# One Experiment Makes a Direct Comparison of Structural Recovery with Equilibrium Relaxation

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**Abstract:** For a molecular glass-former, we compare directly the equilibrium fluctuations, measured as 'structural' relaxation in the regime of linear response, with structural recovery, i.e., field induced physical aging in the limit of a small perturbation. The two distinct correlation functions are derived from a single experiment. Because the relaxation time changes only 2% during structural recovery, no aging model is needed to analyze the results. Although being conceptually different processes, dielectric relaxation and recovery dynamics are observed to be identical for propylene glycol, whereas single-particle dynamics as seen by photon correlation spectroscopy are significantly faster. This confirms the notion that structural recovery and aging is governed by all modes observed by dielectric spectroscopy, i.e., including cross-correlations, not only by single-particle dynamics. A comparison with analogous results for other materials suggests that the relation between relaxation and recovery time scales may be material specific rather than universal.

**Keywords:** dielectric relaxation, physical aging, collective dynamics, material time

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## I. INTRODUCTION

Structural relaxations of supercooled liquids have been studied extensively and by numerous techniques. A key quantity is the average or most probable time-constant of the primary or α-process, which reaches $\tau_\alpha$ = 100 s at the glass transition temperature $T_g$.[1] If measured within the regime of linear response, this α-process reflects the equilibrium fluctuations at the given constant external parameters such as temperature $T$, pressure $p$, and electric field $E$,[2] and thus not a change of structure that is paralleled by changes in the susceptibility, $\chi(\omega)$. By contrast, structural recovery or, similarly, physical aging refers to the process of a system adjusting to a new equilibrium state induced by a change in $T$, $p$ or $E$,[3,4] and is often monitored via the change of $\tau_\alpha$ with aging time. Out of the various parameters that define the susceptibility $\chi(\omega)$, $\tau_\alpha$ is usually the most sensitive to changes of external variables such as $T$, $p$, or $E$. Because each experimental technique aimed at observing the α-process is associated with a specific correlation function and thus a different value for $\tau_\alpha$,[5] it is not immediately clear which relaxation time, if any, is the best predictor for the time scale of physical aging. The analogous problem arises for any material with multiple relaxation processes.[6,7] Interest in this question has recently been renewed by observations capable of disentangling single-particle and collective dynamics in glass forming liquids, which are associated with distinct time constants.[8,9,10]

Physical aging is typically observed via a change of $\tau_\alpha$ in response to a temperature change from above to below $T_g$, and the aging temperature $T_{age}$ is selected such that aging is slow relative to the time required to change temperature, often 100 s or more.[11,12] The equilibrium α-relaxation at $T_{age}$ is therefore very slow and commonly not determined directly by experiment, but rather by extrapolation from higher temperatures. Established models of physical aging such as the Tool-Narayanaswamy-Moynihan (TNM)[13,14,15] and Kovacs-Aklonis-Hutchinson-Ramos (KAHR)[16] approaches are based on the assumption that structural recovery (aging) is governed by equilibrium fluctuations, provided that the change of $\tau_\alpha$ or fictive temperature $T_f$ or material time $\xi$ during aging is accounted for. The fictive temperature $T_f$ is the temperature at which a system in equilibrium has the same property as in the non-equilibrium state at $T \neq T_f$,[13] while the material time concept accounts for the change in rate of approaching equilibrium as $\tau_\alpha$ and $T_f$ change in the course of aging.[14]

The assumptions of the TNM or KAHR models lead to the expectation that structural recovery should follow the α-relaxation response if the perturbation results in only a minute change in structure, i.e., with practically no change in relaxation times and thus the near identity of material and laboratory times.[17] However, several observations argue against this expectation. The feature of heterogeneous dynamics and spectral selectivity observed in many supercooled liquids reveals that fast contributions to the susceptibility spectrum relax (or fluctuate) largely independent of the slower modes.[18,19,20] By contrast, the commonly found characteristic of time - aging time superposition (TaTS) implies that fast and slow modes age at the same rate, i.e., not independently. This feature of TaTS is equivalent to the finding that aging can be described by a single fictive temperature $T_f$ or material time $\xi$.[12,17,21] Moreover, results from field induced aging in the limit of small perturbations have shown that recovery is a factor of 1.4 to 3 slower than relaxation and potentially more exponential.[22] This is consistent with the idea that recovery from a small perturbation is the response that is linked to the equilibrium fluctuations identified as rate exchange,[18] as both processes are related to variations of time constants, shifting or fluctuating.[23,24]

In what follows, we will use the term relaxation for describing the dynamics in equilibrium, while physical aging and structural recovery are associated with the system approaching a new equilibrium state after some perturbation. The term recovery will be used for aging processes in the limit of small perturbations. With the above indications of recovery and relaxation being conceptually distinct processes, a detailed scrutiny of their relation is warranted. In this study, we employ an external electric field for inducing structural recovery, which can be applied in a practically instantaneous manner. As a result, this recovery process can be observed well above $T_g$, where the relaxation times are in the regime of milliseconds. This facilitates an unambiguous comparison of the time scales of equilibrium dielectric relaxation, $P(t)$, and structural recovery, $\tau_\alpha(t)$, under identical conditions, as both correlation decays can be derived from a common data set. Moreover, the overall change in $\tau_\alpha$ is small enough such that modeling of a change in material time is not required. Unlike other supercooled liquids, propylene glycol is found to be characterized by dielectric relaxation and structural recovery following identical response patterns. For this material the kinetic $T_g$ values derived from dielectric relaxation spectroscopy (DRS) and photon correlation spectroscopy (PCS) have been reported as 180 K and 175 K, respectively.[8] This difference can be understood as single particle dynamics being about a factor of six faster than the

collective counterpart, with the implication that aging is governed by collective rather than single-particle dynamics only.[9,25]

## II. EXPERIMENTAL SETUP

Propylene glycol (PG, 1,2-propanediol, 99.5+% A.C.S. reagent, Aldrich) was filled into a sealed capacitance cell ($C_{geo}$ = 105 pF) with titanium electrodes of 17 and 20 mm diameter, separated by a 13 μm thick polyimid ring that leaves an inner 14 mm diameter area for the sample. This cell is kept in a Leybold RDK 6-320 closed-cycle helium refrigerator, equipped with a Lakeshore Mod. 340 temperature controller. Linear response DRS curves are recorded with a Solartron SI-1260 gain/phase analyzer and DM-1360 transimpedance amplifier using a voltage not exceeding 1 $V_{rms}$. The field induced recovery experiment is outlined schematically in Fig. 1, with the applied field pattern consisting of 16 periods of a sinusoidal field without dc-bias, followed by 64 periods of a sine with the same amplitude and frequency $\nu$, but with a large dc-bias field superimposed. For each dc polarity, $V_{pos}(t)$ and $V_{neg}(t)$, the field pattern is repeated 5000 times to allow efficient averaging, with the high field duty cycle not exceeding 5%.

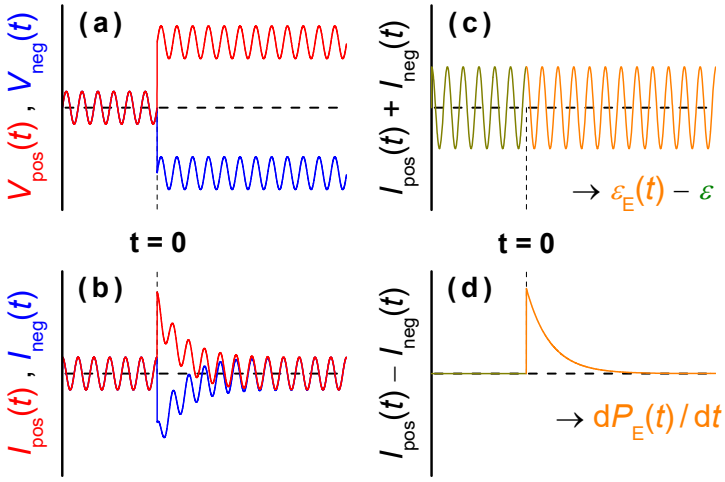


**Fig. 1.** Schematic representation of voltage and current patterns of the field induced aging experiment. (a) Pair of voltage patters, $V_{pos}(t)$ and $V_{neg}(t)$, with positive and negative dc-bias. (b) Current responses $I_{pos}(t)$ and $I_{neg}(t)$ corresponding to $V_{pos}(t)$ and $V_{neg}(t)$, respectively. (c) The sum, $I_{pos}(t) + I_{neg}(t)$, which eliminates the step response. (d) The difference, $I_{pos}(t) - I_{neg}(t)$, which isolates the step response.

From the observed current traces $I_{pos}(t)$ and $I_{neg}(t)$, the dc-field induced change in $\varepsilon''(\nu)$ is derived from the period-by-period Fourier analysis of the 80 periods of the $I_{pos}(t) + I_{neg}(t)$ signal at

the fundamental frequency $\nu$; and from the same data set, the current step response is obtained from the zero-frequency Fourier component of the $I_{pos}(t) - I_{neg}(t)$ signal, see Fig. 1.

## III. RESULTS AND DISCUSSION

The dielectric loss spectra for PG at 183 and 188 K are presented in Fig. 2, together with their fits, each based on a single Havriliak-Negami (HN) profile,[26]

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau_{HN})^\alpha]^\gamma}, \tag{1}$$

with relaxation amplitude $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, characteristic time constant $\tau_{HN}$, and temperature invariant shape parameters $\alpha = 0.98$ and $\gamma = 0.68$. The values for amplitude and time constant are $\Delta\varepsilon = 53.0$ and $\tau_{HN} = 8.25$ ms for $T = 183$ K, and $\Delta\varepsilon = 51.0$ and $\tau_{HN} = 1.50$ ms for $T = 188$ K. For $T = 183$, the two symbol sets in Fig. 2 (blue solid circles and smaller yellow triangles on top) represent the loss profile before and after all high-field experiments, indicating complete reversibility of the field induced changes. The above HN parameters have been translated into the best time-domain equivalents based on the Kohlrausch-Williams-Watts (KWW) or stretched exponential approach, $\phi(t) \sim exp\left[-(t/\tau_{KWW})^\beta\right]$. Using well tested relations,[27] the loss profile shape is represented by $\beta = 0.71$, while the time constants are $\tau_{KWW} = 5.12$ ms for $T = 183$ K and $\tau_{KWW} = 0.93$ ms for $T = 188$ K, i.e., shifted by a factor of 5.5 for this 5 K difference in $T$.

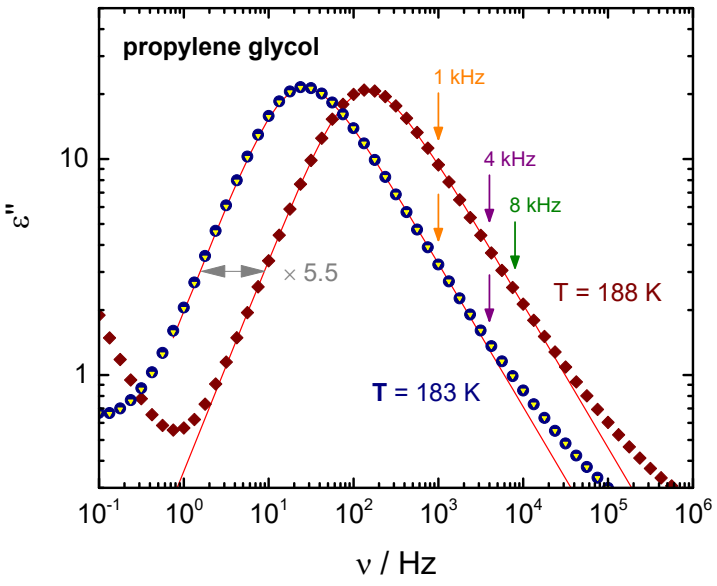


**Fig. 2.** Dielectric loss profiles for PG at temperatures $T = 183$ and 188 K, measured within the regime of linear response. Diamonds are for $T = 188$ K, circles and small triangles on top

are for $T = 183$ K, respectively measured before and after the high-field aging experiments on the same sample. Arrows indicate the test frequencies used for the recovery experiments.

The results of the recovery experiments are compiled as symbols in Fig. 3 for both temperatures, $T$ = 183 and 188 K. The field induced changes are shown as time resolved loss values, $\varepsilon''(t)$, normalized such that unity and zero on the ordinate scale represent the loss level before applying the field and after reaching equilibrium with the high field, respectively. Note that a high dc-bias field shifts the relaxation time to larger values, thus actually reducing $\varepsilon''(\nu)$ for $\nu > \nu_{max}$, as in the present case.[28,29,30] While obscured by the present normalization, note that this is a 'retardation' rather than 'relaxation' type process. For the typical dc-bias field of $E_B$ = 193 kV cm$^{-1}$ used here, the loss level was reduced by 1.3% to 1.8%, equivalent to increases in relaxation time constants by approx. 2%. Originally, these recovery curves start above unity as a result of $\varepsilon''$ initially increasing, due to an increase in dipole or fictive temperature that arises from energy absorption from the time dependent field.[31] This heating-like effect has been corrected for, using an approach that has been verified earlier on a quantitative level.[22,31,32] The impact of this correction amounts to a < 10% correction for the recovery time constants.

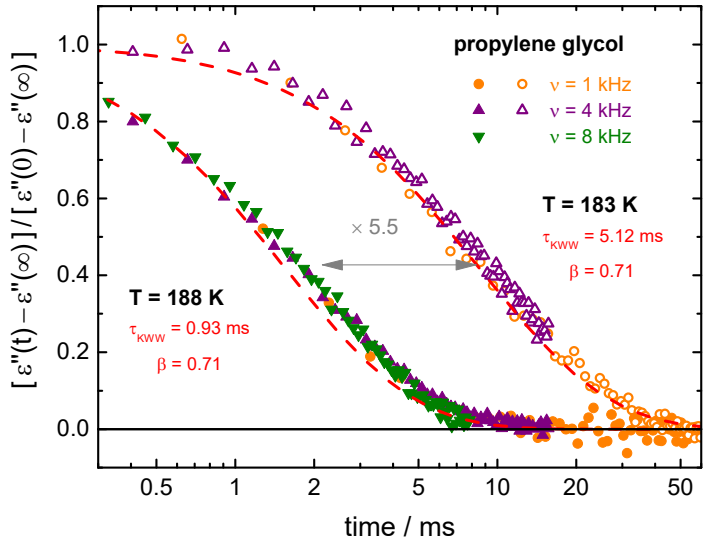


**Fig. 3.** Symbols represent experimental data for the time-resolved change in normalized dielectric loss at a given frequency as indicated. The response is initiated by applying a static electric field at time $t = 0$ to PG at $T = 183$ K (open symbols) and at $T = 188$ K (solid symbols. The dc-bias field amplitude was $E_B$ = 193 kV cm$^{-1}$ in all cases except for $T = 188$ K and $\nu = 1$ kHz, where $E_B$ = 128 kV cm$^{-1}$ was used. The dashed lines are squared stretched exponential rise functions with $\tau_{KWW}$ and $\beta$, with the parameters taken from the fits to the low-field loss spectra of Fig. 2.

In order to compare the recovery represented by symbols in Fig. 3 with the linear response α-relaxation, it needs to be recognized that the response magnitude, $|\varepsilon''(0) - \varepsilon''(\infty)|$, is quadratic in the field amplitude.[31,32] For small perturbations, as in the present case with $\Delta\ln(\tau_\alpha) \approx 0.02$, the amount of relative change regarding $\tau_\alpha$ (and thus $\varepsilon''$) increases with field square, i.e., the 'linear regime' of this aging process is given by $\Delta\ln(\tau_\alpha) \propto E^2$. Therefore, identity of relaxation and recovery kinetics is equivalent to the validity of the following relation:

$$\frac{\varepsilon''(t) - \varepsilon''(\infty)}{\varepsilon''(0) - \varepsilon''(\infty)} = 1 - \left(1 - exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta}\right]\right)^2 . \qquad (2)$$

The dashed lines in Fig. 3 are not fits, but rather predictions of field induced recovery based on the assumption that recovery follows the relaxation pattern, i.e., using Eq. (2) with the KWW parameters $\tau_{KWW}$ and $\beta$ derived from the linear-response loss data of Fig. 2 for the respective temperature. These curves reveal that the recovery process is about 10% slower than the relaxation decay, but associated with the same stretching exponent $\beta$. The observation that Eq. (2) closely captures the relation between relaxation and recovery implies that, in this case of PG, the kinetics of structural recovery matches the equilibrium fluctuation dynamics regarding both $\tau_{KWW}$ (within a 10% margin) and $\beta$. Moreover, this relation between relaxation and recovery is maintained across the present 5 K temperature change.

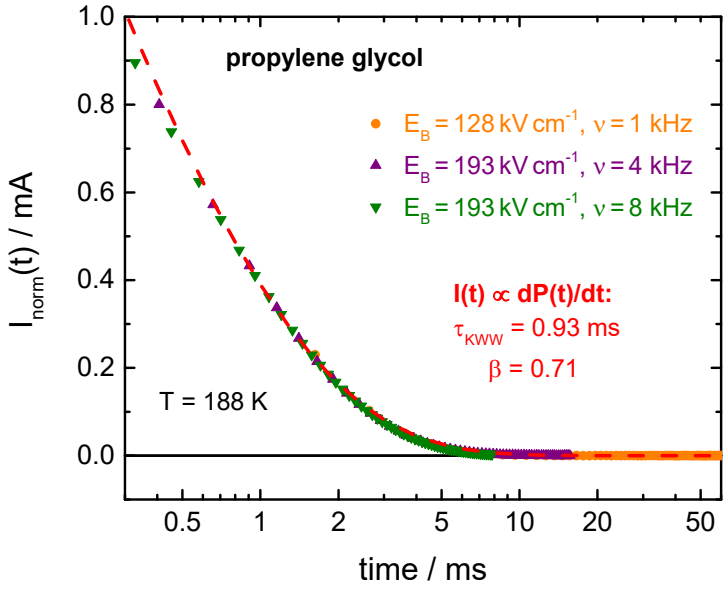


**Fig. 4.** Symbols represent experimental data for the current response, $I(t)$, to a step in the electric field. Measurements using different frequencies $\nu$ (as indicated) are combined to cover

a large time range. Current values are normalized to a common field amplitude of $E_B$ = 193 kV cm$^{-1}$. The dashed line is proportional to the derivative of the stretched exponential decay functions with $\tau_{KWW}$ and $\beta$ derived from the low-field loss spectra, using $I(t) \propto dP(t)/dt$.

With Fig. 4 it is demonstrated that the linear-regime dielectric response could have also been derived with little uncertainty from the high-field experiment. Extracting the response of the current $I(t)$ to the field step as outlined in Fig. 1 facilitates the derivation of the KWW parameters via $I(t) \propto dP(t)/dt$ and assuming stretched exponential behavior for the polarization response $P(t)$. The dashed line in Fig. 4 represents the time derivative of the KWW decay obtained from the HN fit to the $T$ = 188 K loss curve of Fig.2. Thus, practically the same KWW parameters could have been extracted by fitting $I(t)$ with the derivative of a KWW decay, apart from the systematic but small deviation caused by $\tau_{KWW}$ increasing by 2% in the course of the $I(t)$ decay.

Why use an electric field instead of temperature to initiate structural recovery? Similar to a temperature down-jump, increasing the field (with either polarity) leads to an increase of the relaxation time.[28,29,30] Relative to a temperature step, however, an electric dc-bias field can be applied to a sample within a matter of microseconds, facilitating structural recovery experiments for which steady state is reached within 50 ms. This creates the advantage that recovery is measured at a temperature at which the linear response dielectric relaxation can be determined unambiguously. It also allows for the recovery experiment to be repeated thousands of times to obtain a high signal-to-noise ratio, which in turn means that recovery dynamics to very small perturbations can be resolved. Such small perturbations imply that the change of $\tau_\alpha$ in the course of the recovery process is negligible, and comparing relaxation and recovery does not involve models such as the TNM formalism. In cases of much larger excursions from the initial equilibrium as typical for standard temperature down-jump aging experiments, one would need to account for the change in material time or fictive temperature along the aging process. For example, if the relaxation time constant changed from 1 s to 10 s as a result of aging, the approach towards equilibrium would slow down accordingly, equivalent to the material time slowing down relative to real time. In the present experiment with $\tau$ changing only 2% in the course of the recovery, the error resulting from ignoring this change in material time amounts to approximately the width of the dashed lines in Fig. 3, which is negligible for the present purpose.

What do we learn from the present results? The direct comparison of recovery and dielectric relaxation for PG reveals that these distinct processes can be subject to practically identical

dynamics. Analogous experiments on other molecular glass-formers have revealed that recovery is a factor between 1.4 and 3.0 slower than relaxation and possibly more exponential.[22] Together, this is indicative of a material specific rather than universal relation between recovery and relaxation dynamics. Without relying on models of aging, the present data can answer the question whether recovery follows DRS (collective and single-particle modes) or PCS (single-particle modes only) correlation decays more closely.[8,25] Clearly in the case of PG, all modes observed by DRS, thus including cross-correlations, are relevant for structural recovery, thereby confirming the earlier notion advanced by Moch *et al.*[25] that collective modes are involved in the recovery process. The single particle dynamics of PG as revealed by PCS are associated with a six times faster correlation decay relative to DRS dynamics, with only the DRS case matching the recovery time scale.[8] A simple relation between relaxation and aging dynamics will be confined to aging in the limit of small perturbations, with larger excursions requiring at a minimum that the deviation of material time from laboratory time be accounted for.[17]

From the present finding that relaxation and recovery dynamics are practically identical for this particular case of PG, one should not conclude that the two processes are identical in nature. The heterogeneous nature of relaxation implies that fast modes relax independently of the slower ones, whereas it is well established that even the fastest modes recover or age at the same rate as the slowest ones. Thus, fast contributions to the susceptibility, i.e., those with $\tau << \tau_\alpha$, are bound to change their value of $\tau$ on a time scale near $\tau_\alpha$, thus much slower than $\tau$ itself. That said, one should wonder why dielectric hole burning (DHB) was capable of concluding on dynamic heterogeneity, since it is based upon observing that a selected fast mode is subject to a reduction of $\tau$ due to energy absorption from the electric field and thus a rise in $T_f$. The main finding of DHB is that each mode with time constant $\tau$ 'recovers' towards equilibrium on a mode specific time scale, namely $\tau$ itself, contrary to TaTS observed with aging and recovery experiments. A possible explanation for DHB not being associated with a single material time is that DHB involves only a small subset of modes that experience a change in their fictive temperature, namely those selected by the narrow frequency range of the large amplitude sinusoidal field. By contrast, all modes are involved in an aging or structural recovery experiment, because spectral selectivity is absent in a temperature or field step. This observation that TaTS occurs only when all modes are forced to

adapt to a new equilibrium state may serve as a valuable hint to better understand why structural recovery and aging are governed by a single fictive temperature $T_f$ or material time $\xi$.

## IV. SUMMARY AND CONCLUSIONS

In summary, an experiment is realized that facilitates deriving dielectric relaxation and field-induced structural recovery dynamics from a common data set, with each process measured in its respective linear response limit, $P \propto E$ and $\ln(\tau_\alpha) \propto E^2$. For PG it turns out that dielectric relaxation and structural recovery dynamics are virtually identical, which is not the case for field induced recovery of other glass formers. The observation that structural recovery of PG is significantly slower than the single-particle dynamics seen by PCS points towards collective modes originating from cross-correlations and observed by DRS being the most relevant ones for the process of recovery and aging. It is reasonable to assume that recovery from a field or temperature jump yield the same dynamics, with the exception of monohydric alcohols and related materials, where the predominant dielectric relaxation does not reflect the α-relaxation,[33,34] and high fields impact supramolecular structures.[35] It is also pointed out that dielectric hole burning differs from other recovery and aging experiments by its spectral selectivity, resulting in only a small subset of modes experiencing frequency dependent structural recovery. This heterogeneity is not seen in aging or structural recovery experiments and inconsistent with time - aging time superposition, which suggests that the feature of a single fictive temperature $T_f$ or material time $\xi$ requires that all modes concertedly shift towards longer time constants.


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## AUTHOR DECLARATIONS

### Conflict of Interest

The author has no conflicts of interest to disclose.

## DATA AVAILABILITY

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

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