# On the equivalence between the thermodynamic and dynamic measurements of the glass transition in confined polymers

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### ABSTRACT

Understanding why the glass transition temperature ($T_g$) of polymers deviates substantially from 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 necessitates 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 findings 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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## 1. 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, among 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 films [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 the 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 Fig. 1 [26]. For 10 nm thick films supported on a silica substrate, $\Delta T_g$ is ~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

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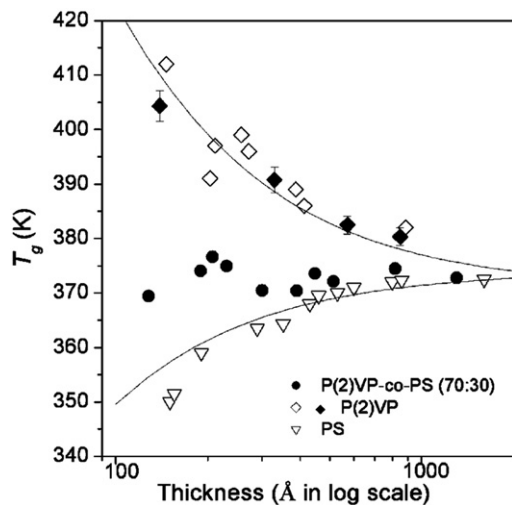
**Fig. 1.** Change in $T_g$ with nanoscale confinement for PS, P2VP, and P2VP–PS copolymer. Reprinted from Park et al. [26].

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.

As it sets the practical use temperature of amorphous polymers, characterizing and understanding $T_g$ of confined polymers are immensely important. The descriptive understanding of the glass transition, in bulk, suggests that a 10-degree change in $T_g$ would be accompanied by an ~1000-fold change in molecular mobility [32]. Thus, it seems intuitive to expect that a change in $T_g$ due to confinement necessitates 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 *dynamics* $T_g$ as one assigned *via* the measurement 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.

## 2. The glass transition: brief phenomenological description

### 2.1. 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 ($\tau$) of the associated thermal fluctuations enter a regime with considerably more pronounced temperature variations. $\tau$ may vary within a relatively small temperature interval by many orders of magnitude. Hence supercooled liquids exhibit highly non-Arrhenius temperature dependence of $\tau$ as shown schematically in Fig. 2B. The temperature dependence of $\tau$ 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 $\tau_0$, $B$ and $T_0$ are the pre-exponential factor, Vogel activation energy and Vogel temperature, respectively. The VFT equation insinuates divergence of $\tau$ at $T_0$. However, this is never observed in experiments. This is due to the fact that, at temperatures not too far from $T_m$, $\tau$ 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
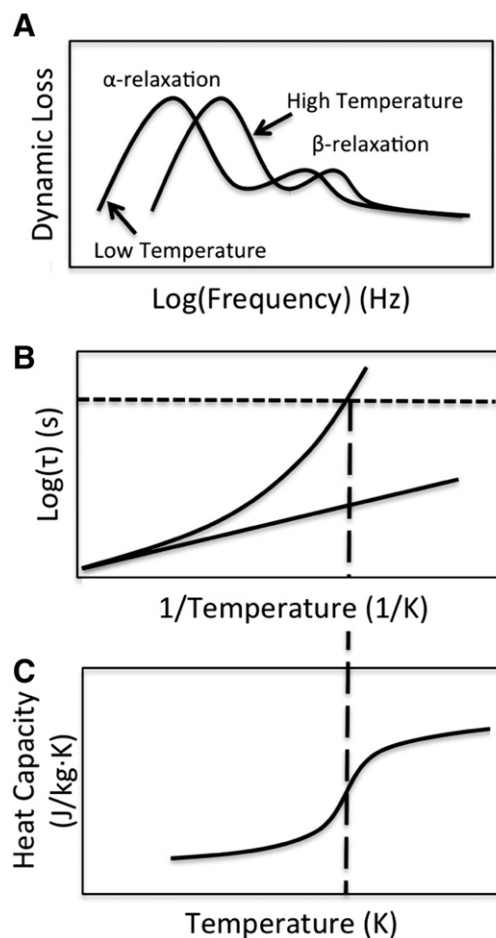


**Fig. 2.** A) Dispersion map of relaxation processes for a general glass former at two temperatures. B) Temperature dependence of the relaxation time of the primary and secondary process in a typical glass former. C) Temperature dependence of heat capacity of a glass former near the glass transition.