

Two-population Rouse models for polymer segmental dynamics in nanocomposites

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Segmental dynamics of polymer chains in a model nanocomposite of poly(ethylene oxide) and silica nanoparticles (NPs) was investigated using quasielastic neutron scattering. The dynamics can be accurately described with the Rouse model. The bulklike polymer far from the NP surface behaves as the neat polymer. However, the slower polymer in the interface close to the NP surface is described either with a second Rouse population with different relaxation time or using the suppressed Rouse model. These simple two-population models accurately reproduce the experimental data, with the suppressed Rouse model describing topological constraints, on average, every 12 beads with an interfacial thickness up to 13.5 beads, and the effect of the interface extending to a layer of thickness comparable to the end-to-end distance of the polymer. This modeling provides an explanation for the observed reinforcement in PNC even at low loadings, consistent with current understanding of the relevance of the interphase.

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I. INTRODUCTION

Polymer nanocomposites (PNCs) can achieve material properties beyond those of either the pure polymer or nanoparticle (NP) due to the enhanced surface area of nanoscale fillers. The mechanism for the mechanical reinforcement of PNCs is not well understood and has been the focus of investigation to aid in the design of these materials [1]. In PNCs with strong attractive interactions between polymer and NP, slowed dynamics in a layer around the NP surface is believed to be important to the PNC property changes [2]. At the smaller dynamical length and time scales of interest in PNCs is polymer segmental dynamics. The most fundamental model for segmental dynamics is the Rouse model (RM): a simple bead spring model. At timescales shorter than the entanglement time, before entangled polymers show the confining effects of their reptation tube, the RM is used commonly to describe the segmental dynamics for polymer melts. RM has been found to provide a good description of the bulk polymer in PNCs [1], especially for poly(ethylene oxide) (PEO) [3–5]. However, whether the RM applies to the interfacial layer has

not been ascertained yet. To improve the design of PNCs, a better understanding of the interfacial dynamics is needed.

In the past, the interface has been treated as glassy [6], though in recent years this approach has changed [7]. Nuclear magnetic resonance (NMR) [1,8], calorimetry [1,9], and broadband dielectric spectroscopy (BDS) [1,9] probing polymer dynamics in the presence of NPs indicate either a distinct interfacial layer slower than the bulk or increasingly slowed average dynamics. When all the polymer is treated as one population, a higher average relaxation time or broadening of either the relaxation time distribution or glass transition region is obtained [1,8,9]. When treating the interface as a second population, BDS observes a slowing of dynamics of 1–2 orders of magnitude in the interface [9,10]. However, this method is insensitive to the length scale of the dynamics. Quasielastic neutron scattering (QENS) can probe the self-motion of hydrogen atoms and is sensitive to the length scale it occurs on (defined by the inverse of the exchanged wave vector, Q , as $\approx 2\pi/Q$). QENS studies for PNCs have been carried out in the literature [3–5,7]. These have found an overall slowing down of dynamics with increased nanoparticle loading when the polymer is strongly attracted to the nanoparticle. Here we perform QENS for a model system of PEO + silica NPs. Elongated NPs have been used to increase the interfacial region for a given NP loading. The excellent data quality allows us to analyze the data in terms of more refined models than used in the past. We will model the neat polymer with the RM, then apply this fit to describe the bulk polymer in the PNC, with a second population used to describe the interface with one of two variants of the RM. These results are

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then physically interpreted to assess plausibility and discuss merits of these variants.

II. METHODS

PEO ($M_n = 35$ kg/mol, $M_w/M_n = 1.08$, Polymer Source Inc.) (calculated radius of gyration $R_g = 6.7$ nm [11]) used here is well above the entanglement mass of $M_e = 2.16$ kg/mol [12]. Elongated silica nanoparticles (coil-like or “string of pearls” in shape, nominal specification from the vendor of 9 nm–15 nm in diameter and 40 nm–100 nm in length) in methyl ethyl ketone (MEK-ST-UP) were provided by Nissan Chemicals America (density $\rho_{NP} = 2.314$ g/cm³ [13]). The PNC was prepared as described in [5], where polymer is strongly adsorbed rather than grafted. To summarize, sample preparation was performed by dissolving the PEO in acetonitrile, mixing with nanoparticle solution, mixing vigorously for two hours, sonicating for 20 minutes, and solution casting in a Teflon dish. The solvent was evaporated overnight in a fume hood and then the samples were annealed for two days at 363 K and then 393 K for one day under vacuum. PNCs with NP volume fractions $\phi = 0.08$, 0.2, and 0.34 ($ID/2R_g = 1.8$, 0.87, and 0.34, respectively) were prepared along with one neat polymer using the same method.

The higher loadings, $\phi = 0.20$ and 0.34, correspond to a highly confined state, where the critical confinement parameter [3] $ID/2R_g < 1$; here ID is the interparticle distance estimated with an equivalent volume sphere representing the NP, and R_g is the polymer radius of gyration. This confinement parameter has been used as a scaling factor to relate diffusion of both the polymer and NP in PNCs with varying chain length and approximately an order of magnitude slower diffusion for highly confined systems ($ID/2R_g < 1$) [14,15].

Using elongated NPs has allowed us to explore the confined region at a different volume fraction than the previously investigated spherical NPs [5]. However, the shape effect of the NP on polymer dynamics is outside the scope of this paper.

A. NP characterization and dispersion

Small angle x-ray scattering (SAXS) measurements were performed on a Xeuss 3.0 HR (Xenocs, Grenoble, France) equipped with an EIGER2R (1 M model) hybrid pixel photon counting detector (Dectris Ltd., Baden, Switzerland) consisting of 1028×1062 pixels with a size of $75 \times 75 \mu\text{m}^2$. The wavelength of the x-ray beam was $\lambda = 1.542$ Å. Calibration of the sample to detector distance was performed using silver behenate ($d = 58.38$ Å). Two sample-to-detector distances, 350 and 1800 mm, were used to access a range of scattering vector, Q , going from 0.004 to 0.9 Å^{-1} , with $Q = (4\pi/\lambda) \sin \theta$ and 2θ the scattering angle. NP solutions in methyl ethyl ketone (MEK) were contained in borosilicate capillaries (WJM GLAS / Muller GmbH, Germany) and sealed with a glue gun while PNC were enclosed in sealed demountable cells using Kapton® foils as windows. The 1D azimuthally averaged scattering patterns were reduced by subtracting the scattering intensity from the blank (capillary plus MEK for the solutions and Kapton® foils for the PNC) and by merging

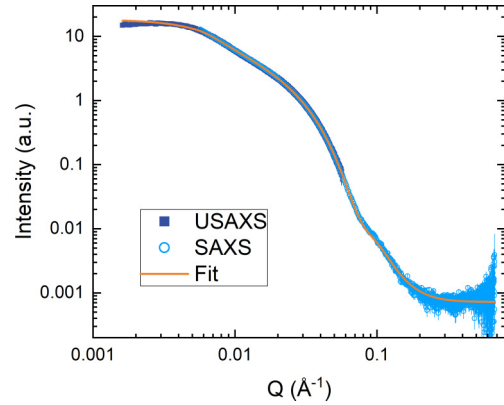


FIG. 1. Fit of a flexible cylinder form factor to SAXS (hollow circle) and USAXS (solid square) spectra of the NP in a solution of MEK at 0.5 vol%.

the curves obtained at the two sample-to-detector distances. Data reduction, normalization, and merging was performed in XSACT (x-ray scattering analysis and calculation tool, Xenocs, France).

USAXS was performed at beamline ID02 at the European Synchrotron Radiation Facility to extend the lower limit of the Q range to 0.0016 Å^{-1} .

The form factor of the nanoparticles is obtained from the combination of SAXS and USAXS patterns in the case of diluted nanoparticle in MEK (i.e., 0.5 vol%). The SAXS curve was shifted vertically to align the region of overlap with the USAXS pattern. The resulting curve is fit with a flexible cylinder model in SasView [16] to capture the coil-like shape of the elongated particles (Fig. 1). Obtained from the fitting was a length of $898 \text{ Å} \pm 1 \text{ Å}$, persistence length of $524 \text{ Å} \pm 1 \text{ Å}$, and mean radius of $51.6 \text{ Å} \pm 0.1 \text{ Å}$. A lognormal polydispersity was applied to the radius of the NP resulting in a PDI of 0.239 ± 0.001 .

Well dispersion of the PNCs was verified with SAXS of the PNC and solution. The structure factor peak corresponds to the interparticle distance (indicated with an arrow in Fig. 2) for randomly packed particles and the lack of a low- Q upturn indicates a lack of aggregation. The similarity between the $\phi = 0.2$ (20 vol%) PNC and 15 vol% solution as well as the $\phi = 0.005$ (0.5 vol%) PNC and 0.7 vol% solution indicates that the NPs do not aggregate when the MEK is replaced by PEO and the shape and interparticle distance are conserved (i.e., there is no change in their arrangement).

The surface area per gram of the elongated nanoparticles was obtained from nitrogen adsorption on the NP surface, fit with Brunauer-Emmet-Teller theory (BET) [17] to be $A_{NP} = 198.6 \text{ m}^2/\text{g}$.

B. QENS measurement of PNC

QENS measurements were performed on the BASIS instrument at Oak Ridge National Laboratory [18]. Samples were placed in a rectangular aluminum foil pouch and shaped with a heat press resulting in a nanocomposite thickness between 0.06 and 0.1 mm, dependent on loading, to achieve $\sim 90\%$ transmission. The rectangular pouches were then shaped as a tube and sealed in an aluminum sample can under

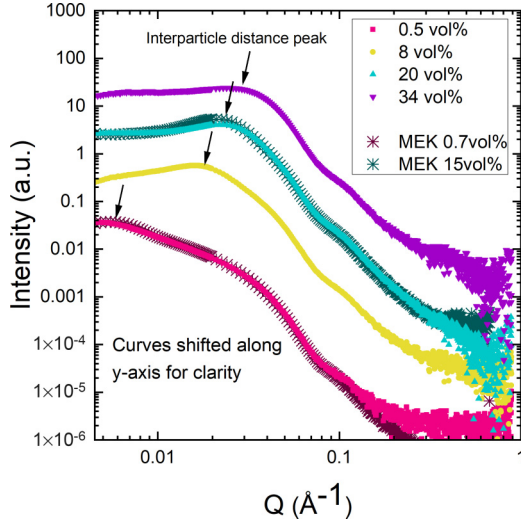


FIG. 2. SAXS curves for the nanoparticles in the polymer nanocomposites and in MEK at two similar loadings. The structure factor peaks are indicated with arrows and correspond to the interparticle distances.

helium. The resolution obtained from vanadium was $3.6 \mu\text{eV}$. Measurement was performed at 400 K over a Q range from $0.3 \text{ \AA}^{-1}$ to $1.9 \text{ \AA}^{-1}$ (only $0.5 \text{ \AA}^{-1}$ to $1.0 \text{ \AA}^{-1}$ were used for analysis) with an energy window of $\pm 200 \mu\text{eV}$ using a repetition rate of 30 Hz.

In the initial analysis of the QENS data, an elastic component was revealed. The hydrogen content of the NP was determined with prompt gamma neutron activation analysis [19] to be $4.57 \cdot 10^{21} \pm 6.7 \cdot 10^{19}$ H atoms per gram of NP. The results (Fig. 3) confirm that, as reported in [5], the Q -independent elastic component in the QENS spectra originates from the hydrogen content of the NPs, which are immobile on the QENS timescale. Fitting was performed in Python using the Bumps fitting package [20] (described in detail in the Supplemental Material [21]).

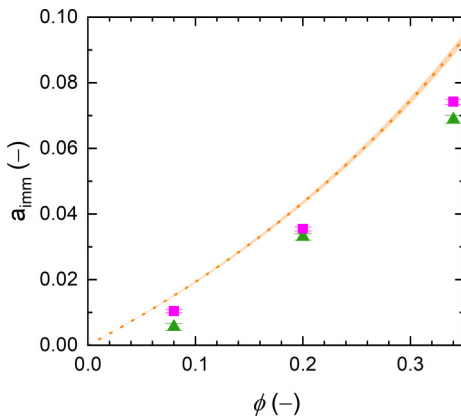


FIG. 3. Predicted immobile component, a_{imm} , from QENS as determined by PGAA (orange dotted line with shaded error bars). The fit a_{imm} for the suppressed model (pink squares) and two relaxation time model (green triangles) are also plotted.

III. RESULTS AND DISCUSSION

In our samples the signal from the hydrogen dominates the other elements in the system because of its very high incoherent scattering cross section. Thus, our experiment probes the single particle dynamics of the hydrogen atoms in the system [22]. Within the RM, the mean squared displacement (MSD) of the polymer segments can be expressed as $\langle R^2(t; p_{\min}, \tau_R) \rangle = \sum_{p=p_{\min}}^N \frac{2b^2N}{\pi^2 p^2} [1 - \exp(-\frac{p^2 t}{\tau_R})]$ [23] where $b = 0.58 \text{ nm}$ [12] is the bead size for PEO, $N = 795$ is the number of beads, p the normal mode index where the p th mode describes a normal mode spanning N/p beads, and τ_R is the Rouse time (with Rouse rate $W = N^2/\pi^2 \tau_R$). Due to the timescale of our measurement, it is not appropriate to simplify the summation as an integral, as it was commonly employed for other QENS experiment (see the SM [21]).

All the spectra have been analyzed using the following equation:

$$S(Q, \Delta E; \tau_{R,\text{bulk}}, \tau_{R,\text{int}}, p_{\min,\text{int}}) = c \cdot [(1 - a_{\text{imm}})a_{\text{bulk}} \cdot \mathcal{F}\{I_{\text{bulk}}(Q, t; p_{\min,\text{bulk}} = 1, \tau_{R,\text{bulk}})\} + (1 - a_{\text{imm}})a_{\text{int}} \cdot \mathcal{F}\{I_{\text{int}}(Q, t; p_{\min,\text{int}}, \tau_{R,\text{int}})\} + a_{\text{imm}}\delta(\Delta E)] \otimes R(Q, \Delta E) + b(Q, t), \quad (1)$$

where $\mathcal{F}$ denotes a Fourier transform, I_{bulk} represents the dynamics of the polymer far away from the interface, and I_{int} represents the dynamics near the nanoparticle. I_{int} and I_{bulk} are the intermediate scattering function (ISF) expressed as $I(Q, t; p_{\min}, \tau_R) = \exp(-\frac{Q^2}{6} \langle R^2(t; p_{\min}, \tau_R) \rangle)$, using the Gaussian approximation [23]. The center of mass diffusion term has been neglected as it takes place far outside our time window. In Eq. (1), $a_{\text{bulk}} + a_{\text{int}} = 1$ are the fractions of the bulk polymer and slow interfacial fraction, respectively. Hydrogen in the NP is represented by a Q -independent elastic component, a_{imm} . Arbitrary scaling, c , and a linear background, $b(Q, t)$, are also applied in the fit. Experimental resolution, $R(Q, \Delta E)$, is obtained from vanadium, which has no observable dynamics at experimental conditions. Fitting is performed over the Q -range $0.5 \text{ \AA}^{-1}$ to $1.0 \text{ \AA}^{-1}$ with lower Q containing a non-negligible amount of coherent scattering and higher Q corresponding to length scales smaller than the bead size where the RM no longer applies.

Fits are performed "globally" to all Q , forcing Q independence for τ_R , $p_{\min}$, a_{bulk} , a_{int} , and a_{imm} . In some cases, spectra for each Q were also fit independently (hereafter referred to as "local fitting") to further validate the fitting. Example fits are shown in Fig. 4 for the neat polymer with the one population model and the $\phi = 0.08$ PNC for the two relaxation time and suppressed Rouse model (discussed in detail later).

Despite this seemingly large selection of fit parameters, we are confident that the fits give useful information about the slow interfacial population of polymer. The Rouse dynamics describe a $S(Q, \Delta E)$ which is symmetric about $\Delta E = 0$, and the slope in the background accounts for instrumental effects without affecting the obtained relaxation time (confirmed with selected zero-slope background fits). Additionally, the region where the interfacial $S(Q, \Delta E)$ is relevant is narrow, so the sloped background will not have a noticeable effect in this energy range. The spectra in Fig. 4 are plotted in log-y scale,

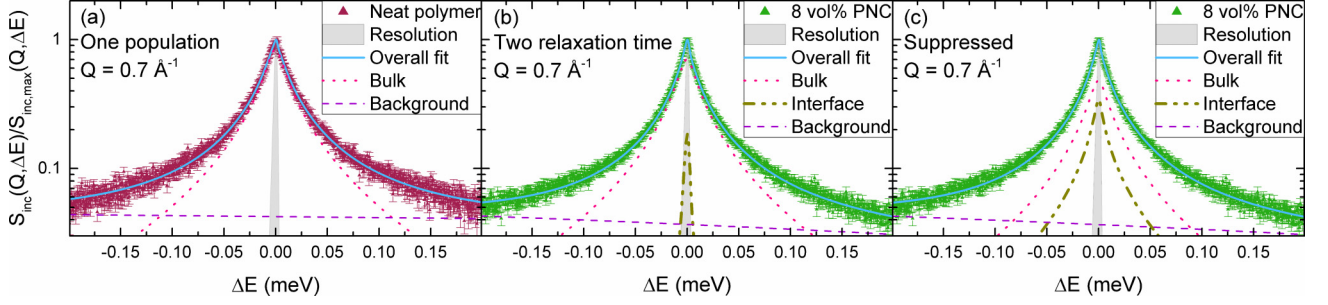


FIG. 4. QENS spectra, normalized to the peak height, at $Q = 0.7 \text{ \AA}^{-1}$ for (a) the neat polymer with one population fit, (b) the 8 vol% PNC with two relaxation time fit, and (c) the 8 vol% PNC with suppressed Rouse fit.

so the scaling applied only shifts the fits vertically without distorting their shape. An example of correlation plots obtained from fitting can be found in the SM [21].

Fitting the neat polymer [Fig. 4(a)] was done by setting $a_{\text{int}} = 0$ (one population model), obtaining the Rouse rate, $W = N^2/\pi^2\tau_R$. Applying this one population model globally for all Q and comparing the resulting τ_R with the value obtained from local fitting justifies the assumption of a Q -independent τ_R , required for the RM (Fig. 5). The global one population fit of the neat polymer results in $W_{\text{bulk}}b^4 = 1.267 \pm 0.006 \text{ nm}^4/\text{ns}$ [24] which is consistent with literature values [3,5,12,25]. Therefore, we confirm the RM is appropriate to describe the bulk polymer.

Moving to the PNC, this analysis is repeated to examine the ability of the one-population RM to describe the PNC (see the SM for example spectra with fits [21]). For this, the highest loading of $\phi = 0.34$ is considered as it illustrates the results most clearly. The Wb^4 obtained from local fitting is strongly Q dependent (Fig. 5), as observed before [5], indicating one population is not able to capture the dynamics of the PNC within the experimental uncertainties of the present measurements and we must consider a second population for the interface.

A. Two relaxation time model

The dynamics of the interfacial population is first described using an unmodified RM with a different τ_R than the bulk. To implement this, the fraction of the bulk population, a_{bulk} , is allowed to be smaller than 1. $\tau_{R,\text{bulk}}$ is fixed to the value obtained from the neat polymer [see example fit in Fig. 4(b)].

The check performed for the one population model in Fig. 5 is repeated for the two relaxation time model (TRM) with global and local fitting (Fig. S5 of the SM [21]).

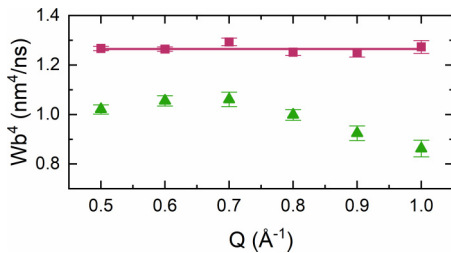


FIG. 5. Fit Rouse times for the single population model fit locally (squares) for the neat polymer and globally for all Q (solid line), as well as $\phi = 0.34$ fit locally (triangles).

The main results of the analysis using the TRM are reported in Fig. 6. The TRM fits reveal that the interfacial dynamics are independent of NP loading and approximately one order of magnitude slower than the bulk ($W_{\text{int}}b^4 = 0.141 \pm 0.005 \text{ nm}^4/\text{ns}$) [Fig. 6(a)]. Consistent with our results, studies using BDS have analyzed their data with a bulk and an interfacial component 1–2 orders of magnitude slower than the bulk [9,10].

This longer relaxation time can be interpreted as an increase in the friction coefficient experienced by the polymer. From the known temperature dependence of the friction coefficient in the bulk, the interfacial dynamics match that of neat PEO at approximately 325 K [12]. This corresponds to a 7% density increase over the bulk polymer [22]. Higher friction coefficients have been used to explain dynamics of polymer grafted to NPs [26], and small density changes at the interface in PNCs have been reported [10]. Consequently, the TRM is consistent with results previously reported.

Previous QENS studies on PNCs [7] have modeled the interface with an elastic component due to resolution limitations and estimate the interface thickness to be 1 nm. Our analysis also provides the fraction of segments displaying slower dynamics, a_{int} , which is identified as polymer in the interfacial layer. From this, an estimate is obtained of the

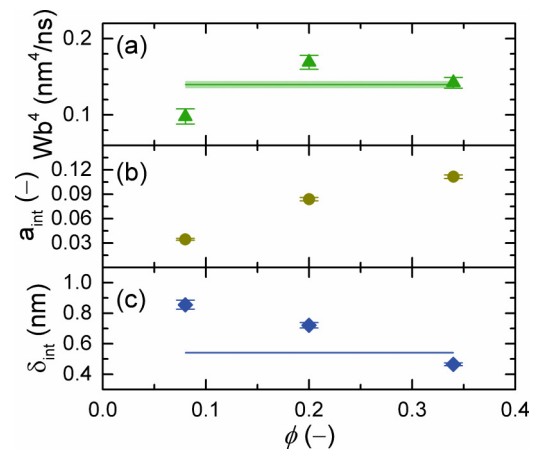


FIG. 6. For the PNC with the TRM the (a) fit Rouse parameter (triangles), (b) fit fraction of polymer in the interface (circles), and (c) calculated interfacial thickness obtained from Eq. (2) (diamonds). Average values (with shaded error bars) can be used to describe the spectra equally well.

interfacial thickness as the ratio of the interface volume to nanoparticle surface area:

$$\delta_{\text{int}} = \frac{(1 - \phi)a_{\text{int}}}{\phi A_{\text{NP}} \rho_{\text{NP}}}. \quad (2)$$

The interfacial thickness slightly varies across the loadings [Fig. 6(b)]. However, the QENS spectra at all loadings can be equally well described by the average value of the thickness $\bar{\delta}_{\text{int}} = 0.55 \pm 0.01$ nm (shown in the SM [21]) which is approximately the size of one polymer bead (0.58 nm [12]). This average is consistent with the previously mentioned estimate from QENS [7] while BDS [9] and simulations [27] have found a thickness as high as four beads.

Simulations have shown a gradient of mobility (which is completely neglected in our model), but they have also shown that this gradient can be approximated as a second population with an interface 1.5–2 beads thick experiencing 1–2 orders of magnitude slower dynamics which is consistent with our results [27]. However, the interpretation of the slower dynamics as due to a density change is somewhat unsatisfactory when this density change is supposed to occur over a scale of one polymer bead.

B. Suppressed Rouse model

This aforementioned shortcoming of the TRM is addressed by considering a model which has been successful in describing the dynamics of polymer chains confined in a nanoporous matrix measured using neutron spin echo, the suppressed Rouse model (SRM) [2]. The SRM cuts off normal modes with $p < p_{\text{min}}$ (where p_{min} is a cutoff parameter) which cover longer length scales as a result of increased topological constraints (e.g., adsorption to the NP), analogous to the well-known effect of entanglement and reptation in the neat polymer [28]. Suppression can propagate away from the surface of the NP through entanglements, allowing chains not directly in contact to the NP to experience suppressed dynamics. The SRM has been used to rationalize QENS results [5], but this is the first investigation to explicitly describe segmental dynamics as observed by QENS with the SRM.

Application of this model to our QENS spectra can be done by setting $\tau_{R,\text{bulk}} = \tau_{R,\text{int}}$, both fixed to the value obtained from the neat polymer, and varying p_{min} . For the suppressed interfacial layer, a loading-independent $p_{\text{min}} = 65$ is observed [Fig. 7(a)]; this is consistent with the idea that the suppressed dynamics originate from the interaction of the polymer chain with the nanoparticle surface. A p_{min} of 65 corresponds to the longest unsuppressed wavelength spanning $N_{\text{min}} = N/p_{\text{min}} \approx 12$ beads (Table I). The adsorbed layer thickness, δ_{ads} , is determined from the end-to-end distance of N_{min} beads: $\delta_{\text{ads}} = b\sqrt{N_{\text{min}}}$. For $N_{\text{min}} \approx 12$, $\delta_{\text{ads}} = 2.01$ nm which is approximately 3.5 bead diameters, consistent with previous reports [2,5]. The total interfacial thickness, δ_{int} , is found using Eq. (2) as before. These results are shown in Fig. 7 and summarized in Table I, with δ_{int} limited by the total amount of polymer at the higher loadings (dashed line in Fig. 7). It should be noted that Eq. (2) does not account for overlap of interfacial layers of neighboring nanoparticles. However, for the loadings that experience interfacial overlap

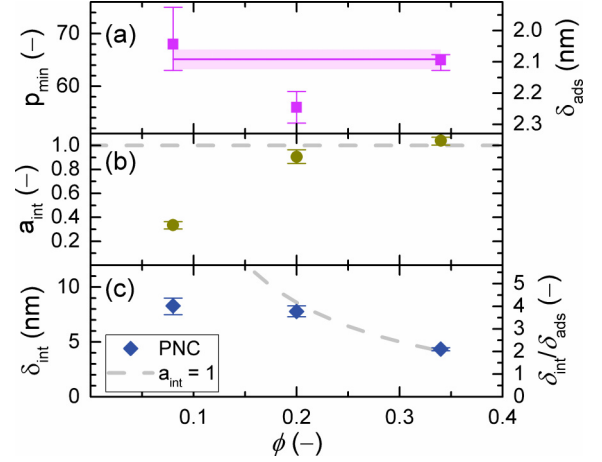


FIG. 7. For the SRM, the obtained (a) fit lowest unsuppressed mode for the PNCs (squares) and their average value (line with shaded error bar) (b) fit fraction of polymer in the interface (circles), and (c) the calculated interfacial thickness (diamonds). The dashed line in (b) and (c) corresponds to the resulting thickness if all the polymer resides in the interface [$a_{\text{int}} = 1$ in Eq. (2)].

($\phi = 0.20$ and 0.34), all segments demonstrate suppressed dynamics, so interfacial overlap is not a concern.

Previous use of the SRM has employed an "interfacial extension parameter" used to describe the interface thickness in terms of adsorbed layer thickness ($\alpha = \delta_{\text{int}}/\delta_{\text{ads}}$) which results from suppression of dynamics propagating away from the nanoparticle surface due to entanglements [2,5]. Krutyeva and coworkers [2], which introduced the SRM for a confined polymer, reported an interfacial extension parameter of 1.9. We find a value that is approximately double, up to $\alpha = 4$ for $\phi = 0.08$ (corresponding to 123% of R_g and 58% of the end-to-end distance for the whole chain), but to the knowledge of the authors, there are few studies investigating the extent parameter at which entanglements can still propagate the suppression of Rouse modes. However, for $\phi = 0.08$ a value of $a_{\text{int}} \approx 0.10$ and a p_{min} value of 146 describes the spectra only marginally worse (3% increase in χ^2 parameter, refer to the SM [21]). This would correspond to $\alpha = 1.9$. These results represent a more stringent minimum acceptable value for α , while $\alpha = 4$ still represents the most likely value within the experimental accuracy and the assumptions of the model.

TABLE I. Main results from the two population models. Interfacial thickness for the SRM taken from a loading of 8 vol%, which is not limited by the amount of available polymer.

	TRM	SRM
$W_{\text{bulk}} b^4$ (nm ⁴ /ns)	1.26 ± 0.01	1.26 ± 0.01
$W_{\text{int}} b^4$ (nm ⁴ /ns)	0.14 ± 0.01	
N_{min} ($-$)		12.1 ± 0.3
δ_{int} (nm)	0.55 ± 0.01	8.2 ± 0.7
δ_{ads} (nm)		2.0 ± 0.3

C. Comparing the TRM and SRM

Even at the lower end of the interfacial thickness range for the SRM, the interface is undeniably thicker than that determined from the TRM, which could explain the large macroscale property changes observed even in low loading PNCs. However, since both models offer a similarly good description of the spectra (and represent an improvement over the one population model), they are further analyzed by decomposing the $I(Q, t)$ into a series of exponentials and finding the distribution of relaxation times, $\rho(\tau)$. As different Q values correspond to different length scales, $I(Q, t)$ and $\rho(\tau)$ are effectively weighted in favor of relaxation processes which occur over that length scale.

This analysis reveals that both models introduce additional slow components to $\rho(\tau)$ which are not present in the bulk. In the TRM, this component originates from a dynamically distinct population at the interphase. The dynamics of these segments have the same Q dependence, i.e., probed lengthscale dependence, as the bulk and therefore the additional slow component is appreciable in $\rho(\tau)$ at all Q . In the SRM, the segments at the interface are forbidden to explore large lengthscales; the lengthscale obtained from this fitting [Fig. 7(a)] is comparable to the lengthscale of ≈ 12 Å of the lowest Q probed, 0.5 Å⁻¹. This originates a small (<0.05) long time plateau in the intermediate scattering function (Fig. S9 of the SM [21]); this feature would result in a delta peak in the QENS spectra at low Q , which disappears as Q is increased. In general, at higher Q , smaller lengthscales are probed and the constraint imposed on the dynamics of the segments by the presence of the PNCs, as described by the SRM, tend to vanish; consequently, at higher Q , $\rho(\tau)$ for the SRM increasingly resembles that of the bulk. However, further experimentation that pushes the timescales accessible will be necessary to conclusively discriminate one model over the other.

IV. CONCLUSIONS

Two population Rouse models can be used to describe the polymer segmental dynamics in the PNC probed by QENS where a one population model fails. A simple TRM yields realistic timescales for the interfacial dynamics but results in a very thin estimated interface thickness of approximately only one bead, consistent with comparable models for other techniques. The SRM offers a more holistic scenario explaining the slowing of interfacial dynamics as arising from increased topological constraints, analogous to entangled polymer melts; it broadens the relaxation time distribution

and results in a greater interfacial thickness. For the SRM, we obtain an adsorbed layer thickness of $\delta_{\text{ads}} = 2.0 \pm 0.3$ nm, corresponding to approximately 3.5 beads, and a total interfacial thickness in the range up to four times that amount. This greater interfacial thickness has important implications for applications in other areas and could explain deviations from the Einstein prediction for suspensions and the large effect of a relatively small amount of NP generally observed in PNCs. We hope this work stimulates further discussion into the modeling of interfacial dynamics in terms of the Rouse model.

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Certain trade names and company products are identified in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best for the purpose.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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