

## SYMMETRY DEPARTURE: DISORDER AND GLASS TRANSITION \*

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### ABSTRACT

It is stated that, for a glass transition to exist in a reorientationally disordered crystal within which a large-amplitude motion is slowed down when temperature decreases, some "symmetry departure" must exist: the different molecular orientations will therefore be discernible, thus entailing a possible disorder that may cause the system to depart from thermodynamic equilibrium. This description has been used to explain and predict glass transitions in some molecular crystals. It has also suggested a two-level system model depending on a symmetry departure parameter. Its behaviour is described in terms of a population temperature  $\theta$  which can be considered as a fictive temperature according to Tool's definition. This model reproduces characteristic properties of systems that vitrify, such as the different variations of  $\theta$  at increasing and decreasing temperatures, respectively, or the shapes of the thermal drift rate curves near the glass transition. It predicts that the activation energies for enthalpy relaxation and for the correlation times for the motion which is frozen at  $T_g$  should be equal: this prediction is fulfilled in all four cases for which sufficient data exist. Finally, the symmetry departure parameters have been calculated from experimental data for the same cases.

### INTRODUCTION

In 1974, Suga and Seki extended the concept of glassy state to the non-equilibrium solid state in general [1]. Adiabatic calorimetry is the surest experimental method to characterize this state by revealing a glass transition, an enthalpy relaxation phenomenon and the existence of a residual entropy at 0 K. Glassy crystals, the first example of which was recognized in crystalline cyclohexanol [2], are such systems. They are glasses from the thermodynamic point of view, but they are still crystals according to radiocrystallographic measurements.

Such model glasses can be obtained by cooling reorientationally disordered crystalline phases and combined thermodynamic, dynamic and

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\* Dedicated to Professor Syûzô Seki in honour of his contribution to Calorimetry and Thermal Analysis.

structural studies led to a coherent description of the quenching mechanism [3,4]. The glassy phase and its dynamically disordered mother phase correspond to the same space and time-averaged crystalline structures, with the same number of possible molecular orientations at each lattice site, with the same occupancy factors and essentially the same mean local disorder [5,6]. From the dynamic point of view, the glass transition is a kinetic phenomenon which can be observed for measuring frequencies ranging from  $10^{-3}$  to  $10^{-5}$  Hz depending on the experimental mode of observation; it is correlated with the "freezing" of the bulkiest large-amplitude-molecular-motion ( $\alpha$  motion). In the compounds which have been studied so far (cyclohexanol [3,4,7], cyclooctanol [4], 1-cyanoadamantane [8,9] and 1,2-difluorotetrachloroethane [4,10]), this motion is the endospherical or quasi-isotropic one. On the other hand, anisotropic, large amplitude motions ( $\beta$  motions) still exist within the glassy phase; they can eventually lead to secondary glass transitions, as it is the case in cyclohexanol [11], when their frequencies reach the above characteristic frequency range.

This is illustrated in Fig. 1. Figure 1a shows the variations of the frequencies of three large-amplitude motions as a function of temperature in crystalline cyclohexanol. Curve D corresponds to self-diffusion which does not seem to be related to any glass transition. Curve  $\alpha$  (illustrating the endospherical motion) and curve  $\beta$  (corresponding to an anisotropic motion, the nature of which is still controversial [4,7]) lead to glass transitions which have been observed by means of calorimetric measurements [11]. On the other hand, in the case of 1-cyanoadamantane (Fig. 1b), it cannot be concluded whether the  $\beta$  motion will lead to a glass transition near 45 K as it could be inferred by linearly extrapolating curve  $\beta$  to the  $10^{-3}$ – $10^{-5}$  Hz range.

This problem is a general one, and the aim of the present paper is to try to define the conditions that a reorientational motion must fulfil to lead to a glass transition when its frequency reaches the above characteristic range.

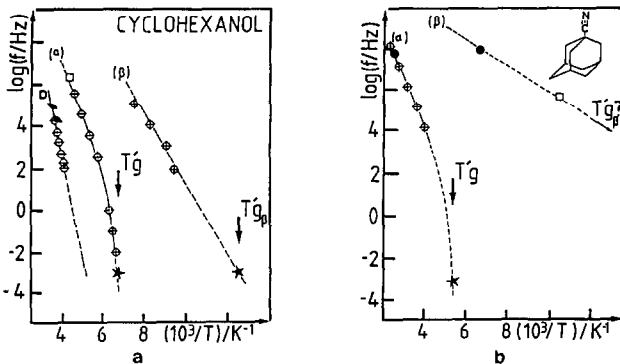


Fig. 1. Relaxation maps for molecular solids leading to glassy crystalline states. (a) Cyclohexanol; (b) 1-cyanoadamantane. These maps have been drawn from ref. 4.

### *Phenomenological description*

We shall present a simple model which is meant to point out how the freezing of a large-amplitude motion can cause the system to depart from thermodynamic equilibrium.

Let us assume that, at each lattice site, each molecule can occupy  $n$  different orientations and 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 temperature  $T_1$ , at which thermodynamic equilibrium is achieved, the system is cooled to  $T_2$ , a temperature at which the mean frequency of the involved reorientational motion is less than  $10^{-5}$  Hz. 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 in the system. The observer will witness a long-time enthalpy relaxation: the lower  $T_2$  is the longer this relaxation will be.

This description illustrates the fact that, according to a formulation stated by Seki and co-workers [12], "the glass transition is not a phase transition. It is a change from a non-equilibrium to equilibrium state" (or vice versa). Thus, departure from thermodynamic equilibrium appears at the result of the convolution of the "observer's time" and the intrinsic evolution kinetics of the observed system.

Let us now consider systems in which all molecular orientational states have the same energies. For instance, it would be the case of a solid within which the molecules would undergo  $2\pi/n$  reorientations around one of their  $C_n$  axes, that are jumps between undiscernible states. Obviously, freezing such a motion would entail no departure from equilibrium. As a matter of fact, crystalline benzene and ferrocene, within which the molecular cycles undergo  $2\pi/6$  or  $2\pi/5$  reorientations around  $C_6$  or  $C_5$  axes [13,14], respectively, exhibit no glass transition [15–17]. In the case of benzene, the number of experimental points in the calorimetric study [15] may not be large enough to warrant that some small thermal step increase did not remain unnoticed; but in the cases of ferrocene- $h_{10}$  [16] and  $-d_{10}$  [17], the calorimetric experimental points are so close to one another that no glass transition could have escaped observation.

Therefore, it may be stated that a glass transition will appear in a crystalline phase within which reorientational molecular motions occur only if some "symmetry departure" exists: the different molecular orientations will therefore be discernible, thus entailing a possible disorder which will allow the system to depart from thermodynamic equilibrium.

A tentative definition may be worded as follows: a symmetry departure will exist if the symmetry group of the molecular orientations in the crystal is not a sub-group of the symmetry group of the molecule (or vice versa), or, if it is, when the respective symmetry axes of these two groups do not coincide.

For instance, if the  $\beta$  motion in crystalline 1-cyanoadamantane (Fig. 1a) consists of  $2\pi/3$  reorientations around the three-fold molecular axis, no symmetry departure is involved and no glass transition will exist. But dielectric measurements [18] suggest that the molecules undergo some precessional motions around the four-fold axes of the crystalline lattice: therefore, calorimetric measurements should reveal a weak secondary glass transition near 45 K [8].

Five-membered heterocyclic compounds yield other examples of glassy crystalline states which can be understood in terms of the above rule of thumb. The glass transitions which have been observed in both phase sequences of crystalline thiophene [19,20] are undoubtedly related to the presence of the sulphur atom which plays the part of a discernibility label. Likewise, the glassy crystalline phases which exist in thiazole, isothiazole and isoxazole [21,22] probably result from the freezing of in-plane reorientational molecular motions between energetically discernible positions.

It will be easy to find further examples to test the predictive value of the symmetry departure rule. We just described the case of 1-cyanoadamantane. It can also be conjectured that the freezing of the precessional motion of the dipolar axes of 1-fluoroadamantane molecules which was recently observed in phase II of this compound [23] will lead to a glass transition near 90 K. Furthermore, reorientational phase I of azaferrocene easily supercools; the variations vs. temperature of its NMR spin-lattice relaxation time  $T_1$  [24] are very similar to the characteristic variations of  $T_1$  for recognized glassy crystals [4,7]. These similarities together with some indications drawn from differential thermal analysis measurements [25] are clues that the discernibility labelling by the nitrogen atom in one of the two molecular five-membered cycles will lead to a glass transition.

We do not know the minimum necessary symmetry departure to bring about an observable glass transition. For instance, it may be debated whether the very weak symmetry departure which exists in monodeuterated-benzene or -ferrocene will be sufficient to lead to what could be called the "minimal molecular glass" in which the departure from thermodynamic equilibrium would be ideally weak. At the moment, these borderline cases correspond to fanciful questions; nevertheless, Atake et al. [26] recently observed non-equilibrium crystalline phases in  $h_{18}$ - and  $d_{18}$ -hexamethylbenzenes within which the discernibility labelling seems to stem out of some dephasing in the rotational motions of the different methyl groups.

It is to be noted that the two classes of orientational crystals we dis-

tinguished with respect to glass transitions (i.e. classes with or without symmetry departure) are essentially the same ones that were described as to what concerns the possible phase transitions towards ordered phases [27]. This could have been anticipated because nucleation of a new phase and slackening of some molecular motion to yield a glass transition are two kinetic mechanisms which compete with each other in many reorientational phases; therefore, they should correspond to some common criteria.

We will now illustrate the above description through a simple two-level system in which symmetry departure corresponds to the energy splitting between the involved levels [28].

### *Symmetry departure: a two-level model*

Let us assume that, in a reorientational crystal, the molecules can occupy orientational states which correspond to two kinds of potential wells separated by an energy equal to  $\Delta E$ , the symmetry departure parameter.  $\Delta E$  and the total number of occupied wells (that is the number of molecules  $N$  in the solid) do not vary with temperature. The transitions between the two kinds of wells are ruled by the crossing of a potential barrier the height of which,  $W$ , is supposed to be temperature-independent ( $W > \Delta E$ ).

At thermodynamic equilibrium, the populations of the lower and higher levels,  $n'$  and  $n''$ , respectively, are given by:

$$n' + n'' = N$$

$$\frac{n'}{n''} = \exp \frac{\Delta E}{kT}$$

Let us now assume that, after an extremely rapid cooling to temperature  $T$ , the two-level populations have not had time to reach their equilibrium values. The higher level is overpopulated by  $n$  excess molecules; obviously,  $n$  also characterizes the underpopulation of the lower levels. The system can momentarily be described by an apparent population temperature  $\theta$  defined by:

$$\frac{n' - n}{n'' + n} = \exp \frac{\Delta E}{k\theta}$$

so that the excess population can be written as:

$$n = N \frac{\exp \frac{\Delta E}{kT} - \exp \frac{\Delta E}{k\theta}}{\left(1 - \exp \frac{\Delta E}{kT}\right) \left(1 + \exp \frac{\Delta E}{k\theta}\right)} \quad (1)$$

The purpose of the ensuing calculations is to describe the variations of  $\theta$ , i.e. the variations of the orientational populations, when temperature changes continuously.

At temperature  $T$ , the system will tend to reach equilibrium. A variation

$dn$  of the excess population will correspond to a change  $d\theta$  of the population temperature such as:

$$dn = \left[ N \frac{\Delta E}{k\theta^2} \exp \frac{\Delta E}{k\theta} / \left( 1 + \exp \frac{\Delta E}{k\theta} \right)^2 \right] d\theta$$

Let the excess population decrease according to:

$$dn = -n \frac{dt}{\tau}$$

in which the relaxation time  $\tau$  is ruled by the crossing of the potential barrier  $W$  referred to before, so that:

$$\tau = A \exp \frac{W}{kT}$$

We get:

$$n dt = -\tau N \frac{\frac{\Delta E}{k\theta^2} \exp \frac{\Delta E}{k\theta}}{\left( 1 + \exp \frac{\Delta E}{k\theta} \right)^2} d\theta$$

hence:

$$\exp \frac{\Delta E}{kT} - \exp \frac{\Delta E}{k\theta} = -\tau \frac{\Delta E}{k\theta^2} \exp \frac{\Delta E}{k\theta} \frac{1 + \exp \frac{\Delta E}{kT}}{1 + \exp \frac{\Delta E}{k\theta}} \frac{d\theta}{dt}$$

Now, let the temperature decrease at a constant rate,  $\sigma > 0$ , according to:

$$\frac{dT}{dt} = -\sigma$$

A simple way to explain what follows is to consider that, during a time  $dt$  at constant temperature  $T$ ,  $\theta$  has undergone a spontaneous change  $d\theta$  which corresponded to a change  $dn$  of the number of orientational states in both levels. After  $dt$  has elapsed, temperature undergoes an *instantaneous* change equal to  $dT = -\sigma dt$  during which no orientational transition occurs, so that  $\theta$  does not change. The value of  $d\theta$  calculated above represents the total change of  $\theta$  for the evolution at  $T$  during  $dt$ , followed by the thermal jump equal to  $dT = -\sigma dt$ . Therefore, we can report the value of  $dt$  in the preceding equation. We get:

$$\exp \frac{\Delta E}{kT} - \exp \frac{\Delta E}{k\theta} = \sigma \tau \frac{\Delta E}{k\theta^2} \exp \frac{\Delta E}{k\theta} \frac{1 + \exp \frac{\Delta E}{kT}}{1 + \exp \frac{\Delta E}{k\theta}} \frac{d\theta}{dT}$$

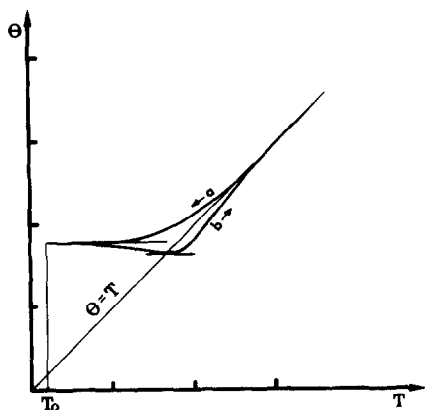


Fig. 2. Variation of population temperature  $\theta$  in a two-level system: temperature decreases first at a constant rate (curve a) and then increases at the same rate (curve b). The populations of the levels are ruled by the crossing of a potential barrier the height of which is independent of temperature.

that we will write as:

$$\exp \frac{\Delta E}{kT} - \exp \frac{\Delta E}{k\theta} = \sigma \tau B \frac{d\theta}{dT} \quad (2)$$

where  $B$  is a positive quantity the variation, vs. temperature, of which is slower than that of  $\tau$  because  $\Delta E < W$ .

During such a continuous cooling, the higher level is systematically overpopulated because reaching thermodynamic equilibrium is not instantaneous, so that  $\theta$  is always higher than  $T$ . Therefore, the first member of eqn. (2) is positive, consequently  $d\theta/dT$  is positive.

At high temperature,  $\tau$  is very weak and the two terms of the first member of eqn. (2) are almost equal. The graph representing  $\theta(T)$  tends towards the straight line  $\theta = T$  with  $\theta > T$ . At low temperature,  $\tau$  becomes very large,  $d\theta/dT$  tends towards zero and  $\theta(T)$  levels off (Fig. 2, curve a).

The cooling is stopped at  $T = T_0$  where  $\tau$  is so large that no evolution of  $\theta$  is observable. Then, the system is heated at the constant rate  $dT/dt = -\sigma$ , with  $\sigma < 0$ .

As the first member of eqn. (2) is initially positive (because  $\theta$  does not change at temperature  $T_0$ ),  $d\theta/dT$  is negative;  $\theta$  begins to decrease (Fig. 2, curve b). It decreases until the first member of eqn. (2) becomes zero, that is when  $\theta = T$ . Then  $\theta$  will increase and will tend towards the straight line  $\theta = T$ , with  $\theta < T$ .

The above model reproduces a number of characteristic features of systems that vitrify. The levelling off of  $\theta$  on cooling reflects the freezing of the high temperature, dynamic orientational disorder. The very existence of a low temperature  $\theta$  limiting value does not depend on the cooling rate, it is a consequence of the very long relaxation times  $\tau$  attained when temperature

decreases. It has been checked by numerical computations that the slower the cooling rate the lower the  $\theta$  limiting value. A corresponding behaviour can experimentally be observed, for instance when measuring volume at a constant cooling rate in a vitrifying system; the slower the cooling rate, the lower the temperature at which the graph  $V(T)$  changes slope.

The curves  $\theta(T)$  obtained on cooling and on heating at the same rate ( $\sigma$ ) are different. This mimics the different behaviours of vitrifying systems at decreasing and increasing temperature. It has also been checked that the  $\theta$  depression on heating depends on the heating rate: the slower the heating rate the lower the  $\theta$  value at  $\theta = T$ .

It is to be noted that the population temperature  $\theta$  strictly conforms to the definition of a “fictive temperature” according to Tool [29], that is: a glassy state at temperature  $T$  can be characterized by a fictive temperature  $\theta$  if, by heating the sample rapidly at temperature  $\theta$ , it regains its thermodynamic equilibrium and, conversely, when bringing it back to temperature  $T$ , it regains its initial state.

We will now examine some more specific consequences of the model.

### *Applications of the symmetry departure model*

Let us first consider the spontaneous thermal evolution of the system at some temperature in the range within which  $\theta$  evolutions begin to be observable on heating. This will happen when the decrease of  $\theta$  can be observed in Fig. 2b, that is for a temperature at which  $\theta > T$ .

In these conditions the higher orientational states are overpopulated and the trend towards equilibrium will result in transitions from the higher levels to the lower ones. Each transition will yield an energy equal to  $\Delta E$ . If the system is placed in adiabatic conditions, in an adiabatic calorimeter for instance, the observer will witness an enthalpy relaxation with a positive thermal drift.

At the temperature for which  $\theta = T$  on curve b of Fig. 2, thermodynamic equilibrium is achieved and no enthalpy relaxation should be observed.

At still higher temperatures,  $\theta < T$ , the lower orientational levels are overpopulated and, to reach equilibrium, transitions from the lower states to the higher ones are necessary. Each transition corresponds to the absorption of an energy equal to  $\Delta E$ , so that the net result will be an enthalpy relaxation with a negative thermal drift. This should happen up to a temperature at which  $\tau$  is short enough for the relaxation to become non-observable under usual experimental conditions.

This behaviour can be compared to what is really observed in calorimetric measurements. For instance, Fig. 3 shows the variations of the spontaneous thermal drift near the glass transition which occurs in the metastable phase sequence of crystalline thiophene [19,20]. Other examples have been published; the shapes of the thermal drift curves may depend on the detailed



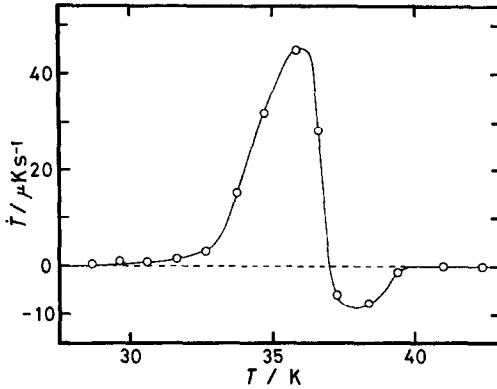


Fig. 3. Temperature drift rate as a function of temperature near the glass transition of the metastable phase sequence of crystalline thiophene.

thermal treatments undergone by the studied samples, but the main characteristics of enthalpy relaxation we just deduced from the model are actually observed.

Moreover, according to our model, the same activation energy  $W$  rules the reorientational motions and the enthalpy relaxation process. Therefore, we must try to compare the corresponding values for real systems. Obviously, the comparison will be valid only for systems in which the freezing of one single motion leads to a glassy phase; furthermore, the corresponding characteristic time  $\tau$  must obey an Arrhenius law. This is the case for compounds in which secondary or secondary-like (as in thiophene) glass transitions exist.

For such systems, Matsuo et al. [30] have described a procedure to analyse the enthalpy relaxation phenomenon. It uses data corresponding to the rising part of the positive temperature drift curve to get an Arrhenius plot of the enthalpy relaxation time such as the one which is represented in Fig. 4 and which has been derived for the glassy crystalline phase of the metastable phase sequence of thiophene. From this plot, an activation

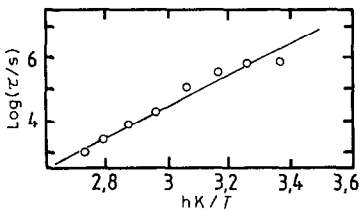


Fig. 4. Least-squares fitted Arrhenius plot for the enthalpy relaxation times in the glassy crystalline phase of the metastable phase sequence of crystalline thiophene.

TABLE 1

Activation enthalpies for enthalpy relaxations and the corresponding NMR correlation times, and symmetry departure parameters  $\Delta E$  for compounds leading to secondary-like glass transitions

	Thiophene (stable sequence)	Thiophene (metastable sequence)	SnCl <sub>2</sub> ·2H <sub>2</sub> O	SnCl <sub>2</sub> ·2D <sub>2</sub> O
$\Delta H_{\text{relax}}$ (kJ mol <sup>-1</sup> )	11 [19,20]	9.4 [19,20]	49.9 [30]	49.8 [30]
$\Delta H_{\text{reor}}$ (kJ mol <sup>-1</sup> )	7 [32] 15.5 [33] 12.7 [19]	11.4 [19]	49 [34] 43.9 [35]	49 [34]
$\Delta E$ (kJ mol <sup>-1</sup> )	3	1.1	4.2	4

enthalpy  $\Delta H_{\text{relax}}$  such as:

$$\tau = \tau_0 \exp \frac{\Delta H_{\text{relax}}}{kT}$$

can be determined.

It has to be compared with the activation enthalpy  $\Delta H_{\text{reor}}$  which rules the reorientational motion which is going to be frozen.  $\Delta H_{\text{reor}}$  can be determined through NMR measurements.

The comparison has been possible in four cases, i.e. SnCl<sub>2</sub>·2H<sub>2</sub>O, SnCl<sub>2</sub>·2D<sub>2</sub>O [30] and the two phase sequences of crystalline thiophene [19,20]. Table 1 shows that the agreement between  $\Delta H_{\text{relax}}$  and  $\Delta H_{\text{reor}}$  is fair for thiophene and excellent for the other two compounds. These equalities (or near equalities) had already been noticed by Matsuo et al. [30] and Figuière et al. [19]. In particular, Matsuo and Suga have written [31]: "The relaxation time derived from the heat evolution and absorption rates has the same activation energy as the correlation time from the NMR  $T_1$  measurements... The same basic mechanism is involved in the two relaxation processes occurring in these quite different time scales". This requirement of the model seems to be fulfilled indeed.

Now, we will try to determine values for the symmetry departure parameter  $\Delta E$ . The more straightforward way to do it would be to try different values of  $\Delta E$  in eqn. (2) to fit the experimental thermal drift curves. But this fitting depends on the thermal histories of the samples which are not accurately known. Instead we shall describe a simple way to get approximate values of  $\Delta E$  by using the enthalpy relaxation phenomenon in the vicinity of the glass transition.

Only part of the total enthalpy of the system is involved in this phenomenon. This part,  $H_c$ , called the configuration enthalpy by Matsuo et al. [30], is the difference between the enthalpy  $H(T, t)$  actually measured at temper-

ature  $T$  and time  $t$  and the equilibrium value  $H(T, t = \infty)$ . According to Matsuo et al.'s model,  $H_c$  is given by:

$$H_c(T, t) = \tau C \dot{T}$$

where  $\tau$  is the corresponding relaxation time,  $\dot{T}$  is the thermal drift rate and  $C$  the heat capacity of the calorimeter cell with the sample inside it.

We will use the following approximation:

$$H_{c,m} = \tau C_{p,m} \dot{T} \quad (3)$$

because the values of  $C_{p,m}$ , the heat capacity of the studied sample (the subscript m stands for molar), are reported in publications relating to calorimetric work.

In our model,  $H_c$  corresponds to the enthalpy that the system would yield at a given temperature to achieve  $\theta = T$ , that is the enthalpy change related to the disappearance of all excess population  $n$ . Therefore, we get:

$$H_{c,m} = \frac{n}{N} \Delta E \quad (4)$$

where  $n/N$ , the molar fraction of excess population, is given by eqn. (1).

This equation has been used to fit  $\Delta E$  so that the configuration enthalpy derived from eqn. (4) is equal to that given by eqn. (3) and which has been determined thanks to experimental data. The value of  $\theta$  is only known for the temperature at which the thermal drift is equal to zero, where  $\theta = T$ , and which corresponds to a minimum value of  $\theta$  so that its variations around that temperature are weak. Consequently, in the four cases for which all data are known and which are the same ones as before,  $H_{c,m}$  was calculated at temperatures near these minima, the values of which were used as approximate values for  $\theta$ .

TABLE 2

Thermodynamic data used to calculate the symmetry departure parameters for compounds leading to secondary-like glass transitions. The symbols are defined in the text. Data for thiophene come from ref. 20 and those for  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SnCl}_2 \cdot 2\text{D}_2\text{O}$  come from ref. 30

	Thiophene (stable sequence)	Thiophene (metastable sequence)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{SnCl}_2 \cdot 2\text{D}_2\text{O}$
$T$ (K)	41.7	35	144.1	149.2
$\theta$ (K)	43.9	37	155	158.4
$\tau$ (s)	1000	5120	61000	52000
$C_{p,m}$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	30.8	25.4	108.6	118.3
$\dot{T}$ ( $\text{K s}^{-1}$ )	$8 \times 10^{-6}$	$4 \times 10^{-5}$	$5 \times 10^{-6}$	$5 \times 10^{-6}$
$H_{c,m}$ ( $\text{J mol}^{-1}$ )	0.25	5.2	33.1	30.8

The experimental data we used are reported in Table 2 and the resulting values of the symmetry departure parameters are reported in Table 1.

The value of  $\Delta E$  for the glassy phase  $V_g$  (stable sequence) of thiophene is higher than that for phase  $II_{2g}$  (metastable sequence). This is consistent with the fact that stable phases are denser than metastable ones. Therefore the steric hindrance should be more important in  $V_g$  than in  $II_{2g}$ , so that  $\Delta H_{\text{relax}}$  and  $\Delta E$  should be higher for the former phase than for the latter one, which is the case.

As for  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and its deuterated analogue, our results suggest that the incompletely long-range-ordered proton (or deuteron) configuration, which, according to Matsuo et al.'s hypothesis [30], is frozen in the glassy state, is related to the existence of two non-equivalent orientations of water molecules. These two different orientations should correspond to a difference of about  $4 \text{ kJ mol}^{-1}$  in the depths of the involved potential wells.

## CONCLUSIONS

To explain how the freezing of large-amplitude reorientational motions can lead to a glassy crystalline phase, some symmetry departure in the original reorientational phase seems necessary.

The existence of glass transitions in the crystalline phases of five-membered heterocyclic compounds has been explained in terms of this concept. It has also been used to predict the emergence of secondary (or secondary-like) glass transitions in 1-cyano- and 1-fluoroadamantane and in azaferrocene; calorimetric studies will be necessary to test these predictions.

This description has suggested what Kovacs would call a zeroth-order model, that is a two-states model in which equilibrium is attained through an exponential law [36], e.g. Bragg and Williams' alloy-quenching model [37]. Symmetry departure is represented by the energy difference between the two orientational levels involved. The behaviour of the systems is described in terms of a population temperature  $\theta$ , the definition of which only depends on the populations of both levels.

The model reproduces characteristic properties of systems that vitrify, e.g. variations vs. temperature of  $\theta$ , which differ on decreasing and increasing temperatures or which depends on the thermal history, or the shapes of the thermal drift rate curves near the glass transition  $T_g$ . It also predicts that the activation energies for enthalpy relaxation and for the correlation times of the motion which is frozen at  $T_g$  should be equal; this prediction is fulfilled for all cases for which sufficient data exist.

It has also been shown that the symmetry departure parameter  $\Delta E$  can be calculated from experimental data.

At the moment, the model gives a good description of secondary or secondary-like glass transitions. It has to be extended to other cases.

Moreover, other characteristic properties of glasses (heat capacity or thermal expansion changes at  $T_g$  for instance) should be related to the model parameters.

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