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Calorimetric investigation on glassy crystals [☆]

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Abstract

The concept of glassy crystals and some of the recent examples are reviewed here to emphasise the wide occurrence of glass transition phenomena in condensed matters not only in liquids but also in crystals. It became apparent that the glass transition is essentially associated with the freezing-in process of any degrees of freedom that a system possesses. The glass transitions which have been observed so far are just one example of the transitions that must be of wide occurrence in solids irrespective of the translational periodicity of the constituent entities. A general relation between the dielectric relaxation and glass transition is considered.

Keywords: Dielectric relaxation; DTA; Enthalpy relaxation; Fullerene; Glass transition; Glassy crystal; Heat capacity; Myoglobin

1. Introduction

Dipolar liquids generally exhibit the dielectric relaxations [1] in their liquid and undercooled liquid states depending on the frequency of the external electric field. The dielectric relaxation is observed when the relaxation time for the configurational change in a liquid becomes of the order of the reciprocal frequency of the field. The dielectric relaxation time τ is defined as $\tau = (2\pi f_m)^{-1}$, where f_m is the frequency at which the dielectric loss reaches its maximum.

There is a class of crystals which exhibits dielectric relaxations. The relaxation derives from freezing-in of orientational polarisation of molecules in the lattice

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which has a three-dimensional periodicity. Again the dielectric relaxation reflects the rate of reorientational motion of the constituent molecule. Thus it can be expected that on cooling the crystal reaches a temperature at which the reorientational motions of the molecules freeze out in a cooperative way, resulting in the disappearance of the contribution of orientation polarisation to the dielectric constant of the crystal. The crystal will show some properties characteristic of a thermodynamically non-equilibrium state.

2. Discovery of glassy crystals

The discovery of glassy crystals can be traced back to 1968 when we measured the heat capacity of cyclohexanol. At that time, we were interested in the determination of dielectric loss of a polar substance by using a specially designed DTA apparatus [2] with built-in electrodes. We found dielectric relaxation in the undercooled high-temperature phase of cyclohexanol. The dielectric behaviour is essentially the same as that of undercooled liquids. The existence of the freezing process of polar molecules in a crystalline substance embarrassed us because the dielectric relaxation is known to be related to the glass transition. Many text-books described the contradictory nature of the concepts between crystals and lqiuids. From careful heat capacity determination [3], we concluded that the undercooled high-temperature phase retained a definite amount of entropy at 0 K and exhibited a large heat capacity jump with relaxational nature at around 150 K. Dielectric measurement [4] of cyclohexanol crystal showed the existence of so-called α and β relaxations which were familiar in many glass-forming liquids [5].

The essential feature of the glass transition is a freezing process of the structural change in a liquid that takes place in response to the variation of an external parameter such as temperature or pressure. This occurs when the relaxation time for structural rearrangement in the liquid crosses the timescale of a particular experimental probe. The same situation might occur in cyclohexanol as in an orientationally disordered crystal with respect to the molecular orientations. Generally the constituent molecules take several orientations in the lattice equi-energetically, leading to the isotropic nature of the system in time- and space-averaged structure. As the temperature is lowered, however, the relaxation time for the reorientational motion is progressively prolonged until it crosses the timescale of the experimental probe. The reorientational motion would freeze out below a particular temperature (T_g) and the remaining disorder manifests itself as a residual entropy.

The latest example of the glassy crystals can be found in isocyanocyclohexane [6]. The molar heat capacity and entropy are shown in Fig. 1. The liquid crystallises into a f.c.c. phase in which the molecules are in an orientationally disordered state. In addition, each molecule in the lattice is known to have two conformations, axial and equatorial. The high-temperature phase is easily undercooled and exhibits three glass transition phenomena. The one occurring at around 160 K is associated with the freezing out of the conversional motion between the axial and equatorial forms

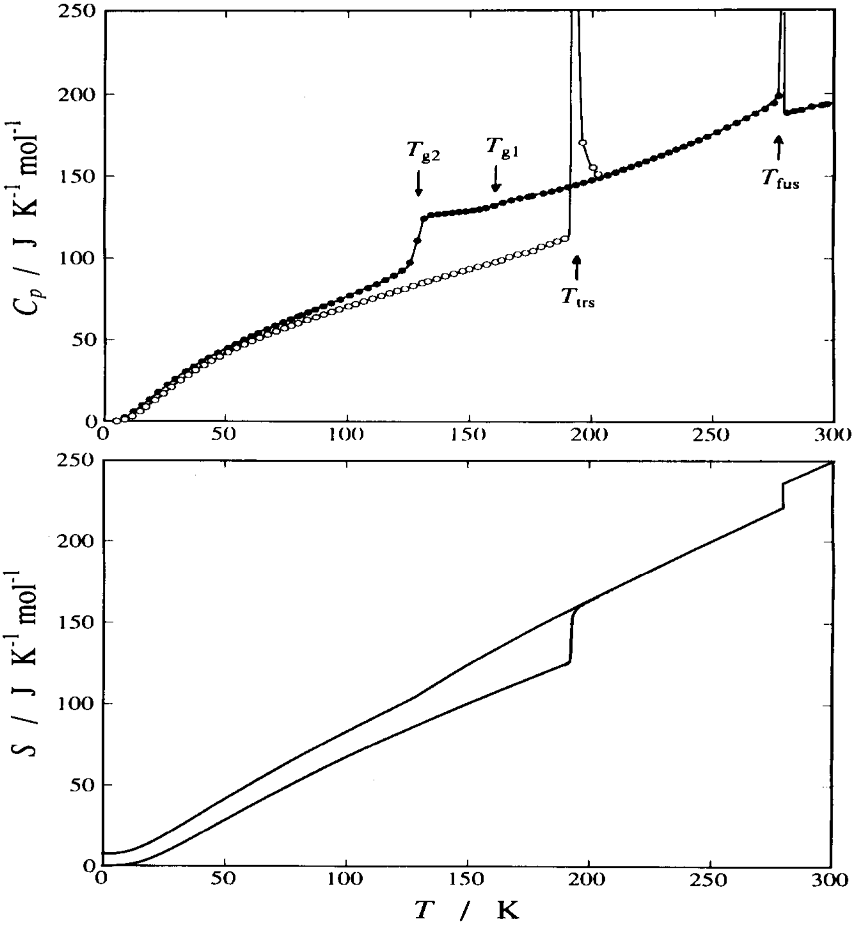

Fig. 1. Molar heat capacity and entropy of isocyanocyclohexane.

[7]. During each equilibration period of the heat capacity measurement, spontaneous changes in sample temperature characteristic of frozen-in systems are observed. An Arrhenius plot of enthalpy relaxation time determined by analysing the rate of temperature change under adiabatic conditions gives an activation energy of 50 kJ mol^{-1} for the kinetic process. The second one is due to freezing out of reorientational motion of molecule and is referred to the main (α) relaxation. The relaxation rate is highly non-exponential and the analysis of relaxation rate is possible only by using the Kohlrausch–Williams–Watts function [8]. The remaining one occurring at 55 K is due to β relaxation and is visible only in an expanded scale. These kinds of multiple glass transitions in a single phase are not uncommon, though they are not usual. The low-temperature ordered phase was realised by annealing the undercooled phase for 3 weeks at 175 K where the interconversional motion is thermally activated to produce an ordered phase composed of molecules with a single conformation.

Ethanol gave the first example of two glass transitions for differently disordered phases in one and the same substance. Ethanol was known to be a good glass-forming liquid. Actually two calorimetric groups [9,10] reported the existence of the glass transition at 97 K. The reported heat capacity data above T_g could not be connected smoothly to those of the liquid above the melting temperature. This unusual behaviour motivated us to re-examine the thermal behaviour of ethanol by DTA experiments under various conditions [11]. Typical runs of the experiments are given in Fig. 2. The Gibbs energy curves that reasonably explain the observed behaviour are given schematically in the same figure. The conclusions we reached can be summarised as follows. The glassy state of liquid is realised only by cooling of liquid with a rate more than 50 K min^{-1}. If the cooling rate is moderate, say

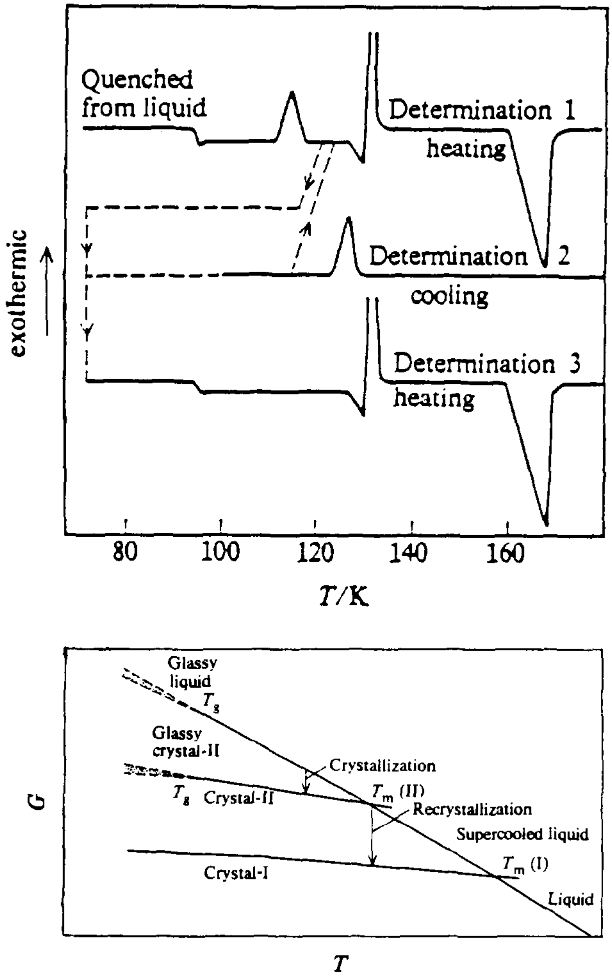

Fig. 2. DTA curves of ethanol under several conditions and Gibbs energy curves of various phases.

5 K min^{-1}, the glassy state of a metastable orientationally-disordered phase is realised. The phase tends to recrystallise into the stable ordered phase after passing its own glass transition and fusion temperatures on heating. Unfortunately, both the T_g values for the liquid and metastable crystal are quite close to each other. Subsequent heat capacity measurement showed that the reported values agree well with those of the glassy crystal. The heat capacity data of the undercooled liquid are much higher than those of the metastable crystal and can be connected reasonably to those of the liquid. Accidentally, both Parks [9] and Kelley [10] produced the glassy crystalline state of ethanol about seventy years ago when people could not imagine the concept of glassy crystals.

3. Glassy crystals in stable phases

There is another category of glassy crystals in which the freezing process occurs in the stable crystalline phase, in contrast to the occurrence in the metastable undercooled phase described above. This situation is similar to the above in that the molecules in the crystal are in an orientationally disordered state at high temperatures. The freezing occurs during cooling before the crystal reaches a hypothetical ordering transition at which the orientational disorder would be removed. The paramount example of this category of the glassy crystals is found in ice. Hexagonal ice I_h has long been known to be a crystal that does not obey the third law of thermodynamics. Giauque and Stout [12] observed a residual entropy of 3.4 J K^{-1} mol^{-1}. The nature of disorder corresponding to the entropy was explained by Pauling [13] in terms of the half-hydrogen statistical model, but the model did not predict anything about the method of realisation of an ordered ice. Debye [14] pointed out difficulty of explaining the large dielectric constant of ice arising from the orientation polarisation if the crystal follows faithfully the "ice rules" proposed by Bernal and Fowler [15]. The absence of any ordering transition in ice I_h has puzzled many scientists over a period of more than fifty years. Onsager [16] suggested using an impure ice sample which might relax the severe constraints imposed on the water reorientational motion by the ice rules, hence realising an ordered ice that obeys the third law.

In fact, an ice specimen doped with a slight amount of KOH exhibited a first-order phase transition at 72 K [17] which removed a substantial fraction of the residual entropy, because the impurity acted as a catalyst to enhance the orientational mobility by creating Bjerrum-type defects in the lattice which remove kinetic hindrance for the observation of the ordering transition in the laboratory time. The relaxation time determined dielectrically for the KOH-doped ice was found to be shorter by a factor of 10^8 at 90 K than that of pure ice [18]. The highly cooperative nature of water reorientational motion under the ice rules in pure ice makes the relaxation time for the motion longer and longer as the temperature is lowered until the motion freezes out at a particular temperature range far above the equilibrium transition temperature. The actual glass transition in pure specimens occurs at around 100 K [19].

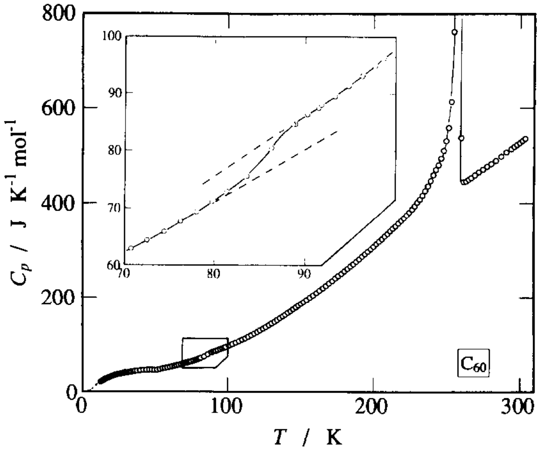

Fig. 3. Molar heat capacity of fullerene C_{60}.

The latest example of this category is fullerene C_{60} crystal [20] which belongs to one of the orientationally disordered crystals at room temperature. On cooling, the crystal undergoes a first-order phase transition at about 260 K into a low-temperature phase of a simple cubic system. According to a neutron diffraction experiment [21], there are two kinds of molecular orientation with a slight energy difference in the low-temperature phase. As the temperature decreases, the fraction of energetically favoured molecules increases exponentially from 0.5 at 260 K to 0.84 at 87 K, below which the fraction ceases to increase any more. The change in dynamic nature of the reorientational motion of the molecule is reflected in the lattice parameter plotted against temperature. The unit cell constant changes its slope at around 87 K. A glass transition due to freezing out of the reorientational motion in the crystal was suspected.

In order to examine the reality, the heat capacity was measured in the temperature range between 10 and 300 K, and the result is given in Fig. 3. The result clearly showed that this was really the case. The heat capacity jump corresponds just to the change in the lattice constant. At the same time, the heat capacity anomaly is accompanied by systematic temperature drifts characteristic of the glass transition in liquid. By simple application of the first law of thermodynamics to the spontaneous temperature changes observed during each equilibration period, the characteristic time for the enthalpy relaxation can be determined. The relaxation time data thus derived are well correlated with those derived from absorption of ultrasonic wave [22] and NMR [23] experiments in an Arrhenius plot, as is shown in Fig. 4. This means that the three independent experiments observed the same molecular dynamics by windows with different timescales. The reorientational motions of molecules freeze out by slowing down before the crystal realises a completely ordered state. The activation energy determined from the slope of the straight line is about 20 kJ mol^{-1}, which is large enough to overcome at low temperatures. The

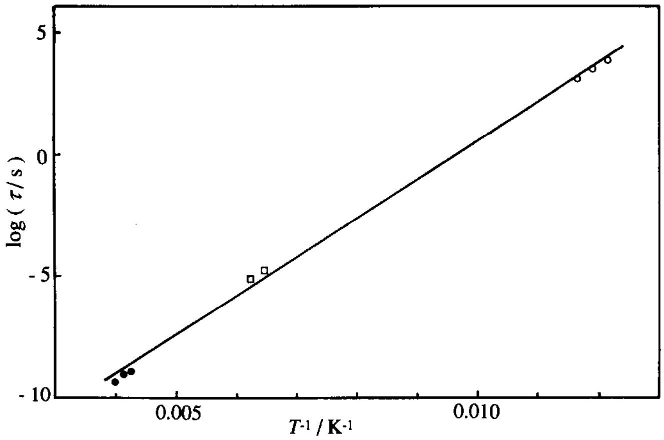

Fig. 4. Arrhenius plot of relaxation times obtained by calorimetry (○), absorption of supersonic wave (□) and NMR (●) experiments.

calculated residual entropy is $-R$ [0.84 ln 0.84 + 0.16 ln 0.16] = 3.65 J K^{-1} mol^{-1}. For C_{60} crystal, we are presently unable to remove the kinetic hindrance in attaining a fully ordered state. Doping of C_{70} molecules would be an interesting experiment.

4. Glass transition in protein crystal

An ensemble of protein molecules with the same conformation in the crystalline state contains a variety of slightly different structures called conformational substates. There are many theoretical and experimental works pointing out that proteins have a stereo map of the Gibbs energy surface composed of a large number of energy valleys separated by energy hills [24]. At physiological temperature the protein fluctuates among these substates as if it were liquid. This fact motivates us to compare protein crystals and glass-forming liquids with respect to fluctuations and relaxations which seem to play important roles in exhibiting biological functions. For example, a change in dynamics of the myoglobin molecule is indicated from Mössbauer spectroscopy [25] at the iron centre at around 200 K when the crystal is cooled from room temperature. The mean-squared amplitude of the iron ion changes its slope about four times, indicating excitation of some degrees of freedom of the biomolecule above that temperature. This biphasic behaviour is also observed in the Debye–Waller temperature factor of ribonuclease A crystal [26] at around 220 K, as revealed by X-ray crystallography. At the same time, the globular protein loses its physiological function. The temperature must correspond to a glass transition associated with immobilisation of the conformational change in the crystal. In order to examine this possibility, it is essential to confirm that the anomalous behaviour is of a relaxational nature. Adiabatic calorimetry is one of the best methods by which this may be verified.

Since the amount of sample is highly limited in quantity, we have used a low-temperature microcalorimeter that enables us to determine the heat capacity of samples of less than 1 g without significant loss of general accuracy and precision of the data [27]. The basic idea of the calorimeter for small samples is to remove a thermometer from a sample cell and transfer the sample temperature to a copper block whose temperature is measured by standard thermometry. This is because the heat capacity of commercial thermometers is too large to obtain accurate data for small samples. Heat exchange through thermometer wires can be removed by this technique. Also a Joule heating effect caused by the thermometric current becomes significant when the sample amount is small. The temperature difference between the sample cell and the copper block is monitored by three pairs of fine thermocouples and the deviation signal is amplified. The output signal is used to control the temperature of the block in order to keep essentially the same temperature with that of the cell. The inaccuracy in the temperature transfer system in an improved version [28] is 1.7 nV which corresponds to 200 μK at 20 K, 60 μK at 80 K and 27 μK at 300 K.

Monoclinic horse myoglobin was chosen for experimentation in view of its rather easy crystallisation from aqueous solution including buffers. The crystal structure is well known [29]. The monoclinic modification has the space group $P2_1$, and the lattice parameters depend on the nature of buffers. The crystallisation procedure reported by Kendrew [29] was followed. A typical size of the obtained crystal was 0.1×0.1 mm^2 and the crystals were found to have the same morphology as that reported by Kendrew [29]. Since water is an important ingredient in the protein crystal, nine types of sample with different water contents were prepared by careful drying of the virgin crystals. The heat capacity of the sample containing 27.3 mass% water is given in Fig. 5.

The initially cooled sample exhibited a large heat capacity jump accompanied by systematic temperature rise and fall arising from enthalpy relaxation at around 185 K. On further heating, an exothermic effect due to crystallisation of some remaining water molecules was found to start at around 220 K. The sample was then annealed at 230 K for two days until the process ceased almost completely. The annealed sample showed the glass transition at about 170 K with smaller heat capacity jump than that of the first one. This indicates clearly that some of the water molecules strongly affect the dynamic nature of protein molecules in the crystalline state. Also it is evident from the analysis of the enthalpy of fusion that there are at least three types of water molecule in the protein crystal. The so-called free water crystallises during the initial cooling. Part of the remaining water is crystallisable only by annealing the crystal above T_g at which the crystals recover their mobility. That remaining is bound water which was completely non-freezable during our experimental time. As the water content decreases, the amount of bound water increases relative to that of free water. Below about 20 mass% water, there is no freezable water. For example, the sample containing 3.0 mass% water exhibited the glass transition at 283 K and no longer exhibited the exothermic effect due to crystallisation of water above T_g.

Temperature drift rates arising from the freezing process are shown in Fig. 6 and these data were analysed to derive the relaxation time. The relaxation time data

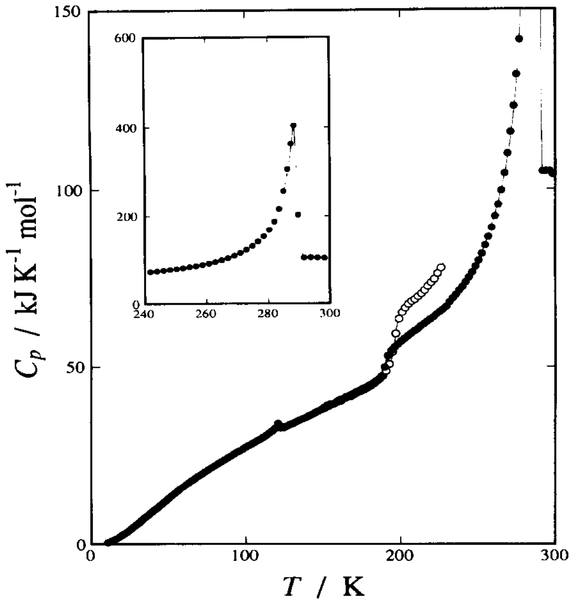

Fig. 5. Heat capacity curves of myoglobin crystal containing 27.3 mass% water for initially cooled (○) and annealed (●) samples.

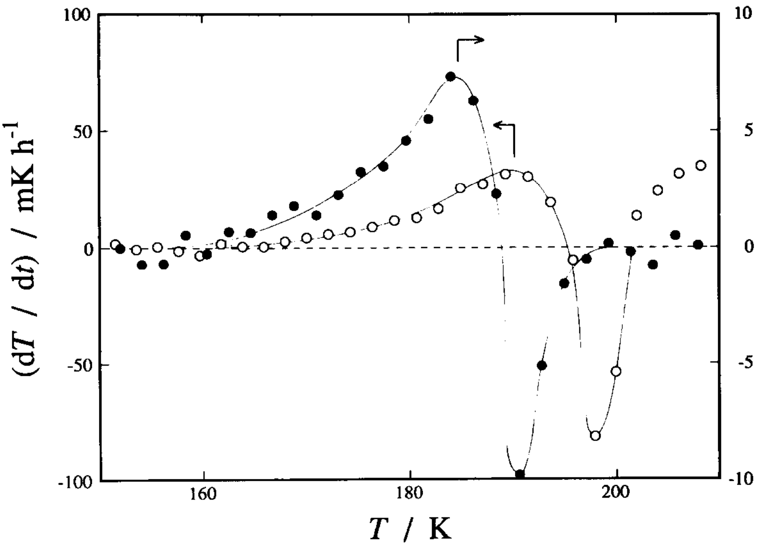

Fig. 6. Spontaneous temperature drift rates of myoglobin crystal for initially cooled (○) and annealed (●) samples.

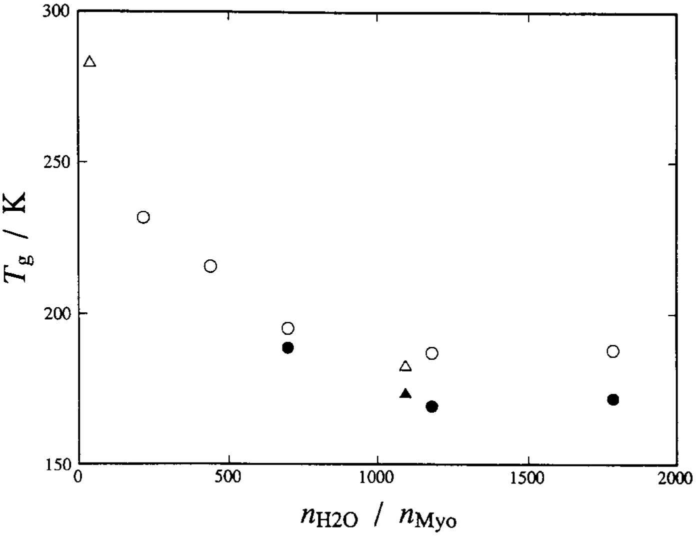

Fig. 7. Glass transition temperatures of myoglobin crystal for initially cooled (○) and annealed (●) samples as a function of water content.

plotted against reciprocal temperature gave a straight line. The corresponding activation energy was found to increase from 50 to 70 kJ mol^{-1} as the water content was decreased and agreed with values obtained from Mössbauer spectroscopy and Rayleigh scattering [25] experiments. The glass transition temperature of myoglobin crystal was determined in this way as a function of the water content and the results are summarised in Fig. 7 [28]. The T_g value increases as the water content is decreased. This can be explained by a loosening effect of water [30]. The hydrated water behaves as a plasticiser to enhance the protein flexibility. If the curve is extrapolated to zero water content, we can recognise that the protein crystal without water is in the glassy state at room temperature. It may be feasible to generalise that any biological materials without water are merely inorganic substances which are unable to exhibit any physiological functions.

We can conclude from these experimental findings that an important aspect of the glass transitions in myoglobin crystals involves the conformational motion of the protein molecules, and the water molecules take part in the cooperative mobility of the giant molecules in an essential way to characterise the actual freezing process. Many examples of glassy crystals have been discovered by the chemical thermodynamic group at Osaka University and they are listed in Table 1. It is now clear that the myoglobin crystal belongs to a novel category of glassy crystals listed in the table in the sense that the two main components in the crystal couple each other in their mobility to determine the dynamic nature of the glass transition. The coupled modes of conformational and configurational degrees of freedom of both molecules are brought into a frozen-in state, keeping the translational invariance of protein molecules with respect to their centres of mass.

Table 1
List of glassy crystals and their glass transition temperatures

Metastable phase	T_g/K	Stable phase	T_g/K
Thiophene	37	Thiophene	42
2,3-Dimethylbutane	76	Buckminsterfullerene C_{60}	87
Isocyanocyclohexanol	55	β-Cyclodextrin $\cdot$ $11H_2O$	150
	130	Ethylene oxide $\cdot$ $6.86H_2O$	85
	160	Tetrahydrofuran $\cdot$ $17H_2O$	85
$CFCl_2$–$CFCl_2$	60	Acetone $\cdot$ $17H_2O$	90
	90	CO	18
	130	RbCN	30
Ethanol	90	$CsNO_2$	42
Cyclohexane I	92	$TlNO_2$	60
III	93	$SnCl_2 \cdot 2H_2O$	150
Cycloheptane I	100	$SnCl_2 \cdot 2D_2O$	155
II	100	H_2O (hexagonal)	105
III	93	(cubic)	140
Cycloheptatriene	106	D_2O (hexagonal)	115
Cycloheptanol	135	pinacol $\cdot$ $6H_2O$	155
Cyclohexanol	150	H_3BO_3	290
$Cs_{0.7}Tl_{0.3}NO_2$	48	D_3BO_3	298
		lysozyme	≈150
		myoglobin	≈170

5. Concluding remarks

Valuable information about disorder in certain dipolar solids has resulted from measurements of the dielectric constant and loss. The dielectric constants of many dipolar liquids drop suddenly at their melting temperatures on cooling, indicating formation of ordered phases. Some liquids can be cooled without crystallisation to realise metastable undercooled phases and exhibit dielectric relaxations. As the temperature of a liquid is lowered under a fixed frequency of external a.c. field, the reorientational motion starts to lag behind the periodical change in the field. This happens when the relaxation time for the motion crosses the reciprocal frequency of the field, resulting in maximum dielectric loss. The molecules in the liquid can no longer respond to the sinusoidal change in the alternating field. The molecular orientation is frozen-in below that temperature as probed by the particular timescale. The actual glass transition temperature corresponds roughly to the relaxation time of 1 ks. This is because the glass transition temperature was determined traditionally by heat capacity measurement, and the timescale of a single heat capacity determination was about 1 ks [31].

The same thing can happen in some orientationally disordered crystals in which the centres of mass of the molecules form a three-dimensional periodic lattice but their orientations are random along several crystallographically unique axes. The reorientational motions are dynamic in nature at high temperatures but become slower and slower as the crystal is cooled. The corresponding freezing process must occur at a particular temperature at which the relaxation time becomes of the order of 1 ks. Many dipolar crystals are known which exhibit the dielectric relaxations, and they are potentially glassy crystals on further cooling. The heat capacity drops suddenly more or less in a narrow temperature range and the associated entropy remains constant below that temperature. Naturally this kind of orientationally glassy state should be extended to crystals which are composed of non-polar molecules; hence their freezing processes cannot be detected dielectrically. Thus the glass transitions are not characteristic properties of liquids but of wide occurrence in condensed matters irrespective of the aperiodic arrangement of the molecules in space [32]. In spite of the paradoxical nature of the concepts involved in the terminology, time is now giving it proof [33] as an intriguing new state of aggregation of molecules.

In this way, the anomalous thermal behaviour observed in seemingly dissimilar compounds such as C_{60} and protein crystal can be analysed on the same thermodynamic basis for irreversible processes. This clearly indicates the power and universality of thermodynamic principles. Also it is worth emphasising that adiabatic calorimetry can be extended to the quantitative study of relaxational process due to stabilisation from a non-equilibrium to the equilibrium state by utilising its high thermal stability and temperature resolution. This opens a new way to the study of ultra-slow dynamics of any irreversible process in a frozen-in disordered system if the process involves even a small enthalpy change.

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