# Computer Modeling and Simulation of the Nanoaggregation and Solubility of Crude Oil Asphaltenes

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*Abstract:* - The methodology of classical molecular dynamics provides useful tools for the simulation of the solution behaviour of asphaltenes. The aggregation and the solubility properties of this class of molecules are studied at a full atomistic level. Average three-dimensional asphaltene models are built on the basis of experimental data, collected 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. Their analysis 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. This is a practical example of obtaining useful physicochemical properties from molecular simulations applied to average asphaltene structures.

Key-Words: - Simulation, Model building, Molecular dynamics, Asphaltene, Oil, Aggregation, Solubility, Hildebrand

## **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 length frequently nanometer scale, 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. The nanoaggregate size and shape in solution were directly measured by small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) in both deuterated aromatic solvents [1-7] and crude oils [8–10], yielding a radius of gyration ranging from 3 to 10 nm, dependent upon the crude oil, asphaltene precipitation method, and the analysis method used [2, 4, 6]. The SAXS and SANS data can be fitted to a number of geometrical form factors, including spheres [1-3, 5], ellipsoids [4, 5] and cylinders [2, 3]. However, because the polydispersity of the nanoaggregates is unknown, these results should be taken with caution. More recently, additional methods have been used to study asphaltene nanoaggregates that have given a smaller size. Investigations of asphaltenes in situ in oil reservoirs under equilibrium conditions gave a radius of  $\sim 1$  nm by buoyancy arguments [11]. Recent ultracentrifugation studies gave similar results, estimating a nanoaggregate diameter of 2.5 nm from the sedimentation speed. Similar sizes have also been estimated from high-Q ultrasonics [12, 13]. These measurements indirectly link the asphaltene molecular structure with the colloidal structure, giving an aggregation number of 4-5. Nuclear magnetic resonance (NMR) diffusion measurements [14] and direct-current (DC) conductivity measurements [15] of asphaltene solutions have been shown to give similar results.

There is little agreement on the internal molecular structures of asphaltene nanoaggregates. 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 model is consistent with smaller nanoaggregate sizes from high-Q ultrasonics measurements [12], which give an aggregation number of approximately 5, which is a reasonable number for  $\pi$ - $\pi$  stacking. However, this model seems incompatible with the nanoaggregate sizes measured by SAXS and SANS, because these sizes require a much greater aggregation number. SAXS and SANS data are generally more consistent with a more "diffuse" model for nanoaggregate structure. It was shown that, for a polydisperse disk form factor to fit the SANS data correctly, one had to include solvent entrainment within the nanoaggregates [2]. The SAXS and SANS data can alternatively be well-interpreted as fractal objects of fractal dimension ~ 2.5, again indicating a diffuse nanoaggregate [8, 16]. The SANS data have been attributed [17, 18] to a solution behavior of asphaltenes as "dynamically varying compositional inhomogeneities".

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The numerous methodologies of molecular modeling and simulation are widely applied in different research fields of chemistry, biophysics and materials science [19-22]. In recent years, there has been an increasing effort to understand the structure of asphaltene aggregation on a molecular level using molecular simulation [23–28]. Initially, asphaltene aggregation was considered in vacuo by molecular mechanics methods. Murgich et al. [29] conducted molecular mechanics calculations using a large asphaltene structure (a single polyaromatic core containing 24 aromatic rings) and showed that aggregation mainly occurred by stacking of aromatic cores. Similarly, Pacheco-Sanchez et al. [23] used molecular dynamics to show that asphaltene aggregation does occur spontaneously for smaller asphaltene molecules (the archetypal Groenzin/Mullins model [30]), forming dimers, trimers, and tetramers during a short 100 ps simulation. The structure of the aggregates formed showed no overriding structure type: face-face, offset stacked, and T-shaped aggregates were observed. Simulations of asphaltene dimers with explicit solvent molecules conducted over 100 ps by Carauta et al. [25] have shown that the asphaltene dimers bind face-face at a distance of  $\sim 3.6$  Å in heptane and  $\sim 5$  Å in toluene. Furthermore, they show that the effect of an increasing temperature (from 323 to 573 K) is to decrease the distance between the asphaltene dimer. A similar temperature dependence has been observed by Zhang et al. [27] from molecular dynamics simulations of asphaltene molecules in model asphalts over 3 ns. The g(r) showed nearest neighbor peaks at lower r at the highest temperatures. The nearest neighbor orientation of asphaltene aromatic cores also showed temperature dependence. Additionally, molecular simulation has been used to study the thermodynamics of asphaltene aggregation by obtaining asphaltene-asphaltene binding energies [31, 32]. Ortega-Rodriguez et al. have conducted coarse-grained simulations [31] representing each asphaltene molecule as a single point with a spherically symmetric interaction potential defined from atomistic molecular mechanics (MM) simulations in vacuo [33]. These atomistic MM calculations gave a high asphaltene-asphaltene binding energy of -130 kJ mol<sup>-1</sup>. From this, they calculated the asphaltene-asphaltene g(r) for course-grained simulations of model asphaltenes and resins, while solvent effects were simplified to a background dielectric constant. From the g(r), the potential of mean force was calculated and the binding free energy was estimated to be  $\sim$  -4kT, considerably less than the binding energy from the MM calculation in vacuo. More detailed atomistic calculations have been conducted between asphaltene pairs in vacuo using the density functional theory by Alvarez-Ramirez et al. [32]. They found an asphalteneasphaltene binding energy of 50-63 kJ mol<sup>-1</sup>.

For any of these simulation studies to yield meaningful results, the model structures used must be representative of asphaltenes as a whole [34-36]. 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 using fluorescence depolarization measurements [40], high-resolution mass spectroscopy [37], and UV absorption and fluorescence emission [38, 39] have convincingly shown the correctness of an asphaltene structure with a single aromatic core (possibly two), containing 4-10 aromatic rings.

Previous studies used "average" model structures that are consistent with experimental data [25, 40, 41]. Sheremata et al. [42] have developed quantitative molecular representation (QMR) as a method for generating a group of structures that best represent experimental data (mass spectrometry, NMR, and elemental analysis), rather than just being consistent with the data. It was shown that 5-6 molecules were needed to represent the experimental data well. The method is based on an algorithm that builds a very large number of asphaltene molecules from building blocks. From this set, the best mixture of 5-6 molecules are chosen that fit the experimental data. This method has recently been updated [36] to allow for the formation of smaller (one aromatic core) and three-dimensional structures. This gives the best fit to experimental data with low-molecular-weight asphaltenes (500-2000 Da). This is quite different from the asphaltene molecular weight used by Sheremata et al. [42], where a molecular weight of  $\sim 4000$  Da, determined from VPO, was used. This tends to the conclusion that asphaltenes have just one or perhaps two aromatic cores, because larger archipelago-type models would have too high of a molecular weight.

This molecular simulation study aims to investigate 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.

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 [43]. 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 [35, 44, 45] in predicting

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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 inter-molecular 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 (mol1a and mol2a: see Results and discussion 3.1) were used and the simulation boxes were filled, respectively, with toluene, tetrahydrofurane, n-pentane or n-heptane. The asphaltene concentrations in the simulation boxes are reported on Table 1.

Table 1	concentration [% w]
mol1a/toluene	30
mol1a/tetrahydrofurane	23
mol1a/n-pentane	30
mol1a/n-heptane	25
mol2a/toluene	25
mol2a/tetrahydrofurane	20
mol2a/n-pentane	25
mol2a/n-heptane	21

From the trajectories, the atomic coordinates and velocities and the associated potential energies were obtained over as long as possible timescales. 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. The pdf is generally defined as the ratio of the local density of atoms at a distance r from an atom at the origin to the average density of atoms in the bulk:  $\rho(r)/\rho$ . In this case, r is the distance between a single atom defined on each asphaltene molecule to represent its center. This allowed to follow the first steps in the spontaneous nanoaggregation process at fixed physicochemical conditions. 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:  $\delta$ =  $(\sqrt{\Delta E^{vap}}/V)$ , 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 [46]. Suitable building blocks were selected among the typical structures and functional groups detected in the asphaltenes by experimental characterization [47, 48]. 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 <sup>1</sup>H and <sup>13</sup>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 experimental asphaltene sample, only the model structure best fitting all available data was chosen as the "average asphaltene" contained in that peculiar sample. Within such collection of average asphaltene models, starting molecules were selected for all 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 (concentrations reported on Table 1) were arranged in a periodic unit cell of appropriate size to start with a density of  $0.1 \text{ g/cm}^3$ . 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 [49] code for parallel MD was used and the atomic parameters from Dreiding [50] 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 run. In two series of simulations, temperature was maintained at 300 and at 350 K using the Nosé-Hoover thermostat [51], while pressure was constantly regulated at 1 atm by the Nosé-Hoover barostat [52]. 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 over 10 ns, at the temperature of 300 K.

#### 2.3 Derivation of solubility parameters

In this set of simulations 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<sup>3</sup>) 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 [53] within MAPS from NVT MD trajectories. The detailed parameters for an effective simulation protocol were tested with pure solvent boxes: the calculated values (see Results and discussion 3.3) were found comparable to reported values of density and Hildebrand  $\delta$ , that were obtained by experiments and other simulation methods [35, 44, 45]. The same protocol was then applied to the asphaltene containing boxes.

## **3** Results and discussion

The following three sections separately report: a) the molecular models of average asphaltene structures obtained by model building; b) an analysis of the molecular dynamics trajectories simulating asphaltene diffusion and aggregation in pure solvents; c) the Hildebrand solubility parameters computed for asphaltenes and for typical asphaltene solvents and precipitants.

## 3.1 Asphaltene model building

A collection of 17 average asphaltene structures were designed by model building, each one corresponding to a single asphaltene sample and a corresponding set of experimental characterization data, as described in the Methodology section. The molecular weight calculated for each asphaltene model is reported on Table 2.

Table 2	MW	
Table 2	[Da]	
mol1a	1519	
mol2a	1467	
mol1b	1439	
mol1c	901	
mol2b	800	
mol2c	1090	
mol2d	945	
mol2e	1045	
mol3a	348	
mol3b	347	
mol3c	590	
mol3d	637	
mol3e	423	
mol3f	534	
mol3g	447	
mol4	1433	
mol5	1625	

The first two model structures are shown in the following Fig.1 (respectively, molla on top and mol2a at the bottom). They were selected for MD simulations of the asphaltene nanoaggregation (see Results and discussion 3.2).





The molecular structures of the other 15 asphaltene models are depicted in the following Fig.2 (ordered according to Table 2).







All produced asphaltene models were subjected to MD simulations to calculate the Hildebrand solubility parameter.

## 3.2 Diffusion and nanoaggregation

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.3 (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.4, 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 npentane and of n-heptane) than in Fig.3, corresponding to more extended or more regular supramolecular structures.

A disordered asphaltene hexamer is shown in Fig.5, 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 [36, 54]. 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.6.



Here the last configuration is reported from the MD simulation at 300K of the mol2a asphaltene in n-pentane (at 20  $%_w$  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.7.



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.7). They were produced by ten asphaltene planes, orderly facing each other within the observed decamer (Fig.6). 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.

#### 3.3 Solubility parameters

The derivation of Hildebrand solubility parameters through MD simulations produced  $\delta$  and density values for 15 solvents: they were ordered according to increasing  $\delta$  and reported on Table 3.

Table 3	$\delta$ [10 <sup>6</sup> Pa <sup>1/2</sup> ]	ρ [g·cm <sup>-3</sup> ]
n-pentane	14.6	0.625
n-heptane	15.3	0.669
pyrrolidine	18.2	0.875
piperidine	18.5	0.863
dichloromethane	18.7	1.314
toluene	18.9	0.846
pyrrole	20.2	0.961
ethanolamine	20.7	1.013
acetone	21.0	0.770
pyridine	21.1	0.981
tetrahydrofurane	21.4	0.857
N-methylpyrrolidone	21.9	1.028
furane	23.2	0.933
dimethyldiethylglycole	23.5	0.937
furfuraldehyde	25.8	1.149

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 4 presents the ordered  $\delta$  and density values obtained for 17 asphaltenes.

Table 4	$\delta$ [10 <sup>6</sup> Pa <sup>1/2</sup> ]	ρ [g·cm <sup>-3</sup> ]
mol3c	17.7	1.006
mol4	18.9	1.145
mol3f	19.0	1.021
mol2c	19.1	1.104
mol1a	19.1	1.106
mol1b	19.4	1.134
mol3e	19.6	1.083
mol5	19.6	1.121

mol3d	19.7	1.078
mol2d	20.0	1.121
mol2e	20.0	1.150
mol2a	20.1	1.194
mollc	20.7	1.173
mol2b	20.7	1.188
mol3g	21.1	1.144
mol3b	23.1	1.251
mol3a	23.4	1.281

The two calculated Hildebrand  $\delta$  series are also plotted in Fig.8.



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 [35, 44, 45] 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.

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