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ABSTRACT

We perform coarse-grained simulations of model unentangled polymer materials to quantify the range over which interfaces alter the structure and dynamics in the vicinity of the interface. We study the interfacial zone around nanoparticles (NPs) in model polymer-NP composites with variable NP diameter, as well as the interfacial zone at the solid substrate and free surface of thin supported polymer films. These interfaces alter both the segmental packing and mobility in an interfacial zone. Variable NP size allows us to gain insight into the effect of boundary curvature, where the film is the limit of zero curvature. We find that the scale for perturbations of the density is relatively small and decreases on cooling for all cases. In other words, the interfaces become more sharply defined on cooling, as naively expected. In contrast, the interfacial mobility scale ξ for both NPs and supported films increases on cooling and is on the order of a few nanometers, regardless of the polymer-interfacial interaction strength. Additionally, the dynamical interfacial scale of the film substrate is consistent with a limiting value for polymer-NP composites as the NP size grows. These findings are based on a simple quantitative model to describe the distance dependence of relaxation that should be applicable to many interfacial polymer materials.

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I. INTRODUCTION

The dynamics of both glass-forming^{1,2} and crystalline materials³⁻⁶ are generally modified by boundaries. Recently, there has been much interest in quantifying the spatial extent over which the interfacial dynamics of materials is perturbed and the factors that influence the dynamics within this interfacial zone.^{1,3-6} The presence of interfacial layers are thought to be especially important in many applications of thin glass-forming polymer films⁷⁻⁹ and nanocomposites^{10,11} and also in the interfacial dynamics of crystalline nanoparticles (NPs)¹² and the grain boundaries of polycrystalline materials.¹³ Here, we focus on the polymer matrix interfacial zones at the interfaces of polymer films and near the surface of nanoparticles without grafted polymer layers. This is a topic of intense experimental investigation because of the relevance of this layer for understanding apparent deviations from the continuum composite theory. From a practical standpoint, these data are useful for controlling property changes in polymer materials through such additives.^{8,9} There are often "multiple" interfacial zones to consider in thin polymer films and nanocomposites (e.g., particle interfacial zone, polymer interfacial zone, and often the interfacial zone of a grafted polymer layer separating the nanoparticle from the surrounding polymer matrix).^{14–18}

Sokolov and co-workers¹⁴⁻¹⁸ have made particularly notable contributions to this problem through their measurement of the spatial extent of the interfacial zone and the change of mobility and other properties within this region of perturbed dynamics based on multiple measurement methods (X-ray scattering, differential scanning calorimetry, broadband dielectric spectroscopy, Brillouin light scattering, and atomic force microscopy).^{14–18} These measurements have indicated that the typical scale of the polymer interfacial region surrounding the nanoparticle is on the order of a few nanometers, and recent measurements further show that this interfacial scale grows slowly upon cooling.¹⁸ While many of their measurements only indirectly measure the interfacial zone width based on models (e.g., layer models in which an interfacial layer around the NP is assumed to have different properties than the glass-forming matrix in which the NP is embedded), Sokolov and co-workers have been able to directly image¹⁷ the interfacial zone in real space by atomic force microscopy and obtained consistent results with the other measurements, providing further support for the model-based interpretations. We thus view some of the essential features of the interfacial zone to be established from an experimental standpoint. However, the problem remains of understanding the factors that control the width of this interfacial zone from a fundamental molecular physics perspective. Molecular simulations offer a means to obtain information complementary to the experiments, facilitating progress on this fundamental problem.

We characterize the dynamical interfacial scale ξ of NPs for a range of NP sizes and thin polymer films, under conditions of both strong and weak interfacial interactions. In doing so, we also quantify the interfacial density scale ξ_{ρ} , which exhibits a rather different temperature dependence from that of the dynamical interfacial scale ξ . These results provide a framework that may potentially be useful to relate interfacial scales to the scales of cooperative rearrangements within the polymer materials.

II. MODELING AND SIMULATIONS

The primary data we analyze come from previous simulations of model polymer nanocomposites¹⁹⁻²² and thin supported polymer films.²³ ²⁶ In our previous work on nanocomposites, we considered an idealized dispersion of NP in the polymer at a concentration corresponding to the dilute limit. These low NP concentrations allow us to study the interfacial zone in the absence of interaction effects between NP. We briefly summarize the key elements of the model, and complete details can be found in the original works.¹⁹⁻²² Polymer chains in the polymer-NP composites are represented by the well-studied Kremer-Grest spring-bead model.²⁷ The chains have N = 20 monomers, which interact via the Lennard-Jones (LJ) potential with strength ε , mass *m*, diameter σ , and a cutoff of interactions beyond $r_c = 2.5 \sigma$; bonded monomers are connected by a finitely extensive nonlinear elastic (FENE) potential with a bond strength $k_{\rm b} = 30 \ \epsilon / \sigma^2$ and bond length $R_0 = 1.5 \ \sigma$. The NPs are modeled by LJ particles arranged in icosahedral shells. The NP is modeled as a collection of beads (identical to the monomers of the polymers) linked together to form an icosahedron. We study three different NP sizes, consisting of 12, 104, or 356 beads, which corresponds to an inscribing sphere with radius 1.6 σ , 3.3 σ , or 5.0 σ , respectively. The LJ size parameter between monomers and NP is $\sigma_{p-NP} = 1.0$, and the LJ attraction strengths are $\varepsilon_{p-NP} = 0.1$ for weak interactions and $\varepsilon_{p-NP} = 1.5$ for strong interactions. All simulations are performed at constant averaged pressure $\langle P \rangle = 0.1$ over a temperature range $0.42 \le T \le 0.80$.

We also analyze data from simulations of polymer films supported by a solid attractive substrate, where the upper interface is free, corresponding to pressure P = 0; thus, the pressure in both composite and film is small. We briefly describe the model details, and a complete description of parameters and simulation protocols are provided in the original work.^{23–25} The polymer chains have 10 beads per chain-half that of the composite-although in a prior study (Fig. S4 in the supplementary material of Ref. 24), we demonstrated that the structural and dynamic properties of polymer segments for chain length 10 and 20 are essentially the same. We use a harmonic spring potential $U_{\text{bond}} = \frac{k_{\text{chain}}}{2} (r - r_0)^2$ to connect nearestneighbor monomers within a polymer chain using the equilibrium bond length $r_0 = 0.9$ and the spring constant $k_{chain} = 1111.^{28}$ The polymer films have 600 polymer chains, resulting in a film thickness $h \approx 15 \sigma$ with dimensions 20 σ in directions parallel to the substrate, where periodic boundary conditions are employed. The substrate is modeled as 528 particles arranged in a triangular lattice (the 111 face of an fcc crystal). These particles are tethered to their equilibrium (zero force) locations via a harmonic spring potential $V_{sub}(r)$ $= (k/2)(r - r_0)^2$, where r_0 is the equilibrium position and k = 50 is the spring constant. We use Lennard-Jones (LJ) interactions between nonbonded monomers and substrate particles. Here, we examine interaction strengths $\varepsilon_{ps} = 0.1$ (weakly attractive interaction) and $\varepsilon_{ps} = 1.5$ (strongly attractive interaction) between monomers and substrate particles. Another way to characterize the range of interfacial interaction strength is that our weakly attractive interfacial interaction strength is a tenth of that of the polymer-polymer interaction strength, while the strongly attractive interfacial interaction strength is 1.5 times that of the polymer-polymer interaction strength.

For both composites and films, we present results in standard LJ reduced units, where ε is the unit of energy, σ is the unit of length, *m* is the unit of mass, $\sigma \sqrt{m/\epsilon}$ is the unit of time, and $\epsilon/k_{\rm B}$ is the unit of temperature (where $k_{\rm B}$ is Boltzmann's constant). To approximately translate to real units, we use $\sigma = 1.0$ nm, the average Kuhn segment length for linear polystyrene (PS), and $\varepsilon = 7.7$ kJ/mol, which leads to $T_{\rm g} \approx 370$ K, so we may loosely view our polymer model as a coarse-grained representation of unentangled PS.^{29,30} Consequentially, the interfacial (polymer-NP and polymer-substrate) interaction strengths in our model map to 0.77 and 11.55 kJ/mol for the weakly and strongly attractive interfaces, respectively. These interaction strengths are within the range shown in Ref. 31, where these authors explored the effects of polymer-NP interaction strength ε on mechanical properties of representative nanocomposites. Additionally, our strongly attractive interface corresponds to an atomically smooth interface having an adhesion energy about 100 mJ/m².³

To quantify the segmental dynamics of the nanocomposites and thin polymer films, we utilize the self-intermediate scattering function,

$$F_{\text{self}}(q,t) \equiv \frac{1}{N} \left\{ \sum_{j=1}^{N} e^{-iq \cdot \left[r_j(t) - r_j(0) \right]} \right\},\tag{1}$$

where r_j is the position of monomer j and q is the scattering vector. We define the characteristic segmental relaxation time τ_{α} by $F_{\text{self}}(q_0, \tau_{\alpha}) = e^{-1}$, where q_0 is defined by the position of the first peak in the structure factor S(q). To quantify the spatial dependence of the nanocomposite dynamics, we compute F_{self} within thin "shells" having a thickness less than a monomer diameter as a function of distance from the NP surface (for composites) or the substrate (for films). We sort monomers into layers based on their location at the time origin, although we could equally well sort them based on their position at time $t = \tau$, since monomers move (on average) less than a monomer diameter on the scale of the relaxation time.³³

III. RESULTS

A. Qualitative effect of interfacial interactions on mobility interfacial zone

Before we quantify the scale of the interfacial zone, we present a qualitative description of the perturbation of the dynamics approaching the interface of the NP or film interfaces. To visualize the phenomenon, Fig. 1 shows a color map of how the segmental relaxation time of the polymer $\tau_{\alpha}(r)$ is perturbed from its value far from the NP interface, Fig. 1(a) shows the strongly attractive interfacial interaction case (where τ_{α} increases near the surface), and Fig. 1(b) shows the weakly attractive case, where τ_{α} is reduced near the surface. We see that τ_{α} changes by a factor of approximately 10-500 approaching the NP interface at the lowest T simulated temperature, i.e., T = 0.42. This factor can become much larger at lower temperature or when the polymer-NP interaction strength becomes larger, leading to significant "bound polymer" effects.³⁴ This effect arises due to a separation of time scales for the binding-unbinding transition of the polymer matrix from the interface.^{21,2} It is visually apparent that the width of the interfacial zone extends over several monomer diameters (σ), which maps to the scale of a few nanometers in laboratory units. This is in qualitative accord with recent measurements on the interfacial zone of well dispersed NPs having an attractive interaction with the matrix to aid in their dispersal. $^{14-18,36-38}$ Our simulation findings thus seem reasonable from a qualitative standpoint.

Importantly, the interfacial scale governing the density variations (ξ_{ρ}) near a surface is generally quite different from the interfacial mobility scale $\xi^{2,20,24}$ We next discuss the interfacial density scale ξ_{ρ} in some detail as we utilize this quantity in the characterization of the interfacial mobility scale ξ . We then quantify ξ as a function of T and the interaction strength between the NP or substrate and the polymer matrix ε in order to better understand the nature of the mobility interfacial zone from a molecular perspective.

B. Variation of interfacial density scale ξ_{ρ} with T and ε

To quantify the interfacial density scale, we start by presenting the density profile for both the polymer-NP composite and the supported film in Fig. 2. The density profiles are locally averaged over the width of a monomer diameter to smooth the packing fluctuations. In all cases, the density reaches a well-defined mean value ρ_{mid} far from the interfaces. We define the interfacial density scale ξ_{ρ} as the length from the interface at which the density reaches within 5% of the density in the steady region, starting from the interface (NP surface, substrate, or free surface). The starting position of the substrate or free surface is defined by the position at which $\rho = 0.05$; and the starting position of the NP surface is at the radius of sphere inscribing the NP, r_{inscribe} . We show the variation of ξ_{ρ} for both model NPs and polymer films for strongly attractive [Fig. 3(a)] and weakly attractive [Fig. 3(b)] interfacial interactions. We find that the boundary interaction has a significant influence on ξ_{ρ} . The interfacial scale ξ_{ρ} is much larger in the case when the interfacial interactions are weak than in the case of the strongly attractive interface; this is sensible since the strongly interacting interface should create a more precisely defined interfacial layer. ξ_{ρ} also exhibits a much stronger T variation for the weakly attractive interface. Specifically, ξ_{ρ} grows on heating in the case of weakly attractive interfacial



FIG. 1. Schematic color map of the ratio $\tau_{\alpha}(r)/\tau_{\text{far}}$ at T = 0.42 for polymer relaxation near the NP surface. A strongly attractive polymer-NP interaction (a) slows down the interfacial dynamics, while a weakly attractive interaction (b) accelerates the rate of relaxation in the interfacial region. The blue color represents $\tau_{\alpha}(r) < \tau_{\text{far}}$. The diameter of the model nanoparticle is about 10 nm in laboratory units based on a unit transformation appropriate for polystyrene.



FIG. 2. The density profile $\rho(r)$ for (a) NPs and $\rho(z)$ for (b) thin films. In panel (b), we illustrate the definition of the interfacial density scale ξ_{ρ} of thin polymer film supported by the substrate with weak substrate-polymer interaction strength $\varepsilon = 0.1$ (black) and strong substrate-polymer interaction strength $\varepsilon = 1.5$ (red) at T = 0.45. See the main text for the definition of ξ_{ρ} .



FIG. 3. The interfacial density scale ξ_{ρ} for polymer-NP and polymer-substrate interfaces having either (a) strong or (b) weak attractive interactions and (c) the free polymer-air interface. ξ_{ρ} of strongly attractive interfaces in the thin film and NP composite increases only slightly with increasing *T*. In contrast, ξ_{ρ} for the weakly attractive interfaces (or free surface) increases much more significantly with increasing *T*. The solid lines are guides for the eve.

interaction for both the polymer films and polymer-NP composites. Additionally, the interfacial density scale ξ_{ρ} increases with decreasing curvature of the interface (increasing NP size) for the weakly attractive interfaces since the flat substrate is equivalent to zero curvature. However, ξ_{ρ} for the strongly attractive interfaces exhibits nonmonotonic variation with the surface curvature, consistent with the density in the hydration shell of proteins.³⁹

C. Quantification of the mobility interfacial scale ξ

Having quantified the scale of perturbations of density near the interfaces, we will use those data to aid in our quantification of the length scale ξ describing the range of altered dynamics near the interface. First, Fig. 4 presents our polymer-NP data for the distance dependence of $\tau_{\alpha}(r)/\tau_{\text{far}}$ as a function of distance r from the particle surface for strong and weak ε values. The interfacial relaxation is much larger or smaller near the NP, depending on the strength of the NP-polymer interactions as has been documented in many earlier works.^{19,21,34,40} The interfacial changes increase substantially upon cooling; note the log scale of the relaxation time ratio, $\tau_{\alpha}(r)/\tau_{\text{far}}$. Similarly, Fig. 5 presents the distance *z* dependence of $\tau_{\alpha}(z)$ for supported polymer films on substrates having strongly attractive or weakly attractive substrate interaction strengths. As in the case of the NP interfacial zone, the relaxation slows down sharply near the strongly attractive substrate and becomes faster near the weakly attractive interface. For both strong and weak substrate interactions, supported films exhibit an enhanced rate of relaxation near the free interface. Accordingly, our methodology to estimate ξ must consider both interfacial regions and their interactions.

To quantitatively extract the dynamical scale, we look to earlier simulation studies for inspiration. These works were motivated by the possibility of identifying a well-defined growing length scale in cooled glass-forming liquids. Consistent with this goal, Scheidler, Kob, and Binder⁴¹ observed a mobility gradient qualitatively similar to Fig. 5(a) near the "free" interface of a model Lennard-Jones glass-forming film, which they quantified by fitting log(τ_{α}) to an exponential function with a decay length ξ describing the interfacial width. Numerous authors subsequently followed this method for



FIG. 4. $\tau_{\alpha}(r)/\tau_{far}$ as a function of *r* from the nanoparticle center; relaxation time is evaluated starting from $\approx 5 \sigma$ from the center of the NP. (a) $\tau_{\alpha}(r)/\tau_{far}$ for strongly attractive NP-polymer interaction. (b) $\tau_{\alpha}(r)/\tau_{far}$ for weakly attractive NP-polymer interaction. We include two representative fits (solid lines) from Eq. (2) in each panel for the lowest and highest temperatures. The color gradient represents the gradient in *T*, ranging from blue at low *T* to red at high *T*. The inset pictures illustrate the dynamical interfacial zone around the NP; the shade of blue represents particles with increased relaxation time (suppressed mobility), while the red color represents particles with diminished relaxation time (enhanced mobility).

estimating the interfacial mobility scale,^{2,42} where evidence correlating this length scale to the apparent temperature dependent activation energy for the film structural relaxation time⁴³ and the extent of cooperative exchange motion with the film,² seemingly confirming the intuition that the mobility interfacial scale might have some relation to the scale of "dynamic heterogeneity" within the film. An issue with the approach of Scheidler et al. is that, for the supported films, the proximity of the substrate and free interface can potentially cause interference between ξ estimated from the substrate or free surface. Accordingly, it is useful to consider a method that simultaneously incorporates both interfaces. In addition, we should also incorporate the scale of density modifications in the formulation so that our estimate of ξ takes into account the structural length scale. Indeed, there is evidence that the mobility interfacial layer correlates with the scale ξ_{ρ} in simulations of proteins in water around room temperature, 39,44,45 suggesting that this scale is somehow related to $\xi,$ even if these quantities are not exactly equal.

Here, we introduce a new functional description to determine ξ that addresses these concerns. We first consider a model for the interfacial mobility near the surface of an isolated NP (or a thick polymer film) and then generalize to systems having multiple interfaces. It is natural to postulate a hyperbolic tangent functional form for the mobility profile, by analogy with the known density profile at the polymer-air interface,³⁵ where the distance from the interface is taken with respect to a reference scale that includes a contribution from the density scale ξ_{ρ} . Specifically, we model our mobility gradient for a NP by

$$\ln \frac{\tau_{\alpha}(r)}{\tau_{\rm far}} = \tau_0 \left[\tanh \left[\frac{r - (r_{\rm NP} + \xi_{\rho})}{\xi} \right] - 1 \right], \tag{2}$$

where $r_{\text{NP}} = a \frac{\sqrt{3}}{12} (3 + \sqrt{5})$ is the radius of a sphere inscribing the icosahedral NP having an edge length *a*. We adapt the same form for the mobility profile near a solid substrate where the distance from



FIG. 5. The relaxation profile $\tau(z)$ for thin polymer films with (a) a strongly attractive substrate-polymer interaction strength ε = 1.5 and (b) weakly attractive substrate-polymer interaction strength ε = 0.1. We include two representative fits (solid lines) from Eq. (3) in each panel for the lowest and highest temperature. The color gradient represents the gradient in *T*, ranging from blue at low *T* to red at high *T*. The inset pictures illustrate the dynamical interfacial zone near the solid substrate and free surface; the shade of blue represents particles with increased relaxation time, while the red color represents particles with reduced relaxation time.

the planar interface *z* replaces *r* in Eq. (2) and where $r_{\text{NP}} = 0$. We fit the layered resolved relaxation time $\tau_{\alpha}(r)$ using Eq. (2) with the explicit value of ξ_{ρ} to obtain the dynamical interfacial scale ξ . We treat the more complex situation of a thin film where the interfaces interact (as in Fig. 5) using the generalized relation for $\tau_{\alpha}(z)$,

$$\ln \tau_{\alpha}(z) = \ln(\tau_0) - c_1 \tanh\left[\frac{z - \xi_{\rho, \text{sub}}}{\xi_{\text{sub}}}\right] - c_2 \tanh\left[\frac{z - (h - \xi_{\rho, \text{int}})}{\xi_{\text{int}}}\right],$$
(3)

where $\xi_{\rho,\text{sub}}$ and $\xi_{\rho,\text{int}}$ are the interfacial density scales of the substrate and free surface, respectively; ξ_{sub} and ξ_{int} are the dynamical interfacial scales of the substrate and free surface, respectively; *h* is the temperature dependent film thickness, defined by the height at which density decreases to 0.05 near the interfaces; c_1 , c_2 , and τ_0 are fitting parameters. We obtain excellent fits with Eq. (3) for all films that we consider.



FIG. 6. The dynamical interfacial scale $\xi(T)$ of thin films and nanocomposites for (a) strongly and (b) weakly attractive interfaces and (c) the free polymer-air interface. The symbols represent the data, and the solid lines are guides for the eve.

We now discuss our results for the dynamical interfacial scales near each interface. In Fig. 6, we show a comparison of ξ estimated for a thin polymer film and our model nanocomposite with variable NP size in the cases of a strongly attractive interface [panel (a)] and weakly attractive solid interface [panel (b)]. We expect that ξ_{sub} in the film substrate should serve as an approximate limit for ξ of the polymer-NP composite in the limit of large NP size. For the case of strong interfacial interactions, ξ of the composite interfacial zone increases with increasing NP size and approaches to that of the film substrate in the large NP limit. This observation is consistent with that observed for the magnitude of the interfacial effect on the relaxation time $\tau_{\alpha}(r)$ reported in Ref. 22 and supported by measurements.³⁶ For the case of weakly attractive interfaces, ξ of the composite only weakly depends on NP size and (like the strongly attractive case) smaller than that of the polymer film substrate. Moreover, the ξ range is diminished for weak interfacial interactions, as compared to the case of strong interactions.

We next consider the behavior of the free interface of the polymer film. Figure 6(c) shows that the width of the mobile interfacial layer near the free interface ξ_{int} increases on cooling, just like that of the substrate. However, the *T* dependence of ξ_{int} is nearly identical for both substrate interactions. This finding is not surprising since the free interface is sufficiently far from the substrate to be largely independent of its effects. Moreover, the magnitude of ξ_{int} is very similar to that of ξ_{sub} of the weakly interacting substrate. This could have been anticipated from the fact that the relaxation profile near the weak substrate is similar to that of a free interface.

These data provide a useful reference for the systematic variation of the interfacial scale in composites and films. In the conclusions, we reflect on how this may relate to other material properties.

IV. CONCLUSIONS

Since nanoparticles have a relatively large interfacial area in comparison to particle additives in bulk materials, the interfacial regions over which the polymer matrix is perturbed can be expected to have an appreciable influence on nanocomposite properties,² despite the relatively small width of this interfacial zone. Our paper focuses on this challenge by quantifying the spatial extent and properties of the interfacial zone around nanoparticles and at the interfaces of a supported thin polymer film. We find that the width of the interfacial zone around nanoparticles is typically a few nanometers when translated to laboratory units appropriate for polystyrene. In all cases, we find that ξ grows progressively upon cooling but remains on the order of a few nanometers. Notably, the width of the interfacial region is sensitive to NP size for strong interfacial interactions but is only weakly dependent on NP size for weak polymer-substrate interactions. That said, the film appears to offer a limiting value for ξ in the limit of very large NP. Our findings broadly accord with the earlier computational study by de Pablo and co-workers⁴⁶ and are also, in general, qualitatively accord with measurements of the interfacial zone width by Sokolov and coworkers.^{14–18,47} We note that the effective size of the nanoparticles in these systems can be altered by a "bound layer" of polymer. The importance of this layer is appreciated when we consider that the interfacial layer thickness can be comparable to dimensions of the nanoparticle.

We briefly compare our estimates of the dynamical interfacial scale ξ in Fig. 7 with experimental estimates of the mobility interfacial zone thickness by Sokolov and co-workers for several glass-forming materials [glycerol, poly(2-vinylpyridine), polypropylene glycol, and polyvinyl alcohol] based on broadband dielectric spectroscopy measurements.^{16,47} To extrapolate the low T behavior of $\xi(T)$ from our simulations, we use the empirical Arrhenius relation $\xi(T) = \xi_0 \exp((\Delta H - T\Delta S)/kT)^{48,49}$ to fit the temperature dependent of ξ from our simulations, where ΔH , ΔS , and ξ_0 are free fitting parameters. We see that the scale and qualitative temperature dependence of these experimental estimates of ξ are reasonably consistent with our coarse-grained simulations; see the work of Cheng et al.^{16,47} for the description of the materials, measurement methods, measurements uncertainties, etc. It is notable that the order of magnitude of the interfacial scale is not sensitive to whether the glass-former is polymeric or not. These experimental estimates are indirect, but later work involving direct imaging of the interfacial region by atomic force microscopy has conformed these observations to a good approximation.¹⁷ The silica NPs used by Sokolov and co-workers¹⁶ in their experimental study has a diameter of 12.5 nm, a value reasonably consistent with our simulated NPs. Quantitative comparisons with the experiment will require estimating the strength of the polymer matrix interaction strength ε .¹

Since the interfacial scale ξ defines the range of the mobility gradient, by definition, it is a scale of dynamic heterogeneity. However, it is not clear how the scale of this mobility gradient may (or may not) relate to the scale of spatially and temporally heterogeneous dynamics that occurs both in films and composites, as well as in structurally homogeneous bulk materials. It has been widely argued, dating back to the pioneering work of Adam and Gibbs,⁵⁵ that the scale of this spatiotemporal heterogeneity can be directly related to the growing activation barrier for molecular rearrangement on cooling. Moreover, it has been argued more recently based on



FIG. 7. Temperature dependence of the interfacial width near the NP $\xi(T/T_g)$ from experiments and simulations. The hollow symbols represent the experiments for glycerol (Gly), poly(2-vinylpyridine) (P2VP), polypropylene glycol (PPG), and polyvinyl alcohol (PVA), and the solid symbols represent the simulation data for variable polymer-NP interaction strengths and NP sizes. The experimental data are derived from broadband dielectric spectroscopy and are taken from Cheng *et al.*⁴⁷ We use an empirical Arrhenius relation to extrapolate the low *T* behavior of $\xi(T)$ from our simulations, a relation approximating the *T* dependence of the extent of cooperative motion (string length, *L*).⁴⁹

simulation evidence that stringlike replacement motions can quantitatively account for the variation in the activation free energy and thus offer a molecular description of abstract "cooperatively rearranging regions" of AG.^{40,56,57} While the variation of ξ in Fig. 6 exhibits the same qualitative trend as the scale of stringlike collective motion in the simulated nanocomposites and thin films,^{56,57} further work is required on both nanocomposite and thin film polymer materials to determine if a quantitative relation exists between these quantities.

We conclude that the width of the interfacial zone near a solid substrate of a supported thin film approximately sets an upper bound of the scale of mobile interfacial zone of a particle with a similar material makeup and stiffness. Furthermore, it is important to consider the scale of interfacial density ξ_{ρ} in determining the dynamical interfacial scale ξ and to distinguish these scales since they exhibit very different variations with molecular and thermodynamic parameters.

To put these findings in context, it is useful to consider the case of water, where there has been significant consideration of interfacial property changes near NPs. For example, the water density profile found in aqueous solutions was found computationally to have a characteristic scale that varies nonmonotonically as a function of NP size,^{39,45} and an enhanced compressibility in the interfacial region of hydrophobic interfaces was also observed in both simulations³ and measurement.^{58,59} Evidently, the interfacial layer (around NPs and even macroscopic interfaces) near the hydrophobic interfaces is more compressible than that of hydrophilic interfaces.^{44,45} Moreover, the density profile exhibits a sensitivity to NP size or interfacial curvature. These observations are somewhat similar to our observations on the interfacial density of NPs where we likewise find the interfacial density scale to vary nonmonotonically with surface curvature in the case of strongly attractive interfaces. Of course, we do not mean to imply that aqueous solutions and polymer fluids are actually equivalent as the interaction potentials are rather different. We note that recent X-ray scattering studies have provided evidence for a zone of modified solvent density around nanoparticles having a scale extending up to about 2 nm beyond the nanoparticle surface,⁵ another experimental trend in qualitative accord with the present work. Measurement of this kind should be helpful in determining the interaction potential between the nanoparticles and the polymer fluid matrix.

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