

CALORIMETRIC MEASUREMENT OF STRUCTURAL RELAXATION IN CHALCOGENIDE AND METALLIC GLASSES

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Some special characteristics of the structural relaxation (SR) in chalcogenide and metallic glasses are presented and the current theories dealing with the physical nature of the SR are recalled. The type of experiments used to measure SR by differential scanning calorimetry are reviewed and some rules to be taken into account when measuring calorimetrically the SR are stressed.

A liquid which has been undercooled to a temperature between the melting point and glass transition point is in a metastable state of equilibrium. In most experiments this state is found to be independent of previous history, so that it is well defined in terms of the usual thermodynamic state variables. Thus, except for very viscous liquids, it can be argued that above the glass transition temperature the relaxation times for molecular movements are very short compared to the experimental time scale. When the liquid is undercooled into the glass transition region, the relaxation towards equilibrium lags behind until, finally, the “freezing” of the liquid diffusive motion occurs and the system falls out of thermal equilibrium. Above the glass transition temperature T_g , the undercooled liquid is allowed to explore all the structures or configurations at equilibrium while below T_g the glass is trapped kinetically in one of such configurations. Since the freezing is a gradual process, the glassy state finally reached depends markedly on the cooling conditions in relation to the relaxational properties of the liquid. As a consequence, practically all physical properties of a glass can be modified to some extent by varying the conditions of the cooling process. This holds for macroscopic properties like density, refractive index or enthalpy as well as for details of molecular structure or short range order observed by spectroscopic (Raman and infrared) and diffraction (X-ray and neutron) methods. Nevertheless, the variation of the glass properties is

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generally rather limited compared with the differences existing between, for instance, two allotropic crystalline phases.

The structural relaxation (SR) of glasses can be easily observed calorimetrically because the apparent heat capacity, $C_{p,app}$ of the sample is very sensitive to structural modifications occurring near the glass transition region. In particular, the use of differential scanning calorimetry (DSC) is very fruitful since in most glasses the same equipment can be used for both the thermal treatment of the sample and the measurement of $C_{p,app}$ values. In this paper the special characteristics of SR in glasses will be presented together with some of the theories dealing with its nature (more information can be found in recent papers dealing with this subject [1, 2]). The type of experiments used to measure calorimetrically the SR in chalcogenide and metallic glasses will be reviewed and some rules to be taken into account in the procedure will be outlined.

Structural relaxation in glasses

Relaxation phenomena show common features across many properties and a range of different glass types including chalcogenide, metallic, oxide and polymeric glasses. There are two kinds of relaxation generally observed: The primary or α relaxation accompanying the glass transition and a secondary or β relaxation occurring at temperatures well below T_g . The β relaxation occurs with relaxation times which are long compared with experimental time-scale and has been often found to exist in binary molecular glasses and many polymer and chalcogenide glasses. It is absent in binary metallic alloys but is observed in ternary and quaternary metallic alloys. In some metallic glasses two distinct regions of β relaxation exist [3]. The sub-sub T_g region corresponds to relaxation occurring at temperatures $T_a < T_g - 100$ K. It consists on configurational rearrangements and is independent of the thermal history of the glass. The sub- T_g region ($T_g - 100 < T_a < T_g$) where many physical properties evolve with annealing time, t_a as $\simeq \ln t_a$ in a continuous manner which suggests the existence of a cooperative non-linear relaxation process. Undercooled liquids with a high viscosity show also, above T_g , a strong deviation of the time dependence of relaxation from the usual exponential form [4].

Phenomenological theories of SR assume that the state of the system in the non-equilibrium range depends not only on the temperature and pressure but also on a number of order (or internal) parameters. Experimentally this is confirmed by the fact that the Prigogine-Defay ratio Γ [5], is greater than 1. In practice, at normal pressure only the fictive temperature T_f , introduced by Davies and Jones [6], is used (the fictive temperature is the temperature at which a glass would be found in

equilibrium with the liquid if brought there from its actual state sufficiently quickly to avoid relaxation to occur). The theory of fictive temperature relaxation was first proposed by Gardon and Narayanaswamy [7, 8] and has proved very useful in describing the relaxation of various properties in the transformation range under different thermal treatments [9, 10]. This theory implies the existence of a spectrum of relaxation times [11] and therefore seems to be adequate to deal with undercooled liquids as well as glasses. In these systems many different molecular environments exist, which may lead to different relaxation rates for locally restricted molecular rearrangements. If it is assumed that each relaxation time is related to an activation energy via an Arrhenius type expression, then this approach merges with the activation energy spectrum (AES) model.

The AES theory has been used extensively to describe mathematically the kinetics of relaxation mostly in chalcogenide and metallic glasses. It assumes the existence of a spectrum of activation energies and was first described in general form by Primak [12]. It may hold in systems, such as disordered solids, which may be considered inhomogeneous with respect to the kind of thermally activated processes occurring, so different activation energies would appear to be associated with different portions of the system. Three categories of behaviour have been explained with the AES model, namely log-time kinetics, reversibility and crossover effects [13]. To simplify the theory it has been recognized that most probably in an amorphous solid low activation energy processes are surrounded by processes with relatively high activation energy. Therefore, this tendency suggests the limiting approximation of an assembly of isolated or weakly coupled two-level systems [13, 14].

Another approach uses as a basis for the kinetics of SR the free-volume theory of molecular transport in liquids and glasses [15, 16]. Thermal density fluctuations give rise to a distribution of molecular volumes, which in turn leads to a broad distribution of the rate of molecular rearrangement. In this theory it is assumed that rearrangements occur at an appreciable rate only if the free molecular volume exceeds a certain critical value. The approach has been applied to metallic glasses by several authors [17–20].

Measurement of structural relaxation by DSC

The primary or α relaxation process can be easily seen by the appearance of an endothermic peak in the DSC curve of a glass previously annealed at temperatures below glass transition. One of the important features of DSC is, as previously mentioned, that the equipment allows to perform successively the heat treatment of the sample and the experimental determination of thermodynamic quantities like

the glass transition temperature and the apparent heat capacity of the glass. Both quantities reflect in general the relaxation effects caused by the previous annealing [21–23]. Measurement of the dependence of T_g on heating and cooling rate allows to get an estimate of the activation energy of the mean relaxation time controlling SR in the sample [21].

One of the major problems in the interpretation of the calorimetric results comes from the fact that within the glass transition region the system is outside equilibrium. On passing through the glass transition region the total change of entropy can be split into two terms

$$\Delta S = \Delta_m S + \Delta_i S$$

where ΔS is the true change of entropy on passing through the glass transition region, $\Delta_m S$ is the measured entropy change due to the exchange of heat with the surroundings, and $\Delta_i S$ (≥ 0) is the creation entropy not provided by external exchange [24]. The relation of the apparent heat capacity with thermodynamic quantities is

$$\Delta H = \int C_{p,\text{app}} dT \quad \text{and} \quad \Delta S \geq \Delta_m S = \int \frac{C_{p,\text{app}}}{T} dT$$

ΔH being the total enthalpy change of the material on passing through the glass transition region.

The most commonly used calorimetric quantity to study the SR is the so called enthalpy of relaxation, ΔH_r , [25–30]. The enthalpy of relaxation is the amount of heat lost by the glass during the annealing. In glasses which show a glass transition on heating, it is obtained by subtracting the heat absorbed on heating an annealed sample through the glass transition region from the heat absorbed in the same temperature interval by a non-treated sample. In glasses which recrystallize on heating before showing the glass transition the standard procedure of obtaining the enthalpy of relaxation is as follows: the as-prepared glass is heated up to a temperature, T_{max} high enough to get almost internal equilibrium but low enough to remain below the crystallization temperature. Then it is cooled at a moderate scan rate (say 20–80 deg/min) to the temperature, T_{min} at which measurement of $C_{p,\text{app}}$ will begin. As a consequence of this preliminary heating of the glass it becomes almost insensitive to the initial quenching rate and can be considered a “pre-conditioned” reference sample without low temperature annealing, or non-treated sample. The difference between the heat absorbed in the temperature interval from T_{min} to T_{max} by the annealed and the non-treated samples gives also the enthalpy of relaxation. However, in general two factors can introduce error in this procedure of measuring ΔH_r :

a) The first factor that can influence the measurement is the problem of the non-equilibrium state of the sample between T_{min} and T_{max} . To test the contribution of

any relaxation at temperatures different from the annealing temperature in the measured value of ΔH_r , the non-treated glass can be cycled between T_{\min} and T_{\max} at a particular scan rate and both the total enthalpy, ΔH^{cy} absorbed and total entropy production, ΔS_i^{cy} in the cycle may be measured as

$$\Delta H^{cy} = \oint C_{p,app} dT \quad \text{and} \quad \Delta S_i^{cy} = - \oint \frac{C_{p,app}}{T} dT$$

The last equality is true only if $\oint dS = 0$, that is, if the system returns after the cycle to the same initial equilibrium state. When both quantities are zero within the accuracy of the measurement one can be sure that there is a negligible contribution of any relaxation in the temperature interval between T_{\min} and T_{\max} when the non-treated sample is cycled at that particular scan rate. Therefore, the standard procedure to obtain ΔH_r for an experiment conducted at that scan rate will reflect the relaxation induced at the annealing temperature.

b) The second factor comes from another irreversible effect which is the eventual crystallization of the sample during the heat treatment. If the crystallization occurs when cycling the non-treated glass without express annealing, the effect can be seen with the measurement of ΔH^{cy} , as pointed out in a). If the crystallization occurs during the anneal it can be detected sometimes by the fact that ΔH_r begins to decrease instead of increase with increasing annealing time. Otherwise microscopic methods like X-ray diffraction or transmission electron microscopy (for very small traces of crystallinity) have to be used.

When the maximum scan temperature that can be chosen to avoid the crystallization is too low to ensure an almost total equilibration of the sample at that temperature it is impossible to avoid the relaxation occurring during the heat treatment needed to obtain the reference value of $C_{p,app}$ and therefore the value measured for ΔH_r is lower than the correct one. One approximation method [31] to give some insight into the relaxation behaviour of the glass is to measure the maximum differential specific heat $\Delta C_{p,max}$ which is approximately related to ΔH_r by the expression

$$\Delta H_r \simeq \Delta C_{p,max}(T_{\max} - T_{\min})/2$$

If the relaxation effects which can affect the reference value of $C_{p,app}$ are most effective at high temperatures and have little influence at temperatures at which the maximum for the differential specific heat occurs, then $\Delta C_{p,max}$ may be a quantity more accurate than the overall curve $C_{p,app}$ versus temperature to obtain ΔH_r . It has been used to study SR, in particular in metallic glasses [29, 31].

Conclusions

A considerable effort has been devoted to the understanding of structural relaxation in glasses. Many properties are sensitive to the thermal treatment of the material and this is particularly true for some thermodynamic quantities such as the glass transition temperature, and the apparent heat capacity of the material or the heat released by the material during heat treatment.

In this paper we have tried to give a thorough description of the relaxation processes within the context of current theories in the subject. The problems related with the measurement of the structural relaxation by differential scanning calorimetry in chalcogenide and metallic glasses have been analyzed. Special attention has been devoted to the results of the measurement of the apparent heat capacity of the sample in the glass transition region. Finally we have mentioned the factors that can influence the correct measurement of the heat lost by the glass during the annealing or the enthalpy of relaxation.

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Zusammenfassung – Es werden einige spezielle Charakteristiken der Strukturrelaxation (SR) von Chalkogeniden und Metallgläsern vorgestellt und die gegenwärtigen Theorien über die physikalische Natur der SR zitiert. Die Art von Experimenten zur Messung von SR mittels DSC wurden kritisch besprochen und einige inbetrachtzuziehende Regeln für die kalorimetrische Bestimmung der SR hervorgehoben.

Резюме — Представлены некоторые особые характеристики структурной релаксации в халькогенидных и металлических стеклах. Пересмотрены теории, касающиеся физической природы структурной релаксации. Приведено обзрение экспериментов, проводимых методом ДСК для измерения структурной релаксации. Подчеркнуты некоторые правила, которые следует учитывать при calorimetрическом измерении структурной релаксации.