Nanoaggregation and Solubility of Crude Oil Asphaltenes from Molecular Dynamics Simulations

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Abstract: - The aggregation and solubility of asphaltenes are studied by classical molecular dynamics simulations. Average three-dimensional atomistic models are built on the basis of experimental data for the asphaltenes from a series of crude oil samples. The simulation of two such asphaltene models in four different solvents puts into evidence the formation of oligomeric clusters and gives clues to the initial stages of asphaltene aggregation at the nanometer scale. The Hildebrand solubility parameter is calculated for the whole collection of asphaltene models, as an example of obtaining practically useful physicochemical properties from molecular simulations applied to average asphaltene structures.

Key-Words: - asphaltene, oil, aggregation, solubility, simulation, molecular dynamics, forcefield, Hildebrand, solvent

1 Introduction
The solubility class of asphaltenes is operationally defined as the non-volatile and relatively polar fraction of crude oil or bitumen that is insoluble in n-alkanes (e.g., heptane) but soluble in aromatic solvents (like toluene). The solubility behaviour of this fraction is complex and often unpredictable. When dissolved in a crude or an aromatic solvent, the asphaltenes are known to form clusters in the nanometer length scale, frequently defined as “nanoaggregates”. There is little consensus in the literature as to the size, shape, and stability of the nanoaggregates and the thermodynamic driving force behind their formation. Moreover, they can form larger aggregates and flocculate. The asphaltene precipitation from the crude is of relevance for many processes in the oil industry, since it can cause such severe problems as fouling of reservoirs, reactors and pipelines.

Asphaltenes are conveniently described as a colloidal system, but their operational definition implies a wide range of different molecules. While the average asphaltene nanoaggregate dimensions are known from experiments (about 1-5 nm) there is less agreement on their internal molecular structures. According to the most prevalent theory asphaltene nanoaggregates are formed from stacking of extended aromatic cores; the stacking is terminated because of steric or entropic considerations.

This study aims to investigate by using molecular simulation the structure of asphaltene nanoaggregates and the driving force behind their clustering in different solvents. Since a full study at the atomistic detail requires too large length scales and too long time scales, only small scale simulations were carried out. These can give information about the aggregation of a small number of molecules and the results obtained for oligomeric structures will possibly lead to the formulation of a comprehensive asphaltene nanoaggregation model. For any of these simulation studies to yield meaningful results, the model structures used must be representative of asphaltenes as a whole [1, 2, 3]. All previous studies have used one or a few “average” model structures that are consistent with experimental data, but a range of different asphaltene molecular shapes have been proposed. All of them fall in either of two general models: archipelago-type structures with multiple small aromatic islands connected by aliphatic chains, or large pericondensed asphaltenes with a single large aromatic core and aliphatic moieties around its border. Recent experimental studies [4] have convincingly shown the correctness of an asphaltene structure with a single aromatic core (possibly two), containing 4-10 aromatic rings.

An easy test of the usefulness of the average molecular representation of asphaltene structures is the derivation of important physicochemical properties from simulation. As an example, a simple method is here presented for calculating the Hildebrand solubility parameter, which is related to the heat of vaporization and the molar volume [5]. This is an important property that was introduced to provide a systemic description of the miscibility behavior of solvents and proved useful for evaluating the extent of interactions occurring in many classes of materials (e.g., pharmaceuticals,
polymers). The Hildebrand solubility parameter is frequently adopted [2, 6, 7] in predicting the miscibility of asphaltenes with a series of liquids, greatly differing either in molecular polarity or aromatic content. While solubility parameters of solvents can be readily obtained from direct experimental measurements, values for asphaltenes must be calculated, because these materials are not volatile and they degrade before reaching their boiling temperature.

2 Methodology
This paper reports on the application of molecular dynamics (MD) to two different series of simulations. Classical MD use intra- and intermolecular potentials and analytical expressions for potential energy components, typically defined in a forcefield, to calculate interatomic forces. The system is allowed to evolve over time by stepwise integration of the equations of motion in a thermodynamic ensemble of choice. It is important that the step size (in this study, 1 fs) be smaller than the time period of the fastest motion in the simulation.

For one simulation set, fairly large 3-dimensional periodic boxes were built, each one containing multiple copies of an asphaltene, surrounded by solvent molecules. Two different, but structurally related, asphaltene structures were used and the simulation boxes were filled, respectively, with toluene, tetrahydrofurane, n-pentane or n-heptane. From the trajectories, the atomic coordinates and velocities and the associated potential energies were obtained over as long as possible timescales. This allowed to follow the first steps in the spontaneous nanoaggregation process at fixed physicochemical conditions. The asphaltene intermolecular radial pair distribution function (pdf) between homologous and heterologous atom types was also calculated, in order to detect the evolution and ordering of small molecular clusters. Eventually the observations and measurements at the nanometer scale could suggest the internal structure of larger aggregates, leading to asphaltene precipitation.

In another simulation set, MD were applied to pure component periodic boxes, assembled from one of 17 different asphaltene structures or of 15 solvent molecules of varying polarity and aromaticity. After proper equilibration at the desired density and temperature, from the potential energy components of the system the cohesive energy density was readily derived and its square root gave the Hildebrand solubility parameter \( \delta \) of the simulated material. More specifically, the Hildebrand parameter is defined as: \( \delta = (\Delta E^{vap}/V) \), where \( V \) is the liquid molar volume and \( \Delta E^{vap} \) is the internal energy of vaporization. Various theoretical frameworks (e.g., regular solution theory, Flory Huggins model) employ the concept of Hildebrand solubility parameter to predict miscibilities and calculate phase diagrams, generally including it in their equations as the square of a difference: \((\delta_1 - \delta_2)^2\), in the case of two components. According to such predictions it can be assumed that, the smaller the difference in \( \delta \) values of two substances, the larger their intermiscibility.

2.1 Model building of an average asphaltene model
The model building of an average asphaltene structure was performed within MAPS [2]. The starting building blocks were selected among the typical structures and functional groups detected in the asphaltenes by experimental characterization [9, 10]. They were arranged into a single molecule in order to fit as well as possible the chemical characterization [unpublished data] of asphaltene samples from different sources. These data consist of quantitative chemical composition (from elemental analysis), average molecular weight (from GPC determinations) and relative content in atom types and their proximities (from \(^1\)H and \(^13\)C NMR experiments). The model building process was repeated to generate a range of molecules, sampling both the pericondensed and the archipelago models. For each asphaltene sample only the model structure best fitting available data was chosen as a starting molecule for subsequent MD simulations.

2.2 Simulation of nanoaggregation
The Amorphous Builder module in MAPS was used to generate completely random starting configurations for the simulation system. 10 asphaltene molecules and 500 solvent molecules (for concentrations varying from 15 to 30 \( \%_{\text{v/v}} \)) were arranged in a periodic unit cell of appropriate size to start with a density of 0.1 g/cm\(^3\). The resulting assemblies (from 7780 to 13800 atoms) were simulated on a multiprocessor (up to 64 CPU cores) cluster computer in times of the order of one week each. The LAMMPS [11] code for parallel MD was used and the atomic parameters from Dreiding [12] were adopted. This forcefield was shown to work well for extensive classes of organic materials in reproducing experimental data. All simulations were conducted in the NPT ensemble. The system was equilibrated in two steps, starting with 20 ps at 100 atm and following with 300 ps, where pressure was allowed to relax to 1 atm and the system smoothly
reached the equilibrium density. The MD trajectories were sampled every 100 ps during the following 10 ns NPT simulation. In two series of simulations, temperature was maintained at 300 and at 350 K using the Nosé-Hoover thermostat [13], while pressure was constantly regulated at 1 atm by the Nosé-Hoover barostat [14]. A limited number of MD simulations were performed without imposing the fast equilibration step at high pressure: in these cases the simulations were allowed to run (at 300 K) over 10 ns.

2.3 Derivation of solubility parameters
The starting periodic box contains a given number of molecules (5-10 in the case of asphaltenes, 20-50 for solvents) that were arranged at a low density (0.1 g/cm$^3$) and in random configurations within MAPS by Amorphous Builder. The same MD code and forcefield were used as for the aggregation studies, but lower system dimensions (~2000 atoms) and much shorter simulation time scales (~200 ps) allowed to complete the set up and data collection very rapidly, even for a larger number of molecular assemblies. Therefore all solubility parameter simulations were performed on a PC, with no parallelization applied. After reaching proper equilibration of the system at 300 K and 1 atm by NPT MD, the cohesive energy of the cell was calculated [15] within MAPS from NVT MD trajectories. The detailed parameters for an effective simulation protocol were tested with pure solvent boxes: the results were found comparable to reported values of density and Hildebrand $\delta$, that were obtained by experiments and other simulation methods [2, 6, 7]. The same protocol was then applied to the asphaltene containing boxes.

3 Results and discussion
A collection of average asphaltene structures were designed by model building, each one corresponding to a single asphaltene sample and a corresponding set of experimental characterization data. Two model structures, respectively labeled mol1a (top) and mol2a (bottom) are shown in the following Fig.1: they were selected for the nanoaggregation MD simulations.

All produced asphaltene models were subjected to MD simulations to calculate the Hildebrand solubility parameter. An easy way to follow the asphaltene nanoaggregation process takes advantage of plotting the pdf profiles of selected intermolecular distances. C/C distances (all C atoms of the aromatic rings) are specifically suitable for the purpose, since their number is large and they are located in a highly regular molecular structure in itself, the extended planar core of the asphaltenes. As an example, the pdf traces shown in Fig.2 (where thf=tetrahydrofurane, tol=toluene, nc7=n-heptane, nc5=n-pentane) were calculated in the last steps along the 10 ns MD trajectory collected at 350K for four mol1a/solvent assemblies.
A well defined three-peak sequence is observed in all four cases, corresponding to the formation of more or less regular tetramers of asphaltene molecules, facing each other through their extended planar cores. Similar results are depicted in Fig.3, where the pdf profiles were drawn for intermolecular aromatic C/C distances calculated of four mol2a/solvent assemblies (same temperature and solvents as for previously presented mol1a results).

Here more peaks are visible (at least five, in the cases of n-pentane and of n-heptane) than in Fig.2, corresponding to more extended or more regular supramolecular structures. A disordered asphaltene hexamer is shown in Fig.4, that reports data from the last configuration from the MD simulation at 300K of the mol1a asphaltene in toluene (at 25 %w concentration) extended over 24 ns.

This is a typical example of the molecular clusters obtained in most nanoaggregation simulations performed for the purpose of this study. Similar asphaltene clusters were already reported in the literature [3, 16]. Frequently more than one cluster
can be detected at the same time in the simulation box, while occasionally the regular facing of the aromatic ring planes is more complete. However, within the whole series of nanoaggregation simulations performed so far, only one simulation revealed a highly ordered structure like the decamer shown in Fig.5.

Here the last configuration is reported from the MD simulation at 300K of the mol2a asphaltene in n-pentane (at 20 %\textsubscript{w} concentration) that were extended over 16 ns.

In this case all asphaltene molecules spontaneously arranged in a single cluster, with the extended asphaltene planar cores neatly contacting each other throughout most of their aromatic surface. The resulting pdf profiles for aromatic C/C and for S/S distances are reported in Fig.6.

Highly regular peak sequences are clearly visible on both plots. Nine maxima mark the C/C profile: the last shoulder peak can be located at 31.9 Å on an expanded scale (inset of Fig.6). They were produced by ten asphaltene planes, orderly facing each other within the observed decamer (Fig.5). The first peak is located at 3.6 Å and, in agreement with the C/C interpeak periodicity, it accounts for the preferred interplanar distance within the asphaltene nanoaggregate. The S/S peak pattern is more irregular in shape, distance and relative height, since there are much less S than aromatic C atoms in the simulation box and their exact location on the asphaltene plane strongly influences their pdf profile. Nevertheless it gives approximately the same repeated interplanar distance observed in the aromatic C/C pdf plot.

The derivation of Hildebrand solubility parameters through MD simulations produced \( \delta \) and density values for 17 solvents: they were ordered according to increasing \( \delta \) and reported on Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>( \delta ) [10(^6) Pa(^{1/2})]</th>
<th>( \rho ) [g·cm(^{-3})]</th>
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</thead>
<tbody>
<tr>
<td>pentane</td>
<td>14.6</td>
<td>0.625</td>
</tr>
<tr>
<td>heptane</td>
<td>15.3</td>
<td>0.669</td>
</tr>
<tr>
<td>toluene</td>
<td>18.2</td>
<td>0.875</td>
</tr>
<tr>
<td>pyridine</td>
<td>18.5</td>
<td>0.863</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>18.7</td>
<td>1.314</td>
</tr>
<tr>
<td>pyrrole</td>
<td>18.9</td>
<td>0.846</td>
</tr>
<tr>
<td>toluene</td>
<td>20.2</td>
<td>0.961</td>
</tr>
</tbody>
</table>
Since these results were found comparable to published data [see Methodology 2.3] the same MD protocol was adopted for the asphaltene simulation boxes. Table 2 presents the ordered δ and density values obtained for asphaltenes.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>δ [10^6 Pa^{1/2}]</th>
<th>ρ [g·cm^{-3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanolamine</td>
<td>20.7</td>
<td>1.013</td>
</tr>
<tr>
<td>Acetone</td>
<td>21.0</td>
<td>0.770</td>
</tr>
<tr>
<td>Pyridine</td>
<td>21.1</td>
<td>0.981</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>21.4</td>
<td>0.857</td>
</tr>
<tr>
<td>Methylpyrrolidone</td>
<td>21.9</td>
<td>1.028</td>
</tr>
<tr>
<td>Ne</td>
<td>23.2</td>
<td>0.933</td>
</tr>
<tr>
<td>Ethyldiethylglycole</td>
<td>23.5</td>
<td>0.937</td>
</tr>
<tr>
<td>Furfuraldehyde</td>
<td>25.8</td>
<td>1.149</td>
</tr>
</tbody>
</table>

The values for the moderately polar and the aromatic solvents fall in the same region (18-22 10^6 Pa^{1/2}) as most asphaltene molecules. On the contrary, the typical asphaltene precipitants n-pentane and n-hexane are located remarkably out of such interval. These results are largely in agreement with published experimental and computational observations [2, 6, 7] and, together with more sophisticated methods, can be used as a guide to the selection of suitable solvents or precipitants for the treatment of oil samples containing asphaltenes.

4 Conclusion

The derivation of a collection of average molecular structures, each describing a different asphaltene sample, was obtained with a specific model building approach. These models can be used in molecular simulations specifically tailored to calculate useful physicochemical properties, like the Hildebrand solubility parameter, or to study the formation of asphaltene nanoaggregates.

Small asphaltene clusters were always detected along MD trajectories produced for the simulation of nanoaggregation in concentrated asphaltene solutions. In the specific decamer case the cluster was observed to grow spontaneously by orderly addition of extended aromatic cores on top of each other, until all available asphaltene molecules entered the nanoaggregate. It is not surprising that
the asphaltenes in this simulation box were soaked in a typical asphaltene precipitant (n-pentane). The results presented in this study hint at highly regular supramolecular structures as starting seeds for much larger asphaltene aggregates. However, the length and time scales that were currently explored prevent the simulation of further cluster evolution. The carefully designed extension of the adopted conditions will possibly lead to a deeper elucidation of the first stages in the nanoaggregation process of asphaltenes.

References:
[8] Scienomics, Sarl