Coupling of Caged Molecule Dynamics to JG β-Relaxation III: Van der Waals Glasses

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Abstract

In the first two papers separately on the polyalcohols and amorphous polymers of this series, we demonstrated that the fast dynamics observed in the glassy state at high frequencies above *circa* 1 GHz is the caged dynamics. We showed generally the intensity of the fast caged dynamics changes temperature dependence at a temperature T_{HF} nearly coincident with the secondary glass transition temperature $T_{g\beta}$ lower than the nominal glass transition temperature $T_{g\alpha}$. The phenomenon is remarkable since T_{HF} is determined from measurements of fast caged dynamics at short time scales typically in the ns to ps range, while $T_{g\beta}$ characterizes the secondary glass transition at which the Johari-Goldstein (JG) β-relaxation time τ_{JG} reaches a long time $\sim 10^3$ s, determined directly either by positronium annihilation lifetime spectroscopy, calorimetry, or low frequency dielectric and mechanical relaxation spectroscopy. The existence of the secondary glass transition originates from the dependence of τ_{JG} on density, previously proven by experiments performed at elevated pressure. The fact that $T_{HF} \approx T_{g\beta}$ reflects the density dependence of the caged dynamics and coupling to the JG β-relaxation. The generality of the phenomenon and its theoretical rationalization implies the

same should be observable in other classes of glass-formers. In this paper III, we consider two archetypal small molecular van der Waals glass-formers, ortho-terphenyl and toluene. The experimental data show the same phenomenon. The present paper extends the generality of the phenomenon and explanation from the polyalcohols, a pharmaceutical, and many polymers to the small molecular van der Waals glass-formers.

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1. Introduction

In Papers I and II of this series, we have reexamined the present and past high frequency measurements in the glassy state of the polyalcohols, a pharmaceutical[1], and many amorphous polymers[2]. The measurements of the fast processes were carried out by quasielastic neutron scattering, quasielastic light scattering, Brillouin scattering, and high frequency dielectric measurements from GHz to THz. In all the glass-formers studied, the Johari-Goldstein (JG) β-relaxation and the α-relaxation are far too slow to be observed in these high frequency measurements at temperatures below $T_{g\alpha}$, the nominal glass transition temperature. The fast processes observed in the glassy state are essentially the vibration and the caged molecule dynamics. The latter was observed in susceptibility measurements as the nearly constant loss (NCL), and in scattering measurements as the elastic scattering intensity, $S(Q, \omega \approx 0)$, where Q and ω are the scattering wave vector and frequency respectively, or the mean square displacement, $\langle u^2 \rangle$. On increasing temperature but still remaining in the glassy state, the caged dynamics measured by either the NCL, $S(Q, \omega \approx 0)$, or $\langle u^2 \rangle$ exhibit a change from a

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weaker temperature dependence at lower temperature to a stronger one on crossing some characteristic temperature T_{HF} ($<T_{g\alpha}$). Arising from this general property is the following interesting question. What is the physical meaning and significance of T_{HF}?

Previous studies of many glass-formers by various experimental techniques over broad range of frequencies have found that the caged dynamics is terminated at lower frequencies[1-8] by the JG β-relaxation[9-11]. Hence the two processes are coupled, and some property of one is transferable to or reflected in the other. One such property is the density dependence of JG β-relaxation strength and relaxation time τ_β or frequency ν_β. The dependence of τ_β on density gives rise to a kinetic secondary glass transition at temperature $T_{g\beta}$ below $T_{g\alpha}$. On cooling below $T_{g\beta}$, τ_β becomes much longer than the laboratory time-scale, and the density coupled to the JG β-relaxation falls out of equilibrium together with τ_β.

The calorimetric and volumetric effects associated with the secondary glass transition at $T_{g\beta}$ is much weaker than the structural α-relaxation at $T_{g\alpha}$, but was observable in some glass-formers by various kinds of precision calorimetry[12-17], and by positronium annihilation lifetime spectroscopy (PALS)[18-21]. These techniques directly determine $T_{g\beta}$. A recent experiment has detected the secondary glass transition and determined $T_{g\beta}$ of a well aged metallic glass by Differential Scanning Calorimetry[16], showing that the non-equilibrium glassy state is characterized by two fictive temperatures: the higher one corresponding to the kinetic freezing of cooperative α-relaxation and the lower one to the kinetic freezing of β-fluctuations.

In glassformers where the τ_β in the glassy state are known from low frequency dielectric or mechanical relaxation measurements, the Arrhenius T-dependence of τ_β can be used to determine $T_{g\beta}$ as the temperature at which τ_β attains an arbitrarily long time such as 10^3 s.[1,22]

Among the findings in Papers I and II, is the good agreement between T_{HF} and $T_{g\beta}$ found in the polyalcohols, a pharmaceutical, and many amorphous polymers. This finding is remarkable because of the ten orders of magnitude or more difference in time scales between the fast dynamics in the GHz-THz range determining T_{HF} and the vitrification at ~10^{-4} Hz at $T_{g\beta}$. Not pointed out before by others, this general property, $T_{HF} \approx T_{g\beta}$, is a new paradigm of fundamental properties of glass transition. It deserves attention from any serious attempt to solve the glass transition problem on a theoretical basis. In Papers I and II we rationalize the finding from the coupling of the caged dynamics to the JG β-relaxation, and the density dependence of the JG β-relaxation as well as that of the caged molecule dynamics. Without the coupling, the caged molecule dynamics would not respond to the secondary glass transition at $T_{HF} \approx T_{g\beta}$, as observed in experiments.

The purpose of this paper is to extend the generality of the findings in Papers I and II to the class of small molecular van der Waals glass-formers. The dynamics of these important class of glass-formers have been extensively studied by various techniques over broad range of time scales. Here we are interested again in the fast process observed in the glass state at high frequency and its connection to the secondary glass transition of these glass-formers. From the experimental measurements reported in the past, we determine the crossover

temperature T_{HF} of the caged molecule dynamics observed at high frequencies, and compare T_{HF} with $T_{g\beta}$ determined by adiabatic calorimetry and/or low frequency dielectric relaxation.

While many more amorphous polymers[2] had been studied by high frequency techniques to find the fast caged dynamics in the glassy state, similar results are available from only four small molecular van der Waals glass-formers. They are o-terphenyl, toluene, propylene carbonate, and tri-naphthyl benzene, which will be considered in the following sections.

2. o-terphenyl

Quasielastic neutron scattering (QENS) is a method to characterize the fast processes as a function of temperature T.[23-25] Directly measured is the incoherent dynamic structure factor, $S(Q,\omega,T)$, which is the Fourier transform of the time dependent density-density correlation function, $\Phi(Q,t)$. From the incoherent scattering function, $S(Q,\omega,T)$, the elastic part of the scattering, $S_{el}(Q,\Delta\omega,T)$, is operationally defined by the integral of $S(Q,\omega,T)$ over ω within -$\Delta\omega < \omega < \Delta\omega$, where Q is the momentum transfer and $\Delta\omega$ is the resolution frequency width. After normalizing $S_{el}(Q,\Delta\omega,T)$ measured at temperature T by its value at $T\approx 0$, $S_{el}(Q,\Delta\omega,T\approx 0)$, one defines a Debye-Waller factor, $W(Q,\Delta\omega,T)$ and a mean square displacement $<u^2(T)>$ of the fast process by

$$S_{el}(Q,\Delta\omega,T)/S_{el}(Q,\Delta\omega,T\approx 0)=\exp[-2\,W(Q,\Delta\omega,T)]=\exp[-<u^2(T)>Q^2/3] \qquad (1)$$

Thus, either the elastic intensity, the Debye-Waller factor, or $<u^2(T)>$ is a measure of intensity of the fast caged dynamics in addition to the vibrational contribution.

Bartsch et al. measured $S(Q,\omega,T)$ of o-terphenyl[23], and from which they obtained the elastic scattering intensity, and $<u^2(T)>$. The spectrometer they used is IN 13 at Institut Laue-Langevin in Grenoble, and the time scales monitored is from 10^{-9} to 10^{-11} s. Their data of

$<u^2(T)>$ are reproduced in Fig.1. The two broken lines are drawn to depict a change of temperature dependence of $<u^2(T)>$ at some temperature T_{HF} in the glassy state. T_{HF} is significantly lower than the calorimetric $T_{g\alpha}$=243 K given by Bartsch et al. and $T_{g\alpha}$=240 K determined from dielectric relaxation, light scattering[26] and adiabatic calorimetry with $\tau_\beta(T_{g\alpha})$=10^3 s by Fujimori and Oguni[12] as shown in the upper panel. The broken line at lower temperatures appropriately represents effectively the vibrational contribution, which at higher temperatures is superseded by the fast caged dynamics as suggested by upper broken line drawn in the figure to guide the eye. The secondary or β glass transition of *o*-terphenyl was successfully observed by the adiabatic calorimetry[12]. At $T_{g\beta}$=133 K, the JG β-relaxation time τ_{JG} is 10^3 s, the value ascertained from the empirical relation between the observed drift rates in adiabatic calorimetry and the relaxation times[12]. This result is presented by the lone star in the upper panel of Fig.1. It is in agreement with τ_{JG} from dielectric relaxation[9] after extrapolating its Arrhenius *T*-dependence to lower temperatures to reach 133 K. The downward pointing arrow in the lower panel of Fig.1 indicates the location of T_{HF} where $<u^2(T)>$ exhibits the change in *T*-dependence. The thin shaded region connecting the two panels indicate possible values of T_{HF}, which are all near $T_{g\beta}$=133 K. Thus the $<u^2(T)>$ data in the lower panel of Fig.1 show either an onset or a change from a weaker *T*-dependence to a stronger one at some temperature close to $T_{g\beta}$. This is the same property we[1] found deep in the glassy state from the THz dielectric loss data[27] of the hydrogen-bonded polyalcohols, and the pharmaceutical flufenamic acid[28], and from quasielastic neutron and light scattering in many amorphous polymers[2]. For OTP we have $T_{g\beta}/T_{g\alpha}$=0.55≈ $T_{HF}/T_{g\alpha}$. Present also in Fig.1 is the much stronger increase of $<u^2(T)>$ at temperatures above $T_{g\alpha}$. This is a well known feature of fast caged dynamics, and has been observed in glassformers of many different kinds[29]. The

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change of temperature dependence at $T_{g\alpha}$ is a general property of any dynamic or thermodynamic variable that is coupled to density and is observed not only by neutron scattering but also other high frequency techniques.

Direct observations of the NCL in the time domain from ps to ns range (note that a relaxation time equal to 1 ps corresponds 1 ps corresponds to 0.16 THz) were made by optically heterodyne detected optical Kerr effect (OHD-OKE) experiments on a variety of small molecular glass-formers including ortho-terphenyl, salol, benzophenone and others at temperatures *above* $T_{g\alpha}$.[30-32] Experiments carried out at lower temperatures will move the secondary relaxation further to longer times, and therefore the NCL certainly will continue to be observed below $T_{g\alpha}$ in the time range from ns to ps, and observed as the fast process by neutron scattering. With the help of the OHD-OKE experimental results, we can be assured that the $<u^2(T)>$ below $T_{g\alpha}$ in Fig.1 come from the caged dynamics and are related to NCL in susceptibility since they were obtained in the time range from 10^{-9} to 10^{-11} s of IN13.

Tölle[24] pointed out that Flinn and coworkers[33] found the first experimental indications of the presence of the fast process in the glassy state of *o*-terphenyl from the temperature dependence of the Debye–Waller factor, $f_Q=\exp[-2\,W(Q,T)]$, obtained by Mössbauer-spectra of ^{57}Fe in ferrocene dissolved in OTP. Tölle replotted the OTP Mössbauer data of $2W(Q,T)$ at $Q = 7.3$ Å^{-1} against T, and fitted the two points at the lower temperatures linearly with a straight line originating from zero value of $2W(Q,T)$ at T=0. Brought out by the fit and noted by Tölle, is the nearly linear temperature dependence at low temperatures, which is followed by an increase starting already at some temperature T_{HF} below $T_{g\alpha}$. These historic data published in 1972 is worth reproducing them in the same version as given by Tölle here in Fig.2. Added are the arrow indicating the locations of $T_{g\beta}$=133 K and $T_{g\alpha}$=240 K. There is not

enough data points of $2W(Q,T)$ to show exactly where the increase starts, but it can be close to $T_{g\beta}$=133 K. From the proportionality relation between $2W(Q,T)$ and $<u^2(T)>$, the results of the Mössbauer experiment are in accord with the neutron data in Fig.1, and together they confirm the caged dynamics changes its T-dependence at or near $T_{g\beta}$.

Schnauss et al.[34] performed ^{2}H-nuclear magnetic resonance spin-lattice relaxation experiments to study the dynamics of perdeuterated o-terphenyl and glycerol in the glassy and the liquid states. In this paper we are interested mainly in the spin-lattice relaxation data in the glassy state. For this reason, their ^{2}H spin-lattice relaxation times T_1 data at temperatures below $T_{g\alpha}$ and only those slightly higher than $T_{g\alpha}$ are reproduced in Fig.3. In this plot of~~against~~ of $\log T_1$ against T ~~T of log T_1~~ obtained at two Larmor frequencies, 15 and 55 MHz,

the data in the glassy state change from a weaker T-dependence to a stronger T-dependence as suggested by the lines drawn to guide the eye. Despite two separate T-dependences, the temperature dependence of T_1 overall is weak and consistent with exp($-T/T_{ref}$). From the fluctuation-dissipation theorem[35], we have $(1/T_1) \propto (kT/\omega)\chi''(\omega)$, and hence it follows that the susceptibility $\chi''(\omega)$ has the weak T-dependence $\sim T^{-1}$exp(T/T_{ref}), which the signature of the NCL.[4-8] Thus the change in T-dependence of T_1 observed at some T_{HF} is tantamount to changed in T-dependence of NCL at the same T_{HF}. In Fig.3 we locate the secondary glass transition temperature $T_{g\beta}$=133 K by the arrow. By inspection of Fig.3, the spin-lattice relaxation times data also supports the relation, $T_{HF}\approx T_{g\beta}$, as found by quasielastic neutron scattering and Mössbauer experiments.

Monaco and coworkers[36] studied extensively the dynamics of o-terphenyl in both the liquid and glassy states by Brillouin light scattering in the frequency range of the order of 10 GHz. The full-width at half-maximum of the Brillouin peak, Γ, obtained from the

measurements as a function of temperature is reproduced in Fig.4. The raw data of Γ show a change in T-dependence at some temperature T_{HF} near $T_{g\beta}$=133 K. The location of $T_{g\beta}$ in the figure is indicated by the downward pointing arrow, while $T_{g\alpha}$=243 K is indicated by the other arrow. Monaco made the ansatz in the glassy state that Γ is the sum of two contributions. One contribution is from a fast process with characteristic time in the 10^{-11} s range and is almost temperature independent, similar to the fast process observed in glassy o-terphenyl by other experimental techniques[37-39]. The other contribution was attributed to the presence of topological disorder in the glass, but we interpret it as coming from the NCL of caged dynamics like in Figs.1-3 by other techniques.

Uvarov et al.[40] applied electron spin echo technique to study transversal spin relaxation of photo-excited triplet state of fullerene C70 molecules in glassy o-terphenyl. In the sub-$T_{g\alpha}$ temperature range, they found the relaxation rate increases sharply above 110 K in o-terphenyl. This value of T_{HF} is some 20 ~~degrees~~ K lower than that found by the other techniques. The discrepancy is not understood at this time.

3. Toluene

Toluene has a prominent JG β-relaxation and its relaxation time τ_β has Arrhenius T-dependence given by $\tau_\beta = \tau_{\infty\beta} \exp (E_\beta/T)$ with $\tau_{\infty\beta}$=10^{-16} s and E_β=3027 K or 25.2 kJ/mol.[41,42] The relaxation times of bulk toluene, τ_β and τ_α, are reproduced from the data given in Hatase et al.[22] but as functions of temperature in the upper panel Fig.5. The values of $T_{g\alpha}$ and $T_{g\beta}$ are 117 K and 69.1 K respectively. The presence of the JG β-relaxation as well as the NCL of toluene can be seen in the isothermal dielectric loss spectra at temperatures below $T_{g\alpha}$ in ref.[42]. At 70 K, the NCL is the only process with frequencies higher than 1 Hz in the loss

spectrum shown in Fig.2 in ref.[42]. Therefore there is no doubt that the process probed at high frequencies by neutron scattering in the glassy state is the NCL of caged dynamics. Hinze and Sillescu[43] measured the ^{2}H-NMR spin-lattice relaxation times T_1 of phenyl ring deuterated toluene as a function of temperature from 75 to 290 K at Larmor frequencies between 13.8 and 55.8 MHz. They found no change of T-dependence of T_1 in the range studied unlike the case of OTP.[34] This difference is readily understood because in their spin-lattice relaxation study of toluene[43] the lowest temperature reached is 75 K, which is above $T_{g\beta}$ =69.1 K. Nevertheless, the T_1 data in the glassy state in a plot of logT_1 vs. 1000/T in Fig.5 of ref.[43] originate from the NCL because the activation energy ranges from 2.2 to 3.9 kJ/mol is much smaller than the E_β=25.2 kJ/mol of the JG β-relaxation of toluene. Hence the observed T_1 deep in the glassy state has to be identified with the NCL, and not with the β-relaxation of toluene as incorrectly done in ref.[43].

The first study of toluene by neutron scattering was published by Frick et al.[44] using the sample, toluene-d3, in which the hydrogen in the methyl group is replaced by deuterium. By this strategy, the unwanted fast contributions to the scattering from the dynamics of the methyl groups are practically absent. The objective of that publication is to study the finite-size effect on the dynamics of toluene in confinement. In Fig. 5 we reproduce the temperature dependence of the mean squared displacement $<u^2(T)>$ for toluene-d3 in MCM-41 matrices of different pore size. The IN10 spectrometer at ILL was used to acquire the data with high energy resolution of about 1 μeV, corresponding to observation times of the order of 4 ns. The $T_{g\alpha}$ of confined toluene-d3 determined by DSC is higher than the bulk $T_{g\alpha}$=117 K, and the difference increases on decreasing the pore size. The increase of $T_{g\alpha}$ of toluene-d3 in confinement is caused by surface interaction with the confining MCM-41 which slows down

the cooperative α-relaxation. The effect penetrates layer by layer into the pore volume, causing the α-relaxation to be spatially heterogeneous, and in turn $<u^2(T)>$ to increase smoothly over a broad temperature region centered at the $T_{g\alpha}$ determined by DSC. On the other hand, the surface interaction and confinement has practically no effect on the caged dynamics because these are local processes, particularly in the glassy state. We cannot exclude the possibility that the averaged $T_{g\beta}$ of confined toluene-d3 could be slightly increased from the bulk value, but the change is not expected to be significant. Hence we can use the $<u^2(T)>$ of confined toluene-d3 in the lower panel of Fig.5 to look for the change in temperature dependence at T_{HF}, and $T_{g\beta}$ of bulk toluene-d3 should still be a good estimate of T_{HF} if the relation $T_{HF} \approx T_{g\beta}$ holds for toluene. The shaded region connecting the upper and lower panels indicates where $<u^2(T)>$ of the confined toluene-d3 exhibits a change of temperature dependence in the glass state. The possible values of T_{HF} lie within the shaded region, and are all near $T_{g\beta}$=69.1 K of bulk toluene. Thus the fast caged dynamics in in toluene show either an onset or a change from a weaker T-dependence to a stronger one at some temperature T_{HF} which is nearly equal to $T_{g\beta}$. The property, $T_{HF} \approx T_{g\beta}$ holds in the case of toluene. For toluene we have $T_{g\beta}/T_{g\alpha}$=0.59 $\approx$ $T_{HF}/T_{g\alpha}$.

A most recent paper on the dynamics of confined toluene is by Audonnet et al.[45], where more MSD data from neutron scattering experiments of bulk and confined toluene-d3 were published. Like the data in Fig.5, the new results were obtained by using the IN16 spectrometer at ILL. We have reproduced the entire sets of data in Fig.6, and place the red~~magenta~~ arrow at the location to indicate $T_{g\beta}$=69.1 K of the bulk toluene. Despite the spread of the MSD data of bulk toluene-d3, a change of its T-dependence seems to occur somewhere near $T_{g\beta}$=69.1 K. The MSD of the confined toluene-d3 show similar trends as in

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Fig.5 and exhibit change of T-dependence in the glassy state at some T_{HF} not far from the bulk $T_{g\beta}$=69.1 K. This goes as expected because the surface interaction in confined toluene has little effect on the caged dynamics particularly in the glassy state, and hence the value of T_{HF} is about the same as in bulk toluene.

4. Discussion and Conclusion

The study of fast dynamics of small molecular van der Waals glassformers in the past by quasielastic neutron scattering, , Brillouin scattering, and ^{2}H spin-lattice relaxation were limited to a few cases. This is particularly so when the interest is on the fast process in the glassy state. The neutron scattering community had chosen o-terphenyl, tri-naphthyl benzene (TNB)[25], toluene, and propylene carbonate. TNB is a classic case studied in the early years in the liquid state by Plazek and Magill[46]. This may be the reason why it was chosen for neutron scattering study, where the onset of fast caged dynamics was found in the glassy state of TNB[25] as in o-terphenyl, and toluene. However TNB is apolar and difficult to synthesize, and the sample is not readily available to others for additional measurements to find the JG β-relaxation and to determine $T_{g\beta}$. For our purpose to verify the relation, $T_{HF}\approx T_{g\beta}$, , we also need to know the secondary glass transition temperature $T_{g\beta}$, but it is not available for TNB. This extra requirement restricts our considerations to the glass-formers discussed in the previous sections 2 and 3.

Börjesson et al.[47,48] performed incoherent quasielastic neutron scattering experiments on propylene carbonate using the IRIS spectrometer at the pulse spallation source ISIS, Rutherford-Appleton Laboratory, UK, with resolution (FWHM = 12 μeV). The focus of these authors are on data at temperatures above $T_{g\alpha}$=157 K to compare with Mode Coupling

Theory. Consequently few data were taken in the glassy state of propylene carbonate. The limited amount of data obtained below $T_{g\alpha}$ does not give any clear idea of T_{HF} where occurs the change in T-dependence of the fast caged dynamics. Hence the scanty neutron scattering data published by Börjesson et al.[47,48] cannot be used to determine T_{HF}. The secondary glass transition temperature $T_{g\beta}$ determined by adiabatic calorimetry was reported by Fujimori and Oguni to be 64 K.[13] On the other hand, PALS experiment by Bartoš et al.[49] shows possibly $T_{g\beta}$ is about 130 K. If we adopt the $T_{g\beta}$=64 K from adiabatic calorimetry[13], we are surprised by the low value of $T_{g\beta}/T_{g\alpha}$=0.41 for propylene carbonate in view of the larger values of the polyacohols[1] including glycerol, the pharmaceuticals[1], and the polymers[2]. However the value of $T_{g\beta}\approx$130 K from PALS give $T_{g\beta}/T_{g\alpha}$=0.82, which is more in line with the trend found from the other glass-formers. This leads us to question the verity of the value of $T_{g\beta}$=64 K given in ref.[13]. Actually the value of $T_{g\beta}$=64 K defining the freezing of JG β-dynamics had already been questioned by Qi and co-workers[50]. They employed deuteron nuclear magnetic resonance on propylene carbonate samples selectively deuterated at the methyl group. By this means they were able to show that the methyl group rotation time attains the timescale of 10^3 s just around 65 K and hence this transition observed at 64 K by adiabatic calorimetry[13] originates from the methyl group and should not be ascribed to the universal JG β-relaxation of propylene carbonate. The values of both $T_{g\beta}$ and T_{HF} of propylene carbonate are unknown at this time. This should stimulate others to make new measurements of these quantities in the future. Throughout the discussion in this paragraph we have assumed the existence of the JG β-relaxation in propylene carbonate, although it has not been resolved by dielectric[51] or mechanical spectroscopy[52]. The reason for not able to resolve the JG β-relaxation is because of the small separation in time-scale of it from the α-relaxation as indicated by a prediction of

the Coupling Model (CM)[3,7,10,11,53]. It presence is suggested by the excess loss (or excess wing) on the high frequency flank of the α-loss peak[51], suggesting it is the unresolved JG β-relaxation. By performing long term aging experiment[51], the excess wing was changed to become a shoulder, which was taken by Schneider et al.[51] as evidence of the presence of the β-relaxation.

The most complete sets of data in the family of small molecular van der Waals glass-formers are found in the case of o-terphenyl. The collections of high frequency measurements by quasielastic neutron scattering, Mössbauer-spectra of ^{57}Fe in ferrocene dissolved in OTP, ^{2}H-nuclear magnetic resonance spin-lattice relaxation, and Brillouin scattering have provided consistent evidences for the change of T-dependence of the caged dynamics at some temperature T_{HF} below $T_{g\alpha}$. The secondary glass transition of o-terphenyl had been found by adiabatic calorimetry, and its transition temperature $T_{g\beta}$ determined and supported by dielectric relaxation measurements of the JG β-relaxation time, τ_{β}, when extrapolated to 10^{3} s. There is good agreement between $T_{g\beta}$ and T_{HF}, indicating the change of T-dependence of the GHz caged dynamics at T_{HF} is in response to the secondary glass transition at $T_{g\beta}$ of the JG β-relaxation with $\tau_{\beta}(T_{g\beta})=10^{3}$ s. Before closing, it is worthwhile to point out that the ratio $T_{g\beta}/T_{g\alpha}$ of propylene carbonate with value of 0.82 is significantly larger that 0.59 of toluene and 0.55 of OTP. This is an example of the trend of finding smaller value of $T_{g\beta}/T_{g\alpha}$ in glass-former having larger coupling parameter n of the CM[7] appearing in the Kohlrausch correlation function of the α-relaxation, $\phi(t) = \exp[-(t/\tau_{\alpha})^{1-n}]$. We have seen this trend before from the polyalcohols in Paper I,[1] and can be deduced from data of the amorphous polymers in Paper II.[2] The trend is consistent with or derivable from the well established correlation[7,10,11] at temperatures above $T_{g\alpha}$ between n and the ratio of the α- and the JG β-

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relaxation times, τ_α/τ_β, which is a prediction of the CM. Since $T_{HF}/T_{g\alpha} \approx T_{g\beta}/T_{g\alpha}$, we can expect the trend of smaller $T_{HF}/T_{g\alpha}$ in glass-former with larger n.

In conclusion, all available high frequency experimental data of small molecular van der Waals glass-formers in the glassy state have shown there is change of T-dependence of the fast caged dynamics at or near the secondary glass transition temperature. The property was found previously in the polyalcohols, a pharmaceutical, and many amorphous polymers in Papers I and II. The generality of the property becomes more evident by showing it applies to the family of small molecular van der Waals glass-formers. Thus it has impact on the fundamental understanding of the fast and slow processes in the search of a comprehensive solution of the glass transition problem. Our explanation of this property of the small molecular van der Waals glasses is the same as that given before in the previous two papers. Firstly, the occurrence of the secondary glass transition at $T_{g\beta}$ originates from the density and configurational entropy dependences of the JG β-relaxation[16,54,55]. Secondly, due to the coupling with the JG β-relaxation, the caged dynamics changes its temperature dependence in response to the secondary glass transition at some temperature T_{HF} nearly the same as $T_{g\beta}$.

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Table of contents graphic.
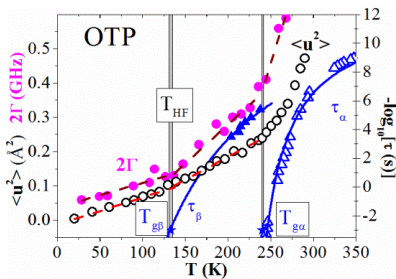
TOC. Left side: mean square displacement, $<u^2>$, (open black circles) and linewidth of Brillouin peak, Γ, (closed magenta circles) of OTP plotted as a function of temperature. Data are from ref.[23, 36] and redrawn. The grey vertical thick line shows T_{HF}. Right side:

logarithm of the reciprocal of α- and JG β-relaxation times (blue open and closed circles respectively) from ref.[12].
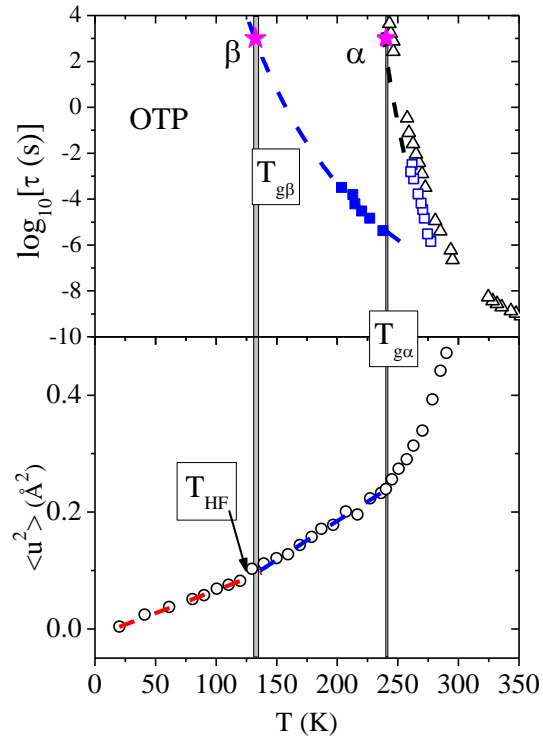
Fig.1. Upper panel: The α and β relaxation times determined by adiabatic calorimetry (magenta star) and dielectric relaxation plotted as a function of temperature. The data are taken from ref.[12].(squares from dielectric data[9], triangles from Brillouin scattering data[26], blue and black dashed lines are from fitting Arrhenius and Vogel-Fulcher-Tamman functions respectively). The adiabatic calorimetric value of $T_{g\alpha}=241$ K and $T_{g\beta}=133$ K. **Lower panel:** Mean square displacement in Å^2 of *o*-terphenyl as a function of temperature. Data are from Bartsch et al.[23] and redrawn. The two dashed lines are linear regressions optimized in the low and intermediate temperature region. The arrow indicates the location of T_{HF} as obtained from the crossing of the two linear regressions. The shaded region connecting the upper and lower panels is devised to show the property $T_{HF}{\approx}T_{g\beta}$ holds for *o*-terphenyl.
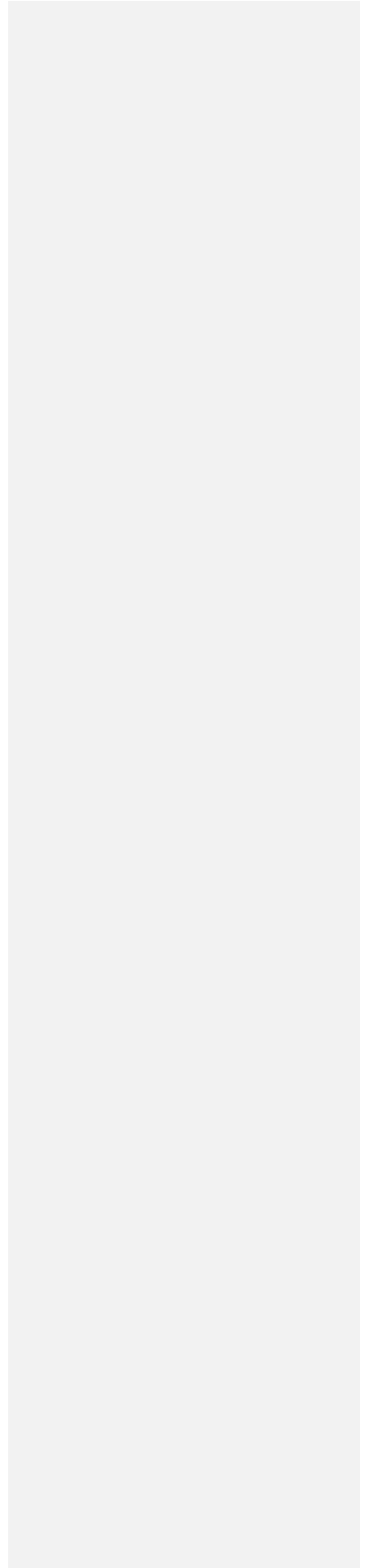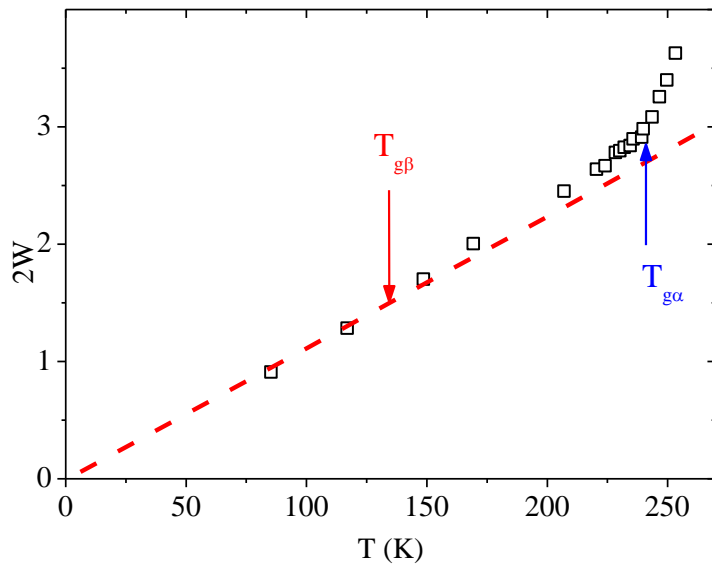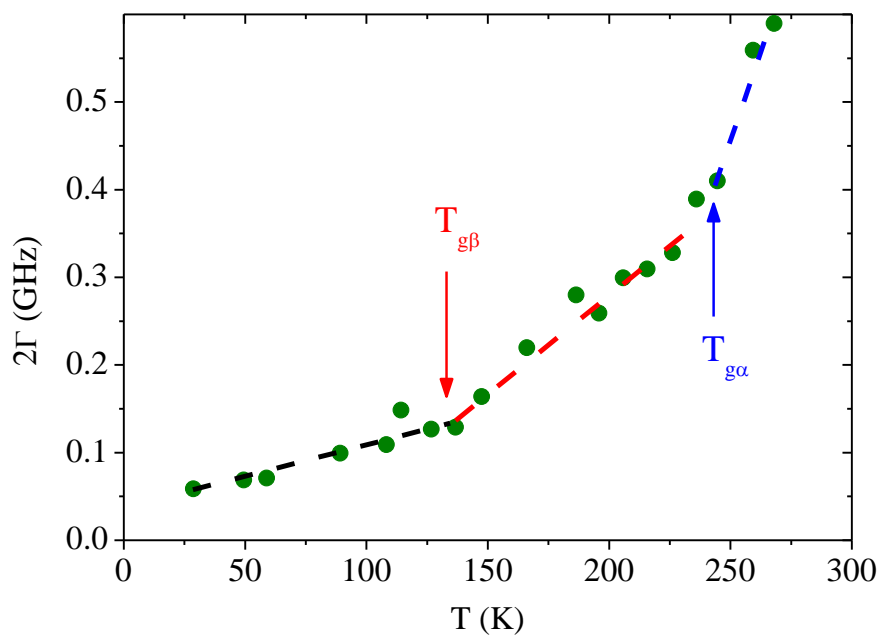
Fig.2. A plot of the temperature dependence of the Debye–Waller factor, obtained by Mössbauer-spectra of ^{57}Fe in ferrocene dissolved in OTP given by Tölle[24]. The line was reproduced exactly as done by Tölle. The arrows indicate the primary and secondary glass transition temperatures, $T_{g\alpha}$=243 K and $T_{g\beta}$=133 K, respectively of o-terphenyl.
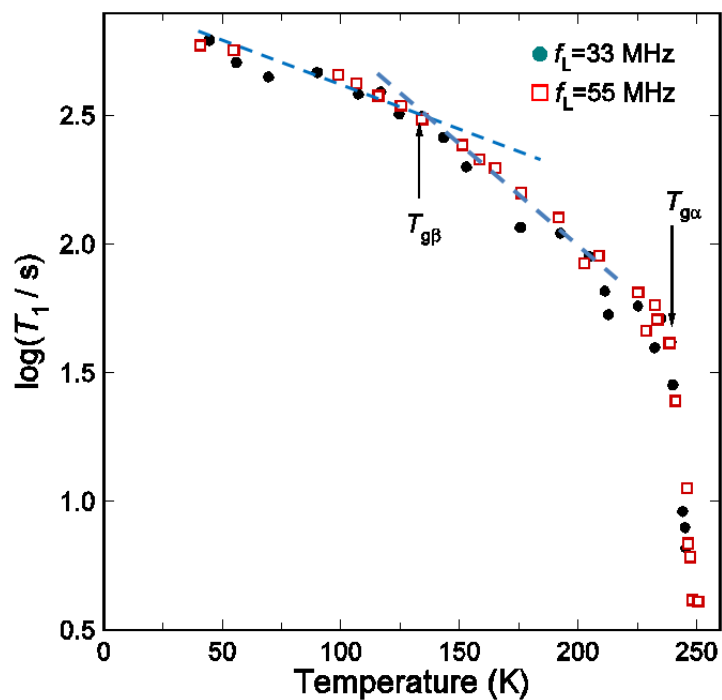
Fig.3. ^{2}H NMR spin-lattice relaxation times of *o*-terphenyl as a function of temperature. Data from Schnauss et al.[34] and redrawn. The lines are drawn to indicate change in the *T*-dependence at the primary and secondary glass transition temperatures. The arrows indicate the primary and secondary glass transition temperatures, $T_{g\alpha}$ =243 K and $T_{g\beta}$ =133 K, respectively of *o*-terphenyl.

Fig. 4. Temperature dependence of the measured linewidths in *o*-terphenyl in the glassy and liquidus states. Data are taken from Monaco et al.[36] and redrawn. The lines are drawn to indicate change in *T*-dependence at the primary and secondary glass transition temperatures. The arrows indicate the primary and secondary glass transition temperatures, $T_{g\alpha}$=243 K and $T_{g\beta}$=133 K, respectively of *o*-terphenyl.
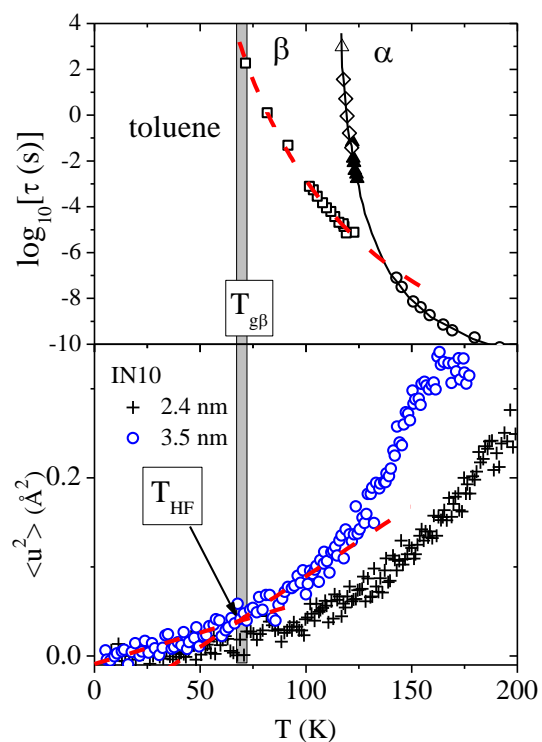
Fig. 5. Upper panel: Plot of relaxation times, τ_α and τ_β, of bulk toluene taken from Hatase et al.[22] and replotted as a function of temperature. Red dashed line and black continuous line are from fitting Arrhenius and Vogel-Fulcher-Tamman function respectively, as reported in literature[22]. **Lower panel:** Mean squared displacement of toluene-d3 confined in 3.5 nm and 2.4 nm pores as a function of temperature. The methyl group is deuterated and its relaxation contribution is removed. Data from Frick et al.[44] and redrawn. The two dashed lines are linear regressions optimized in the low and intermediate temperature region. The arrow indicates the location of T_{HF} as obtained from the crossing of the two linear regressions. The shaded region connecting the upper and lower panels is devised to show the property $T_{HF} \approx T_{g\beta}$ holds for toluene.
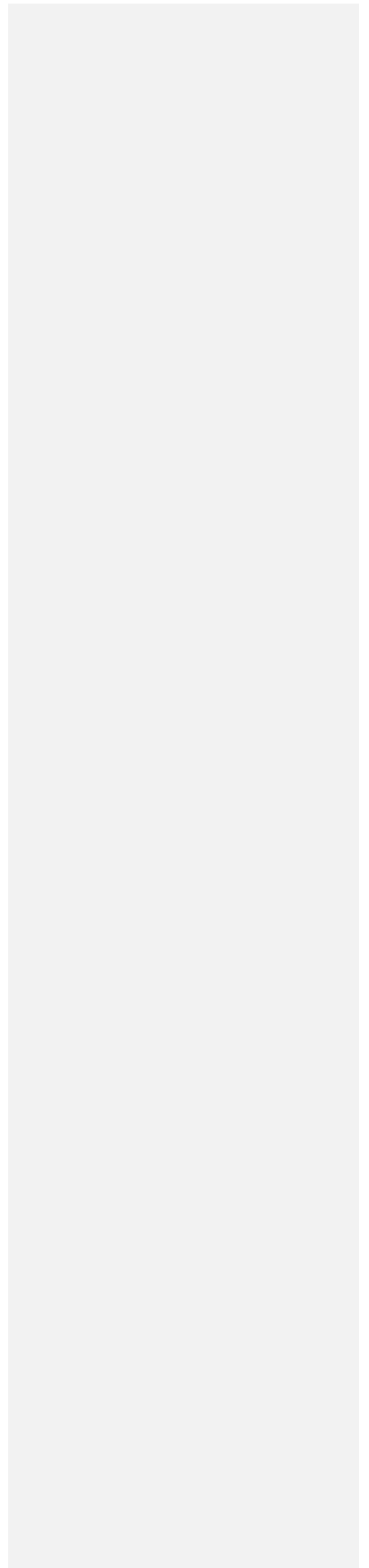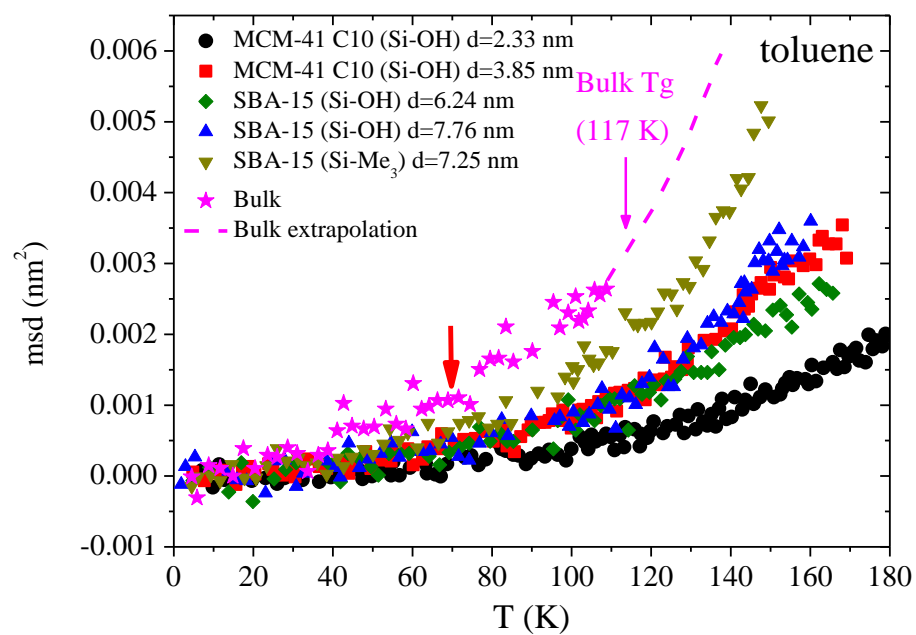
Fig. 6. Mean square displacement of partially deuterated toluene (toluene-d3) as a function of the temperature in the bulk state and in four different confining environments. Data are from Audonnet et al.[45] and redrawn. The arrows indicate the primary and secondary glass transition temperatures of bulk toluene.