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# Interfacial Free Volume and Vitrification: Reduction in $T_g$ in Proximity of an Adsorbing Interface Explained by the Free Volume Holes Diffusion Model

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The reduction in glass transition temperature ( $T_g$ ) in ultrathin polymer films is commonly explained in terms of the presence of free surfaces (interface with a gas or vacuum), which, accelerating the structural dynamics,<sup>1</sup> shift the mean relaxation time ( $\tau$ ) and its distribution toward shorter values. For polystyrene (PS)<sup>2</sup> and poly(methyl methacrylate) (PMMA)<sup>3</sup> it was experimentally verified that in the region extending for 2–3 nm from the free surface the structural relaxation takes place on time scales more than 10 orders of magnitude shorter than in bulk.<sup>4</sup> However, lower glass transition temperatures were also detected in the case of capped films<sup>5,6</sup> and for nanocomposites,<sup>7</sup> where free surfaces are not present. Moreover,  $T_g$  values larger than in bulk can be detected at the free surface of high functionality star-shaped polymers due to an improved packing of the interfacial chains.<sup>8</sup> These observations question the universality of the correlation between a reduction in  $T_g$  and the presence of a free surface. An alternative molecular picture should be proposed to rationalize this experimental evidence.

In this regard, recent models assume that the faster dynamics is the result of an excess in free volume<sup>9</sup> in the thinner films. Possible sources of this effective packing frustration were related to larger specific volume upon confinement,<sup>10,11</sup> longer interchain distances,<sup>12</sup> or the formation of an irreversible adsorbed layer onto the substrate.<sup>5</sup> The reduction in  $T_g$  is then related to the lower value in interfacial monomer density of as spin-coated films.<sup>13–16</sup> Thermal treatment, required after spin-coating to remove residual solvent and release mechanical stresses,<sup>17</sup> favors an increase in the adsorption degree, which leads to a reduction in free interface (space available at the polymer/solid interface due to incomplete surface coverage).<sup>18</sup>

Usually, the annealing step is performed at time scales comparable to those of technological interest (minutes, hours), while the formation of a polymer/solid interface denser than the bulk takes place on the time scale of chain adsorption, which in the case of PS might require several days at temperatures well above bulk  $T_g$ .<sup>5,19</sup> Consequently, chains located in the proximity of these partially unhealed interfaces, although firmly adsorbed onto a solid substrate, can explore a larger volume (lesser steric hindrance), which yields a reduction in  $T_g$ . Direct evidence of this unusual behavior was reported for poly(4-*tert*-butylstyrene) (PTBS), an analogue of PS where the hydrogen in the para position is replaced by a bulky side group, promoting packing frustration as demonstrated by a drop in density by 9%.<sup>20</sup> Confined at the nanoscale level, films of PTBS capped in between aluminum layers (no free surfaces) show a

reduction in  $T_g$  which was rationalized via the presence of an excess in free volume located in between the interfacial immobilized layer and the bulk core.<sup>21</sup> Further proof of the role of interfacial free volume on the properties of thin films comes from the observation that well-annealed films of poly(vinyl acetate) (PVAc) exposed to controlled humidity do not uptake as much water as films annealed at shorter times.<sup>22</sup> The transition from a hydrophilic to a hydrophobic character was justified considering that well annealed films might achieve density larger than in bulk and thus have less free volume for the diffusion of water molecules.

Similar results were found in experiments permitting to determine the gradient in relaxation time and orientational polarization (a probe for adsorption) in ultrathin films of PS capped between Al layers.<sup>23</sup> At short annealing times the interfacial  $T_g$  (averaged over the first 14 nm) was lower than in bulk, while prolonged annealing yielded a neat increase in  $T_g$  and in the adsorption degree. This qualitative picture was confirmed by a successive study, which highlighted a strong correlation between the thickness of the adsorbed layer and the shift in  $T_g$ .<sup>5</sup> Considering that the thickening of the adsorbed layer proceeds via a continuous filling of the unoccupied sites on the surface of the substrate,<sup>24</sup> it was proposed and then experimentally verified that the thickness of the adsorbed layer should be a probe for the free interface<sup>5</sup> and that the reduction in the  $T_g$  of thin films is correlated to the excess free volume at the polymer/solid interface.<sup>18</sup> Although these correlations are intuitive, a suitable theoretical framework capable to justify these results is still missing.

In this Note we demonstrate that the free volume holes diffusion (FVHD) model<sup>25</sup> is able to catch simultaneously the following experimental observations in Al-capped PS films:<sup>18</sup> (i) the magnitude of  $T_g$  depression and interfacial free volume are linearly correlated; (ii) surface/volume ratio and interfacial interactions are not sufficient in determining the deviations from bulk behavior.

The FVHD model—originally developed to describe physical aging of glassy “bulk” PVAc<sup>25</sup> and recently revitalized to describe physical aging and  $T_g$  depression in free-standing PS films<sup>26–29</sup> and polymer nanocomposites<sup>30–32</sup>—predicts that equilibrium is ensured on cooling, as long as free volume holes can diffuse and annihilate at the interface. The major limitation

Received: July 1, 2013

Revised: September 2, 2013

Published: September 26, 2013



of the model was the presence of an ill-defined “internal length scale” necessary to account for the lack of size effects on the  $T_g$  and physical aging of bulk glasses. Conversely, this approach permits to rationalize the acceleration of physical aging<sup>25,27,29,30,33,34</sup> and  $T_g$  depression<sup>29,30,33</sup> in glasses with typical length scale smaller than several micrometers. In fact, according to the FVHD model, larger free interfaces between the glass and its environment correspond to a reduction in the distance required by free volume holes to maintain equilibrium upon cooling. Hence, from a qualitative point of view, nanostructured glasses having shorter typical length scale (that is, larger surface/volume ratio or larger free interfaces) will be able to resist against vitrification more efficiently. Therefore, the  $T_g$  of these systems will be lower in comparison to the bulk.

From a quantitative point of view, one can express  $\langle x^2 \rangle$ , the mean-square displacement of free volume holes in one dimension, i.e., the component relevant for films, as a function of time via the expression

$$\langle x^2 \rangle = 2D(T)t \quad (1)$$

where  $D(T)$  is the thickness-independent, temperature-dependent diffusion coefficient of free volume holes. In a free-standing film, where the entire interface of the film is available for free volume removal, the glass transition at a given cooling rate  $q \sim t^{-1}$  occurs when  $\langle x^2 \rangle$  equals half the thickness of the film,  $h$ :

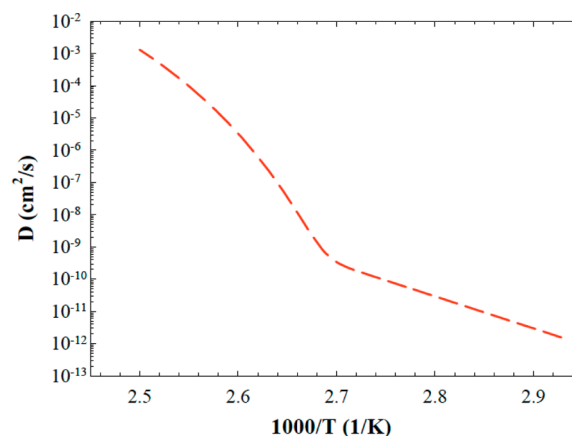
$$\left(\frac{h}{2}\right)^2 = 2D(T_g)q^{-1} \quad (2)$$

For films thinner than about 100 nm,  $h$  corresponds with the real film thickness. For thicker films,  $h$  is replaced by an equivalent thickness,  $h_{eq}$ , evaluated accounting for the lack of thickness dependence of the  $T_g$  for films larger than several micrometers. Formally, this can be done introducing an internal thickness,  $h_{int}$ , which, in the case of PS, was found to be  $\sim 1750$  nm.<sup>29</sup> In doing so, the equivalent thickness is evaluated as  $h_{eq} = hh_{int}/(h + h_{int})$ . Further details regarding this point can be found in ref 29.

From eq 2, it is possible to extract  $D(T)$  from measurements of the cooling rate dependence of  $T_g$ .<sup>29</sup> The temperature dependence of the diffusion coefficient of free volume holes for PS is shown in Figure 1.

$D(T)$  crosses from super-Arrhenius, at relatively high temperatures ( $>370$  K), to Arrhenius behavior at lower temperatures. Interestingly, the former can be suitably described by a Vogel–Fulcher–Tammann (VFT) law with Vogel temperature and activation energy equal to those of the  $\alpha$ -process of bulk PS, whereas the Arrhenius law exhibits activation energy typical of the secondary process of PS.<sup>29</sup>

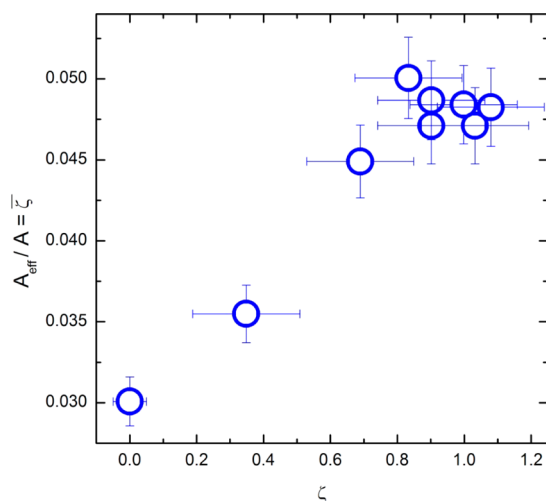
While application of the model to free-standing films is straightforward, the presence of a solid substrate requires a specific treatment, considering the changes in free interface due to irreversible chain adsorption.<sup>18,35–39</sup> In this geometry, only a portion (if any) of the polymer/substrate interface is available to free volume holes removal. In the extreme scenario where, upon sufficiently long annealing, the monomer density in the adsorbed layer reached, without exceeding, bulk values, no  $T_g$  depression should be detected. A further clarification about the application of the FVDH model in capped films should be done. The key factor allowing elimination of free volume holes to keep equilibrium when cooling down a melt is the presence of a free surface. This is obvious in free-standing as well as



**Figure 1.** Temperature dependence of the free volume holes diffusion coefficient of PS taken from ref 29. The diffusion coefficient is calculated as a sum of a VFT and an Arrhenius law:  $\log D = \log D_{0(VFT)} + B/(T - T_0) + \log D_{0(Arr)} + E_a/kT$ , with  $B = 1000$  K,  $T_0 = 341$  K,  $D_{0(VFT)} = 302$  cm<sup>2</sup>/s,  $E_a = 190$  kJ/mol, and  $D_{0(Arr)} = 1.8 \times 10^{15}$  cm<sup>2</sup>/s.

supported films. In the case of capped films, instead, free interfaces provide a sink for free volume holes removal. Conversely, the chains being adsorbed onto the substrate exhibits infinite energetic barrier, not amenable to be overcome by free volume holes.

In the molding experiment of Napolitano et al.,<sup>18</sup> a controlled annealing procedure permitted to tune the adsorption degree of PS, and thus the free interface, while keeping the interfacial interactions and the thickness of the sample constant. These experimental conditions are thus optimal to test the validity of the FVHD model. From a quantitative point of view, to take into account the reduction in free interface upon adsorption, in eq 2 we replace the film thickness with an effective thickness  $h_{eff}$  corresponding to an effective free interface  $A_{eff}$ . We employed the values of  $T_g$  of Al-capped films annealed at 423 K for different times<sup>18</sup> to evaluate via eq 2  $h_{eff}$  and therefore  $A_{eff}$  at different adsorption degrees. The so-obtained  $A_{eff}$  were then used to determine the fraction of free interface,  $\zeta = A_{eff}/A$ , where  $A$  is the surface of a slab of the same thickness. This last quantity was finally compared with the amount of free interface  $\zeta$  experimentally determined via tracer diffusion experiments of labeled PS in adsorbed layers of PS. Such a comparison is displayed in Figure 2. The amount of free interface determined by the FVHD model via the analysis of  $T_g$  data scales linearly with the experimental values of excess in interfacial free volume obtained via diffusion of labeled PS. Moreover, the results of Figure 2 provided a strong proof of the ability of the model to capture the magnitude of  $T_g$  depression. In fact, the capped film with the largest  $T_g$  depression ( $\sim 5$  K) has a content of free interface limited to 5%, which corresponds to freely standing films with an equivalent thicknesses on the order of  $\sim 670$  nm; remarkably in these systems the shift in  $T_g$  was limited to 5 K.<sup>29</sup> Such a correlation strengthens the idea that the structure of the interface governs the effects of confinement on thin films and that the thickness, acting as an averaging parameter, plays a secondary role. Moreover, these evidences prove the robustness of the FVHD model also in the case of adsorbed thin films and buried interfaces and demonstrate the possibility to predict the properties of confined systems without invoking a change of the segmental dynamics.<sup>40–42</sup>



**Figure 2.** Fraction of interfacial free interface as a function of the experimentally determined interfacial free volume.<sup>18</sup>

Finally, our findings are also in line with the hypothesis that the deviations from bulk behavior originate from the different conformations assumed by polymer chains upon confinement.<sup>43</sup> In particular, the observation that the shift in  $T_g$  can be correlated to a change in the interfacial free surface suggests that the changes in the thermal  $T_g$  arise from the way interfacial conformations affect the local free volume.<sup>44</sup>

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

D.C. acknowledges the University of the Basque Country and Basque Country Government [Ref No. IT-436-07, Depto. Educación, Universidades e investigación; and Spanish Government (Grant No. MAT2012-31088] for their financial support.

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