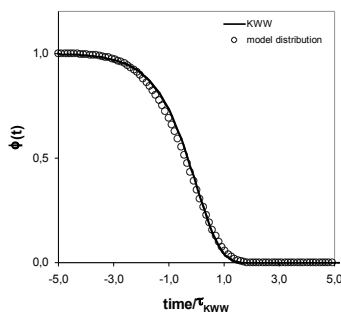


# Phenomenological theory of structural relaxation based on a thermorheologically complex relaxation time distribution.

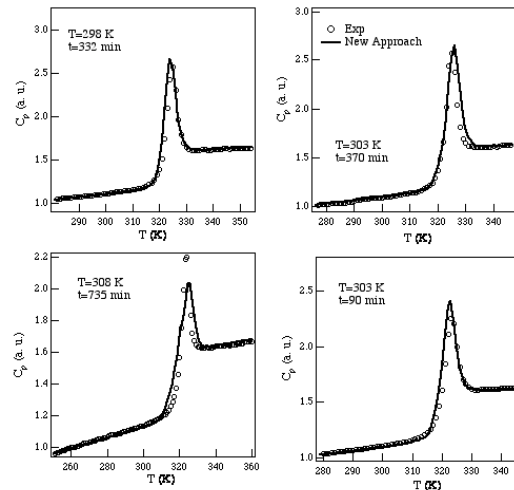
The structural relaxation (or physical ageing) is the slow co-operative dynamic process attempting to restore thermodynamic equilibrium in a glass. Such a process is of fundamental importance on both a practical and theoretical point of view being strictly related to the glass transition phenomenon.

Phenomenological approaches to the study of structural relaxation have yielded several models [1]. A series of assumptions are common to most of these models, the main of them being: (i) The linearization of the relaxation process using the reduced time concept (ii) An asymmetric distribution of relaxation times (iii) The double dependence of the position of the relaxation time distribution in the time axis on both temperature,  $T$ , and on the structure, the latter usually characterized by the fictive temperature,  $T_f$ . (iv) The shape of the distribution of relaxation times has been considered to be independent of  $T$  and  $T_f$  i.e., the process has been considered thermorheologically simple (v) The limit at infinite time of the isothermal structural relaxation is the equilibrium state at that temperature obtained by extrapolation of the experimental data above the glass transition, i.e.,  $T_f = T$ . Four-parameter models such as the TNM model [1] have been applied to many different substances. In generally, these models are able to qualitatively describe the ageing process, but evident quantitative discrepancies have been found in several cases, so that possible extension and/or modifications of these models have been developed [2]. The most part of such modified approach adds a free parameter by changing the treatment of non-linearity effects. On the contrary the development of phenomenological models recognizing thermoreological complexity (i.e addressing the assumption iii) is still missing. We have recently tried to develop such a model testing it by means of Differential Scanning Calorimetry (DSC) experiments on a PVAc sample. We assumed a discrete distribution of 19 exponential relaxation times corresponding to the well known (KWW) stretched exponential relaxation function (see fig. 1)



**Fig. 1:** theoretical stretched exponential relaxation function (KWW) corresponding to a stretching  $\beta=0.5$ , and numerical discretization adopted in our work.

The underlying idea is that the system is composed by an ensemble of small but macroscopic regions characterised by different relaxation time. Each one of these regions is thought to evolve independently of the others with a mechanism essentially equivalent to that provided by TNM model. The single dynamical components are assumed to have the same temperature dependence at equilibrium being characterised only by different prefactors. In this way the regions are characterised by different glass transition temperature and the out of equilibrium behaviour of each dynamical component is different so that the shape of the relaxation time distribution is constant only at equilibrium. In figure 2 we show the fitting of 4 different DSC thermograms recorded on heating a PVAc sample after different thermal histories. We can see the experimental curves are quite well reproduced.



**Fig. 2:** DSC experimental thermograms recorded on a PVAc sample after different thermal treatments together with the best fits obtained with the thermorheologically complex approach.

## References

- [1] I.M Hodge, *J. Non Cryst Solids*. **169**, 211 (1994).
- [2] L.Andreozzi, M.Faetti, M. Giordano, D. Palazzuoli, F. Zulli, *Macromolecules*. **36**, 7379 (2003)

## Authors:

L. Andreozzi (a,b), M. Faetti (a,b), M. Giordano (a,b) J.L. Gomez Ribelles ( c)

(a) polyLab-CNR, Pisa (Italy)

(b) Dipartimento di Fisica, Universita' di Pisa (Italy)

(c) Depto. De Termodinámica aplicada, Universidad Politécnica de Valencia (Spain)