RHEOLOGICAL AND THERMODYNAMIC PROPERTIES OF MODEL ASPHALT USING FFT AND GROUP CONTRIBUTION METHODS

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RHEOLOGICAL AND THERMODYNAMIC PROPERTIES OF MODEL ASPHALT USING FFT AND GROUP CONTRIBUTION METHODS

BY

MOHAMMAD MASOORI

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
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DOCTOR OF PHILOSOPHY DISSERTATION

OF

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UNIVERSITY OF RHODE ISLAND
2015
Asphalt is an amorphous material whose mechanical performance relies on viscoelastic responses to applied strain or stress. High quality pavement can enhance the commute experience and also can reduce the risk of accidents as well as preventing air pollution. Furthermore, it also can reduce the need for expensive reconstruction and maintenance of roads. Having a broad understanding of asphalt chemistry is the key to understand and improve mechanical properties of this material. Although asphalt is a widely seen material, our knowledge about its molecular structure and properties is limited. Molecular simulations of asphalts can be exploited to infer how the actions of individual molecules contribute to the nanoscale mechanical behavior of a model system.

In this work, chemical composition and its effect on the viscoelastic properties of asphalts have been investigated by computing complex modulus from molecular dynamics simulation results for two different model asphalts (Zhang, L., & Greenfield, M. L. (2008). Energy Fuels, 22(5), 3363–3375 [ZG08] and Li, D. D., & Greenfield, M. L. (2014). J. Chem. Phys., 140(3), 034507 [LG14]) whose compositions each resemble the Strategic Highway Research Program AAA-1 asphalt in different ways. Results from equilibrium molecular dynamics simulations these have been interpreted by converting the stress relaxation modulus $G(t)$ to the complex modulus and phase angle delta. Complex modulus at different temperatures have been calculated using fast Fourier transform to study the effect of temperature on viscoelastic properties of asphalt models. Because of inherent noise, any comparison was challenging. To remove the noise, signal processing techniques have been exploited. Signal processing techniques enhanced the clarity of the results and enabled removing the noise from the modulus results. The LG14 system contains larger molecules, and its results have shown a very good agree-
ment with the low and high frequency scaling limits of the Maxwell model within the frequency ranges spanned by the molecular dynamics simulations, while results for the ZG08 model asphalt only follow the high frequency scaling limits of the Maxwell model. A Black plot or van Gurp-Palman plot of complex modulus vs. phase angle for the LG14 system suggests some overlap among results at different temperatures for less high frequencies, with an interdependence consistent with the empirical Christensen-Anderson-Marasteanu model. Both model asphalts are thermorheologically complex at very high frequencies, where they show a loss peak that appears to be independent of temperature and density.

While molecular simulation can provide relatively accurate results, it is computationally expensive. To provide a faster approach to determine the relationship between the asphalt chemistry and macroscale properties, an equation of state (EOS) can be used. Most equations of state need critical properties which are not always available for all compounds. Since most molecules within the ZG08 and LG14 model asphalts are hypothetical molecules and no experimental data are available for them, a group contribution method by Nannoolal et al. (Nannoolal, Y., et al. (2004). Fluid Phase Equilib., 226, 45–63; Nannoolal, Y., et al. (2007). Fluid Phase Equililib., 252(1-2), 1–27; Nannoolal, Y., et al. (2008). Fluid Phase Equilib., 269(1-2), 117–133) has been applied for all molecules in both model asphalts to determine their critical properties and acentric factors. These provide the required properties to use in a common cubic EOS, e.g., Peng-Robinson (PR), to predict phase behavior of multicomponent systems. The results for densities and thermal expansion have been compared to experimental results. Since cubic equations of state do not predict liquid density precisely, COSTALD volume translation has been applied to improve density predictions. The results from PR EOS were quite good but the results from molecular dynamics were better. This fact should
not devalue the EOS results because an EOS calculation is much faster and takes a fraction of one step of molecular simulation time. The result from PR without COSTALD volume translation for thermal expansion was even better than results from molecular dynamics. By knowing asphalt phase behavior, one can predict its performance in the real world. For example, rutting of asphalt is usually related to the waxy molecules within asphalt mixture. Precipitation of waxes can cause the cracking of asphalt pavement as well as increase asphalt mixture viscosity during compaction of asphalt pavement. To predict this phenomenon, precipitation of squalane was investigated. The chemical potential of pure squalane (as a waxy compound) and squalane in the multicomponent system have been estimated. To calculate the Gibbs free energy required to study phase behavior of asphalt, the critical properties of molecules were calculated using the Nannoolal et al. correlations. The chemical potential of pure squalane somewhat below its melting point was lower than its chemical potential in the multicomponent system, which suggests that squalane will precipitate below its melting point. The temperature that the wax precipitates can help to choose the right asphalt binder for a specific location.

In total, the approaches used here provide ways to model how differences in asphalt can affect thermodynamic and mechanical properties. Signal processing can help remove the noise from data which leads to a better understanding and interpretation of the results. Having equation of state parameters for a system will help to predict phase stability of the asphalt systems at different conditions.
ACKNOWLEDGMENTS

This work presented was conducted with Prof. Michael L. Greenfield as my academic advisor. I want to especially thank Prof. Greenfield for all the inspiration and discussion throughout the work. He has helped me become a better person not just being a better researcher. I also have to thank Prof. Richard J. Vaccaro, my defense chair for his valuable comments. I also have to thank Prof. Samantha A. Meenach, my defense committee member, for her comments and her books! I wish to express my sincere gratitude to all faculties for their help and what they taught me. I would also thank my friends for their help and support during my studies. I have to thank all the staffs of the Department of Chemical Engineering and University of Rhode Island for their efforts and help during my graduate school. I would also like to thank Mr. and Mrs. Harrison for supporting me during my stay in the United States and helping me to feel like home, I will always remember them as my grandparents not my neighbors. I would also like to thank Mr. and Mrs. Ferguson for their help during my settlement in the States. Last but definitely not the least, I would like to thank Federal Highway Administration and Asphalt Research Consortium through the Western Research Institute and the Rhode Island Department of Transportation for their financial support.
To those who have always supported me.
PREFACE

This thesis is in manuscript format. The following journal paper has been published from the research work presented and it is included in this thesis as chapter 1:

1. Masoori, M. & Greenfield, M. L. (2014). “Frequency analysis of stress relaxation dynamics in model asphalts”, The Journal of Chemical Physics, 141(12), 124504. doi:10.1063/1.4895972

The following journal papers are under preparation to be submitted from the research work presented:

1. Masoori, M. & Greenfield, M. L. (2015). “Using Signal Processing Techniques to Reduce Noise in Computed Correlation Functions”, In preparation for The Journal of Chemical Physics

2. Masoori, M. & Greenfield, M. L. (2015). “Equation of State Modeling of Bitumen Thermodynamic Properties”, In preparation for Industrial & Engineering Chemistry Research

The following presentations and posters have been presented from this research work:

1. Greenfield, M. L., Masoori, M., Li, D. D., & Zhang, L. (2014). Detailed Molecular Simulations Of Model Bitumens To Inter-relate Chemistry And Mechanical Properties. In 15th International Conference on Petroleum Phase Behavior and Fouling. Galveston, TX, USA.

2. Masoori, M. & Greenfield, M. L. (2013). Frequency Interpretation of Molecular Asphalt Relaxation Processs. In Petersen Asphalt Research Conference. Laramie, Wyoming, USA.
3. Masoori, M. & Greenfield, M. L. (2013). Storage and Loss Modulus of Model Asphalts. In Graduate Research Symposium, University of Rhode Island. Kingston, RI, USA.

4. Masoori, M. & Greenfield, M. L. (2013). Thermorheological Behavior of Model Asphalt. In The AIChE Annual Meeting. San Francisco, CA, USA.

5. Masoori, M. & Greenfield, M. L. (2012). Effects of Asphalt Compositions on Nanoscale Properties by Molecular Simulation. In The AIChE Annual Meeting. Pittsburgh, PA, USA.

6. Masoori, M. & Greenfield, M. L. (2012). Multiscale Modeling of Asphalt System. In Graduate Research Symposium, University of Rhode Island.

7. Masoori, M. & Greenfield, M. L. (2012). Storage and Loss Modulus of Model Asphalts. In Foundation Of Molecular Modeling and Simulation (FOMMS). Portland, Oregon, USA.
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MANUSCRIPT 1

Frequency Analysis of Stress Relaxation Dynamics in Model Asphalts

The following manuscript has been published in The Journal of Chemical Physics.

• Masoori, M. & Greenfield, M. L. (2014). “Frequency analysis of stress relaxation dynamics in model asphalts”, The Journal of Chemical Physics, 141(12), 124504. doi:10.1063/1.4895972.
1.1 Abstract

Asphalt is an amorphous or semi-crystalline material whose mechanical performance relies on viscoelastic responses to applied strain or stress. Chemical composition and its effect on the viscoelastic properties of model asphalts have been investigated here by computing complex modulus from molecular dynamics simulation results for two different model asphalts whose compositions each resemble the Strategic Highway Research Program AAA-1 asphalt in different ways. For a model system that contains smaller molecules, simulation results for storage and loss modulus at 443 K reach both the low and high frequency scaling limits of the Maxwell model. Results for a model system composed of larger molecules (molecular weights 300 to 900 g/mol) with longer branches show a quantitatively higher complex modulus that decreases significantly as temperature increases over 400 to 533 K. Simulation results for its loss modulus approach the low frequency scaling limit of the Maxwell model at only the highest temperature simulated. A Black plot or van Gurp-Palman plot of complex modulus vs. phase angle for the system of larger molecules suggests some overlap among results at different temperatures for less high frequencies, with an interdependence consistent with the empirical Christensen-Anderson-Marasteanu model. Both model asphalts are thermorheologically complex at very high frequencies, where they show a loss peak that appears to be independent of temperature and density.

1.2 Introduction

Asphalt has been a widely used material since ancient eras. Roberts et al.[1] cite the use of asphalt in shipbuilding in Sumeria as long ago as 6000 B.C, for example. Despite this long history, a thorough description of how asphalt chemistry directly impacts its mechanical properties has been incomplete. Progress in understanding asphalt[2, 3, 4] and asphaltene[5] chemistry is enabling advances that link
asphalt chemistry to physics and mechanics. Achieving such a deep understanding of asphalt mechanical properties can help to understand pavement mechanical behavior and to improve pavement performance and durability.[6]

The aim of this paper is to calculate viscoelastic properties of proposed model asphalt systems via frequency analysis of stress relaxation dynamics. Stress correlations from equilibrium molecular dynamics simulations[7, 8] using two different model systems [9, 10] that each represent the atomic composition of asphalt AAA-1 of the Strategic Highway Research Program (SHRP)[11] have been investigated by calculating storage and loss moduli from stress relaxation modulus data. Results are compared to simulation results of others and to experimental results available in the literature for real asphalts.

The SHRP revolutionized the mechanical tests that are employed to characterize asphalts and bitumens.[12] Tests such as viscometry and penetration were found to be inadequate for estimating asphalt performance. Instead, thermal and rheological tests such as complex modulus and viscosity were found to provide a more thorough understanding of asphalt characteristics, including estimates of asphalt mechanical performance and elasticity.[1] While magnitude and temperature dependence of complex modulus and viscosity describe many asphalt mechanical properties,[12] asphalts with comparable complex modulus under certain conditions show different performance in “real world” pavement applications because of independent behaviors of other mechanical properties.[1, 6, 13]

Another challenge of asphalt is the composition of its components. Because different asphalts come from different crude oil sources, they have different chemical components and different properties.[1] Asphalt generally contains approximately $10^5$ to $10^6$ different molecule types.[14] It can be separated into at least three different fractions — asphaltenes, resin, and maltene — that range from least non-
polar and most viscous to most non-polar and least viscous. Asphaltene molecules are considered to have a great role in the viscosity of bitumen. [1, 6] Asphalt nano-scale structure also affects its properties. [4] Aging asphalt changes its properties further. [2]

Asphalts have been characterized since the SHRP by using complex modulus. Storage modulus, $G' (\omega)$, is a measure of energy stored and recovered per cycle of sinusoidal deformation and can be related to stress relaxation modulus $G(t)$ by [15]

$$G' (\omega) = G_e + \int_0^\infty [G(t) - G_e] \sin(\omega t) \, dt \quad (1)$$

$G_e$ is the equilibrium tensile modulus and can be calculated by $G_e = \lim_{t \to \infty} G(t)$, and it equals zero for viscoelastic liquids. [15] The angular frequency $\omega$ is defined using frequency as $\omega = 2\pi f$. Loss modulus, $G'' (\omega)$, is a measure of energy lost per cycle of sinusoidal deformation and can be calculated by [15]

$$G'' (\omega) = \int_0^\infty [G(t) - G_e] \cos(\omega t) \, dt \quad (2)$$

$G'(\omega)$ and $G''(\omega)$ can be merged to define complex modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$, [15] which in asphalt rheology is represented by its magnitude and phase angle, [15]

$$|G^*(\omega)| = [G'(\omega)^2 + G''(\omega)^2]^{1/2} \quad (3)$$

$$\tan \delta = G''/G' \quad (4)$$

In an oscillatory shear experiment, $|G^*(\omega)|$ corresponds to the ratio of stress and strain amplitudes. Phase angle $\delta(\omega)$ corresponds to the difference in phase between stress and strain oscillations, and it represents the ratio between viscous and elastic responses during the shearing process. [15] Complex modulus and $\delta$ can also indicate glass transition ($T_g$) and secondary molecular relaxation. [15]

Dynamic rheology tests are conducted so deformation data are in the linear viscoelastic region. Often the results can be expressed well by master curves that
use the time-temperature superposition principle (TTSP). However many distress mechanisms such as failure, cracking, moisture damage, and tertiary creep are nonlinear.[16] Extra relaxation mechanisms that reflect morphological alterations can lead to TTSP not applying to low frequencies or high temperatures.[16] To use TTSP successfully, all contributing viscoelastic mechanisms must follow the same temperature dependence. If TTSP is applicable to a material, the material is called thermorheologically simple.[17, 18] The Black (or van Gurp-Palman) plot,[19] which encompasses phase angle and complex modulus, can be used to test the applicability of TTSP.

In general, a relaxation log-log plot of $G'(\omega)$ and $G''(\omega)$ vs. frequency has four typical regions: terminal zone, plateau zone, transition zone, and glassy zone.[15] The terminal zone corresponds to flow at low frequencies (i.e. long times).[15] One general characteristic of the plateau zone is a relatively small change in moduli over the frequency region. Another is that $G'$ is always at least as large as $G''$, with phase angle passing through a minimum. This property is characteristic of networks, such as entangled or cross-linked polymers, and may be missing if a network does not exist over the measurement time scale.[15] Furthermore, in polymer modified asphalts, the width of this plateau is a measure of compatibility of an elastomeric polymer and the asphalt.[16] Moduli increase by several order of magnitude in the transition zone from rubber-like to glass-like and remain higher as a function of frequency. Another characteristic of the transition zone is that at a given frequency, storage modulus rises rapidly with decreasing temperature, and the lower the chosen frequency, the steeper the rise.[15] A large maximum in phase angle occurs when the transition from rubber-like to glass-like consistency is crossed.[15] The temperature of the midpoint $T_M$ of the primary transition can be roughly specified by the inflection in $G'$. In the glassy region, the viscoelastic
properties reflect local molecular motions that include rotation around backbone bonds, configurational rearrangement of side chains, and rotations of terminal groups.[15]

Viscoelastic relaxation corresponds to altering the distributions of torsional fluctuations, bending and stretching of bonds, and of intermolecular arrangements over the time scale of mechanical deformation.[15] Local motions are studied by high-frequency viscoelastic measurements above $T_g$ rather than by low-frequency below $T_g$. These two types of studies usually give closely related but not quite identical information. Above $T_g$, the local structure changes with temperature far more than below $T_g$, leading to a larger thermal expansion coefficient. As a result, the temperature dependence of the magnitude of relaxation may be different above and below $T_g$. Normally, at higher temperatures molecules need less time to relax.[15]

Molecular simulations have previously been applied to isolated asphaltenes and to bitumens, as recently reviewed.[20] Boek et al.[21, 22] developed a computer algorithm to create and optimize quantitative molecular representations of asphaltenes on the basis of experimental data. Their algorithm can generate both archipelago and peri-condensed structures. The former have several small aromatic domains (a few fused rings) and are interconnected by alkane chains. The latter have one larger aromatic domain that contains more fused rings; both have alkane branches. Their algorithm followed prior work on asphaltene quantitative molecular representations by Klein and co-workers,[23, 24] Kowalewski et al.[25], and Sheremata et al.[26] Headen and Boek used molecular dynamics to calculate the potential of mean force of an asphaltene molecule on a calcite surface.[27] Headen et al.[28] have investigated the nanoaggregation of asphaltene in toluene and in heptane as well as asphaltene-asphaltene potential of mean force from molecu-
lar dynamics simulations. Jian et al. simulated the effects of different side chain lengths for a model asphaltene with a 9-ring core and two ester substituents.[29]

Our group proposed combinations of compounds to represent asphalt systems, focusing on asphalt as a system rather than asphaltenes as a solubility class. Initial work employed ternary systems.[30] A system with a larger number of more polar molecules was proposed next;[9] its molecules were later found to be too small.[7] A new set of yet larger molecules was proposed recently.[31, 10] A coarse-grained four-component “Cooee bitumen” system was recently proposed by Hansen and co-workers.[32, 33] Stress relaxations up to nanosecond time scales were shown for simulations at 452 and 603 K, with a long-time limit reached at the higher temperature.[32] Chemical aging was then simulated via changes in asphaltene and resin content.[33] The long durations of these simulations enabled independent estimates of stress relaxation modulus over widely separated time periods. The work presented here provides further interpretations of our prior molecular dynamics simulations.[7, 8]

1.3 Methods

Molecular simulations[34] evaluate statistical mechanical averages numerically, given a force field that represents intermolecular potential energy among molecules. The work described here entails further post-processing analysis of results from molecular dynamics simulations that were described in earlier papers.[9, 7, 10, 8] There, the optimized potentials for liquid simulations (OPLS)[35, 36, 37] all-atom force field was chosen because its parameters have been optimized for liquid state properties and because it works sufficiently well[38] for aliphatic and aromatic hydrocarbons as well as sulfur compounds. In those prior simulations,[9, 31, 10] a fixed number of molecules, volume, and temperature (NVT ensemble) and the Nose-Hoover[39, 40] thermostat in molecular dynamics (MD) were used, with a
time step $\Delta t$ of 1 fs and fluctuations sampled for at least 4 ns. The volume was equal to the average volume that resulted from simulations at constant temperature and pressure (1 atm). A single simulation was run at each state point because in our prior work we obtained similar results from multiple independent simulations.

Two model asphalt systems simulated in prior work had been devised so their chemical compositions resembled those of an asphalt termed “AAA-1” in the SHRP. Simulation results from those two different model asphalt systems are investigated here. The earlier of these model asphalts\cite{9} used relatively small molecules to represent the different SARA (saturate, aromatic, resin, asphaltene) fractions of real AAA-1 asphalt. In this work, we refer to that model asphalt system\cite{9} as ZG08. It contained 18 linear C$_{22}$ alkane chains as a saturate; these were consistent with the size range invoked by Kowalewski et al.\cite{25} 100 ethyltetralin molecules were used as a naphthene aromatic. 113 molecules of one- to three-ring aromatics based on thiophene, quinoline, and benzothiophene represented resins. The latter compounds were suggested by Masson and Lacasse\cite{41} and from degradation studies by Strausz.\cite{42} 9 molecules that used a structure proposed by Groenzin and Mullins\cite{43} represented asphaltenes. The ZG08 system matched the atomic composition reported in experiments on real AAA-1 asphalt,\cite{11} but it led to a predicted viscosity that was too low and relaxation times that were too fast,\cite{7} compared to experimental data. A polymer modified version of ZG08 was also simulated, in which the composition was augmented by one molecule of polystyrene, which was selected to represent the more polar fraction of the styrene-butadiene-styrene (SBS) co-polymers that are used in practice to modify asphalts.\cite{44} In this work we refer to that polymer modified system as ZG08p.

In a newer model asphalt system\cite{10} representative of real AAA-1 asphalt, the asphaltene structure of Groenzin and Mullins was replaced with three types of
asphaltene molecules proposed by Mullins[45] that are considered more consistent with experimental characterizations and quantum mechanics studies. Some side chain positions were changed to alleviate high energy “pentane effect” overlaps.[46] Five types of polar aromatics compounds were chosen that were consistent with geochemistry studies.[47, 48, 49, 50, 51] Two types of naphthene aromatics were taken from previously proposed asphalt models.[52, 53] Saturates were chosen to be consistent with characterizations by Netzel and Rovani;[54] a notable change from our prior models is the use of branched and naphthenic compounds (squalane and hopane[55]), because the cited measurements[54] reported that 97 to 99 wt% of alkanes are branched or cyclic in real AAA-1 asphalt. In this work we refer to this system as LG14. It contains 72 molecules among the 12 molecule types. Full details and discussion of its composition are available elsewhere.[10]

Time-dependent stress relaxation modulus data were taken from stress fluctuations calculated in the prior molecular dynamics simulations.[7, 8, 31] There they were calculated by

\[ G(t) = \frac{V}{10k_BT} \sum_{u,v} \left\langle \sigma_{u,v}^{\text{st}}(0)\sigma_{u,v}^{\text{st}}(t) \right\rangle \]

in which \( V \) is volume, \( k_B \) is the Boltzmann constant, \( T \) represents temperature, and \( \sigma^{\text{st}} \) is a symmetric traceless stress tensor that was calculated using the molecular virial.[56] The stress tensor \( \sigma \) is averaged with its transpose and has the pressure subtracted from each diagonal component; the pressure equals one third of the trace of \( \sigma \). Then summations over directions \( (x, y, z) \), indicated by indices \( u \) and \( v \), average over all 9 components of the symmetric, traceless stress tensor. This Green-Kubo method[34] obtains the stress relaxation modulus from spontaneous fluctuations in stress under zero shear conditions, rather than by imposing a prescribed time-dependent strain.

The time integral of Eq. (20) was proposed[57, 58] for use in estimating zero
shear viscosity from shear fluctuations. Symmetrizing the stress tensor, removing
the trace, and summing all components was found to yield a more accurate and
quickly converged viscosity estimate, compared to averaging a single off-diagonal
component of the stress tensor.[57, 58] We assumed here that fluctuations of the
stress tensor can be quantified by fluctuations of its symmetric, traceless form.

Equations (21) and (22) with $G_e = 0$ indicate that numerical integration,

$$G^* = i \int_0^\infty G(t)e^{-i\omega t} dt \approx i \sum_{n=0}^{N-1} G(n\Delta t)e^{-i\omega n\Delta t} \Delta t$$

(6)

enables discrete Fourier cosine and Fourier sine transforms to be applied to calcu-
late storage and loss moduli. The time equals the number of equal time intervals,
$t = n\Delta t$, and the corresponding angular frequencies are $\omega = 2\pi(n/N)/\Delta t$. The
maximum time available for $G(t)$ equals $N\Delta t$ and is of order nanoseconds, which
leads to minimum frequencies of order $10^{-3}$ rad/ps.

Since Eq 24 provides a large amount of equally spaced numerical data, the
transforms can be performed using a fast Fourier transform (FFT), which re-
quires of order $(N \log_2 N)$ operations.[59] The fastest Fourier transform in the
west (FFTW) package has been exploited in this paper. Its detailed algo-
rumth and method are described in the package documentation[60] and in the
literature.[61] An FFT calculates a discrete Fourier transform[61], which by defi-
nition is periodic,[59, 62] meaning that the FFT algorithm implicitly treats $G(t)$
data as being periodic over the time domain considered. Thus $G(t)$ data were
augmented for all times $t$ by $G(-t) = -G(t)$ for storage modulus (Fourier sine
transform, odd function) and by $G(-t) = G(t)$ for loss modulus (Fourier cosine
transform, even function).

Several facts must be taken into account while using FFT and interpreting
data. The fewer MD results for longer time differences in $G(t)$ lead to a poor signal-
to-noise ratio at low frequencies, though for a given set of time data, results from
FFT for lower frequencies are more accurate than for higher frequencies. Vratsanos and Farris[63] suggest that the frequency range used in FFT should be ten times larger than the highest frequency result that can be used reliably. Considering the Nyquist-Shannon sampling theorem[64] and the MD time step of $\Delta t = 1$ fs, the highest reliable frequency range is $\omega < 10^2$ THz. Data beyond the first 10% ($\omega > 10^2$ rad/ps) of the FFT output are not shown for this reason.

Next, to smooth the results and to avoid small fluctuations, a moving average filter was applied to all frequency domain results. The moving average was conducted over a lead and lag of 100 data points. These parameters were chosen such that high frequency noise has been removed from the FFT outputs. Whenever not enough points were available for the lead or lag direction, the extent of the lead and lag were both reduced to the available number of points. Applying a moving average on the frequency domain was found to be a better method that led to reasonable and smooth results, while applying a moving average to $G(t)$ data led to complex modulus results that still contained harmonic noise.

The Maxwell model for viscoelastic liquids has been employed as a reference for comparison. The Maxwell model for stress relaxation in viscoelastic liquids is[65]

$$G(t) = \sum_{i=1}^{m} G_i e^{-t/\tau_i}$$  \hspace{1cm} (7)$$

where $G_i$ is the $i$-th stress modulus term and $\tau_i$ is the $i$-th relaxation time, for a set of $m$ discrete relaxations. The storage and loss moduli for the Maxwell model can be written as[65]

$$G'(\omega) = \sum_{i=1}^{m} \frac{G_i \omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}$$  \hspace{1cm} (8)$$

$$G''(\omega) = \sum_{i=1}^{m} \frac{G_i \omega \tau_i}{1 + \omega^2 \tau_i^2}$$  \hspace{1cm} (9)$$

For low frequencies, Eqs. (8) and (9) simplify to $G'(\omega) = \omega^2 \sum_{i=1}^{m} G_i \tau_i^2$ and
\[ G''(\omega) = \omega \sum_{i=1}^{m} G_i \tau_i, \]
with slopes of +2 and +1 on log-log scales. For high frequencies, Eqs. (8) and (9) simplify to \[ G'(\omega) = \sum_{i=1}^{m} G_i \] and \[ G''(\omega) = \frac{1}{\omega} \sum_{i=1}^{m} G_i / \tau_i, \]
with slopes of 0 and -1.

1.4 Results and Discussion

Stress relaxations for the LG14, ZG08, and ZG08p systems have been calculated using Eq. (20) and are illustrated in Figs. B.1 to 3. The relaxation shown at each time \( t \) was obtained by averaging over all terms within the stress tensor and over all time intervals \( t \equiv (t_j - t_i) > 0 \) obtainable from times \( t_i \) and \( t_j \) within the equilibrated simulation. Random fluctuations increase at longer relaxation times \( t \) because fewer intervals of duration \( t \) are available. Figure B.1 shows the first picosecond of \( G(t) \). Values at longer times are illustrated in Figs. 2 and 3, which show the stress correlations fluctuate rapidly in a wide range of \( \pm 4 \times 10^7 \) Pa after 400 ps. Ideally the \( G(t) \) reaches a plateau of zero for a viscoelastic liquid, but converging to this limit at all times is beyond the capability of the duration of our molecular dynamics simulations. Integrals of \( G(t) \) lead to viscosity and reach well-defined plateaus at high enough temperatures, as shown in prior work [9, 8, 66] and discussed in Fig. 11 below. Insets in Figs. 2 and 3 indicate results obtained by averaging \( G(t) \) over \( \pm 10 \) ps. This reduces noise significantly and illustrates the trends and fluctuations about an eventual zero limit.

Figures 2 and 3 illustrate that the stress relaxation modulus of the LG14 system is more than twice as large as that of the ZG08 and ZG08p systems at the same temperature (443 K). Figures B.1 and 3 show that incorporating polymer into the ZG08 model asphalt increased its stress relaxation modulus by a factor of up to 1.5. Furthermore, the higher the temperature for LG14, the smaller the relaxation modulus and the shorter the relaxation time.

To interpret zero-shear rheological behavior of model asphalts, Fourier sine
Figure 1. First ps of the stress relaxation modulus of both AAA-1 model asphalts. Temperature suffixes ¥ and þ indicate the ZG08 and ZG08p systems;[9, 7] others refer to the LG14 system.[8]

and cosine transforms have been applied on the $G(t)$ data to calculate storage and loss moduli. To examine thermorheological simplicity, complex modulus and phase angle results are shown together as a Black (or van Gurp-Palmen) plot in Fig. 4. Because of large temperature differences, a vertical shift of $|G^*|$ has been applied by considering $T = 533$ K as reference. Over a $|G^*|(V/V_{ref})(T_{ref}/T)$ range of 0.1 to $3 \times 10^8$ Pa, phase angle decreases with increased modulus for each temperature, with a few exceptions. The results below $3 \times 10^8$ Pa show some coarse overlap among different temperatures. Results at higher complex moduli show a peak in phase angle (a loss peak) that does not overlap. In contrast, better overlap for this peak is found when applying a “reverse vertical shift”, $|G^*|(V_{ref}/V)(T/T_{ref})$, which corresponds to removing the volume and temperature factors in Eq. (20). The origin of this peak is a subject of follow-up work. Because the curves at different temperatures do not overlap completely, the LG14 system does not follow thermorheological simplicity over the entire frequency range of the simulation. In other words, this model asphalt is thermorheologically complex and TTSP does not
Figure 2. 1 ps to 1 ns of the stress relaxation modulus of the LG14 system.

necessarily apply to it. The fact that these model asphalts are thermorheologically complex does not imply the models follow thermorheological complexity for all other temperatures. Even if the data at higher frequencies do not superpose, the data at lower frequencies may follow thermorheological simplicity.[15, 18]

Figure 4 also qualitatively compares the simulation results with Black (or van Gurp-Palman) plots for two asphalts described in the literature. da Silva et al.[16] modeled their rheology measurements of AC-1 and AC-2 bitumen systems at 313 K by using the Christensen-Anderson-Marasteanu (CAM) rheological model,[16, 67] which relates complex modulus and phase angle to frequency as

\[
|G^*| = G_g \left[ 1 + (\omega/\omega_0)^{-\nu} \right]^{-w/\nu} \\
\delta = \frac{\pi w}{2} \frac{1}{1 + (\omega/\omega_0)^\nu}
\]

(10)

(11)

where \( \nu \) and \( w \) are parameters. While bitumens AC-1 and AC-2 differ from the AAA-1 asphalt of SHRP, the intent of this comparison is to assess if the simulation results follow trends known to occur for real asphalts. Phase angle-complex modulus curves calculated over frequencies of \( 10^1 \) to \( 10^8 \) rad/s are shown in the figure, with a temperature and density shift applied to \( |G^*| \) using a thermal expansion
Figure 3. 1 ps to 1 ns of the stress relaxation modulus of the ZG08 and ZG08p systems at 443 K.

The coefficient of $\alpha = 5.9 \times 10^{-4} \text{K}^{-1}$.[68] The $G_g$ parameter needed to be increased by a factor of 10 so the numerical results would match those shown in the figures of da Silva et al.[16]; other parameters for the CAM model were taken directly from their paper. The simulation results at frequencies below $\sim 1 \text{rad/ps}$ follow the qualitative trend of the CAM model fits. The CAM model does not incorporate the capability to display a loss peak, such as the peak found in the simulations.

Figure 5 shows the averaged frequency-dependent moduli and phase angle of the LG14 system at 400 K. Over a frequency range of $7 \times 10^{-4} \text{rad/ps}$ to $1.5 \text{rad/ps}$, storage modulus is larger than loss modulus and phase angle is passing through a minimum, which suggests that this is the plateau zone of the LG14 system. The fact that storage modulus is changing slowly and smoothly in this frequency range supports this idea as well. The presence of a plateau between $10^{-2}$ and $10^0 \text{rad/ps}$ suggests that the model system acts entangled over simulation time scales of order $\sim 1/\omega \sim 100 \text{ps}$ at 400 K. Such entanglement is consistent with the decrease of rotation autocorrelation functions from 1 to 0.8 over $\sim 100 \text{ps}$.[8]

Figure B.6 illustrates moduli for both ZG08 and LG14 systems at 443 K.
Across the whole frequency range, the complex modulus magnitude is greater for the LG14 system than the ZG08, which consists of smaller molecules. These results show that using larger molecules leads to higher moduli and thus a stiffer model asphalt. The storage and loss moduli in the LG14 system are comparable, while in the ZG08 system the loss modulus accounts for almost all of the complex modulus ($G^\ast \Upsilon$ and $G'' \Upsilon$ curves nearly overlap).

Figure 7 compares the ZG08 and the ZG08p systems. These results show a slight increase in all moduli upon adding polystyrene to the model asphalt. The sudden drops in storage modulus in Fig. 7 arise from occasional negative values. We interpret these as simulation artifacts of a poor signal to noise ratio for this nearly viscous material. Analogous findings of a negative loss modulus for a nearly elastic material have been reported.[63]

All moduli and phase angle of the LG14 system at 533 K are illustrated in Fig. 8. Over a frequency range of $9 \times 10^{-4}$ to 3 rad/ps, we find comparable relative increases in storage and loss moduli and a minimum in phase angle. Loss modulus
Figure 5. Moduli and phase angle of the LG14 system at $T = 400$ K.

is larger than storage modulus over this range, indicating more viscous than elastic behavior. A zero-shear viscosity can be estimated at this temperature.\[8\]

To have a more thorough investigation of temperature effects on mechanical properties, the storage modulus, loss modulus, and $|G^*|/\omega$ are separately illustrated for all systems in Figs. B.9 to 11. To make these comparisons more informative while retaining clarity, phase angle results above $2 \times 10^{-2}$ rad/ps are plotted in all figures. The results for all systems and at each temperature all show a similar phase angle peak at very high frequency, with the slope of the lower frequency side of the peak decreasing with increasing temperature. A phase angle peak indicates a relaxation mechanism and thus potentially indicates a transition from rubber-like to glass-like over the time scale of the simulation. For LG14, the highest peak (largest viscous contribution) corresponds to the highest temperature (533 K). The slopes of all moduli with frequency show faster rises with frequency at higher temperatures. Furthermore, storage modulus at a given frequency rises rapidly with decreasing temperature, and the lower the chosen frequency, the steeper the rise. Corresponding rises in loss modulus are smaller.

Figures B.9 to 11 can be used to compare the effect of composition on rheo-
Figure 6. Moduli and phase angle of the ZG08 (¥) and LG14 systems at T = 443 K.

logical properties of model asphalts. Comparing the moduli of ZG08 and LG14 at 443 K shows that these compositions differ in mechanical properties by factors of 5 to 10. Furthermore, the ZG08 system at 443 K has a bigger viscous to elastic ratio than the LG14 system for frequencies below \( \sim 10 \) rad/ps, as indicated by its larger phase angle. Its smaller molecules lead to a lower loss modulus (Fig. B.10) and much lower storage modulus (Fig. B.9). Storage moduli at all different temperatures converge in the transition zone (5 to 20 rad/ps) and then they remain more than 2 orders of magnitude larger than at lower frequencies. This trend occurs for loss moduli and \(|G^*|/\omega\) as well.

To interpret model asphalts at extreme frequency limits, the limiting slopes of the Maxwell model are shown in Figs. B.9 and B.10. In Fig. B.9, all systems approach the zero slope high frequency limit of the Maxwell model. The slopes for the ZG08 and ZG08p model asphalts are similar to the low frequency Maxwell model limit \( \sim \omega^2 \), and the LG14 system at 533 K is close to this limit. The LG14 system for lower temperatures has not yet reached this limiting behavior. Instead, its relaxation times are long enough that contributions \((\omega \tau_i)^2\) remain comparable
Figure 7. Moduli and phase angle of the ZG08 and ZG08p systems at $T = 443$ K. $|G^*|$ and $G''$ for the ZG08 system (¥) overlap below $\omega \sim 10^{-1}$ rad/ps.

to unity at 443 K and 400 K.

Results in Fig. B.10 are analogous. Both model asphalts begin to approach the high frequency limiting slope $-1$ of the Maxwell model. The slopes for LG14 at 533 K, ZG08, and ZG08p model asphalts are close to the low frequency $\sim \omega$ limit. The LG14 model asphalt at lower temperatures again has not reached the low frequency Maxwell model limit.

High frequency results of Hansen et al.[32] for a four-component bitumen model may be compared to these results. The model storage and loss moduli at $T = 603$ K for their four-component model are in the same modulus range as those for the LG14 system ($10^7 < G', G'' < 10^8$ Pa). Furthermore, the four-component model over $8 \times 10^9 < \omega < 3 \times 10^{10}$ Hz shows $G' \propto \omega^{1/4}$. The LG14 system shows scaling similar to $G' \propto \omega^{1/4}$ at 400 K and frequencies of $10^{-3}$ to 1 rad/ps, while for 443 K the storage modulus scaling increases faster, as $G' \propto \omega^{0.7}$.

The axes of Fig. 11 enable comparing complex modulus results with zero-shear viscosity $\eta_0$ via the relationship $\lim_{\omega \to 0} |G^*|/\omega = \eta_0$. The zero shear viscosities calculated previously[9, 8] using the Green-Kubo approach are plotted along with the
new results for all systems. $|G^*|/\omega$ for the LG14 system at 400 and 443 K continues to increase as frequency decreases, which indicates that the limiting values of the zero-shear viscosities at low frequency have not yet been reached. $|G^*|/\omega$ shows a slow rise with decreasing frequency at 533 K, with a semiquantitative approach toward the Green-Kubo value calculated previously.[8] The ZG08 and ZG08p systems shows good agreement at lower frequencies with the prior Green-Kubo results.[9] Also, the magnitude of complex moduli of the LG14 system at 400 and 443 K are larger by more than a factor of 10 at lower frequencies compared to the ZG08 and ZG08p systems, and they remain larger for higher frequencies as well. This again shows an effect of the larger molecules used for the LG14 system. The corresponding plot for the four component model of Hansen et al. showed convergence for frequencies below $10^9$ Hz at 603 K. Experimental data for the zero-shear viscosity at temperatures within 10 degrees of 400 and 443 K for two asphalt systems described in the literature[69, 32] are shown on the y-axis of Fig. 11. Differences between the two systems reinforce that “asphalt” refers to a class of materials for which their range of mechanical properties depends on the chemical constitution, molecular weight, and microstructure. The measured viscosities are higher than
Figure 9. Storage modulus of all systems (solid line for $G'$ and dashed line for $\delta$).

those calculated in the simulations at the least high frequencies, which is consistent with the rising trend with decreasing frequency that is seen in the simulation results. The frequency at which the rise converts to a plateau, as seen in the range $-1.5 < \log \omega < -0.2$ for the 533 K system, cannot be predicted directly.

To show another effect of adding polymer on rheological properties of the model asphalt, Fig. 12 illustrates a Black (or van Gurp-Palman) plot for the ZG08 and ZG08p systems at 443 K. In the simulation, adding polymer to the asphalt increases the viscous contributions to the modulus at higher frequencies. Over $2 \times 10^7 < |G^*| < 5 \times 10^8$ Pa, the systems show significant overlap. At lower complex modulus (lower frequencies), the elastic contribution is stronger in the system with the polymer.

1.5 Conclusions

Molecular simulations of model asphalts provide a method to understand how molecular motions contribute to viscoelastic response to applied strain or stress. Storage and loss moduli were calculated using stress relaxation modulus $G(t)$ data from previous equilibrium molecular dynamics simulations of model asphalt sys-
Figure 10. Loss modulus of all systems (solid line for $G''$ and dashed line for $\delta$).

tems ZG08, ZG08p,[9, 7] and LG14.[10, 8, 31]. Storage and loss moduli were then converted to complex modulus and phase angle. A Black (or van Gurp-Palman) plot of $|G^*|$ vs. $\delta$ for the LG14 model asphalt shows some overlap of results for frequencies less than 1 rad/ps over temperatures of 400 to 533 K, with qualitative similarity to trends of the empirical CAM model. Results showed deviations from thermorheological simplicity above 1 rad/ps that were consistent with a temperature- and density-independent loss peak found in both systems. The ZG08 and ZG08p systems, composed of smaller molecules, show a quantitatively lower complex modulus magnitude, while the LG14 system shows higher complex modulus magnitude with relatively longer molecules. Storage modulus plays a much more significant role in the LG14 system with its larger molecules. Differences are smaller in loss modulus between the two systems. The ZG08 and ZG08p model asphalts essentially reach the low and high frequency scaling limits of the Maxwell model within the frequency ranges spanned by the molecular dynamics simulations, while the LG14 model asphalt only reaches the low frequency limit for the loss modulus at the highest temperature simulated of 533 K. Both model asphalt systems show good agreement with Green-Kubo estimates of zero shear
Figure 11. $|G^*|/\omega$ of all systems. Dashed lines show Green-Kubo method low frequency limits.[9, 8] Squares indicate experimental data[69] for a PG 64–22 asphalt at 398 (filled) and 443 K (open). Left-pointing triangles indicate experimental data[32] for a 70/100 bitumen at 409 K (filled) and 433 (open).

viscosity for temperatures at which that approach has converged.[9, 8] Polystyrene added to the ZG08 system increased the modulus of modified asphalt and led to a less frequency-dependent phase angle, showing some compatibility. Qualitative trends are similar to those reported recently for a four-component united-atom model bitumen system of smaller molecules at a high temperature and pressure.

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Figure 12. Black (or van Gurp-Palman) plot for the ZG08 and ZG08p systems.

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Using Signal Processing Techniques to Reduce Noise in Computed Correlation Functions

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2.1 Abstract

Signal processing and its application in removing inherent noise in a correlation function has been investigated. Signal is a property that depends on at least one independent variable (e.g., time) and that carries information about the behavior or attributes of some phenomenon. Correlation function data for stress relaxation modulus obtained by equilibrium molecular dynamics simulations were used as the input signal. Fast Fourier transform was used to get the frequency domain data of the correlation function which are required to have a better understanding of the data. Because of inherent noise in the correlation function, understanding of the information behind it was almost impossible. To remove the noise, signal processing techniques have been exploited. Signal processing techniques enhanced the clarity of the results and removed the noise from our results. Noise removal can improve the signal to noise ratio and lead to more clear interpretation of results such as correlation functions. Removing insignificant components of the Fourier-transformed signal had a great effect and is should be considered in any enhancement of frequency domain results. While applying moving average on time domain data did not lead to improvements when used alone, it is required to get the best results for a given set of data. Moving average is required in both time domain and frequency domain to extract the best results.

2.2 Introduction

Using data in the presence of large fluctuations is always challenging. The challenges of temperature measurements under environmental or apparatus noise, convergence of a correlation function in the presence of noise, or even tracking of an item price under marketing uncertainties are all examples of presence of noise in information.

Usually noise is the unwanted part of input data or any unwanted modification
of original data. Noise is an unavoidable part of our everyday lives and we have to deal with it everyday. Every measurement has some degree of uncertainty or noise in it.[1] Since 17th century, some techniques have been developed to remove these noise from our data. These techniques became the foundation of a science we call “signal processing” today.[2]

Signal is a property that depends on at least one independent variable (e.g., time) and that carries information about the behavior or attributes of some phenomenon. A signal is not necessarily electrical and can be anything like an acoustic wave, thermometer output, pH-meter output, or even an electromagnetic wave.[3] To use already established techniques of signal processing, one can consider these data as signals. The act of doing some operations on a signal to produce another signal is known as signal processing.[3]

Several methods can be applied to remove the noise from a given signal. Noise removal can improve the overall quality of the original signal and consequently a signal processing procedure can improve the result. The reliability of any result from any signal processing techniques depends on how well it deals with noisy input signal. Consequently, the performance of signal processing systems are limited by noise.[1]

The aim of this chapter is to show how to remove noise from data. Removing noise from data enables researchers in many disciplines to have better understanding of their data. To show the generality of signal concept and to show the applicability of signal processing techniques on a real life problem, the estimation of rheological properties of asphalt has been chosen here. Recently, our team has published a series of papers[4, 5, 6, 7, 8, 9, 10, 11] on application of molecular simulation on asphalt to predict its properties.

Some attributes of a signal can be determined in the time domain. To fully
characterize the signal, the signal needs to be examined in frequency domain. One of the biggest advantages of frequency domain analysis is the ease of distinguishing between noise and signal. Removing noise in frequency domain can be done by truncating the data after a certain frequency.[1]

Frequency analysis needs frequency domain data corresponding to time domain data; the first step is to convert time domain signal to frequency domain data.[12] If \( f(t) \) is piecewise continuous in every finite interval, has a right-hand derivative and a left-hand derivative at every point, and is absolutely integrable, then \( f(t) \) can be represented by a Fourier integral,

\[
f(t) = \int_{0}^{\infty} [A(\omega) \cos \omega t + B(\omega) \sin \omega t] \, d\omega
\] (12)

where \( A(\omega) \) and \( B(\omega) \) are Fourier cosine and sine transforms respectively,[12]

\[
A(\omega) = \frac{1}{L} \int_{-\infty}^{\infty} f(t) \sin \omega t \, dt
\] (13)

\[
B(\omega) = \frac{1}{L} \int_{-\infty}^{\infty} f(t) \cos \omega t \, dt
\] (14)

and \( L \) is the data acquisition time duration. The discovery of Fourier series and Fourier transform (FT) had a great influence on mathematics as well as our understanding about functions and integration theory.[13] Fourier transform is a powerful tool to calculate various problems including calculating complex integrals.[14]

Fourier transform by definition can be applied on well-defined functions. In many cases we are interested in applying Fourier transform on a series of data that is not considered as a well-defined function, like equally spaced numerical data. This situation happens in many scientific and engineering applications like telecommunications, simulation problems, and data series.[15, 16, 17, 12] These necessities led mathematicians to develop the discrete Fourier transform (DFT).[12]

For discrete times, (13) and (14) lead to

\[
A(\omega_n) = \frac{1}{L} \sum_{k=0}^{N-1} f(k \Delta t) \sin \omega_n k \Delta t
\] (15)
B(\(\omega_n\)) = \frac{1}{L} \sum_{k=0}^{N-1} f(k\Delta t) \cos \omega_n k\Delta t \quad (16)

N is the total number of sampled data.

For large \(N\), the calculation of Eqs. (15) and (16) is laborious. DFT requires \(O(N^2)\) operations and is computationally expensive. The modern digital world entered another era by introducing the fast Fourier transform (FFT).\([12]\) The FFT algorithm requires only \(O(N \log_2 N)\) operations.\([15, 12]\) It converts a function efficiently to the frequency domain, which makes it straightforward to separate noise from actual signal.\([18]\) Because Fourier transform is a linear operator and noise is additive, the acquired signal is the sum of the noise-free signal and the noise.\([19]\)

FFT codes calculate a discrete Fourier transform,\([16]\) which by definition is periodic.\([12, 20]\) This means that the FFT algorithm implicitly treats data as being periodic over the time domain considered. This assumption causes the information to repeat beyond the given period.\([19]\) The details of the theory and algorithm can be found elsewhere.\([15, 16, 17, 12]\)

Fourier transform of a real function will give a complex function. Having just the magnitude of the transformed function in frequency cannot uniquely reconstruct the sinusoidal data in time domain. The other complementary information is called phase angle \(\delta\). Phase angle can be calculated using both an imaginary \((\beta)\) and real part \((\alpha)\) of a complex number \((\zeta = \alpha + i\beta\) in general),\([12]\)

\[
\delta(\omega) = \tan^{-1}(\beta/\alpha) \quad (17)
\]

The phase angle is usually represented in a 0 to \(2\pi\) interval; this system is called “modulo \(2\pi\) phase.”\([19]\)

Understanding signals is not always straightforward. Several facts must be taken into account while using FFT and interpreting data. Sometimes errors are in the results, but it is claimed that more often the errors are simply misinterpretation.
of the results.[19]

The rate at which data are being sampled determines how well those data become defined in either the time domain or frequency domain. Assuming the number of samples remains the same, increasing definition in the time domain causes a decrease in frequency domain definition. This comes from the reciprocal relationship between the time domain sample spacing, $\Delta t$, and the corresponding frequency domain sample spacing, $\Delta f$. If you decrease $\Delta t$ for more time resolution, then $\Delta f$ increases for less frequency resolution.[19]

Having a larger set of time domain samples for a given sampling duration will increase the resolution of time domain but conversely affects the FFT calculation speed. Fewer time domain samples for a given sampling duration leads to a poor signal-to-noise ratio at low frequencies, though for a given set of time samples, results from FFT for lower frequencies are more accurate than for higher frequencies.[19, 21] Vratsanos and Farris[22] suggest that the frequency range used in FFT should be ten times larger than the highest frequency result that can be used reliably.

Fundamental frequency is the lowest frequency that can be reached by a given data acquisition duration,[12]

$$f_0 = \frac{1}{L} \quad (18)$$

This value is very important and will dictate the resolution in frequency domain,[19]

$$\Delta f = f_0 \quad (19)$$

Each frequency axis value is an integer multiple of this fundamental frequency and is referred to as a “harmonic.” Since $\Delta f$ has a reciprocal relation with the length of sampling duration, increasing $L$ can increase the resolution in the frequency domain.
The signal can be sampled in finite time duration. This interval can be selected by multiplying the signal by a function which is zero outside of the interested interval; this function is called a window function or simply a window.[18] Limiting the integral to a short interval or window is the same as multiplying the signal by a square pulse having a width equal to the interval of integration.[19]

Limiting the length of the data acquisition time interval of the signal causes smearing of frequency domain spectral components to adjacent frequencies. This phenomenon is known as spectral leakage or simply leakage.[19, 18] Leakage errors occur when the data period is not harmonically related to the total sampling duration. Leakage only occurs when the FFT is used to estimate the discrete line spectra associated with periodic and almost periodic signals (a signal that it starts and ends at the same value within a certain error in each period). Almost periodic signals have line spectra, but the components are not harmonically related. In case of non-repetitive signal, specifically pulses.[19, 18]

Leakage is not a universal problem. It does not affect transient data as long as the transient data are fully contained in the window. The actual source of leakage is the window function used in acquiring the data. The amount of leakage depends upon the window shape and how the data fit into the window. Since almost periodic data do not have a definite period, one can choose a window with a start and end at the same level. Another alternative is to use a different window type.[19, 23]

The Nyquist frequency \((1/2\Delta t)\) is the highest frequency that can be defined by the \(1/\Delta t\) sampling rate. The rule for proper sampling is referred to as the “Nyquist sampling theory,” which states that the sampling rate must be at least twice the frequency of the highest frequency component in the data being sampled.[23] In other words, there must be at least two samples per cycle for any frequency com-
ponent one wishes to define.

It is impossible to have a sampling rate that assures two samples per cycle for all frequencies. However, in most cases the high-frequency portion of a windowed data spectrum drops to what can be considered an insignificant level at higher frequencies. Then all one needs to do is to select a sampling rate such that several samples per cycle occur for the highest frequency of significance. There are some cases where data are not high-frequency limited. The ideal square wave is one example.

Noise, leakage, and periodicity are all related to implementing the FFT in general. They really are not FFT errors. In fact, they are errors associated with the analog data and how it is acquired and sampled. Each approach to acquisition and sampling has specific errors unique to that approach.[19]

There are few techniques toward improving FFT results; signal averaging in time domain is one of them. When the signal is repetitive and the noise random, signal averaging can substantially improve the signal to noise ratio. The technique of signal averaging is straightforward. A repetitive signal is acquired a number of times and then the average of them will be reported. For truly zero-mean noise, the improvement in signal to noise ratio for \(2^n\) signals is \(\approx 4.239n\).[19, 23]

Sampling using a higher rate than Nyquist sampling rate is another technique to improve FFT results. This technique is called “oversampling.” Using sampling rate greater than twice the highest frequency can improve the results taken from FFT. A time-domain interpolation can be used to create more finely spaced data from existing data.

To improve pavement performance, it is useful to have a deep understanding of its properties.[24] The Strategic Highway Research Program (SHRP)[25] categorized different asphalts using their complex modulus and viscosity. Recently,
our team proposed a model system[10] (named as LG14) to represent molecular composition of SHRP AAA-1 asphalt. Stress relaxation modulus data have been obtained by equilibrium molecular dynamics simulations[10] for LG14 model asphalt. The storage and loss moduli as well as complex modulus of this model has been investigated later on.[11]

In current study, some advanced signal processing techniques have been employed to enhance the results in frequency domain. The results have been compared to previous results.

Complex modulus and viscosity describe many asphalt mechanical properties,[26] but because of independent behaviors of other mechanical properties, asphalts with comparable complex modulus under certain conditions show different performance in pavement.[27, 24, 28] Different performance might be related to the fact that different asphalts come from different crude oil sources and different chemical components.[27]

Complex modulus is used to characterized asphalts by the SHRP. The complex modulus has two parts: storage modulus and loss modulus. Storage modulus, $G'(\omega)$, is a measure of energy stored and recovered per cycle of sinusoidal deformation. Storage modulus can be calculated by Fourier transform from stress relaxation modulus ($G(t)$). The stress relaxation modulus can be related to stress tensor by

$$G(t) = \frac{V}{10k_BT} \sum_{u,v} \left\langle \sigma^{st}_{u,v}(0)\sigma^{st}_{u,v}(t) \right\rangle$$

$V$ is volume, $k_B$ is the Boltzmann constant, $T$ represents temperature, and $\sigma^{st}$ is a symmetric traceless stress tensor that was calculated using the molecular virial,[29] which incorporates the forces between molecule centers of mass and the kinetic energy of each molecule. The stress tensor $\sigma$ is averaged with its transpose and has the pressure subtracted from each diagonal component; the pressure equals
one third of the trace of $\sigma$. Then summations over directions ($x, y, z$), indicated by indices $u$ and $v$, average over all 9 components of the symmetric, traceless stress tensor. The storage modulus is related to stress relaxation modulus $G(t)$ by[30]

$$G'(\omega) = G_e + \omega \int_0^\infty [G(t) - G_e] \sin(\omega t) \, dt \tag{21}$$

$G_e$ is the equilibrium tensile modulus and can be calculated by $G_e = \lim_{t \to \infty} G(t)$. For viscoelastic liquids, $G_e = 0$. The angular frequency $\omega$ is defined using frequency as $\omega = 2\pi f$. Loss modulus, $G''(\omega)$, is a measure of energy lost per cycle of sinusoidal deformation and can be calculated by[30]

$$G''(\omega) = \omega \int_0^\infty [G(t) - G_e] \cos(\omega t) \, dt \tag{22}$$

Phase angle ($\delta(\omega)$) corresponds to the difference in phase between stress and strain oscillations, and it defines as the ratio between viscous and elastic responses during the shearing process.[30] Using Eq. (17) the phase angle is defined as $\tan \delta = G''/G$.[30]

Calculating Eqs. (21) and (22) by definition is very tedious. Instead of using numerical integration to calculate $G'(\omega)$ and $G''(\omega)$ one can use Fourier transform. $G'(\omega)$ and $G''(\omega)$ can be merged to define complex modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$,[30] which in asphalt rheology is represented by its magnitude and phase angle,[30]

$$|G^*(\omega)| = [G'(\omega)^2 + G''(\omega)^2]^{1/2} \tag{23}$$

$|G^*(\omega)|$ corresponds to the ratio of stress and strain amplitudes.

Equations (21) and (22) are in the same form of Eqs. (15) and (16) respectively; instead of using numerical integration to calculate $G'(\omega)$ and $G''(\omega)$ one can use FFT to accelerate the calculations.
2.3 Methods

Time-dependent stress relaxation modulus data of LG14 were taken from stress fluctuations calculated in the prior constant volume molecular dynamics simulations.[9, 31] This Green-Kubo method[32] obtains the stress relaxation modulus from spontaneous fluctuations in stress under zero shear conditions, rather than by imposing a prescribed time-dependent strain.

Numerical simulations have sampled continuous $G(t)$ data to obtain discrete results; therefore the digital signal processing must be applied here instead of analog signal processing to interpret the results. $G(t)$ data are the input correlation function that is used as our input signal here. Equations (21) and (22) with $G_e = 0$ indicate that numerical integration,

$$ G^* \approx i\omega \sum_{n=0}^{N-1} G(n\Delta t)e^{-i\omega n\Delta t} \Delta t $$

(24)

enables discrete Fourier cosine and Fourier sine transforms to be applied to calculate storage and loss moduli. The time equals the number of equal time intervals, $t = n\Delta t$. The maximum time available for $G(t)$ equals $N\Delta t$ and is of order of nanoseconds, which leads to minimum frequencies of order $10^{-3}$ rad/ps.

$G(t)$ data were augmented for all times $t$ by $G(-t) = -G(t)$ for storage modulus (Fourier sine transform, odd function) and by $G(-t) = G(t)$ for loss modulus (Fourier cosine transform, even function). This extension has been employed to prevent leakage. In this strategy, the beginning and end of the $G(t)$ function are at the same level.

Since $G(t)$ does not go to zero in longer times, as for liquid viscoelastic liquids, a window function has been applied to $G(t)$ data. The following window function has been applied

$$ \chi(n\Delta t) = \begin{cases} 1 & n\Delta t \leq a \text{ ps} \\ \exp[-\zeta(n\Delta t - a)/(b - a)] & n\Delta t > a \text{ ps} \end{cases} $$

(25)
ζ is decaying factor and considered to be 10. \( a \) is the start point of damping and considered to be 1 ps. This \( a \) value has been chosen to have the least effect on data for which we have more confidence about them. \( b \) is the sampling duration and it is 3500 ps. ζ is chosen in this way to have the least damping effect while forcing the window function to go to zero at its end.

Applying this window function leads to some suppression of frequency response magnitude. To restore the magnitude of frequency response, the results have to be divided by coherent gain. Coherent gain of a given window function is calculated by

\[
κ = \frac{\sum_{n=0}^{N-1} \chi(n\Delta t)/N}{N} \tag{26}
\]

One of the most common filters to remove random noise is the moving average filter. The moving average is the fastest digital filter available. Moving average is the optimal filter for removing random noise while retaining a sharp step response. As the number of points involved in the moving average increases, the noise becomes lower, and the edges of sharp step response becomes smeared. The moving average filter provides the least noise possible while retaining a given edge sharpness and it is optimal for removing random noise while retaining a sharp step response. It can reduce the noise by square-root of number of points used in the averaging.

To smooth \( G(t) \) data, a moving average filter was applied to \( G(t) \) data beyond the first 1ps. The moving average was conducted over a lead and lag of 0.1ps. Whenever there were not enough points available for the lead or lag direction, the extent of the lead and lag were both reduced to the available number of points.

The fastest Fourier transform in the west (FFTW) package has been exploited in this paper to accelerate the calculations. It is based on FFT to reduce the computational cost. The detailed algorithm and method are described in the
Using FFTW, the $G(t)$ data have been used to calculate $G'(\omega)$ and $G''(\omega)$. To calculate storage modulus, $G(t)$ was extended as an odd function for negative time span to use Fourier sine transform. An even function generalization has been applied to calculate loss modulus using Fourier cosine transform. Using these two moduli and Eqs. (17) and (23) the phase angle and complex modulus magnitude were calculated.

Low magnitude noise are unavoidable because of digitizing the input signal as well as computer round-off error. Fast rises (large slopes) in time domain corresponds to high frequencies in the frequency domain. By only considering the low frequency components one can remove high frequency components (noise).

Low-level noise components can make significant contribution to the phase angle results. A small number divided by a small number is the same as a large number divided by a large number. At each frequency we have to remove insignificant frequency components. The corresponding phase angle for any insignificant component must be removed from phase angle plot as well.

2.4 Results

Using Eq. (20), stress relaxation modulus has been calculated for LG14 system. The stress relaxation tensor has been averaged over all their elements to have one scalar stress relaxation at each time. The first nanosecond of stress relaxations for the LG14 system has been plotted in Figs. 1 and 2 in the previous paper. The fluctuations at longer times were in the range of $\pm 8 \times 10^8$ Pa after 400 ps. These high amplitude fluctuations in the $G(t)$ data after 400 ps will introduce spectral leakage in FFT results. To reduce the increasing random fluctuations at longer relaxation times, which is caused by a decreasing number of available time separations in the signal averaging of Eq. (20), a moving average of $\pm 0.1$ ps has
been applied to all relaxation times beyond 1 ps. This moving average can reduce the spectral leakage in FFT results. The stress relaxation data beyond 1 ps for LG14 system after applying moving average on it is shown in Fig. 13. Since the data within first picosecond of stress relaxation data were the most reliable part, no operation has been applied to this part.

![Graph showing stress relaxation modulus](image)

Figure 13. 1 ps to 3.5 ns of the stress relaxation modulus of the LG14 system at 533 K after applying moving average on $G(t)$ data.

Stress relaxation in Fig. 13 does not go to zero at longer time. This cause spectral leakage in frequency domain. Furthermore, from the physics of viscoelastic liquid it is expected that $G(t)$ goes to zero at longer times. To make this decay happen, the window function of Eq. (25) has been applied here. This window function has the benefit of not changing the first picosecond of stress relaxation data while damping the data beyond it in a way that has the least change on data which have more certainties. The data at longer times, which have less certainties, will change more.

Figure 14 shows the effect of this window function (Eq. (25)) on $G(t)$ signal. The applied window function did not change the first 10 ps of $G(t)$ data that much. Between 10 ps and 100 ps, the noise damping effect of the applied window
starts to be noticeable. Beyond 100 ps, the noise have been damped a lot and the transformed signal reached 0 Pa after 1000 ps. This window function forced the $G(t)$ to meet the 0 Pa limit of stress relaxation modulus of viscoelastic liquids.

![Graph](https://example.com/graph.png)

Figure 14. 1 ps to 3.5 ns of the stress relaxation modulus of the LG14 system at 533 K after applying moving average and window function on $G(t)$ data.

FFTW has been applied to calculate Fourier sine and cosine transforms of $G(t)$ data. These calculations have provided storage and loss moduli. For cases in which a window function was used on $G(t)$ data, the FFTW output (storage modulus and loss modulus) were divided by the coherent gain ($\kappa$). From storage and loss moduli, the phase angle and complex modulus magnitude were calculated.

Storage and loss moduli for the LG14 system at 533 K have been plotted in Fig. 15. This figure shows the raw results without any attempt to remove the high amplitude fluctuations. It is impossible to conclude any useful information from this plot because of the low signal to noise ratio. To show the effect of different noise reduction techniques, the step by step enhancement of the results using signal processing techniques are shown in Figs. 16 to 20.

To enhance the moduli results, several strategies have been investigated here. Significant improvement steps are shown in the main text. Additional combinations
are provided in supplementary material. Applying only a moving average on $G(t)$ data prior to the FFT had no significant effect. Removing insignificant components in the frequency domain, as defined by negative storage or loss moduli, without any other technique has improved the signal to noise ratio, as shown in Fig. 16. The effect of removing insignificant components on loss modulus, and consequently on phase angle, is significant. The high amplitude fluctuations in both loss modulus and phase angle have disappeared. Applying moving average on $G(t)$ data and removing insignificant components in frequency domain did not improve the results in comparison to only removing insignificant components in the frequency domain.

The first major enhancement of the results can be seen by applying the window function (Eq. (25)) and moving average on $G(t)$ data in conjunction with removing insignificant components in frequency domain. Figure 17 shows the improvement in the moduli results, especially for loss modulus. The noise in moduli have lessened significantly and the phase angle data have become more clear. The phase angle is not fluctuating between the minimum and maximum limit anymore. This improvement is more obvious for loss modulus since it has less noise in it in all frequencies. The storage modulus still shows noise, especially for the frequency range of 3 to 30 rad/ps.

To improve the results further, a moving average filter has been applied on all moduli results as well applying the aforementioned methods. Applying moving average only on moduli results was investigated previously.[11] Applying moving average on $G(t)$ data along with applying moving average on moduli results did not improve the results significantly in comparison to the previous case. This confirmed that removing insignificant components is very important.

Applying the window function on $G(t)$ data along with applying moving average on moduli results and removing insignificant components led to additional
improvements in the results. Figure 18 shows the results of these techniques. In
this case, the severe fluctuations in storage modulus as seen in Fig. 17 in frequency
range of 3 to 30 rad/ps have disappeared.

The best improvement was after applying the window function and moving av-

erage on $G(t)$ data plus removing insignificant components from frequency domain
data and applying moving average on all moduli while sampling at highest rate.

Figure 19 shows the result that was obtained after applying all these techniques.

Phase angle has no high amplitude fluctuation and moduli are smooth.

To show the effect of sampling rate on the frequency domain results, the same
techniques that were applied in Fig. 19 have been applied to $G(t)$ and all moduli
data with a lower sampling rate of 1 sample per 5 fs, compared to 1 sample per
1 fs in previous case. The results are shown in Fig. 20. Using a lower sampling
rate induces some low amplitude fluctuations especially in storage modulus and
consequently phase angle and particularly at frequencies above 1 rad/ps.

Figure 19 is clear enough to investigate asphalt rheological properties at 533 K.

The fact that storage modulus is less than loss modulus for frequencies below
200 rad/ps shows that asphalt is more viscous than elastic at this temperature.

For frequencies above 200 rad/ps, the elastic components are more dominant. The
less noisy data should also enable investigating time-temperature superposition
more clearly.

2.5 Conclusions

Noise removal can improve the signal to noise ratio and lead to more clear
interpretation of results such as correlation functions. Removing insignificant com-
ponents of the Fourier-transformed signal has a great effect and is should be con-
sidered in any enhancement of frequency domain results. While applying moving
average on time domain data did not lead to improvements when used alone, it is
required to get the best results for a given set of data.

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Figure 15. Storage modulus and loss modulus that correspond to raw $G(t)$ data for LG14 at 533 K.
Figure 16. Effect of removing insignificant components from results.
Figure 17. Effect of applying window function and moving average on $G(t)$ data.
Figure 18. Effect of window function on $G(t)$ data and removing insignificant components from frequency domain results and applying moving average on the results.
Figure 19. Effect of window function and moving average on $G(t)$ data and removing insignificant components from frequency domain results and applying moving average on the results.
Figure 20. Effect of lower sampling rate on Fig. 19 results.
MANUSCRIPT 3

Equation of State Modeling of Bitumen Thermodynamic Properties

The following manuscript is prepared for submission to the journal of Industrial & Engineering Chemistry Research.

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3.1 Abstract

Critical properties, saturated pressure, and acentric factors of the components in two model asphalts have been estimated. These parameters are required by most cubic equations of state. The simplicity and acceptable accuracy of cubic equations of state in predicting phase equilibria make them useful in research and industry. Since bitumen is the bottom residue of crude oil refineries, having these properties will enable researchers to use cubic equations of state in thermodynamic simulations that require properties of amorphous bitumen phases, including phase field models of wax crystallization. The method of Nannoolal et al. which is based on group contribution has been implemented to calculate critical properties and acentric factors of the model compounds. The estimated critical properties have been used in a cubic equation of state to predict densities and thermal expansions of asphalt models. The results for thermal expansion show a good consistency with molecular simulation results as well as experimental results. The critical properties along with Peng-Robinson equation of state have been used to predict precipitation of wax in asphalt mixture. Precipitation of waxes create big problems in pavement and cause cracking. To predict this phenomenon, precipitation of squalane as a wax was investigated. In a specific temperature, the chemical potential of pure squalane below its melting point was lower than its chemical potential in the multicomponent system which suggests that squalane will precipitate below its melting point. The temperature in which an asphalt model precipitate is different for each models. This confirms that the chemistry of asphalt can effect its mechanical properties.

3.2 Introduction

Bitumen is a widely seen material nowadays but it is not a new discovery. It has been used since ancient era.[1, 2] It has been used in shipbuilding in Sumeria around 6000 B.C.[2] and as cement or adhesive material in sculptures by Sumerians
and Babylonians.\cite{1} The term “asphalt” is traced back to Babylonians and means “secure” or “firm”, which implies its application as an adhesive material.\cite{1} The first record of using asphalt in pavement was in Babylon around 625 B.C.\cite{3} This material has been used without a thorough understanding of its composition and properties. Understanding chemistry \cite{4,5,6,7}, viscoelastic properties,\cite{8,9,10,11,12,13,4,14,15,16,17,18} and thermodynamics\cite{11,19,20,21,22,23,24} of phase behavior asphalts and asphaltenes are routes toward improving its performance and durability. Recently the chemistry of asphalt and its impact on its properties have been investigated by several authors.\cite{5,6,4,7}

The aim of this paper is to provide required parameters for corresponding states\cite{25} based equations of state (EOS) to enable predicting thermodynamic properties of bitumen. As one example, the density and thermal expansion will be calculated without molecular calculations or experiments. A second example will demonstrate the driving force for precipitation of wax from the bitumen, a problem known from experiments. Waxes are undesirable high molecular weight alkanes in petroleum and petrochemical industries.

The quality and performance of asphalt depends on crude oil source, and therefore depends on chemical composition of asphalt.\cite{11} Naphthenic based crude oils are known to yield high quality asphalt while paraffinic crude oils are known to show poor performance on roads.\cite{26} The major point of this paper is to demonstrate a multiscale method that can account for the effects of chemistry while modeling asphalt properties.

The first step in molecular simulation of any system is to define the molecules in the system. Asphalt is a mixture of $10^5$ to $10^6$ different molecule types.\cite{27} Doing molecular studies on a system containing this huge number of molecule types is laborious if not impossible. Instead, we use a small set of components
that represents the asphalt properties. Several representative models have been introduced. [28, 29, 30, 31, 32]

Several researchers using advanced EOS like SAFT[33, 34] have been carried out on asphaltene and asphalt recently.[21, 19, 22, 20, 23, 35, 24] While these methods are supposed to be more accurate, they need lots of experimental data to estimate unknown parameters. Ting et al.[19] have predicted stability boundaries of asphaltene in reservoir conditions. Gonzalez et al.[20, 22] have applied PC-SAFT EOS to predict instability of asphaltene under gas injection conditions. Aguilera-Mercado et al.[21] have used Monte Carlo method to predict asphaltenes and resins aggregation in a molecular model for the crude oil. Vargas et al.[36] have proposed a general approach for modeling asphaltene stability. They have exploited PC-SAFT to generate simulation data for crude oil containing different asphaltenes instead of experimental data. Then they have provided correlations bubble point and onset of asphaltene precipitation. They demonstrated the agreement of their method to predict onset of precipitation of asphaltenes for different crude oils. They have investigated the precipitation of asphaltene in crude oil and density prediction of crude oil as a function of temperature, pressure, and compositions.[37] Panuganti et al.[38, 39] have provided an extensive procedure to characterize crude oil using PC-SAFT EOS. They have provided phase envelopes which had good consistency with experimental data. They have tested their model over a wide range of conditions and the model were robust enough.

Molecular simulation can be used to study thermodynamic behavior of asphaltene models. The liquid-vapor phase behavior of asphaltene-like molecules have been investigated by Rane et al.[24] using molecular simulation. They have calculated the saturated densities, vapor pressures, and enthalpies of vaporization of several asphaltene model molecules over a wide range of temperatures. One of the
biggest disadvantages of molecular simulation is the fact that it is computationally expensive. By virtue of these issues we have decided to choose a common cubic EOS in this research.

The Strategic Highway Research Program (SHRP) introduced and named different asphalt binders for research studies. The temperature dependent complex modulus and viscosity were used by SHRP to characterize different binders.[40, 11] Although magnitude and temperature dependence of complex modulus and viscosity describe many asphalt mechanical properties,[40] asphalts with comparable complex modulus show different performance in pavement applications because of independent behaviors of other mechanical properties.[2, 11, 41]

Our group proposed several combinations of compounds that represent asphalt as a system rather than asphaltenes as a solubility class. Initial work employed ternary systems.[28] A system with a larger number of more polar molecules[29] was proposed next to represent atomic composition of AAA-1 asphalts in SHRP classification. Here, it has been referred as ZG08. Its molecules were later found to be too small.[42] A new set of yet larger molecules was proposed recently[43, 30] to represent SHRP asphalts AAA-1, AAK-1, and AAM-1 (labeled here as LG14A, LG14K, LG14M) as composition variations of the same compounds. Details that motivate these model representations of AAA-1, AAK-1, and AAM-1 can be found elsewhere.[29, 30]

The critical properties of several hundreds of general compounds are available in the literature. [44, 45] But the critical properties of interest are not always available in the literature for all the molecules we need for modeling asphalt. Although experimental methods are available for measuring critical properties of materials,[46, 47] measuring these properties are sometimes costly [48] or require special techniques for unstable materials. [49, 50, 51, 52, 53] Sometimes experi-
mental methods are not even possible because some molecules in the models are hypothetical and are nontrivial to produce as pure compounds.

An alternative way of finding unknown critical properties is group contribution (GC) methods, which have been shown to be a great alternative. [54, 55, 56] The underlying theory behind GC methods is that the properties of a compound can be calculated from the properties of its fragments (groups) [57]. Full discussion about different methods and their parameters can be found elsewhere.[44, 45, 58, 59, 60, 61, 62, 54, 55, 56]

A relationship between critical temperature and normal boiling point has been studied for more than 100 years and was first reported by Guldberg[63] in 1890. This relation has been modified several times and almost all GC methods follow Guldberg’s relation.[63]

\[ T_c = 1.5 T_b \]  

(27)

where \( T_c \) and \( T_b \) are in Kelvin.

A GC method for critical properties has been introduced by Riedel,[57] and since then several modifications[64, 65, 66, 67, 54, 55, 56] have been introduced to improve the accuracy and reliability of prior approaches. Joback and Reid [64] assumed that there are no interactions between groups. The Joback method includes summing the frequency of each group times its structure-based contribution. [64] Because Joback method (and all similar methods) assumes no interaction between groups (called a first-order assumption), it suffers from low accuracy. In addition, this method cannot distinguish between isomers. [68, 66] Joback et al. did not claim high accuracy of this method, though it became very popular because it is extremely easy to use.

Some improvements were introduced in a group interaction contribution (GIC) method by Constantinou et al. [59, 60, 61, 62], but the range of applicability is quite
limited and requires symbolic calculations. Marrero-Morejón et al. improved the accuracy of the Constantinou et al. method. They have claimed that a GIC method leads to a more accurate result than GC methods for all chemical classes. Marrero-Morejón et al. proposed another method based on a three-order GC method. Both methods can estimate physical properties of simple molecules, but the earlier method results in poor estimates for alcohols, phenols, and large heterocyclic compounds. The later method used a logarithmic dependence for $T_b$, which can cause large errors for small and large molecules. Recently, Nannoolal et al. proposed an approach that outperforms other GC methods and was selected by Perry’s Chemical Engineers’ Handbook as the most accurate method for boiling point estimation. Their method is based on previous work by Cordes and Rarey.

The method of Nannoolal et al. has been employed here to estimate the critical properties of the ZG08 and LG14 model asphalts. The composition of ZG08 and LG14 model asphalts are listed in Tables 3 and 4 respectively. The details and discussion of these model asphalts are available elsewhere.

### 3.3 Methods

The relationship between temperature ($T$), pressure ($P$), and molar volume ($v$) can be described by an equation of state. One of the most common equations of state (EOS) in both academia and industry is the Peng-Robinson (PR) equation of state. The PR EOS can be written for a pure component as

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}$$

(28)

$a$ is the energy parameter and is a function of mole fractions and critical properties, [69]

$$a = \sum_{i}^{n} \sum_{j}^{n} x_i x_j a_{ij}$$

(29)
where $a_{ij}$ is [69]

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2}$$  \hspace{1cm} (30)$$

$k_{ij}$ is a binary interaction parameter between species $i$ and $j$. Here we set all $k_{ij} = 0$ for simplicity. $a_i$ and $a_j$ are pure component parameters and can be calculated by critical properties [69]

$$a_i = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha_i$$  \hspace{1cm} (31)$$

$R$ is the universal gas constant, $T_c$ is critical temperature, $P_c$ is critical pressure, $T_r = T/T_c$, and $\omega$ is acentric factor. [69] $\alpha_i$ is calculated from reduced temperature by [69]

$$\alpha_i = [1 + \kappa_i(1 - T_r^{1/2})]^2$$  \hspace{1cm} (32)$$

$\kappa_i$ is a function of acentric factor only, [69]

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$  \hspace{1cm} (33)$$

$b$ is the mixture volume parameter, [69, 70]

$$b = \sum_i^n x_i b_i$$  \hspace{1cm} (34)$$

$b_i$ is the pure component volume parameter which can be estimated by [69]

$$b_i = 0.07780 \frac{RT_{c_i}}{P_{c_i}}$$  \hspace{1cm} (35)$$

Since most of the compounds in the models are hypothetical compounds, their critical properties are unknown. To estimate unknown critical properties, the method of Nannoolal et al. [54, 55, 56] has been used. This method was chosen because of its generality, reliability, and accuracy. This method is a three-order method: [54, 55, 56]

1. The first-order is just like any other basic GC method. The first order contribution is calculated by summing the occurrence frequency of any group multiplied by its contribution value.
2. The second-order contribution accounts for contributions from some special functional groups as well as isomers.

3. The third-order accounts for interactions between different groups.

We have implemented the method of Nannoolal et al. [54, 55, 56] in Microsoft Excel VBA. To check the reliability of this method and our code, we have examined several known material (including but not limited to examples provided by Nannoolal et al.), and in all cases we obtained very good agreement with the corresponding literature data.

Nannoolal et al. improved Guldberg’s method by replacing the simple coefficient factor of 1.5 by a more complicated group contribution expression. [55]

A corresponding states related parameter that is required by most cubic equations of state is the acentric factor, \( \omega \), which is a measure of the non-sphericity of the molecules. [71, 72, 25] While this parameter was not provided directly in papers by Nannoolal et al., they have provided an expression for saturation pressure \( (P^*) \) that we have exploited to calculate acentric factor. Their expression for saturation pressure in \( atm \) is [56]

\[
\log P^* = (4.1012 + dB) \left( \frac{T_{rb} - 1}{T_{rb} - (1/8)} \right)
\] (36)

where \( T_b \) is the normal boiling point temperature, \( T_{rb} = T/T_b \), and

\[
dB = \left( \sum_i N_i C_i + GI \right) - 0.176055
\] (37)

\( GI \) is a third-order group interaction contribution, which is [54]

\[
GI = \frac{2}{n(m-1)} \left( \sum_{i=1}^{m} \sum_{j=i+1}^{m} C_{i-j} \right)
\] (38)

\( m \) is the total number of interacting groups and \( n \) is the number of atoms in molecule excluding hydrogen atoms. The notation \( C_{i-j} \) indicates the contribution from interactions between group \( i \) and group \( j \); it is not a subtraction. We
calculated acentric factor using its definition, \[71, 25\]

\[
\omega \equiv -1.0 - \log P_r^*|_{T_r=0.7}
\]  \hspace{1cm} (39)

where \(P_r^* = P^*/P_c\). The temperature \(0.7T_c\) required for acentric factor can be written using the expression from Nannoolal et al. for critical temperature \[55\] as

\[
T_{rb,\omega} = 0.7 \left( \frac{T_c}{T_b} \right) = 0.7 \left( 0.6990 + \frac{1}{0.9889 + \left( \sum_i N_i C_i + GI \right)^{0.8607}} \right)
\]  \hspace{1cm} (40)

Substituting \(T_{rb,\omega}\) in Eq. (36) and using the definition of acentric factor with the expression from Nannoolal et al. for critical pressure leads to

\[
\omega = -1 - \log \left( 101.325(4.1012+dB) \left( \frac{T_{rb,\omega} - 1}{T_{rb,\omega} - (1/8)} \right) \left( 0.00939 + \sum_i N_i C_i + GI \right)^2 M^{0.14041} \right)
\]  \hspace{1cm} (41)

\(M\) is the molecular weight in g/mol. The \(C_i\) and \(GI\) terms in equations 37 and 41 are different, and all \(C_i\) and \(C_{i-j}\) have separate values that can be found elsewhere. \[54, 55, 56\]

Unfortunately, most cubic equations of state do not predict liquid volume accurately.\[73, 74, 75\] Several methods have been developed\[76, 77, 78, 79, 80, 81, 73, 82\] that improve liquid density results without altering phase equilibria.

In this paper, the COSTALD \[81\] method has been used for calculating saturated liquid volume. The COSTALD correlation, \(V_s/V^\circ = V_R^{(0)} \left[ 1 - \omega V_R^{(\delta)} \right]\), requires only reduced temperature, acentric factor, and a characteristic volume which can be estimated from critical properties of each pure compound.\[81\] \(V_s\) is saturated liquid volume and \(V_R^{(0)}\) and \(V_R^{(\delta)}\) are\[81\]

\[
\begin{align*}
V_R^{(0)} &= 1 - 1.52816(1 - T_r)^{1/3} + 1.43907(1 - T_r)^{2/3} - 0.81446(1 - T_r) + 0.190454(1 - T_r)^{4/3} \\
V_R^{(\delta)} &= [-0.296123 + 0.386914T_r - 0.0427258T_r^2 - 0.0480645T_r^3] / (T_r - 1.00001)
\end{align*}
\]  \hspace{1cm} (42)

\(V^\circ\) is the characteristic volume for each pure component. If no experimental value
available for the characteristic volume, the following expression can be used,[81]

\[ V^\circ = \frac{RT_c}{P_c} (a + b\omega + c\omega^2) \]  

(43)

Constants \(a\), \(b\), and \(c\) are listed for nine classes of fluids by Hankinson and Thomson.[81] For a multicomponent system, \(T_c\) and \(\omega\) are replaced by \(T_{cm}\) and \(\omega_m,\)[81]

\[ T_{cm} = \sum_i \sum_j x_ix_j V_{ij}^\circ T_{cij} \]  

(44)

\[ V_m^\circ = 1/4 \left[ \sum_i x_i V_i^\circ + 3 \left( \sum_i x_i V_i^{2/3} \right) \left( \sum_i x_i V_i^{1/3} \right) \right] \]  

(45)

\[ V_{ij}^\circ T_{cij} = (V_i^\circ T_{ci} V_j^\circ T_{cj})^{1/2} \]  

(46)

\[ \omega_m = \sum_i x_i \omega_i \]  

(47)

All EOS calculations have been carried out in Aspen HYSYS 13.2 by defining hypothetical components for the compounds of the model bitumens.

Existence of wax in asphalt binder can be related to several problems. At high temperatures, the viscosity of wax decreases and make the binder prone to rutting. At low temperatures, it make the binder brittle and increase the chance of thermal cracking.[26] The hydrophobic character of wax reduce the ability of bitumen to wet the aggregate and that may decrease the adhesion between aggregate and bitumen.[26] Furthermore, it makes the compaction of the binder on the road more difficult because of sudden increasing viscosity.[26]

Precipitation of a solid phase cannot be predicted using only a conventional cubic equation of state. Here, experimental data for the heat of fusion and pure component melting point \((T_m)\) have been used to provide approximate guidance about wax precipitation in a bitumen. The enthalpy of fusion for a pure component was not estimated by Nannooolal et al., so we used the method proposed by Joback.
\[ \Delta H_{\text{fusion}} = -0.88 + \sum_i N_i C_i \] (48)

Here \( \Delta H_{\text{fusion}} \) is in units of kJ/kgmol. \( N_i \) and \( C_i \) are the occurrence frequency of group \( i \) and the group contribution of group \( i \) respectively. \( C_i \) parameter can be found in the Joback and Reid paper.[64] The solid phase free energy for a pure component has been estimated away from \( T_m \) by assuming that \( \Delta H \) and \( \Delta S \) are independent of temperature over a moderate range. This leads to

\[ \frac{G_S}{T} = \frac{G_L}{T} - \Delta H_{\text{fusion}} \left( \frac{1}{T_m} - \frac{1}{T} \right) \] (49)

The subscripts \( S \) and \( L \) indicate pure solid and liquid phases, with liquid phase properties obtained from the equation of state. The pure component chemical potential equals \( \bar{G}_i \) (intensive free energy). Squalane was chosen from the compounds in LG14 as a representative component for wax precipitation. Its chemical potential in the multicomponent bitumen has been calculated using the usual EOS approach.

### 3.4 Results

Published data exist for some of components involved in this study.[83, 84, 85, 53] The estimated critical properties and acentric factor of them have been listed in Table 1. The absolute relative difference percentage (ARD%), which is defined as \( 100|\text{exp.val.} - \text{est.val.}|/\text{exp.val.} \), of estimated critical properties and acentric factors of components in both model asphalts for which experimental data are available are summarized in Table 2. These results suggest that the Nannoolal method can estimate the thermodynamic and critical properties accurately.

The estimated properties have been used in Aspen HYSYS 13.2 environment for all components, even for compounds such as \( nC_{22} \) that exist in the software component library. This makes our approach consistent for all components while
Table 1. Estimated values of each property for known compounds.

| Compound       | $T_b$ | $T_c$ | $P_c$ | $\omega$ | Exp. data source       |
|----------------|-------|-------|-------|----------|------------------------|
| nC$_{22}$      | 635   | 780   | 9.62  |          | Nikitin et al. [83]    |
| 1-ethyltetralin| 513   |       |       |          | Karo et al. [84]       |
| 7,8-benzoquinoline | 613 |       |       |          | chemicalbook.com[85]  |
| Squalane       | 688   | 806   | 6.47  | 1.16     | Nikitin and Popov [53] |

Table 2. ARD% with respect to experimental data for known compounds.

| Compound       | $T_b$ | $T_c$ | $P_c$ | $\omega$ | Exp. data source       |
|----------------|-------|-------|-------|----------|------------------------|
| nC$_{22}$      | 1.03  | 0.7   | 2.01  |          | Nikitin et al. [83]    |
| 1-ethyltetralin| 0.25  |       |       |          | Karo et al. [84]       |
| 7,8-benzoquinoline | 0.32 |       |       |          | chemicalbook.com[85]  |
| Squalane       | 7.32  | 1.7   | 7.61  | 2.83     | Nikitin and Popov [53] |

modeling ZG08 and LG14 model asphalts.

The estimated critical properties and acentric factors of components in ZG08 model asphalt are summarized in Table 3 and of LG14 model asphalts in Table 4. The ranges of critical properties and acentric factors of asphaltene molecules in both ZG08 and LG14 model asphalts are of the same order. Among all asphaltene molecules in LG14 model, asphaltene-pyrrole has the most similar properties as the asphaltene molecule used in ZG08 model asphalt. This similarity might be because both of these two molecules have almost the same number of aromatic carbon atoms that are bound to three aromatic neighbors (14 for asphaltene molecule in ZG08 model asphalt and 16 for asphaltene-pyrrole in LG14 model asphalt). For LG14 model asphalts, the saturates have the lowest normal boiling points and critical temperatures while asphaltenes molecules have the highest normal boiling points and critical temperatures. These are consistent with the fact that asphaltene molecules are the largest molecules in the model. Molecular structures of these compounds are available elsewhere.[29, 30]

ZG08 and LG14 thermodynamic properties of compounds in model AAA-1 asphalts have been calculated using PR EOS using critical properties listed in Ta-
| Molecule                  | No. of molec. | $T_b$ [K] | $T_c$ [K] | $P_c$ [bar] | $V_c$ | $\omega$ |
|--------------------------|---------------|-----------|-----------|-------------|-------|----------|
| $nC_{22}$                | 18            | 635       | 780       | 9.62        | 87.56 | 0.94     |
| 1-ethyltetralin          | 100           | 513       | 721       | 25.77       | 86.67 | 0.49     |
| 7,8-benzoquinoline       | 43            | 613       | 893       | 38.10       | 86.63 | 0.47     |
| Ethylbenzo thiophene     | 20            | 535       | 778       | 34.38       | 86.56 | 0.45     |
| 3-pentyl thiophene       | 50            | 478       | 685       | 30.10       | 86.59 | 0.46     |
| Asphaltene 2             | 9             | 1115      | 1128      | 2.71        | 91.11 | 2.98     |

Table 3. Molecule types, number of molecules, and estimated thermodynamic properties for compounds in ZG08. \[28, 29\]

| Molecule                  | No. of molec. in LG14 | $T_b$ | $T_c$ | $P_c$ |
|--------------------------|------------------------|-------|-------|-------|
|                         | AAA-1 | AAK-1 | AAM-1 |       |       |
| Squalane                 | 4     | 2     | 1     | 688   | 806   | 6.47    |
| Hopane                   | 4     | 2     | 1     | 714   | 885   | 8.86    |
| PHPN                     | 11    | 10    | 20    | 812   | 949   | 8.3     |
| DOCHN                    | 13    | 10    | 21    | 753   | 900   | 8.8     |
| Quinolinohopane          | 4     | 4     | 10    | 821   | 968   | 8.32    |
| Thioisorenieratane       | 4     | 4     | 10    | 847   | 914   | 4.81    |
| Trimethylbenzeneoxane    | 5     | 4     | 10    | 714   | 832   | 7.47    |
| Pyridinohopane           | 4     | 4     | 10    | 769   | 921   | 8.94    |
| Benzo bisbenzothiophene  | 15    | 12    | 4     | 749   | 1049  | 34.76   |
| Asphaltene-phenol        | 3     | 3     | 1     | 926   | 1024  | 6.52    |
| Asphaltene-pyrrole       | 2     | 2     | 1     | 1125  | 1139  | 2.96    |
| Asphaltene-thiophene     | 3     | 3     | 1     | 1002  | 1063  | 4.56    |

Table 4. Molecule types, number of molecules, and thermodynamic properties for compounds in LG14. \[30\] The units for properties are the same as Table 3.
bles 3 and 4 and with all $k_{ij}$ set to zero in Aspen HYSYS. Figure 21 shows the temperature-dependent density predictions for both ZG08 and LG14 asphalt models. Experimental density data and thermal expansion coefficient[86] for SHRP AAA-1 asphalt binder are shown in this figure. The density of AAA-1 asphalt at different temperatures were previously[29, 30] calculated using molecular dynamics (MD) and the OPLS[87, 88, 89] all-atom force field for both ZG08 and LG14 model asphalts at different temperature. The density of AAA-1 asphalt binder represented by ZG08 model asphalt using the PR EOS shows almost 40% ARD compared to the experimental density. The density of LG14 model asphalt representation of AAA-1 asphalt binder using PR EOS shows a slightly less poor ARD (35%). This improvement in density prediction can be related to the fact that the molecules are of higher molecular weight. Using the COST ALD correlation significantly improved the density predictions: 20% and 13% ARD% underprediction respectively for ZG08 and LG14 representations of AAA-1 asphalt binder. MD results show better predictions in all cases. Molecular dynamics for AAA-1 asphalt binder represented by ZG08 shows 10% ARD and 6% for AAA-1 asphalt binder represented by LG14. Although MD results are outperforming, they require a huge amount of CPU time, while EOS calculations can be done in a fraction of a second.

The density predictions enable calculating thermal expansion coefficients $\alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P$ using different models. Results are shown in Table 5 along with the experimental and MD results for AAA-1 asphalt.

For ZG08 model asphalt, COST ALD correlation can provide the most accurate thermal expansion prediction. The PR EOS prediction for thermal expansion is better than MD prediction but it is not as good as COST ALD prediction. COSTALD and MD predictions for LG14 model asphalts are equally good while
Figure 21. Density vs. temperature for AAA-1 asphalt binder determined for ZG08 and LG14 models using MD (solid line), PR EOS (dashed), and COSTALD (dotted) compared to experimental data (dot-dashed).

| Asphalt model | ZG08 | LG14 | ZG08 | LG14 |
|---------------|------|------|------|------|
| MD [29, 30]   | 11.3 | 8.4  | 88   | 40   |
| COSTALD       | 3.8  | 3.4  | 37   | 43   |
| PR            | 2.5  | 1.3  | 58   | 78   |

Table 5. Thermal expansion of AAA-1 asphalt binder and its absolute relative error with respect to experimental data.
Figure 22. The chemical potential of squalane in mixture and as a pure component PR EOS shows poor result for thermal expansion prediction. Generally, COSTALD correlation is the most reliable method for thermal expansion prediction for both ZG08 and LG14 model asphalts.

Figure 22 illustrates the squalane chemical potential in LG14 representations of AAA-1, AAK-1, and AAM-1 model asphalt binders. Chemical potential results for pure liquid and solid squalane are based on precipitation at the squalane melting point of 235K, as reported by Nikitin and Popov. Whenever the chemical potential of squalane in the mixture is less than pure solid squalane, squalane does not precipitate. Below 235 K, the chemical potential of pure solid squalane becomes more negative than the chemical potential of squalane within the multicomponent systems. This indicates a free energy driving force for squalane to precipitate at low enough temperatures.

The temperature at which the solid squalane chemical potential becomes lowest depends on the composition of the multicomponent system. To show this effect of chemistry on wax precipitation more clearly, the ratio of chemical potential of squalane in different mixtures and of squalane as a pure liquid has been plotted. Figure 23 predicts that squalane would precipitate from AAA-1 at a higher temper-
Figure 23. The ratio of chemical potential of squalane in different mixtures and squalane as a pure component.

ature (226 K) compared to from modeled AAK-1 or AAM-1. Squalane is predicted to precipitate from the modeled AAM-1 at lowest temperature (219 K). This figure can help to predict precipitation of wax which is a key part of determining the performance of an asphalt binder.

Figure 24 compares the specific enthalpies calculated from MD for AAA-1 asphalt binder represented by LG14 model asphalt with the enthalpies calculated for AAA-1, AAK-1, and AAM-1 asphalt binders represented by LG14 model asphalt. While AAA-1, AAK-1, and AAM-1 show almost the same enthalpies at different temperatures, they are lower than the enthalpies calculated using MD for AAA-1 asphalt binder represented by LG14 model asphalt. The deviation is larger at higher temperatures.

Figure 25 illustrates the TP phase envelopes of AAA-1 using two model asphalts. A T-P phase envelope indicates the corresponding bubble point pressure and dew point pressure at each temperature. This figure shows that the ZG08 model provides a wider two-phase region than LG14 model asphalt. Figure 25 can help us estimate the mixture critical point. The mixture critical temperature for
ZG08 model asphalt is 814 K and its critical pressure is 31 atm. The mixture critical temperature for AAA-1 is 955 K and the mixture critical pressure is 11 atm. Figure 25 and Tables 3 and 4 can be used to conclude that ZG08 molecules are more volatile in asphalt processing condition. The ZG08 model asphalt bubble point at 1 atm is 500 K, and bitumen processing usually extracts volatile species at 800 K.\cite{90} This is a further indication that the molecules in the ZG08 model asphalt are too small and volatile and are not suitable for being used specially in distillation column conditions and asphalt processing conditions.

### 3.5 Conclusions

The critical properties and acentric factors of all components involved in both ZG08 and LG14 model asphalts have been estimated using the methods of Nannooolal et al. \cite{54, 55, 56} The densities and the thermal expansions of both model asphalts were calculated in Aspen HYSYS 13.2 using these estimated properties and the PR EOS. LG14 model asphalt predicted densities and thermal expansion coefficient more accurate with respect to experimental data. The calculated densities from MD is better than results from PR EOS corrected by COSTALD
Figure 25. T-P envelope of modeled AAA-1. BPP stands for bubble point pressure and DPP stands for dew point pressure.

correlation. But the calculation cost is which smaller using the EOS. The PR EOS is not performing very well in predicting densities, which is common in cubic equations of state. On the other hand, PR EOS without volume translation is predicting thermal expansion of asphalts much better than any other methods. Comparing the squalane chemical potential in the multicomponent system to that of pure liquid or solid squalane shows that the chemistry of an asphalt binder can affect the temperature at which waxes can precipitate.

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APPENDIX A

Nannoolal method for critical property calculations

One of the most important physical properties of a compound is the normal boiling point. It can be estimated by [1]

\[
T_b = \frac{\sum_i N_i C_i + GI}{n^{0.6583} + 1.6868} + 84.3395
\]  (A.1)

where \(N_i\) is the frequency of the group \(i\) in the molecule, \(C_i\) is the group contribution of group \(i\), and \(n\) is the number of atoms in molecule excluding hydrogen atoms. \(GI\) is the group interaction contribution (third-order), which is [1]

\[
GI = \frac{2}{n(m-1)} \left( \sum_{i=1}^{m} \sum_{j=i+1}^{m} C_{i-j} \right)
\]  (A.2)

\(m\) is the total number of interacting groups. The notation \(C_{i-j}\) indicates the contribution from interactions between group \(i\) and group \(j\); it is not a subtraction.

While \(T_b\) does not appear directly in the EOS, its value is required for critical temperature calculations.

The relation between critical temperature and normal boiling point is known for more than 100 years and was first reported by Guldberg[2] in 1890. This relation has been modified several times and almost all GC methods follow Guldberg’s relation,[2]

\[
T_c = 1.5 T_b
\]  (A.3)

where \(T_c\) and \(T_b\) are in Kelvin. Nannoolal et al. improved Guldberg’s method by replacing the simple coefficient factor of 1.5 by a more complicated expression [3]

\[
T_c = T_b \left( 0.6990 + \frac{1}{0.9889 + \left( \sum_i N_i C_i + GI \right)^{0.8607}} \right)
\]  (A.4)
The critical pressure ($P_c$) is another parameter which is used by equations of state based on "principle of corresponding states."[4] This value can be calculated by [3]

$$P_c = \frac{M^{-0.14041}}{\left(0.00939 + \sum_i N_i C_i + GI\right)^2}$$  

(A.5)

which $P_c$ is in kPa and $M$ is the molecular weight in g/mol.

The critical volume can be calculated based on Nannoolal method as [3]

$$V_c = \frac{\sum_i N_i C_i + GI}{n^{-0.2266}} + 86.1539$$  

(A.6)

The dimension for critical volume is $10^{-6}m^3mol^{-1}$.

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APPENDIX B

Improved results for chapter 1

This appendix is showing the updated results of Chapter 1 after applying some signal processing techniques to improve the frequency domain results.

Figure B.1. First ps of the stress relaxation modulus of both AAA-1 model asphalts. Temperature suffixes \( \¥ \) and \( \dagger \) indicate the ZG08 and ZG08p systems;[1, 2] others refer to the LG14 system.[3]

Figure B.2. 1 ps to 1 ns of the stress relaxation modulus of the LG14 system.
Figure B.3. 1 ps to 1 ns of the stress relaxation modulus of the ZG08 and ZG08p systems at 443 K.
Figure B.4. Black (or van Gurp-Palman) plot for the LG14 system for different temperatures. Lines indicate a qualitative comparison with CAM model fits reported[4] for AC-1 and AC-2 asphalt systems and shifted to 533 K.

Figure B.5. Moduli and phase angle of the LG14 system at T = 400 K.

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Figure B.6. Moduli and phase angle of the ZG08 (\(\chi\)) and LG14 systems at \(T = 443\) K.

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Figure B.7. Moduli and phase angle of the ZG08 and ZG08p systems at T = 443 K.

Figure B.8. Moduli and phase angle of the LG14 system at T = 533 K.
Figure B.9. Storage modulus of all systems (solid line for $G'$ and dashed line for $\delta$).

Figure B.10. Loss modulus of all systems (solid line for $G''$ and dashed line for $\delta$).
Figure B.11. $|G^*|/\omega$ of all systems. Dashed lines show Green-Kubo method low frequency limits. [1, 3] Squares indicate experimental data [5] for a PG 64–22 asphalt at 398 (filled) and 443 K (open). Left-pointing triangles indicate experimental data [6] for a 70/100 bitumen at 409 K (filled) and 433 (open).

Figure B.12. Black (or van Gurp-Palman) plot for the ZG08 and ZG08p systems.
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