

# Molecular Dynamics Simulations of Asphaltenes at the Oil–Water Interface: From Nanoaggregation to Thin-Film Formation

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## S Supporting Information

**ABSTRACT:** We have investigated the interfacial behavior of asphaltene molecules at the oil–water interface using molecular dynamics simulations. Oil precipitants and solvents are represented by heptane and toluene, respectively. It was found that asphaltenes are preferably distributed in the oil phase in the case of pure toluene, whereas they accumulate at the oil–water interface for pure heptane. Interestingly, the interfacial tension (IFT) of the interfacial system containing a small amount of asphaltene molecules is close to that of a pure heptane–water system, while the IFT of the system containing a large amount of asphaltene molecules is much reduced,  $\sim 12$  mN/m. Further, it was shown that the reduced IFT results from a complete asphaltene film formed at the oil–water interface when asphaltenes are abundant. In addition, it was found that a small amount of asphaltene molecules stacked their aromatic planes and formed a nanoscale aggregate, which exhibited an exotic molecular oscillation behavior of asphaltene molecules at the oil–water interface.

## ■ INTRODUCTION

In the petroleum industry, it is of essential importance to better understand interfacial systems between crude oil and underground fluids.<sup>1–4</sup> Stable water-in-oil emulsions form during the production of oil, which must be resolved to fit the specified product quality.<sup>4–6</sup> Asphaltenes and resins in the crude oil are known as major components to stabilize the emulsions.<sup>4–6</sup> The aggregation status of asphaltene molecules at the oil–water interface is, therefore, one of the most important interfacial properties being investigated.<sup>4–8</sup> It has been shown that asphaltenes stabilize water-in-oil emulsions only if they are close to or above the point of incipient flocculation.<sup>4–6</sup> This is consistent with the speculation that the asphaltene film is two-dimensional in nature at low concentrations in the oil but changes to three-dimensional at high asphaltene concentrations.<sup>8</sup> However, there is still a lack of a fundamental understanding of the interfacial films (of asphaltenes) with detailed molecular structures.

Asphaltenes are part of extra heavy oil components and, by definition, are a solubility class of materials that is insoluble in heptane but soluble in toluene.<sup>9</sup> They may be precipitated from petroleum reservoir fluids as a highly viscous and sticky material that is likely to cause deposition problems in reservoir rock, production wells, and pipelines. Experiments and computational simulations have been performed to obtain a fundamental understanding of asphaltenes, including molecular structure, hierarchical colloidal structures, interfacial properties, and chemical reactivity.<sup>10–19</sup> According to the modified Yen model, asphaltene molecules form nanoaggregates in solvent (with an aggregation number of  $\sim 6$ ) and with a single offset polycyclic aromatic stacking in the interior with peripheral aliphatic chains. Furthermore, asphaltene nanoaggregates can form clusters (with aggregation numbers estimated to be  $\sim 8$ ).<sup>10,11</sup> This is further supported by recent surface X-ray scattering<sup>12</sup> and small-angle neutron scattering<sup>13</sup> data portrayed

as a diffuse nanoaggregate. A similar conclusion has been reached by other measurements, such as centrifugation as well as computational studies.<sup>14,16</sup> The adsorption of the asphaltene molecules,<sup>4–8,20,21</sup> especially at the oil–water interface,<sup>4–8</sup> has also improved our knowledge on interfacial asphaltenes. The focus of this study will be to investigate the interfacial structures of asphaltenes for a single asphaltene molecule, an asphaltene nanoaggregate, an asphaltene cluster, and a complete asphaltene film.

Molecular dynamics (MD) simulations have been performed to study static and dynamic interfacial phenomena and the wetting behavior of liquids, including asphaltenes<sup>22–25</sup> and asphalts *in vacuo*<sup>26–29</sup> and in a solvent.<sup>30</sup> A range of different asphaltene models have been employed in various studies.<sup>31–37</sup> In this study, we have used three types of asphaltene molecules generated from an updated quantitative molecular representation (QMR) method, which was optimized to most of the available experimental data with low-molecular-weight asphaltenes (500–2000 amu).<sup>36</sup> Using MD simulations, we have investigated the interfacial phenomena and the dynamic behavior of the asphaltene molecules at the oil–water interfaces. The aim is to describe the interfacial structures and the dynamics of the asphaltene from a single asphaltene molecule, the accumulated nanoaggregates, and finally, the thin asphaltene film at the oil–water interface and visualize the behavior of the asphaltene molecules at the nanoscale.

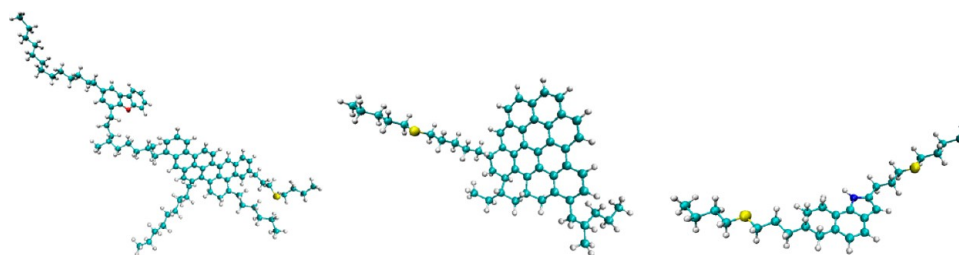
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**Figure 1.** Asphaltene molecules employed in this study: (left) archipelago type, (middle) island type, and (right) resin type.

## COMPUTATIONAL METHODS

MD simulations have been used to investigate the interfacial phenomena and behavior of the asphaltene molecules at the oil–water interface.<sup>38</sup> Basically, the interface system in this work consists of three slabs, which are oil, asphaltene, and water. By changing the type and number of the asphaltene molecules, we have investigated the asphaltene status from nanoaggregate to thin film at the oil–water interface.

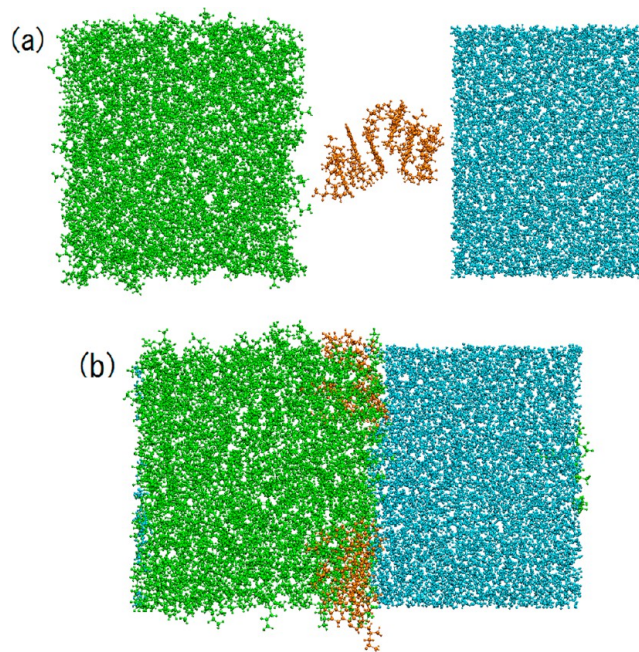
**Molecular Models.** Asphaltene molecules consist of the three components. The first component is the aromatic core containing many polycyclic aromatic rings, because the asphaltene molecule has one or more rigid planes. This core constrains the molecular behavior. The second is the aliphatic chain, and the third one is the heteroatom, for example, nitrogen, sulfur, or oxygen. Therefore, the chemistry of the asphaltene molecule is defined by the number, size, and kind of these components. In this work, three types of asphaltene models have been used. These models can be generated from an improved QMR method.<sup>36</sup> The essence of the method is to generate a group of ~10 000 asphaltene molecules that make chemical sense. An optimization algorithm is then used to select a mixture of 5–6 structures and their proportions in the mixture that best match the experimental data. The set of the three models, as employed in this study, are the best representatives of the asphaltenes in the mixtures (>95%).

These three molecules are called “archipelago type” ( $C_{90}SOH_{120}$ ; MW = 1248), “island type” ( $C_{53}SH_{58}$ ; MW = 726), and “resin type” ( $C_{26}NS_2H_{41}$ ; MW = 431), as shown in Figure 1. The archipelago-type molecule has two condensed aromatic cores connected by the aliphatic chains and has one oxygen atom and one sulfur atom. The island-type molecule is one large aromatic core with three aliphatic chains and has one sulfur atom. The resin-type molecule has a few aromatic rings as well as nitrogen and sulfur atoms. Of the three structures studied, the “island type” is the asphaltene with its structure best matched to experimental and theoretical studies of asphaltene ultraviolet (UV) fluorescence emission and absorption spectra, namely, with aromatic core sizes of approximately 7 rings. Therefore, this structure is considered in more detail than the other two.

The oil solvents are represented by heptane and toluene. We have used the optimized potentials for liquid simulations—all atom (OPLS-AA) force field parameters<sup>39,40</sup> for all of the hydrocarbon molecules. The water molecule is modeled by single-point charge/extended (SPC/E).<sup>41</sup>

**Details of MD.** Basically, we have used oil–asphaltene–water interface systems in the calculations. This interface system can be obtained by combining the three slabs, which are oil, asphaltene, and water. Two kinds of asphaltene slabs are used in this work. One is composed of only island-type asphaltene molecules. The other is a mixture of 3 types of asphaltene molecules, in which the ratio of the molecules is 2 archipelago-type molecules/3 island-type molecules/6 resin-type molecules. Thus, the base unit has 11 asphaltene molecules. Figure 2a shows the initial configuration of the oil–asphaltene–water interface system, in which the oil is represented by heptane and the asphaltene slab has 6 island-type asphaltene molecules.

The interface systems have been simulated using isobaric, isothermal, and iso-interfacial-area calculations ( $NAnPT$  ensemble calculation). The temperature was maintained at 300 K by the Nose–Hoover thermostat,<sup>42</sup> and pressure was kept constant at 1 bar by the Parrinello–Rahman barostat,<sup>43</sup> in all calculations in this work. The



**Figure 2.** Interface system (heptane–6 island-type asphaltene–water): (a) initial configuration and (b) final configuration. Green molecules (left) represent heptane, and blue molecules (right) represent water.

particle-mesh Ewald summation<sup>44</sup> was used for the electrostatic interactions, and a cutoff of 1.1 nm was used for the calculation of the van der Waals interactions. A 1.0 fs time step was used, and output coordinates were obtained every 1.0 ps. The box length in the two directions along the interface is fixed at 5.4 nm during the calculations. Calculations run for 4.0 ns showed a sufficiently close approach to equilibrium, as indicated by the rolling average of the interfacial tension (IFT) (shown in Figure S1 of the Supporting Information). Snapshots of molecular distributions were prepared by the visual molecular dynamics (VMD) software.<sup>45</sup> The IFT can be calculated by the following equation:<sup>22,23</sup>

$$\gamma(t) = \frac{1}{n} \int_0^{L_z} \{P_{zz}(z, t) - ((P_{xx}(z, t) + P_{yy}(z, t))/2)\} dz \quad (1)$$

where  $n$  is the number of interfaces in the system and  $L_z$  is the  $z$  length of the system. With two identical interfaces perpendicular to the  $z$  axis, this gives

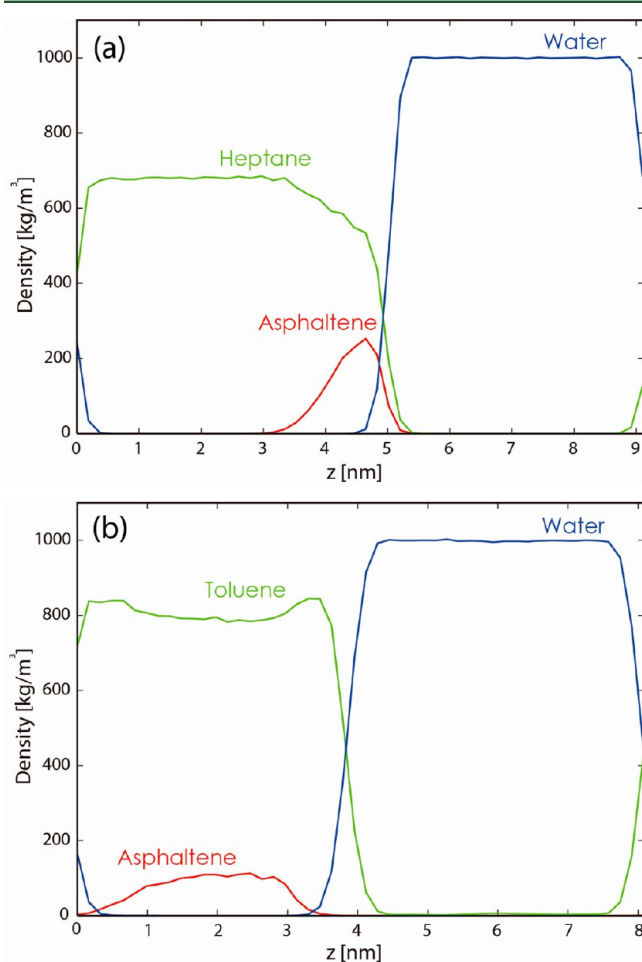
$$\gamma = \frac{1}{2} (P_z - ((P_x + P_y)/2)) L_z \quad (2)$$

in which  $P_\alpha = p_{\alpha\alpha}$  ( $\alpha = x, y, \text{ and } z$ ) are the diagonal elements of the pressure tensor and  $L_z$  is the box length in the  $z$  direction used in the calculations. In this work, the IFT of the pure heptane (toluene)–water interface was calculated by eq 2. In the case of the heptane–asphaltene–water system, the IFT of the heptane–water interface with asphaltene molecules was obtained by the total IFT value (i.e.,  $2\gamma$ )

minus the pure heptane–water IFT value. The calculated IFTs of heptane and toluene with SPC/E water are 51.9 and 37.6 mN/m, respectively. These values are in good agreement with experimental data and previous calculations.<sup>22</sup> This indicates that MD simulations successfully predict the interaction between water and different hydrocarbons.

## RESULTS AND DISCUSSION

**Comparison of Asphaltenes in Heptane–Water and Toluene–Water Interfacial Systems.** In this section, only the island-type asphaltene molecule was used in the asphaltene phase and we calculated two interface systems, namely, heptane–6 island-type asphaltenes–water and toluene–6 island-type asphaltenes–water. The number of heptane and toluene molecules is determined by the oil/asphaltene ratio of 7% asphaltene by weight. The initial and final configurations of the heptane–6 island-type asphaltenes–water system are shown in Figure 2. The density profile can be obtained by taking the time average over the latter 2 ns of the 4 ns calculation. As the density profile of the systems (Figure 3)



**Figure 3.** Density profiles of (a) heptane–6 island-type asphaltenes–water and (b) toluene–6 island-type asphaltenes–water.

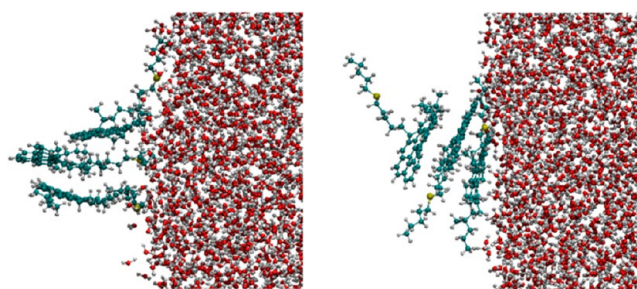
shows, the asphaltene molecules can be detected at the oil–water interface in the heptane–6 island-type asphaltenes–water case. On the other hand, the asphaltene molecules were distributed inside the oil phase in the toluene case. This result is consistent with the fact that asphaltenes are insoluble in heptane but soluble in toluene.<sup>9</sup> In a previous study, the

asphaltenes were immersed in the pure heptane and toluene phase, where the asphaltenes form dimers and trimers in both toluene and heptane.<sup>16</sup> The difference is that the nanoaggregates persist for longer in heptane than in toluene. Hence, the result presented here serves further evidence that the asphaltene models in our study correspond to the solubility class definition. To be sure that the accumulation of asphaltene at the heptane–water interface is not dependent upon the initial configurations, an initial configuration with asphaltene molecules inside the heptane solvent was also studied. We observe that asphaltene molecules do move to the interface within 4 ns (shown in Figure S2 of the Supporting Information).

We do not observe a thin film of asphaltenes at the toluene–water interface as reported previously.<sup>7</sup> Very likely, the reason is that the asphaltene models employed in this study do not contain carboxylic acid or other proton-donating polar functional groups. To this end, it has been documented that thin films at the toluene–water interface are very dependent upon the crude oil source.<sup>7</sup>

**Dynamic Behavior of a Nanoaggregate at the Heptane–Water Interface.** Many asphaltene molecules can make it complicated for us to understand the asphaltene behavior. Thus, we calculated two simple systems to investigate the behavior of the asphaltene molecules at the heptane–water interface. One system is heptane–1 island-type asphaltene–water, and the other is heptane–3 island-type asphaltenes–water. This island-type molecule (Figure 1) has only one aromatic core, and this aromatic rigid plane can constrain the dynamic behavior of this molecule.

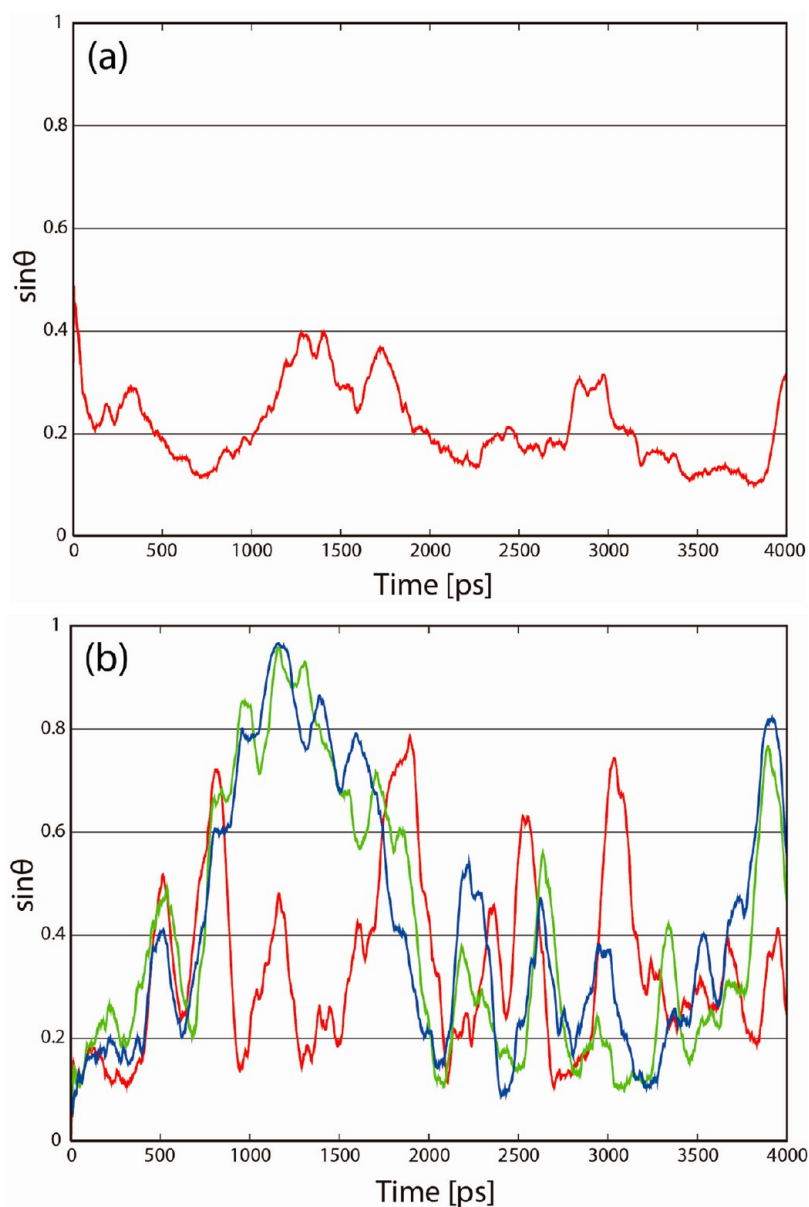
In the 1-island-type asphaltene case, the aromatic plane is attracted toward the interface by the interfacial water molecules. The aromatic plane forms a stable structure parallel to the water interface (as shown in Figure S3 of the Supporting Information). On the other hand, 3 island-type asphaltene molecules can form a nanoaggregate and change this stable position relevant to the interface, i.e., from a vertical structure to a parallel structure (as shown in Figure 4).



**Figure 4.** Asphaltene aggregate configurations at the oil–water interface: (left) vertical structure and (right) parallel structure.

We have then calculated the angle between the aromatic plane and the oil–water interface. In the 1-island-type asphaltene case (Figure 5a), this angle is kept low during the calculation, where the highest value is 0.4, which is about 24°. This means that the parallel structure is stable in the 1-island-type asphaltene case. In the 3-island-type asphaltenes case (Figure 5b), the angles can take a higher value and the amplitude of the fluctuation is larger than that of the 1-island-type asphaltene case. This result shows that 3 island-type asphaltene molecules can oscillate and adopt a vertical structure



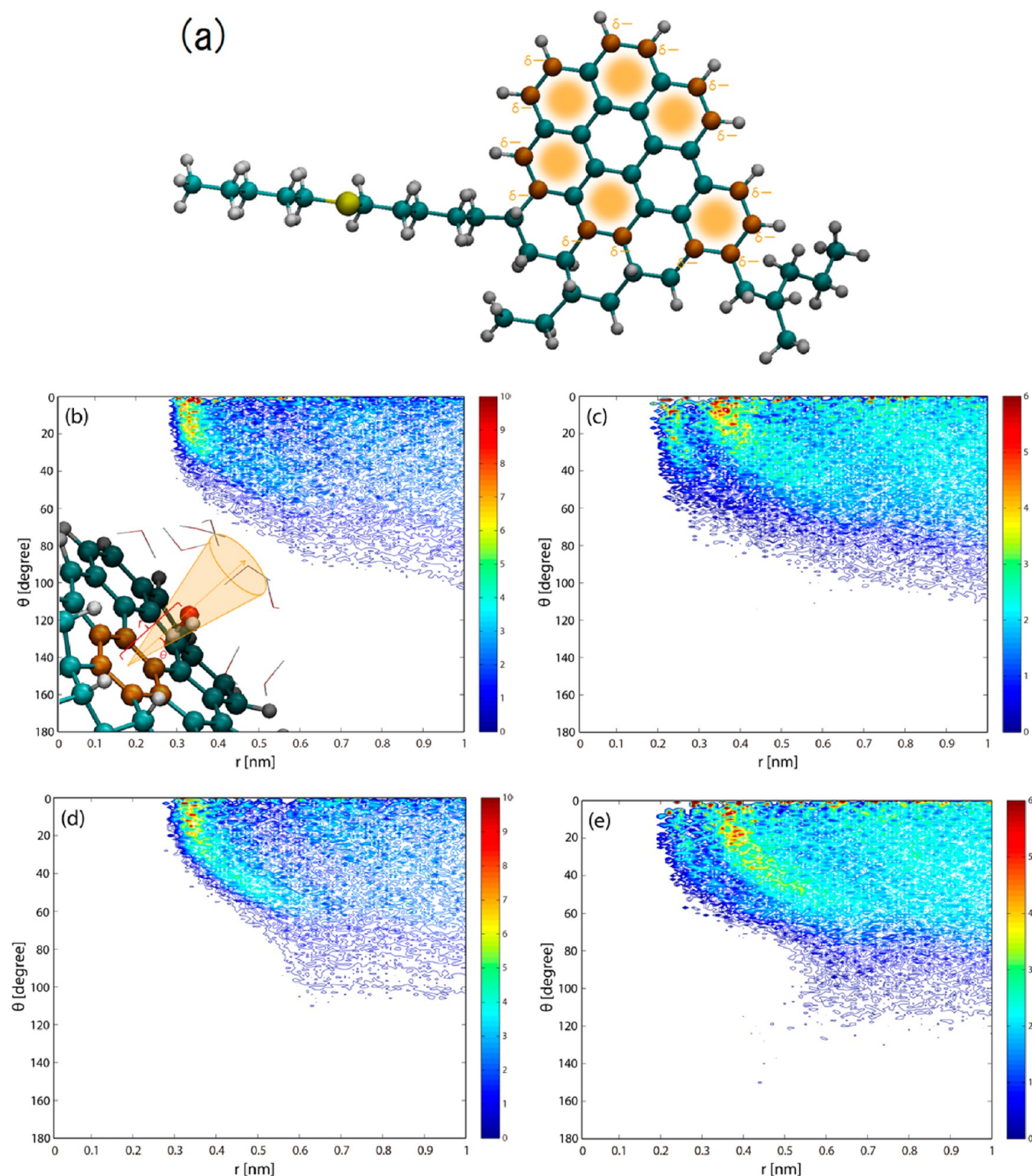


**Figure 5.** Temporal evolution of angles between the asphaltene aromatic plane and the oil–water interface for the systems including (a) 1 island-type asphaltene molecule and (b) 3 island-type asphaltene molecules. The angle is defined on the basis of the normal of the interface and the normal of the aromatic plane of the island-type asphaltene molecule.

with respect to the oil–water interface (Figure 4). The difference between these two systems is only the number of asphaltene molecules. Thus, the molecular oscillation can be caused by the nanoaggregate formed by a few asphaltene molecules.

The interaction between a negatively charged aromatic ring and a proton of a water molecule has been clarified by “weak hydrogen bonding” in the case of light oil–water interfaces.<sup>22</sup> Furthermore, it has been shown in ref 22 that the attractive nature of this “weak hydrogen bonding” is the reason that aromatics have a lower IFT with water than the other hydrocarbons and the reason that the aromatics accumulate at the oil–water interface. Figure 6 shows the angle-dependent radial distribution functions from the center of the aromatic ring to the oxygen (panels b and d) or hydrogen (panels c and e) in the water molecules using the 1-island-type asphaltene calculation result. The base direction was set normal to the

aromatic ring plane. This island-type asphaltene molecule has two different aromatic rings: charged versus non-charged. The orange carbon atom in Figure 6a is the edge of the aromatic binding to a hydrogen atom and has a negative charge. Thus, the aromatic rings including this negatively charged carbon atom will have an overall negative charge. On the other hand, the other rings will have no charge. The first peak of hydrogen is around 0.23 nm, and the first peak of oxygen is around 0.33 nm (Figure 6). This shows that the water molecule points the hydrogen atom toward the center of the aromatic ring. This is the main interaction causing the attraction between the aromatic plane and the water interface. As Figure 6 shows, the charged aromatic ring (panels b and c) has a clearer first peak than the non-charged aromatic ring (panels d and e). This is because the negatively charged ring and the positive charge of hydrogen in the water molecule are attracted to each other and form “weak hydrogen bonding”.

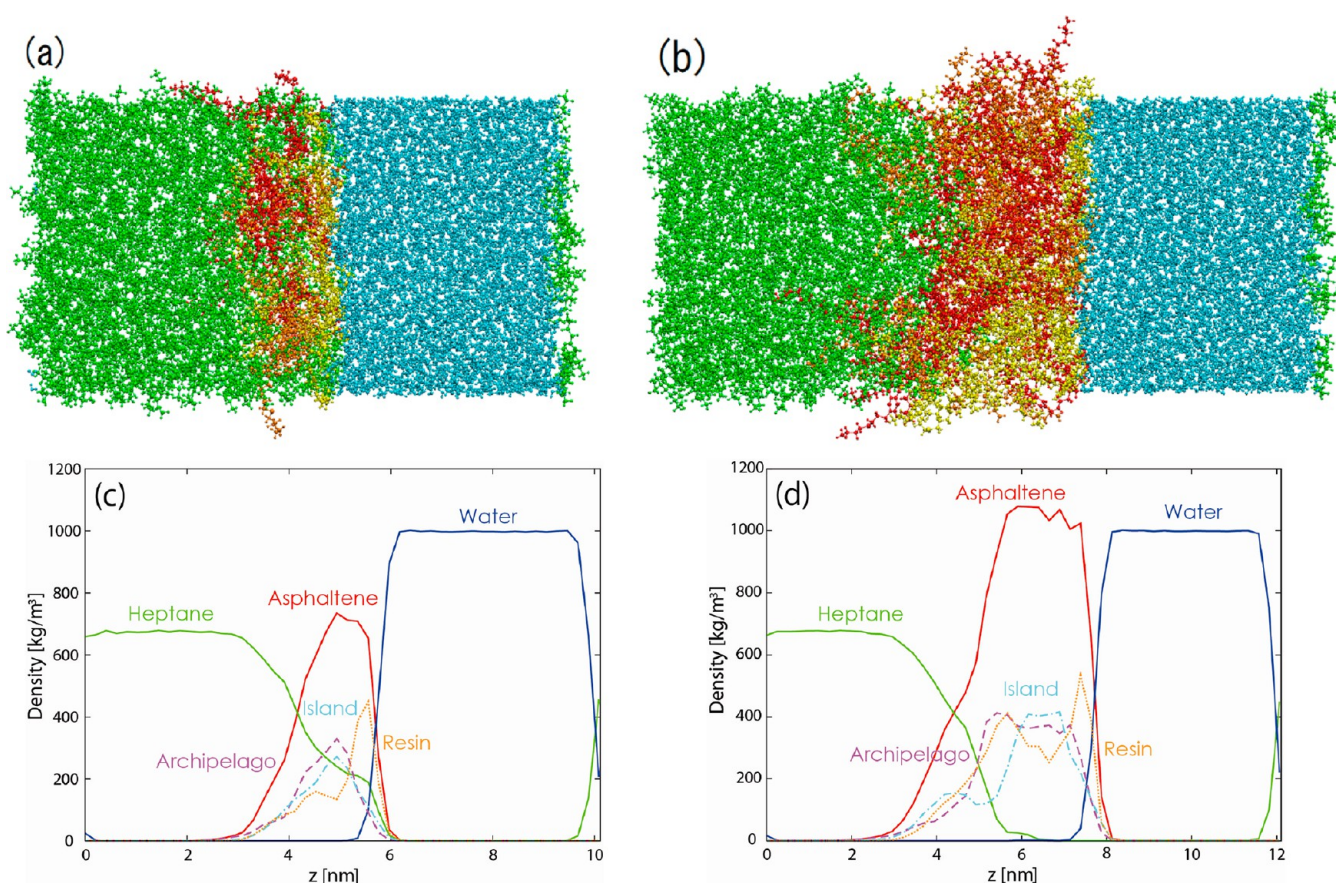


**Figure 6.** Angle-dependent radial distribution functions. (a) Island-type asphaltene molecule in which the orange carbon atom has a negative charge. The angle-dependent radial distribution functions from the center of the charged aromatic ring (b and c) and non-charged aromatic ring (d and e) to the oxygen (b and d) or hydrogen (c and e) in the water molecules using the 1-island-type asphaltene calculation result. The base direction was set normal to the aromatic ring plane.

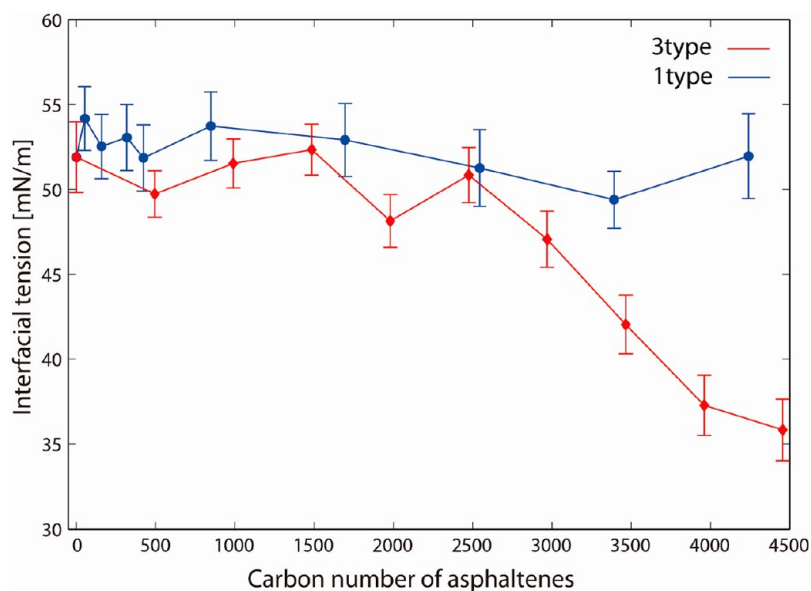
**From Nanoaggregation to Thin-Film Formation.** By increasing the number of asphaltene molecules, the asphaltene slab grows thicker. Finally, a thin asphaltene film can appear between the oil phase and the water phase. In the mixture of 3 types of asphaltene cases, the numbers of asphaltene molecules

are 11, 22, 33, 44, 55, 66, 77, 88, and 99, keeping the same ratio. In the island-type case, those are 1, 3, 6, 8, 16, 32, 48, 64, and 80 molecules. Heptane was used as an oil in this section.

Figure 7a shows the final configuration of the calculation system including 3 types of asphaltene molecules (33



**Figure 7.** (a) Final configuration including 33 asphaltene molecules with (c) corresponding density profile and (b) final configuration including 88 asphaltene molecules with (d) corresponding density profile. Red solid line, asphaltene phase; green solid line, heptane phase; and blue solid line, water phase. In the asphaltene phase, the purple dashed line, light blue dash-dotted line, and brown dotted line represent archipelago-type, island-type, and resin-type structures, respectively.



**Figure 8.** IFT with an increasing number of asphaltene molecules for a set of 3-type asphaltenes (red diamonds) and only island-type asphaltenes (blue circles). A set of asphaltene molecules (2 archipelago-type molecules, 3 island-type molecules, and 6 resin-type molecules, in total, 11 molecules) has 495 carbon atoms.

molecules). In this figure, the red molecule is archipelago-type, the orange molecule is island-type, the yellow molecule is resin-type, the green molecule is heptane, and the blue molecule is

water. As shown in Figure 7c, the asphaltenes are not a complete film but a nanoaggregate, which is penetrated by the heptane phase. On the other hand, it is found that the system



including 88 asphaltene molecules (Figure 7b) forms a complete thin film of asphaltenes as shown by the corresponding density profile (Figure 7d).

Because the IFT is so influential with capillarity of the oil or underground fluids in the reservoir rocks, it is one of the most important interfacial properties in the oil production. For this reason, we have calculated the IFT for interfaces, including asphaltenes with an increasing number of asphaltene molecules for both the 1-type case (only island) and the 3-type case (archipelago, island, and resin). The IFT calculation results are shown in Figure 8, in which the horizontal axis is the total carbon number of the asphaltene molecules in the system. This result shows the drop of IFT using 3-type asphaltene molecules (red line in Figure 8) around a 3500 carbon number. This decrease indicates a complete thin film of asphaltene, and the result is in good correspondence with the experimental studies.<sup>4,5</sup> A comparison here is made only in a qualitative manner, because the oil precipitant (heptane) is different from those in the experiments, cyclohexane and heptane–toluene mixture. Furthermore, it is well-known that the adsorption of asphaltene at the oil–water interface exhibits a strong aging effect because of a slow diffusion of asphaltene in the oil phase toward the interface, while in our simulations, all of the asphaltenes are initially located at the interface. The drop of the IFT has not occurred for the 1-type case. This means that the accumulation of resin-type molecules at the interface is the cause of the decreased IFT (as shown in Figure 7d and Figure S4 of the Supporting Information) and implies that a set of molecules (3 types) is needed to represent asphaltenes correctly. We have also calculated the IFT for the oil–water interface with 52 archipelago-type molecules (i.e., with 4680 carbon atoms) and 179 resin-type molecules (i.e., with 4650 carbon atoms). The total carbon number of asphaltenes with such a choice is a little above 4500. It is shown that the resin-type molecule has indeed led to a reduction of IFT of  $\sim 44.8$  mN/m, while the archipelago-type molecule instead increases the IFT to  $\sim 61.8$  mN/m. In comparison, the IFT with 3 types of asphaltenes and 99 molecules (i.e., around 4500 carbon atoms) is  $\sim 35.8$  mN/m. This further reduction of the IFT might be induced by the rearrangement of interfacial resin structures, when coexisting with the other two asphaltene molecules. Finally, we remark that a complete thin film is necessary to decrease the IFT significantly because, otherwise, the heptane phase will penetrate through the diffuse asphaltene aggregate and make contact with water.

It has been shown experimentally that emulsions stabilized by individual asphaltene molecules are of little significance, when compared to stabilization by colloiddally dispersed asphaltenes.<sup>4–6</sup> Moreover, it has been shown that asphaltenes stabilize water-in-oil emulsions only if they are close to or above the point of incipient flocculation. From our study, it seems that the integrity of the thin film (i.e., complete thin film) is formed with an increasing amount of asphaltenes, which might indicate an enhanced stability of water-in-oil emulsions. Although it has been argued that the main function of interfacial asphaltene molecules is not the lowering of the IFT, the interface can behave elastically to resist the coalescence.<sup>3</sup> We show here that resin and asphaltene mixtures might be able to lower their interfacial energy, as shown by the calculated IFT (Figure 8).

## CONCLUSION

In this work, we have calculated oil–asphaltene–water interface systems to investigate the interfacial phenomena of the oil–water interface with asphaltene molecules by MD simulations. The asphaltene molecules in the system using heptane as oil accumulate at the oil–water interface. Both 1- and 3-island-type asphaltene calculations show that the aromatic plane is attracted by the interfacial water molecules to form stable parallel structures, but the nanoaggregates can change this positional relation and cause molecular oscillations.

Additionally, we succeeded to reproduce the asphaltene status from nanoaggregates to a thin film between oil and water using MD simulations. In the case that the number of asphaltene molecules in the interface system is enough to form a complete thin film, the IFT can fall sharply. The resultant effects on the emulsion, including elastic and viscous contributions, will be discussed in the near future.

## ASSOCIATED CONTENT

### Supporting Information

Temporal evolution of the IFT for the heptane–asphaltene–water system, snapshots, and density profiles of some other relevant systems (Figures S1–S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Moore, F. G.; Richmond, G. L. Integration or segregation: How do molecules behave at oil/water interfaces? *Acc. Chem. Res.* **2008**, *41*, 739–748.
- (2) Benjamin, I. Molecular structure and dynamics at liquid–liquid interfaces. *Annu. Rev. Phys. Chem.* **1997**, *48*, 407–451.
- (3) Jungwirth, P.; Finlayson-Pitts, B. J.; Tobias, D. J. Introduction: Structure and chemistry at aqueous interfaces. *Chem. Rev.* **2006**, *106*, 1137–1139.
- (4) Sjoblom, J.; Aske, N.; Auflem, I. H.; Brandal, O.; Havre, T. E.; Sather, O.; Westvik, A.; Johnsen, E. E.; Kallevik, H. Our current understanding of water-in-crude oil emulsions. Recent characterization techniques and high pressure performance. *Adv. Colloids Interface Sci.* **2003**, *100–102*, 399–473.
- (5) Fan, Y.; Simon, S.; Sjoblom, J. Interfacial shear rheology of asphaltenes at oil–water interface and its relation to emulsion stability: Influence of concentration, solvent aromaticity and nonionic surfactant. *Colloids Surf., A* **2010**, *366*, 120–128.
- (6) McLean, J. D.; Kilpatrick, P. K. Effects of asphaltene aggregation in model heptane–toluene mixtures on stability of water-in-oil emulsions. *J. Colloid Interface Sci.* **1997**, *196*, 23–34.
- (7) Zhang, L. Y.; Lopetinsky, R.; Xu, Z.; Masliyah, J. H. Asphaltene films at a toluene/water interface. *Energy Fuels* **2007**, *21*, 274–285.

- (8) Li, M.; Xu, M.; Ma, Y.; Wu, Z.; Christy, A. A. Interfacial film properties of asphaltenes and resins. *Fuel* **2002**, *81*, 1847–1853.
- (9) Petersen, K. S.; Christensen, P. L. *Phase Behavior of Petroleum Reservoir Fluids*; CRC Press (Taylor and Francis Group): Boca Raton, FL, 2007.
- (10) Dickie, J. P.; Yen, T. F. Macrostructures of the asphaltic fractions by various instrumental methods. *Anal. Chem.* **1967**, *39*, 1847–1852.
- (11) Mullins, O. C. The modified Yen model. *Energy Fuels* **2010**, *24*, 2179–2207.
- (12) Headen, T. F.; Boek, E. S.; Stellbrink, J.; Scheven, U. M. Small angle neutron scattering (SANS and V-SANS) study of asphaltene aggregates in crude oil. *Langmuir* **2009**, *25*, 422–428.
- (13) Barre, L.; Simon, S.; Palermo, T. Solution properties of asphaltenes. *Langmuir* **2008**, *24*, 3709–3717.
- (14) Mostowfi, F.; Indo, K.; Mullins, O. C.; McFarlane, R. Asphaltene nanoaggregates studied by centrifugation. *Energy Fuels* **2009**, *23*, 1194–1200.
- (15) Boek, E. S.; Ladva, H. K.; Crawshaw, J. P.; Padding, J. T. Deposition of colloidal asphaltene in capillary flow: Experiments and mesoscopic simulation. *Energy Fuels* **2008**, *22*, 805–813.
- (16) Headen, T. F.; Boek, E. S.; Skipper, N. T. Evidence for asphaltene nanoaggregation in toluene and heptane from molecular dynamics simulations. *Energy Fuels* **2009**, *23*, 1220–1229.
- (17) Boek, E. S.; Wilson, A. D.; Padding, J. T.; Headen, T. F.; Crawshaw, J. P. Multi-scale simulation and experimental studies of asphaltene aggregation and deposition in capillary flow. *Energy Fuels* **2010**, *24*, 2361–2368.
- (18) Headen, T. F.; Boek, E. S. Molecular dynamics simulations of asphaltene aggregation in supercritical carbon dioxide with and without limonene. *Energy Fuels* **2011**, *25*, 503–508.
- (19) Gray, M. R.; Tykwinski, R. R.; Stryker, J. M.; Tan, X. Supramolecular assembly model for aggregation of petroleum asphaltenes. *Energy Fuels* **2011**, *25*, 3125–3134.
- (20) Wang, S.; Liu, J.; Zhang, L.; Masliyah, J.; Xu, Z. Interaction forces between asphaltene surfaces in organic solvents. *Langmuir* **2010**, *26*, 183–190.
- (21) Zahabi, A.; Gray, M. R. Kinetics and properties of asphaltene adsorption on surfaces. *Energy Fuels* **2012**, *26*, 1009–1018.
- (22) Kunieda, M.; Nakaoka, K.; Liang, Y.; Miranda, C. R.; Ueda, A.; Takahashi, S.; Okabe, H.; Matsuoka, T. Self-accumulation of aromatics at the oil–water interface through weak hydrogen bonding. *J. Am. Chem. Soc.* **2010**, *132*, 18281–18286.
- (23) Kunieda, M.; Liang, Y.; Fukunaka, Y.; Matsuoka, T.; Takamura, K.; Loahardjo, N.; Winoto, W.; Morrow, N. R. Spreading of multi-component oils on water. *Energy Fuels* **2012**, *26*, 2736–2741.
- (24) Kuznicki, T.; Masliyah, J. H.; Bhattacharjee, S. Molecular dynamics study of model molecules resembling asphaltene-like structures in aqueous organic solvent systems. *Energy Fuels* **2008**, *22*, 2379–2389.
- (25) Kuznicki, T.; Masliyah, J. H.; Bhattacharjee, S. Aggregation and partitioning of model asphaltenes at toluene–water interfaces: Molecular dynamics simulations. *Energy Fuels* **2009**, *23*, 5027–5035.
- (26) Zhang, L.; Greenfield, M. L. Molecular orientation in model asphalts using molecular simulation. *Energy Fuels* **2007**, *21*, 1102–1111.
- (27) Zhang, L.; Greenfield, M. L. Relaxation time, diffusion, and viscosity analysis of model asphalt systems using molecular simulation. *J. Chem. Phys.* **2007**, *127*, 195502.
- (28) Pacheco-Sanchez, J. H.; Zaragoza, I. P.; Martinez-Magadan, J. M. Asphaltene aggregation under vacuum at different temperature by molecular dynamics. *Energy Fuels* **2003**, *17*, 1346–1355.
- (29) Pacheco-Sanchez, J. H.; Alvarez-Ramirez, F.; Martinez-Magadan, J. M. Morphology of aggregated asphaltene structural models. *Energy Fuels* **2004**, *18*, 1676–1686.
- (30) Carauta, A. N. M.; Seidl, P. R.; Chrisman, E. C. A. N.; Correia, J. C. G.; de O. Menechini, P.; Silva, D. M.; Leal, K. Z.; de Menezes, S. M. C.; de Souza, W. F.; Teixeira, M. A. G. Modeling solvent effects on asphaltene dimers. *Energy Fuels* **2005**, *19*, 1245–1251.
- (31) Li, D. D.; Greenfield, M. L. High internal energies of proposed asphaltene structures. *Energy Fuels* **2011**, *25*, 3698–3705.
- (32) Greenfield, M. L. Molecular modeling and simulation of asphaltenes and bituminous materials. *Int. J. Pavement Eng.* **2011**, *12*, 325–341.
- (33) Artok, L.; Su, Y.; Hirose, Y.; Hosokawa, M.; Murata, S.; Nomura, M. Structure and reactivity of petroleum-derived asphaltene. *Energy Fuels* **1999**, *13*, 287–296.
- (34) Groenzin, H.; Mullins, O. C. Molecular size and structures of asphaltenes from various sources. *Energy Fuels* **2000**, *14*, 677–684.
- (35) Sheremata, J. M.; Gray, M. R.; Dettman, H. D.; McCaffrey, W. C. Quantitative molecular representation and sequential optimization of Athabasca asphaltenes. *Energy Fuels* **2004**, *18*, 1377–1384.
- (36) Boek, E. S.; Yakovlev, D. S.; Headen, T. F. Quantitative molecular representation of asphaltenes and molecular dynamics simulation of their aggregation. *Energy Fuels* **2009**, *23*, 1209–1219.
- (37) Al Halwachi, H. K.; Yakovlev, D. S.; Boek, E. S. Systematic optimization of asphaltene molecular structure and molecular weight using the quantitative molecular representation approach. *Energy Fuels* **2012**, *26*, 6177–6185.
- (38) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J. Chem. Theory Comput.* **2008**, *4*, 435–447.
- (39) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- (40) Jorgensen, W. L.; Laird, E. R.; Nguyen, T. B.; Tirado-Rives, J. *J. Comput. Chem.* **1993**, *14*, 206–215.
- (41) Berendsen, H.; Grigera, J.; Straatsma, T. The missing term in effective pair potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.
- (42) Nose, S. A molecular dynamics method for simulations in the canonical ensemble. *Mol. Phys.* **1984**, *52*, 255–268.
- (43) Parrinello, M.; Rahman, A. Strain fluctuations and elastic constants. *J. Chem. Phys.* **1983**, *76*, 2662–2666.
- (44) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. A smooth particle mesh Ewald method. *J. Chem. Phys.* **1995**, *103*, 8577–8593.
- (45) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* **1996**, *14*, 33–38.