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Calorimetric study of frozen-in disordered solids

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Abstract

The freezing-in phenomena that occurred in some orientationally disordered crystals and liquid crystals, either in the metastable or in the stable state, are described in comparison with those in liquids. These observations indicate clearly that the glass transitions observed exclusively in liquids are just one example of ‘transitions’ which must occur widely in condensed states of matter, irrespective of the structural regularity. The interplay between phase and glass transitions in crystals is discussed in relation to useful dopants that accelerate some molecular motions resulting in failure to maintain equilibrium at low temperatures. The structural relaxation occurring in vapour-quenched amorphous solids is studied using an adiabatic calorimeter operated as a low-frequency spectrometer. The anomalous behaviour of the configurational entropy S_c observed for some molecular systems is discussed. The solid-state vitrification of molecular crystals caused by mechanical milling and the formation of molecular alloys for some binary systems are described, with potential applications.

1. Introduction

The states of aggregation of molecules are divided into gases, liquids, and solids depending on the mechanical properties. Further division of the solids into non-crystalline and crystalline states is based on the structural aspects. The division of metastable liquids below their fusion points into glassy and undercooled liquid states is based on the non-equilibrium or equilibrium nature derived from thermodynamic reasoning. Thus the criteria of classification are multifarious. It has become possible to study non-crystalline solids prepared by various kinds of non-equilibrium processing [1]. The intellectual fascination with the non-crystalline solids arises from the basic understanding of the states of aggregation of the constituent entities. Since the diffraction techniques are generally not powerful for solids lacking periodic structures, thermodynamic characterization of non-crystalline solids became important in creating a conceptual picture for frozen-in disordered solids.

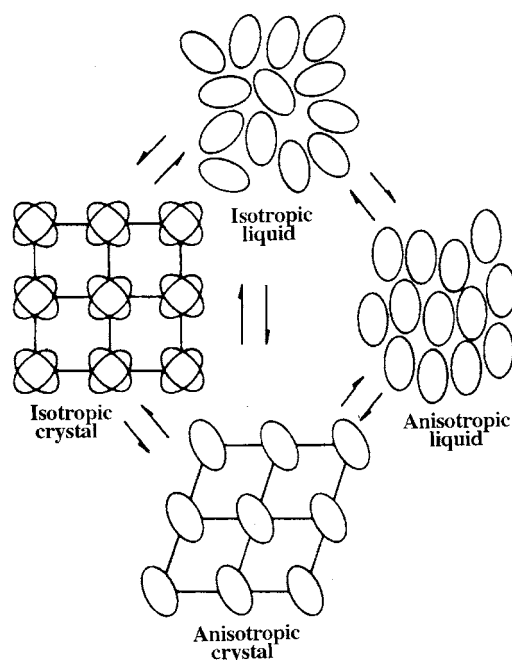


Figure 1. A schematic drawing of various states of aggregation of molecules in the equilibrium state.

A molecular assembly differs from other systems in being composed of discrete molecules that are held together in condensed states by weak intermolecular interactions. The rich polymorphisms observed in molecular crystals arise partly from the marked contrast between the intramolecular and intermolecular interactions [2]. When a molecular crystal undergoes a transition, there is often a considerable increase in disorder that is reflected in a large entropy of transition compared to the small entropy of fusion. Thus the ordered crystals in this category are considered to melt in two steps through intermediate disordered phases called mesophases. There are two kinds of mesophase: isotropic crystals (or orientationally disordered crystals) and anisotropic liquids (or liquid crystals), as depicted schematically in figure 1. What will happen if the mesophases with relevant disorder are cooled too rapidly to transform into the ordered crystal? This is an interesting problem analogous to that of the formation of glasses by rapid cooling of liquids [3].

2. Frozen-in disorder in the mesophase

Liquid cyclohexanol crystallizes at 299 K into an fcc system. The high degree of crystallographic symmetry implies several equi-energetic orientations of the molecule in the cubic lattice. The fcc phase transforms at 265 K into a monoclinic phase on cooling. The highly disordered nature of the fcc phase is reflected by the large entropy of transition, $33.2 \text{ J K}^{-1} \text{ mol}^{-1}$, compared to the small entropy of fusion, $5.96 \text{ J K}^{-1} \text{ mol}^{-1}$. The fcc phase undercools easily with a moderate cooling rate and exhibits a discontinuous heat capacity jump at 150 K [4]. The frozen-in orientational disorder is clearly evidenced by the residual entropy of $4.72 \text{ J K}^{-1} \text{ mol}^{-1}$, as shown in figure 2. The large jump and the long tail of the heat capacity at and below T_g are noticeable. A dielectric experiment showed the existence

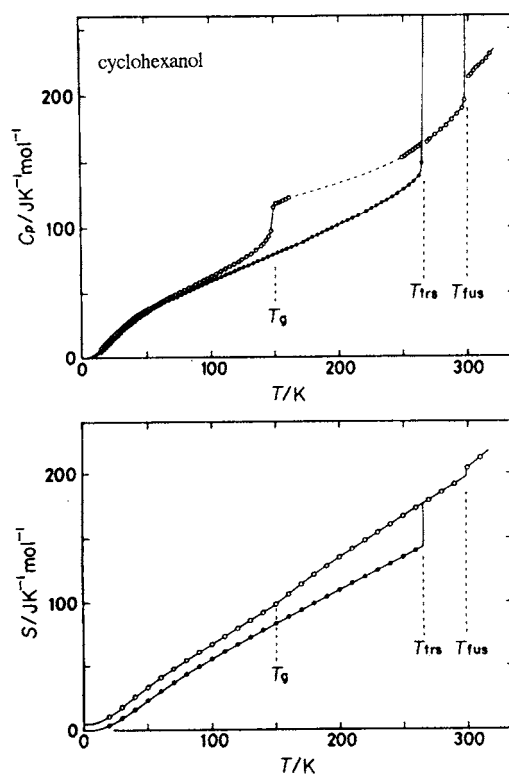


Figure 2. The heat capacity (upper) and entropy (lower) of cyclohexanol in various states. The symbols \bullet are for the stable crystalline phase and the symbols \circ are for the undercooled fcc phase.

of β -relaxation below T_g . These properties resemble closely those of glass-forming liquids. The only difference between the glasses and the glassy state of cyclohexanol is that there is translational invariance with respect to the centres of masses of molecules in the latter state. The name 'glassy crystals' was given to the crystals possessing some frozen-in disorder. Glass transition and residual entropy are characteristic properties of glasses. The fusion and ability to give x-ray diffraction peaks are typical of crystals. Two seemingly contradictory properties are realized in this novel state of aggregation of molecules.

Ethanol gave the first example of realization of the glassy crystalline and glassy liquid states, depending on the cooling rate [5]. The latter could be produced only when the liquid was cooled at a rate above 50 K min^{-1} . Interestingly, the glass transitions took place at essentially the same temperature of 97 K for both the glassy crystal and the glassy liquid. This may imply that the reorientational motion of the molecules primarily governs the kinetic property of both freezing processes. In this way, two kinds of glass transition were observed for different states of one and the same substance. The two glassy states of ethanol were confirmed recently by x-ray diffraction and Raman spectroscopy [6]. The low-temperature behaviour of protonated and deuterated ethanols was clarified by calorimetric measurement [7]. The difference in relaxational dynamics between the two glassy states was studied by means of dielectric measurements [8].

A rich polymorphism of molecular crystals is exemplified by *N-p-n*-hexyloxy-benzylidene-*p'-n*-butylaniline. The phase sequence clarified by our measurement shown in

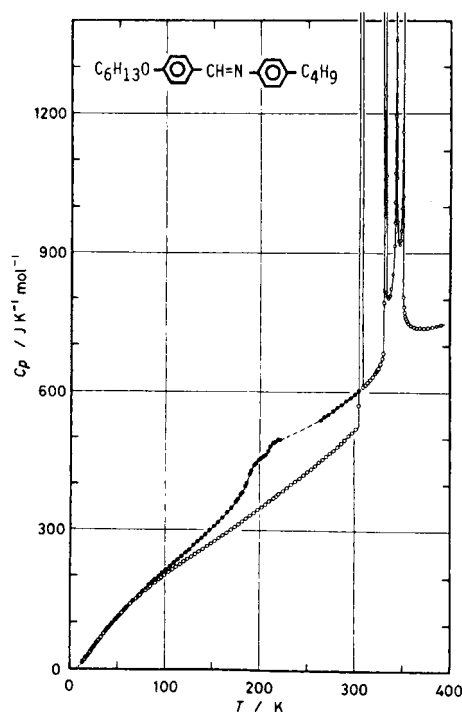


Figure 3. The heat capacity of *N-p-n*-hexyloxybenzylidene-*p'-n*-butylaniline (HBBA).

figure 3 is as follows; crystal-(306.6 K)-smectic G-(331.6 K)-smectic B-(332.9 K)-smectic A-(343.2 K)-nematic-(351 K)-isotropic liquid (IL) [9]. Six different phases appear in a narrow temperature range of 50 K. The highly disordered nature of the smectic G phase is quantified by the large entropy of transition $\Delta_{irs}S(\text{cr} \rightarrow S_G)$ of $75.98 \text{ J K}^{-1} \text{ mol}^{-1}$ which exceeds the sum of the remaining entropies of transition: $[2.53(S_G \rightarrow S_B) + 10.14(S_B \rightarrow S_A) + 9.37(S_A \rightarrow N) + 5.37(N \rightarrow \text{IL})] \text{ J K}^{-1} \text{ mol}^{-1}$. The smectic G phase readily undercools and exhibits a glass transition at around 200 K with two steps. The frozen smectic G state is characterized by residual entropy of $7.51 \text{ J K}^{-1} \text{ mol}^{-1}$. The origin of the double glass transition is unclear. One characteristic feature of smectic phases as differentiated from other liquid crystalline phases is that molecules are arranged in layer structures. Therefore, at least one of the glass transitions should have its origin in a freezing of molecular modes characteristic of a layered structure, either the undulation mode of a layer or anisotropic translational diffusions parallel and perpendicular to a smectic layer.

Thus the glass transition is not a characteristic property of liquid, but occurs widely in condensed phases, irrespective of the spatial arrangement of the molecules. The discovery of glassy crystals requires in particular renewal of the concept of the glass transition. This is because glasses and crystals are two extremes in our concept of structural regularity. Table 1 lists the T_g -values for the glassy crystals discovered by us. There exist two kinds of glassy crystal—realized either in the metastable undercooled phase or in the stable crystalline phase. A paramount example of the latter is given by ice I_h that has long been known to deviate from the third law of thermodynamics. The residual entropy for ice I_h was interpreted in terms of the half-hydrogen statistical model [10] based on the ‘ice conditions’ [11]. Each water molecule possessing two proton-donating and two proton-accepting facilities can have

Table 1. Glass transition temperature T_g of various glassy crystals.

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·11H ₂ O	150
	130	ethylene oxide·6.86H ₂ O	85
	160	tetrahydrofuran·17H ₂ O	85
CFCl ₂ -CFCl ₂	60	acetone·17H ₂ O	90
	90	CO	18
	130	RbCN	30
ethanol	90	CsNO ₂	42
cyclohexene	92	TiNO ₂	60
	93	SnCl ₂ ·2H ₂ O	150
cycloheptane	100	SnCl ₂ ·2D ₂ O	155
	100	H ₂ O (hexagonal)	105
	93	H ₂ O (cubic)	140
cycloheptatriene	106	D ₂ O (hexagonal)	115
cycloheptanol	135	pinacol·6H ₂ O	155
cyclohexanol	150	H ₃ BO ₃	290
Cs _{0.7} Tl _{0.3} NO ₂	48	D ₃ BO ₃	298
		lysozyme	about 150
C ₂ Cl ₆ in thiourea adduct	59	myoglobin	about 170

six orientations under the tetrahedral coordination. Owing to the ice conditions, however, reorientational motion of a water molecule is possible only when simultaneous reorientational motions of the neighbouring molecules occur in liaison. It is this highly cooperative nature of the reorganization motion that prevented us from observing a hypothetical ordering transition at a low temperature.

In fact, a glass transition with a small heat capacity jump was observed at 100 K, at which the dielectric relaxation time for orientation polarization becomes of the order of 1 ks [12]. The temperature is high enough compared to a hypothetical ordering temperature predicted to be 60 K based on a mean-field calculation of the dipolar interactions [13]. It is necessary therefore to accelerate the motion by doping with some kinds of lattice defect that relax the severe constraints imposed by the ice rules. Some alkali hydroxides doped into the ice lattice were found to shorten the dielectric relaxation time [14]. When an ice specimen was doped with KOH in the mole fraction of 10^{-4} and annealed at 65 K for some days, a first-order phase transition appeared at 72 K [15]. The transition removed a substantial fraction of the residual entropy. In a perfect ice crystal, proton rearrangement can only be accomplished by infringement of the ice rules. A real crystal contains some kinds of lattice defect that facilitate such rearrangement in the lattice. Doping of KOH will increase the number of effective lattice defects, and induce the phase transition which has escaped experimental observation for kinetic reasons.

Proteins are known to have a free-energy landscape possessing a large number of energy valleys, arising from the conformational change of a protein chain, separated by energy mountains [16]. At physiological temperatures the protein fluctuates among these valleys as if it were liquid, and the fluctuation is believed to play an essential role in various biological functions. Obviously such fluctuation becomes dormant at low temperatures, as in the case of liquids. In fact, a glass transition was observed in egg-white lysozyme crystal [17]. It must be recognized, however, that water is an important ingredient in constituting the tetragonal protein

lattice. Water is considered to affect the mobility of the protein molecule in a cooperative way. Calorimetric measurements were done on several lysozyme crystals with different water contents. T_g was found to increase as the amount of water is decreased, showing that the mobility of globular protein depends strongly on the water content. Below a certain content of water, the glass transition took place at temperatures higher than 300 K. This means that the conformational and orientational degrees of freedom of both molecules are frozen in at our physiological temperatures without showing any biological function.

3. Rate of enthalpy relaxation

Constant temperature of a sample kept in an adiabatic calorimeter is a prerequisite for thermal equilibrium. If any spontaneous temperature changes are observed during the equilibration periods, this is a clear indication that the sample is in a frozen-in disordered state undergoing structural relaxation. Part of the configurational enthalpy is released during the process and this will induce a spontaneous temperature change of the sample under adiabatic conditions. Here, the enthalpy of glassy solid was divided into vibrational and configurational parts, depending on the different response times against temperature jump. The spontaneous change of calorimetric temperature is well reproduced by the following equation [18]:

$$dT/dt = a + bt + c \exp[(-t/\tau)^\beta]. \quad (1)$$

Here a small correction term bt due to residual heat leakage was taken into account. This equation is simply derived by recognizing that the enthalpy ($H = H_{vib} + H_c$) is kept constant under adiabatic conditions and that the rate of enthalpy relaxation is described by the Kohlrausch–Williams–Watts (KWW) equation [19]:

$$\Delta H_c(t) = \Delta H_c(0) \exp[(-t/\tau)^\beta], \quad (2)$$

where ΔH_c is the configurational enthalpy to be relaxed, τ the average relaxation time, and β the non-exponential parameter representing a distribution of the relaxation times. Thus the least-squares fitting of the calorimetric temperature observed during each equilibration period to this equation gives the two parameters τ and β governing the relaxation at that temperature.

Figure 4 depicts (upper panel) the enthalpy of a glassy solid and (lower panel) the rate of spontaneous change in calorimetric temperature dT/dt near its T_g . The oblique segment in the upper figure represents the temperature rise due to a Joule heating and the slope corresponds to the quasi-equilibrium heat capacity. The horizontal segment shows a spontaneous temperature change arising from the enthalpy relaxation. At low temperatures where the ΔH_c to be relaxed is large but τ is long, the length is short. At temperatures near T_g where τ is short but ΔH_c is small, the length is again small. There exists a temperature at which the exothermic drift rate reaches a maximum value. Above T_g the drifts change their sign, because the actual enthalpy of the sample is temporarily less than the equilibrium liquid. Thus the sample temperature exhibits a series of exothermic followed by endothermic drift rates during the heat capacity measurements with an intermittent heating mode. If the sample is well annealed at a certain temperature from point a to b as shown in the figure, the sample exhibits only endothermic effects above that temperature.

A typical example of this behaviour was observed in acetone (Ac) clathrate hydrate $(\text{CH}_3)_2\text{CO} \cdot 17\text{H}_2\text{O}$ [20]. Reorientational motion of the host water molecules freezes out at around 90 K, as in the case of ice I_h . One of the spontaneous temperature changes observed for this crystal at 80 K is shown in figure 5 as a function of time. Analysis of the data using equation (3) gives the following kinetic parameters; $\tau = 25.1$ ks and $\beta = 0.71$. The value of β is similar in magnitude to those for glassy liquids. The τ -data thus obtained can be correlated

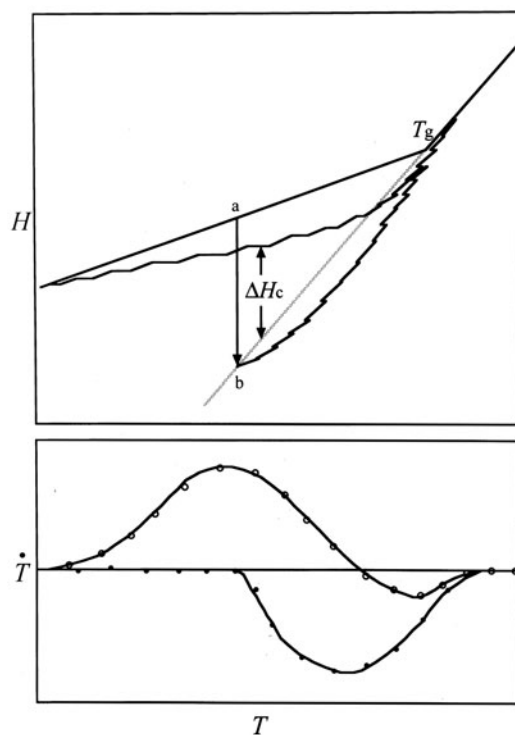


Figure 4. Upper panel: a schematic drawing of the enthalpy H versus temperature T curve of a substance that undergoes a glass transition at T_g . The zigzag line indicates the path that a sample follows during the actual heat capacity measurement. Lower panel: the rate of spontaneous change in calorimetric temperature observed during equilibration periods.

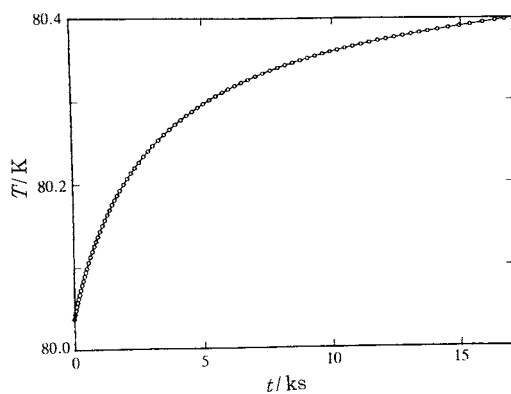


Figure 5. Spontaneous temperature change observed at 80 K for acetone clathrate hydrate.

well with dielectric relaxation times in an Arrhenius plot over a wide range of temperature. The activation energy determined from the slope, 21 kJ mol^{-1} , is similar to that of ice I_h , 20.9 kJ mol^{-1} .

The enthalpy relaxation can be observed generally in the temperature interval of 20 K around T_g for many glassy liquids. However, the process is observable at temperatures far

below T_g for vapour-deposited solids. In this method, a sample vapour is condensed onto a cold substrate. During the deposition the kinetic energies of molecules are effectively removed without passing the ‘crystallization-dangerous’ region that is inherent in the liquid quenching. A vapour-condensed (VC) solid of butyronitrile was prepared at a substrate temperature of 67 K [21]. The VC solid turned out to have a high fictive temperature T_{fic} [22] of 119 K as determined from its excess enthalpy. The high values can be compared with 100 K for the glassy liquid (LQ) realized by a cooling rate of 3 K min^{-1} . Enthalpy relaxation was observed only in the temperature range between 85 and 105 K for the LQ solid. The same process turned out to start just above the deposition temperature for the VC solid. Analysis of the relaxation rate was performed using the KWW equation. The value β is 0.07 at 83.8 K, 0.11 at 89.7 K, and 0.21 at 95.0 K, and these values are quite small compared to the values 0.6–0.9 observed for many LQ solids. It can be concluded that the KWW equation can describe the relaxation rate for a vitreous solid far from the equilibrium liquid, and that the small values of β reflect a wide distribution of the structural relaxation times. The glass transition took place at essentially the same temperature for both the VQ and LQ solids, because the excess ΔH_c for each solid has relaxed towards similar levels during the measurements before they could reach the glass transition region.

4. Configurational entropy

Adam and Gibbs [23] derived the following AG equation for the structural relaxation time based on a statistical model:

$$\tau = A \exp[N_A \Delta\mu s_c^*/kT S_c(T)], \quad (3)$$

where $S_c(T)$ is the macroscopic configurational entropy of liquid, $\Delta\mu$ the chemical potential per molecule hindering the cooperative rearrangement of a cluster, z^* the number of molecules constituting the cluster, s_c^* the configurational entropy of the smallest group that can undergo the rearrangement, and N_A Avogadro’s constant. The theory asserts that τ depends not only on T but also on $S_c(T)$. The non-Arrhenius behaviour may arise from the fact that the number z^* increases with falling temperature and approaches the total number of molecules in the system at the Kauzmann temperature T_K , at which τ will diverge in the equilibrium liquid.

According to a classical view, the configurational entropy S_c should keep at a constant value $S_c(T_g)$ at temperatures below T_g , because of the freezing in of all degrees of freedom. One may notice, however, a long tail of the excess heat capacity of the glassy state over the stable crystalline phase. This long tail, observed not only for liquids but also glassy crystals and glassy liquid crystals, certainly causes S_c to change over a considerable range of temperature below T_g . There must be some common physical basis for this behaviour that will be inherent in the glassy states. It is hard to imagine the tailing effect to be of vibrational origin, since there is no counterpart in the heat capacity of the stable crystal. At high temperatures, the molecules are fluctuating among many configurational substates. As the temperature is lowered, the fluctuation becomes sluggish and ultimately freezes at T_g . Even in this case, small-scale fluctuation is possible among the substates if the barrier heights separating them are less than the molecular thermal energy kT .

It was pointed out recently that the configurational entropy S_c for polymers is not constant but decreases with lowering temperature below T_g down to T_K [24]. The theory assumed that the configurational entropy S_c could be divided into two terms, one depending on the temperature T and the other on the fictive temperature T_{fic} :

$$S_c(T, T_{fic}) = x_s S_c(T) + (1 - x_s) S_c(T_{fic}). \quad (4)$$

Here x_s ($0 \leq x_s \leq 1$) is an entropic non-linear parameter analogous to the parameter x involved in the Tool–Narayanaswamy–Moynihan (TNM) equation [25, 26] for the structural relaxation time $\tau(T, T_{fic})$:

$$\tau(T, T_{fic}) = \tau_0 \exp[x \Delta h/RT + (1 - x) \Delta h^*/RT_{fic}]. \quad (5)$$

In order to examine the reality of the low-temperature behaviour of S_c below T_g , the heat capacities of the stable and undercooled fcc phases of cyclohexanol were analysed carefully. This is because thermal properties of a crystal at low temperatures can be calculated accurately within the harmonic approximation whenever the distribution function of the normal mode frequencies is known [27]. The heat capacity of the stable crystal was calculated as the sum of the contributions from (1) intramolecular vibrations, (2) lattice vibrations, and (3) the expansion correction $C_p - C_V$. The first part $C(1)$ was calculated as the sum of the Einstein functions with the following normal mode frequencies taken from the spectroscopic data. They are as follows (in cm^{-1} with the weight given in parentheses): 220 (1), 240 (1), 338 (1), 406 (1), 454 (19), 481 (1), 556 (1), 650 (1), 786 (1), 832 (1), 843 (1), 860 (1), 888 (1), 924 (19), 970 (1), 1025 (1), 1033 (1), 1048 (1), 1200 (9), 1400 (10), 3000 (12). The only unknown mode among 51 intramolecular degrees of freedom was the torsion of the OH group ω_t . The second part $C(2)$ was approximated by the Debye heat capacity function with weight 3 for the translational vibrations and the Einstein function with weight 3 for the torsional vibrations. The third part $C(3)$ was approximated using the empirical equation $C_p - C_V = AC_p^2 T$. The heat capacity data between 15 and 200 K were used to determine four parameters by the method of least squares. The best-fitting values were $\Theta_D = 110.7 \pm 1.3$ K, $\Theta_E = 136.3 \pm 1.3$ K, $\omega_t = 294 \pm 6$ cm^{-1} , and $A = 1.13 \pm 0.09 \times 10^6$ mol J^{-1} , where Θ_D and Θ_E are the Debye and Einstein characteristic temperatures, respectively. The same values of A and ω_t were used to determine the Debye and Einstein temperatures in the glassy crystalline state. The C_p -data employed in the least-squares fitting were between 15 and 55–90 K. The temperature interval 55–90 K of the data used in the calculation was chosen to test the validity of the model functions. All the calculations using the data in this temperature interval gave essentially the same parameters: $\Theta_D = 86.3 \pm 0.8$ K, $\Theta_E = 132.8 \pm 0.9$ K. The results of the calculations are summarized in figure 6.

The curve with the data points \circ in figure 7 represents the excess entropy determined experimentally. The dotted line shows the differences in vibrational entropies, and is subtracted from the first curve to derive the configurational entropy S_c . The S_c -value at T_g , 7.1 $\text{J K}^{-1} \text{mol}^{-1}$, decreases slowly to 4.71 $\text{J K}^{-1} \text{mol}^{-1}$ at 70 K, and then the value is kept constant down to the lowest temperature. Recent neutron scattering experiments have revealed several characteristic features of glass-forming liquids. One of these characteristics is the fast process that has been found by neutron and Raman scattering studies in various kinds of glassy state [28, 29]. More experiments extending to the glassy crystals will be necessary to clarify the nature of the mobility of molecules in the glassy states. In this way, the glass transition phenomena in solids prepared by various non-equilibrium processes were studied calorimetrically. Table 2 lists the T_g -values of these solids. Among other features, solid-state vitrification by mechanical milling is unique in the sense that the starting substances are crystals.

5. Formation of molecular alloys

Mechanical alloying is a non-equilibrium process and has been used in the development of new materials in the field of metallurgy [30]. This can be done by milling of a mixture composed of two or more metals at room temperature. This low-temperature route of vitrification is particularly favourable for the molecular crystals that are prone to undergo

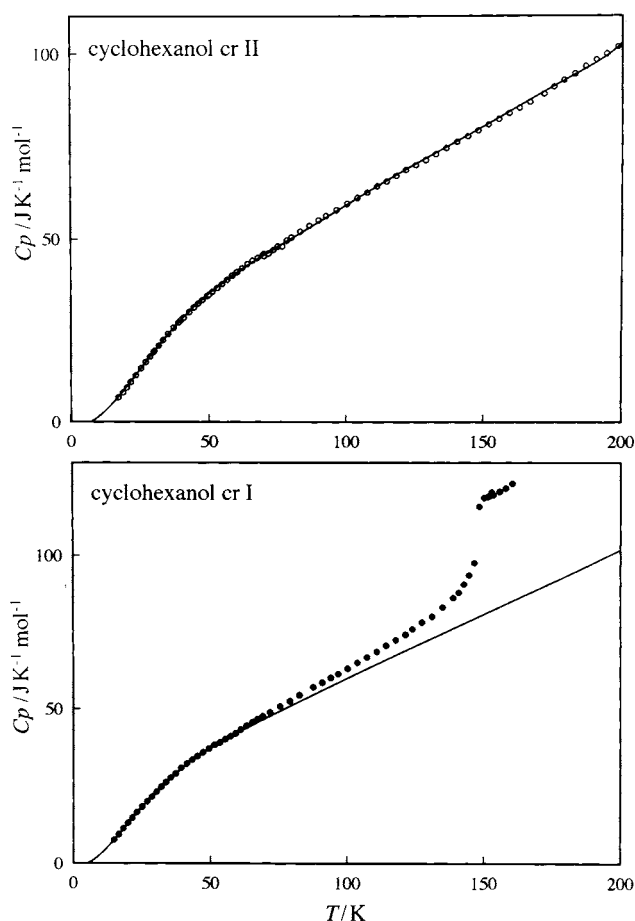


Figure 6. Reproduction of the heat capacities for stable and glassy states of cyclohexanol crystal.

thermal decomposition. In contrast to the case for metals, milling of molecular crystals produces vitreous solids even in a single system. For example, tri-*O*-methyl- β -cyclodextrin (TMCD) [31], salicin and others [32], deoxycholic acid (DCA) [33], and trehalose [34] have been vitrified in single system by this process.

Supply of mechanical energy to a crystalline substance beyond a critical level induces lattice instability of the crystal and freezes it in an energized state that has lost the original periodicity [35]. Obviously the process must be carried out at temperatures below a 'crystallization-dangerous' region of the resulting vitreous solid. The nature of the vitreous solids turned out to depend on the milling time. The T_g -value and the crystallization peak area were found to increase asymptotically with the milling time, while the x-ray diffraction halo of the resulting solid did not change significantly even after some time, say 20 min. The increased peak area of crystallization indicates an increased amount of vitreous solid. The increased T_g can be interpreted in terms of an increased fictive temperature T_{fic} of the resulting solid as the external mechanical energy is accumulated progressively [36]. For some binary molecular crystals, milling of a mixture resulted in the formation of molecular alloys with a single T_g varying continuously with the composition. The component molecules mixed

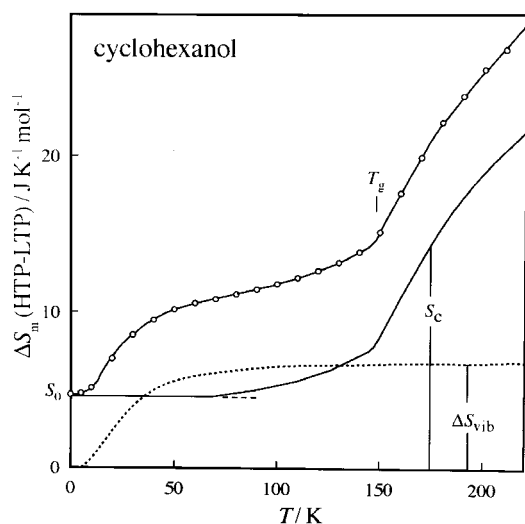


Figure 7. Variation of the configurational entropy S_c with temperature in the glassy crystalline state of cyclohexanol.

Table 2. Glass transition temperature T_g of various non-crystalline solids. LQ: liquid quenching; VC: vapour condensation; CR: chemical reaction; MM: mechanical milling of crystal; DH: dehydration of hydrate crystal.

Substance	T_g (K)	Method	Substance	T_g (K)	Method
propane	46	VC	butyronitrile	97	LQ
(propane) _x (propene) _{1-x}	46–55	VC	methanol	103	VC
propene	55	VC	vinyl acetate	123	LQ
	55	LQ	isopropylbenzene	126	LQ
(propene) _x (1-butene) _{1-x}	55–60	VC	H ₂ O	135	VC
1-butene	60	VC	<i>m</i> -cresol	200	LQ
	60	LQ	resorcinol	250	LQ
(propene) _x (1-pentene) _{1-x}	55–72	VC	salicin	333	MM
(butane) _x (1-butene) _{1-x}	60–62	VC	sucrose	342	MM
(1-butene) _x (1-pentene) _{1-x}	60–72	VC	tri- <i>O</i> -methyl- β -cyclodextrin (TMCD)	352	LQ
1-pentene	72	VC	phenolphthalene	362	MM
CCl ₄	60	VC	TMCD+benzoic acid	337	LQ
isopentane	65	LQ		337	MM
CHCl ₃	79	VC	brucine	359	MM
3-methylpentane (0.1 MPa)	77	LQ	deoxycholic acid (DCA)	363	MM
(108 MPa)	85	LQ	trehalose	384	MM
(198 MPa)	92	LQ	magnesium acetate	469	DH
ethanol	90	LQ	As ₂ S ₃	477	CR
cyclohexene	92	LQ		477	LQ
dichloromethane	93	LQ	Sb ₂ S ₃	489	VC
1-propanol (0.1 MPa)	97	LQ	polytetrahydrofuran	185	LQ
(108 MPa)	104	LQ	polyoxacyclobutane	193	LQ
(198 MPa)	109	LQ	polyoctamethyleneoxide	255	LQ
butyronitrile	97	VC			

uniformly on a molecular level to exhibit a single relaxation process over the whole vitreous solid. A binary mixture, TMCD + DCA, exhibited a maximum value of T_g at the equimolar

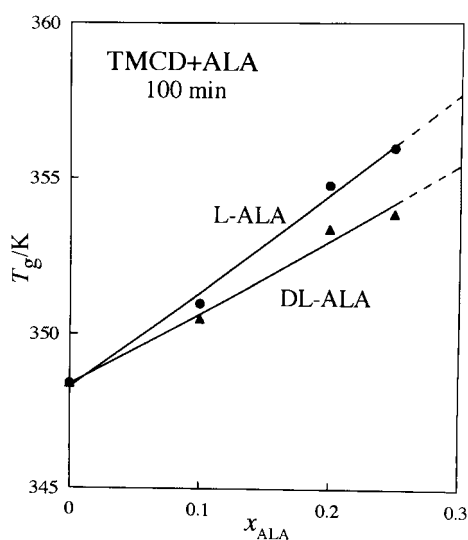


Figure 8. Variation of T_g with composition in TMCD + alanine binary solids.

composition. Study of the phase diagram of this system clarified that the prolonged relaxation time of the equimolar mixture compared to those of pure solids arose from the formation of a 1:1 intermolecular compound of the solids. Formation of solid solutions in the crystalline state is highly limited by many factors, such as the shared crystal symmetry, and the similar sizes of the unit cells and similar molecular shapes [37]. Alloying of otherwise immiscible substances in the solid state is possible only under non-equilibrium conditions.

Some molecular crystals are unable to vitrify by this method. For example, glucose alone cannot be vitrified by this process. Many publications describe glucose as a good glass-forming liquid, but the situation is not simple. Glucose changes into a mixture of α - and β -pyranose on melting [38]. There is a tendency for the glass-forming ability to be greater for binary or ternary systems than for single systems. Thus the 'glassy glucose' does not contain original glucose molecules. Even in this case, glucose can form molecular alloys over a limited composition range when the crystal is milled simultaneously with appropriate crystals that form vitreous solids in single systems. For example, a binary system (trehalose + glucose) forms molecular alloys up to $x_{GLU} = 0.5$. The mutual miscibility depends strongly on the entropies of both systems. In the gaseous phase where the entropy is the largest, all the binary systems can mix under normal conditions. Most of the binary systems can mix in their liquid state, where the disorder is intermediate. A vitreous solid is in a disordered state with extremely high viscosity, and can dissolve any second crystalline component to some extent up to the saturated solubility.

Figure 8 shows another example of molecular alloys formed in a limited composition range. Alanine crystal alone does not vitrify even after a long milling. When TMCD crystal is added, formation of molecular alloys between them is possible up to $x_{ALA} = 0.25$. Alanine is an optically active substance. L-alanine and DL-alanine behave in different manner as regards the variation of T_g with composition. Simple extrapolation of these data to $x_{ALA} = 1$ shows that the T_g of L-alanine is about 7 K higher than that of DL-alanine. Unfortunately, the fusion of the two crystals is accompanied by decomposition, so experimental verification of this difference is impossible. It will be not inappropriate to consider DL-alanine as a mixture of the D and L optical isomers and therefore as having different packing and mobility as compared to the optically pure system [39].

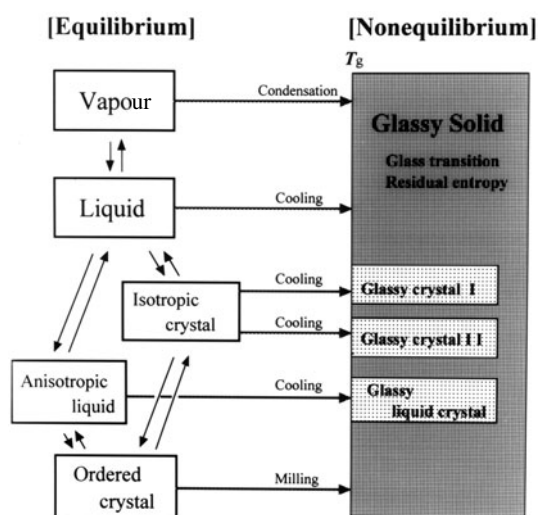


Figure 9. Subdivision of glassy states as clarified by calorimetric measurements.

This feature of formation of the molecular alloys for a poor glass-former, even in a limited concentration range, will find some applications in the pharmaceutical industry. Properties of drugs can be modified by vitrification. Thus the solubility and the rate of dissolution into relevant solvents are substantially increased by virtue of the excess Gibbs energy stored in a vitrified solid compared to the crystalline state. However, the chemical stability will be decreased by the increase in the surface area which makes attack of the molecules by moisture etc easier. Also a vitrified drug exhibits enthalpy relaxation or crystallization during storage. These problems will be overcome by embedding the drug on a molecular level into a stable vitreous solid possessing a high T_g , such as TMCD and DCA. For example, the T_g -value of indomethacin increases with the amount of TMCD, thus reducing the rate of enthalpy relaxation during storage. Development of novel functional materials is possible by the formation of molecular alloys with various combinations of two or more molecular crystals.

Figure 9 summarizes all the observed states of aggregation of molecules in the equilibrium as well as non-equilibrium states, as revealed by our calorimetric measurements. Molecular assembly can produce various states of aggregation that are much richer than we had anticipated. The subdivision of the glassy state will deepen our basic understanding of the substance and require renewal of the concept of glass transition. Freezing processes in seemingly dissimilar substances could be analysed on the same thermodynamic basis for the irreversible process, indicating the power and universality of the underlying thermodynamic principles. A new realm of amorphous solid-state science with many unsolved problems is confronting us and must be challenged.

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