

GLASS PHYSICS

A wing explained

The origin of a well-known feature in relaxation data seen in many glass-forming materials has now — possibly — been resolved by means of computer simulations.

Reiner Zorn

In a correspondence in 1995 P. W. Anderson wrote:¹ “The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition.” Unfortunately, the prediction in the next sentence in his letter did not come to pass: “This could be the next breakthrough in the coming decade.” Indeed, many questions in this field remain open. One of the most important is the spectral shape of the so-called α relaxation, the process dominating the dynamic properties of a material, such as its viscosity, close to the glass transition. Writing in *Nature Physics*, Benjamin Guiselin and colleagues² now provide insights into the mechanism of the α relaxation, signifying an important step towards a better understanding of the glass transition.

The dynamics of a glass-forming liquid is usually studied by measuring its dynamic complex susceptibility. An oscillating field (for example, electric or mechanical stress) is applied to the sample and its response (polarization or strain) is measured. When the imaginary part χ'' of the resulting susceptibility is plotted against the frequency ω , one typically finds a number of peaks. Traditionally, the peaks are labelled in ascending order of frequency using Greek letters. Usually, the α peak shows the same temperature dependence for all susceptibilities. Therefore, it is assumed that this peak originates from the fundamental relaxation process in a glass-forming liquid — accordingly named α relaxation.

Phenomenological descriptions of the α relaxation are usually based on functions (as that proposed by Kohlrausch already in 1854³) that produce an $\omega^{-\beta}$ ($\beta < 1$) decay of $\chi''(\omega)$ for high frequencies in the spectrum. Since the 1990s it has been known that for many materials a transition to $\omega^{-\sigma}$ takes place for even higher frequencies, where $\sigma < \beta$ (ref. 4). From its appearance in a log–log plot of $\chi''(\omega)$, this feature is called excess wing (EW).

Two ‘schools’ have emerged with different views on the origin of the EW. While one school considers the EW a part of the α relaxation⁴, the other takes it as a ‘buried’

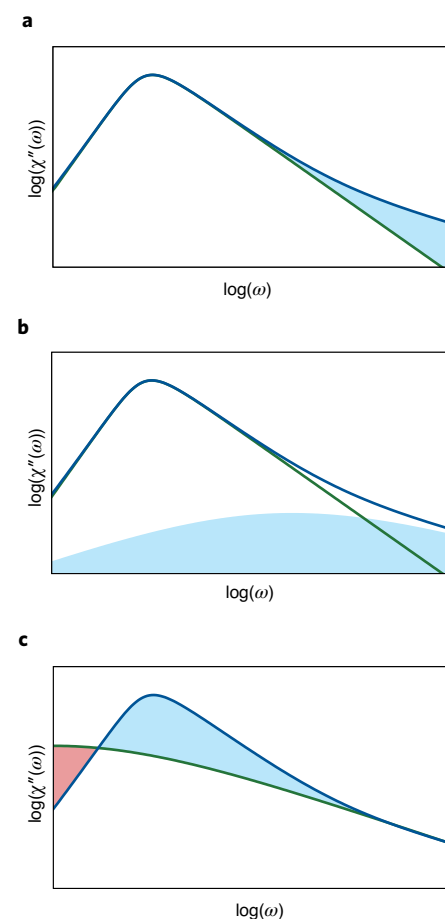
peak from the β relaxation⁵, a faster process that is often present in glass-forming materials in addition to the α relaxation (Fig. 1a,b). There have been numerous attempts from both sides to prove their point. For example, a common temperature scaling of the α peak and the EW has been demonstrated for many materials^{4,6}. This would suggest that both are in fact a single feature. On the other side it was possible to decompose the compound of the α peak and EW into separate α and β peaks by ageing for other materials⁷. Ultimately, these attempts have not been able to settle the debate.

Most experimental studies of the EW are done by means of dielectric spectroscopy (DS) because it provides an enormous frequency range, often up to 12 decades. In principle, the problem can also be tackled by molecular dynamics (MD) simulations. But these face two problems resulting from the limited simulation time. Firstly, the α relaxation becomes extremely slow near the glass transition. In fact, the glass transition temperature is empirically defined as the temperature where the α relaxation time exceeds 100 seconds, a value that is out of reach for MD simulations. Secondly, it often takes an even longer time for a sample to reach equilibrium after cooling.

The second problem has recently been overcome by a procedure devised by Ludovic Berthier, co-author of the article² now published in *Nature Physics*, the ‘swap algorithm’⁸. The algorithm speeds up the ageing processes tremendously by ‘unphysical’ particle swaps in addition to conventional Newtonian dynamics. (Of course, these are switched off during the ‘production runs’ from which correlation functions are calculated.) Guiselin and colleagues have now used this technique to prepare deeply cooled systems that clearly show an EW in the relaxation spectra. Compared to macroscopic methods like DS, MD has the additional benefit of offering insight into the motion of individual

Fig. 1 | Explanations of the excess wing (EW) seen in relaxation spectra of glass-forming liquids.

The blue line schematically represents the experimental $\chi''(\omega)$ curve. The green line indicates the assumed ‘bare’ α relaxation. **a**, In one traditional explanation, the EW results from a change of the slope in the high-frequency wing, but is an integral part of the α relaxation. **b**, In another traditional interpretation, the EW results from an additional relaxation, the peak of which is buried (blue shading) under the α relaxation wing. **c**, In the explanation now offered by Guiselin and colleagues², the fundamental spectrum (green line) is very broad and identical to the EW for high frequencies. The facilitation mechanism sweeps up low frequency modes (red shading) and displaces them into the feature that appears as the α relaxation peak (light blue shading). Figure adapted from ref. 2, Springer Nature Ltd.




particles. By looking at snapshots of the individual mobilities and calculating their statistics, the authors uncovered a two-step process. In the first step, small mobile regions pop up at sparse positions. Later, the regions grow, coalesce, and finally span the whole sample. Relating the times of the snapshots to the frequencies in the spectrum, they connect the first step with the EW and the second with the α peak. This is supported by the statistical analysis of the waiting time for the first step, which shows the same exponent σ as the EW in the spectrum.

In order to distil the essence of the mechanism, the authors then constructed a surprisingly simple model based on dynamic facilitation. They started from a trap model, that is, an energy landscape with maxima of equal height but minima of randomly distributed depth. The bare version of the model can be easily solved analytically by converting the distribution of energy barriers into one of relaxation times. The crucial ingredient the authors add is that all trap depths are shifted randomly if any one of them has relaxed. This situation can only be solved numerically. The obtained spectra were strikingly similar to those from the MD

simulations and also to spectra obtained in DS experiments. The low frequency part of the spectrum is 'swept up' into a peak with the high frequency part remaining as a wing (Fig. 1c).

The conclusion is that the EW is not an 'offshoot' of the α peak, but that it is the other way around: the α peak results from a small fraction of relaxed particles assisting the relaxation of others, a mechanism often dubbed dynamic facilitation, modifying the extremely broad spectrum that results from the trap distribution. In one way this supports the 'integral school' in their claim that α relaxation and EW are inseparable phenomena. But at the same time, it turns the conditionality around: the $\omega^{-\sigma}$ spectrum is the fundamental feature and the α peak with its $\omega^{-\beta}$ wing the modification.

This conclusion is revolutionary in the literal sense of turning something around. Considering the time the discussion of this issue has already lasted, I am not sure whether it will be the final word. Probably, there will be more MD simulations of different systems. Maybe it will even be possible to deploy methods like quasielastic neutron scattering, which allow direct

insight into the molecular dynamics of real materials. In any case, it is a fresh point of view that will rekindle the efforts to come to a final answer to questions pertinent to the glass transition. 

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Competing interests

The author declares no competing interests



QUANTUM MATERIALS

Controlling ferroelectricity below the surface

Optical control of material properties is usually limited to the region that absorbs the light. Coupling to lattice vibrations that travel close to the speed of light allows ultrafast modulation of polarization deep inside a ferroelectric material.

Elsa Abreu

Quantum materials exhibit many intriguing properties that arise from complex interactions between electronic, structural, spin and orbital degrees of freedom. One such phenomenon is ferroelectricity — the emergence of an internal electric polarization within the material caused by opposite displacements of ions with different charges. The ferroelectricity can be controlled using low-frequency vibrations of the ionic lattice of the material, which can be excited through nonlinear coupling with optically active lattice modes at higher frequencies. Writing in *Nature Physics*, Meredith Henstridge and co-workers show how the ferroelectricity can be controlled in spatial

regions of the material that cannot be reached by the initial optical excitation¹.

Until recently, studies of the dynamics of the lattice in a variety of condensed-matter systems have relied on optical photoexcitation of the electronic subsystem followed by transfer of this energy to the vibrational modes of the lattice — called phonons — via electron–phonon coupling. Another route towards ultrafast control of structural dynamics is by resonant excitation of phonons. One version of this is based on the nonlinear phononics approach² which has been enabled through the development of high-intensity tabletop sources of mid-infrared radiation. In a typical

nonlinear phononics experiment, an ultrafast light pulse in the mid-infrared frequency range excites an infrared-active phonon mode. When this excitation is strong, a nonlinear coupling to other phonons, typically in the terahertz range, becomes significant and indirectly drives these phonons. The corresponding terahertz lattice vibrations occur around a displaced position of the ions. This scheme has been used to control a variety of quantum material responses, such as magnetism³, superconductivity⁴ and ferroelectricity⁵.

One common concern of irradiating the sample with a laser is that it leads to heating, which modifies the state of the system and can potentially induce