Why Volume and Dynamics Decouple in Nanocomposite Matrices: Space that Cannot Be Accessed is Not Free

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Polymer nanocomposites have important material applications and are an ongoing focus of many molecular level investigations, however, puzzling experimental results exist. For example, specific volumes for some polymer nanocomposite matrices are 2% to 4% higher than for the neat polymer; in a pure polymer melt this would correspond to a pressure change of 40 to 100 MPa, and a decrease in isothermal segmental relaxation times of 3 to 5 orders of magnitude. However, the nanocomposite segmental dynamics do not show any speed up. We can explain this apparent uncoupling of dynamics from specific volume, and the key is to consider the system expansivity, i.e., the temperature dependence of the volumetric data, together with the concept of limiting volume at close liquid packing. Using pressure, volume, temperature data as a path to both, we are able to predict the effect of nanoadditives on the accessible, i.e., free, space in the material, which is critical for facilitating molecular rearrangements in dense systems. Our analysis explains why an increase in specific volume in a material may not always lead to faster segmental dynamics.

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Molecular level segmental dynamics in polymers and polymer nanocomposites [1–7] are fundamentally important in driving the processes that lead to their characteristic material properties [8–14]. These molecular motions affect mechanical and rheological behavior, glass formation (vitrification and devitrification), transport properties, viscosity, diffusion, energy dissipation, etc. Two independent thermodynamic variables control the segmental relaxation time: volume (V) and temperature (T), [8,9] and there has been extensive study over recent decades into understanding the effect that changing thermodynamic conditions [8–14] have on the rate of segmental dynamics. Quantities of particular interest include the α-relaxation time, τ (e.g., via dielectric spectroscopy or scattering techniques), and the related glass transition temperature T_g, the point where upon cooling τ becomes longer than the typical laboratory observation timescale.

Some recent experimental data on nanocomposites have revealed [15–20] counterintuitive and, as yet, unexplained trends which appear to indicate a decoupling of the expected connection between volume and dynamics. The implication is that the specific volume of the polymer matrix in a nanocomposite can be significantly higher than that of the corresponding neat polymer, while the segmental dynamics remain unchanged, or even slow down a little. In this Letter we explain those seemingly contradictory results.

Normally, segmental relaxation rates increase (τ decreases) when V is increased, and when T is increased. The latter effect is due to the increased available thermal energy for surmounting activation barriers. The former effect relates to the added free space for segmental motion, which reduces the need for cooperativity and therefore effectively reduces the activation energy. The independent control that T and V have on relaxation times is reflected in the general form [21,22]

$$\tau(T,V) \propto \exp[f(T) \times g(V)], \tag{1}$$

where there is a T-based contribution $f(T)$ and a V-based contribution $g(V)$.

Over the decades there have been many experiments [8,9] on a wide variety of polymer and small molecule systems whose results support the correlation between increasing volume and faster segmental relaxation. This has been most effectively accomplished by following the dynamics as pressure is changed under isothermal conditions, thereby resolving the V-based contribution. This correlation between τ and V (as well as T) has been described using density scaling theory [8,9,14,23–29]. Application involves fitting a key material-specific parameter γ, such that in a plot of τ vs TV^{γ} all pressure-dependent dynamics data can be collapsed into a single curve. In terms of Eq. (1), the density scaling formalism is consistent with a volume-based contribution of $g(V) \propto 1/V^{c}$, with a positive-valued exponent, $c \propto \gamma$ [21,24,30]. It is clear from this form of $g(V)$ that the relaxation rates must increase (τ decreases) whenever the volume increases, as expected.

It would therefore seem that the puzzling nanocomposite results cannot be resolved through density scaling analysis, which correlates relaxation data with system volume. However, it is important to consider that an increase in

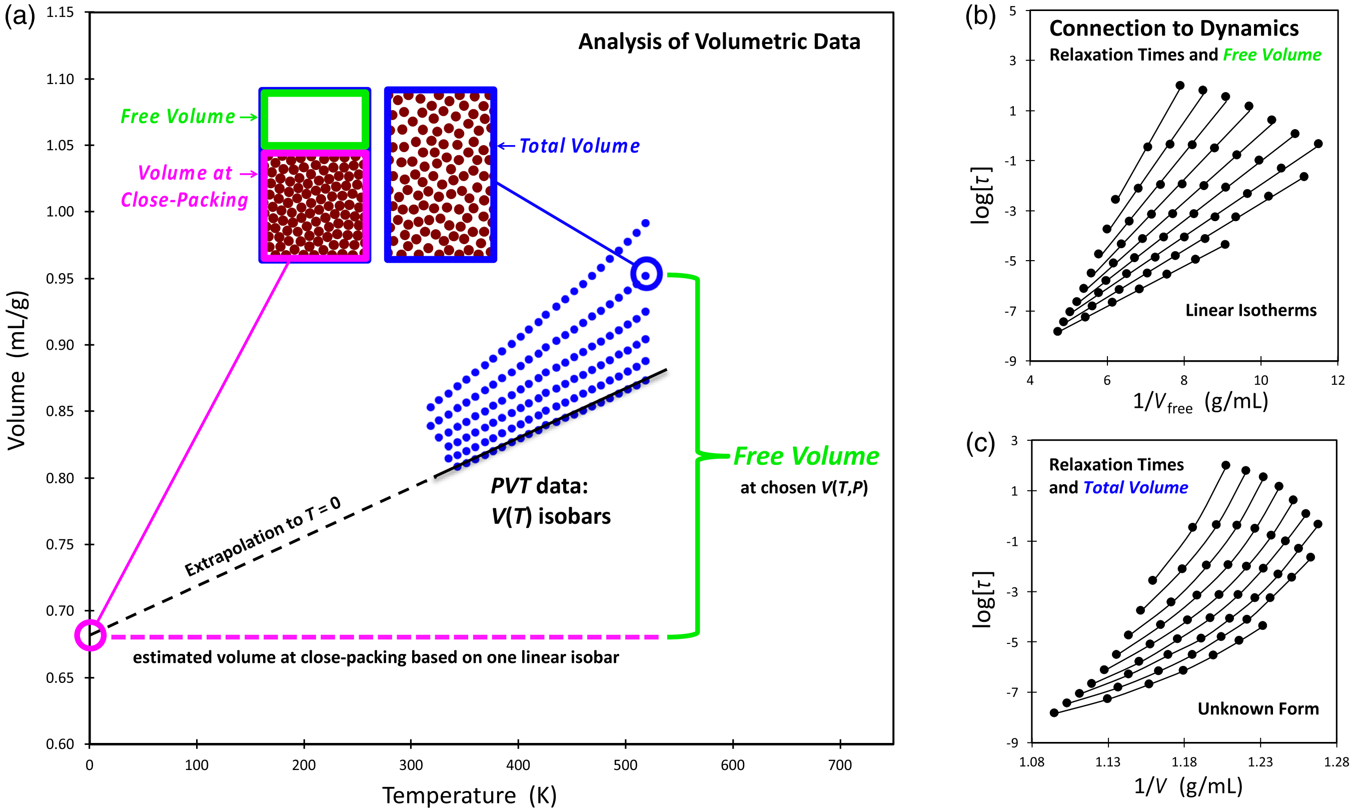

FIG. 1. (a) PVT data for a polyvinylacetate melt [35] plotted in the form of $V(T)$ isobars at $P = 0, 40, 80, 120, 160$, and 200 MPa, and diagrams depicting how to define and estimate free volume, $V_{\mathrm{free}}(T,P)$ [Eq. (2)]. (b) T, P dependent segmental relaxation times [36] correlated against $V_{\mathrm{free}}(T,P)$ estimated via the method in panel (a); plot shows $\log\tau(T,P)$ vs $1/V_{\mathrm{free}}(T,P)$ on isotherms of varied T (333 to 413 K). (c) Same relaxation times correlated against total volume, $\log\tau(T,P)$ vs $1/V(T,P)$.

overall system volume may not *necessarily* mean more free space for segmental motion. One should instead ask what is happening to the effective "free volume" in going from pure polymer to the matrix material in the nanocomposite systems.

Free volume, V_{free}, is a natural variable for describing the volume-based contribution in Eq. (1). Once it is clear how to determine V_{free} from volumetric measurements, e.g. pressure, volume, temperature (PVT) data, it can be connected with dynamics and we have demonstrated the effectiveness of the simple form [22,30–33], $g(V) \propto 1/V_{\mathrm{free}}$, which leads to some *a priori* insight before even measuring the dynamics.

The choice of free volume definition is important because multiple definitions exist in the research community [22,31,34]. We define V_{free} as the difference between the system's total volume V and its volume at the limiting state of random (liquidlike) close packing, V_{hc}:

$$V_{\mathrm{free}} = V - V_{\mathrm{hc}}. \tag{2}$$

V and V_{free} both depend on T, P, while V_{hc} is a constant. This simple definition is graphically illustrated in Fig. 1(a), which includes an example of an experimental system's PVT data, plotted in the form of $V(T)$ isobars, as well as schematics depicting the total volume, close-packed volume, and the corresponding remaining free space V_{free}.

The figure demonstrates that we can approximate the system's volume at close packing by extrapolating one of its $V(T)$ isobars down to zero temperature, an important result for our purposes here. This route to determining the close molecular (segmental) packing in real experimental systems is supported by our simulation results and analysis of PVT data for spherical molecular segments. We have shown that the result using an extrapolated isobar does indeed lead to a limiting volume that is quite close to the volume of the spheres at random close packing [22,32,33]. In terms of the choice of isobar to extrapolate, we have found that higher pressure isobars, being strongly linear, give a very reliable lower bound estimate of V_{hc}; Ref. [22] considers this topic in depth, but for our purposes here any isobar could be chosen because the results are similar enough to demonstrate the main physical arguments. Another route to the volume at close packing and thus V_{free} is to analyze the system's PVT data using the LCL equation of state [34], which has molecular level parameters (related to the size of the molecules) that yield the system's characteristic V_{hc} value; this more formal analysis will be applied below.

Figure 1(b) illustrates the strong correlation that results from the analysis using the independently determined V_{free}, calculated *a priori* from the PVT data. The linear $\log\tau$ vs $1/V_{\mathrm{free}}$ isotherms demonstrate that in Eq. (1) we can write $g(V) \propto 1/V_{\mathrm{free}}$; the increasing isotherm slopes with decreasing T result from the changing $f(T)$ contribution. The kinetics leading to this general form of behavior have been explained in terms of the cooperative free volume (CFV) rate model which predicts these trends [22,30,32]. For comparison, in Fig. 1(c), we show the more conventional plot against inverse total volume ($\log\tau$ vs $1/V$), instead of inverse free volume. The isotherms do exhibit a consistent monotone relation, but the nonlinear functional form (related to the γ parameter) is system specific, and not known until after the dynamics are measured. The strong *a priori* connection between V_{free} and segmental relaxation time is what will allow us to understand the impact of nanoparticle addition on matrix dynamics.

In particular, we consider two experimental systems that were studied in Refs. [15,18–20]: polyvinyl acetate (PVAc) with silica nanoparticles at multiple nanoparticle concentrations ranging from $\phi_{\mathrm{s}} = 0.018$ to 0.282, and, polystyrene (PS) with silica nanoparticles at a concentration of $\phi_{\mathrm{s}} = 0.042$. Relaxation times and T_{g} measurements on both of these systems demonstrate that the segmental dynamics of the polymer nanocomposite matrices are not faster than the corresponding neat polymer, and the glass transitions show little or no change. For example, the T_{g} of the PS/silica system studied in Tao and Simon [19] was found via DSC to be 102 °C compared to $T_g = 99\,^{\circ}\mathrm{C}$ for the neat PS. [19] For the PVAc/silica nanocomposites in Bogoslovov *et al.* [18] all silica nanoparticle concentrations gave the same T_g as the neat PVAc ($40.4 \pm 0.7\,^{\circ}\mathrm{C}$ via MDSC). In the dielectric spectroscopy measurements of Cheng *et al.* [15] the relaxation spectrum (see, e.g., Fig. 1 of that Letter) shows little change in the peak location (relaxation time) when comparing neat PVAc to a PVAc/silica nanocomposite sample of $\phi_{\mathrm{s}} = 0.205$ (and molecular weight, $M_{\mathrm{w}} = 40$ kg/mol).

Cheng *et al.* [15] were the first to observe that the specific volume of the polymer matrix (i.e. just the polymer-containing portion of the overall nanocomposite) is higher than that of the corresponding neat polymer, which as discussed above is unexpected given the system's observed dynamics behavior. Those authors performed density measurements on PVAc/silica systems using gas pycnometry. Converting to the corresponding specific volume for just the polymer matrix ($\phi_{\mathrm{s}} = 0.205, M_{\mathrm{w}} = 40$ kg/mol) showed that it was about 2% higher than that of the neat PVAc, and up to 4% higher for samples with higher molecular weights. Following this lead, we now consider the volumetric behavior in more detail by analyzing the full nanocomposite PVT datasets that were reported in Bogoslovov *et al.* (PVAc/silica) [18] and Tao and Simon (PS/silica) [19,20].

The first step is to map the PVT data [18,19], which correspond to the specific volumes for the *overall* nanocomposite, into the PVT behavior corresponding to the polymer matrix, alone. Specifically, we must calculate the polymer matrix specific volume, $v_{\mathrm{m}} = (v_{\mathrm{nc}} - y_{\mathrm{s}} v_{\mathrm{s}})/(1 - y_{\mathrm{s}})$, at each T, P datum point based on the value of the overall nanocomposite specific volume (v_{nc}), the specific volume of the silica nanoparticles (v_{s}), and the mass fraction of the silica (y_{s}). Further details on these calculations, including the assumptions involved, and the effect of the value of the silica nanoparticle density, are available in the Supplemental Material [37], which includes additional Refs. [38–40]. (Note going forward, the detailed variable notation for the matrix specific volume, v_{m}, is not used elsewhere in the text or figures, i.e., simply using "V" for specific volume will suffice).

Figure 2 shows the resulting plots of PVT behavior for the polymer matrices of the PVAc/silica ($\phi_{\mathrm{s}} = 0.153$) and PS/silica ($\phi_{\mathrm{s}} = 0.042$) nanocomposites, along with the corresponding data for the neat polymers. The plots are of specific volume as a function of T for isobars at $P = 0$, 20, 40, 60, and 80 MPa. The isobar at $P = 0$ is indicated for each system by a heavy solid curve; these are approximately the same as the ambient isobars (i.e., $P \approx 1$ atm). The isobars at higher pressures are marked with lighter dashed curves.

Comparison of the ambient ($P = 0$) isobars shows clearly that the polymer matrices in both the PVAc/silica and PS/silica nanocomposites have a higher specific volume than that of the corresponding neat polymer. At a given T the matrix specific volume is between 2 to 4 percent higher than that of the neat polymer, which is a large change in a condensed liquidlike or solidlike phase. Such an isothermal volume change in a polymer melt would be associated with external pressure changes of about 40 to 100 MPa. The corresponding effect on the dynamics (τ), at a temperature say about 25° above T_g, would be to decrease relaxation times by roughly 3 to 5 orders of magnitude. (See the Supplemental Material [37] for detailed examples these estimates.) The differences between matrix and neat specific volumes shown in Fig. 2 are in agreement with the results based on the gas pycnometry measurements in Cheng *et al.* [15]. The latter represent an independent estimate at a single T,P. The T dependence from the PVT data will be the key however to explaining the apparent disconnect between volume and dynamics.

While Fig. 2 shows that for both nanocomposites the polymer matrix has a higher specific volume than the neat polymer, this does not necessarily translate into additional *free* volume. To explain this we use $V(T)$ diagrams similar to Fig. 1(a) and consider two systems "1" and "2" in two different scenarios shown in panels (a) and (b) of Fig. 3. In each of these scenarios, system "2" is observed (at any given T) to have a larger specific volume than that of system "1" ($V_2 > V_1$). As the schematics show, there is more than one underlying rationale for how this can arise. In panel (a), system "2" has a higher tendency to expand

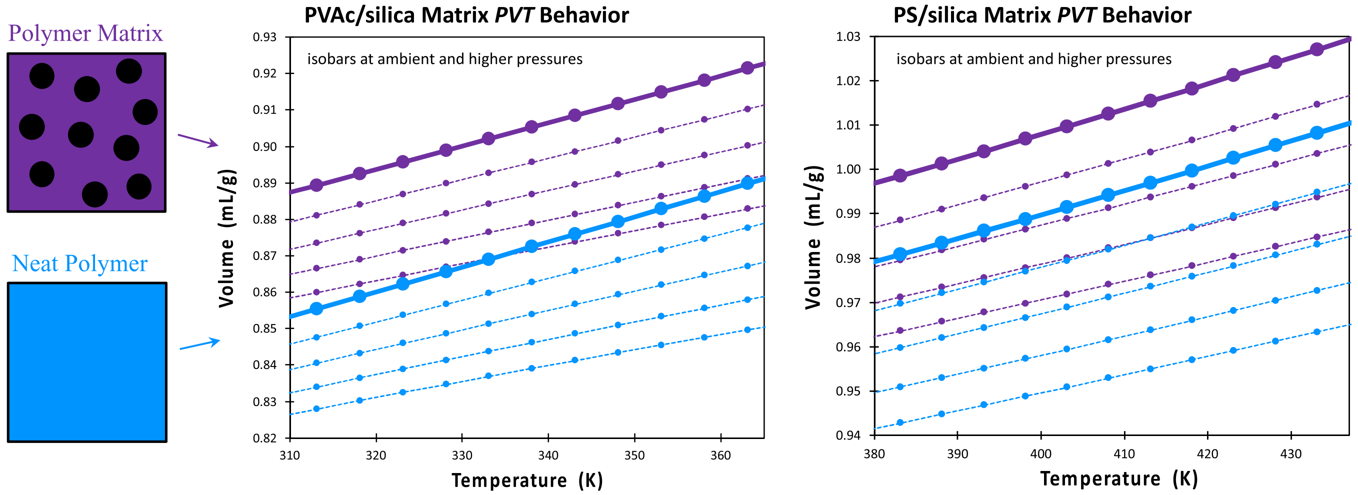

FIG. 2. *PVT* behavior of the polymer matrices in PVAc/silica ($\phi_s = 0.153$) and PS/silica ($\phi_s = 0.042$) nanocomposites, compared with corresponding neat polymers. $V(T)$ isobars at $P = 0$, 20, 40, 60, and 80 MPa, based on original measurements from Bogoslovov *et al.* [18] and Tao and Simon [19].

than system "1," while both systems have the same (constant) close packed volume. Since $\mathrm{d}V_2/\mathrm{d}T > \mathrm{d}V_1/\mathrm{d}T$, it follows that $V_2 > V_1$ for $T > 0$, and so $V_{\mathrm{free}2} > V_{\mathrm{free}1}$; the free volume difference is a consequence of there being a significant difference in $\mathrm{d}V/\mathrm{d}T$.

The other possibility [panel (b)] is that the two systems could have essentially the same $\mathrm{d}V/\mathrm{d}T$ but, because there is a difference in their volume at close packing ($V_{\mathrm{hc}2} > V_{\mathrm{hc}1}$), we will observe $V_2 > V_1$ at experimental temperatures $T > 0$. The converse way of stating this latter scenario is that, if, we observe $V_2 > V_1$ at experimental temperatures, and, if, a significant difference in $\mathrm{d}V/\mathrm{d}T$ is *not* observed, then, we can conclude that the $V_2 > V_1$ observation must be from the significant difference in the volume at close packing (V_{hc}). As shown in the diagram, an important consequence of this latter scenario (b) is that it will not correspond to a large difference in free volume between the two systems. With these two scenarios in mind, we can analyze both the matrix and neat *PVT* behavior using the LCL equation of state, which will allow us to identify the difference in *free* volume between the two.

Referring back to the actual *PVT* behavior in Fig. 2, it can be seen that the nanocomposite matrix and corresponding neat polymer do not show much of a difference in $\mathrm{d}V/\mathrm{d}T$, i.e., the slopes of the isobars compared at the same P are very similar. This situation is a close match to scenario (b) from Fig. 3, and so, we anticipate that the LCL predictions for the free volume of matrix and neat polymer will be similar.

We can verify these arguments by fitting the LCL EOS to the *PVT* data for both the matrix and the neat polymer. The resulting molecular parameters lead to the characteristic value of the volume at close packing (V_{hc}) for each; recall this quantity is independent of temperature and pressure. The free volume follows from Eq. (2), $V_{\mathrm{free}} = V - V_{\mathrm{hc}}$. See the Supplemental Material [37] for details on applying the LCL EOS to the matrix *PVT* behavior for all nanoparticle concentrations; we additionally cover a free volume analysis applied directly to the overall nanocomposite data, and leading to the same conclusions.

Figure 4 gives the results of the LCL EOS analysis, showing the impact that nanoparticle presence has on the total specific volume, close-packed volume, and free volume of the polymer matrix [panel (a): PVAc/silica [50 °C, 1 atm], panel (b): PS/silica [140 °C, 1 atm]]. For each plot, the point at zero value on the abscissa marks the result for the neat polymer, and the points moving progressively to the right show the result for the matrix in the presence of increasing nanoparticle concentration. Consistent with the scenario in panel (b) of Fig. 3, the LCL results clearly show that as the total volume of the matrix increases with nanoparticle addition, so does the system's volume at close packing. The result is that there is little change in the system's corresponding free volume. These results, based solely on thermodynamic analysis, lead us to conclude that the segmental dynamics

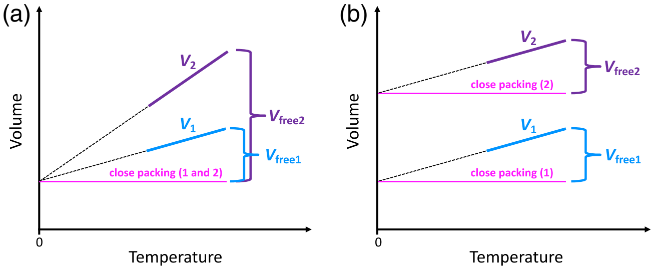

FIG. 3. Diagrams of two scenarios, (a) and (b), both where "system 2" has greater specific volume than "system 1," but where scenario (b) does not lead to a difference in free volume due to little difference in expansivity, $\mathrm{d}V/\mathrm{d}T$.

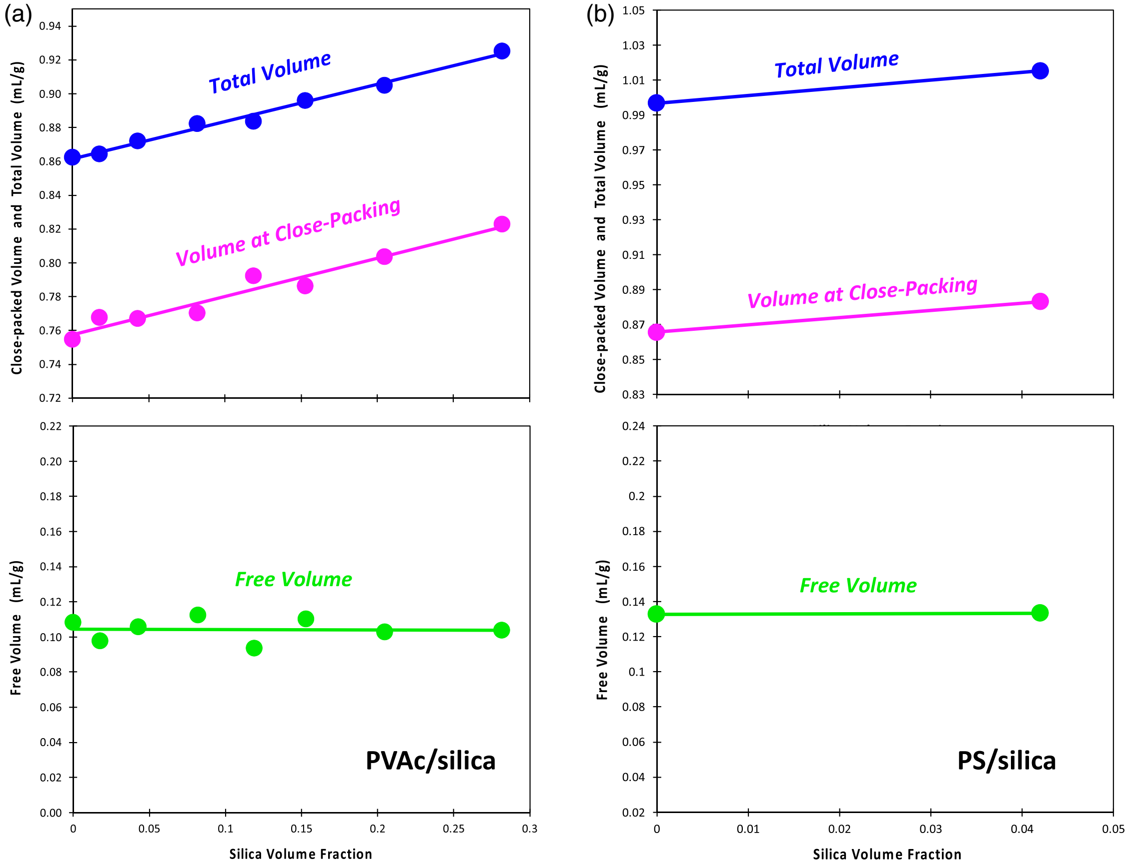

FIG. 4. Free volume predictions for polymer matrices as a function of silica nanoparticle loading: Free volume, total volume, and volume at close packing, based on LCL EOS analysis of matrix PVT data. Calculations at $T = 50\,^{\circ}\mathrm{C}$ and $P = 1$ atm for PVAc/silica, and $T = 140\,^{\circ}\mathrm{C}$ and $P = 1$ atm for PS/silica.

in a nanocomposite matrix should not be much different than that of the neat polymer and, indeed, that is what the experimentally measured dynamic relaxation data show.

We have noted above that for a given system the volume at close packing is independent of temperature and pressure. The results of Fig. 4 show that for these nanocomposites it does depend on nanoparticle concentration. Evidently, the presence of nanoparticles reduces the packing efficiency of the polymer matrix. We can speculate on how and why this might be happening. For example, findings from x-ray and neutron scattering experiments in Genix *et al.* [16,17] turn out to be aligned with the present analysis. These authors obtained local density profiles which showed a clear decrease (over a ~2 nm region) near the nanoparticle surface and they concluded it is driven by inefficient chain packing and folding. This points to the influence of polymer chain connectivity, e.g., polymer segments attached to the nanoparticle surface causing an effect on the configurations of the remaining mutually connected chain segments. If this is the case, then one might expect molecular weight to play a role, and the results from Cheng *et al.* [15] do clearly show this. Lower oligomeric molecular weight material did not exhibit any increase in specific volume, while the polymeric samples did. It was speculated [15,16] that the former can more readily adjust their conformation and achieve an efficiently packed equilibrium adsorption state, while the latter may be stuck in a quasistable nonequilibrium state.

An additional influence that might occur in some nanocomposites at higher nanoparticle concentrations is an excluded volume effect, e.g., from three or more nanoparticles coming together and excluding the space between them from the polymer segments. In such a case, the resulting excluded volume would show up in our analysis as having become part of V_{hc}, i.e., not contributing toward V_{free} because it does not contribute to segmental thermal expansivity.

Our thermodynamic analysis shows there to be little to no change in matrix free volume, therefore the CFV rate model noted above, $\tau \propto \exp[f(T) \times (1/V_{\mathrm{free}})]$, predicts there to be little to no change in dynamics. Other models that connect with thermodynamic aspects of molecular packing can do so through quantities such as the system's bulk compressibility (κ). The ECNLE model of Schweizer and co-workers [41,42] accounts for elastic contributions between the segments, as embodied in κ. Here, for the PVAc matrix there does not appear to be much change in κ upon nanoparticle addition, while for

PS, it appears to decrease a little, say, from about 0.00065 to 0.0006/MPa.

In summary, we have explained seemingly counterintuitive results where the specific volume of a polymer matrix in a nanocomposite was found to be significantly higher than that of the corresponding neat polymer, while the segmental dynamics remained unchanged. Analysis of independent *PVT* data for both systems showed a notable increase in the close-packed volume due to the presence of the nanoparticles in the composite. This additional volume, however, cannot be accessed by the molecular segments. Therefore the volume increase does not make it any easier for the segments to move around each other and rearrange; dynamic relaxation will not speed up if the increased amount of space in a material is not actually free.

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