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Cite this: *Phys. Chem. Chem. Phys.*, 2017, **19**, 29905

Why is surface diffusion the same in ultrastable, ordinary, aged, and ultrathin molecular glasses?†

K. L. Ngai,*[a] Marian Paluch[ab] and Cristian Rodríguez-Tinoco *[ab]

Recently Fakhraai and coworkers measured surface diffusion in ultrastable glass produced by vapor deposition, ordinary glass with and without physical aging, and ultrathin films of the same molecular glass-former, *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD). Diffusion on the surfaces of all these glasses is greatly enhanced compared with the bulk diffusion similar to that previously found by others, but remarkably the surface diffusion coefficients D_S measured are practically the same. The observed independence of D_S from changes of structural α-relaxation due to densification or finite-size effect has an impact on the current understanding of the physical origin of enhanced surface diffusion. We have demonstrated before and also here that the primitive relaxation time τ_0 of the coupling model, or its analogue τ_β, the Johari–Goldstein β-relaxation, can explain quantitatively the enhancement found in ordinary glasses. In this paper, we assemble together considerable experimental evidence to show that the changes in τ_β and τ_0 of ultrastable glasses, aged ordinary glasses, and ultrathin-films are all insignificant when compared with ordinary glasses. Thus, in the context of the explanation of the enhanced surface diffusion given by the coupling model, these collective experimental facts on τ_β and τ_0 further explain approximately the same D_S in the different glasses of TPD as found by Fakhraai and coworkers.

Received 7th August 2017,
Accepted 13th September 2017

DOI: 10.1039/c7cp05357f

rsc.li/pccp

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1. Introduction

Surface diffusion coefficients $D_S(T)$ of several molecular glass-formers including indomethacin (IMC), nifedipine (NIF), and *ortho*-terphenyl (OTP),[1–3] and a canonical metallic glass, $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (Pd_{40})[4] were measured at temperatures slightly above and mostly below the bulk glass transition temperature T_g using the method of surface-grating decay. The surface diffusion coefficients $D_S(T)$ are found to be many orders of magnitude larger than the bulk diffusion coefficients $D_V(T)$ at the same temperature. The size of the enhancement of D_S over D_V depends on the glass-former, as shown by nearly the two orders of magnitude greater enhancement in the case of OTP than that in IMC. In all these previous studies[1–4] at temperatures below T_g the glasses were formed ordinarily by rate cooling or liquid quenching, and are referred to as ordinary glass (OG) to distinguish from a new class of ultrastable glasses (SG) produced by physical vapor deposition. Several theoretical models were proposed to address this huge enhancement of surface mobility of small molecule OGs[5–7] and metallic glass.[8]

Recently Fakhraai and coworkers[9–11] have investigated the effect of variations in bulk dynamics on the surface diffusion of the molecular glass, *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD) with its ordinary T_g = 330 K. Using the tobacco mosaic virus as a probe particle, they measured $D_S(T)$ on glasses of the same composition but with a large difference in bulk relaxation dynamics and in the glass transition temperature. The glasses of TPD include the ordinary glass (OG) obtained by liquid quenching, annealed glass after physical aging at $0.9T_g$ for a week, ultrastable glass (SG) fabricated by physical vapor deposition at various substrate temperatures, and 12 to 30 nm thin films. The fictive temperature T_f is reduced in aged glass and much reduced in the SG. The onset temperature for the transformation from the stable glass to the supercooled liquid, T_{on}, is significantly higher than the T_g of the OG. These changes imply orders of magnitude increase of the structural α-relaxation time τ_α in the SG. It is generally believed that the high surface mobility or the much larger surface diffusion coefficients $D_S(T)$ rather than $D_V(T)$ plays a critical role in allowing the formation of highly stable glasses.[12,13] Glasses of higher stability will be formed in systems where surface diffusion is faster. This is borne out by OTP[2] having a larger $D_S(T_g)$ than IMC[1] and also having formed a more stable glass than IMC.[12,13] However, despite the large difference in the bulk dynamics of SG, OG, and annealed OG of TPD, the surface diffusion coefficients of these glasses measured[9–11] turn out to be nearly identical at two temperatures below the T_g of bulk OG. These results have led

[a] *Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1, 41-500 Chorzow, Poland. E-mail: kiangai@yahoo.com, cristian.rodriguez-tinoco@smcebi.edu.pl*
[b] *Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cp05357f

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Fakhraai and coworkers to suggest that surface diffusion has no dependence on the bulk relaxation dynamics when measured below T_g, and to question the validity of theories proposed to account for the size of the $D_S(T)$.

Furthermore, Fakhraai and coworkers[11] measured the average α-relaxation dynamics in ultrathin films of molecular glass TPD supported on a silicon substrate with film thickness h in the range 12 nm $< h <$ 53 nm. As the film thickness is decreased, T_g decreases rapidly, and the average relaxation time of the films is shorter by 6–14 orders of magnitude, depending on the measuring temperature below T_g of bulk TPD. The enhancement of relaxation in the TPD thin films also originates from the high mobility of the free surface, which induces faster dynamics of the film interior as concluded from studies of the reduction of the glass transition temperature of polymer thin films.[14–20] Surface diffusion of the thin films was measured by Fakhraai and coworkers.[11] Again, surprisingly they found that the surface diffusion coefficients $D_S(T)$ are approximately the same, in spite of the large variations of the averaged film relaxation dynamics for film thicknesses in the range of 12 nm $< h <$ 400 nm. Even more surprising, the $D_S(T)$ of the thin films are practically the same as that of the SG and OG, indicating a complete decoupling of the average film relaxation and surface diffusion.[11]

Collectively the results from the studies of Fakhraai and coworkers have an impact on the research on surface diffusion, ultrastable glasses, and dynamics of thin films. The results also challenge theories of surface diffusion enhancement, and may yield insight into the α-relaxation dynamics of the ultrastable glass, which cannot be directly measured. The basic question is why is the surface diffusion coefficient $D_S(T)$ approximately the same despite widely different structural α-relaxation dynamics in the different cases? Part of the answer is at hand if a mechanism for the enhanced $D_S(T)$ can be found and is present in all cases. The answer is complete if the mechanism can give quantitatively the size of the enhanced $D_S(T)$ with approximately the same value for all cases. In this paper, we provide such a mechanism in the primitive relaxation of the coupling model[21–25] or its analogue the Johari–Goldstein (JG) β-relaxation[25–29] exemplified in experiment and simulations.[21] It has been demonstrated before[6,8] that the primitive relaxation time τ_0 or the JG β-relaxation time τ_β can account for the size of the enhanced $D_S(T)$. In this paper, we show directly from experiments that these relaxation times have approximately the same values in all cases, and thus provide an answer to the question why the measured $D_S(T)$ all have approximately the same value. Moreover, the change of τ_β in ordinary glasses at ambient pressure and under high pressures up to 500 MPa is shown to be similar to that found between τ_β in SG and τ_β in OG. We use this result to support our explanation of the roughly invariant surface diffusion coefficient in SG, OG, and annealed OG as well as in nanometer thin films.

2. Evidence from experiments

The basic question from the findings of Fakhraai *et al.* is why the surface diffusion coefficient $D_S(T)$ is approximately the same in SG, OG, aged OG, and nanometer thin films, despite widely different bulk structural α-relaxation dynamics. One way to answer this question is to identify the mechanism that is omnipresent, and can account quantitatively for the size of the surface diffusion enhancement, $D_S(T)/D_V(T)$, in all four cases. But before doing that, one must be able to have a mechanism working in the simpler case of bulk OG before showing it continues to work for the other three more sophisticated cases, particularly the SG. Here we consider the mechanism from the primitive relaxation of the coupling model (CM) and its analogue, the JG β-relaxation.

A. OG

In our previous applications of the CM to surface diffusion in OG,[6] it was assumed at the surface that intermolecular cooperativity of the α-relaxation is totally removed and the many-body relaxation is reduced to the primitive relaxation.[21–25,28,29] Consequently, the α-relaxation time at the surface is given by the primitive relaxation time $\tau_0(T)$, which can be many orders of magnitude shorter than $\tau_\alpha(T)$ in the bulk according to the time-honored CM equation,

$$\tau_\alpha = [t_c^{-n}\tau_0]^{1/(1-n)}, \quad (1)$$

if n is not zero. In eqn (1) t_c is the onset time of classical chaos[21–24] and its magnitude depends on the interaction potential. Its value is ≈1 to 2 ps for soft matter including molecular glass-formers and polymers and was determined by quasielastic neutron scattering experiments and molecular dynamics simulations.[21] The parameter $(1 - n)$ is the fractional exponent of the Kohlrausch correlation function,

$$\varphi(t) = \exp[-(t/\tau_\alpha)^{1-n}]. \quad (2)$$

According to the CM, τ_0 is the α-relaxation time that the structural relaxation would have if all the cooperativity associated with the many-body α-relaxation had been removed, and the coupling parameter n is reduced to zero. In fact from eqn (1), it is clear τ_α is reduced to τ_0 when n becomes equal to zero. The JG β-relaxation is an analogue of the primitive relaxation,[21,25,28,29] and their relaxation times are found in general to be approximately equal,

$$\tau_\beta(T) \approx \tau_0(T) \quad (3)$$

This relation has been verified multiple times in many glass-formers of different types since the first paper in 1998,[25] and is justified by both the primitive relaxation and the JG β-relaxation being non-cooperative precursors of the structural α-relaxation and having similar properties.[21]

Free of neighboring molecules and totally free space to explore on one side, molecules diffusing on the surface are not slowed down by intermolecular coupling, provided there is no widespread hydrogen bonding and extensive penetration of the molecules into the interior to constrain and retard surface diffusion. Thus, at the surface the coupling parameter n can become zero or nearly zero. The α-relaxation time, $\tau_S(T)$, at the surface is obtained by substituting $n = 0$ into eqn (1), and therefore is the same or nearly the same as $\tau_0(T)$,

$$\tau_S(T) = \tau_0(T) \quad (4)$$

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From eqn (4) and the relation of $\tau_S(T)$ to the surface diffusion coefficient, $D_S(T)$, given by $D_S(T) = d^2/4\tau_S(T)$, the CM immediately predicts $D_S(T)$ quantitatively by

$$D_S(T) = d^2/4\tau_0(T) \quad (5)$$

where d is the size of the molecule. Taking relation (3) into consideration, we have

$$\tau_S(T) \approx \tau_\beta(T), \quad (6)$$

and alternatively, $D_S(T)$ can be determined from the JG β-relaxation time by

$$D_S(T) \approx d^2/4\tau_\beta(T) \quad (7)$$

Predicting $D_S(T)$ by eqn (5) requires calculating the primitive $\tau_0(T)$ from eqn (1), which needs the input of $\tau_\alpha(T)$ and n. By contrast, eqn (7) directly determines $D_S(T)$ from the experimental $\tau_\beta(T)$ without performing any calculation. This is worth emphasizing at the outset because we shall apply it to surface diffusion in SG, OG, annealed OG, and thin films later on.

Although eqn (5) and (7) are straightforward, the magnitude of d is not exactly known. This indeterminate parameter is eliminated if the enhancement of surface diffusion given by the ratio, $D_S(T)/D_V(T)$, is considered. Incidentally, the experimental values of this ratio at T_g for several molecular glass-formers are published in the literature.[1–4,30] If $D_S(T)/D_V(T)$ is the same as the ratio $\tau_\alpha(T)/\tau_S(T)$ or $\tau_\alpha(T)/\tau_0(T)$ except for a factor 3/2 which is insignificant for the consideration herein and henceforth is neglected, then *via* eqn (1) $D_S(T)/D_V(T)$ is given by

$$\frac{D_S(T)}{D_V(T)} = \frac{\tau_\alpha(T)}{\tau_s(T)} = \frac{\tau_\alpha(T)}{\tau_0(T)} = \left[\frac{\tau_\alpha(T)}{t_c}\right]^n. \quad (8)$$

Furthermore from eqn (6), we have approximately

$$\frac{D_S(T)}{D_V(T)} = \frac{\tau_\alpha(T)}{\tau_s(T)} \approx \frac{\tau_\alpha(T)}{\tau_\beta(T)}. \quad (9)$$

For ordinary glasses, the values of $\tau_\alpha(T)$ and n are known at temperatures above and below T_g from dielectric relaxation. For indomethacin (IMC), the value of n = 0.41 was determined.[6] Using this value together with t_c = 1 to 2 ps for soft matter and the choice of $\tau_\alpha(T_g) = 10^2$ or 10^3 s, the CM eqn (1) gives $\tau_0(T_g) = 10^{-3.62}$ and $10^{-3.03}$ s respectively. Assuming d = 1 nm, eqn (5) predicts $D_S(T_g) = 10^{-15.16}$ and $10^{-15.75}$ m^2 s^{-1} compared to the experimental value of $D_S(T_g) = 10^{-14.3}$ m^2 s^{-1} (see inset of Fig. 1). The discrepancy can be due to the arbitrary choice of the value of d. On the other hand, after eliminating d, eqn (8) yields $\tau_\alpha(T_g)/\tau_S(T_g) \approx 10^6$ s, which is in order of magnitude agreement with the experimental value of $D_S(T_g)/D_V(T_g)$.[1] The temperature dependence of $\tau_0(T)$ is also about the same as that of the $D_S(T)$ data below T_g = 314 K of OG, indicating $\tau_0(T)$ continues to match $\tau_S(T)$ in value in the OG of IMC. The JG β-relaxation of IMC is not resolved at ambient pressure (albeit resolved at a high pressure of 400 MPa), and its relaxation time $\tau_\beta(T)$ at ambient pressure cannot be determined exactly.

In this paper we test the CM further by considering the new case of OTP, which had its JG β-relaxation resolved in the OG,[27,31] and the experimental values of $\tau_\beta(T)$ can be used to directly predict $D_S(T)$ *via* eqn (7).

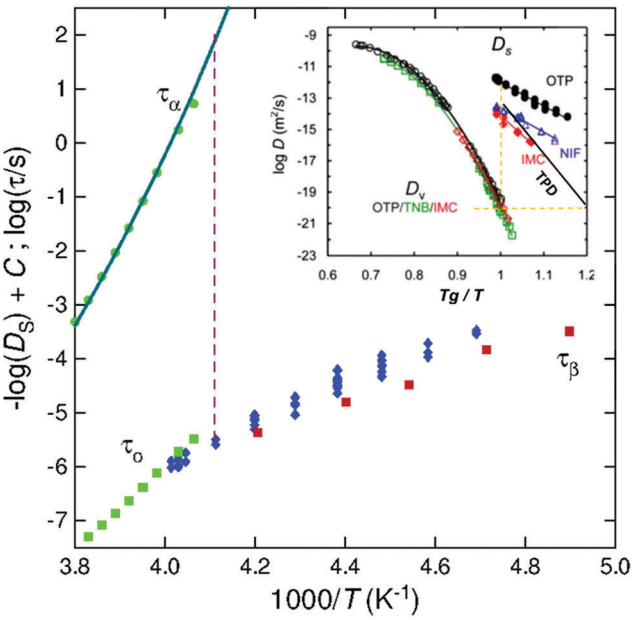


Fig. 1 Green closed circles and squares are the α-relaxation times $\tau_\alpha(T)$, and the primitive relaxation times $\tau_0(T)$ (calculated), and the red closed squares are the β-relaxation times $\tau_\beta(T)$ of bulk OTP. The blue closed diamonds represent $-\log D_S(T) + C$ with $C = -17.35$ and the original data of $D_S(T)$ are from ref. 2. The inset showing $D_S(T)$ and $D_V(T)$ is reproduced from ref. 2. Added is the line, which is a fit of the $D_S(T)$ of the OG of TPD by the Arrhenius dependence.

OTP has a larger value of n = 0.50 than IMC at a temperature near T_g.[32] The dielectric $\tau_\alpha(T)$ and a Vogel–Fulcher fit are shown in Fig. 1 together with $\tau_\beta(T)$, the calculated $\tau_0(T)$, and $D_S(T)$ after it was shifted by a constant to match roughly $\tau_0(T)$ above T_g. Although $\tau_0(T)$ can only be obtained above T_g, $\tau_\beta(T)$ was determined experimentally below T_g. By extrapolating the Arrhenius temperature dependence of $\tau_\beta(T)$ back to T_g the relationship $\tau_\beta(T) \approx \tau_0(T)$ is verified. Hence, from eqn (8) and (9), we have at T_g. the CM predicted value of

$$D_S(T_g)/D_V(T_g) = \tau_\alpha(T_g)/\tau_S(T_g) = \tau_\alpha(T_g)/\tau_0(T_g) = 10^{7.5}, \quad (10)$$

and

$$D_S(T_g)/D_V(T_g) = \tau_\alpha(T_g)/\tau_S(T_g) \approx \tau_\alpha(T_g)/\tau_\beta(T_g) \approx 10^{7.5} \quad (11)$$

This prediction of enhanced surface mobility based on $\tau_0(T)$ and $\tau_\beta(T)$ is to be compared with the experimental value of $D_S(T_g)/D_V(T_g) \approx 10^{7.6}$ at T_g shown in the inset of Fig. 1 taken from the paper of Zhang *et al.*[2] Deeper into the glassy state, the shifted $D_S(T)$ and $\tau_\beta(T)$ are within half a decade apart and can be considered the same if the uncertainty of $\tau_\beta(T)$ determined from the broad frequency dispersion of the JG β-relaxation is taken into consideration. Thus eqn (8) and (9) for $T \leq T_g$ in OG of OTP is verified.

We can obtain $D_S(T_g)$ of OTP directly from the experimental value of $\tau_\beta(T_g)$ by using eqn (7) and again assuming d = 1 nm. The Arrhenius extrapolation of $\tau_\beta(T)$ in Fig. 1 determines

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$\tau_\beta(T_g) = 10^{-5.56}$ s. Hence the predicted value of $D_S(T_g)$ is $10^{-13.22}$ m^2 s^{-1}, which is smaller than the experimental value of $10^{-12.1}$ m^2 s^{-1}. Assumed in eqn (5) and (7) is that $\tau_s(T_g)$ is the same as the CM primitive relaxation time $\tau_0(T_g) \approx \tau_\beta(T_g)$ in the OTP bulk. But the actual value of $\tau_0(T_g) \approx \tau_\beta(T_g)$ at the surface can be shorter, due to more free space, and hence the actual value of $D_S(T_g) = 10^{-13.22}$ m^2 s^{-1} calculated by eqn (7) can underestimate the real enhancement. It can be seen from Fig. 1 that $\tau_\beta(T)$ continues to describe well the temperature dependence of $D_S(T)$ deep into the glassy state of OTP. This means the $D_S(T)$ from eqn (7) not only agrees with the experimental value at T_g but also at temperatures below it.

The exercise presented in the above in the case of OTP demonstrates that the experimental data of $\tau_\beta(T)$ can be used directly *via* eqn (7) to determine $D_S(T)$. Therefore, if there is no or little change in $\tau_\beta(T)$ in glasses of different origins, we can immediate conclude that the surface diffusion coefficients $D_S(T)$ measured in these glasses will be practically the same. This point is relevant for understanding the collection of studies of the surface diffusion of SG, OG, and annealed OG of TPD in the following subsections B and C.

Shown in the inset of Fig. 1 is the Arrhenius fit of the measured tracer surface diffusion coefficients of the OG of TPD.[10] The enhancement $D_S(T_g)/D_V(T_g)$ of TPD at T_g lies in between that of the surface self-diffusion of IMC and OTP. If the tracer surface diffusion of TPD measured is not too different from self-diffusion, the approximately same order of magnitude of the enhancement at T_g of TPD and OTP can be understood from the comparable value of $n = 0.50$ and 0.48 for TPD and OTP respectively.

B. Aged OG

From the previous Section A we have validated eqn (6) and (7) and established that the JG β-relaxation time $\tau_\beta(T)$ is a quantitative indicator of the enhanced surface diffusion coefficient $D_S(T)$ for $T \leq T_g$ in the OG. Now, if the OG is densified by physical aging over a long period of time, any change of $D_S(T)$ will be observed by the corresponding change in $\tau_\beta(T)$. It is known from the classical study of physical aging of 43.3 mol% toluene in pyridine glass at several temperatures[33] that there is practically no change of the β loss peak frequency, $f_\beta = (1/2\pi\tau_\beta)$, except a reduction of the amplitude of the loss. A slight increase of the peak frequency was found on aging the JG β-relaxation of glassy polyvinylethylene.[34] On the other hand, a small increase of peak frequency was found on aging of dipropyleneglycol dibenzoate.[35] In all cases, including others not mentioned, there is either no change or a small change of τ_β by physical aging. From this general aging property of $\tau_\beta(T)$, it follows from eqn (6) and (7) that $\tau_S(T)$ and $D_S(T)$ of the aged TPD glass are nearly the same as that of OG, as found by Fakhraai and coworkers.

C. SG

The key for continued use of eqn (6) and (7) to predict the enhancement of surface diffusion at T_g or T_{on} in SG is to have data on $\tau_\beta(T)$ of SG. The onset temperature T_{on} is defined as the intersection of the extrapolated glassy line and the tangent of the transformation from the glassy state to the supercooled liquid state. Among the SGs produced by vapor deposition, only the SG of toluene[36,37] has been studied by dielectric relaxation and reported.[38] Toluene is a rigid molecule and its sole secondary relaxation is the JG β-relaxation.[28] The relationship between the α- and the β-relaxations of toluene is in accord with the CM eqn (1)–(3) as shown by an example in the inset of Fig. 2. Shown there is the reported dielectric loss spectrum of toluene at 119 K with $f_\alpha = 0.2$ Hz[39] and the Kohlrausch fit with exponent $(1 - n) = 0.52$. The calculated primitive frequency $f_0 = (1/2\pi\tau_0)$ is about half a decade higher than $f_\beta = (1/2\pi\tau_\beta)$, verifying the approximate eqn (3).

The experimental data of $\tau_\beta(T)$ of a toluene SG deposited at a substrate temperature 98 K (= $0.84T_g$) from Yu *et al.*[38] are reproduced in Fig. 2. The value of T_{on} of the SG is 123 K,[36] and the corresponding $1000/T_{on}$ is located in Fig. 2 by the vertical black broken line. The other vertical broken line is at $1000/T_g$ with $T_g = 117$ K. Shown also are $\tau_\beta(T)$ and $\tau_\alpha(T)$ of the toluene OG from dielectric and NMR measurements.[40,41] Remarkably, $\tau_\beta(T)$ of the SG is longer than the OG by less than a decade at the same temperature, and the T-dependence of both are Arrhenius with the activation energies $E_\beta = 27 \pm 3$ and 25 ± 2 kJ mol^{-1} respectively. From these experimental facts, eqn (6) and (7) of the CM readily explain why the surface diffusion time $\tau_S(T)$ and coefficient $D_S(T)$ of the SG are practically the same as those of the OG.

We have extrapolated the Arrhenius T-dependence of $\tau_\beta(T)$ in the SG to higher temperatures to intersect $1000/T_{on}$. The intersection determines $\tau_\beta(T_{on}) = 10^{-4.31}$ s for the SG, while a similar

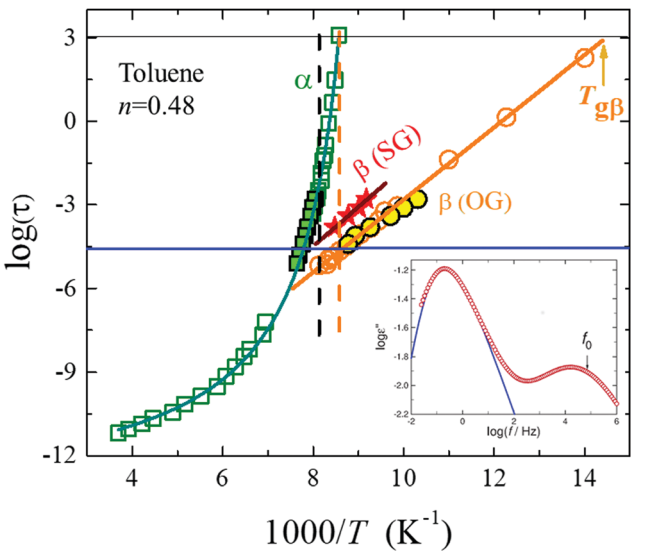


Fig. 2 The main figure is reproduced from Yu *et al.*[38] It shows logarithmic relaxation times of α and β processes of ordinary glass (open symbols), and the relaxation times for the vapor-deposited samples (solid symbols) *vs.* reciprocal temperature. Added are the two vertical lines located at $1000/T_g$ and $1000/T_{on}$. Inset: The dielectric loss spectrum of toluene, the fit by the Fourier transform of the Kohlrausch function with $n = 0.48$, and the calculated value of the primitive frequency f_0.

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operation determines $\tau_\beta(T_g) = 10^{-4.57}$ s for the OG. The nearly same value of τ_β suggests also $\tau_S(T)$ of the SG at T_{on} is similar to $\tau_S(T)$ of the OG at T_g.

D. Nanometer thin films

Zhang and Fakhraai[11] measured average α-relaxation time in ultrathin films of molecular glass TPD supported on a silicon substrate with film thicknesses ranging from 12 nm to 400 nm. The film T_g decreases rapidly with decreasing film thickness. They also measured the tracer surface diffusion coefficient $D_S(T)$ of all the films and found that the $D_S(T)$ are all enhanced at all temperatures by the same orders of magnitudes as the $D_S(T)$ of OG and SG, despite the fact that the average film α-relaxation time decreases significantly with decreasing film thickness.

It is generally agreed that the enhanced surface mobility in supported or freestanding polymer thin films is primarily the cause of the decrease of the film T_g as thickness is decreased. The enhanced surface mobility with the fast relaxation time $\tau_S(T)$ is transmitted into the interior of the film but the effect is attenuated layer by layer.[19] The substrate may have an opposite effect on the mobility if physical or chemical interaction with the film exists at the interface. Consequently, the averaged α-relaxation of the film measured is slower than at the surface, and the effective relaxation time is longer than $\tau_S(T)$ as in the study of Zhang and Fakhraai. However, the JG β-relaxation is a local process and its relaxation time $\tau_\beta(T)$ is not sensitive to changes of film thickness, as is supported by experiments. For example, dielectric measurements of poly(methyl methacrylate) (PMMA) thin films show little change of $\tau_\beta(T)$ for thickness down to 20 nm. The $\tau_\beta(T)$ of the 15 nm, and 9.5 nm thick films are only about a factor of 5 and 8 respectively shorter than the thick 1070 nm film, while the change of T_g is more than 20 K.[42] Direct measurement of surface relaxation of syndiotactic (PMMA) films by lateral force microscopy also finds the $\tau_\beta(T)$ at the surface shorter than the bulk by about 1 decade at higher temperatures of measurements.[43] Thus, from eqn (6) and (7), the small difference between $\tau_\beta(T)$ in thin films and in bulk explains the same for the surface diffusion $D_S(T)$ observed in glassy thin films of TPD compared to OG.

It is worthwhile mentioning a related experimental fact of the average segmental relaxation time, τ_α^{nano}, measured by dielectric relaxation on a 40 nm, and by PCS on a 22 nm freestanding polystyrene (PS) thin film. The values of $\tau_\alpha^{nano}(T)$ were shown to match the primitive relaxation times $\tau_0(T)$ in the glassy state of bulk PS.[44] In these ultrathin freestanding films the high mobility of the two free surfaces dominate in determining τ_α^{nano}, and hence the finding of $\tau_\alpha^{nano}(T) \approx \tau_0(T)$ supports the fact that $\tau_S(T)$ is the same as $\tau_0(T)$, or eqn (4).

The cooperative α-relaxation in nominal glass-formers such as OTP at 10 degrees above T_g has a length-scale of the order of 20 nm already.[45] Therefore, when the film thickness is much reduced to the order of 1 nm, not only the surface mobility dominates the entire film but also the interior is also removed of the cooperativity provided that the substrate has no effect. The ideal situation is realized in the 1.5 nm thin films of poly(methylphenylsiloxane) confined in galleys of nanocomposites[19,46] or poly(dimethylsiloxane) confined in 2 nm glass pores,[47] and the calculated $\tau_0(T)$ by eqn (1) from the bulk is in quantitative agreement with the experimental $\tau_S(T)$ as shown in ref. 19 (see Fig. S1 for the 1.5 nm thin film in the ESI†). Thus eqn (4) is verified and, *via* eqn (5), it supports the explanation of the nearly no change of $D_S(T)$ to change of film thickness.

3. Comparing SG at ambient pressure with OG at elevated pressures

Studies of the structure of vapor-deposited SG have shown the differences from OG, which include higher density, different local packing and orientations of the molecules.[48,49] Since higher density is a primary cause of the stability of SG, it is profitable to consider the glasses formed by applying very high pressure to the liquid and comparing some properties. This task is relevant in view of a recent experiment,[50] which compares the pressure dependence of the onset of devitrification, T_{on}, between the SG and OG of IMC. The dynamics and thermodynamic stabilities of the two glasses are very different at ambient pressure. Ultrastable glasses of IMC have densities up to 1.4% more than the liquid-cooled glass.[13,37] The two glasses have different dT_{on}/dP values at low pressures, but become nearly the same when T_{on} of the OG approaches that of the SG with increase of pressure to 300 MPa.[50]

At about 75 MPa, the increase of T_{on} of OG with pressure has caught up with the T_{on} of SG at ambient pressure. From this, we can expect at higher pressures, such as a few hundred MPa routinely reached in dielectric studies of the dynamics of glass-formers, that T_{on} as well as the density of the pressurized OG is significantly higher than the UG at ambient pressure. Thus, the difference in $\tau_\beta(T)$ between the pressurized OG and OG at ambient pressure in the glass state should be larger than that between the SG and OG at ambient pressure. This can be verified by examining some experimental $\tau_\beta(T)$ data of OG at ambient and elevated pressure such as poly(phenylglycidylether) (PPGE),[51] diglycidyl ether of bisphenol-A with M_w = 380 g mol^{-1} (also known as EPON 828),[52] and di-propylene glycol dibenzoate (DiPGDB).[35] In Fig. S2–S4 (ESI†) are the data of τ_β and τ_α of the three glass-formers shown at a fixed temperature as a function of pressure, and at a fixed pressure as a function of temperature. From these plots, T_g changes by 54 K for EPON 828 with the increase in pressure of 400 MPa; by 43 K and 77 K for DiPGDB with increase of 268 and 530 MPa respectively; and by 17 and 64 K for PPGE with increase of 95.5 and 500 MPa respectively. The T_g change of 17 K at 95.5 MPa matches the difference between T_g = 242.3 K and T_{on} = 259 K for the most stable glass of OTP vapor-deposited at $0.85T_g$.[12] Even for the much larger increase of pressure up to 500 MPa, it only changes τ_β by one to two orders of magnitude in the glassy state at a fixed temperature in all cases. The change of τ_β is even less at pressures lower than 100 MPa to match the increase in density with that of the IMC SG at ambient pressure. This we can use as corroborative evidence to support the small difference in τ_β

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between SG and OG at ambient pressure, and the use of the CM eqn (6) and (7) to explain the same surface diffusion coefficient for the two glasses. The properties of pressurized OG and SG produced by vapor deposition are the same as long as the pressure on the former is maintained, and the common cause is significant densification of the glass. By no means do the similar properties diminish the achievement of vapor-deposited SG in producing glassy materials with properties very different from OG at ambient pressure. By contrast, when the pressure is released, the pressurized glass returns to OG. Nevertheless, the physics of the pressurized glass is the same as SG as far as the comparison is confined to their glassy states. The analogy is no longer valid when the relationship of the glassy state to the equilibrium liquid is considered. For example, during transformation of the SG, the emerging liquid phase is at ambient pressure, and cannot be compared to the transformation of pressurized OG, where both the glass and liquid phases are under high pressure. Consequently, SG and pressurized OG do not exhibit the same transformation behavior. More importantly, the limiting fictive temperature (T_f') of a SG is lower than the OG, while the T_f' of the pressurized OG is higher than that of the OG at ambient pressure (note that this does not contradict the higher density of the pressurized OG than the ambient pressure OG). To be more specific, when calculating the T_f' of a SG, one considers the corresponding liquid at ambient pressure, while the T_f' of the pressurized OG refers to the liquid at the corresponding pressure. Again, since the definition of T_f' of either glass involves the corresponding equilibrium liquid, the mentioned analogy is not applicable in this point.

It is worthwhile to point out from the data shown in Fig. S2–S4 (ESI†) that $\tau_\beta(T,P)$ has approximately the same value at any arbitrary chosen long time $\tau_\alpha(T,P)$, independent of the choice of the fixed T as a function of P, or the choice of fixed P as a function of T.[35,51,52] The relationship $\tau_\beta(T,P) \approx \tau_0(T,P)$ has also been verified.

4. Conclusions

The findings of practically no change of the surface diffusion coefficient $D_S(T)$ on ultrastable glass (SG), ordinary glass (OG) with and without physical aging, and nano-meter glassy thin films of TPD by Fakhraai and coworkers are interesting, and certainly have an impact on identifying the mechanism of enhanced surface diffusion. They suggest that fast surface diffusion is decoupled from the bulk dynamics, although the exact mechanism of this decoupling merits further investigation. We show the mechanism of decoupling is the removal of intermolecular coupling or cooperativity in relaxation and diffusion of molecules at the surface, resulting in the surface relaxation time $\tau_S(T)$ being the same as the primitive relaxation time $\tau_0(T)$ of the coupling model (CM), and orders of magnitude shorter than the bulk α-relaxation time $\tau_\alpha(T)$. The enhanced surface diffusion is given by $D_S(T) = d^2/4\tau_S(T) = d^2/4\tau_0(T)$ where d is the size of the molecule. In the case of OG at T_g, the values of $\tau_\alpha(T_g)$ and the coupling parameter n are known, and the calculated $D_S(T_g)$ are in semi-quantitative agreement such as in the case of IMC,[4] OTP herein, and ethylcyclohexane (ECH).[53] $D_S(T_g)$ of ECH is several orders of magnitude less enhanced than that of IMC and OTP,[53] but it is still consistent with the CM eqn (8) because ECH has a smaller $n \leq 0.32$ than IMC and OTP. From the fact that the Johari–Goldstein β-relaxation is the analogue of the primitive relaxation, and its relaxation time $\tau_\beta(T)$ is approximately the same as $\tau_0(T)$ as proven in many materials, one can take the values of $\tau_\beta(T)$ from experiment and directly calculate the enhanced surface diffusion in the glassy state by $D_S(T) \approx d^2/4\tau_\beta(T)$. The crux of our explanation of the approximate invariance of $D_S(T)$ in SG, OG with and without physical aging, and nano-meter glassy thin films of TPD is the corresponding approximate invariance of $\tau_\beta(T)$, despite the huge differences in the bulk α-dynamics. This property of $\tau_\beta(T)$ is demonstrated directly from experimental data in all these different glasses. It is perhaps unsurprising since both the primitive relaxation and the JG β-relaxation are local process without cooperativity, although a more in-depth study to substantiate it theoretically is needed and will be forthcoming. We compare also the change of $\tau_\beta(T)$ in some other ordinary glasses by elevating the pressure up to 500 MPa. The advantage of studying OG under pressure is because $\tau_\beta(T)$ is resolved in the glassy state of many glass-formers. Pressure below 100 MPa is able to densify the OG to the same level and have a similar T_{on} as the best SG deposited at $0.85T_g$. The change of $\tau_\beta(T)$ in the pressurized OG is found to be small. Much higher T_{on} is found in OG pressurized at higher levels above 100 MPa. Notwithstanding, the change of $\tau_\beta(T)$ is still not large. This comparative study of $\tau_\beta(T)$ in OG at elevated pressures lends support to the explanation for the ultrastable glass.

In this paper we use eqn (5)–(7) exclusively and directly from the experimental τ_β or the theoretical τ_0 to compare with the experimental value of $D_S(T)$ of SG like TPD. The CM eqn (1) need not be used to calculate τ_0 from the structural α-relaxation time τ_α. The exception is the previous work on indomethacin (IMC)[6] where τ_α is known from experiment above and below T_g, and OTP above T_g in Fig. 1 herein. This situation in IMC and OTP confers the benefit of predicting the size of the enhancement by the ratio, τ_α/τ_0, and comparing with the experimental value of $D_S(T)/D_V(T)$, as successfully done for IMC and OTP. In the case of SG prepared by vapor deposition, τ_α is not known and eqn (1) cannot and need not be used to calculate τ_0 or τ_β in the stable glass.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank Prof. Ranko Richert and Prof. Haibin Yu for sharing with us their data on the secondary relaxation in the ultrastable glass of toluene. C. R.-T. acknowledges support from the National Science Centre through the Polonez scheme (Grant No. DEC-2015/19/P/ST3/03540/2). This project has received

funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 665778.

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