On the Equivalence Between the Thermodynamic and Dynamic Measurement of the Glass Transition in Confined Polymers

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Abstract

Understanding why the glass transition temperature (T_g) of polymers deviates substantially for the bulk with nanoscale confinement has been a 20-year mystery. Ever since the observation in the mid-1990s that the T_g values of amorphous polymer thin films are different from their bulk values, efforts to understand this behavior have intensified, and the topic remains the subject of intense research and debate. This is due to the combined scientific and technological implications of size-dependent glassy properties. Here, we discuss an intriguing aspect of the glassy behavior of confined amorphous polymers. As experimentally assessed, the glass transition is a dynamic event mediated by segmental dynamics. Thus, it seems intuitive to expect that a change in T_g due to confinement necessitate a corresponding change in molecular dynamics, and that such change in dynamics may be predicted based on our understanding of the glass transition. The aim of this perspectives article is to examine whether or not segmental dynamics change in accordance with the value of T_g for confined polymers based on bulk rules. We highlight past and recent finding that have examined the relationship between T_g and segmental dynamics of confined polymers. Within this context, the decoupling between these two aspects of the glass transition in confinement is emphasized. We discuss these results within the framework of our current understanding of the glass transition as well as efforts to resolve this decoupling. Finally, the anomalous decoupling between translational (diffusion) and rotational (segmental) motion taking place in the proximity of attractive interfaces in polymer thin films is discussed.

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Highlights:

- We review the relationship between the dynamic and pseudo-thermodynamic measurements of the glass transition in confined polymers.
- The free volume diffusion model and irreversible chain adsorption offer insights into the properties of confined glassy polymers.

I. Introduction

The study of confined amorphous polymers, those with a reduced length scale in one or more dimensions, has become increasingly important because these systems enable numerous technologies in which miniaturization is paramount. As an example, thin polymer films (with thickness (*h*) < 100 nm) are being exploited for use as templates in microelectronics,[1] active layers in photovoltaic cells,[2] non-biofouling protective coatings,[3] and membranes in separation technologies.[4] Polymer nanoparticles (with diameter (*d*) < 500 nm) are being explored for use as vehicles in drug delivery,[5] components in fluorescent imaging,[6] performance reinforcing additives,[7] and components in photonic structures.[8] Polymer nanocomposites (with interparticle distance (*ID*) < 100 nm) are being engineered to enhance structural, barrier, flame resistance, electro-optical, and bactericidal properties, amongst many others.[9,10] If the physical properties of polymers change due to physical confinement or interfacial effects, our understanding of such effects will be essential in assessing their potential use in nanotechnology, including the above mentioned.

The discovery, in the early 1990s, that the glass transition temperature (T_g) can deviate significantly from the bulk for nanoconfined molecular[11] and polymer[12] glass formers exposed a new aspect of glassy behavior that continues to provide challenges for fundamental understanding.[13] For the case of polymer glasses, the material of attention for this perspective, it is now recognized that systematic deviations in T_g may be observed for thin film[14-18], nanoparticles[19,20] and nanocomposites.[21,22] Deviations in T_g with confinement are generally explained to be a result of (or lack of) interfacial interactions between the polymer and the interface.[12,16,19,22-25] When attractive interactions between the polymer and interface (substrate) persist, enhancements in T_g may be observed.[22-24] On the other hand, repulsive or free/soft interfaces can lead to a reduction in T_g with confinement.[12,16,19,25] By tuning the interfacial interactions between the substrate and confined polymer, it is possible to systematically change T_g.[24,26] This effect is highlighted in Figure 1.[26] For a 10 nm thick films supported on a silica substrate, ΔT_g ~ 35 K and ~ - 20 K for poly(vinyl pyridine) (P2VP) and polystyrene (PS), respectively. Nevertheless, a 70:30 P2VP-PS copolymer exhibits a T_g that is invariant with film thickness. We note, that recent work has opened to the possibility of tuning T_g by varying the adsorption degree, while keeping interfacial interactions and thickness constant.[27]

How interfaces modify T_g remains an intriguing and open question.[13,28,29] One possible scenario is that the presence of the free surface acts to locally reduce the requirement for cooperativity of segmental dynamics, thereby reducing T_g while, in contrast, the presence of attractive polymer–substrate or polymer–nanoparticle interactions, *e.g.,* hydrogen bonds, increases the requirement for cooperativity in the dynamics associated with the glass transition, leading to a T_g increase.[23,30,31] Because deviations in T_g have been reported for thin films and nanoparticles with thicknesses and diameters greater 100 nm and 400 nm, respectively, perturbations to dynamics originating from interfaces must propagate over a long length-scale (h > 10 nm), a fact that would require a completely new picture of glassy dynamics (the cooperative length scale is generally predicted to be of the order of nanometers[32]). Understanding how interfaces may influence glassy dynamics over tens-of-nanometers remains a challenge and brings into question our understanding of structural relaxation, which is believed to be localized to a few nanometers.

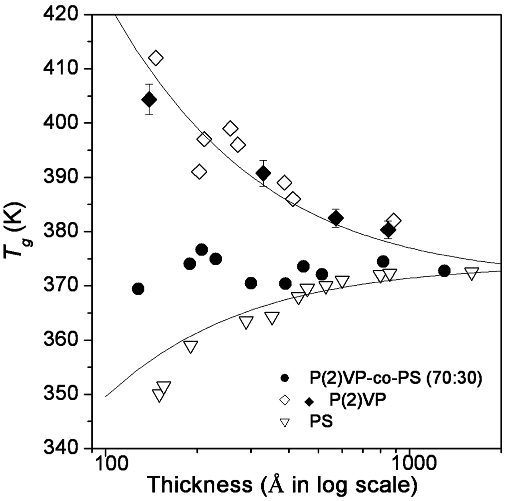

Figure 1: Change in T_g with nanoscale confinement for PS, P2VP, and a P2VP-PS copolymer. Reprinted from Park *et al.*[26]

As it sets the practical use temperature of amorphous polymers, characterizing and understanding T_g of confined polymers is immensely important. The descriptive understanding of the glass transition, in bulk, suggests that a 10-degree change in T_g would be accompanied by a 1000-fold change in molecular mobility.[32] Thus, it seems intuitive to expect that a change in T_g due to confinement necessitate a corresponding change in molecular dynamics, and that such change in dynamics may be predicted based on our understanding of the glass transition. *The aim of this* *perspectives article is to examine whether or not segmental dynamics change in accordance with the value of T_g for confined polymers based on bulk rules.* Here, we define the *dynamic* T_g as one assigned *via* the measurements of molecular dynamics, *e.g.,* dielectric relaxation spectroscopy. The *thermodynamic* value of T_g is assigned based on monitoring a thermodynamic property (or proxy) as a function of temperature, *e.g*., calorimetry and dilatometry. We first briefly discuss the phenomenology of glass formation. Next, we highlight prior and recent findings that examined the relationship between T_g and molecular dynamics of confined polymer and an anomalous decoupling between translational (diffusion) and rotational (segmental) motion taking place in the proximity of attractive interfaces. We discuss the results within the context of our understanding of the bulk glass transition. Finally, we end with concluding remarks.

II. The Glass Transition: Brief Phenomenological Description

Dynamics Description

The glass transition is a dynamic event. The viscosity of liquids above their melting temperature, T_{m}, generally exhibits Arrhenius temperature dependence. This behavior changes considerably once the liquid is cooled down below T_{m}, provided that crystallization is avoided, that is when a supercooled liquid is formed. In this case the viscosity and the relaxation time (τ) of the associated thermal fluctuations enter a regime with considerably more pronounced temperature variations. τ may vary within a relatively small temperature interval by many orders of magnitude. Hence supercooled liquids exhibit highly non-Arrhenius temperature dependence of τ as shown schematically in Figure 2b. The temperature dependence of τ is generally described by the empirical Vogel-Fulcher-Tammann (VFT) law[33-35]:

$$\tau = \tau_0 \exp \frac{B}{T - T_0} \tag{1}$$

where τ_0, B and T_0 are the pre-exponential factor, Vogel activation energy and Vogel temperature, respectively. The VFT equation insinuates divergence of τ at T_0. However, this is never observed in experiments. This is due to the fact that, at temperatures not too far from T_{m}, τ becomes larger than seconds. Hence, for laboratory observation times, generally of the order or smaller than seconds, the system cannot rearrange to maintain equilibrium and a non-equilibrium glass is formed. The temperature at which this occurs is known as the glass transition temperature (T_{g}). Below such temperature, glasses slowly evolve toward equilibrium. The kinetics of equilibrium recovery is normally addressed as physical aging.[36,37]

Apart from the dynamical process responsible for the glass transition, supercooled liquids normally exhibit additional relaxation processes. In particular, virtually all glass formers exhibit at least one secondary fast relaxation, so-called β–relaxation, associated with localized motion, see Figure 2a.[38,39] In Figure 2b, together with the primary glass-transition related process, a typical secondary relaxation, exhibiting Arrhenius temperature dependence, is schematically drawn. The relevance to the glass transition of secondary relaxations is a matter of open debate, particularly for those secondary relaxations related to the motion of the overall structural units.[40]

Among the several facets of the dynamics of the glass transition, its heterogeneous[41-43] and cooperative[44] nature and decoupling phenomena[42] are currently subject of intense debate. This is generated by the search for a comprehensive understanding of the dynamics of the glass transition, which is at present missing.

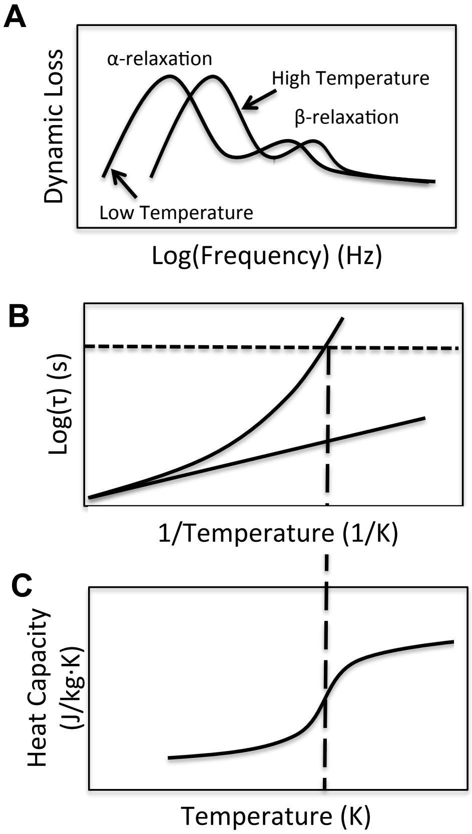

Figure 2: a) Dispersion map of relaxation processes for a general glass former at two temperatures. b) Temperature dependence of the relaxation time of the primary and secondary process in a typical glass former. c) Temperature dependence of heat capacity of a glass former near the glass transition.

Thermodynamic Description

Though the glass transition is a dynamic event, there are signatures similar to a second-order phase transition. In the previous description on the dynamics of glass forming systems, the occurrence of the glass transition has been described from the point of view of dynamics, that is, a phenomenon taking place on cooling once the rate of spontaneous fluctuations becomes too slow in comparison to the experimental time scale. This has deep implications in the thermodynamics of glass formers.[45,46] In particular, the freezing in of the molecular motion associated to the glass transition implies that the configurational contributions to thermodynamic coefficients (e.g., heat capacity, thermal expansion coefficient, and compressibility) are removed. This implies that, when crossing the glass transition, a jump in thermodynamic coefficient is observed. As an example, the jump of the specific heat around the glass transition is schematically drawn in Figure 2c. As can be seen due to the freezing-in of configurational degrees of freedom, the specific heat in the glassy state is considerably smaller than that of the corresponding melt.

The jump of the specific heat at the glass transition is reminiscent of a second order thermodynamic transition. However, this interpretation must be discarded due to the fact that a transition in a strict thermodynamic sense occurs at a fixed temperature, whereas the T_g is cooling rate dependent. Moreover, the Prigogine-Defay ratio of the glass transition systematically exceeds one, that is, the value expected for a second order thermodynamic phase transition.[32] The relatively low specific heat in the glassy state does not mean that configurational degrees of freedom are frozen in over all time scales, but only over that of the calorimetric experiment, that is, the applied cooling rate. Thus the observed evolution toward the equilibrium state during physical aging is driven by the slow configurational rearrangement on long time scales. This, together with the cooling rate dependence of the T_g, is a manifestation of the kinetic nature of the glass transition.

Connection Between Dynamic and Thermodynamic Descriptions of Glass Transition

In the previous sections, the intimate link between the dynamics and thermodynamics has been anticipated. In particular, it has been emphasized how the presence of a discontinuity in thermodynamic coefficients underlines a correlation between the crossover from an equilibrium to an out-of-equilibrium glass and spontaneous fluctuations in the glass former. Nonetheless, it is important to remark that the time scale of such fluctuations and the time scale of equilibration (e.g., the time needed to recover equilibrium or the cooling rate in a calorimetric experiment) are two distinct concepts. In particular, the former is an intrinsic property of the glass former and can be probed by applying a linear perturbation. This provides a so-called molecular relaxation time

τ_{mol}. Conversely concepts like restoring equilibrium in the aging regime or leaving equilibrium when cooling a glass former through T_g imply that a perturbation beyond the linear regime is applied. In this case, an equilibration time τ_{eq} is rather obtained.[47] This conceptual difference emerges, for instance, in the experimental observation that values of τ at the calorimetric T_g at a given rate are widely scattered, that is, in a range of at least 3-4 orders of magnitude in time scale.[48] Notwithstanding the previous considerations, in bulk glass formers, numerous studies indicate that the two concepts are one-to-one related. In particular, the kinetics of recovery in the physical aging regime has been shown to be related to the rate of spontaneous fluctuations.[36,37] Furthermore, in bulk glass formers, it is well-established that the dependence of the T_g on the cooling rate can be described by the VFT law. Importantly, it has been shown that the parameters τ_0 and T_0 fitting the cooling rate as a function of the T_g are identical to those describing the time scale of spontaneous fluctuations.[49-51] The present Perspective aims to highlight recent results on these aspects in confinement. We anticipate that in such case the mentioned interdependence is not as trivial as in bulk systems and propose possible interpretation and developments.

III. Highlights of Past and Recent Observations

When polystyrene is confined to the nanometer length scale its glass transition temperature can deviate dramatically from the bulk. In fact, suppressions in the T_g of confined PS have been observed in freestanding films, supported films, nanoparticles, and nanocomposites by a range of dissimilar techniques. In essence, the influence of size on T_g of PS is near universally observed.[29,52,53] Are accompanying changes in molecular dynamics universally observed?[13] This question has recently received significant attention in the literature as unifying scenarios emerge as well as the aim at reconciliation with opposing viewpoints.[54] Here, key literature results pertaining to this important question are highlighted.

Ideally, intrinsic molecular mobility and T_g should be measured within the same experiment. This is important to ensure that both parameters are measured in samples that are subjected to the identical thermal history, environmental conditions and interfacial interactions. In this case, dielectric relaxation spectroscopy (DRS) combined with capacitive dilatometry (CD) offers a unique possibility to probe the glass transition of confined polymers as both molecular mobility and T_g can be obtained in single experiment. The first study to simultaneously measure these two aspects of the glass transition was that by Fukao *et al.*[18] In their seminal study, the confinement behavior of PS films supported between Al substrates was investigated. The T_g was observed to decrease as a function of film thickness at an onset value of ~ 60 nm. The dependence of T_g on thickness occurred continuously such that a 30 nm thick film exhibited an ~ 25 K change of T_g in comparison to the bulk value. However, the peak temperature of the segmental dynamics, denoted as, T_α, remained constant until a critical thickness of ~ 15 nm at which point a drastic reduction in T_α was observed. As noted by Fukao *et al.*[18] the thickness dependence of T_g was not related to the characteristic relaxation time. Supporting this claim was the later work of Lupascu *et al.*[55] In their study, DRS and CD was employed to measure the glassy dynamics of PS thin film supported between Al-layers. While the T_g as measured by CD exhibited a pronounced thickness dependence similar to that observed by Fukao *et al.*[18] a very modest speed-up in molecular dynamics was observed with reducing film thickness. In fact, for a film of thickness ~ 500 nm, $T_g = 90^\circ$C and $T_\alpha = 95^\circ$C, while for a film of thickness ~ 10 nm, $T_g = 60^\circ$C and $T_\alpha = 85^\circ$C.

Recently, several studies have revealed either a less-than-expected behavior or lack of positive correlation between the thickness dependence of the T_g and cooperative segmental mobility. The observations appear independent of sample geometry, as similar phenomenon has been observed in thin films, nanospheres and nanocomposites. As an example, Sharp *et al.* found no discernible shift or broadening in the α-relaxation peak (at frequency of 1 kHz) for isotactic PMMA for thicknesses approaching 7 nm, whereas the ellipsometric T_g was shown to decrease significantly with decreasing film thickness.[56] In another case, Svanberg applied DRS to measure T_α of PS thin films immersed in glycerol.[57] An enhancement in the segmental relaxation dynamics of ultrathin films relative to bulk was observed. Yet, the magnitude for the increase in mobility was "less than expected from previous observations of T_g for free-standing films" as noted by Svanberg.

In a series of investigations, the decoupling between T_g and segmental dynamics in thin films and nanocomposites has been thoroughly examined by Cangialosi, Boucher and coworkers.[58-61] In one study, DRS, CD, conventional differential scanning calorimetry (DSC) and AC-calorimetry were applied to measure glassy dynamics in PS thin films subjected to the same preparation procedure and measured under identical environmental conditions.[58] In doing so, they observed a complete decoupling in the size-dependent segmental mobility and T_g. Segmental mobility as measured by AC-calorimetry and DRS was invariant with thickness down to 15 nm. In contrast, T_g, underlying the equilibrium to out-of-equilibrium, exhibited a clear depression with decreasing film thickness as measured by DSC and CD. A summary of these finding are illustrated in Figure 3. Figure 3a displays the relaxation map obtained from both DRS and AC-calorimetry, in which the characteristic relaxation time was determined as $\tau = 1/(2\pi f)$, where f is the frequency of the maximum of the imaginary part of the susceptibility, for PS films in the freestanding and Al-capped geometries. No discernible thickness dependence of the temperature-dependent relaxation time was observed within the temperature range probed for either geometry.

Figure 3b plots the T_g vs. film thickness for freestanding and Al-capped PS films. A thickness dependent T_g was observed for both geometries though the magnitude in deviations was greater for freestanding films. Here, we note that freestanding films represent the stacked film geometry. In order to obtain sensitivity of the measurement the stacking of films is required, as originally illustrated by Simon *et al.*[62] As detailed in refs.[58,62,63], stacked films behave similar to a single freestanding film, provided that very high molecular weight polymers are employed. In such a case, if the sample temperature is kept low enough to avoid promotion of chain dynamics polymer films do not interdiffuse and can be mechanically separated after measurement.

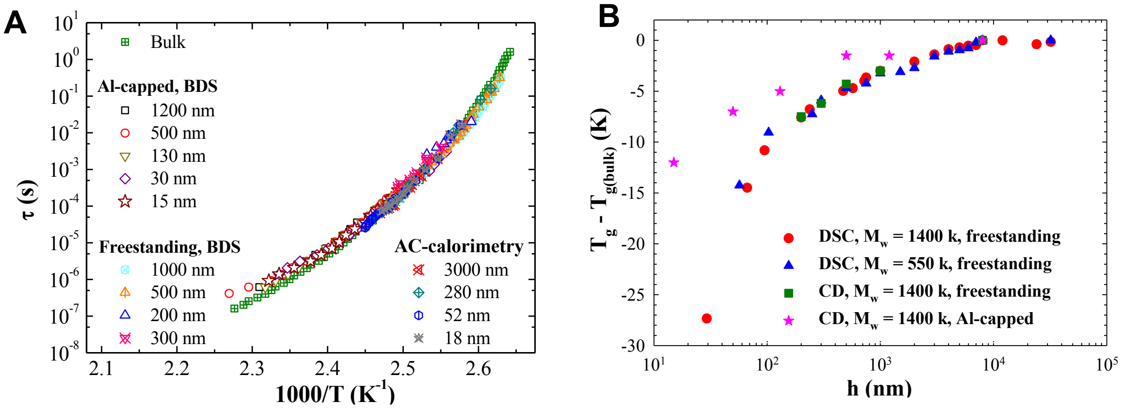

Figure 3: a) Temperature dependence of the characteristic relaxation time for thin films of PS measured by DRS and AC-calorimetry. b) Thickness dependence of the deviation in T_g for thin film PS measured by DSC and CD. Reprinted from Boucher *et al.*[58]

In a collaborative effort, Priestley and Cangialosi investigated the segmental dynamics and T_g of PS nanospheres using CD and DRS, respectively.[64] Here, a film of dried PS nanospheres was prepared between Au electrodes using a Teflon spacer. The films were dried under vacuum at room temperature to remove residual water. We note that the presence of void space within the film, which is due to nanosphere packing, only serves to reduce the effective dielectric strength of the film. *Via* CD, it was illustrated that films of PS nanospheres with diameters (d) less than 400 nm exhibited suppressions in T_g that increased with decreasing the confinement length scale. Remarkably, the size-dependent T_g of PS nanospheres as measured by CD was nearly identical to that revealed by calorimetry measurements.[19] While T_g was impacted by confinement, in the range 130 nm < d < 400 nm, in stark contrast, the cooperative segmental mobility, *i.e.*, the peak position of the α-relaxation process was not. These results are reprinted in Figure 4. They highlight that the observed decoupling between T_g and cooperative segmental mobility in not limited to the thin film geometry but is also observed in nanospheres. Interpretations of the decoupling were discussed in terms of techniques averaging over a gradient in dynamics in a different manner[27,55] or within the framework of equilibrium *vs*. non-equilibrium effects.[65] Both are discussed in more detail in the next session.

Finally, it is important to point out that complete decoupling between segmental dynamics and the thermodynamic measurement of T_g are not always experimentally observed. In the case of ultrathin PS films, changes in T_g with confinement have been reported in which changes of the segmental dynamics, *i.e.,* a shift in the α-relaxation peak temperature, and broadening of the distribution of relaxation times are observed, although not to the extend based on bulk rules. Recently, a more intimate coupling between T_g and segmental dynamics has been observed for PS thin films.[63] We note, this observation is made possible only if one extrapolates the relaxation times, via VFT fits, between five and six decades. Nevertheless, understanding the differences between these results and others remains a major challenge. One argument is that the extrapolation of high temperature dynamics to the measured value of T_g for confined systems is not valid; this should be investigated in the future. Another argument is that the source of such differences could be due to minute variances in sample preparation in which difference in chain conformations and residual stresses may manifest and alter confined polymer properties.

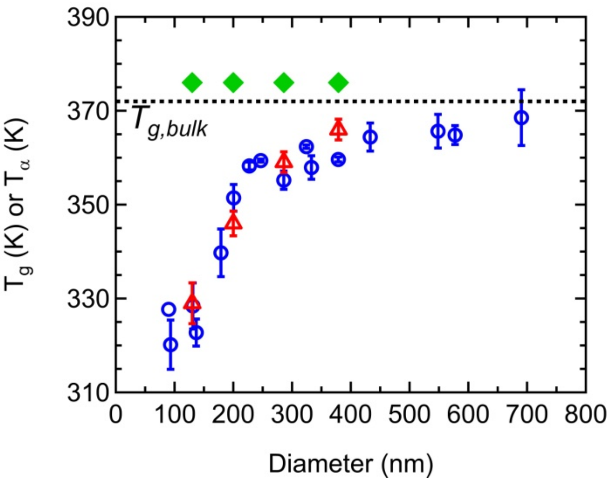

Figure 4:) Glass transition temperature versus PS nanosphere diameter measured by CD (red triangles; error bars represent repeated linear fittings of raw data) and MDSC (blue circles; error bars represent repeated measurements). The latter are taken from Zhang *et al.*[19] The dynamic glass transition temperature, T_α, taken as the temperature at which ε'' is maximum at 0.5 Hz, is also plotted as a function of nanosphere diameter (green diamonds). Reprinted from Zhang *et al.*[64]

Here, we introduce another exotic decoupling appearing as a peculiar behavior of polymers under confinement, where an unperturbed segmental motion is accompanied by a severe reduction in mass transport. Molecular diffusion is intrinsically bound to the viscosity of the environment via the Stokes-Einstein (SE) relation, fixing an equality between the energetic barrier for translational motion and that for rotational motion. This relation, valid for melts at equilibrium, usually breaks down upon supercooling in proximity of the glass transition. As a common feature of the glassy dynamics, diffusion is enhanced compared to the viscosity and the segmental relaxation.[66] At temperatures well above T_g, in fact, the translational and rotational motion of simple liquids are correlated via the SE relation, here written in the case of a solid sphere of radius a immersed in a fluid of viscosity η:

$$D_t = \frac{k_B T}{6\pi a \eta} \tag{2}$$

where D_t is the diffusion coefficient for translational motion. Similar forms of equation 2 can be written replacing D_t and η by the crystallization time in the regime of cold crystallization ($\sim D_t^{-1}$), t ($\sim \eta$) or the charge conductivity ($\sim D_t$). Large experimental evidence have shown that such a simple relation does not hold in proximity of T_g, where equation 2 is replaced by a fractional form of the type

$$D_t \left(\eta/T\right)^{\xi} = const \tag{3}$$

with ξ the fractional SE coefficient, falling in the interval (0.5, 1.0). The molecular mechanism yielding to condition $\xi < 1$ is still under debate[67,68]

Extensive investigation of the impact of confinement on water confirmed the typical scenario observed in bulk liquids.[69] On the contrary, thin polymer films revealed an unusual deviation from bulk behavior. In the proximity of adsorbing interfaces, polymers under 1D confinement show a severe reduction in transport properties coupled to an invariant segmental mobility, leading to the exotic condition $\xi >> 1$. Here, we list recent experimental evidence supporting the anomalous breakdown of the SE relation at the nanoscale. *Crystallization experiments:* Vanroy *et al.* reported an increase in the crystallization time of ultrathin films of poly(ethylene terephthalate), PET, capped between aluminum layers,[70] not justified by a comparable increase in τ. A similar trend was found for poly(L-lactide acid)[71] and poly(hydroxy butyrate).[72] *Confinement effect on the $\alpha-$relaxation and the normal mode:* investigation by BDS of thin layers of poly(cis-1,4-isoprene) revealed that the segmental dynamics is unaffected by film thickness, while the normal mode (diffusion) is strongly reduced in the thinner films.[73]

Molecular motion in irreversibly adsorbed layers: the segmental time of irreversibly adsorbed layers of PS assume bulk values,[27] while the diffusion of gold markers into similar films is reduced by several orders of magnitude.[74] *Tracer diffusivity experiments:* the diffusion of small molecules (tracer diffusion) dispersed into thin supported films of PS is heavily reduced in comparison to thicker films, up to distances exceeding by 10 times the macromolecular size,[75] while τ shows minor reductions upon confinement. Remarkably, the shift in T_g corresponding to the reduction in tracer diffusion followed the same thickness dependence of the T_g obtained via CD; see Figure 5. In the case of freestanding films, a tremendous acceleration in the segmental dynamics[76] is accompanied by the lack of thickness dependence in the tracer diffusion coefficient, at least down to 20 nm.[77]

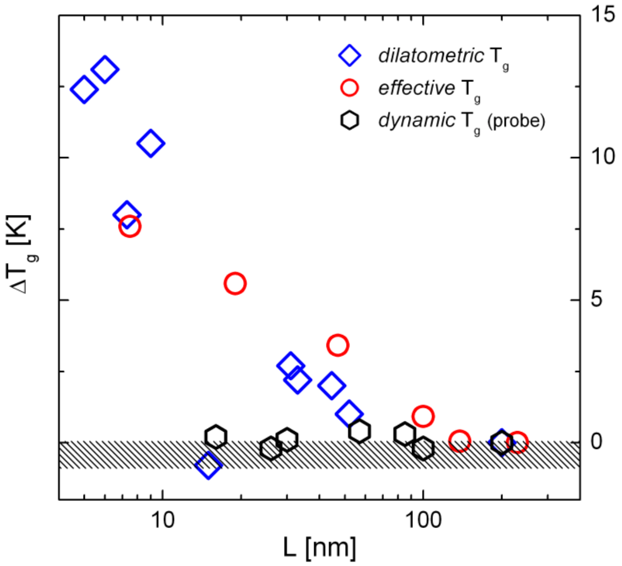

Figure 5: Comparison between the increase in "effective" T_g of the PS (matrix) related to the shift in the glass transition temperature necessary to justify the observed reduction in tracer diffusivity, T_g obtained by CD for single layers of PS160 capped between aluminum electrodes[78] and the "dynamic" T_g of single layers of l-PS (probe) as deduced by the temperature dependence of the segmental mobility. The formal procedure to obtain the effective T_g is provided in ref.[79] The shadow area indicates the variation in the "dynamic" T_g of ultrathin films of PS of different molecular weight[80] Errors are smaller than the symbol. Reproduced from Napolitano et al.[79] with permission from Wiley-VCH.

IV. Discussion of Observed Decoupling

The previous section demonstrated that the out-of-equilibrium dynamics in terms of T_g variations in confinement couldn't be exclusively described based on a modification of the molecular mobility. Recently, Ediger and Forrest elaborated on one interpretation for the decoupling between T_g and segmental dynamics in thin films in the following manner.[13] There is a region near the free surface of thin films with enhanced segmental mobility. The thickness of the mobile layer, which is thought to range from 1-10 nm, increases upon heating toward T_g. The temperature dependence of the mobile layer segmental dynamics is weaker than the bulk below T_g but merge at high temperature. The state-of-affairs suggest a highly temperature dependent confinement (interface) effect. That is, the length scale at which the free surface perturbs dynamics is small above bulk T_g. Cangialosi and Priestley also recently expressed a similar interpretation.[64] They noted that T_g has been found to be independent of size when measured at high heating/cooling rates[81]; therefore under certain experimental conditions, no decoupling between segmental mobility and T_g for confined polymer is observed. We stated: "*One could rationalize this effect by utilizing the temperature dependence of the length-scale of cooperative segmental mobility. The use of a high heating/cooling rate to measure T_g would probe a smaller length-scale of mobility that would be less cooperative. Such suppression in cooperative segmental mobility could suppress the impact of interfaces and confinement on the measured value of T_g.*" Yet, as noted by Ediger and Forrest this interpretation has some shortcomings that should be addressed in the future.

Other qualitative explanations for the decoupling between segmental mobility and T_g have been put forth. For instance, the decoupling has been explained in terms of the ability of different techniques to distinguish specific relaxation processes within confined polymer.[27,55,82] In this framework, dynamic measurements (*e.g.*, DRS) and pseudo-thermodynamic measurements (*e.g.*, CD) average over a mobility gradient away from an interface differently. However, it should be mentioned that in the temperature range in which both enhanced and bulk-like dynamics are observed, one generally does not find the signature of two T_gs, *i.e.,* one each representing enhanced and bulk-like dynamics, respectively. Within the context of the well-documented two-layer model this would be expected.

Another possible explanation, and the one we discuss in more detail, is that the decoupling originates from the conceptual difference between the time scale of equilibration τ_{eq} that is that relevant for T_g and the time scale of spontaneous fluctuations τ_{mol}. This has been discussed in detail in Section II. It has been evidenced how, for bulk glass-former, $\tau_{eq} \sim \tau_{mol}$. Our current knowledge on the dynamics of glass formers in confinement indicates that in this case the proportionality between τ_{eq} and τ_{mol} cannot be considered ~~unity~~. In other words, geometric aspects, that is the confinement length scale h, play a major role in determining the time scale of equilibration. This can be quantitatively expressed as: $\tau_{\mathrm{eq}} \sim g(h)\tau_{\mathrm{mol}}$; where $g(h)$ is a function depending of the confinement length scale. Therefore, theoretical activity aiming to understand glassy dynamics in confinement should seek for the physics behind the function $g(h)$.

From theoretical approaches recently developed to explain the glass transition in confined polymers, it is worth of remark that models based on percolation arguments[83,84], that is, purely geometric arguments, are in principle adequate to describe alteration of the out-of-equilibrium dynamics. Recently, Wool and co-workers showed that the twinkling fractal theory (TFT) predicts a confinement effect on T_g in the absence of a size-dependence on segmental mobility.[85,86] This is due to the fact that such relaxation occurs at length scale of the order the monomer size. However, according to the model, the relaxation time relevant for the T_{g} and the recovery of equilibrium in the aging regime involves percolating clusters with sizes up to 100 nm.[85] The model provides a rationale for why effects on the out-of-equilibrium dynamics are seen for typical length scales at which no modifications of the rate of spontaneous fluctuations exists.

Among the theoretical approaches able to catch the phenomenology of glassy dynamics in confinement, the free volume holes diffusion (FVHD) model represents a good candidate.[87] According to it, when a glass-former is perturbed beyond the linear regime, the thermodynamic equilibrium is recovered via diffusion of free volume holes through the sample free interface. This implies that, according to this model, the T_{g} of a glass former is the temperature at which free volume holes are not able to diffuse out of the sample free interface in the experimental time scale of the experiment (e.g., the cooling rate). Once in the physical aging regime, a glass recovers equilibrium according to the same mechanism. From a qualitative point of view, it is easily realized that a glass with short confinement length scale is able to maintain equilibrium efficiently and, therefore, exhibits reduced T_{g} and faster achievement of equilibrium in the physical aging regime.

The FVHD model was first proposed in the early 1980 by Simha and co-workers.[87] In its original version, it did not receive much attention due to the fact that it required the presence of an "internal length scale" to account for the absence of size dependent rates of physical aging for macroscopic samples. The FVHD model was later revitalized[60,88] after the observation of accelerated physical aging in nanostructured glasses with typical confinement length scale of the order of or shorter than several microns.[59,61] The basic equations to apply the FVHD model are: i) Fick's second diffusion expression:

$$\frac{\partial f_v(r,t)}{\partial t} = \nabla(D\nabla f_v(r,t)) \tag{4}$$

and ii) an equation expressing the mean square displacement (MSD) ($<x^2>$) as a function of time for one-dimensional linear diffusion:

$$\langle x^2 \rangle = 2Dt \tag{5}$$

where f_{v} is the fractional free volume and D is the diffusion coefficient of free volume holes. Equation 4 can be employed to describe the spatio-temporal evolution of the free volume during physical aging. For moderate variations of thermodynamic properties, that is, in the vast majority of cases of typical equilibrium recovery experiments, proportionality between the variation of f_{v} and that of thermodynamic properties such as the enthalpy can be established.[89] Employing equation 5, a description of the T_{g} can be performed. The reason is that, according to the FVHD model, the glass transition occurs when $<x^2>$ in the experimental time scale, $t = q^{-1}$ in typical experiments aiming to determine the T_{g}, is of the order of the confinement length scale, that is, when $h^2 \sim 2\mathrm{D}q^{-1}$ where h is the film thickness.

In freestanding thin polymer films, where the entire interface is available for diffusing out free volume holes, the confinement length scale corresponds to the film thickness.[61,90] Figure 6 shows a test of the FHVD model to describe the T_{g} depression of freestanding thin PS films.[61] As can be observed, the model is able to catch the overall phenomenology of the out-of-equilibrium dynamics with a thickness-dependent diffusion coefficient, that is, with no need to invoke any change in the polymer segmental dynamics in confinement.

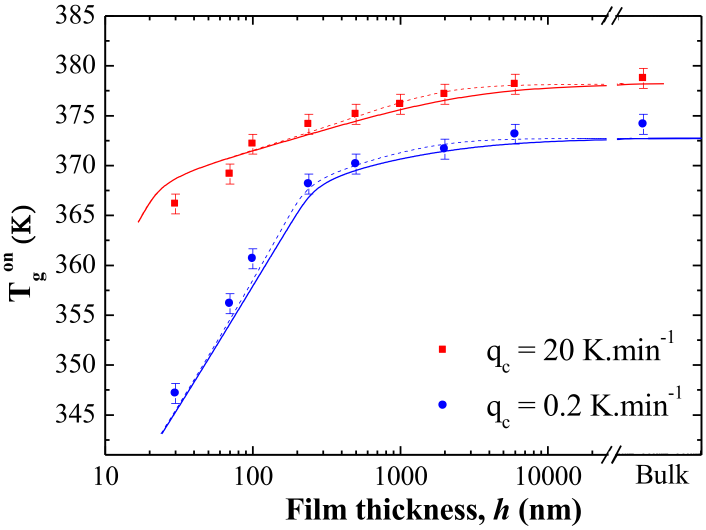

Figure 6: T_g as a function of film thickness and applied cooling rate (q) for freestanding thin PS films. Continuous and dashed lines are the fits of the FVHD model to the experimental data (solid squares) via two different approaches. Reprinted from Boucher et al.[61]

The FHVD can be also applied to supported thin polymer films[59,91] or, in general, a range of confinement conditions where a solid interface exists between the glass former and the external environment. However, in this case, the portion of polymer adsorbed on the solid surface represents an infinitely high potential energy barrier to be overcome by free volume holes.[91] Therefore, only part of the interface, that is, the free interface, will be available to free volume holes diffusion. Once the total interface is replaced by the free interface, the model can be successfully applied. Finally, the impressive agreement between dilatometric T_g and the effective T_g, presented in Fig. 5, related to the change in dynamics necessary to justify the reduction in tracer diffusion, hints at an intimate correlation between the two quantities. Future work should address the extension of the FVHD model to this type of experiments.

An alternative, yet related explanation for the decoupling in molecular dynamics is related to the different impact of irreverisble chain adsorption on the molecular mechanisms responsible for segmental mobility and diffusion. The reduction in translation motion is, in fact, active only if supported interfaces are present, we can relate the molecular origin of the reduction in mass transport properties to the presence of adsorbed layers. We propose that this anomalous decoupling could be related to the content and distribution of free volume in proximity of free surfaces[76] and adsorbing interfaces[92]. Recent experimental evidence and theoretical models support, in fact, the idea that the deviation from bulk behavior are strictly connected to the local content in free volume. Under this framework, a reduction in T_g should be related to an increase in packing frustration[91], *e.g.,* as in the first stages of adsorption, and the consequent larger free volume content compared to the bulk[93]. This hypothesis is in line with recent simulations by Tito *et al.* showing that the glassy dynamics is affected by the propagation of colonies of free volume.[94,95]

Cangialosi and coworkers[60,61,65,91,96] proposed that, by means of the ~~free volume holes diffusion~~ model, that the shift in T_g of thin films and polymer-based nanocomposites is correlated to the effective surface available for diffusion of free volume holes. Similarly, we can imagine that the reduction in tracer diffusion is related to a different distribution of free volume holes, not permitting their diffusion as efficiently as in bulk. Such a condition could be, for example, achieved via a discontinuity in packing density. Thin adsorbed layers are, in fact, characterized by non-equilibrium chain conformations with a bimodal energy landscape.[97] In the early stage of adsorption, chains pin onto the substrate with a large number of monomers/macromolecule, which induces the formation of a depletion zone rich in free volume. Adsorption of further chains is possible only upon reduction of the excess in free volume, and pinning with a smaller number of contact/molecule. Such a heterogeneous morphology provides a distribution of chain conformations severely different than that of bulk melts at thermodynamic equilibrium, and consequently to a new interplay between structure and dynamics.

VI. Conclusions

This perspectives article has focused on emphasizing the correlation or lack thereof between the thermodynamic and dynamic measurements of the glass transition temperature of confined polymers. Specifically, we highlighted past and recent literature contributions that undertook investigations in which simultaneous measurements of the thermodynamic and dynamic T_g where obtained. The results illustrate either a less-than-expected or lack of positive correlation between the size-dependence of T_g as measured by calorimetric means and cooperative segmental mobility, as measured by T_α for amorphous polymers. That is, under identical experimental conditions while the value of T_g has dramatically deviated from the bulk, the cooperative segmental dynamics are unchanged. Clearly, the relationship between the two measurements of the glass transition does not conform to bulk rules and suggest a more complicated non-trivial relationship. We highlighted several phenomenological and theoretical models aimed at rationalizing this confined induced decoupling between the calorimetric and dynamic measurements of T_g. In addition, we discussed the anomalous decoupling between rotational and translational motion taking place in proximity of adsorbing interface, where a tremendous reduction in transport properties (*e.g.,* crystallization growth, tracer diffusion) can occur at constant structural relaxation time. We proposed an explanation for this intriguing phenomenon, focusing on the specific impact of the irreversibly adsorbed layers on the molecular dynamics at different time and lengthscales. Finally, we suggest that future work should aim at localized interfacial measurements of the thermodynamic and dynamic properties. The role of processing on the decoupling phenomenon should also be examined. In this way, we gain an understanding for the significance that processing contributes to property modifications, *i.e.*, the connection between processing and interfacial properties. Theoretical efforts should also accompany new experiments to understanding the physics behind this decoupling in T_g measurements in confinement.

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