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Glassy crystals: correlation between molecular symmetry and glass transition ☆

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Abstract

Using the symmetry departure concept, a tentative classification of molecular glassy crystals is presented. In particular, it is shown that plastic crystals of symmetrical molecules which do not lead to glassy crystals have their counterparts in plastic crystals of homologous substituted molecules which do. Other classes take into account heterocyclic molecules, incompatible symmetries and molecular interconversion motions. An extension of this classification is suggested to handle the cases of fullerene C_{60} and of some molecular mixtures.

Keywords: Glass transition; Glassy crystal; Plastic crystal; Symmetry

1. Introduction

In 1974, Suga and Seki extended the concept of the glassy state to the non-equilibrium solid state in general [1] which can be characterized by the existence of a glass transition, of enthalpy and volume relaxation phenomena, and of a residual entropy at 0 K.

Glassy crystals, the first example of which was recognized in crystalline cyclohexanol [2], belong to such systems: they are glasses from the thermodynamic point of view, and they are still crystals according to radiocrystallographic measurements. They can be obtained by cooling orientationally disordered crystalline phases. In the cases of

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☆ Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

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cyclohexanol [3] and cyanoadamantane [4], it has been shown that the glassy phases and their dynamically disordered mother phases correspond to the same space and time-averaged structures, with the same number of possible molecular orientations at each lattice site, the same occupancy factors, and essentially the same mean local disorder.

From the dynamic point of view, the glass transition is a kinetic phenomenon which is correlated with the "freezing" (more accurately "the slowing down") of a large-amplitude motion [5,6]. For instance, in cyclohexanol [5,6,7], cyclooctanol [6], 1-cyanoadamantane [8,9] and 1,2-difluorotetrachloroethane [6,10], the main (or α) glass transition corresponds to the freezing of the endospherical or quasi-isotropic molecular motion.

To describe the conditions that a reorientational motion must fulfill to lead to a glass transition, let us consider [11] the plastic crystal model according to which each molecule at its lattice site can reorient between n different orientations [12]. The symmetry group of these orientations contains the site symmetry, because the "mean molecule" which is constructed by superimposing the real one in all orientations at a given site must comply with the crystalline symmetry. Let us assume that each orientation corresponds to a different potential depth. These potential wells will be separated by energy barriers the crossing of which will be ruled by energy fluctuations within the solid. At thermodynamic equilibrium, the populations of these different energy levels will comply with Boltzmann's law.

Starting at the temperature T_1 at which thermodynamic equilibrium is achieved, the system is cooled down to T_2, a temperature at which the mean characteristic time of the involved reorientational motion is larger than 10^3 s. The energies of the orientational states at equilibrium may be slightly modified, because of thermal contraction for instance, but mainly the populations of these states will change. In particular, the occupancy factors of the lowest energy states will increase at the slow pace of the effective energy fluctuations within the system. The observer will witness a large-time enthalpy relaxation: the lower the T_2, the larger this relaxation will be. This of course illustrates the fact that "the glass transition is not a phase transition. It is a change from a non-equilibrium to equilibrium state" [13].

Let us now consider systems in which all molecular orientational states correspond to the same energies. This would be the case of a solid within which the molecules would undergo $2\pi/n$ reorientations around one of their C_n axes. Obviously, freezing such a motion would entail no departure from equilibrium.

Therefore, it may be stated that a glass transition will arise in a crystalline phase within which reorientational molecular motions occur only if some "symmetry departure" exists. This will be so if the symmetry group of the molecular orientations in the crystal is not a subgroup of the symmetry group of the molecule or, if it is, when the respective symmetry axes of these two groups do not coincide. As the referee has noted, this will also be the case when the site symmetry is higher than the molecular one. As a result, the different molecular orientations will be discernible, thus entailing a possible disorder which will allow the system to depart from thermodynamic equilibrium.

2. Tentative classification of glassy crystals

In this paper, we present a tentative classification of glassy crystals. As a result of what we have just described, molecular symmetry is the key element [14].

2.1. Symmetry departure through molecular substitution

In a crystal within which the molecules reorient around one of their symmetry elements which is common with a symmetry element of the crystal or a crystal in which the molecules undergo $2\pi/n$ reorientations around one of their C_n axes, the molecular orientations are not discernible and there is no definite disorder. For instance, this is the case for ethane, neopentane, cyclohexane, benzene, adamantane and ferrocene.

Substituting one chemical group or heteroatom in the above molecules will result in a symmetry departure; in most cases, a symmetry center will disappear and the different molecular orientational positions at their lattice sites will become discernible: as a consequence, a glassy crystal will emerge at low temperature.

Therefore, plastic crystals of symmetrical molecules which do not lead to glassy crystals have their counterparts in plastic crystals of homologous substituted molecules which do. Table 1 shows this correspondence.

No glass transition has ever been observed in mono-deuterated benzene which is reported in Table 1 and which exhibits a very weak symmetry departure indeed. Nevertheless, NMR measurements [19] reveal a non-symmetrical ln T_1 vs. $1/T$ curve which is typical of glassy crystalline behavior [20, 21]. It is likely that a glass transition, if it exists in this crystal, would not be intense enough to be observable.

2.2. Heterocyclic molecules

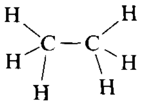
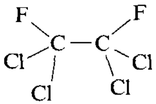
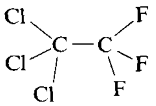
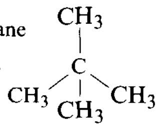
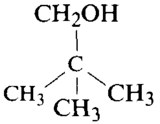
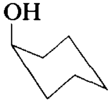
Solids of plane five-membered heterocyclic molecules were investigated first because their molecular shape favors the existence of quasi-five-fold reorientational motions in the cyclic plane and because it was originally thought that the uncrystalline five-fold symmetry would help to generate glassy states. But it was soon understood [22] that the quasi-five-fold symmetry of thiophene does not entail glassy states, but it is probably the origin of the incommensurate phases which are observed in both phase sequences of thiophene [23, 24].

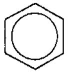
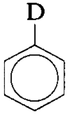
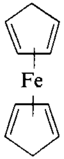
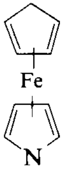
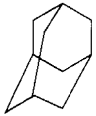
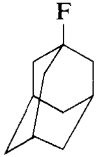
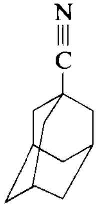
However, the heteroatom plays the part of a discernibility probe : it is the source of disorder which entails a glass transition.

Glass transitions have been observed in both crystalline phase sequences of thiophene near 40 K [25, 26] and in crystalline thiazole [27, 28], isothiazole, and isoxazole [28].

Other derivatives of these compounds also exhibit glassy crystalline phases : 2-methylthiophene [29], 2-chloro- [30] and 2-bromothiophene [31], 3-bromo-thiophene, and 2,5-dimethylthiophene [32]. Many others are still to be found.

Table 1
Substitutions of symmetrical molecules leading to glassy crystalline phases

Symmetric molecules giving reorientational phases	Molecular symmetry	Space group and site sym.	Subsituted molecules leading to glassy crystals		Molecular symmetry	Ref.
Ethane C_2H_6 	D_{3h} or D_{3d}	Im3m m3m	1, 2 Difluorotetrachloroethane $Tg \simeq 90$ K III Trichloro–222 Trifluoroethane $Tg < 77$ K	 	C_{2v} C_{3v}	[15]
Neopentane C $(CH_3)_4$ 	T_d	Fm3m m3m	Neopentanol C $(CH_3)_2CH_2OH$ $Tg \approx 150$ K		C_3	[16]
Cyclohexane C_6H_{12} 	D_{3d}	Fm3m m3m	Cyclohexanol $Tg \approx 150$ K Fluorocyclohexane $Tg \approx 137$ K Cyanocyclohexane $Tg \approx 134.7$ K Isocyanocyclohexane $Tg \approx 128.6$ K		C_{2v} C_{2v} C_{2v} C_{2v}	[2] [17]

Benzene C_6H_6		D_{6h}	Pbca $\bar{1}$	Mono-deuterated benzene T_g ?		C_{2h}	[11]
Ferrocene $(C_5H_5)_2Fe$		D_{5d} or D_{5h}	$P2_1/a$ 2/m	Azaferrocene $T_g \approx 185$ K		C_1	[14]
Adamantane $C_{10}H_{14}$		T_d	Fm3m m3m	Fluoroadamantane $T_g \approx 90$ K ?		C_{3v}	[11]
				Cyanoadamantane $T_g \approx 177$ K		C_{3v}	[18]

2.3. Incompatible symmetries

Crystals of the ferrocenium salt $Fe(C_5H_5)(C_6H_6)^+(PF_6)^-$ exhibit two glass transitions, whereas crystals of $Fe(C_5H_5)_2^+(PF_6)^-$ have none [33]. This example can be viewed as a special case of symmetry departure through substitution : a benzene group has been substituted for a cyclopentadienyl group. It can be noted that the symmetries of the two cycles which reorient rapidly (around the C_6 and C_5 axes, respectively) cannot be made compatible, which also entails a symmetry departure.

Similar examples should be observed in other metallocene derivatives in the future.

2.4. Molecular interconversion motions

In the case of flexible molecules such as substituted cyclohexane, the different conformers are discernible. Observed glass transitions in crystals have been correlated with the slackening of the interconversion motions between the axial and equatorial conformers of cyano- and isocyanocyclohexane [17] and between the trans and gauche varieties of 1,2-difluorotetrachloroethane [15].

These assumptions have yet to be proved.

3. Discussion and conclusion

In this short review, we have tried to show how to determine, from symmetry alone, whether a molecule can lead to glassy crystalline states. The necessary symmetry departure can most easily be attained through chemical substitution of some symmetrical molecule which yields a reorientational crystalline phase.

Obviously, the validity of such a criterion is limited in several ways : first, the substituent must not be too cumbersome because the resulting molecule has to reorient at its lattice site for a glass transition to be generated from freezing its motion; then the symmetry departure should be great enough for a glass transition to be observable. A glass transition in crystalline mono-deuterated benzene or ferrocene is probably beyond observation, but it would be interesting to define the tiniest symmetry departure which leads to an observable glass transition.

The example of fullerene C_{60} illustrates cases our classification cannot foresee. According to our one-molecule model, the high symmetry of the C_{60} molecule could not have allowed the emergence of a glass transition in the C_{60} crystal. However, a transition observed near 90 K through neutron diffraction measurements [34] was soon demonstrated to be a glass transition by means of thermal diffusivity experiments [35] and heat capacity measurements [36]. This conclusion was supported by thermal expansion [37] and radiocrystallographic [38] determinations in particular.

Only a model in which C_{60} molecules enter two different two-molecule configurations [34] could take into account the neutron diffraction data. Obviously, the one-molecule model we presented above cannot cope with such a case. David et al. [34] showed that the respective populations of these two configurations vary with temperature down to $\sim$ 90 K and stay frozen at lower temperature. These two two-molecule configurations which correspond to two different energy levels are indeed the origin of the glass transition.

Meingast and Gugenberger [39] have recently written a review of the properties of crystalline C_{60} as a glassy crystal. They suggest that the 90 K transition could be the minimal glass transition such as that which can be modeled through the freezing of a Schottky anomaly [40].

Another way to introduce disorder in crystals of symmetrical molecules would be to add some other compound which syncrystallizes with the first one. An example is given by mixtures of thiophene and benzene : adding benzene to thiophene slightly modifies the temperature of the $\sim$ 40 K glass transition [41]. But conversely, one wonders how much thiophene has to be introduced into benzene to produce enough symmetry departure in order to observe the corresponding glass transition which will then be considered as the glass transition of (not very pure) benzene.

The classification we have presented is meant to predict the glassy crystals which can be formed through modifications of very symmetrical molecules by substituting some chemical groups. The last two examples we describe do not enter this classification; however, they indicate how to generalize it by considering configurations of two or more molecules, each corresponding to different energy levels, which can be attained dynamically through fluctuations of the system. The freezing of the corresponding motions will lead to glass transitions. Again some symmetry departure will be responsible for the disorder which is the source of the formation of a glass.

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