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.

"The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition", wrote P. W. Anderson in a correspondence in 1995 [1]. 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* [2], Benjamin Guiselin and colleagues 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 glass forming liquids is usually studied by measuring its dynamic complex susceptibility. An oscillating field (e.g. 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 1854 [3]) which 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 places for even higher frequencies, where $\sigma < \beta$ [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 relaxation [4], the other takes it as a 'buried' peak from the β relaxation [5], a faster process which is often present in glass-forming materials in addition to the α relaxation (Figure 1). 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 α peak and EW into separate α and β peaks by ageing for other materials [7]. 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 range in frequencies, 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 which 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 by Ludovic Berthier, co-author of the article now published in *Nature Physics* [2], 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 which clearly show an EW in the relaxation spectra. Compared to macroscopic methods as DS, MD has the additional benefit of offering insight into the motion of individual 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 distill the essence of the mechanism, the authors then constructed a surprisingly simple model based on dynamic facilitation. They started from a trap model, i.e. 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 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 (Figure 2).

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 which will rekindle the efforts to come to a final answer to questions pertinent to the glass transition.
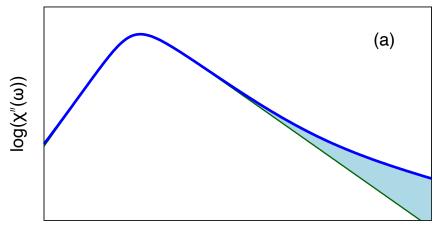
Reiner Zorn

Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science (JCNS-1) and Institute for Biological Information Processing (IBI-8), 52425 Jülich, Germany
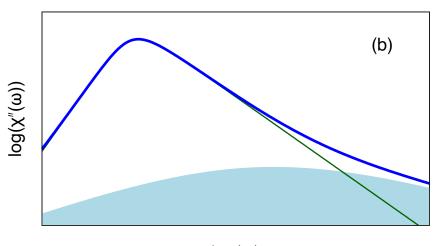
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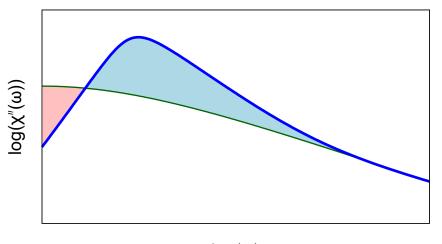
Figure 1: Explanations of the excess wing (EW) seen in relaxation spectra of glass-forming liquids. The blue line schematically represents the experimental $\chi''(\omega)$ curve. The green line indicates the assumed 'bare' α relaxation. (a) In one traditional explanation, the EW results from a change 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 colleagues [2], 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). (Adapted from figure 4(c) in ref. 2.)

(a)

(b)