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Mechanism of fast surface self-diffusion of an organic glass

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Zhu *et al.* [L. Zhu, C. W. Brian, S. F. Swallen, P. T. Straus, M. D. Ediger, and L. Yu, Phys. Rev. Lett. **106**, 256103 (2011)] measured the surface self-diffusion for an organic glass former, indomethacin, and found surface diffusion is more than 10^6 times faster than bulk diffusion at temperatures around T_g. With the help of dielectric relaxation and differential scanning calorimetry measurements on bulk indomethacin, and analysis of the data using the coupling model, we provide a quantitative explanation. We find the bulk α-relaxation time is longer than the primitive relaxation time also by about six orders of magnitude in a range of temperature above and below the bulk T_g. Thus, the cause of the fast surface diffusion is the nearly vanishing of intermolecular coupling of relaxation and diffusion at the surface. The results of related experimental studies of enhanced relaxation and diffusion at the surface of other glass formers also have been analyzed and quantitatively explained. Our predictions on surface diffusion from the coupling model are compared with that given by the random first order transition theory.

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I. INTRODUCTION

Recently Zhu *et al.* [1] used the surface grating decay method and successfully measured the surface diffusion on an organic glass former, indomethacin [1-(p-chlorobenzoyl)-5-methoxy-2-methyl-indole-3-acetic acid]. Indomethacin (IMC) has been studied by a variety of experimental methods for its structure [2,3], dynamics, and other properties [4–12]. IMC is also one of the highly stable glasses that can be produced by vapor deposition, an area of research of much current interest [13–16]. The purpose for studying surface diffusion in IMC is to find out if it is the mechanism of formation of highly stable glasses by vapor deposition [1]. By elegant experimental technique together with a thorough analysis of the data, Zhu *et al.* showed that surface diffusion accounts for the grating decay rates at temperatures T below $T_g + 12$ K and down to about 20 K below $T_g = 315$ K of bulk IMC. They compared the surface diffusion coefficient, D_s, with the bulk diffusion coefficient, D_v, over this temperature range, and found D_s is about 10^6 times larger than D_v. The result proves that surface diffusion is responsible for the surface evolution of IMC at micrometer to nanometer length scales, resulting in the formation of the ultrastable glass. In view of the relevance of surface diffusion for formation of ultrastable glass and the dynamics of ultrathin films and nanoconfined glass formers of interest to a broader research community, it is important to explain quantitatively the origin of the six orders of magnitude increase of diffusion coefficient at the surface. It is the objective of this paper to give a full quantitative explanation of this effect.

II. COMPARISON OF DIFFUSION DATA WITH DIELECTRIC AND CALORIMETRIC DATA

If the correlation time and mean square displacement associated with the molecular motion for surface diffusion are τ_s and $\langle x^2\rangle$, respectively, D_s is the ratio of τ_s and $\langle x^2\rangle$, and hence data of D_s alone cannot determine the specific characteristics of the molecular motions. To overcome this difficulty, we supplement surface and bulk diffusion data with dielectric relaxation data of bulk IMC at ambient and elevated pressures [8–11], with the assistance of data from differential scanning calorimetry (DSC) [4–7], thermal stimulated depolarizing current (TSDC) [12], and theoretical analysis.

Dielectric measurements were made by Carpentier *et al.* [8] and Bhugra *et al.* [9] at ambient pressure, and by Wojnarowska *et al.* [11] at ambient and elevated pressures. In all studies, the structural α-relaxation responsible for glass transition is the most prominent feature in the dielectric loss spectra at temperatures above T_g. The $T_g = 315$ K was determined by a DSC scan at the rate of 1 K/min [6]. Additional isothermal dielectric loss spectra of IMC with respect to those published by Wojnarowska *et al.* [11] at temperatures above $T_g = 315$ K are presented in Fig. 1 as a master curve obtained after time-temperature superposition has been applied to data in the temperature range $315 \leqslant T \leqslant 355$ K. It shows the frequency dispersion of the α-loss peak does not change over this extended temperature range. At the lowest temperature 315 K, the τ_α reaches a long time duration of the order of 100 s. Good fits to the isothermal dielectric α-loss peak of the master curve were obtained by the one-sided Fourier transform of the Kohlrausch-Williams-Watts (KWW) function,

$$\varphi(t) = \exp[-(t/\tau_\alpha)^{1-n}], \qquad (1)$$

with $n = 0.41$. From the invariance of n down to $\tau_\alpha = 100$ s, we can safely assume the same $n = 0.41$ applies to IMC in the glassy state.

From the fit of τ_α so determined, it was found that the value of τ_α is 100 s at $T_g = 315$ K, to be compared with $T_g = 316.25$ K by Carpentier *et al.* using the same criterion. The values of dielectric T_g are in rough agreement with that given by Zhu *et al.* [1], and thus we can directly compare the diffusion data with the dielectric data. Correia *et al.* [12] employed TSDC to study molecular mobility in IMC below its

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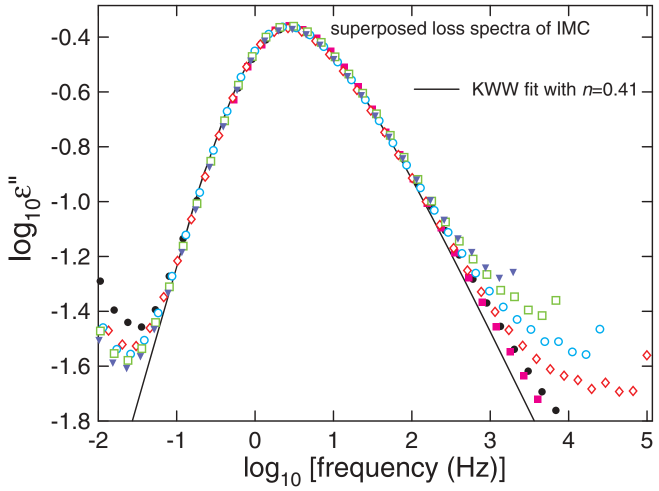

FIG. 1. (Color online) Dielectric loss data of IMC above T_g at six temperatures within the range $315 \leqslant T \leqslant 355$ K all shifted to have the same frequency and height at the peak as the data at $T = 327$ K. The excellent superposition of the data shows that there is no change of frequency dispersion of the main α-loss peak over the range. The line is the KWW fit with $(1-n) = 0.59$.

$T_g = 315$ K. By this technique, they were able to determine τ_α over some range of temperatures below T_g. Hancock *et al.* [6] determined $T_g = 315$ K at the midpoint of the glass transition by DSC at a heating rate of 1 K/min, in agreement with $T_g = 314$ K reported earlier by Andronis and Zografi [4]. The heating rate of 1 K/min in Ref. [6] corresponds to $\tau_\alpha = 200$ s [17]. In another study by DSC, Hancock *et al.* [5] gave the value of 180 kJ/mol for the activation energy of τ_α in the glassy state of IMC. The dielectric, TSDC, and DSC data of τ_α at temperatures above and below T_g are plotted all together in Fig. 2.

III. THE JOHARI-GOLDSTEIN β-RELAXATION AND THE PRIMITIVE RELAXATION OF THE COUPLING MODEL

As shown repeatedly before in many glass formers, there is a slow secondary relaxation that involves the motion of the entire molecule, has strong connection with the α-relaxation, and is fundamentally important for glass transition [18–20]. To distinguish this fundamentally important secondary relaxation of intermolecular origin from other trivial ones involving intramolecular degree of freedom, it is called the Johari-Goldstein (JG) β-relaxation. Acting as the precursor of α-relaxation, the presence of the JG β-relaxation is supposed to be universal in all glass formers and supported by experiments [19]. In the case of IMC, the contribution of JG β-relaxation is not easily resolved in loss spectra in the liquid state, due to the convolution with other processes. Notwithstanding, Carpentier *et al.* [8] found the JG β-relaxation in IMC by isothermal dielectric measurements above T_g, and in the glassy state was obtained by a rapid and deep quench in the isochronal spectra at 10 Hz. The JG β-relaxation of amorphous IMC at temperatures below T_g was also detected using differential scanning calorimetry by Vyazovkin and Dranca [7]. It appears as a small endothermic feature when reheating the quenched sample after annealing in the temperature region from 253 to 278 K [7]. Wojnarowska *et al.* [11] was able to resolve the JG β-relaxation by performing isobaric measurements at $P = 400$ MPa over a wide range of temperatures in the glassy state.

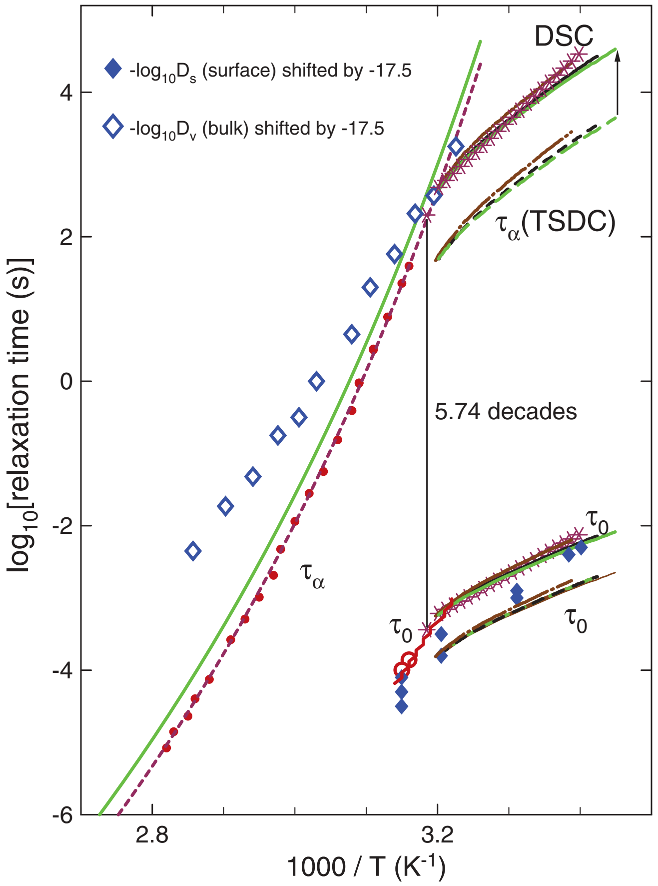

FIG. 2. (Color online) Dielectric α-relaxation times, τ_α, from the following sources. Red filled circles together with the VFT fit (dashed purple line) are τ_α from Ref. [11]. Green line is VFT fit to data of τ_α from Ref. [8]. The green, black and brown lines labeled TSDC are τ_α from Ref. [12]. The companion lines on top are the TSDC data shifted upward to match with the data from Ref. [11]. The purple stars on top are τ_α from DSC measurements [5,6]. The first asterisk on the upper left corresponds to $\tau_\alpha = 200$ s at 315 K. The rest of the asterisks represent τ_α in the glassy state with activation energy of 180 kJ/mol (see text). In the lower part of the figure, the red open circles together with the red dashed line are the calculated primitive relaxation times τ_0 from τ_α (red closed circles and purple dashed line). The two sets of green, black, and brown lines at the bottom are τ_0 calculated from the original and shifted TSDC data of τ_α in the upper part of the figure. The purple asterisks at the bottom are the primitive relaxation times τ_0 calculated from τ_α obtained by DSC [5,6]. The vertical line indicates ($\log_{10}\tau_\alpha$–$\log_{10}\tau_0$) at $T_g = 315$ K is 5.74 decades. The open and closed blue diamonds are $\log_{10}(1/D_v)$ and $\log_{10}(1/D_s)$ data from Ref. [1] shifted downward by 17.5 decades to place $\log_{10}(1/D_v)$ at approximately the same locations as $\log\tau_\alpha$. Note that the same shift superposes $\log_{10}(1/D_s)$ to $\log_{10}\tau_0$. Note that the units of D_v and D_s are m^2/s, different from the units of the relaxation times, which are seconds.

From the experimental studies by different groups, the existence of the JG β-relaxation in IMC is certain, albeit it is difficult to resolve it in the dielectric spectra to determine its relaxation time, τ_{JG}, even in the glassy state at ambient pressure. Nevertheless, there is a way to estimate τ_{JG} from the relaxation time τ_α and the Kohlrausch stretch exponent, $\beta = (1-n)$, of the α-relaxation correlation function appearing in Eq. (1). Verified before in many glass formers [18–21] is the good correspondence between the most probable JG β-relaxation time, $\tau_{\mathrm{JG}}(T)$, from experiments and the primitive relaxation time, τ_0, calculated from the key equation of the coupling model (CM) [19,22–24],

$$\tau_\alpha = \left[t_c^{-n}\tau_0\right]^{1/(1-n)}. \tag{2}$$

In Eq. (2) t_c is a constant $\approx$2 ps for molecular glass formers and polymers as determined by quasielastic neutron scattering experiments and molecular dynamics simulations [19]. According to the CM, τ_0 is the α-relaxation time that the structural relaxation would have if the cooperativity associated with many-body relaxation had been removed entirely. For this reason, its value is very similar to that of the local and noncooperative JG relaxation time τ_{JG}, as found in many glass formers by experiments. After having calculated $\tau_0(T)$ from Eq. (2) with $n = 0.41$ for $315.15 \leqslant T \leqslant 355.15$ K for IMC [11], values of $\tau_{\mathrm{JG}}(T)$ are obtained from the calculated $\tau_0(T)$ via the approximate equality, $\tau_{\mathrm{JG}}(T) \approx \tau_0$. Previously, Carpentier *et al.* [8] had found that the calculated values of $\tau_0(T)$ are consistent with $\tau_{\mathrm{JG}}(T)$ deduced from their isothermal and isochronal spectra.

For IMC, the value of $(1-n) = 0.59$ determined by fitting dielectric loss data [8,11] is constant over a range of temperature above T_g. Although there are no data of the frequency dispersion of the α-dispersion below T_g, the same value of $(1-n) = 0.59$ should apply because of vitrification, and also it is justified by the invariance of the loss peak over the range $10^2 > \tau_\alpha > 10^{-5}$ s (see Fig. 1). We have calculated $\tau_0(T)$ by Eq. (2) with a constant value of $(1-n) = 0.59$ and $\tau_\alpha(T)$ from the experimental data. Above T_g, $\tau_\alpha(T)$ are taken from the isothermal data of bulk IMC and Vogel-Fulcher-Tammann (VFT) fit of Wojnarowska *et al.* Below T_g, the data of $\tau_\alpha(T)$ from the DSC by Hancock *et al.* [5,6] and from TSDC by Correia *et al.* are used. The results of $\tau_0(T)$ are shown also in Fig. 2, and can be considered as good approximations of $\tau_{\mathrm{JG}}(T)$. There is a change of temperature dependence of $\tau_0(T)$ on crossing T_g which is a typical behavior of $\tau_{\mathrm{JG}}(T)$, mimicking the same for the α-relaxation when falling out of equilibrium [18–20]. At T equal to the DSC $T_g = 315$ K, there is an almost perfect match of $\tau_0(T_g)$ calculated from the $\tau_\alpha(T_g)$ of dielectric and DSC, but not with the $\tau_0(T_g)$ calculated with $\tau_\alpha(T_g)$ taken from the center of the spectrum of τ_α reported in the TSDC experiment. A better match would be obtained had we taken the longer τ_α within the TSDC spectrum. Nevertheless, we continue to use the chosen values of τ_α in the central part of the TSDC spectrum, and shift them uniformly upward by 0.95 decade to match $\tau_\alpha(T)$ defined by the VFT fit to the dielectric $\tau_\alpha(T)$. Consequently two sets of $\tau_0(T)$ data are reported in Fig. 2 for TSDC, corresponding to the original and the shifted $\tau_\alpha(T)$ from TSDC. This is shown in Fig. 2 to serve the purpose that the calculated $\tau_0(T)$ with $\tau_\alpha(T_g)$ from TSDC can be taken within these two bounds at temperatures below T_g.

IV. QUANTITATIVE EXPLANATION OF THE DIFFERENCE BETWEEN SURFACE AND BULK DIFFUSION

In light of the various relaxation processes in IMC in the equilibrium liquid and the glassy state obtained by dielectric, TSDC, and DSC techniques, we now reexamine the surface and bulk diffusion data of Zhu *et al.* [1]. The relation $\tau_v(T) = \langle x_v^2\rangle/6D_v(T)$ holds between the bulk diffusion coefficient $D_v(T)$, the mean square displacement $\langle x_v^2\rangle$, and the characteristic diffusion time $\tau_v(T)$. Assuming at $T = T_g = 315$ K that $\tau_v(T_g)$ is the same as $\tau_\alpha(T_g) \approx 10^2$ s from the dielectric spectroscopy and DSC, and with the value of $D_v(T_g)$ given by Zhu *et al.*, $\langle x_v^2\rangle$ is calculated. Its value is approximately 3.1 Å, which is comparable to the nearest neighbor distance of 4.7 Å from the pair distribution functions measured by x-ray diffraction [2,3]. Thus this justifies that indeed $\tau_v(T_g) \approx \tau_\alpha(T_g) \approx 10^2$ s. Because of this, and the fact that $\tau_v(T)$ is proportional to $1/D_v(T)$, it follows that $\log_{10}\tau_v(T)$ can be obtained from $-\log_{10} D_v(T)$ by a downshift of 17.5 decades to a good approximation. The same downshift of 17.5 decades is applied to $-\log_{10} D_s(T)$ in Fig. 2 to obtain $\log_{10}\tau_s(T)$. The operation brings the surface and bulk diffusion data for comparison with the data of $\tau_\alpha(T)$ from dielectric relaxation, DSC, and TSDC of bulk IMC together with the primitive relaxation time $\tau_0(T)$. Albeit the units of $1/D_v$ and $1/D_s$ are different from dielectric relaxation times, the difference in log scale of $\tau_\alpha(T)$ and $\tau_0(T) \approx \tau_{\mathrm{JG}}(T)$ at $T = T_g = 315$ K is about 5.74 decades, comparable to the difference of about six decades between $\log_{10}(1/D_v)$ and $\log_{10}(1/D_s)$ at the same temperature. The relation of surface $D_s(T)$ to bulk $D_v(T)$ is like that between $\tau_0(T) \approx \tau_{\mathrm{JG}}(T)$ and $\tau_\alpha(T)$. There are approximate agreements between the values of $\log_{10}\tau_0(T)$ and the downshifted values of $-\log_{10} D_s(T)$ over the entire temperature range of measurements of the latter. In the CM, $\tau_0(T)$ is the relaxation time without the effect of slowing down by intermolecular cooperativity. Thus the good correspondence between $\tau_0(T)$ and the downshifted value of $-\log_{10} D_s(T)$ suggests that the molecular mechanism of the fast surface diffusion observed in IMC is the translational diffusion in the absence of intermolecular coupling, i.e., the primitive diffusion. The drastic reduction of intermolecular cooperativity of the α-relaxation at the free surface compared to the bulk is likely due to the nonexistence of molecules on one side. Free of neighboring molecules and having totally free volume to explore on one side, molecules on the surface are not slowed down by intermolecular coupling. In the CM, this means that the coupling parameter n in Eq. (2) goes to zero, and $\tau_\alpha(T)$ is reduced to become the same or nearly the same as the noncooperative $\tau_0(T)$. This conclusion has independent support from experiments on 2-nm-thin polymer films confined in galleys of nanocomposites [25,26], and polymers confined in 2.5–5-nm silanized glass pores [25], where reduction of $\tau_\alpha(T)$ to $\tau_0(T) \approx \tau_{\mathrm{JG}}(T)$ was verified.

It is worthwhile to point out that $\tau_0(T)$ shown in Fig. 2 are calculated from $\tau_\alpha(T)$ of bulk IMC, and $\tau_0(T)$ exhibit a change of temperature dependence at $T_g = 315$ K of bulk

IMC, a behavior found experimentally also in $\tau_0(T) \approx \tau_{\mathrm{JG}}(T)$ of many glass formers in the bulk [19,20]. This behavior of $\tau_0(T) \approx \tau_{\mathrm{JG}}(T)$ on crossing T_g reflects the same property of $\tau_\alpha(T)$, and the similarity is a consequence of the strong connection between these faster relaxations and the structural α-relaxation in bulk glass formers [19,20]. However, surface diffusion is decoupled from the bulk, and $\tau_s(T)$ does not sense the glass transition temperature of bulk IMC. In fact, from the good agreement between $\tau_0(T)$ and the shifted $D_s(T)$ shown in Fig. 2, we infer that surface diffusion of IMC transpires in the absence of intermolecular cooperativity. Therefore $\tau_s(T)$ or $D_s(T)$ is not expected to assume the slightly stronger temperature dependence on crossing $T_g = 315$ K of bulk IMC from below as exhibited by $\tau_0(T)$ in Fig. 2. Surface diffusion data of $D_s(T)$ at temperatures higher than those shown in Fig. 2 are not available at the present time to shed light on this point.

The relation between the fast surface diffusion and $\tau_0(T) \approx \tau_{\mathrm{JG}}(T)$ can be used to calculate the mean square displacement $\langle x^2 \rangle$ at the surface with the assumption that characteristic surface diffusion time $\tau_s(T)$ is the same as the rotational relaxation time $\tau_0(T) \approx \tau_{\mathrm{JG}}(T)$ deduced from dielectric measurements. Taking the data of $D_s \approx 5 \times 10^{-14}$ m^2/s at the one temperature above T_g from Zhu *et al.* where $\tau_0(T) \approx \tau_{\mathrm{JG}}(T) = 6.3 \times 10^{-5}$ s, we can get an estimate of $\langle x^2 \rangle$ from the product $\tau_0(T) D_s$, which gives the result $\sqrt{\langle x^2 \rangle} = 17.7$ Å. This length is about three times the nearest neighbor distance of 4.7 Å from the pair distribution functions measured by x-ray diffraction, identified as the thickness of the IMC molecule, and it is slightly more than two times the width of the IMC molecule, ~7.3 Å [2,3]. The assumption $\tau_s(T) = \tau_0(T)$ made above may not be exact. Translation can be still faster than rotation even in the absence of intermolecular coupling because their correlation functions are different, and $\tau_s(T)$ may be shorter than $\tau_0(T)$. A factor of 3 shorter $\tau_s(T)$ will bring $\sqrt{\langle x^2 \rangle}$ down to 10 Å. In any case, the estimated mean displacement corresponding to $\tau_s(T)$ is physically reasonable, and this can be considered as additional support of the proposed molecular mechanism for surface diffusion.

V. SURFACE AND BULK DIFFUSION DATA OF OTHER GLASS FORMERS

The possibility to provide a quantitative explanation for enhanced surface dynamics in terms of noncooperative intermolecular relaxation is intriguing. Let us consider other experiments [27–32] where measurements of a dynamic variable $X(=\tau_\alpha,\eta,1/D,$etc.) were made, each by the same technique, in the bulk and at the surface. Depending on the condition of the experiment employed to measure X at the surface, cooperativity of X at the surface may not be totally removed. The remnant of the cooperativity of X at the surface is indicated by the magnitude of n_s in the fit to the correlation function measured by the KWW function, $\varphi_s(t) = \exp[-(t/\tau_s)^{1-n_s}]$. In the consideration of the experimental data of IMC by Zhu *et al.* [1] where $X \equiv D$, we have made two reasonable assumptions. (i) The ratio $X_{\mathrm{bulk}}/X_s = \tau_\alpha/\tau_s$ at T_g, where τ_α and τ_s are the relaxation times measured in the bulk and at the surface, respectively. (ii) The CM Eq. (2) is also valid for τ_s and its primitive τ_0 is the same as the bulk, but of course the surface coupling parameter n_s has to be used. If τ_s coincides with τ_0, we can infer immediately from Eq. (2) that n_s is zero, as is likely the case in the experiment on IMC of Zhu *et al.* [1]. In general for all possible n_s less than n of the bulk, based on (i) and (ii) it is straightforward to derive from Eq. (2) the following relations at T_g:

$$\log_{10}\left(\frac{X_{\mathrm{bulk}}}{X_s}\right) \cong \log_{10}\left(\frac{\tau_\alpha}{\tau_s}\right) = \log_{10}\left(\frac{\tau_\alpha}{t_c}\right)\left(\frac{n-n_s}{1-n_s}\right) = 13.7\left(\frac{n-n_s}{1-n_s}\right) = 13.7n^*. \tag{3}$$

The factor, 13.7, comes from $\log_{10}(\tau_\alpha/t_c)$ with $\tau_\alpha = 10^2$ s at T_g, and $t_c = 2$ ps. Thus, the ratio between the bulk and surface dynamic variable X at T_g is proportional to $n^* = (\beta_s - \beta)/\beta_s = (n - n_s)/(1 - n_s)$, i.e., the normalized difference between either the coupling parameters n and n_S or the stretching parameters β and β_s in the bulk and at the surface, respectively. If the removal of cooperativity is total at the surface ($n_s = 0$), then n^* is just n of the bulk. This is possibly the case of IMC because $13.7n^* = 5.7$ if $n^* = n = 0.41$, matching the order of magnitude of the data [1].

Figure 3 is a plot of $\log_{10}(X_{\mathrm{bulk}}/X_s)$ against n^* with data coming from several experiments on different glass formers [1,27–32], where data on X from both bulk and surface were reported in the region around T_g. The values of n^* were calculated from n and n_s, the values of which were either given in the Refs. [27–32] or obtained ourselves from the fits to the time and frequency dependence of the correlation function. The values for the different dynamic variables $X(=\tau,\eta,1/D,\ldots)$ obtained at T_g and the related

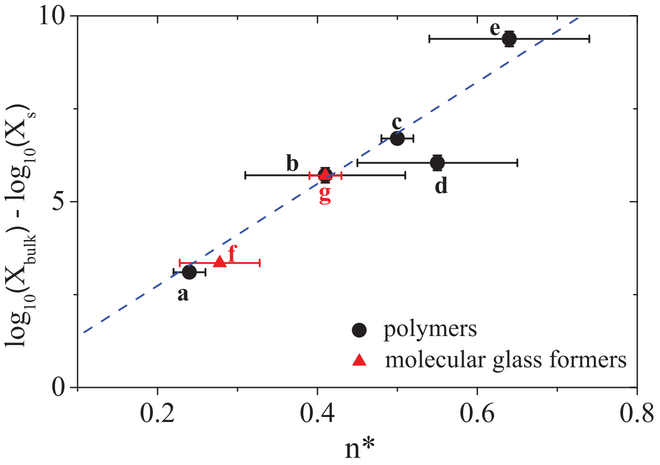

FIG. 3. (Color online) Difference at T_g between bulk and surface dynamics plotted versus the normalized coupling parameter n^* Eq. (3). Dashed line is from CM prediction Eq. (3). $X(=\tau_\alpha,\eta,1/D,$ etc.) indicates the measured dynamic variable. Data are related to (a) reorientation of N,N′-bis(2,5-di-*tert*-butylphenyl)3,4,9,10perylenedicarboximide (BTBP) in polystyrene [27], (b) lateral force microscopy (LFM) on polystyrene [28], (c) time evolution of surface capillary waves in nonentangled polystyrene [29], (d) LFM on polystyrene [30], (e) scanning viscoelasticity microscopy on polystyrene [31], (f) X-ray Photon Correlation Spectroscopy (XPCS) relaxation rate in dibutyl phthalate [32], (g) self-diffusion in indomethacin [1].

TABLE I. Numerical values used for Fig. 3 of the manuscript. Data, calculated at T_g, are related to (a) reorientation dynamics of BTBP in polystyrene by optical photobleaching (OPh) technique [27], (b) lateral force microscopy (LFM) on polystyrene [28], (c) time evolution of surface capillary waves (SCW) in nonentangled polystyrene [29], (d) LFM on polystyrene [30], (e) scanning viscoelasticity microscopy (SVM) on polystyrene [31], (f) XPCS capillary waves relaxation rate $\lambda = G/\eta$ in dibutyl phthalate [32], (g) self-diffusion from surface grating decay (SGD) in indomethacin [1]. For data (a) n was provided by the authors [27], while n_s was fixed to 0; n for entangled (data b, d, e) and nonentangled polystyrene (data c) were from [33,34], respectively; n for data (f) and (g) are from [11,35], respectively; n_s for data (b), (d), (f) were provided by the authors; n_s for data (c), (e), (g) was estimated null from the shape of the relaxation function.

Material	Reference	Technique	X	n^*	n	n_s	$\log_{10}(X_{\text{bulk}})$	$\log_{10}(X_s)$
(a) BTBP + polystyrene ($M_w = 160$ kg/mol)	[27]	OPh	τ_{rot}	0.24	0.24	0	4.8	1.7
(b) Polystyrene ($M_w = 223$ kg/mol)	[28]	LFM	τ_M	0.41	0.64	0.39	2	−3.71
(c) Polystyrene ($M_w = 2.4$ kg/mol)	[29]	SCW	η	0.5	0.5	0	13	6.3
(d) Polystyrene ($M_w = 140$ kg/mol)	[30]	LFM	τ_M	0.55	0.64	0.2	2	−4.04
(e) Polystyrene ($M_w = 140$ kg/mol)	[31]	SVM	τ_M	0.64	0.64	0	2	−7.38
(f) Dibutyl phthalate	[32]	XPCS	$1/\lambda$	0.28	0.35	0.1	2	−1.35
(g) Indomethacin	[1]	SGD	$1/D$	0.41	0.41	0	−19.7	−14.0

β and β_s parameters for the different experiments are shown in Table I. The predictions according to Eq. (3) shown by the line are in agreement within experimental errors for the different systems and techniques.

VI. COMPARISON OF THE CM AND THE RFOT EXPLANATIONS

Zhu *et al.* had compared part of their experimental data with the prediction on surface relaxation given by Stevenson and Wolynes (SW) [36] from the random first order transition (RFOT) theory [37,38]. It could be of interest to compare our predictions on surface diffusion with that of the RFOT theory. For bulk glass formers, RFOT has the structural α-relaxation time,$\tau_{\alpha,\text{bulk}}(T)$, given by

$$\tau_{\alpha,\text{bulk}} = \tau_\infty \exp\left[F_{\text{bulk}}/k_B T\right]. \tag{4}$$

Here τ_∞ is the prefactor that, originally in Ref. [36], was denoted by τ_0 by SW. To avoid confusion with the same symbol τ_0 used in the CM to denote primitive relaxation time, we replace τ_0 by τ_∞ in Eq. (4). F_{bulk} is the free energy barrier for reconfiguration events in the bulk and is inversely proportional to $T s_c(T)$, where $T s_c(T)$ is the configurational entropy. In the deeply supercooled region, Eq. (4) has the Vogel-Fulcher dependence, $\tau_{\alpha,\text{bulk}} = \tau_\infty \exp[B/(T - T_K)]$, where T_K is the Kauzmann temperature. SW suggested for a free surface with no structural modifications that the transition state of RFOT would rearrange a region of hemispherical shape and the free energy barrier is reduced from F_{bulk} by a factor of 2 [36]. With the assumption that the prefactor is the same for bulk and surface, the surface relaxation time, τ_s, is related simply to the bulk value, $\tau_{\alpha,\text{bulk}}$, given by

$$\tau_S = \sqrt{\tau_\infty \tau_{\alpha,\text{bulk}}}. \tag{5}$$

On the other hand, our predicted surface relaxation time from the CM Eq. (2) is

$$\tau_S(t) \approx \tau_0(t) = (t_c)^n [\tau_{\alpha,\text{bulk}}(t)]^{1-n}, \tag{6}$$

where $(1 - n) = 0.59$.

Zhu *et al.* [1] have fitted their data to the Arrhenius dependence, $D = D_0 \exp(-Q/RT)$ over a common temperature range of D_s and D_v in Fig. 2 to obtain the respective activation energies Q_s and Q_v. The obtained ratio of the activation energies for surface and bulk diffusion, Q_s/Q_y, is consistent with either the value of 0.5 predicted by Eq. (5) from RFOT or 0.59 from Eq. (6) of the CM since $(1 - n) = 0.59$. This is due to the limited temperature range in which both D_s and D_v were determined as well as the uncertainties of the measurements.

We have shown from the CM equation (6) that the ratio, $\tau_{\alpha,\text{bulk}}/\tau_0$, can account quantitatively for the nearly six orders of magnitude increase of D_s compared with D_v observed experimentally at temperature near the T_g of bulk IMC. Let us examine the prediction of the RFOT theory on the ratio, $\tau_{\alpha,\text{bulk}}/\tau_s$, also at the T_g of bulk IMC. To do this, the RFOT equation (5) is rewritten as

$$\log_{10}(\tau_{\alpha,\text{bulk}}/\tau_s) = 0.5[\log_{10}(\tau_{\alpha,\text{bulk}}) - \log_{10}(\tau_\infty)]. \tag{7}$$

To account for the six orders of magnitude difference between $\tau_{\alpha,\text{bulk}}$ and τ_s at the T_g of bulk IMC, where $\tau_{\alpha,\text{bulk}}(T_g) = 10^2$ s, Eq. (7) requires τ_∞ to have the value of 10^{-10} s. The fit to the IMC dielectric data of $\tau_{\alpha,\text{bulk}}$ by the Vogel-Fulcher equation gave $\tau_\infty = 10^{-19.4}$ s [11], which is much shorter than the value of 10^{-10} s required. A survey has been made of the literature data of the Vogel-Fulcher fits to $\tau_{\alpha,\text{bulk}}(T)$ of glass formers having fragility index m comparable to the value of 82.8 for IMC [11]. The values of τ_∞ are usually at least several orders of magnitude shorter than 10^{-10} s. The problem is more serious if Eq. (7) is applied to surface diffusion in the cases (a) and (f) shown in Fig. 3. There are only about three orders of magnitude in enhancement of surface dynamics, and an anomalously long value of 10^{-4} s for the prefactor τ_∞ is required to account for the experimental observation.

There is also one important difference between the RFOT theory and the CM. The RFOT theory applies exclusively to dynamics of liquids and glasses, and glass transition, whereas the CM is concerned with the many-body relaxation and diffusion dynamics in interacting systems, which include glass-forming substances, but it has been applied to other systems having nothing to do with glass transition [19].

VII. CONCLUSION

In summary, using dielectric relaxation, DSC, and TSDC data of the structural α-relaxation time $\tau_\alpha(T)$ above and below

T_g of bulk IMC, we have calculated the primitive relaxation time, $\tau_0(T)$, from the coupling model, which is about six orders of magnitude shorter than the τ_α in the neighborhood of T_g. The difference between $\tau_0(T)$ and $\tau_\alpha(T)$ matches that between D_s and D_v. This result indicates fast surface diffusion is due to nearly or totally vanishing of intermolecular cooperativity at the surface, resulting in the surface diffusion correlation time having the same order of magnitude as $\tau_0(T)$, and the characteristic length of diffusion of about two or three times the nearest neighbor distance. Support of the reality of $\tau_0(T)$ is provided by the universal Johari-Goldstein β-relaxation found in bulk IMC with relaxation time $\tau_{JG}(T)$ nearly the same as $\tau_0(T)$. The same explanation has been applied successfully to data relating surface and bulk dynamics obtained on different systems by different experiments.

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