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Rotational relaxation times of individual compounds within simulations of molecular asphalt models

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The dynamical properties of a complex system incorporate contributions from the diverse components from which it is constituted. To study this relationship in a multicomponent system, relaxation times based on rotation autocorrelation functions in molecular dynamics simulations were analyzed for molecules in two sets of unmodified and polymer-modified model asphalt/bitumen systems over 298–473 K. The model asphalt systems were proposed previously to approximate the chemical and mechanical properties of real asphalts. Relaxations were modeled using a modified Kaulrausch–Williams–Watts function and were based on the third Legendre polynomial of normal vector time correlation functions for aromatic species (asphaltene, polar aromatic, naphthene aromatic). Both the end-to-end vector and the longest axis eigenvector of the radius of gyration matrix were used for time correlation functions of chain molecules (C_{22} , polystyrene). Decreases in temperature induced large increases in relaxation time consistent with the Vogel–Fulcher–Tammann equation. The presence of a polymer slowed the decay of each correlation function to some extent. The product of relaxation time and diffusion coefficient revealed qualitative differences between larger and smaller molecules in the same system. These relaxation mechanisms remained coupled for small molecules, while the larger asphaltene and polymer molecules revealed significant slowdowns in rotation compared to translational diffusion at lower temperatures. Smaller values of the stretched exponential parameter β for asphaltenes compared to smaller molecules suggested a broader range of relaxation times and were consistent with this distinction. Difficulties in converging polymer chain relaxation times are discussed in terms of fluctuations in the magnitude and orientation of the end-to-end vector and chain axis eigenvector. Viscosity results suggested by the Debye–Stokes–Einstein relationship are consistent with trends shown in the literature for true bitumen systems. © 2010 American Institute of Physics. [doi:10.1063/1.3416913]

I. INTRODUCTION

Condensed phase systems of practical interest differ in many ways from idealized single-component counterparts. Such systems include petroleum and its derivatives, formulated polymers, and heterogeneous catalysts. Understanding such systems from a fundamental perspective requires knowledge of how different molecules within them contribute to overall dynamic response and functionality. First principles theories are lacking for how contributions among numerous molecule types combine into a rheological response function. In this work we resort to molecular simulations to quantify the dynamics of individual molecules within multicomponent systems that represent the chemical structures found in bitumen (termed asphalt in the US).

The chemistry of bitumen, which mainly comes from crude oil distillation and is widely used in road pavement,¹ plays an important but not always recognized role in mechanical properties. Bitumens are chemically classified based on their solubility in different solvents into asphaltene, resin, and maltene components. Asphaltenes have the largest sizes and make strong contributions to viscosity and polarity,

while maltenes are the least polar. Polar resins make intermediate contributions to viscosity. The balance of polarity² helps asphaltenes, resins, and maltenes intermix, keeping the system stable. Bitumens from different sources likely differ in their detailed chemistry but may have similar mechanical properties. Understanding the connections among rheology, the underlying chemistry and physics, and the influence of additives would aid with selecting bitumens and designing modifiers more effectively. Understanding the mechanisms by which single molecules impact bulk properties would have widespread applications beyond bitumen systems.

This work is part of an effort to understand the links between chemical composition and bitumen mechanical properties through computational models. It follows our earlier study³ on estimating viscosity at lower temperatures, where it cannot be predicted directly due to long molecule relaxations, via Debye–Stokes–Einstein (DSE) relationships among viscosity, self-diffusion coefficient, and rotational relaxation time; the latter properties are more amenable to numerical convergence and accurate estimation over a range of temperatures. The results are of more broad interest in terms of how relaxations of different molecules in a mixture respond to changes in temperature. Similar questions motivated by petroleum-derived systems were pursued by

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Freed,^{4–6} who investigated how the diffusion coefficients of n-alkanes in an n-alkane mixture depend on the distribution of chain lengths found in the mixture. Decoupling between translation and rotation was described by Lombardo *et al.*⁷ in a single-component glass-forming system. The results here that are of most general interest illustrate qualitatively significant decoupling between translational and rotational diffusion as a function of molecule size.

One challenge is to relate viscosity to single-molecule properties from a fundamental basis. Analysis of solvent drag on a sphere relates mixture and pure solvent viscosity using particle size, e.g., intrinsic viscosity in polymer solutions. The separation of length scales in this continuum analysis restricts applying it to mixtures in which molecule sizes are distributed across a range of sizes that lack a discrete/continuum gap.

Many past studies of small to moderate size molecules have interrelated viscosity η , self-diffusion coefficient D , and rotational relaxation time τ_r . Dote *et al.*⁸ formulated a DSE model relating viscosity, rotational relaxation time, and free space V_f per molecule,

$$\tau_r = KV_r\eta/k_B T. \quad (1)$$

The proportionality constant K included terms related to the shape and volume of the rotating molecule. They found good agreement among experimental data for numerous liquids. Pastor and co-workers⁹ and Mondello and Grest¹⁰ found in simulations of neat alkanes of short to moderate chain length that the viscosity/temperature ratio and rotational relaxation time scaled similarly, as implied by Eq. (1). Mondello and Grest further observed that diffusion occurred more quickly than expected from the relationship

$$\eta/T \sim 1/D, \quad (2)$$

in which the proportionality constant includes k_B and depends on radius of gyration and the molecular friction factor. They determined τ_r based on relaxation of the eigenvector corresponding to the smallest eigenvalue of the radius of gyration matrix. Ngai¹¹ explained that enhanced diffusion, compared to rotational relaxation time and viscosity, arises because different types of dynamical behavior are influenced differently by intermolecular cooperativity. For a mixture, he showed theoretically that significant diffusion enhancement occurs when the molecule under study and the overall system have comparable relaxation times; small Kaulrausch–Williams–Watts (KWW) exponents β occur under the same conditions. Smaller β also leads to a larger temperature dependence of the relaxation time for rotation and viscosity. Bedrov *et al.*¹² found better correlation of viscosity with diffusion coefficient than with rotational relaxation time at very high temperature for a complicated ring compound. Gordon^{13,14} correlated diffusion coefficient and viscosity via a drag coefficient and found scaling prefactors that depended on molecular shape. The product $D\eta/T$ was relatively insensitive to temperature and exhibited a density dependence that was sensitive to molecular structure. Lombardo *et al.*⁷ illustrated how several measures of translational and rotational diffusion decoupled as temperature decreased within simulations of o-terphenyl, with rotational relaxation time and vis-

cosity increasing by orders of magnitude compared to smaller slowdowns in diffusion rate. Kioupis and Maginn¹⁵ obtained viscosities, rotational relaxation times, and self-diffusion coefficients from simulations of hexane/hexadecane mixtures at 298.15 K. Their results can be described using a linear relationship between viscosity and rotational relaxation time of either component, and the $\tau_r D$ product was essentially constant for both components over a range of mole fractions. A common feature of these works on pure compounds and two-component mixtures is the analysis of mechanical relaxation via viscosity, self-diffusion, and rotational relaxation time.

Bitumen chemistry of model asphalts was represented within molecular simulations in our prior work^{16,17} by choosing one or several compounds to represent each solubility class of asphalt. The amounts of each molecule were chosen to replicate several compositional measures and properties (both physical and mechanical) of real asphalts. Next,³ viscosity was calculated at a high temperature directly from the instantaneous stress fluctuations in a molecular dynamics simulation. Changes in rotational relaxation time, determined from extrapolations of fits of the normal vector correlation function for asphaltene molecules, were used to estimate viscosities at low temperatures using a DSE relationship. The temperature dependences of DSE-based viscosity predictions for model asphalts were similar to those reported from experiments on various real asphalts. When applying the same procedure to naphthalene, our simulation results and DSE estimates agreed well with viscosity data from the literature.

The specific objective of this paper is to compare how the relaxations experienced by the many different molecules found in multicomponent systems simultaneously do or do not follow the DSE relationship. The complex bitumen systems chosen as examples include an n-alkane, small aromatics, complex aromatic compounds, and in some cases a polymer chain. Visualizations of the aromatic compounds, extracted from 400 K bulk simulations without polystyrene, are shown for reference in Fig. 1. These illustrate just a small number of the sizes and chemistries of molecules found in true bitumens.¹⁸ Two model asphalt systems are compared: a ternary system based on what we elsewhere labeled¹⁷ the “asphaltene2” molecule (a molecular structure first proposed by Groenzin and Mullins¹⁹) and a six-component system¹⁶ targeted toward asphalt AAA-1 of the Strategic Highway Research Program (SHRP).²⁰ Chemical details are provided in Sec. II. Two examples of polymer-modified systems were built by adding one polystyrene chain (50 repeat units and 2 hydrogen ends) to each of these systems;¹⁶ this was chosen since it is one block of the common styrene-butadiene-styrene (SBS) asphalt modifier. Computational limits prevented using a larger chain or more chains in order to probe system size effects. Our work contrasts with bitumen simulations of others in that we have focused on multicomponent systems rather than pure asphaltenes or “average” asphalt molecules.^{21–26}

Rotational relaxation time depends on molecular size. Small molecules relax quickly, while the largest molecules (asphaltene and polystyrene) have the longest relaxation times among all components.³ Surrounded by large and small

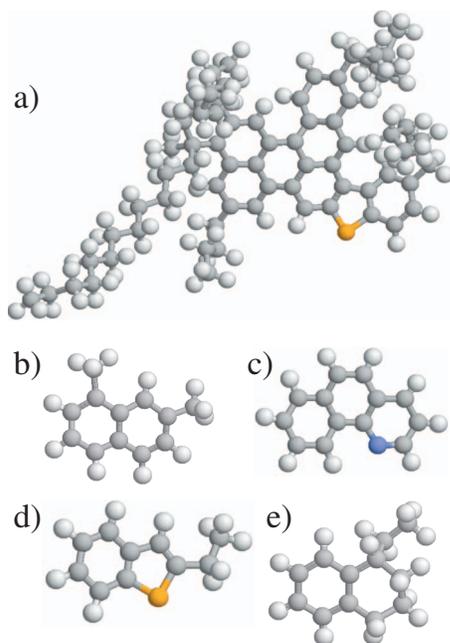


FIG. 1. Structures of (a) asphaltene2, (b) dimethylnaphthalene, (c) benzoquinoline, (d) ethylbenzothiophene, and (e) ethyltetralin, in configurations taken from within bulk simulations at 400 K. Intermediate and light shadings indicate carbon and hydrogen atoms. Dark shadings in (a) and (d) indicate sulfur and in (c) indicate nitrogen.

aromatic compounds and aliphatic chains, a polystyrene chain influences the local dynamics of surrounding molecules, and its local dynamics are influenced too. The effect of environment on all molecules is specifically addressed here. To quantify the contribution of polymer local dynamics to modification of asphalt properties, polymer correlation functions and relaxation times at different temperatures were investigated. Results are compared to those for asphaltene2 molecules, the second largest molecule present, and for smaller molecules. Large and small molecules are shown to display qualitatively different combinations of rotation and diffusion as temperature decreases.

II. SIMULATION DETAILS

Two model asphalt systems were investigated, and details about building them were described in earlier work.^{16,17} The system here termed modified “asphalt2” has polystyrene added to what was originally^{17,27} a ternary system (dimethylnaphthalene as a naphthene aromatic and n-C₂₂ as a saturate added to the asphaltene2 molecule). The modified AAA-1 system¹⁶ has polystyrene added to six components (asphaltene2; benzoquinoline, ethylbenzothiophene, and 3-pentylthiophene as polar aromatics; ethyltetralin as a naphthene aromatic; n-C₂₂ as saturate). It was originally devised to improve agreement with the chemical speciation²¹ of the SHRP AAA-1 system. Five and seven conditions were simulated in AAA-1 to analyze the temperature dependence of modified asphalt2 and AAA-1 systems: 473.15 (AAA-1 only), 458.15, 443.15, 400, 358.15, 333.15 (AAA-1 only), and 298.15 K. 443 K corresponds to the “hot mix” temperature reached during construction. The few simulations at higher temperatures were conducted to test the temperature

dependence of rotational relaxation times. Lower temperatures were chosen to assess a range of conditions down to ambient temperature. All simulations were at 1 atm pressure.

Molecules were initially placed on a cubic lattice, and conformations and positions were randomized in an isothermal-isobaric Monte Carlo simulation (Towhee program^{28,29}) for a small number of moves. Molecular dynamics simulations based on the all-atom OPLS-aa forcefield^{30,31} (as implemented in Towhee) and using LAMMPS (version 2001)^{32,33} were then conducted in order to equilibrate systems further. First, a velocity rescaling method in a constant volume and temperature ensemble was used for 100 ps with a time step of 0.5 fs to dissipate high energy interactions between molecules. Then, keeping the same time step, the isothermal-isobaric (*NPT*) ensemble using the Nosé-Hoover thermostat and barostat³⁴ was used to continue the simulation for at least 2 ns. After the system reached an equilibrium state, indicated by consistent and steady instantaneous volume fluctuations about the average volume, *NVT* simulation was continued for at least 8 ns with a timestep of 1.0 fs, with atom position data collected every 1 ps and stress-tensor data output every timestep. A molecular formalism³⁵ was used to describe the stress tensor. The modified asphalt2 system was rerun at 443.15 and 400 K starting from a different initial system configuration and polymer conformation. Initial polymer conformations were selected from a distribution calculated using the rotational isomeric state model³⁶ with an in-house code.

Correlation functions of unit vectors were calculated in order to analyze local dynamics. Based on our earlier work,³ we used the unit normal vector of aromatic rings for asphaltene2 molecules and small aromatic ring compounds. For chain molecules, we compared the end-to-end vector and the eigenvector that corresponds to the largest eigenvector of the radius of gyration matrix (following earlier studies^{10,13,14}). The end-to-end vector only incorporates atom position information of two atoms; full chain modes, which are the slowest, are neglected beyond their effects on end-group positions. More direct accounting for motions along the chain was accomplished by using the eigenvector, as described in detail by Gordon.^{13,14} Dot products of eigenvectors based on consecutive configurations were used to ensure that a consistent direction was followed; this was important for rare circumstances in which the first- and second-longest chain dimensions swapped temporarily. As in earlier work,³ we used the averaged time-dependent third order correlation function $\langle P_3(x) \rangle = (5\langle x^3 \rangle - 3\langle x \rangle) / 2$ to analyze the local dynamics of the unit vector correlation function $x(t) = \hat{u}(t) \cdot \hat{u}(0)$. P_3 correlation function results were regressed to a modified KWW (mKWW) function (weighted sum of exponential and stretched exponential),^{37,38}

$$P_{\text{mKWW}}(t) = \alpha \exp(-t/\tau_0) + (1 - \alpha) \exp(-(t/\tau_{\text{KWW}})^\beta), \quad (3)$$

using the same methods as earlier³ for nonlinear curve fitting and estimating standard deviations. The correlation time $\tau_c = \alpha\tau_0 + (1 - \alpha)\tau_{\text{KWW}}(1/\beta)\Gamma(1/\beta)$ was calculated through analytic integration of the mKWW regression function; at lower

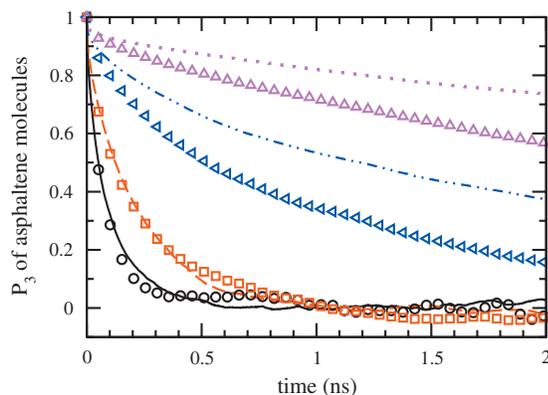


FIG. 2. Correlation functions for asphaltene2 molecules in unmodified and polymer-modified AAA-1 systems. Symbols indicate unmodified systems at (○) 443.15 K, (□) 400 K, (◁) 333.15 K, and (△) 298.15 K, while lines indicate modified systems at (—) 443.15 K, (— —) 400 K, (— · —) 333.15 K, and (·· ·) 298.15 K.

temperatures this included (often significant) extrapolation of the fit beyond the simulation time. From the Debye rule, this correlation time is related to the rotational relaxation time τ_r that is based on the first-order Legendre polynomial by $\tau_r = 6\tau_c$. The KWW stretched exponential relaxation corresponds to an approximation of the results found from exponential relaxations when there exists a distribution of relaxation times; a smaller exponent β corresponds to a wider distribution. Interpretations of bitumen rheology³⁹ are consistent with the presence of a broad distribution of exponential relaxation times. Efforts to infer the underlying distribution were not made in this work, beyond determining the average time τ_c and the approximate width information contained in β .

Self-diffusion coefficients were calculated from the mean-squared displacement of the center of mass, averaged over all molecules of the same type and over multiple time origins; results were reported previously.¹⁶ In previous work^{3,16} to calculate viscosity of polymer-modified systems, Green-Kubo and Einstein methods were used to calculate high temperature viscosity directly from stress fluctuations. Viscosity estimates at lower temperatures were made here using the scaling implied by Eqs. (1) and (2), neglecting temperature dependence of terms other than τ_c and D .

III. RESULTS AND DISCUSSION

A. Asphaltene and resin correlation functions

The third order rotational correlation functions P_3 in both polymer-modified model asphalt systems were calculated to analyze the effects of a neighboring polymer chain on asphaltene and resin dynamics. In both unmodified and modified AAA-1 systems (Fig. 2), asphaltene2 correlation functions showed a consistent increase in rotational relaxation time as temperature decreased, as found for ternary model asphalts that lack a polymer.³ At 443.15 and 400 K, the correlation function remained similar in the presence of a polymer. At 333.15 and 298.15 K, the correlation function decayed more slowly with a polymer present and exhibited a longer relaxation time.

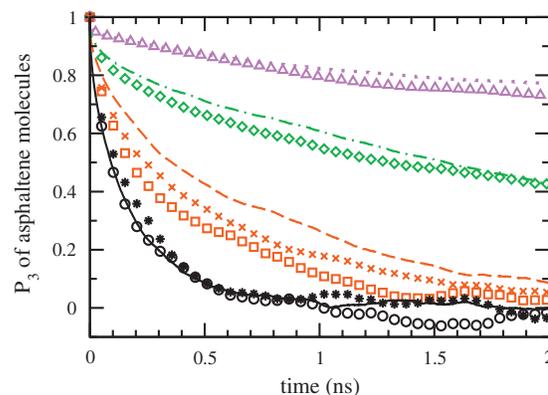


FIG. 3. Correlation functions for asphaltene2 molecules in unmodified and polymer-modified asphalt2 systems. Results at 358.15 K are indicated as (◇) unmodified and (— —) modified; results from run B are at (*) 443.15 K and (×) 400 K. Other symbols and lines match Fig. 2.

Asphaltene2 correlation functions have a consistent temperature dependence in unmodified and modified asphalt2 systems as well (Fig. 3). Repeating the simulation using different initial configurations emphasized similar results for unmodified and modified systems at 443.15 K. At 400 K (in two independent runs) and 358.15 K, the correlation function decay slowed in the presence of a polymer chain; the slowdown was apparent only at longer times at 298.15 K. This change in asphaltene2 relaxation contrasts with the larger decrease at low temperatures in the presence of a polymer in the AAA-1 system.

The effect of a polymer chain on resin molecule dynamics was analyzed using the P_3 correlation function as well. A typical result is shown in Fig. 4 for dimethylnaphthalene in the asphalt2 system. The P_3 correlation function relaxed to zero much more quickly than for asphaltene molecules. The presence of one polystyrene chain slowed rotational motions. Simulations starting with alternate polystyrene configurations at 443 and 400 K led to the same correlation function decays, suggesting convergence. Model fits using the mKWW function describe each correlation function well, and the logarithmic time axis emphasizes the distinction between the fast initial decay ($P_3=1$ at $t=0$) and the slow stretched exponential decay. The stretched exponential func-

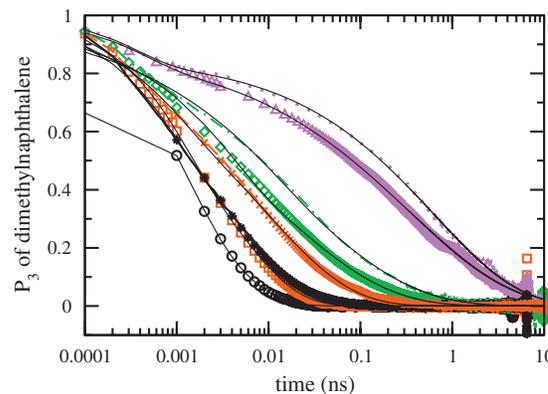


FIG. 4. Correlation function for dimethylnaphthalene molecules in unmodified and polymer-modified asphalt2 systems. Lines and symbols match those defined earlier. Thin lines indicate mKWW fits.

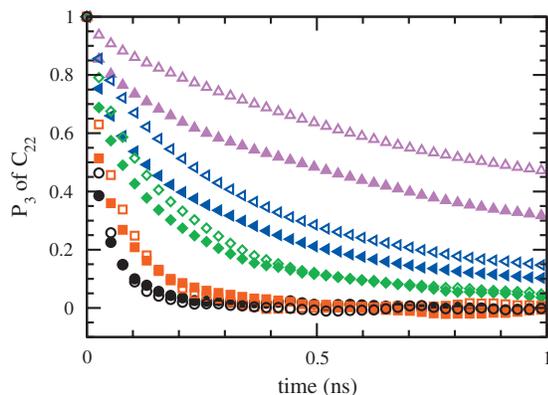


FIG. 5. Comparison of correlation functions based on eigenvector and end-to-end unit vector for $n\text{-C}_{22}$ molecules in the AAA-1 system at (○) 443.15 K, (□) 400 K, (◇) 358.15 K; (◁) 333.15 K, and (△) 298.15 K. Open symbols indicate end-to-end vector results while filled symbols eigenvector results.

tion is an empirical way to describe via few parameters the shape taken on by a system that relaxes via an underlying distribution of relaxation times.

The P_3 functions for benzoquinoline, ethylbenzothiophene, ethyltetralin, and pentylthiophene in the AAA-1 system show qualitatively similar behavior. The higher the temperature, the smaller the change in relaxation rate in the presence of a polymer. The larger the molecule, the more the relaxation time increased at lower temperatures. Results are shown in the supplementary material⁴⁰ and elsewhere.⁴¹

B. Chain molecule correlation functions

The local dynamics of polystyrene and $n\text{-C}_{22}$ chain molecules were analyzed using two different unit vectors. The end-to-end vector should relax with the longest relaxation time.⁴² An alternative is to analyze relaxation of the eigenvector that corresponds to the longest molecular axis.^{10,13,14} Those two methods should have consistent correlation results since they describe similar molecule movements from different viewpoints.

Results in Fig. 5 show that correlation functions based on the eigenvector and end-to-end vector for $n\text{-C}_{22}$ in the AAA-1 model asphalt system without polymer have moderate quantitative differences. Both show a consistent temperature dependence and the eigenvector correlation functions decay to zero consistently faster than end-to-end vector correlation functions at each temperature. The partial motions included in eigenvector dynamics speed relaxation compared to dynamics of the entire chain defined by the end-to-end vector. These results from $n\text{-C}_{22}$ provide confidence that both unit vectors can lead to qualitative trends for chain molecules, after sufficient averaging.

The presence of a polymer in AAA-1 systems had little effect on $n\text{-C}_{22}$ relaxations (Fig. 6). The end-to-end vector correlation functions decayed only slightly more slowly. In the asphalt2 system, the correlation functions for $n\text{-C}_{22}$ molecules also decayed slightly more slowly in the presence of a polymer at the two higher temperatures (Fig. 7). At the lower temperatures, a spontaneous crystallization event occurred during the simulations.⁴³ Chains that joined the crystallite

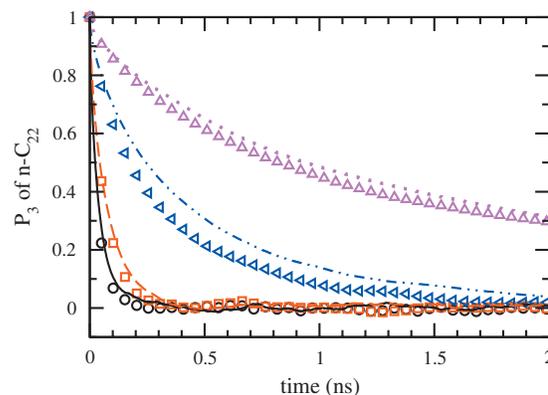


FIG. 6. End-to-end correlation function for $n\text{-C}_{22}$ in unmodified and polymer-modified AAA-1 systems.

ceased rotating, leading to a plateau in the P_3 correlation function. Results tabulated using only chains outside of the crystallite showed faster decays than in the presence of a polymer, consistent with results shown here for asphaltene, and the relaxation differences were more significant in magnitude than found for the model AAA-1 system.

We analyzed the eigenvector and end-to-end vector correlation functions for the polystyrene chain in the modified AAA-1 and asphalt2 systems at different temperatures. Detailed $\langle P_3 \rangle$ results and discussion are shown in the supplementary material.⁴⁰

C. Relaxation times and mKWW function

To determine rotational relaxation times for polymer and asphaltene2 molecules in AAA-1 and asphalt2 systems, nonlinear regression was performed using the mKWW function, Eq. (3), to describe the third order correlation function P_3 . This leads to parameters α , τ_0 , τ_{KWW} , and β . Here α represents the contributions of fast decaying rotational relaxations with a corresponding average relaxation time τ_0 . $(1-\alpha)$ represents contributions of the slow stretched decays.

Local relaxation times in polymers are influenced by both conformational dynamics and overall molecular reorientation.^{42,44} The longer the chain, the more conformational dynamics dominates the whole relaxation process. For long chain molecules, conformational dynamics dominates,

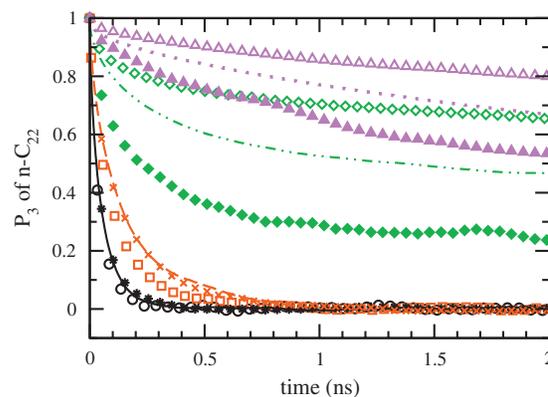


FIG. 7. End-to-end correlation function for $n\text{-C}_{22}$ in unmodified and polymer-modified asphalt2 systems. Filled symbols indicate results for chains that do not crystallize.

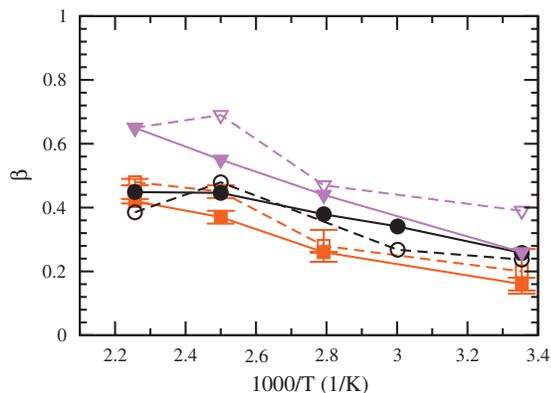


FIG. 8. mKWW parameter β for (∇) dimethylnaphthalene and for asphaltene2 molecules in the (\square) asphalt2 and (\circ) AAA-1 systems. Filled symbols and solid lines indicate polymer-modified systems.

so stretched decaying contributes most to polymer relaxation; i.e., $(1-\alpha)$ is closer to unity. As temperature decreases, relaxation time for conformational dynamics increases and τ_{KWW} increases. In addition, a decreased β corresponds to a broader relaxation time distribution.

Figure 8 shows the β parameters for asphaltene2 and some resin molecules. As temperature decreases, β decreases in a similar manner in each system. The β values for smaller molecules in these systems, such as the example shown for 1,7-dimethylnaphthalene, begin closer to unity and decrease similarly with temperature. The smaller values for asphaltene are consistent with the larger temperature dependence of its relaxation time, as described by the theory of Ngai.¹¹

Results for τ_0 and τ_{KWW} are shown in the supplementary material⁴⁰ and are summarized here. For small molecules such as dimethylnaphthalene, reorientation of overall molecules as a rigid body dominates the whole decaying process, so α is close to unity, especially at high temperatures. As temperature decreased, τ_0 increased. For multiaromatic compounds such as asphaltene, both parts are important and as temperature decreased, both τ_0 and τ_{KWW} increased.

The temperature dependences of relaxation times τ_c in different systems are shown in Fig. 9. The asphaltene2 molecule relaxation time–temperature relationship can be described by the Vogel-Fulcher-Tammann (VFT) equation, as shown earlier for the asphalt2 system.³

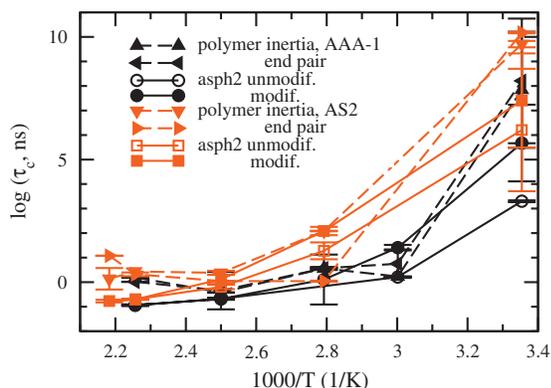


FIG. 9. Relaxation times for polymer (dashed lines, triangles) and asphaltene2 (solid lines, circles and squares) in model AAA-1 and asphalt2 unmodified (open symbols) and polymer-modified systems (filled symbols).

Figure S12 in the supplementary material⁴⁰ shows relaxation times for model resin and saturate molecules. C_{22} results are based on the end-to-end vector and are limited to molecules that do not crystallize. Compared to asphaltene and polymer results, the saturate and resin molecules show an Arrhenius-like dependence, as found earlier¹⁶ for self-diffusion coefficients in these systems. The exceptions to Arrhenius behavior for C_{22} at 358 K likely relate to more poor statistics for the few molecules that have not yet joined the crystallite and for a crystallization driving force that slows relaxation.

Different molecules show a different sensitivity to compositional change. In the AAA-1 system with a polymer, asphaltene2 relaxation time increased by a factor of 200 at 298.15 K compared to the system without polymer; increases were smaller at higher temperatures. In asphalt2 systems at 298.15 K, asphaltene2 relaxation time in the presence of a polymer increased by a factor of $10^{1.2} \approx 16$ compared to the unmodified case, while dimethylnaphthalene relaxation time increased by $10^{0.07}$ times and $n\text{-}C_{22}$ increased by $10^{0.3}$ (for chains not joining the crystal). In terms of absolute magnitude, asphaltene2 molecules increased their relaxation time the most, although considering that its τ_c standard deviation among different mKWW fits can reach 10^9 , its difference in relaxation time is relatively small. The relative changes for dimethylnaphthalene and $n\text{-}C_{22}$ molecules are smaller. The asphaltene2 relaxation time increased more in the modified system than in the unmodified system as temperature decreased, and the increase was by a larger factor than in AAA-1.

D. Polymer analysis and discussion

Relaxation times determined using the eigenvector and end-to-end vector for polystyrene show inconsistent relaxation time–temperature dependences in both systems. These polymer relaxation times (dashed lines in Fig. 9) follow the approximate trends shown by the asphaltene relaxation times (solid lines), although results at higher temperatures are inconsistent with each other. Specifically, polymer relaxation time in the AAA-1 system at 333.15 K is shorter than at 443.15 K. In asphalt2 systems, polymer relaxation time is longer than that of asphaltene2 molecules at 298.15, 443.15, and 458.15 K, while at 358.15 and 400 K the polymer relaxation time is shorter. The inconsistency is problematic in part because it interferes with using temperature-dependent changes in relaxation time to estimate viscosity via the DSE equation,^{8,14} as done in the absence of a polymer.³

The inconsistent polymer temperature behavior can be related to several causes. One is poor statistics. Both model asphalt systems contain only one polymer chain, and it needs a longer simulation time than an asphaltene to relax. A single chain may be insufficient for properly sampling configuration space and evaluating time correlation functions. A second reason could be anomalous local dynamics of the chain start and end. If the polymer start and end are close to each other and are surrounded by smaller, faster moving molecules, then the end-to-end correlation function could decay to zero faster than it would when averaged over many pos-

TABLE I. Average polymer end-to-end distances in AAA-1 and asphalt2 systems

System	Temperature (K)	Average distance (Å)	Standard deviation (Å)
AAA-1	443.15	30.0	12.0
	400	17.3	5.7
	358.15	15.7	2.6
	333.15	22.3	4.0
	298.15	31.9	9.9
Asphalt2	458.15	33.9	10.5
	443.15, run A	37.3	11.9
	443.15, run B	37.7	10.3
	400, run A	16.8	7.4
	400, run B	27.2	4.8
	358.15	16.5	8.4
	298.15	32.3	3.1

sible configurations. That can cause an abnormally fast apparent polymer relaxation. Another possible reason could arise from changes in physical properties. For example, a glass transition or plasticizing effect induced by local concentration of other molecules could occur in the temperature range studied. Bulk polystyrene has its glass transition temperature at 373 K, which is in the middle of the temperature range simulated, and Bauer *et al.*⁴⁴ have found that polystyrene exhibits a plasticizing effect at specific solvent concentrations. Nonrandom concentrations of smaller molecules near the chain start or end that differ with temperature (due to poor sampling) could induce anomalously fast relaxation for those portions of the chain. Several calculations were performed to investigate these hypotheses about the inconsistent polymer time–temperature behavior.

The average polymer end-to-end distance and its standard deviation were calculated to assess differences in configuration. The widely disparate values, shown in Table I, indicate that a chain in a single simulation was unable to sample over the full range of possible configurations. The standard deviations thus represent fluctuations about local minima. In a theta solvent, a polystyrene chain of this size would have a root-mean-square end-to-end distance of 48.9 Å, based on a characteristic ratio of 10.2 (Ref. 45) and 100 bonds of 1.53 Å. The smaller average magnitudes indicate configurations here that are more characteristic of poor solvent behavior. This is more likely an artifact of the configurations chosen than of chain rearrangement in response to solvent environment.

In the AAA-1 systems, two different initial polymer configurations were used. Simulations at 400, 358.15, and 333.15 K based on one initial configuration led to end-to-end distances and standard deviations that are smaller than those at 443.15 and 298.15 K, which were initiated using the other configuration. Since the two ends are closer, smaller collective motions can lead to faster correlation function decays, even while the whole molecule only occasionally experiences large-scale conformational motions. The small chain size leads to artificially fast relaxation at those temperatures,

which leads to relaxation times whose dependence parallels the end-to-end distance rather than the temperature.

Similarly, in the asphalt2 systems at 358.15 and 400 K (run A), the average end-to-end distances are smaller than those at the other three temperatures. The distance fluctuations at 358.15 K span a wider range than that at 400 and 298.15 K. The end-to-end distances at 443.15 K are consistent with each other, but the chain size is a bit larger than in the AAA-1 system at 443.15 K or in the asphalt2 system at 458.15 K. The shorter and comparable relaxation times at 400 and 358.15 K, respectively, compared to 443.15 K, are likely a consequence of their smaller end-to-end distance.

Sampling of the end-to-end vector can be probed by studying its orientation in addition to its magnitude. Orientation was defined by the spherical coordinate angles of the end-to-end vector compared to the edge vectors of the simulation box (i.e., the laboratory frame). The angle $\phi = \cos^{-1}(r \cdot z)$ indicates orientation relative to the z axis while θ (the angle between the x axis and the x – y projection of r) indicates motions in the x – y plane. The more motions that occurred, the better the sampling, as long as the end-to-end distance is large enough.

Figure S8 in the supplementary material⁴⁰ shows that at 400 and 358.15 K in the modified asphalt2 system, the end-to-end unit vector experienced more significant fluctuations than that at 443.15 K in both angles. The end-to-end distance indicates that this is possible since the vector magnitude is much smaller at 400 and 358.15 K than at 443.15 K. This reinforces how local vibration movements at 400 and 358.15 K enable apparent conformational relaxation despite relatively small position changes. Figures S6 and S7 in the supplementary material⁴⁰ show time correlation function relaxations based on vectors from the chain center to both ends, in both AAA-1 and asphalt2. These averaged results (two halves per chain) relax at rates that are more consistent with the temperature dependences found for other molecules. Sampling of more widely spaced regions of polymer chain configuration space are required to obtain more accurate averaged time correlation functions for polymer conformation.

E. Translation–rotation diffusion product

The product of rotational relaxation time and diffusion coefficient probes how temperature affects translational and rotational modes of mechanical motion. The DSE relationships [Eqs. (1) and (2)] suggest viscosity exhibits direct and inverse relationships with τ_c and D , respectively; thus the product $\tau_c D$ should remain constant when rotational and translational diffusion contribute similarly to viscosity. Breakdowns in this relationship have been theorized¹¹ and observed previously⁷ in simulations of a pure compound.

Results for the $\tau_c D$ product are shown in Fig. 10 for the polymer, asphaltene, and resin molecules in the model asphalt systems. All four of the modified and unmodified systems show a similar pattern. The $\tau_c D$ product increases by orders of magnitude for the polymer and asphaltene2 molecules as temperature decreases, particularly at 358 K and cooler. Assuming that viscosity relates more directly to rotation than to translation when this decoupling occurs, as sug-

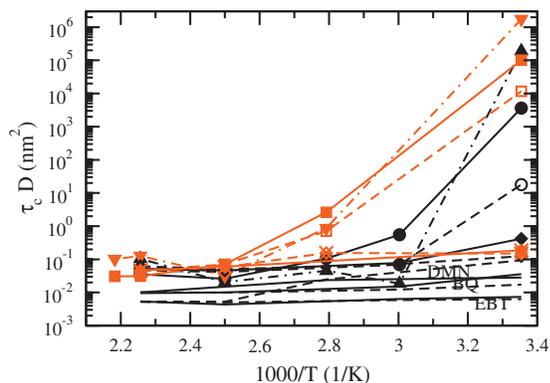


FIG. 10. Product of single-molecule rotational relaxation time and self-diffusion coefficient in (open symbols and dashed lines) unmodified and (filled, solid) polymer-modified model asphalt systems for (triangles) polymer, (O, \square) asphaltene, (\diamond) saturate, and (no symbol) model resin molecules (DMN) dimethylnaphthalene, (BQ) benzoquinoline, (EBT) ethylbenzothioophene. Downward triangles, squares, and diamonds with an overlapping \times symbol indicate asphalt2 systems.

gested by Mondello and Grest,¹⁰ Lombardo *et al.*,⁷ and Ngai¹¹ when interpreting their simulations and theory, this indicates polymer and asphaltene center-of-mass self-diffusion that occurs more quickly than expected based on the system viscosity. This also suggests that either asphaltene or polymer relaxation time may be used to estimate system viscosity. The $\tau_c D$ products for the saturate chain and the model resin molecules remain closer to constant across this temperature range, with a slight increase for dimethylnaphthalene in the asphalt2 system. Rotation and self-diffusion remain coupled for these smaller compounds across the range of temperatures simulated. The presence of a polymer changes the quantitative $\tau_c D$ product but does not affect its general trend. This qualitative change as a function of molecule size indicates a breakdown in the mechanistic relationships among diffusion coefficient, rotational relaxation time, and viscosity, since not all of the scalings $\eta/T \sim \tau_c \sim 1/D$ can be maintained. The $\tau_c D$ temperature dependence is a key difference between larger and smaller molecules in model asphalt systems. More generally, it indicates that molecules of disparate sizes in a multicomponent system may show qualitatively different dynamic behavior upon cooling, even without passing through a glass transition. Translation and rotation can decouple for larger molecules while they remain coupled for smaller molecules.

F. Viscosity prediction

The rotational relaxation times and viscosity at high temperature were next used to estimate the viscosity of model asphalt systems at lower temperatures. In earlier work,³ we estimated viscosity for unmodified ternary asphaltene2-based and asphaltene1-based systems (i.e., asphalt2 and the asphalt1 equivalent) at 400, 358.15, and 298.15 K based on the temperature dependences of the DSE relationship, with an assumption that the molecule volume and system-dependent numerical prefactor have a qualitatively negligible temperature dependence. In those model asphalt systems, the as-

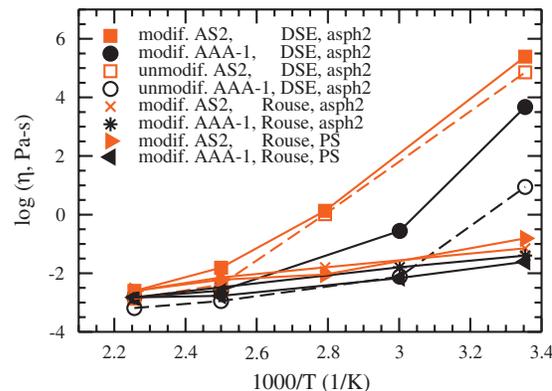


FIG. 11. Viscosity estimated from DSE Eq. (1) and Rouse/SE Eq. (2). Dashed and solid lines indicate results in unmodified and polymer-modified systems.

phaltene molecules are the largest and have the longest relaxation times, so they provided the basis for viscosity estimates.

Here we apply that technique to the AAA-1 model asphalt system. In earlier work,¹⁶ we directly calculated a AAA-1 system viscosity of 6.5×10^{-4} Pa s at 443.15 K, using both Green-Kubo and Einstein methods. Applying the DSE relationship using the asphaltene relaxation times at different temperatures, we estimate a viscosity that reaches 8.77 Pa s at 298.15 K (Fig. 11). This room temperature viscosity is almost three orders of magnitude lower than those of asphalt2 and model ternary asphaltene1-systems³ and is also much lower than SHRP AAA-1 asphalt.

In polymer-modified systems, the same approach suggests using the polymer relaxation time to scale the viscosity to lower temperatures. At 458.15 K in the polymer-modified systems, the simulation time is less than the asphaltene relaxation time $\tau_r \approx 6\tau_c \approx 6 \times 10^{0.2}$ ns estimated from molecule reorientation (P_3) calculations. Thus the stress correlation times are not long enough to estimate viscosity from Green-Kubo or Einstein calculations; results in other systems^{10,46,47} suggest that durations of over 100 relaxation times are required for accurate direct viscosity estimates. The viscosities from longer simulations at 443.15 K are used instead. These were estimated in earlier work¹⁶ using Green-Kubo and Einstein methods as 1.5 and 2.5 cP for the modified AAA-1 and asphalt2 system viscosities, respectively. In polymer-modified AAA-1 and asphalt2 systems, polystyrene replaced asphaltene as the largest molecule and its relaxation time is expected to be longer than that of asphaltene2. The inconsistent temperature dependence discussed above for the polymer relaxation time results raises concerns about the feasibility of using the DSE equation to estimate the viscosity of polymer-modified systems. An alternative using asphaltene relaxation is pursued below, and an approach using free volume is being pursued elsewhere.⁴⁸

In both polymer-modified AAA-1 and asphalt2 systems, the asphaltene2 is the second largest molecule and its correlation function shows a consistently slower relaxation as temperature decreases, as shown in Figs. 2 and 3. Furthermore, trends for τ_c and the $\tau_c D$ product were similar for the polymer and asphaltene molecules. Thus one alternative is to

use asphaltene2 relaxation times in polymer-modified systems for estimating viscosity using the DSE equation. Results are shown in Fig. 11.

At each temperature, the predicted viscosity of both systems increased after adding one polymer. At 298.15 K, the viscosity increased by factors of $10^{2.7}$ for the AAA-1 system (circles) and $10^{0.6}$ for the asphalt2 system (squares). The reason for the smaller relative increase in the asphalt2 system is not known. We suspect it is due to the higher viscosity of the unmodified asphalt2 system, making the increase in viscosity upon adding a polymer larger in absolute terms but smaller in relative terms. The increase in viscosity at low temperature beyond a linear Arrhenius dependence, which was calculated for both systems, is consistent with the fragile viscosity–temperature dependence reported⁴⁹ for a real asphalt.

The Rouse model⁴² relates viscosity and diffusion coefficient for chain molecules; thus in both polymer-modified systems it is possible to estimate temperature dependence of viscosity based on the polymer chain diffusion coefficient. Such results here neglect any temperature dependence of the density and radius of gyration, which are expected to be small in comparison. Temperature effects on radius of gyration taken directly from our simulation results are neglected due to the poor statistics discussed above. The Rouse temperature dependence is consistent with the Stokes–Einstein relationship, Eq. (2). Polystyrene showed the slowest diffusion rate at each temperature, but the temperature dependence of its diffusion coefficients showed some noise,¹⁶ so for both systems we compared using asphaltene2 and polymer diffusion coefficients to estimate the viscosity. All four sets of results are shown in Fig. 11. The estimated viscosity changes based on diffusion coefficients are similar to one another and are much smaller than those estimated using rotational relaxation time. These results are consistent with our prior results³ for unmodified model asphalts. Using polymer diffusion coefficients led to higher viscosity estimates at 298.15 K in the asphalt2 system (right-pointing triangle) but lower viscosity in the AAA-1 system (left triangle), compared to estimates based on asphaltene2 diffusion coefficients.

The asphalt2 system viscosity at 298.15 K calculated earlier³ is lower than that of true SHRP asphalts.⁵⁰ The viscosity calculated for model AAA-1 asphalt is much lower than those calculated for asphalt2 and asphalt1 systems and thus much lower than that of SHRP asphalts at room temperature. What could be responsible for this low viscosity prediction? We think the lower viscosity most likely resulted from the large number of small molecules in the model AAA-1 system. Compared to the asphalt2 system, the number of asphaltene2 molecules in AAA-1 almost doubled while the number of small molecules almost tripled. Thus each asphaltene2 molecule had more small molecule neighbors on average than in the asphalt2 system. Those large number of small molecules can relax quickly, which leads to faster asphaltene2 relaxation. Based on an inverse relationship between viscosity and the rates of translation and rotation through which stress is transmitted, the predicted viscosities of AAA-1 systems decreased a lot. In future studies,

choosing larger resin molecules for model asphalt systems and controlling their concentration (relative to asphaltenes) are important to ensure satisfactory viscosity results. The importance of molecule size is supported by experiments of Storm *et al.*,⁵¹ who found that temperature and asphaltene concentration are vital factors influencing asphalt viscosity.

IV. CONCLUSIONS

In order to compare relaxations of different size compounds within a multicomponent system and to analyze effects of a polymer on model asphalt properties, temperature-dependent local relaxation dynamics in asphalt2 and AAA-1 systems were analyzed via rotational correlation functions and self-diffusion coefficients determined from molecular dynamics simulations. In both asphalt2 and AAA-1 systems, the large asphaltene2 and small aromatic molecules have consistent relaxation time–temperature dependences. Consistent correlation function results were obtained for n-C₂₂ at different temperatures using either a major axis eigenvector or end-to-end vector, with eigenvector correlation functions decaying consistently faster than those of the end-to-end vector. Overall relaxation time τ_c followed a VFT dependence for asphaltene and polymer molecules, consistent with the fragile nature reported⁴⁹ for asphalt viscosity. Relaxation times for smaller molecules followed an Arrhenius dependence.

The product $\tau_c D$ of rotational relaxation time and diffusion coefficient indicated qualitative differences between large and small molecules within the multicomponent systems simulated. The larger molecules (polymer and asphaltene) showed dramatically slower rotations as temperature decreased; translation decoupled and slowed less at lower temperature. Smaller resin molecules maintained coupling between rotation and translation, as evidenced by a near-constant value of the $\tau_c D$ product across the range of temperatures simulated. This breakdown indicates that the larger molecules control the temperature dependence of viscosity. Smaller mKWW β values for the asphaltene were consistent with this interpretation. The temperature-dependent viscosity of AAA-1 systems was much lower than viscosity reported in experiments on real asphalts.

The eigenvector and end-to-end vector correlation function results for an added polystyrene chain were not consistent; instead there was an inconsistent relaxation time–temperature dependence over the temperature range simulated. Analysis revealed that inconsistent relaxations for the polymer could come from significant differences in average chain size, which indicates insufficient sampling in modified systems for the single polymer molecule, which is the largest and slowest moving. End-to-end distance showed that some chains were in conformations with close ends, making the end-to-end vector relax anomalously quickly compared to the major axis eigenvector. By subdividing a polymer into two halves and analyzing average correlation function temperature dependence, a consistent temperature dependence in AAA-1 system was observed. A further contribution could arise from a plasticization-type effect in which portions of the polymer chain that neighbor smaller

molecules relax quickly compared to portions near less small molecules. Such a distinction in relaxation along the backbone could be an artifact of a total simulation time that is shorter than the overall chain relaxation time.

In total, adding one polymer into the asphalt2 and AAA-1 systems exerted quantitative slowdowns on the relaxation rates but did not invoke qualitative modifications to the dynamics, as probed by rotational correlation functions.

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