Transport Properties of Waxy Crude Oil: A Molecular Dynamics Simulation Study

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1. INTRODUCTION

Crude oil plays an important role in global energy supply. Waxy crude oil is the most common type of crude oil, for example, accounting for 90% of the total production in China.1 The presence of paraffin is responsible for the waxy behavior of crude oil. Paraffin refers to the mixture of n-alkanes and iso-alkanes with the carbon number ranging from C_{20} to C_{46}.2 It precipitates from crude oil when the temperature is below the wax appearance temperature (WAT),4 and such precipitation can cause an increase of viscosity and a decrease of flow ability during the transportation process.3,6 The relationship between the content of paraffin and the properties of crude oil has been previously investigated experimentally. Multiple factors can influence viscosity changes in oil and oil/water emulsions, for example, paraffin crystallization,7 aggregation of nanoparticles,8 and so forth. However, very little is known about molecular level mechanisms that lead to WAT and changes in viscosity. Therefore, recently, the understanding of crude oil at the microscale has attracted attention from researchers,9 including the application of molecular dynamics (MD) simulations that have been used to study hydrocarbons and organic molecules.11 With the advancements in high-performance computing, an increased number of simulation studies of alkanes, paraffins, and crude oil has been reported. For example, Mondello and Grest12,13 calculated self-diffusion coefficients and viscosity of n-decane and n-hexadecane. The simulated diffusion coefficients were found to be higher than experimental values while the predicted viscosity was lower compared to the experiment. McCabe et al.14 used MD simulations to study the rotational relaxation time and viscosity of 9-octylheptadecane and accurately predicted the transition from Newtonian to non-Newtonian behavior. Lin and Rao15 considered n-C_{20} as the representative of the paraffin molecule and investigated bulk thermal conductivity and phase behavior. Liu et al.16 constructed a mixture model consisting of paraffin (n-C_{28} and n-C_{22}) and polystyrene to study the heat and mass transfer of this system using the nonequilibrium MD (NEMD) method. Makrodimitri et al.17 studied the viscosity of pure n-

ABSTRACT: To study the effects of paraffin on viscosity of waxy crude oil and transport properties of small molecules, light and waxy crude oil models were investigated at atmospheric pressure and 293–323 K temperature range using atomistic molecular dynamics simulations. The optimized parameters for liquid simulations all-atom (OPLS-AA) and atomistic polarizable potential for liquids, electrolytes, and polymers (APPLE&P) force fields were employed. The self-diffusion coefficients, viscosity, and paraffin configurations were compared for two oil models and between the two employed force fields. However, the behavior of paraffin molecules predicted by two force fields was quite different. Simulations using the OPLS-AA force field showed crystallization of longer paraffin molecules below 323 K, while a homogeneous mixture down to 293 K. To provide additional validation of the employed force fields, the density, diffusion coefficient, and crystallization of pure alkanes were compared with experimental data. The density and diffusion coefficients of n-C_6 and n-C_{14} simulated with the APPLE&P force field were found to be in much closer agreement with the experimental data. The OPLS-AA force field was found to overestimate the crystallization temperature of pure alkanes. Therefore, simulations with the APPLE&P provide more realistic description of the waxy oil structure and transport properties. In this temperature range, the paraffin molecules are homogeneously distributed in the mixture, and viscosity of the system increased by a factor of two compared to light oil. Crystallization of paraffins requires lower temperatures or/and the presence of other components such as nanoparticles or asphaltene molecules to facilitate nucleation.
alkanes from \( n-C_8 \) up to \( n-C_{96} \) by MD simulations and found good agreement between viscosities predicted from simulations and the available experimental data at various temperatures. While these studies extensively sampled structural and transport properties of these single or only few component systems, they were not concerned about the ability of the employed force fields to accurately capture the phase behavior and specific crystallization in these materials. Using a coarse-grained force field, Shahrudin et al.\(^\text{18}\) showed how sensitive the determination of crystallization temperature of \( n \)-alkanes can be to the details of simulation protocol, system composition, and chain length.

MD simulations of \( n \)-alkanes and their mixtures showed that simulations can be an efficient tool to study both microscopic characteristics as well as to predict macroscopic properties. However, crude oil is a complex mixture consisting of numerous hydrocarbon molecules. It is widely accepted that alkanes, cycloalkanes, and aromatic hydrocarbons are essential components in a crude oil model.\(^\text{19}\) Miranda et al.\(^\text{20,21}\) constructed a model for light oil from Japanese oil fields using eight types of hydrocarbons mixed at a certain ratio in order to study accumulation of aromatic molecules at the oil–water interface. Gao et al.\(^\text{22}\) added asphaltene molecules into the light oil model proposed by Miranda. The mixture was regarded as asphalt-based crude oil, and the aggregation configuration of asphaltene molecules in crude oil was discussed. Sedghi et al.\(^\text{23}\) considered crude oil as a mixture of \( 14 \) types of nonpolar (saturated and aromatic fractions) and \( 12 \) types of polar molecules (resin and asphaltene fractions); the specific composition was correlated to the saturates, asphaltene, resins, and aromatic fractions and the gas chromatography analysis of a crude oil sample. The influence of polar components on interfacial tension between the crude oil and brine was determined. Gan et al. investigated the dissolution of paraffin crystals in model waxy crude oil as a function of pressure.\(^\text{24}\) Most of the MD simulations of crude oil described above were related to the asphalt-based crude oil, either focusing on the behavior of polar components in crude oil or the interactions between oil and water. However, very limited number of simulations has focused on waxy crude oil and the behavior and role of paraffin molecules in crude oil. Moreover, very little or no attention has been paid to the influence of employed simulation force fields to the accuracy of property predictions.

The objective of this study is to determine the influence of long-chain paraffin molecules on transport properties of waxy crude oil and to assess the sensitivity of these predictions to the choice of the force field utilized in simulations. In Section 2, we provide description of two different force fields that were used in simulations, details on system compositions representing the light oil and waxy crude oil, and the analysis procedures to sample self-diffusion coefficients, configuration of paraffin chains, and viscosity. Section 3 summarizes the obtained results for viscosity, self-diffusion coefficients, and phase behavior of paraffin molecules in model oils as a function of temperature. Section 3 also discusses additional efforts to validate the two force fields by comparing the density, diffusion coefficients, and crystallization of pure alkanes (\( n-C_6 \), \( n-C_{14} \), and \( n-C_{38} \)) obtained from the simulations and experiment. Finally, Section 4 provides the summary and conclusions of the results obtained from this work and discusses the gained molecular level understanding of properties of waxy crude oil.

### 2. SIMULATION DETAILS

#### 2.1. Molecular Models and Simulation Setup

In this paper, both the light and waxy crude oil models were constructed. The light oil is based on the model proposed by Kunieda et al.\(^\text{25}\) and includes alkanes (72 hexane, 66 heptane, 78 octane, and 90 nonane), cycloalkanes (48 cyclohexane and 78 cycloheptane), and aromatic (78 toluene and 30 benzene) molecules. The waxy crude oil was modeled as a mixture of light oil and paraffin molecules (20 \( n-C_{20} \) and 20 \( n-C_{26} \)). The type and content of paraffin molecules correlate with the data from differential scanning calorimetry and the carbon number distribution analysis of a waxy crude oil sample.\(^\text{26}\)

MD simulations were performed with optimized parameters for the liquid simulations all-atom (OPLS-AA) force field\(^\text{26}\) using the large-scale atomic/molecular massively parallel simulator (LAMMPS)\(^\text{27}\) and the atomistic polarizable potential for liquids, electrolytes, and polymers (APPLE&P) force field using the Wasatch Molecular, Inc. (WMI) software package.\(^\text{28}\) Simulations were carried out at atmospheric pressure and a temperature range from 293 to 323 K. Isothermal–isobaric (NPT) ensemble simulations were initially performed for 20 ns to obtain the equilibrium configuration at each temperature. These configurations were then used as the starting point for 30 ns production simulations in the isothermal–isochoric (NVT) ensemble. The Nosé–Hoover thermostat and barostat were used for controlling the temperature and pressure with an integration step of 1 fs in LAMMPS and WMI codes.\(^\text{29,30}\) The dispersion forces of van der Waals interactions were represented by the Lennard-Jones potential function in the LAMMPS and by modified exp-6 potential in the WMI code.\(^\text{31}\) The long-range Coulombic interactions were evaluated by the particle–particle–particle-mesh\(^\text{32}\) method with an accuracy value of \( 10^{-4} \) in the LAMMPS and by Ewald summation\(^\text{33}\) in the WMI code. Periodic boundary conditions were employed in \( x, y, \) and \( z \) directions. A cutoff of 10 Å was used for the intermolecular interactions. The open visualization tool (OVITO)\(^\text{34}\) and Jmol\(^\text{35}\) were employed to visualize configurations of the simulated systems.

#### 2.2. Calculation of Viscosity

The zero-shear viscosity can be computed by equilibrium MD (EMD) and NEMD methods.\(^\text{36,37}\) In this study, to calculate viscosity, we employed the Einstein relation to analyze results of EMD simulations. The formula for this relation is given in eq \( 1 \):\(^\text{38}\)

\[
\eta = \lim_{t \to \infty} \frac{V}{20k_B T t} \int_0^t \sum_{\alpha \neq \beta} \frac{q_{\alpha \beta} \int_0^t P_{\alpha \beta}(t') dt'}{\left(\frac{r_{\alpha \beta}^3}{r_{\alpha \beta}^2}\right)^2} dt
\]

where \( V \) and \( T \) are the volume and temperature of the system, \( k_B \) is the Boltzmann constant, \( q_{\alpha \beta} \) is a weight factor (\( q_{\alpha \beta} = 1 \) if \( \alpha \neq \beta \), otherwise, \( q_{\alpha \beta} = 4/3 \)), \( P_{\alpha \beta} \) is the component of the stress tensor, \( t \) is the integration time, and \( r \) is the sampling frequency of \( P_{\alpha \beta} \).

### 3. RESULTS AND DISCUSSION

#### 3.1. Viscosity of Light and Waxy Crude Oils

Calculation of viscosity (eq \( 1 \)) relies on the integration of stress tensor fluctuations with respect to time, and therefore, the stress tensor output and integration step have to be selected appropriately. The time evolution of the \( P_{xy} \) component of the stress tensor for one of the systems is plotted in Figure 1 with the output frequencies of 1, 5, 10, and

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20 fs. It can be seen that the sampling frequencies of 1 and 5 fs provide almost the same evolution of the stress tensor, capturing all features of high-frequency oscillations. However, outputs with 10 and 20 fs result in missing certain oscillations, and hence, the time integral obtained by the numerical integration (and hence viscosity estimate) would not be accurate. Therefore, the sampling frequency of 5 fs was chosen for all viscosity calculations.

Figure 2 shows an apparent viscosity of light and crude oils as obtained from analysis of MD simulations using the APPLE&P force field as a function of integration time at temperatures ranging from 293 to 323 K. In the viscosity analysis using the Einstein relation, the apparent viscosity is expected to reach a plateau value at longer integration times, which corresponds to the zero shear rate value of viscosity. It can be seen that the apparent viscosities of light oil reach a well-defined plateau when the integration time is larger than 100 ps. The viscosities of crude oil at 323 and 313 K also reach a plateau at an integration time of 300 ps. However, for 293 and 303 K, it takes about 800 ps integration time to reach reasonable saturation. The viscosities of light and crude oils (extracted as plateau values from Figure 2) obtained from simulations using APPLE&P and OPLS-AA force fields are summarized in Table 1 and plotted versus inverse temperature in Figure 3. For light oil, both force fields show an Arrhenius behavior in the temperature range investigated. Simulations of crude oil with the APPLE&P force field show close to Arrhenius dependence, although some change in slope between high and low temperature data points can be observed. However, simulations of crude oil with OPLS-AA show a much stronger and non-Arrhenius dependence.

Because of the lack of experimental data available for validation, the viscosities of light oil obtained from MD simulations were compared with empirical estimates. We adopted the empirical relation proposed by Kendall and Monroe, as shown in eqs 2 and 3

\[
\eta_{\text{m}}^{1/3} = \sum_{i=1}^{n} x_i \eta_i^{1/3} 
\]

(2)

\[
\ln \eta_{\text{m}} = \sum_{i=1}^{n} x_i \ln \eta_i 
\]

(3)

where \(\eta_{\text{m}}\) is the empirical viscosity of light oil, \(\eta_i\) is the experimental viscosity of each component in light oil, and \(x_i\) is

![Table 1. Viscosity of Light and Crude Oil Obtained from MD Simulations with OPLS-AA and APPLE&P Force Fields](image)

**Figure 2.** Apparent viscosity of light (a) and crude (b) oil systems as a function of integration time at different temperatures. Horizontal dash lines indicate plateau values used to define converged viscosity values.

**Figure 3.** Viscosity as a function of inverse temperature as obtained from MD simulations using two force fields. Lines are for the eye guidance.
the corresponding mole fraction. According to this empirical relation, the mixture viscosity \( \eta_m \) can be calculated from the mole fraction and the experimental viscosities of each component in light oil (as shown in the Supporting Information). For our light oil mixture, the \( \eta_m \) at 293 K was found to be \( 6.61 \times 10^{-4} \) and \( 6.33 \times 10^{-4} \) Pa s as calculated by eqs 2 and 3, respectively. The slightly higher values of APPLE&P predictions are therefore closer to this empirical estimate of viscosity than the OPLS-AA values.

3.2. Dynamics of Small Molecules. The self-diffusion coefficient of species is usually inversely proportional to viscosity. Therefore, it is instructive to examine the effect of paraffin on the self-diffusion coefficients of small molecules. The light and crude oils contain aromatic, cycloalkane, and linear alkane molecules. We choose toluene, cycloheptane, and nonane as representatives for each type of molecules. The self-diffusion coefficients of these compounds in light and crude oils are shown in Figure 4. The diffusion coefficients of small molecules in the light oil calculated using OPLS-AA are systematically (10–30%) higher than those predicted by the APPLE&P force field, which is consistent with the viscosity results that showed that the light oil viscosity predicted by OPLS-AA is lower than APPLE&P results. Both force fields show consistent temperature dependence of self-diffusion coefficients, that is, monotonically increasing with temperature.

As expected, because of the presence of paraffin chains, the diffusion coefficients of molecules in crude oil are smaller than that in the light oil. However, the slowing down is less than a factor of two compared to light oil. Moreover, both force fields predict similar temperature dependence despite the fact that simulations with OPLS-AA showed a very sharp jump in viscosity upon decreasing temperature below 323 K. No corresponding jump in diffusion of small molecules has been observed in OPLS-AA simulations.

The observed temperature trends for transport properties of light and crude oils show perplexing trends. On the one hand, both force fields show qualitatively consistent trends for the self-diffusion coefficients of small molecules; on the other hand, viscosities predicted from OPLS-AA and APPLE&P are qualitatively different. For the light oil, both force fields predict consistent behavior, while for the crude oil, the viscosities show very different behavior.

3.3. Crystallization of Paraffin and Transport Property Analysis. In order to explore the cause for significant deviation of viscosity predictions by two models, the configurations and distribution of paraffin molecules were analyzed and are displayed in Figures 5 and 6. The OPLS-AA simulations show that paraffin molecules crystallize as temperature decreases. At 323 K, some paraffin molecules aggregate, while the rest are distributed randomly through the system. However, at 313 K, the aggregated paraffin molecules tend to crystallize, adopting primarily all-trans conformations. With a further decrease of temperature, the crystal domain becomes well-defined and consumes all molecules in the system. However, simulations with the APPLE&P force field (Figure 6) do not show any sign of crystallization at any of the temperatures. The paraffin molecules are well-distributed in the crude oil system.

Comparing these observations with the viscosity results, it becomes clear that the sharp increase in viscosity and non-Arrhenius behavior for OPLS-AA systems occur in systems...
where the paraffin molecules start to crystallize. Such viscosity behavior is qualitatively consistent with experimental observations when paraffins undergo crystallization in waxy oil mixtures, albeit it is expected to occur at lower temperatures than what observed in simulations. Taking into account that because of periodic boundary conditions the formed crystal domain is semi-infinite, applicability of the Einstein relationship for viscosity calculation becomes questionable in this case. This is also consistent with the observed trends for self-diffusion of small molecules. While crystallization of paraffin molecules can affect the stress tensor correlations and hence viscosity, the mobility of small molecules is only slightly affected by the phase of the paraffin.

We would like to point out that brute force MD simulations are not well suited for studying phase transition, particularly crystallization, because of limited observation times (multiple nanoseconds) and finite size effects. Hence, often in MD simulations, the system has to be significantly overcooled/overheated in order to generate stable nucleation of a new phase. However, if MD simulations predict crystallization at higher temperatures than typically observed in experiments, that would be an indication that the force field employed to describe inter- and intramolecular interactions might be at fault.

Taking into account that the two models effectively predict different phase behavior of paraffins in crude oil, the next key question is which of those observed behaviors is more realistic? To address this issue, we have examined properties of pure alkanes using both force fields and validated them against available experimental data.

### 3.4. Force Field Validation

In order to validate which the force field is suitable for hydrocarbon systems, several properties of pure alkanes were simulated and compared with the experimental data. The phase-transition temperature of bulk n-C14 and n-C38 was estimated from brute force simulations and compared with the experimental melting temperature. The n-C14 and n-C38 systems were first heated to 1000 K to ensure random distribution of molecules. Then, the systems were cooled to different temperatures in steps of 50 K and production runs of 10 ns. This is not a rigorous method to determine the phase-transition temperature. For the first-order phase transition, one would expect that the brute force cooling in MD simulation leads to a noticeable overcooling of the system below the melting temperature before any crystallization would be visible in simulation.

The snapshots of simulated systems with OPLS-AA are shown in Figure 7 and with APPLE&P in Figure 8 at several temperatures. The experimental melting temperatures of n-C14 and n-C38 are 279.25° and 351.7 K, respectively. Simulations with OPLS-AA indicate that n-C14 and n-C38 begin to crystallize at temperatures higher than the experimental melting point. The n-C14 shows crystallization at 313 K which is about 34° higher than the experimental melting temperature. The n-C38 crystallizes at 383 K which is also about 30° higher than its melting temperature. On the other hand, simulations using the APPLE&P force field do not show any sign of crystallization even at temperatures below the experimental melting temperature, which would be expected for this brute force cooling estimate. These simulations indicate that the employed OPLS-AA model overestimates the crystal phase of n-alkanes compared to the liquid phase.

We also compared the density and diffusion coefficient of n-C6 and n-C14 which are summarized in Table 2 and compared to the experimental data at 298 K. The diffusion coefficients were determined using the Einstein relation between the time-
Table 2. Simulated and Experimental Density and Self-Diffusion Coefficients of n-Alkanes at 298 K

| Alkanes | Properties | Simulation | Experiment |
|---------|------------|------------|------------|
| n-C6    | density (g/cm³) | 0.6335     | 0.6628     | 0.6548<sup>a</sup> |
|         | diffusion coefficient (×10<sup>-5</sup> cm<sup>2</sup>/s) | 4.745      | 4.361      | 4.44<sup>b</sup> |
| n-C14   | density (g/cm³) | 0.8397     | 0.7562     | 0.7590<sup>c</sup> |
|         | diffusion coefficient (×10<sup>-5</sup> cm<sup>2</sup>/s) | 0.5797     | 0.60<sup>d</sup> | 0.58<sup>e</sup> |

<sup>a</sup>From ref 45. <sup>b</sup>From ref 46. <sup>c</sup>From ref 47. <sup>d</sup>From ref 48.

...dependent mean square displacement and self-diffusion. A finite size correction<sup>24</sup> is given as

\[
\Delta D = \frac{2.837k_B T}{6\eta nL}
\]

where \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(L\) is the length of the cubic simulation cell, and \(\eta\) is the experimental viscosity (0.309 cP for C6 and 2.028 cp for C14 at 298 K) applied. Table 2 shows that the density and self-diffusion coefficients of n-C6 and n-C14 predicted from simulations using the APPLE&P force field are in a closer agreement with the experimental data compared to OPLS-AA. The OPLS-AA underestimates the density and overestimates the self-diffusion coefficient of n-C6. As the n-C14 system has crystallized at 298 K, the simulated density is much higher than the experimental data, and an estimate of the diffusion coefficient is meaningless for this system at 298 K.

Overall, both the APPLE&P and OPLS-AA force fields are imperfect, but the APPLE&P force field better captures the expected phase behavior and predicts diffusion coefficients closer to experiment.

4. SUMMARY AND CONCLUSIONS

In this paper, the effects of paraffin on viscosity of waxy crude oil and the transport property of small molecules were investigated in the 293–323 K temperature range using MD simulations with OPLS-AA and APPLE&P force fields. To compare and validate the two force fields, the properties of pure alkanes were investigated and compared with the experimental data. The main conclusions can be summarized as follows.

1. Simulations with the OPLS-AA force field show that the paraffin molecules in the crude oil model crystallize at temperatures lower than 323 K, while simulations with the APPLE&P do not show any signs of crystallization.

2. The validation of force fields based on simulations of alkane melts showed that the OPLS-AA force field noticeably overestimates the crystallization temperature. The density and diffusion coefficients of bulk n-C6 and n-C14 liquids simulated with the APPLE&P force field are closer to the experimental data. The differences in the description might be attributed to the fact that APPLE&P is a polarizable force field that explicitly takes into account Debye type polarization interactions, while OPLS-AA is not. Although, the importance of Debye-induced polarization interactions in these systems should be minor because there are no ionic species that could result in substantial polarization of molecules. It is more likely that the observed difference in phase behavior is due to differences in parameters describing the London dispersion forces of van der Waals interactions.

3. Taking this into account, we believe that the results from simulations using the APPLE&P force field are more reliable for sampling waxy crude oil. Specifically, these simulations show that paraffin molecules are homogeneously distributed in the light oil mixture of small molecules without a noticeable tendency for aggregation. In the investigated temperature range, the presence of paraffin chains increases the viscosity of waxy oil and reduces the mobility of smaller molecules by no more than a factor of two.

Taking these observations into account, we believe that the presence of paraffin molecules in crude oil, by itself, is unlikely to be the source of a significant increase in viscosity, which is often observed for waxy crude oils in field operations. It is likely that crystallization of paraffins requires cooling to lower temperatures or/and the presence of other components such as nanoparticles, asphaltene molecules, or other contaminants to facilitate nucleation. More importantly, our work demonstrates that prediction from MD simulations can be quite sensitive to the accuracy of the model used and hence particular care has to be taken for the force field selection and validation when studying such complex multicomponent systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00070. Mole fraction and the experimental viscosities of each component in light oil (PDF)

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Notes

The authors declare the following competing financial interest(s): Prof. Bedrov is one of the co-founders of Wasatch...
Molecular Inc which develops and distributes the APPLE&P force field for molecular dynamic simulations.

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