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Cancellation of dipole moment of models of asphaltene aggregates as a mean for their dispersion in toluene and THF calculated using molecular dynamics

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Abstract

The study of the behavior of asphaltenes in solution has focused on their tendency to form aggregates and less importance has been given to describing and understanding what allows the formation of asphaltene aggregates that remain stably dispersed. Using molecular dynamics simulations we calculated that the dipole moment of models for asphaltene aggregate tend to zero when the number of molecules in the aggregate tends to large values. In other words such dipole moment cancellation would be the mean where by asphaltene aggregates are keep stable in solution.

1 Introduction

In view of the deleterious effects that asphaltene aggregation causes in the different stages of crude oil processing, a very large number of research reports dealing with this subject could be found in the literature and a very small number of these could be found in the Reference part below.¹⁻⁹ No doubts such interest has provided a large knowledge on the theme and controversies about basic concepts are common. For instance, whereas many conjectures could be proposed to account for aggregate formation of different sizes there is no consensus regarding the stability of these aggregates in solution. In this work we used a molecular dynamics method and polycyclic aromatic models containing heteroatom to simulate both aggregate formation and stability. We found that our simulation is coherent with formation of aggregates with dipole moments (μ) equal or close to zero. Moreover, we also found that $\mu \rightarrow 0$ when the number of molecules within the aggregate tends to a large number.

The study of asphaltenes has always been involved in some difficulties due to their complex constitution. Because of this, his studies on solutions are debated in two main theories, the colloidal solution theory or colloidal model,¹⁰ this theory helps to explain the presence of small, and dense nanoaggregates in solution. It has also been the pillar of many structural models.¹¹⁻¹³ The phase theory for multicomponent mixtures or thermodynamic model is also involved in the behavior of asphaltenes in solution,^{14,15} especially in studies concerning

the solubility parameter.¹⁶⁻¹⁸ This shows the dual nature of asphaltenes depending on the concentration present, partially dissolved, partially colloidal.¹⁹⁻²¹

Molecular dynamics simulations provide us with an ideal technique to study the behavior of a system at nanometer scales, where intermolecular interactions are present. These simulations allow us the sampling of a system in time by generating a set of configurations where the conditions of temperature, pressure and species are constant. This is helpful in observing the behavior of asphaltene aggregates in solution.^{10,14} However, due to the large family of compounds present, it is difficult to devise structural models. Recent work, using Atomic Force Microscopy (AFM) has isolate real asphaltene molecules⁹ which resulted to be polycyclic aromatic compounds (PAC) largely similar to empirical aromatic models used to represent the behavior of asphaltenes in solution.⁶

Using the below described molecular dynamics methods and appropriate molecular models we calculated here that cancellation of dipole moments of aggregates is a principal factor in the stability of asphaltene aggregates containing many molecules.

2 Methods

Two different models, type A1 and type A2 were used for asphaltene simulations. Figure 1 shows the 3D molecular models employed for A1, A2 and aggregate composed by 50% of each one. The molecular dynamics calculations were performed in toluene and THF at room conditions. 80 asphaltenes molecular models were randomly introduced in an 8x8x8 nm³ toluene or THF box which was equilibrated during 60 ns, before performing the molecular dynamics. Once the molecular dynamics of the system were completed the aggregates formed in the system were analyzed and characterized. All simulations were carried out using the GROMOS96 force fields with 53A6 parameter set,¹¹ using the GROMACS 2019.3 computer package^{5,11}. The main feature of this force field is its united-atom (UA) parameter which allows an increase in the size of system without losing computer time. Other characteristics

of the system could be found in the literature.^{3,22–26}

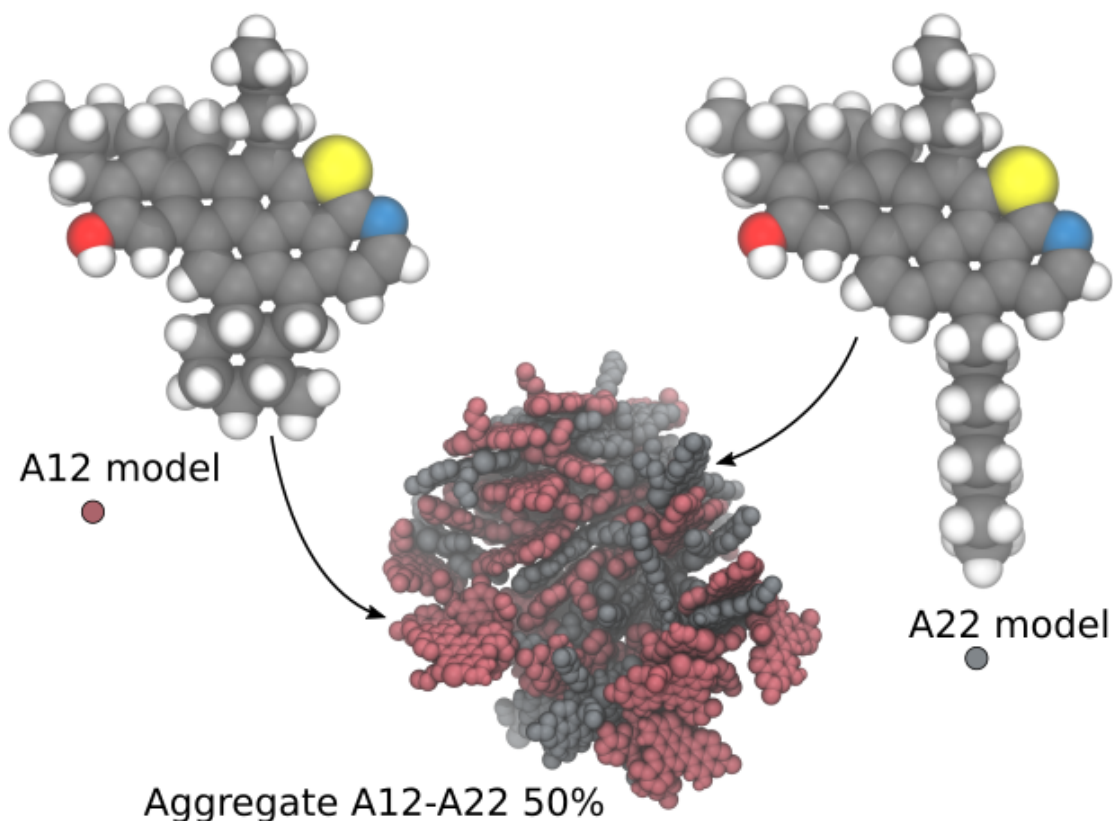


Figure 1: Structural representation of models A12 and A22 and aggregate with a 50 % mixture of both. The yellow spheres are S, the blue N and the red OH groups

Figure 1 shown the molecular structure base of the asphaltenes molecules used in this study for the subfractions A1 and A2. All models have the same basic structure, consisting of an aromatic core, with a general island-like architecture. These are based on those proposed by Acevedo,²⁷ shown in Figure 1. The main difference between the A1 and A2 structures is the exchange of a side chain (n-octyl) for two alkyl cycles, which produces a decrease in the H/C ratio and increases the DBE producing a more rigid structure for A1 and a more flexible one for A2.²⁸ The presence of a sulfur atom, nitrogen atom, hydroxyl group on the aromatic nucleus and the addition of a carboxyl group on the side chain were considered.

Charge of atoms for all atoms in each aggregate were calculated using the semiempirical AM1 program.^{29–31} These charges were then used for dipole moment calculation. These DM

values were certified using model molecules with well known charge.

3 Results

Figure 2 shows the dipole moment changes of the A12 aggregates relative to the number of molecules. Calculations were done for both toluene and tetrahydrofuran (THF). As depicted, when the number of model molecules in the aggregate increases their dipole moments decrease. In most cases the decrease is very fast. The dipole moments reach values close to zero for a number of molecules close to 45. In general, the dipole moment curve drops to a sort of plateau close to zero both for toluene and THF.

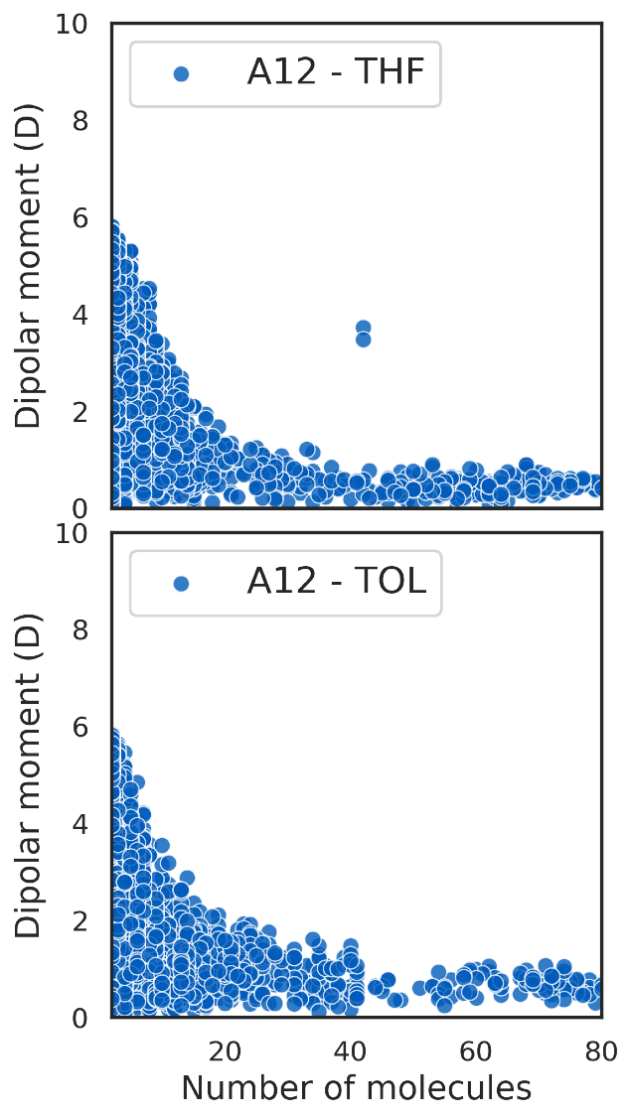


Figure 2: Reduction of the dipole moment with the increase of the number of molecules in the aggregate according to the simulation. Here we observe similar results for models A12 and A22 in toluene and THF.

Figure 3 shows various arrays of aggregates for the A12 model. Dipole moments of these arrays and corresponding number of molecules are listed in Table 1. As the number of molecules increases, the dipole moment decreases. Arrows indicate the direction of the dipole moment corresponding to molecular models. Random array of these leads to cancellation of the dipole moment of the aggregate.

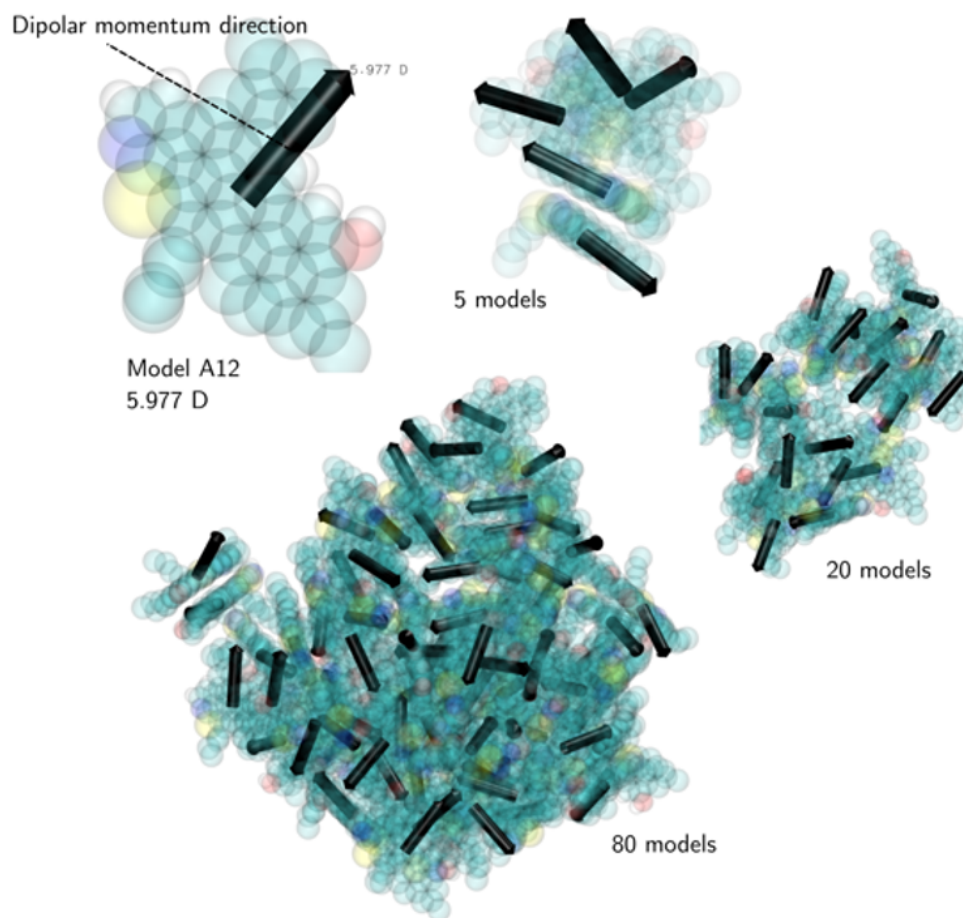


Figure 3: Array of molecular models corresponding to a single molecule and various aggregates for A12 model.

Table 1: DM as a function of N

DM as a function of N	
N	DM(D)
1	5.97
5	2.11
20	0.78
80	0.39

Dipole Moments in Debyes

It should be noted that dependence of dipole moment with N in THF is similar to the one observed in toluene see below Figure 4.

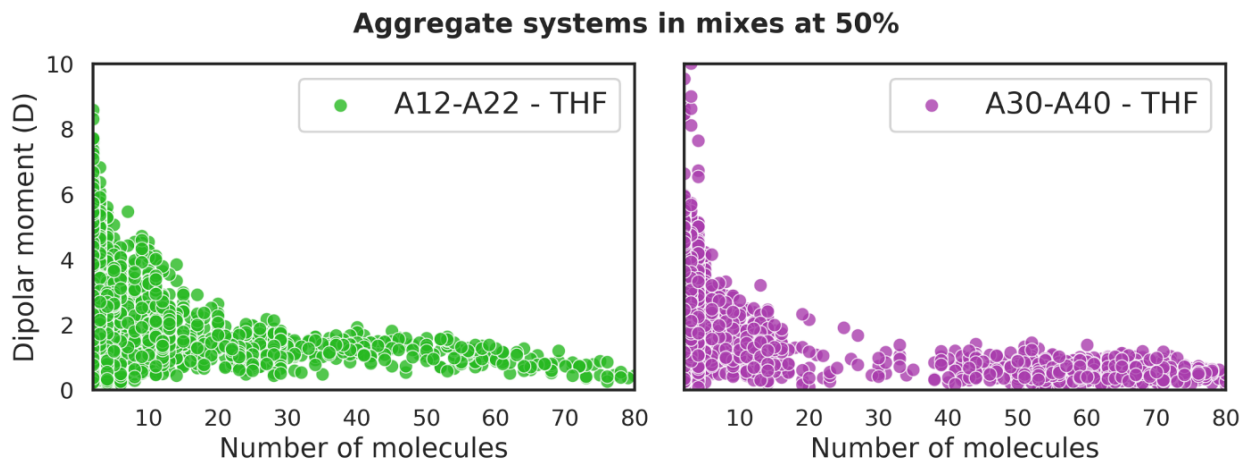


Figure 4: Mixtures of the model shown in THF solvent.

Figure 4 shown mixtures of the model in THF solvent. As was the case for single models shown in Figures 4, the dipole moment of aggregates also tends to zero when the number of molecules increases.

In the Figure 5 is presented a sketch of the array of molecular models corresponding to a single molecule and various aggregates. As shown in Table 1, as the number of molecules increases, the dipole moment decreases. Arrows indicate the direction of the dipole moment corresponding to molecular models. Random array of these leads to cancellation of the dipole moment of the aggregate

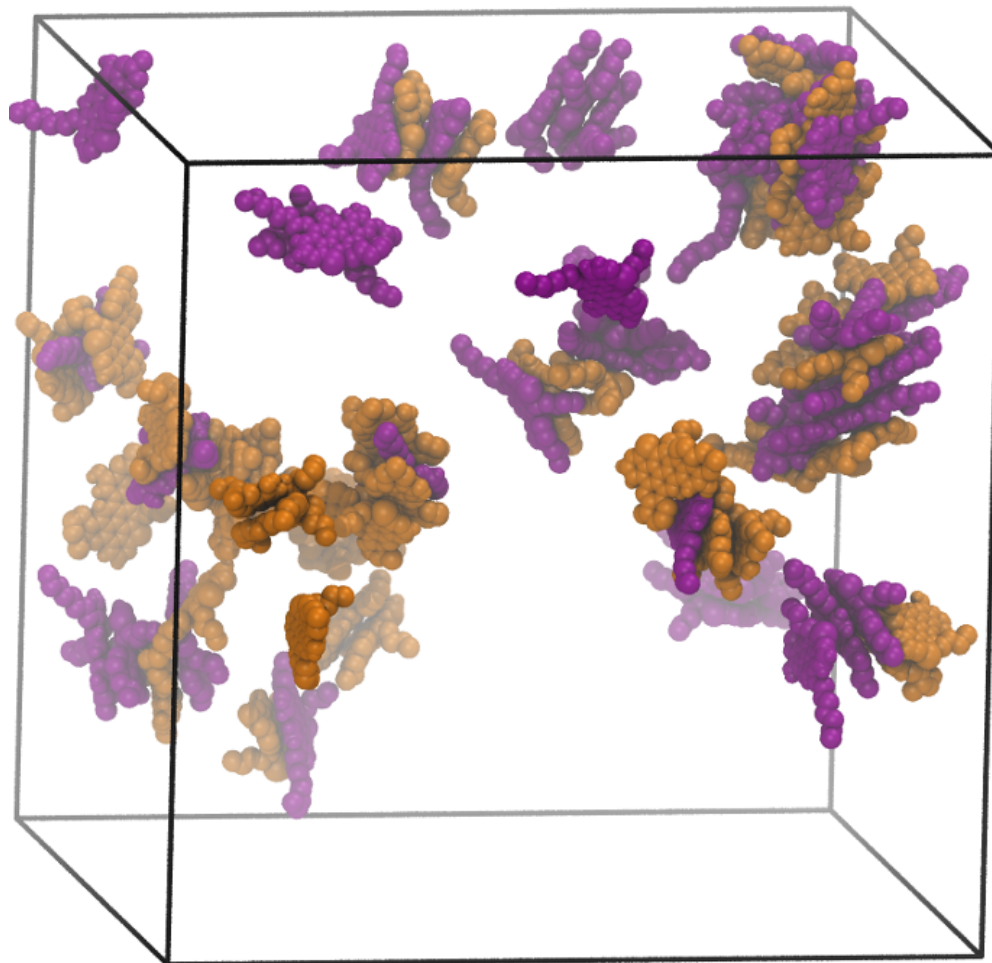


Figure 5: Section of Molecular display corresponding to mixture A12 (in brown) +A22 (in pink). Solvent (not shown) is toluene

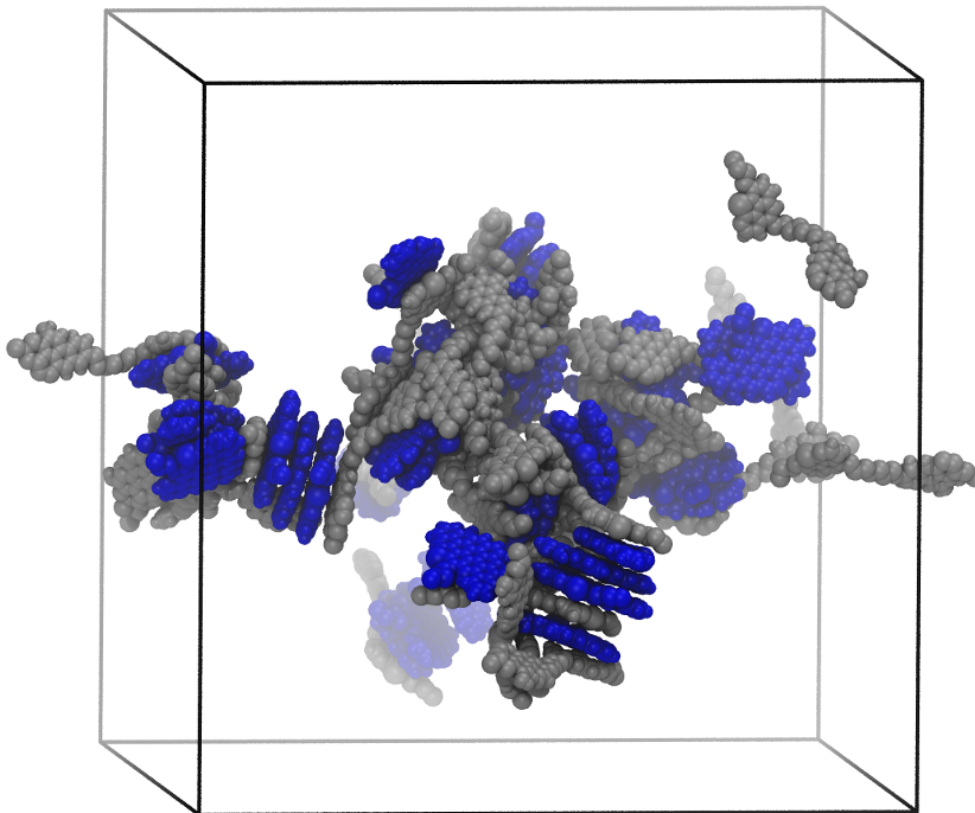


Figure 6: Section of Molecular display corresponding to mixture A30 (in brown) +A40 (in pink). Solvent (not shown) is toluene

Figures 5 and 6 are representatives of aggregates after finishing the molecular dynamics.

4 Discussion

Stability of aggregates in toluene, required for its successful dispersion has been calculated using molecular dynamics method, employing both toluene and THF. For this, cancellation of the dipole moment of aggregates is required. The dipole moment cancellation ($\mu = 0$) is produced by randomly orientation of molecules within the aggregate. This cancellation would be the largest while the largest would be the number of calculated molecules inside the aggregate. In other terms:

Dispersion stable $\mu = 0$; when N is a large number

N is the number of molecules in aggregate.

To our knowledge, in the literature there is no mention of the above condition ($\mu = 0$) to account for dispersion stability of asphaltene. We found this to be the case in 22 experiments similar to the one described above for the A12 case. Although this is a welcome finding, more research is highly recommended before such a concept gain more consensuses. For instance what would be the results in the case of mixtures of molecular models.

According to the above results asphaltenes could be considered as self-assembling materials where the usual several physical factors such as hydrogen bonding, dispersion and polar effects promote aggregate formation and growing (increase N_{Agg}) and simultaneously such increase in promotes cancellation or annulment of dipole moment thus suppressing aggregate formation. This compromise between these opposite effects (N_{Agg}) would be responsible for the stability of the dispersion.

5 Conclusions

Calculation of dipole moments of model aggregates in solutions, both in toluene and THF, using the above described molecular dynamics technique constitutes a valid approach to understand both formation and stability of these solutions. In view of them in being a stable dispersion of large and small aggregates, the proposal regarding dipole moment cancellation, linked to intermolecular attraction of molecules within the aggregates completes the required steps to obtain the corresponding dispersion.

References

- (1) Headen, T. F.; Boek, E. S.; Jackson, G.; Totton, T. S.; Müller, E. A. Simulation of Asphaltene Aggregation through Molecular Dynamics: Insights and Limitations. *Energy & Fuels* **2017**, *31*, 1108–1125.
- (2) Santos Silva, H.; Alfarra, A.; Vallverdu, G.; Bégué, D.; Bouyssiére, B.; Baraille, I.

- Asphaltene aggregation studied by molecular dynamics simulations: role of the molecular architecture and solvents on the supramolecular or colloidal behavior. *Petroleum Science* **2019**, *16*, 669–684.
- (3) Jiang, B.; Zhang, R.; Yang, N.; Zhang, L.; Sun, Y.; Jian, C.; Liu, L.; Xu, Z. Molecular Mechanisms of Suppressing Asphaltene Aggregation and Flocculation by Dodecylbenzenesulfonic Acid Probed by Molecular Dynamics Simulations. *Energy & Fuels* **2019**, *33*, 5067–5080.
- (4) Headen, T. F.; Hoepfner, M. P. Predicting Asphaltene Aggregate Structure from Molecular Dynamics Simulation: Comparison to Neutron Total Scattering Data. *Energy & Fuels* **2019**, *33*, 3787–3795.
- (5) 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.
- (6) Villegas, O.; Salvato Vallverdu, G.; Bouyssiére, B.; Acevedo, S.; Castillo, J.; Baraille, I. Molecular Cartography of A1 and A2 Asphaltene Subfractions from Classical Molecular Dynamics Simulations. *Energy & Fuels* **2020**, *34*, 13954–13965.
- (7) Silva, H. S.; Sodero, A. C. R.; Bouyssiére, B.; Carrier, H.; Korb, J.-P.; Alfarra, A.; Vallverdu, G.; Bégué, D.; Baraille, I. Molecular Dynamics Study of Nanoaggregation in Asphaltene Mixtures: Effects of the N, O, and S Heteroatoms. *Energy & Fuels* **2016**, *30*, 5656–5664.
- (8) Chmiela, S.; Saucedo, H. E.; Müller, K.-R.; Tkatchenko, A. Towards exact molecular dynamics simulations with machine-learned force fields. *Nature Communications* **2018**, *9*, 1–10.
- (9) Schuler, B.; Meyer, G.; Peña, D.; Mullins, O. C.; Gross, L. Unraveling the Molecu-

- lar Structures of Asphaltenes by Atomic Force Microscopy. *Journal of the American Chemical Society* **2015**, *137*, 9870–9876.
- (10) Leontaritis, K. J.; Mansoori, G. A. Asphaltene Flocculation During Oil Production and Processing: A Thermodynamic Colloidal Model. SPE International Symposium on Oilfield Chemistry. 1987; p 16258.
- (11) Mullins, O. C. The Modified Yen Model. *Energy & Fuels* **2010**, *24*, 2179–2207.
- (12) 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.
- (13) Acevedo, S.; Castillo, J.; Vargas, V.; Castro, A.; Delgado, O.; Cortés, F. B.; Franco, C. A.; Bouyssiere, B. Suppression of Phase Separation as a Hypothesis to Account for Nuclei or Nanoaggregate Formation by Asphaltenes in Toluene. *Energy & Fuels* **2018**, *32*, 6669–6677.
- (14) Painter, P.; Veytsman, B.; Youtcheff, J. Asphaltene Aggregation and Solubility. *Energy & Fuels* **2015**, *29*, 2120–2133.
- (15) Andersen, S. I.; Speight, J. G. Thermodynamic models for asphaltene solubility and precipitation. *Journal of Petroleum Science and Engineering* **1999**, *22*, 53–66.
- (16) Acevedo, S.; Castro, A.; Vásquez, E.; Marcano, F.; Ranaudo, M. A. Investigation of Physical Chemistry Properties of Asphaltenes Using Solubility Parameters of Asphaltenes and Their Fractions A1 and A2. *Energy & Fuels* **2010**, *24*, 5921–5933.
- (17) Rogel, E. Theoretical Estimation of the Solubility Parameter Distributions of Asphaltenes, Resins, and Oils from Crude Oils and Related Materials. *Energy & Fuels* **1997**, *11*, 920–925.
- (18) Redelius, P. Bitumen Solubility Model Using Hansen Solubility Parameter. *Energy & Fuels* **2004**, *18*, 1087–1092.

- (19) Leontaritis, K. J.; Kawanaka, S.; Mansoori, G. A. Descriptive accounts of thermodynamic and colloidal models of asphaltene flocculation. *Proceedings of Symposium on Thermodynamic and Transport Properties of Fluids*. **1988**, *33*, 196–204.
- (20) Balestrin, L. B. S.; Loh, W. Recent Developments on the Elucidation of Colloidal Aspects of Asphaltenes and Their Relevance to Oilfield Problems. *J. Braz. Chem. Soc.* **2020**, *31*, 230–243.
- (21) Kawanaka, S.; Leontaritis, K. J.; Park, S. J.; Mansoori, G. A. *Oil-Field Chemistry*; 1989; Chapter 24, pp 443–458.
- (22) Faraji, M.; Solaimany Nazar, A. R. A study of the dynamic evolution of asphaltene aggregate size distribution using Monte Carlo simulation. *Energy & Fuels* **2010**, *24*, 4952–4960.
- (23) Kundarapu, L. K.; Choudhury, S.; Acharya, S.; Vatti, A. K.; Pandiyan, S.; Gadag, S.; Nayak, U. Y.; Dey, P. Combined experimental and molecular dynamics investigation of 1D rod-like asphaltene aggregation in toluene-hexane mixture. *Journal of Molecular Liquids* **2021**, 116812.
- (24) Aray, Y.; Hernández-Bravo, R.; Parra, J. G.; Rodríguez, J.; Coll, D. S. Exploring the Structure–Solubility Relationship of Asphaltene Models in Toluene, Heptane, and Amphiphiles Using a Molecular Dynamic Atomistic Methodology. *The Journal of Physical Chemistry A* **2011**, *115*, 11495–11507.
- (25) Tarefder, R. A.; Arisa, I. Molecular Dynamic Simulations for Determining Change in Thermodynamic Properties of Asphaltene and Resin Because of Aging. *Energy & Fuels* **2011**, *25*, 2211–2222.
- (26) Li, R.; Du, H.; Fan, Z.; Pei, J. Molecular Dynamics Simulation to Investigate the Interaction of Asphaltene and Oxide in Aggregate. *Advances in Materials Science and Engineering* **2016**, *2016*, 1–10.

- (27) Acevedo, S.; Escobar, O.; Echevarria, L.; Gutiérrez, L. B.; Méndez, B. Structural Analysis of Soluble and Insoluble Fractions of Asphaltenes Isolated Using the PNP Method. Relation between Asphaltene Structure and Solubility. *Energy & Fuels* **2003**, *18*, 305–311.
- (28) Acevedo, S.; Cordero, J. M.; Carrier, H.; Bouyssiére, B.; Lobinski, R. Trapping of Paraffin and Other Compounds by Asphaltenes Detected by Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-TOF MS): Role of A1 and A2 Asphaltene Fractions in This Trapping. *Energy & Fuels* **2009**, *23*, 842–848.
- (29) Jakalian, A.; Jack, D. B.; Bayly, C. I. Fast, efficient generation of high-quality atomic charges. AM1-BCC model: II. Parameterization and validation. *Journal of Computational Chemistry* **2002**, *23*, 1623–1641.
- (30) Thompson, J. D.; Cramer, C. J.; Truhlar, D. G. Parameterization of charge model 3 for AM1, PM3, BLYP, and B3LYP. *Journal of Computational Chemistry* **2003**, *24*, 1291–1304.
- (31) Jakalian, A.; Bush, B. L.; Jack, D. B.; Bayly, C. I. Fast, Efficient Generation of High-Quality Atomic Charges. AM1-BCC Model: I. Method. *Journal of Computational Chemistry* **2000**, *21*, 132–146.