


# Time in a glass

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Ageing is a non-linear, irreversible process that defines many properties of glassy materials. Now, it is shown that the so-called material-time formalism can describe ageing in terms of equilibrium-like properties.

Glasses are ubiquitous in everyday life. Yet, the spontaneous temporal evolution, or ageing, of their properties imposes important limitations on numerous technological applications, as it can lead to ductile-to-brittle evolution and even fractures. Owing to the out-of-equilibrium nature of glasses, predicting the time evolution of their properties is a formidable challenge – but one of the fundamental necessities to ensure safe application with optimized performance. Now, writing in *Nature Physics*, Till Böhmer and colleagues describe ageing in terms of stationary and reversible equilibrium properties, using the concept of an internal clock that triggers the dynamics of a glass. This result has profound implications for the field of disordered systems<sup>1</sup>.

When a liquid glass-former is cooled below its glass transition temperature, it solidifies into an out-of-equilibrium state that spontaneously evolves toward a metastable equilibrium phase. This temporal evolution, called physical ageing, is a highly nonlinear process involving irreversible changes in the glass's thermodynamic state and microscopic structural reorganizations<sup>2</sup>. Most studies on ageing are concerned with the temporal evolution of a given observable, such as enthalpy, volume or elastic constants<sup>3</sup>. The temporal evolution of these observables, structure–property relationships and scaling laws can be measured, but such measurements often remain limited to the specific material under investigation and the technique used.

Introduced in 1971, the concept of material time allows one to linearize the irreversible ageing process: real time is replaced by an internal time inherently related to the glass via its relaxation rate, which changes during ageing<sup>4</sup>. More recently, the material-time approach has been used to successfully rescale ageing data in molecular glasses obtained after a temperature jump from a few millikelvin to several kelvin, starting from an equilibrium configuration<sup>5,6</sup>. These studies mainly focused on the thermal response of the glass, where the time evolution of the glass's thermodynamic state was monitored.

Approaches based on characterizing spontaneous fluctuations during ageing typically rely on the application of a small perturbation, for instance of the mechanical<sup>2</sup> or the electric field<sup>7</sup>, in the time domain or in the frequency domain. As ageing is monitored in the glassy state, where the typical timescales of fluctuations largely exceed a second, these methods only allow one to access the short-time and high-frequency portion of the glass relaxation spectrum, thus preventing access to the overall features of the glass's linear response, as accessing larger times/lower frequencies would provide the response of an evolving system<sup>2</sup>.

Böhmer and colleagues used a challenging experimental and data-analysis approach to apply the concept of material time to a

variety of ageing materials, including molecular glasses, polymerizing systems, colloidal gels and numerically simulated glass-formers. They employed the multi-speckles approach used in visible-light and X-ray photon correlation spectroscopy experiments<sup>8,9</sup> to obtain almost 'instantaneous' time-resolved intensity auto-correlation functions, which describe the long-time decay of the density fluctuations, thus probing the ageing of the main  $\alpha$  structural relaxation process during equilibrium recovery. The latter represents the microscopic structural reorganizations that occur in the material, and the characteristic time of these rearrangements is proportional to the shear viscosity of the system.

This approach allowed Böhmer and colleagues to obtain the material time of each glass from the measured autocorrelation functions, without making any a priori assumptions about the underlying relaxation mechanism controlling ageing. This unprecedented result stands in contrast to previous studies, which assumed that the structural  $\alpha$  relaxation was the underlying mechanism mediating ageing<sup>5,6</sup>. In this way, the authors validated the material-time formalism and rescaled all data to a single curve, thus linearizing the ageing process.

Remarkably, the concept of material time, when applied to temperature jumps of a few Kelvin, is thus shown to describe the ageing of different families of systems, independent of the experimental technique used to measure it. Furthermore, the authors demonstrated the occurrence of equilibrium properties during ageing by validating the triangular relation of materials at thermodynamic equilibrium, which establishes the time-reversibility of the signal, and also by considering the statistical stationarity of the intensity fluctuations as a function of material time.


The ability to describe an out-of-equilibrium process in terms of reversibility and stationarity, normally valid at equilibrium, represents an important step forward for our understanding of ageing in complex systems, with strong theoretical implications, complementing previous research in which the material-time concept was applied to the description of the time-dependent variation of the glass thermodynamic state<sup>5</sup>. At the same time, as with any new important advancement in science, the work raises several questions, which should be addressed in future studies.

The material time framework concerns only the evolution of the  $\alpha$  relaxation process. However, additional secondary or microscopic processes generally referred to as non- $\alpha$  relaxation are active in glasses and can contribute to equilibrium recovery. These processes can lead to a failure of ageing linearization, especially for large temperature jumps from the supercooled liquid into the deep glassy state<sup>6</sup>, where the  $\alpha$  relaxation rate tends to vanish.

An indication of the role of other relaxation processes is already offered by Böhmer and colleagues in the case of a concentrated colloidal suspension of laponite (lithium sodium magnesium silicate), which features an almost stationary secondary relaxation process at time scales shorter than, but still relatively close to, those associated with the  $\alpha$  relaxation process<sup>10</sup>, and also in the case of a simulated Lennard-Jones glass, where the time scale for structural reorganization is close to that of additional microscopic processes.

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## Competing interests

The authors declare no competing interests.