq} .

temperature, $T_f(0)$ —in our case, the fictive temperature after cooling at 1000 K/s—by the following equations:

$$V(0) = V_0(1 - \alpha_g(T_f(0) - T_a)) \quad (6)$$

and

$$V_{eq} = V_0(1 - \alpha_l(T_f(0) - T_a)), \quad (7)$$

where α_g and α_l are the coefficients of thermal expansion in the glassy and liquid states, respectively. Here, we have implicitly assumed that T_f from enthalpy relaxation experiments coincides with that of volume relaxation, which was shown to be approximately correct.^{11,42,52,53} In analogy to Eq. (6), as depicted in Fig. 4, the time-dependent volume is connected to the time-dependent fictive temperature by

$$V(t) = V_0(1 - \alpha_l(T_f(0) - T_f(t)) - \alpha_g(T_f(t) - T_a)). \quad (8)$$

Before expressing the instantaneous volume during aging, $V(t)$, as a function of $T_f(t)$, we define the normalized relaxation function, varying between the unity, at the beginning of aging, and zero, once aging is completed,

$$R(t) = \frac{T_f(t) - T_a}{T_f(0) - T_a}. \quad (9)$$

Hence, combining Eqs. (7)–(9), we obtain the following expression, where the aging time dependence is exclusively contained in $R(t)$,

$$V(t) = V_0(1 - \Delta T_f(\alpha_l - \Delta \alpha R(t))), \quad (10)$$

where $\Delta \alpha = \alpha_l - \alpha_g$ and $\Delta T_f = T_f(0) - T_a$.

From the explicit aging time dependence of $V(t)$, the relaxation time at a given aging temperature and time can be written combining Eqs. (5) and (10),

$$\tau(T_a, t) = \tau_0 \exp \frac{C}{T_a(V_0(1 - \Delta T_f(\alpha_l - \Delta \alpha R(t))))^\gamma}, \quad (11)$$

and analogously, the equilibrium relaxation time is given by

$$\tau_\infty = \tau_0 \exp \frac{C}{T_a(V_0(1 - \alpha_l \Delta T_f))^\gamma}. \quad (12)$$

Combining Eqs. (11) and (12), the aging time-dependent relaxation time can be rewritten as

$$\ln \tau(T_a, t) = \ln \tau_\infty(T_a) + \frac{C}{T_a V_0^\gamma} \times \left(\frac{1}{(1 - \Delta T_f(\alpha_l - \Delta \alpha R(t)))^\gamma} - \frac{1}{(1 - \alpha_l \Delta T_f)^\gamma} \right). \quad (13)$$

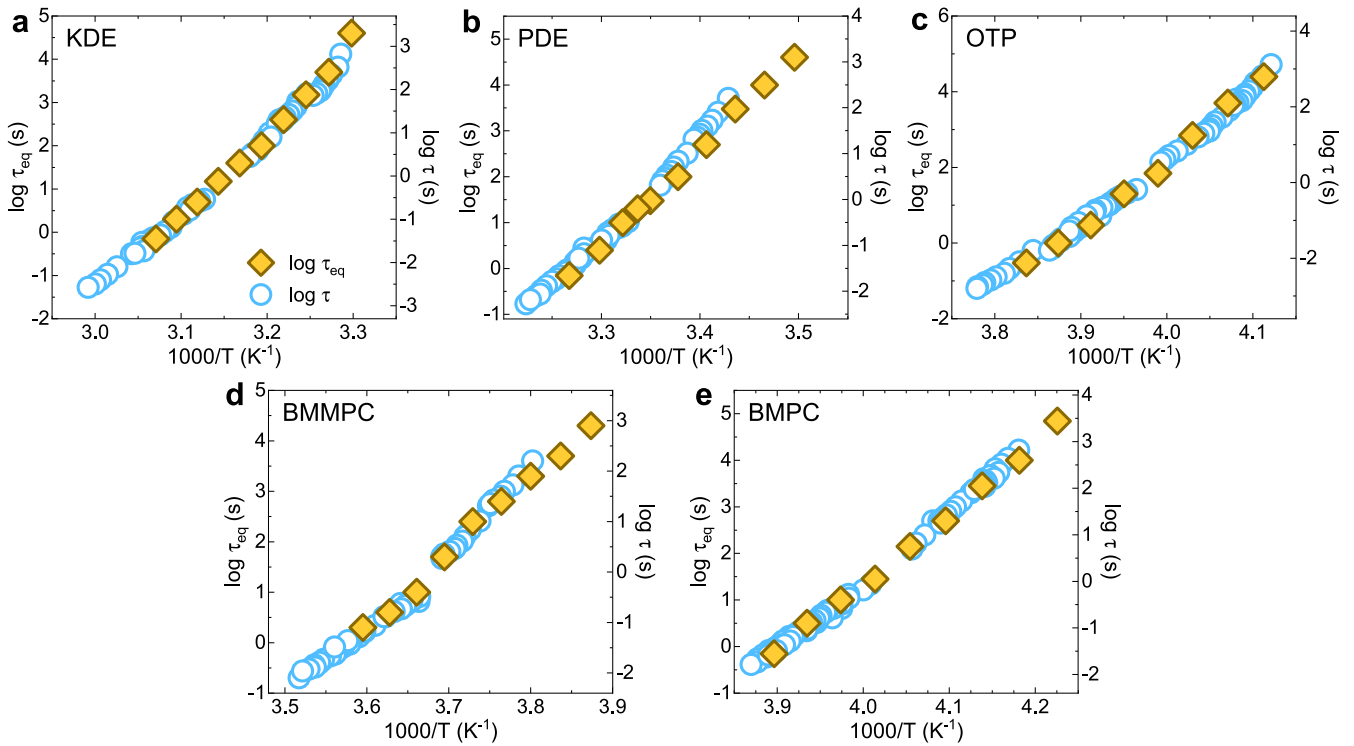


FIG. 3. Time scale to reach equilibrium (left axis) and relaxation time of the α relaxation (right axis) as a function of the inverse temperature for all investigated glasses.

We now define the following function of $R(t)$, corresponding to the second addend of the right-hand side of Eq. (13):

$$g(R(t)) = \frac{C}{T_a V_0^\gamma} \left(\frac{1}{(1 - \Delta T_f (\alpha_l - \Delta \alpha R(t)))^\gamma} - \frac{1}{(1 - \alpha_l \Delta T_f)^\gamma} \right). \quad (14)$$

In such a way, the aging time and temperature-dependent relaxation time are expressed by

$$\ln \tau(T_a, t) = \ln \tau_\infty + g(R(t)). \quad (15)$$

For temperature down-jumps, where the relaxation time during aging is always smaller than or equal to τ_∞ , $g(R(t)) \leq 0$.

To model physical aging results of a given glass, the knowledge of the normalized relaxation function at a reference aging temperature $R_1(t)$ is required. This can be obtained by interpolating or fitting with an appropriate function experimental aging data at that temperature. The reduction in the non-linear response after an arbitrarily chosen temperature jump to the linear response after a jump smaller than the amplitude of spontaneous thermal fluctuations²⁹ implies that the normalized relaxation function is a unique function of the material time: $R_1(\xi) = R_2(\xi)$. This implies that a generic normalized relaxation function after an arbitrary temperature jump can be derived from the relaxation function at a reference temperature.²⁹

The equality of $R(\xi)$ after different jumps holds for the derivatives, too,

$$\frac{dR_1(\xi)}{d\xi} = \frac{dR_2(\xi)}{d\xi}, \quad (16)$$

which can be rewritten in terms of absolute time considering Eq. (4),

$$\frac{dR_1(t_1^*)}{dt_1^*} \tau_1(t_1^*) = \frac{dR_2(t_2^*)}{dt_2^*} \tau_2(t_2^*). \quad (17)$$

Here, $\tau_1(t_1^*) = \tau(T_1, t_1^*)$ and $\tau_2(t_2^*) = \tau(T_2, t_2^*)$. Hence, combining Eq. (17) with Eq. (15), we obtain

$$\frac{dR_1(t_1^*)}{dt_1^*} \tau_{1,\infty} \exp(g(R_1(t_1^*))) = \frac{dR_2(t_2^*)}{dt_2^*} \tau_{2,\infty} \exp(g(R_2(t_2^*))). \quad (18)$$

If we consider identical changes in the normalized relaxation function, $dR_1(t_1^*) = dR_2(t_2^*)$, we can deduce the time increment for aging at the target temperature rearranging Eq. (18),

$$dt_2^* = \frac{\tau_{2,\infty}}{\tau_{1,\infty}} \exp[g_2(R) - g_1(R)] dt_1^*, \quad (19)$$

where $g(R_1(t_1^*))$ and $g(R_2(t_2^*))$ are replaced by $g_1(R)$ and $g_2(R)$, respectively. Integrating Eq. (19), we obtain

$$t_2 = \int_0^{t_2^*} dt_2^* = \frac{\tau_{2,\infty}}{\tau_{1,\infty}} \int_0^{t_1^*} \exp[g_2(R) - g_1(R)] dt_1^*. \quad (20)$$

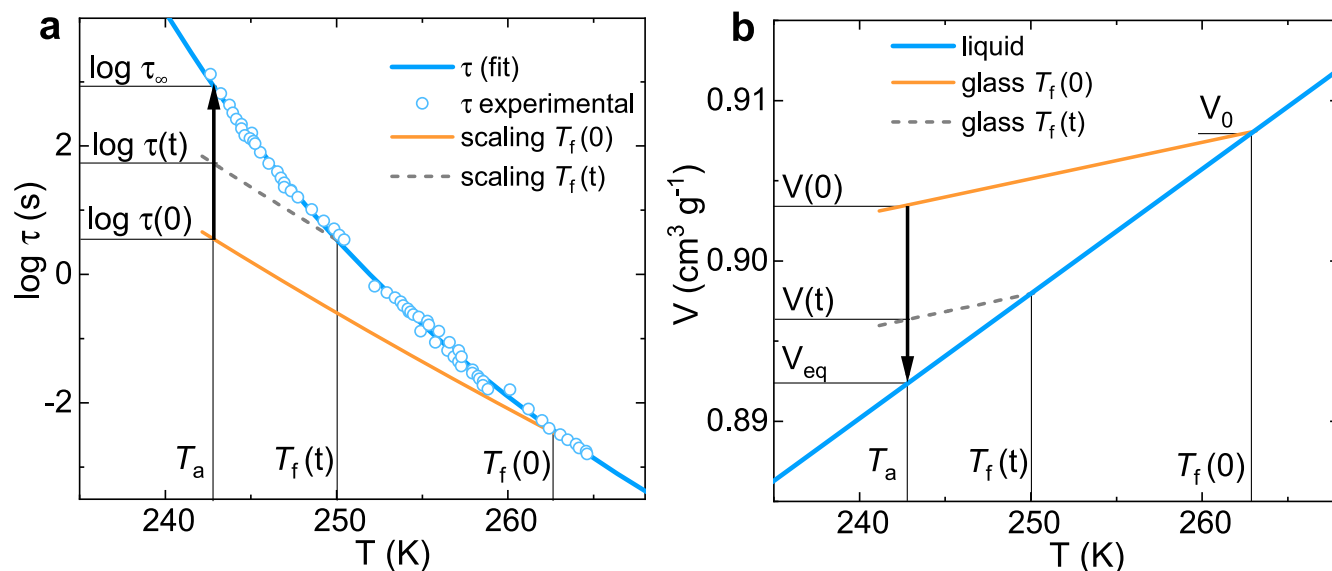


FIG. 4. Temperature dependence of the α relaxation time—described by the density scaling approach (lines) and experimental function (points)—[panel (a)] and the specific volume [panel (b)], and their relation with the fictive temperature, at equilibrium, after quenching at 1000 K/s to T_a , and after quenching under the same condition and aging for a given time for OTP.

TABLE II. Data required to obtain the α relaxation time within the density scaling approach for KDE,⁵⁴ PDE,⁵⁶ OTP,^{54,55} BMMPC,⁵⁷ and BMPC.⁵⁷

Glass formers	$T(0)$ (K)	V_0 (cm ³ /g)	α_l (kK ⁻¹)	α_g (kK ⁻¹)	γ	C (K (g/cm ³) ^{γ})
KDE	330.5	0.87	0.505	0.25	4.5	7 100
PDE	306.5	0.735	0.765	0.25	4.5	8 100
OTP	263	0.905	0.87	0.25	4	12 000
BMMPC	277	0.91	0.635	0.25	8.5	6 100
BMPC	259	0.9	0.765	0.25	7	4 550

Hence, Eq. (20) allows converting a discrete set of experimental data points, the time vector $\mathbf{t}_1 = (t_1^1, t_1^2, \dots, t_1^n)$, corresponding to a set of normalized relaxation function vectors $\mathbf{R} = (R^1, R^2, \dots, R^n)$, to a second set of data points corresponding to a different aging temperature, the time vector $\mathbf{t}_2 = (t_2^1, t_2^2, \dots, t_2^n)$. Plotting R vs t_2 delivers the model prediction at any aging temperature from the knowledge of the normalized relaxation function at a reference temperature. Importantly, this does not require any fitting parameter.

Before presenting the outcome of the model prediction, it is worth remarking that the description of $R(t)$ at the reference temperature contains the intrinsic non-exponential relaxation of the glass plus the non-linear behavior at that temperature. The magnitude of non-linearity, depending on the aging temperature, is tuned by the function $g(R)$ [see Eq. (15)]. Having summarized these general aspects of the model, the implementation within the density scaling description of the α relaxation time requires the knowledge of several inputs, which are reported in Table II. In the same table, we also report $T_f(0)$, that is, the fictive temperature after the

quench at 1000 K/s and the specific volume at that temperature, V_0 . The values reported in Table II are taken from the available literature data.^{54–57} Due to data scarcity, the coefficient of thermal expansion in the glassy state was fixed at 2.5×10^{-4} K⁻¹, that is, the value reported for OTP.⁵⁵ This choice is highly reasonable as 2.5×10^{-4} K⁻¹ lies in the tiny range of variation of small molecule glass formers.⁵⁸

The outcome of the application of the model is shown in Fig. 5, where the experimental normalized relaxation functions (symbols) and those predicted by the model (lines) as a function of aging time and temperature are presented. Figure 6 shows the difference between the model prediction and $R(t)$ data from measured T_f , thus providing a representation of how much the models deviate from experiments. A common general observation that applies to all glasses is that the model is able to accurately catch the experimental data at high aging temperatures, specifically for temperatures larger than 313.2 K for KDE, 298.2 K for PDE, 250.7 K for OTP, 263.2 K for BMMPC, and 246.7 K for BMPC. At lower temperatures,

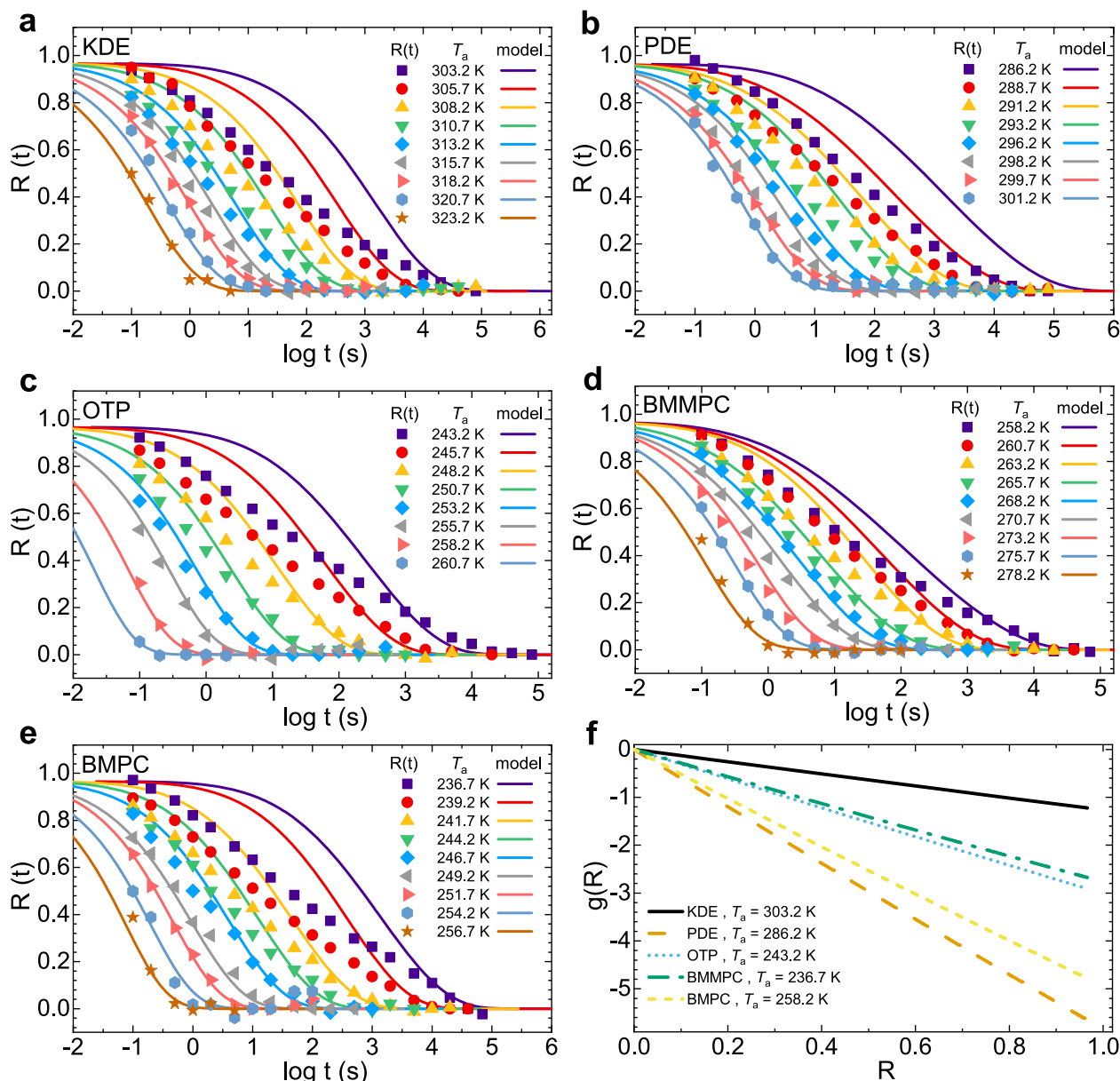


FIG. 5. [Panels (a)–(e)] Experimental (points) and predicted (lines) normalized relaxation function vs aging time for all investigated temperatures and glasses. [Panel (f)] $g(R(t))$, providing the deviation of τ from its equilibrium value [see Eq. (15)], as a function of $R(t)$ at the lowest investigated aging temperatures.

the model fails to capture the entire time evolution of $R(t)$ in both the shape and typical time scale of the relaxation. In all cases, the experimental $R(t)$ appears to be way more stretched than the model prediction. Altogether, the model predicts largely slower aging time evolution of the glass thermodynamic state than the experimental outcome. However, for all glasses except PDE, while failing to describe the whole aging behavior, the model is able to accurately catch the ultimate stages of approach to equilibrium. As an exception, the approach to equilibrium for PDE is found to be always

faster than that predicted by the model, even at the final stages of the aging process.

A complementary way of visualizing how the model based on the α relaxation deviates from experimental aging data relies on depicting the normalized relaxation function vs the material time, ξ , which, as discussed, linearizes the aging response [see Eq. (4)]. This is shown in Fig. 7, where it can be observed that experimental data at high aging temperatures collapse on a single curve, which perfectly overlaps with that predicted by the

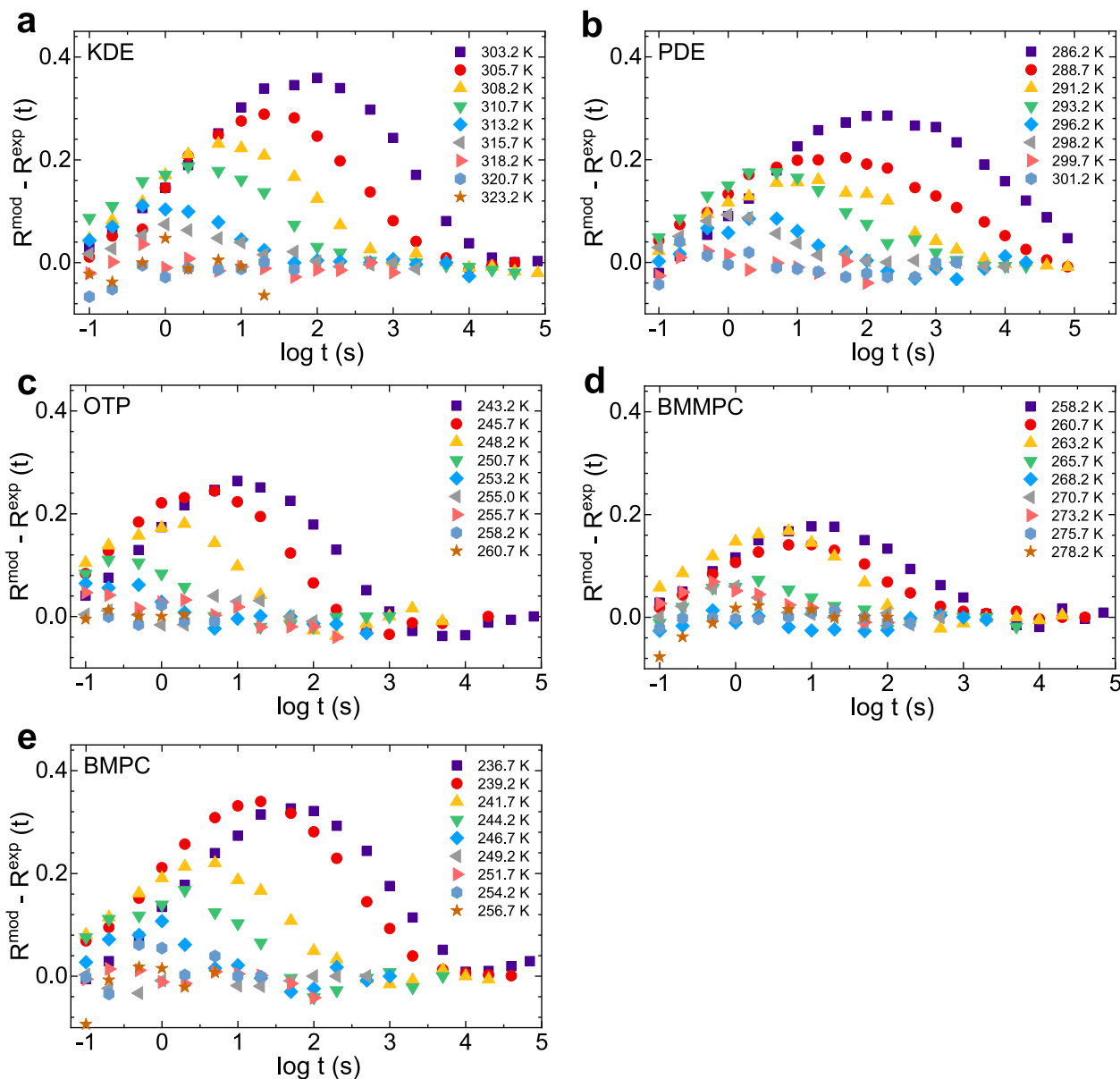


FIG. 6. Difference between the predicted and experimental relaxation function vs time for all investigated temperatures and glasses.

model. Experimental aging data gradually shift to lower ξ with decreasing aging temperatures. This way of showing data provides a plastic representation of how, in this low temperature regime, only the final part of aging is accurately caught by the α relaxation, whereas the overall aging response is more stretched and anticipated with respect to the prediction based on the α relaxation.

Before closing this section, it is worth pointing out that fitting of our data by the original SPA model^{27–29} provides analogous deviations as those of our model based on density scaling. Furthermore,

the $g(R)$ function, providing the deviation of $\ln \tau$ from its equilibrium value, varies linearly with $R(t)$ [see Fig. 4(f)], as in the original SPA model. However, apart from the absence of any fitting parameter, there are at least two reasons why it is worth including density scaling to describe our data: (i) the most important is that, within the original version of the model, it would have been unclear whether deviations from the model predictions were due to the inadequacy of the α relaxation alone to describe aging significantly below T_g or rather due to the inadequacy of the simple proportionality between $\log \tau$ and T_f ; (ii) second, while for not too fragile systems and for

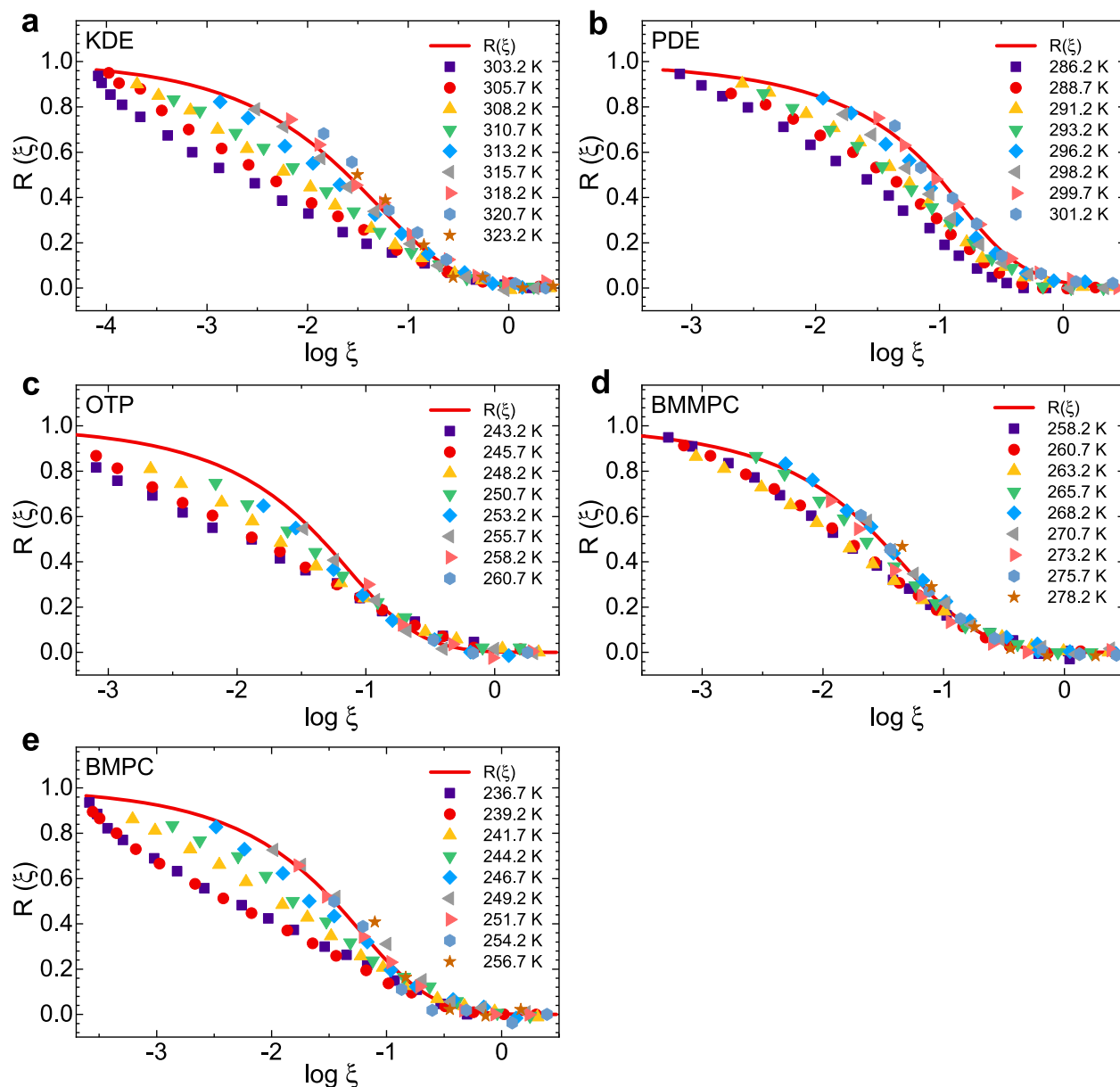


FIG. 7. Experimental (points) and predicted (red line) normalized relaxation function as a function of material time ξ for all investigated temperatures and glasses.

not too large temperature jumps, the proportionality between $\log \tau$ and T_f may be acceptable [see Fig. 4(a)], this is not the case for highly fragile glass formers, such as polymers, and/or for very large temperature jumps.

IV. DISCUSSION

In Sec. III, we have presented a systematic characterization of physical aging in glasses made of small molecules via FSC, which permitted covering a wide range of time scales and tem-

peratures. In such a way, the current understanding of physical aging has been challenged employing two different approaches: a model-independent one exclusively based on the time scale to reach equilibrium and an approach based on a model originally known as SPA.^{27–29} Within both approaches, the aging behavior at the highest investigated temperatures is completely caught considering exclusively the α relaxation. This is evidenced by the aging temperature dependence of the time scale to reach equilibrium (see Fig. 3), which exhibits the same super-Arrhenius behavior as the α relaxation, and by the ability of the model to catch com-

pletely the time evolution of the glass thermodynamic state. The latter result is in line with previous reports in which SPA was fitted to aging data after small temperature steps.^{27–29} Furthermore, the adequacy of the α relaxation to describe physical aging in the high temperature regime agrees with findings where aging is investigated in a limited temperature interval in the proximity of T_g .^{12–15}

If we consider our model-independent approach at low aging temperatures, the temperature dependence of τ_{eq} generally mimics that of the α relaxation. This is certainly the case for KDE, OTP, BMMP, and BMPC, whereas PDE appears to exhibit minor deviations from the super-Arrhenius temperature dependence of the α relaxation. Consistently with the analysis based on τ_{eq} , with the exception of PDE, the model prediction for these glasses close to equilibrium catches the experimental late stage evolution of the thermodynamic state. Regarding the anomalous behavior of PDE, we tentatively ascribe it to the poor extrapolation of equilibrium τ of the α relaxation to the lowest temperatures at which aging was investigated.⁵⁹ However, importantly, low aging temperatures, corresponding to large jumps in the fictive temperature, entail a considerable increase in the complexity of the overall kinetics of equilibrium recovery. Indeed, the common feature of the aging behavior of all glasses is that, when the description of the whole normalized relaxation function is realized in the low temperature regime, the prediction based exclusively on the role of the α relaxation largely fails for all investigated glasses. In particular, the experimental normalized relaxation function is way more stretched than the predicted behavior and, above all at the early stages of aging, exhibits a faster evolution than expected only accounting for the α relaxation.

The failure of the α relaxation as the only mechanism involved in glass equilibration after large temperature jumps has been shown in several studies where different variants of the TNM-KAHR models were applied.^{60–64} The inadequacy of this class of models was explained as resulting from the need for refining/modifying the explicit analytical form expressing the non-linearity of physical aging. Here, we rather show that even introducing non-linearity without making an explicit assumption on its mathematical form brings about large discrepancies between model prediction and experimental data. Hence, our findings indicate that the inadequacy of the TNM-KAHR models to describe physical aging after large temperature jumps must be sought not so much in their analytical expressions *per se* but in the fact that they exclusively contain one time scale, namely that of the α relaxation.

The reason for the discrepancy between the predicted and experimental behaviors after large temperature jumps, especially at the beginning of aging, must be sought in the role of fast non- α molecular mechanisms triggering physical aging. Their role has been documented for a variety of glasses, including polymers,^{19,20,65,66} metal alloys,^{23,24} chalcogenides,²² and glycerol,²⁵ where multiple decays toward equilibrium could be separated. Here, even if the splitting of multiple decays cannot be clearly discerned, the pronounced stretching of the normalized relaxation function indicates the presence of multiple steps not yet well separated in the approach to equilibrium. A close inspection of data at the lowest aging temperature actually hints toward a splitting of the approach to equilibrium

in two steps. In particular, for all glasses at their lowest investigated aging temperature, a slowdown of relaxation takes place at about 10^3 s, followed by a late evolution to the final equilibrium (see Fig. 5). Importantly, this observation rules out the possibility that deviations of experimental data from the model could originate from the inaccurate description of the α relaxation time by the density scaling.

To understand the decoupling between aging behavior and α relaxation, the conceptual difference between the non-linear and linear responses can be invoked.^{67,68} This interpretation agrees with the experimental findings,^{27–29} including ours, showing that for limited temperature jumps, the α relaxation contains all the information to describe weakly non-linear aging. However, the evidence that there exists an underlying molecular non- α mechanism triggering aging under certain conditions requires a suitable explanation on why this is unresolved in linear measurements. Here, it is worth pointing out that our characterization of the glass linear response relies on the obtainment of the thermal susceptibility, that is, the complex specific heat, a second-order thermodynamic property. Instead, monitoring the time-dependent fictive temperature in the aging regime implies that the evolution of a first-order thermodynamic property, in this case, the enthalpy, is monitored. If one of the molecular motions triggering physical aging involves a temperature independent number of degrees of freedom, its associated entropy, $S(T)$, will be temperature independent, too.⁶⁹ As a result, the signature of this relaxation will deliver a null contribution to the specific heat as $C_p(T) = T \left. \frac{\partial S(T)}{\partial T} \right|_p$. This scenario is fully compatible with the inability of linear response—delivering a thermal susceptibility and containing information exclusively on the α relaxation—to describe equilibrium recovery in glass aging, where a first-order thermodynamic property as the enthalpy is monitored.

According to the previous considerations, fluctuations related to non- α relaxation processes may remain unidentified in thermal susceptibility measurements. However, those fluctuations may be visible if the susceptibility is obtained applying different fields, for instance, dielectric or mechanical linear perturbations.⁷⁰ The most immediate candidates to explain the fast evolution of the glass thermodynamic state are secondary β relaxations, generally detected by dielectric and mechanical spectroscopies below T_g .⁷¹ These are well characterized in all glasses investigated by us.^{40,72,73} PDE,⁴⁰ OTP,⁷² and BMPC⁷³ exhibit a secondary relaxation, whereas KDE⁴⁰ and BMMP⁷³ do not. In contrast, deviations of experimental aging behavior from the prediction expected considering exclusively the α relaxation are common to all glasses and, therefore, insensitive to the presence of secondary relaxations. Furthermore, the OTP β relaxation attains time scales of the order of seconds below 200 K,⁷² that is, way below the temperatures at which we observe a strong influence of non- α mechanisms on OTP glass equilibration. All these arguments are at odds with the explanation of fast aging as triggered by the β relaxation.

The relaxation mechanism responsible for accelerated aging with respect to predictions based only on the α relaxation must bear large potential to equilibrate and exhibit time scales compatible to such a fast evolution. In this sense, a suitable candidate to explain the fast non- α relaxation can be a recently identified slow Arrhenius process (SAP), which has been shown to play a role of utmost

importance in the kinetics of equilibration of different phenomena, including physical aging, polymer adsorption, and dewetting.⁷⁴ A stringent test of the role of SAP would require an analysis on the activation energy of fast equilibration at aging temperatures lower than those of the present study and for longer times, where a complete splitting with the step of equilibration due to the α relaxation is attained.

The evidence of an additional mechanism of glass equilibration raises the question of how to apply the concept of material time under those conditions at which the α relaxation is insufficient to catch the overall aging behavior. The natural consequence of our findings is that the material time is tuned by the time scale of both α and non- α relaxation mechanisms. Hence, Eq. (4) should be rewritten as $d\xi = (a\tau_\alpha^{-1} + (1-a)\tau_{non-\alpha}^{-1})dt$. The implementation of the material time requires the knowledge on how much potential of equilibration is borne by each relaxation mechanism, contained in the parameter a , and the temperature dependence of $\tau_{non-\alpha}$.

A final important implication of our findings is that they open the door to accessing glasses with low energy. Within the scenario of physical aging exclusively driven by the α relaxation, the tremendous growth of the associated time scale with decreasing temperature would imply that aging would disappear not too far from T_g , thereby preventing the exploration of low energy states. In contrast, physical aging is known to exhibit pronounced effects even way below T_g ,^{2,75–81} which can be rationalized considering non- α relaxations, whose potential to equilibrate glasses survives where the α relaxation is completely frozen. Importantly, reducing the sample size may significantly shorten the time scale of glass relaxation via fast non- α mechanisms, as shown in glasses with largely diverse nature, such as polymers^{17,68} and metallic glasses.¹⁸ In such a way, topics of extraordinary importance, such as the existence of the ideal glass transition⁸² at the Kauzmann temperature,^{83,84} can be explored reducing the sample size and employing fast non- α mechanisms to reduce the glass energy over time scales amenable to the experimental practice.^{85,86}

V. CONCLUSIONS

We have presented an extensive characterization of the kinetics of physical aging in five small molecule glasses interacting via van der Waals forces, exploiting the ability of FSC to access a wide range of time scales. In this way, we have covered a wide spectrum of aging time, covering about six decades. With the aim of challenging the role of the α relaxation, we have adopted two different approaches to obtain insights into the underlying molecular mechanisms mediating physical aging: (i) a model-independent approach based on the time to reach equilibrium and (ii) a model, previously addressed as SPA, where the non-exponentiality and non-linearity of physical aging are considered without providing an explicit mathematical form. Here, we have implemented the SPA model employing the density scaling approach to connect the aging time-dependent α relaxation time with the glass thermodynamic state.

The model-independent approach based on the equilibration time generally shows that the final equilibrium is attained in ways compatible with the exclusive role of the α relaxation. In the same way, the final stages of physical aging are reasonably captured by the

modified SPA model. Furthermore, the whole experimental relaxation function at the highest investigated aging temperatures is accurately described by the model. However, the central finding of the present study is that, at low aging temperatures, corresponding to large jumps in the fictive temperature, the model based on the exclusive role of the α relaxation largely fails to describe the whole relaxation function. In particular, the experimental relaxation function is vastly more stretched than that predicted by the model, implying that, at the beginning of the equilibration process, aging proceeds faster than predicted by the model. The main consequence of our results and their analysis is that physical aging in glasses aged significantly below T_g cannot be described as exclusively triggered by the α relaxation and, therefore, other fast mechanisms of equilibration must be considered. As a consequence, physical aging can survive with rates amenable to the experimental practice even way below T_g , where the α relaxation is frozen, a result that, under certain conditions, may convey glasses to low energies.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Daniele Cangialosi: Conceptualization (lead); Data curation (equal); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Methodology (equal); Writing – original draft (lead); Writing – review and editing (equal). **Valerio Di Lisio:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review and editing (lead). **Vasiliki-Maria Stavropoulou:** Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review and editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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