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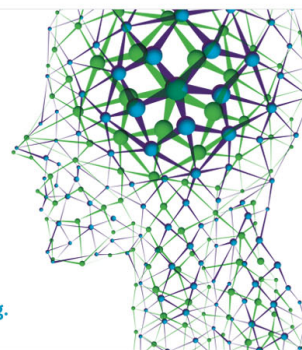
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Structural fluctuations and orientational glass of levoglucosan—High stability against ordering and absence of structural glass

Elpidio Tombari¹ and G. P. Johari^{2,a)}

¹*Istituto per i Processi Chimico-Fisici del CNR, via G. Moruzzi 1, 56124 Pisa, Italy*

²*Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada*

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To investigate whether a non-exponential relaxation always indicates 2–4 nm-size regions of dynamic heterogeneity, we studied the kinetic freezing and unfreezing of structural fluctuations involving the rotational modes in orientationally disordered crystal (ODIC) of levoglucosan by calorimetry. The heat capacity, C_p , of levoglucosan measured over the 203 K–463 K range shows that its low-temperature, orientationally ordered crystal (ORC) transforms to ODIC phase on heating, which then melts to a low viscosity liquid. On cooling, the melt transforms to the ODIC which then does not transform to the ORC. Instead, the ODIC supercools. Fluctuations resulting from hindered (random) rotations of levoglucosan molecules confined to the lattice sites and from their conformational changes become progressively slower on cooling and an orientational glass (O-G) forms showing the sigmoid shape decrease in C_p characteristic of structural arrest like that of a glass. On heating the O-G state, rotational fluctuations begin to contribute to C_p at T_{o-g} of 247.8 K and there is an overshoot in C_p and thermal hysteresis (characteristic of physical ageing) in the temperature range of 230–260 K. The non-exponential relaxation parameter, β^{cal} , determined by fitting the C_p data to a non-exponential, nonlinear model for relaxation of a glass is 0.60, which is similar to β^{cal} found for polymers, molecular liquids, and metal-alloy melts in which Brownian diffusion occurs. Such $\beta^{cal} < 1$ are seen to indicate 2–4 nm-size dynamically heterogeneous domains in an ultraviscous liquid near the glass formation, but its value of 0.60 for ODIC levoglucosan, in which Brownian diffusion does not occur, would not indicate such domains. Despite the lack of Brownian diffusion, we discuss these findings in the potential energy landscape paradigm. Levoglucosan melt, which is believed to vitrify and to stabilize a protein's disordered structure, did not supercool even at 200 K/min cooling rate. The findings have consequences for reports on the dielectric relaxation studies that indicated that levoglucosan melt supercools to form a structural glass of T_g of ~ 245 K, and for computer simulation of its dynamics. Levoglucosan is the ninth ODIC that forms O-G. It does so more easily than the other eight. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4913759>]

I. INTRODUCTION

In our current understanding of the liquid to glass transition, density and structural fluctuations in a liquid become progressively slower as it is cooled, and its viscosity increases until the liquid becomes rigid: a structural glass. These fluctuations occur at a constant volume and energy and, as the configurational entropy and free volume decrease on cooling, they become slower and the viscosity, η , increases. The increase in η is related to decrease in the configurational entropy¹ or in free volume in their respective models.^{2,3} The liquid-glass-liquid transition is investigated by measuring η , the specific heat C_p , and the thermal expansion coefficient. Dielectric, mechanical, and C_p relaxation spectra^{4–6} have shown that the fluctuation dynamics has an asymmetric distribution of relaxation times which becomes broader as fluctuations become slower, the non-exponential response parameter, β , decreases^{4,5} and a second type of fluctuations, with its own distribution of relaxation times, evolves. These features were observed usually by spectroscopy^{4–6} and, in some cases, by analyzing the C_p against T

plots.^{7,8} When a glass is heated η decreases, β increases, and the two temporally separated fluctuations begin to merge.^{3–6}

Similar changes in C_p have been observed on heating the quench-cooled state of some crystals with atomic disorder in a binary metal alloy.^{9,10} It is also known that molecular crystals occur as polymorphs, most of which are orientationally ordered crystal (ORC) phases which differ in their phonon properties, density, energy, and entropy. Diffusion of point defects in their structures also causes structural fluctuations and one expects that there would be a decrease in C_p on kinetic freezing of these fluctuations on cooling, similar to that observed on cooling through the liquid-glass transition range, albeit almost unobservably small. Some crystal polymorphs differ also in their configurational properties. In these polymorphs, the centre of mass of a molecule remains at the lattice site, and the molecule as a whole undergoes random orientational motions, or it transform between its two isomeric states. The molecules may also undergo mutarotation, the process of change in the equilibrium between two anomers when the corresponding stereo-centers interconvert. Such crystals are known as orientationally disordered crystals (ODICs) or plastic crystals,¹¹ the latter because they are soft and plastically deform easily at

^{a)}Email: joharig@mcmaster.ca

high temperatures. ODICs are generally isotropic, have a cubic or hexagonal structure with lattice dimensions of 0.6-1 nm, have low entropy of fusion (4-20 J/mol K), low volume of fusion, and high molecular diffusion coefficient near the melting point. On cooling, they transform to the ORC phase, an occurrence analogous to crystallization of a liquid. Structural fluctuations in some of the ODICs become rapidly slower on cooling until they become unobservable, and at lower temperature, they are said to form a glassy crystal.¹² According to Yamamuro *et al.*,¹³ only eight such crystals have been quenched or rapidly cooled to form glassy crystals. These glassy crystals were renamed as orientational glass (O-G). Molecular motions in ODICs and O-Gs are localized at the lattice sites.

Although soft and easily deformed, ODICs do not show Newtonian viscosity, as is known from numerous previous studies *e.g.*, ice, the most abundant ODIC, shows only a crystal axis-dependent plastic deformation evident in the motions of glaciers. Their dynamics is, therefore, necessarily studied by calorimetry or by dielectric relaxation and nuclear magnetic resonance (NMR) spectra. Because of their rapid transformation to the ORC phase on cooling and a high stability of the ORC phase, slowing of their structural fluctuations has been difficult to study. Only the gradual *unfreezing* of structural fluctuations on heating their quench-formed O-G state could be studied because the (equilibrium) ODIC phase began to cold-transform to the ORC phase,¹² a process analogous to cold-crystallization on heating some supercooled liquids. Most such studies were performed by measuring C_p on the heating path by adiabatic calorimetry, and their residual entropy was determined.¹² The *unfreezing* of orientational fluctuations appears as a C_p endotherm, which is qualitatively indistinguishable from the *glass to liquid* transition C_p endotherm.¹² It is of historical interest that sigmoid shape increase in C_p on heating the O-G state of cyclohexanol was studied by Kelley¹⁴ in 1929, and its detailed studies were performed by Adachi, *et al.*¹⁵ in 1968, who determined its residual entropy and investigated its enthalpy relaxation. In some investigations, orientational unfreezing was studied by thermal conductivity.¹⁶

Here, we report a study the C_p features during the gradual *freezing* of orientational fluctuations on cooling and during

their gradual unfreezing on heating. We also determine these changes for different cooling and heating rates. We chose levoglucosan (1,6-anhydro- β -D-glucose or 1,6-anhydro- β -D-glucopyranose, see structure in Fig. 1 inset) for this study. Levoglucosan is formed by removing one water molecule from the hexose structure and its highly strained molecule exist in only two conformations, one boat and one chair, in its solid state.¹⁷ Solid levoglucosan itself exists as two crystal phases:¹⁸ its low-temperature phase is the ORC phase in space group, $P2_1 2_1 2_1$. Its high-temperature phase is the ODIC phase. The enthalpy of its ODIC phase is 23.3 kJ/mol higher than that of its ORC phase. Broad line NMR and IR spectra have shown that ODIC-levoglucosan has decreased hydrogen bonding than glucose.¹⁸ These properties were briefly reviewed in Ref. 19.

We chose levoglucosan also for other reasons: (i) its ORC phase, highly stable at 298 K, transforms to ODIC phase on heating, and the ODIC phase then melts—most ORC phases do not transform to ODIC phase on heating. (ii) Our preliminary study showed that the levoglucosan melt did not supercool—it formed the ODIC phase on cooling—but dielectric relaxation studies of levoglucosan were interpreted, like those of glucose, to conclude that levoglucosan forms a *structural* glass with T_g of 245 K, ~ 60 K lower than T_g of glucose.²⁰ (iii) A small amount of levoglucosan "... is found to stabilize the activity and/or the native structure of freeze-dried lysozyme and catalase, despite the processing temperatures being above T_g' of excipient-protein mixtures."²¹ (iv) It is believed that in addition to stabilizing a protein against degradation, levoglucosan may increase the solubility rate of biopolymer pharmaceuticals.²¹

In this calorimetric study of the rotational fluctuations (without Brownian diffusion) and of their hysteretic behavior on the cooling and heating paths, we fit the non-exponential, nonlinear structural relaxation model used for liquids to the C_p data of levoglucosan's ODIC phase and determine the non-exponential parameter, β^{cal} . We then consider our findings of β^{cal} *vis-a-vis* the non-exponential relaxation response observed in ultraviscous liquids in which Brownian diffusion is postulated to produce dynamic heterogeneity, *i.e.*, temporally and spatially separated nm-size regions where fluctuation rates differ by several orders of magnitude. Our inability to form

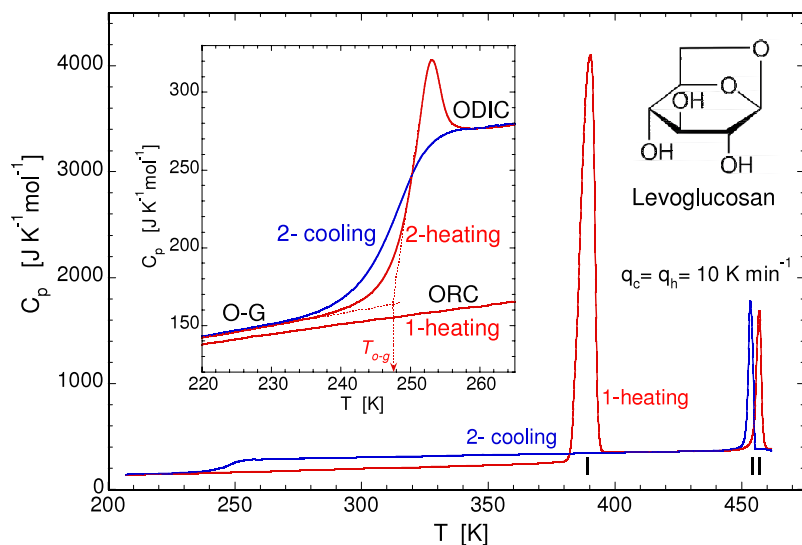


FIG. 1. The C_p against T plot (curve 1-heating, red) of the as-received ORC levoglucosan obtained by heating at 10 K/min rate. The first endotherm is due to the ORC to ODIC phase transformation and the second due to the melting of the ODIC phase. Curve 2-cooling (blue) is for the cooling of the melt from 463 K to 203 K that first transformed to ODIC phase then by supercooling to the O-G phase. By taking into account the negative dT/dt value for cooling, the crystallization exotherm of the melt to ODIC phase in the C_p plot is shown on the same side as the endotherm observed on heating. The inset shows the plots on cooling (2-cooling) and a successive heating (2-heating) through the orientational freezing on cooling (blue) and then unfreezing (red) on heating through the temperature range in which equilibrium levoglucosan ODIC becomes O-G and O-G becomes equilibrium ODIC phase. Also plotted is the C_p of ORC phase of levoglucosan measured on the first heating (1-heating) of the as-received sample. The inset shows the structure of levoglucosan.

a structural glass and the finding that levoglucosan forms an orientational glass at about the same T as the dielectrically estimated T_g ²⁰ bears upon the merits of the simulations of its melt's dynamics and of its slowing to form levoglucosan structural glass.²⁰ Levoglucosan is the ninth ODIC that supercools to form O-G. It supercools more easily and is more stable against ordering than the other eight.¹³

II. EXPERIMENTAL METHODS

Levoglucosan ($C_6H_{10}O_5$, mol wt. 162.14 Daltons) is known as an intermediate product formed on pyrolysis of cellulose and starch. It is also formed by dehydration of D-glucose which removes one H_2O molecule from D-glucose molecule and inserts an oxygen bridge into the carbohydrate ring. We purchased it as powder of 99% purity from Aldrich Chemicals and kept in hermetically sealed dry condition until use. This precaution is important because the sample absorbs moisture from air, which promotes ORC phase formation on cooling the ODIC phase, thus changing the calorimetric features.

We used Perkin-Elmer Differential Scanning Calorimeter DSC 8500 equipped with IntraCooler III as refrigerating system. The instrument was calibrated for temperature with high purity indium, naphthalene, and cyclohexane as standards according to the standard procedure used for DSC. For enthalpy, the calibration was performed with indium. The sample mass of 18–22 mg was contained in a sealed aluminum DSC pan. Nitrogen was used as purge gas at a rate of 30 mL min^{-1} . Baseline was obtained for the empty DSC pan and the DSC signal was corrected accordingly to obtain the C_p values. Measurements were performed during both cooling and heating of the sample at various fixed rates. A fresh sample was employed for each analysis to minimize the effects of degradation that could occur on repeated thermal cycling.

III. RESULTS

To characterize the formation conditions of the levoglucosan's ODIC phase and to compare the enthalpy and entropy changes on phase transformations against the literature values,^{18,19} we first cooled the as-received sample from 298 K to 203 K at 10 K/min rate and, thereafter, heated it at the same rate to 463 K. The C_p of levoglucosan measured on heating at 10 K/min is plotted against T as curve 1 in Fig. 1. It shows two endotherms, I and II. As in previous studies,^{17–19} we attribute the low temperature endotherm to transformation of the ORC phase to ODIC phase and the second endotherm to the melting of the ODIC phase. Repeated visual observations in this study were consistent with the liquid and the two crystal states of levoglucosan. Plastic solid nature of ODIC phase at 298 K is already known.^{17,18} Transformation of the ORC phase to ODIC phase begins at T_t of $383.3 \pm 0.3 \text{ K}$ (endotherm I) and the melting of the ODIC phase begins at T_m of $454.9 \pm 0.3 \text{ K}$ (endotherm II). The $C_p - T$ plot of endotherm I was integrated to obtain the enthalpy change, $\Delta H_t = 24.2 \pm 0.3 \text{ kJ/mole}$, and the $C_p - \ln(T)$ plot of endotherm I was integrated to obtain $\Delta S_t = 62.2 \pm 0.6 \text{ J/(mole K)}$, by using a straight line as the baseline for the endotherm in both cases. The $C_p - T$ plot of

endotherm II was integrated to obtain the enthalpy change, $\Delta H_m = 3.31 \pm 0.05 \text{ kJ/mole}$ and the $C_p - \ln(T)$ plot of endotherm II was integrated to obtain $\Delta S_m = 7.25 \pm 0.7 \text{ J/(mole K)}$, again by using a straight line as the baseline for the endotherm. These values are close to the value given by Rocha *et al.*¹⁹ $T_t = 384.9 \pm 0.3 \text{ K}$, $\Delta H_t = 23.2 \pm 0.4 \text{ kJ/mol}$, $\Delta S_t = 60.4 \pm 1.0 \text{ J/(mol K)}$, $T_m = 455.4 \pm 0.1 \text{ K}$, $\Delta H_m = 3.3 \pm 0.2 \text{ kJ/mol}$, and $\Delta S_m = 7.3 \pm 0.4 \text{ J/(mol K)}$ for 0.9993 (mass fraction) pure levoglucosan heated at 2 K/min. (Note that Rocha *et al.*,¹⁹ who provided a detailed review of the studies of levoglucosan and a comparison against previously published thermodynamic data,¹⁸ determined ΔS_t by the relation, $\Delta S_t = \Delta H_t/T_t$ and ΔS_m by the relation, $\Delta S_m = \Delta H_m/T_m$. We determined ΔS_m by integrating the area of the $C_p - \ln(T)$ plots.) Measurements of C_p for different cooling and heating rates using different samples taken from two different stocks gave the same values of T_t , T_m , ΔH_m , and ΔS_m . The same amount of increase in enthalpy on heating and the decrease in enthalpy on cooling shows that the reversible transformation is between a liquid and (ODIC) solid without thermal hysteresis

Figure 1 also shows the typical plot (curve 2 in blue) obtained on cooling the melt from 463 K to 203 K at 10 K/min rate, a procedure required for determining phase transformations, but not used previously.^{17–19} By taking into account the negative dT/dt value for cooling, the crystallization exotherm of the melt to ODIC phase in the C_p plot is shown on the same side as the endotherm observed on heating. It shows the beginning of the exotherm at the same T as T_m , and, within experimental errors, the same area as the melting endotherm, thus establishing that (i) the melting and freezing transitions are equilibrium transitions, and (ii) the melt does not supercool. The same amount of increase in enthalpy on heating and the decrease in enthalpy on cooling through $T_m = 455.4$ shows that the reversible transformation is between a liquid and (ODIC) solid without thermal hysteresis. None of the cooling paths, up to 200 K/min for several sample studied, showed indication of supercooling of the melt or of crystallization of the melt to the original levoglucosan's ORC phase. Instead, the melt transformed to the ODIC phase which supercooled. On cooling further through the 230–260 K range, the ODIC phase showed a sigmoid shape decrease in C_p and thereafter on the second heating, it showed a sigmoid shape curve with a C_p overshoot. The first cooling and second heating in the sigmoid shape C_p change region showed the detailed features which are plotted on an enlarged scale in the inset in Fig. 1, for cooling (in blue) and heating (in red). The plots show hysteresis and crossing of the two curves which are characteristic features of liquid-glass-liquid transition. In the case of levoglucosan, it indicates orientational freezing of the ODIC phase to form O-G. Here, we have also plotted the C_p of ORC phase of the as-received levoglucosan measured on the first heating.

We use the C_p endotherm's feature for studying, (i) the gradual freezing of localized fluctuations in levoglucosan's ODIC phase as it loses internal equilibrium on cooling and forms the O-G state, and (ii) the gradual unfreezing of localized fluctuations of its O-G state as it returns to the equilibrium state of ODIC phase on heating. The plot also shows the C_p of levoglucosan ORC phase measured during the first heating from 203 to 463 K. To distinguish the orientational freezing

temperature from the T_g of a (structural) glass, we denote the onset temperature of orientational unfreezing on heating as T_{o-g} , which is 247.8 K for the 10 K/min rate, as obtained from drawing the lines as shown in Fig. 1 inset.

To further investigate whether or not the melt can be supercooled or ODIC phase formed can be transformed to ORC phase, we did one further set of experiments according to the $T-t$ profile given in the inset of Fig. 2. First, the ORC phase was heated from 203 K to 408 K at 20 K/min and after the ODIC phase had formed, as seen by the endothermic heat flow (path a), it was cooled to 373 K (path b) and annealed for 15 min (path c) and then heated to 473 K (path d). The heat flow against T is plotted in Fig. 2. It shows no features in paths b, c, and d. The ODIC phase did not transform to the ORC phase on annealing at 373 K, which is 10 K below its T_t of 383 K. This shows that the ODIC phase of levoglucosan readily supercools and remains stable on cooling to 203 K. We then thermally cycled the sample three times between 473 K and 433 K at 20 K/min rate. In this cycling, it showed endothermic and exothermic heat flows in a reversible manner. The levoglucosan melt did not supercool. Instead, it reversibly crystallized to ODIC phase at the same T at which the ODIC phase had melted. The overshoot in C_p due to enthalpy recovery before the equilibrium C_p value is reached in the heating curve in Fig. 1 (inset), and in the plots shown in Fig. 3 demonstrates that the enthalpy decreases as O-G structurally relaxes (physically ages) during the time period of the measurements. Hysteresis of the cooling and heating paths in C_p is also due to structural relaxation on the cooling and heating paths.

Once we found the overshoot in C_p and established the hysteresis for 10 K/min heating/cooling rate, there was no need to obtain the plots for the cooling path in other scans. Therefore, to examine the C_p - T features in detail, we performed a third set of experiments in which we measured the corresponding endotherms on heating. For this purpose, we heated a new, as-received ORC phase from 203 K to 463 K at 20 K/min and transformed it to the ODIC phase and then cooled the ODIC phase to 273 K at the same rate. Thereafter, we cooled the ODIC phase to 203 K transforming it to the O-

G state and then thermally cycled it between the O-G state and its equilibrium state as described in the inset in Fig. 3. The final cycle was repeated at 20 K/min rate to ascertain that the ODIC sample had not transformed to the ORC phase during the previous two hours of thermal cycling. The cycling was performed for heating and cooling at the same rate in the sequence 20, 80, 40, 20, 10, 5, 2, and finally again at 20 K/min. (We found that for 80, 40, and 20 K/min cooling, the automated system lost control at 273 K, 243 K, and 213 K, respectively, while the heating was always under control.) The $C_p - T$ plots for the different heating rates are shown in Fig. 3, where the plot for cooling is included only for 10 K/min rate. The C_p for different thermal histories plotted here confirms the value plotted in the inset in Fig. 1 for the ODIC phase.

IV. DISCUSSION

A. Thermal hysteresis and its cyclic integral

As fluctuations become progressively slower on cooling through the liquid-glass transition range, properties of an ultraviscous melt change not only with T but also with time. On heating the glass, fluctuations become more rapid, becoming observable at a certain T , known as T_g , and their rate also changes with time until the equilibrium melt state is reached. Thus the rate of fluctuations changes with time on both the cooling and the heating paths, and a configurations-related property shows a thermal hysteresis that characterizes the liquid-glass-liquid transition and the structural relaxation during glass formation on cooling the liquid and during heating a glass. According to the first law of thermodynamics, the cyclic integral between the cooling and heating paths in a C_p against T plot should be zero, and it was found to be zero within the experimental and analysis errors.^{22,23}

According to the Clausius inequality, the cyclic integral on the irreversible paths in a C_p against $\ln(T)$ plot between two temperatures, one at $T < T_{o-g}$ and the other at $T \gg T_{o-g}$, cannot be used to determine the entropy change. We violate this premise and determine the cyclic integral of the C_p against

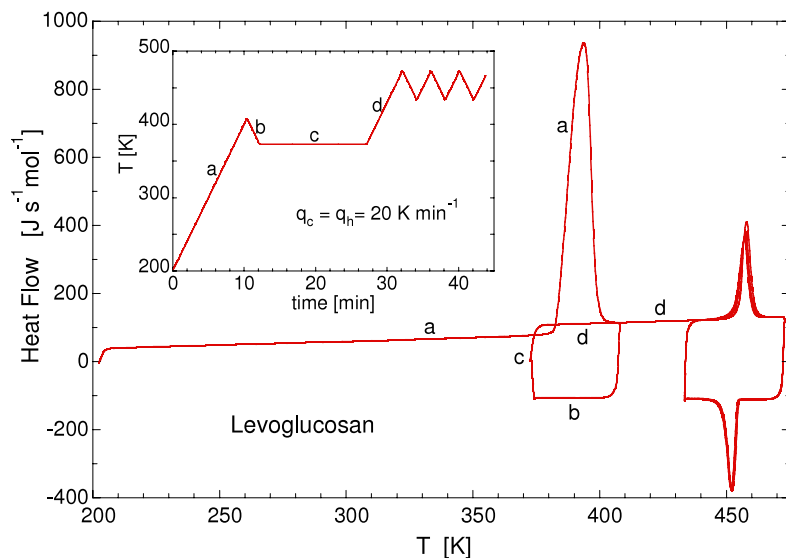


FIG. 2. The heat flow against T plots during heating and cooling at 20 K/min rate of the as received levoglucosan heated at from 203 K to 408 K, then cooled to 373 K, kept for 15 min, and heated to 473 K. Also shown is the thermal cycle in which the melt was cooled from 473 K to 433 K, heated back to 473 K and cycled three times. The $T-t$ protocol has been given as inset.

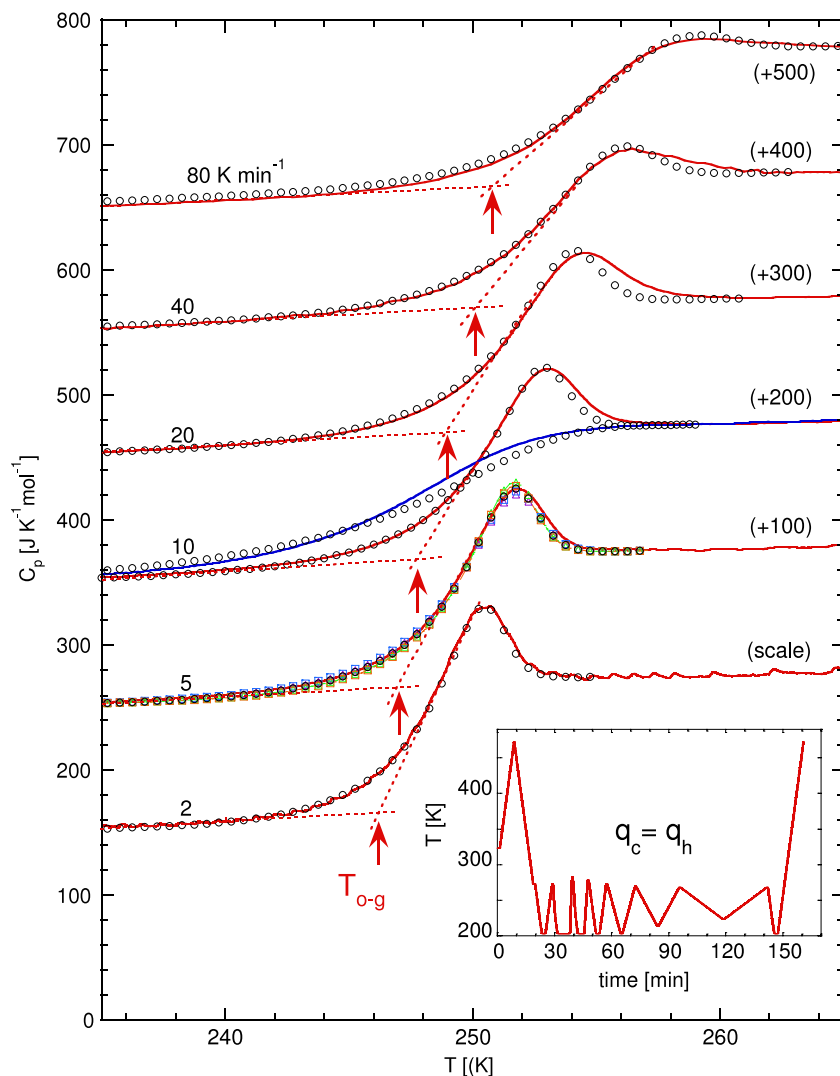


FIG. 3. The C_p against T plots of the ODIC phase of levoglucosan heated in the range from 203 K to 283 K at rates of 2, 5, 10, 20, 40, and 80 K/min after cooling at the same rates (except for 80 K/min and 40 K/min for which the automated system lost control at 273 K and 243 K, respectively), as shown by the inset. The rates are noted. The plot for 10 K/min rate includes the cooling curve and is the same as in Fig. 1 inset. Circles are the fit of the TNM model for non-exponential nonlinear model. The curves are vertically shifted by the units indicated. To show the sensitivity of the fit to β^{cal} and x values, we calculated the curves for $\beta^{cal} - x$ pairs of (i) 0.61-0.42, (ii) 0.61-0.40, (iii) 0.65-0.42, (iv) 0.65-0.44, and (v) 0.63-0.42 for the 5 K/min heating curve. These show (see for enlargement Ref. 29) that we could resolve the adequacy of the fit to within ± 0.02 of β^{cal} and x values.

$\ln(T)$ plot from

$$\Delta\sigma (\text{ODIC} \rightarrow \text{O-G} \rightarrow \text{ODIC}) = \oint C_p d(\ln T) = 0.12 \text{ J}/(\text{mol K}) \quad (1)$$

representing the $C_p d \ln(T)$ integral as σ , to distinguish it from the Clausius entropy relation. The cyclic integral contains the irreversibility of both the vibrational and configurational parts of σ , and its value is 0.12 J/(mol K) in Eq. (1). To estimate the $C_p d \ln(T)$ integral approximately from 0 K to 260 K, we use half the C_p value at 260 K, which is ~ 137 J/(mol K), and multiply it by $\ln(260)$ to obtain 762 J/(mol K). The value of 0.12 J/(mol K) from Eq. (1) is at most 0.02% of this approximate entropy. Therefore, the value from Eq. (1) is too small to have an effect on our calculations. Experiments performed previously^{22,23} also showed that the cyclic integral of the C_p against $\ln(T)$ plot was small enough that the entropy change along the path could be estimated in the hysteretic region of the C_p against $\ln(T)$ plots. It also shows that thermodynamic consequences of slowing of fluctuations in levoglucosan's ODIC phase are similar to those of slowing of the fluctuations in liquids. The residual entropy is not known, but given the large excess heat capacity difference of 104 J/(mol K) at 255 K, one expects it to be relatively high.

As in the ORC phase, the levoglucosan molecules in the ODIC phase are hydrogen bonded to the neighboring molecules. They are known to have only one boat and one chair conformation¹⁷ but may have more conformations in the gas state. The number of orientations a molecule confined to the lattice site may have would be numerically related to its configurational entropy, and this number is not known. But any conformational and configurational change is expected to occur in an intermolecular environment and, therefore, would involve overcoming intermolecular barriers. As mentioned earlier here, levoglucosan is produced by removing one water molecule from the glucose molecule, which introduces an oxygen bridge in the structure. The oxygen bridge causes strains in its molecular structure and, by affecting the steric hindrance in the pyranose ring and the orientation of the remaining three hydroxyl groups, it has an effect on the formation of intermolecular hydrogen bonds. The ODIC (high entropy) phase of levoglucosan indicates a greater vibrational contribution and a considerable configurational and conformational contribution to its specific heat. Therefore, one expects that the change in the fluctuations with time in the ODIC \leftrightarrow O-G temperature range should be a combined effect of at least four occurrences: (i) change in the rotational degree of freedom and in the available orientations, (ii) change in

the molecular conformation equilibrium, (iii) change in the hydrogen bonding and (iii) change in the phonon frequencies and anharmonic forces. The conformational contribution in the high temperature phase would be the same as in the low temperature phase if intermolecular hydrogen bonding did not change.

B. Non-exponential response parameter from model fitting

Non-exponential response parameter, β , of value between 0 and 1, is generally seen as an asymmetric distribution of relaxation times occasionally written as the sum of single relaxation times. Since there is no *a priori* way of estimating its value, it is determined by fitting the relaxation spectra of an equilibrium state. When the structure reversibly changes with T and does not change with time, β may be determined from the real and imaginary components of the complex C_p measured at a fixed frequency as a function of T , as in temperature modulated scanning calorimetry.²² Nevertheless, both β and the characteristic relaxation time, τ_0 , of a material depend upon the probe used for studying its dynamics, and the β value has been qualitatively related to the non-Arrhenius variation of τ_0 . (The subject and the importance of β for understanding the evolution of molecular motions in liquids were described in detail in a recent article, where it was argued⁶ that variation of β with T provides more insight into the relaxation processes than the variation of τ_0 with T .)

We use the Tool-Narayananaswamy-Moynihan²⁴⁻²⁷ (TNM) model for liquids to calculate the value of β over the temperature range of the ODIC to O-G state and back to ODIC transition of levoglucosan. Its formalism is written as^{26,27}

$$\tau_0 = A \exp \left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f} \right], \quad (2)$$

where τ_0 is the characteristic (calorimetric) relaxation time of the calorimetric α -relaxation process, A is a parameter equal to τ_0 when both T and T_f are formally infinity and Δh^* is the activation energy. The quantity x , whose value is between zero and 1, is the nonlinearity parameter, which takes into account the dependence of τ_0 on a liquid's structure or, conceptually, its fictive temperature, T_f . The T_f itself is defined as the temperature at which the observed property would be the equilibrium state property and its value is determined usually by extrapolation. It was noted²⁷ that Eq. (2) is empirical, and the parameters x and Δh^* have no clear physical interpretation. Glasses of a material obtained by different cooling/heating paths, or those prepared by physically or chemically different methods, may have the same T_f , but not the same configurational or the same vibrational properties. Its history dependence renders T_f as a parameter of phenomenological convenience rather than an accurate measure of the configurational and vibrational state of a glass structure. For $x = 1$, Eq. (2) becomes an Arrhenius equation, $\tau_0 = A \exp[\Delta h^*/RT]$ as it does when $T = T_f$. The relaxation function used for fitting of the model is written as, $\phi(t) = \phi(0) \exp[-(t/\tau_0)^\beta]$. (In an alternative approach, Kovacs *et al.*²⁸ treated the non-exponential relaxation as a sum of exponentials with relaxation times and weighting factors defined by the rela-

tions $\phi(t) = \int_0^\infty g(\tau) \exp-(t/\tau)d\tau$ and normalized such that $\int_0^\infty g(\tau)d\tau = 1$. They used differential equations, one for each relaxation time, to define the departure from the equilibrium and solved the coupled, nonlinear differential equations for different thermal histories.²⁸) The parameter $\beta < 1$ indicates a distribution of relaxation times, which is interpreted as a distribution of the heights of energy barriers that separate minima of equal depth in the potential energy landscape description.^{29,30} Because of its simplicity, we determined β from fitting to the TNM model by a method described in Refs. 6 and 27, where we discussed the approximations made in this fitting and critically discussed their consequences. As usual, β is taken to remain constant with changing T_f , although it would be affected by the time and temperature-dependent approach to the equilibrium state in the T -range of the T_{o-g} endotherm. In view of the approximations in the TNM model, we take this β value as an average value in the narrow T -range of the C_p endotherms in Fig. 3 and denote this β as β^{cal} at T_{o-g} of levoglucosan. The fitting of the model is shown in the C_p against T plots in Fig. 3, and the values of the best fit parameters – $-\ln(A)$, β^{cal} , x , and Δh^* obtained by the fit for different heating rates, q_h , are listed in Table I. The data for 10 K/min cooling and heating rate are: $\ln A = -200$, $x = 0.39$, $\beta^{cal} = 0.60$, $\Delta h^* = 421.0$ kJ/mol. Their values for other heating rates are expected to be the same within experimental and analytical errors, but in Table I, they differ. The differences, although small, may indicate the simplicity of the model itself.^{26,27} We also calculated T_f from the C_p -plots for the heating paths by using the area matching method as used before.²³ These values are also listed in Table I. To show the sensitivity of the fit to β^{cal} and x values, we calculated the data points for $\beta^{cal} - x$ pairs of (i) 0.61-0.42, (ii) 0.61-0.40, (iii) 0.65-0.42, (iv) 0.65-0.44, and (v) 0.63-0.42 for the 5 K/min heating curve.³¹ The plots show that we can detect the effects of variation of ± 0.02 in the β^{cal} and x values in fitting the data, thus confirming the estimated uncertainty in these values.

As mentioned earlier here, previous studies^{17,18} showed that ODIC phase is solid, and our studies showed that it is hard and opaque solid (due to the small ODIC crystals) at 273 K, i.e., at T far above its T_{o-g} . It does not flow like a liquid and could not be penetrated by a fine needle. Nevertheless, its state, in which Brownian diffusion does not occur, may still be described in terms of the potential energy barrier picture,²⁹ i.e., the potential

TABLE I. The parameters obtained by fitting the TNM formalism for non-exponential nonlinear structural relaxation to the data for levoglucosan heated at different rates q_h in K/min after cooling at the same rate. T_{o-g} is the temperature determined by drawing lines as shown in Fig. 3 and T_f is the fictive temperature determined by area matching of the heating curves. The β^{cal} and x values are within ± 0.02 , T_{o-g} and T_f are within ± 0.2 K.

q_h (K/min)	T_{o-g} (K)	T_f (K)	$-\ln(A)$	x	β^{cal}	Δh^* (kJ/mol)
2	246.1	245.7	200	0.43	0.66	420.5
5	246.9	246.8	200	0.42	0.63	420.6
10	247.8	247.8	200	0.39	0.60	421.0
20	248.8	249.0	200	0.39	0.57	421.5
40	249.9	251.4	200	0.50	0.50	422.7
80	250.8	254.5	200	0.85	0.40	424.7

energy landscape,³⁰ though few computations have attempted to do so. In this picture, each of the minima separated by energy barriers represents a specific state point of the levoglucosan's ODIC phase with its specific hindered rotations of molecules on lattice sites, its molecular conformations and its hydrogen-bond equilibrium. By definition, there is no change in the volume or energy when fluctuations occur among the various state points. On cooling through T_{o-g} , the state point for a rotational structure becomes trapped in one deep minimum, but still some molecular mobility corresponding to the short time of the distribution of relaxation times persists in the O-G state, and this mobility prevents the state from becoming entirely non-ergodic, an aspect argued for a structural glass.³² The potential energy U of a liquid itself is not a function of temperature, only of coordinates, but the probability distribution for potential energy of a state point of course is, through the Boltzmann factor, $\exp(-U/kT)$, whose integral over all coordinates of the landscape is the configuration integral which determines the shape of its T_{o-g} endotherm.²⁹ If one ignores the co-ordinates of each atom of a molecule and also of the center of its mass relative to the lattice point in the energy landscape corresponding to an ODIC phase, U of the phase would be a function of the orientation vector of a molecule.

C. Density and structure fluctuations

One expects that density (volume) fluctuations would also occur in the structure of ODIC and would become slower on cooling until they become unobservable below T_{o-g} and then become *observable* on heating from a low temperature though T_{o-g} , i.e., an ODIC would show an increase in the thermal expansion coefficient on heating above its T_{o-g} .

It is easy to envisage the source of structural fluctuations in levoglucosan, or another ODIC phase. This source may be the temperature-dependent random orientation of molecules on the lattice sites producing different configurations or temperature dependent positions of the atoms of each molecule confined to the lattice site. The onset of these fluctuations increases C_p , yielding $\Delta C_p > 0$ on heating through the T_{o-g} range. But it is difficult to envisage density or volume fluctuations that would produce $\Delta\alpha_p > 0$. One may consider that in a given spherical volume with lattice unit cell at the center, the change in the orientation of the neighboring molecules would cause the number of molecular parts in that sphere to fluctuates locally as the orientations of the neighboring molecules randomly change at a constant energy and constant volume. Thus thermal fluctuations may produce local mass density fluctuations in ODICs, as they do in liquids. According to Graessly,³³ "the dynamic environment of a molecule within a domain slow or fast depends on the density of its domain high or low." Stochastic fluctuations (meaning that a system's subsequent state is determined both by the process's predictable actions and by a random element) of thermally activated molecular orientations in levoglucosan can produce fluctuations of mass density, but the dynamic environment of the domains in levoglucosan's ODIC phase would seem to be extremely small. Therefore, the domains would not be of 2-4 nm in size, as suggested for liquids,³⁴ but may be close to the much smaller size of the unit cell of an ODIC. At a microscopic

level, density fluctuations can be seen as fluctuations in the volume of the unit cell of an (equilibrium) ODIC phase, and the temperature derivative of this volume decreases when an ODIC becomes an O-G because the decrease in the volume would be due to decrease in the size of the unit cell, as for most crystals. When the O-G state is heated through T_{o-g} , the temperature derivative of the volume of the unit cell would increase in a time-dependent manner until equilibrium ODIC is reached. Measurements of thermal expansion coefficients of ODICs have rarely been performed by diffraction or other measurements. Such measurements may be helpful in relating the entropy fluctuations with the volume fluctuations. Because of its unusual stability, levoglucosan can be studied more easily than other crystals.

D. Structural fluctuations and dynamic or static heterogeneities

On the premise that some molecules in an ultraviscous liquid move orders of magnitude faster than those a few nanometers away, dynamic heterogeneity³⁴ is also referred to as spatially heterogeneous dynamics. Mackowiak *et al.*³⁵ described it thus: "spatial heterogeneity refers to the presence of distinct regions in the supercooled liquid, each exhibiting exponential relaxations, but with time constants that may differ significantly. Temporal heterogeneity refers to alterations in the dynamics of the system or a given spatial region within the system over time." The non-exponential response comes from a sum of parallel exponential processes and these processes may be spatially separated or temporally separated. In modeling non-exponential relaxation as a sum of exponential relaxations, Majumdar³⁶ considered that each molecule has its own exponential relaxation and the relaxation time varies as the molecular environment varies. In contrast, a collection of molecules form a domain in the dynamic heterogeneity view and each domain has its own exponential relaxation, its configuration changing with time, and slower domains of this type become faster over (macroscopic) time and faster domains become slower, two domains close to each other may have relaxation times differing by orders of magnitude. The size of these domains has been estimated to be 2-4 nm³⁴ close to the value estimated for the co-operatively rearranging regions.¹ For a review related to the effect of addition of 2 nm size particles see Ref. 37. There we also pointed out that light scattering intensity measurements on multi-component ultraviscous melts used by Moynihan and Schroeder's³⁸ and by Bokov³⁹ to conclude that structure of these (ultraviscous) melts consists of heterogeneities. But after performing further experiments, Bokov concluded:⁴⁰ "The results obtained illustrate that the universal character behavior of the visible light scattered intensity exhibited as a peak in the glass transition region of oxide glass may be explained by the non-equilibrium part of the scattered intensity produced by the temperature gradient arising from the sample at the initial moments after the temperature rise." This new finding puts into question the basis used for inferring structural heterogeneity of ultraviscous liquids.

To consider the relevance of these views to ODICs, we envisage each molecule of levoglucosan on its lattice site to

have a different rotational fluctuation rate, depending upon its already fluctuating environment, with the reference molecule being a part of the environment formed by the neighboring molecules on the lattice sites. But, still it is difficult to envisage formation of 2–4 nm size heterogeneous or homogeneous domains separated spatially as well as temporally from other domains with order of magnitude difference in the fluctuation rates that can produce a non-exponential response or a distribution of relaxation times in the levoglucosan's ODIC phase.

One of us noted⁶ that the ODICs generally show a non-exponential response in their dielectric relaxation studies,^{41,42} which is intriguing because ODIC of 1-cyanoadamantane, a rigid molecule, also has shown a non-exponential dielectric relaxation.⁴³ A basic difficulty in reconciling non-exponential relaxation with the dynamic heterogeneity view here is that translational (Brownian) diffusion of molecules is needed for forming dynamically heterogeneous domains and for increasing their size on cooling. Moreover, before slower domains could become faster and faster domains become slower, intermolecular distance should change. But molecules in levoglucosan ODIC occupy fixed lattice sites and as described here, it does not show viscous flow. Therefore, although levoglucosan's ODIC phase has a configurational entropy, its β^{cal} of 0.60 may not be explained by suggesting dynamically heterogeneous domains in its structure. Since β^{cal} is expected to decrease with decrease in T_f and the fluctuations to become slower with time in the temperature range of orientational slowing in the T_{o-g} range, one would expect that such domains would become larger with time at a fixed T in this range. But the Brownian diffusion needed for this occurrence is absent in levoglucosan's ODIC phase.

Oriental fluctuations also occur in molecular liquids. Whether or not, they always have a role in determining the dynamics of liquids is uncertain, because reorientation of a spherically symmetric ideal molecule is *not* a fluctuation. Since, an atom has no orientation and therefore no orientational fluctuations, the observed non-exponential behavior of viscoelastic relaxation of metal alloy glasses must be due only to fluctuations arising from Brownian motions. We also note that optical Kerr effect spectroscopy studies of noble-elements have shown that relaxation of argon, krypton, and xenon liquids is non-exponential with β of about 0.66.⁴⁴ Therefore, it would seem that Brownian diffusion is needed for producing a non-exponential response; orientational motions are not needed. But there is no Brownian diffusion in ODIC levoglucosan, still it shows β^{cal} of 0.60. We argue that β^{cal} of the ODIC levoglucosan represents the sum of exponential thermal relaxations of molecules on the lattice sites with a distribution of barrier heights that vary with the intermolecular environment of the molecule.

E. Structural glass of levoglucosan or orientational glass

In this study, we find that levoglucosan melt does not supercool or form a structural glass even for cooling at 200 K/min rate. Instead, the melt crystallizes to its ODIC, which on further cooling transforms to the O-G state. The transformation between the ODIC-OG-ODIC states resembles

a liquid-glass-liquid transition. Previous studies^{17–19} had also found no evidence for the melt persisting at room temperature. However, Kaminski *et al.*²⁰ interpreted their dielectric relaxation study of levoglucosan as if it was a study of its supercooled liquid that vitrified or formed a structural glass on further cooling. The melt contained in a dielectric cell was quenched to room temperature in their study, and the dielectric relaxation spectra were measured during slowly cooling the dielectric cell. Their computer simulation of the relaxation processes in levoglucosan was also based on the assumption that levoglucosan melt supercooled and formed a structural glass.

The dielectric relaxation time data of levoglucosan yielded T_g of 245 K,²⁰ and the dielectric loss spectra peak (at ca 0.01 Hz at ~ 243 K)²⁰ yields a relaxation time of 16 s. We find that T_{o-g} is 246.1 K for cooling-heating rates of 2 K/min and T_{o-g} is 248.8 K for 20 K/min rate (see Table I for T_{o-g} s for other cooling-heating rates). The agreement between T_g in Ref. 20 and T_{o-g} here indicates that the levoglucosan they had studied²⁰ may have been in its ODIC phase. Nevertheless, we also note that calorimetric T_g (= 97 K) of ethanol was found to be the same as its calorimetric T_{o-g} (= 97 K).^{45,46} Haida *et al.* pointed out⁴⁵ that the ODIC phase of ethanol was not known in 1929, and therefore its C_p decrease on orientational freezing was reported as the glass transition of liquid ethanol.⁴⁷ Benkhoff *et al.*⁴⁸ reported that at 107 K, the dielectric relaxation time of ODIC ethanol is at least 10-times of that of its liquid and similar differences were found by others.^{49,50} So, one may argue that T_g and T_{o-g} of levoglucosan can also be similar. There is, however, one major difference between levoglucosan and ethanol: ethanol's liquid and ODIC phases rapidly crystallize to the ORC phase, and the liquid had to be quenched to form the glassy state and to avoid formation of the ODIC or the ORC phase. Also, in order to avoid formation of the ORC phase, the ODIC ethanol itself had to be quenched to the O-G state. In our study, levoglucosan melt could not be supercooled to 300 K, it crystallized to ODIC phase. On that basis, we suggest that levoglucosan's ODIC phase and not its supercooled melt were studied in Ref. 20. A better characterized state of levoglucosan may resolve the dielectric features of its ODIC phase from that of its melt.

We also consider the value of β^{cal} against the value of the Cole-Davidson asymmetric distribution parameter, β_{CD} , determined by a comprehensive dielectric studies by Brand *et al.*⁴² They found that its value ranges between 0.5 and 0.8 for the six plastic crystals they had studied. The β^{cal} of 0.6 for the slowest heating rate reported here for levoglucosan is within this range 0.5–0.8 of β_{CD} .⁴² A discussion of the role of the distribution of relaxation time is already provided in detail in Ref. 6, Sect V(G), where numerous explanations for the non-exponential relaxation were critically reviewed and it was argued that the change in the distribution of relaxation time with T is perhaps more meaningful in understanding the glass formation than the extent of non-Arrhenius temperature dependence of the viscosity. That conclusion has been extended to ODICs here. It should be noted also that an intrinsically nonexponential relaxation, rather than a distribution, would require that all molecules have the same time-dependence of the relaxation time. Since there is no Debye response or a

single relaxation time, each molecule is expected to show the same non-exponential response. While it is conceivable that the distribution is not the sum of multiple Debye-responses, it seems improbable that all molecules would have the same non-exponential response, especially when no two molecules have identical environment even in ODICs. As discussed earlier,⁶ there is a need to investigate the source of the non-exponential response.

V. CONCLUSIONS

The ORC phase of levoglucosan is stable at ambient temperature. It transforms to the ODIC phase on heating, and the ODIC phase melts on further heating. On cooling, the melt crystallizes to the ODIC phase, but the ODIC phase does not transform to the ORC phase even when cooled at 2 K/min or annealed at 10 K below the temperature at which it had been formed on heating the ORC phase. Only the melting and crystallization is found to have an equilibrium temperature. Unlike glucose, levoglucosan melt does not supercool and vitrify even when cooled at 200 K/min cooling rate; it rapidly crystallized to the ODIC phase. The levoglucosan's ODIC phase is more stable and over a wider T range than any other known ODIC phases, which had to be rapidly quenched to form the O-G state.

On orientational freezing during cooling of levoglucosan's ODIC phase, C_p changes in the sigmoid manner and there is a thermal hysteresis of the C_p plots on the cooling and heating paths. The orientation unfreezing temperature is 247.8 K for 10 K/min cooling and heating rates. Entropy change in the hysteretic thermal cycle, whose estimate is not permitted by the Clausius theorem, is negligibly small. The $C_p - T$ plots for cooling and heating at 10 K/min can be fitted to the non-exponential, nonlinear relaxation model, and β^{cal} is 0.60. In its configurational thermodynamics, orientational freezing of levoglucosan's ODIC phase resembles the freezing of Brownian motions in polymer, molecular and metal-alloy melts, and glasses.

Previously, we had found that fructose, glucose, and galactose crystals spontaneously liquify when kept at T significantly below their melting points according to a mechanism in which a vacancy diffusing from site to site in crystal lattice increases the energy of the neighboring molecules which then tautomerize.⁵⁰ The tautomer no longer fits the lattice site nor can it revert to its original state. This produces locally disordered, liquid-like regions in the lattice; the population and size of such regions grow with time; the regions become connected and ultimately merge, thus causing their crystals to liquify without heating. This may occur in ORC or ODIC phases of levoglucosan mainly because its (dehydrated glucose) molecular structure is highly strained.

Slowing of the orientational fluctuations on cooling and the resulting C_p features on formation of O-G state may be envisaged as belonging to that part of the potential energy landscape that corresponds to the orientational-configuration states. It is argued that thermal expansion coefficient would also decrease in the same manner as C_p decreases on kinetic freezing of orientational fluctuations, but the molecular mechanism for it is difficult to envisage. Brownian motion of

molecules is needed to cause the (nm-size) slower domains to become faster and faster domains to become slower. In the absence of such motions, it seems difficult to reconcile the non-exponential enthalpy fluctuations in levoglucosan's ODIC phase.

Because they lack positional disorder, orientational glasses are considered as simplified models of structural glasses. Yamamuro, *et al.*¹³ noted that there are eight ODICs that can be quenched or rapidly cooled to form an O-G. The molecules that form O-Gs are, ethanol ($T_{o-g} = 97$ K), cyclohexanol ($T_{o-g} = 150$ K), cyanocyclohexane ($T_{o-g} = 135$ K), isocyanocyclohexane ($T_{o-g} = 129$ K), 1,2-difluorotetrachloroethane ($T_{o-g} = 90$ K), 2,3-dimethylbutane ($T_{o-g} = 76$ K), cyanoadamantane ($T_{o-g} = 170$ K), and cyclo-octanol ($T_{o-g} = 168$ K), whose thermodynamic, dielectric, and NMR studies were performed for the purpose of investigating their orientational relaxation and the O-G formation. On examining the behavior of these ODICs, we find that the ninth molecule, levoglucosan, is the easiest one to supercool and to form an orientational glass. It remains stable against ordering.

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