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MODELING OF ASPHALTENE AGGREGATION IN CRUDE OIL BY DISSIPATIVE PARTICLE DYNAMICS (DPD)

By

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A thesis submitted to the

Graduate School-New Brunswick

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Master of Science

Graduate Program in Chemical and Biochemical Engineering

Written under the direction of

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And approved by

New Brunswick, New Jersey

October, 2016

ABSTRACT OF THE THESIS

Modeling of Asphaltene Aggregation in Crude Oil by Dissipative Particle Dynamics (DPD) by TIANYING MA

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In this work we model aggregation of heavy polyaromatic hydrocarbons in solution of aliphatic and aromatic hydrocarbons, effectively mimicking crude oil using dissipative particle dynamics. It has both fundamental and methodological aspects. First of all, this is the first (as far as we know) attempt to model solutions of geometrically complex molecules. Polyaromatic molecules are geometrically complex compared to, for example, common surfactants modelled by DPD due to presence of polyaromatic cores that form flat sheets in thickness of only one carbon. The anisotropy of molecules translates into anisotropic structures of the aggregates where the cores "stack" on the top of each other, therefore, computationally efficient DPD simulations should use beads of different effective diameters. The first part of the thesis describes the experience of building models of solutions of polyaromatic compounds using differently sized beads. We generally follow the "top-down" approach: the parameters are chosen to provide the best match to common thermodynamic properties of reference bulk solutions of hydrocarbons: molar volumes, activity coefficients, and solubilities. Bonded parameters are chosen from the geometrical considerations and atomistic simulation results.

Having developed the DPD forcefield, we compose models of characteristic asphaltenes of different molecular mass and geometry and model their aggregation. The results show that the behavior of polyaromatic systems cannot be described with a single characteristic asphaltene

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model. The presence of archipelago and big asphaltenes considerably increases the size of the aggregates and makes the shape much more complex; we could follow the birth of fractalic structures typical during the asphaltene precipitation process. At the same time, the toluene insoluble fractions only weakly influences by the presence of smaller asphaltenes. The presence of smaller polyaromatic compounds with higher hydrogen to carbon ratio indeed substantially increase the dispersity of the system hindering asphaltene aggregation.

Acknowledgement

I would first like to thank my thesis advisor Research Associate Professor Vishnyakov of Department of Chemical and Biochemical Engineering at Rutgers, the State University of New Jersey, whose enthusiastic passion and discrete attitude towards computational chemistry and molecular simulations inspired me a lot. Dr. Vishnyakov is always patient to help me with questions related to simulations processing and thesis writing and guided me in the right way towards the ultimate accomplishment whenever he thought I needed it.

I would also like to express my grateful feelings to distinguished Professor Neimark and his research groups of Department of Chemical and Biochemical Engineering at Rutgers, the State University of New Jersey, who consistently provided me research resources and give me valuable advice during my researches. I would like to thank Dr. Ming-Tsung Lee, a former PhD candidate in Professor Neimark's group, who guided me on molecular simulations in the primaries.

Finally, I must express my truly deeply gratitude to my parents and my little brother for providing me with sufficient support and continuous trust throughout my years of study and through my pursuit of Master degree in Chemical Engineering at Rutgers University. Thank you.

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Chapter 1 Introduction

Saturates, aromatics, resins and asphaltenes (SARA¹) are widely acknowledged as the major components in crude oil. Among SARA, asphaltenes form the enigmatic component, not only because of the wide variety of structures, but it majorly contributes to problematic and complicated behavior of crude oil. Asphaltenes are widely defined as a solubility class of molecules that precipitate in paraffinic solvents but dissolve in toluene¹⁻³. This component combines poly-aromatic rings, aliphatic hydrocarbon, and hetero (O, S, and N) functional groups. The structures of asphaltenes are characterized by the average molecular mass, elemental composition, including hydrogen/carbon H/C ratio⁴. The MW reported ranges from a few hundred to dozens of thousands⁵⁻⁹. Barrera et al.⁶ divided the asphaltenes into two kinds, the lighter cuts have lower molecular weight that is from 900 to 4300, and the heavy cuts have high molecular weight from 12300 to 38000. Speight et al.⁷ collected sources and estimated the average of about 2000, which could represent the asphaltenes in highly polar solvents that prevent aggregation. The element compositions are in general consensus while differences remain between different oil^{7, 8,10-12}. The H/C ratio was measured by many authors: from 1 to 1.5 by Tanaka et al.¹⁰, 1 to 1.1 by Oh et al.⁸, 1.1-1.3 by Zhang et al.⁵. It is commonly agreed that H/C ratio in asphaltenes is close to 1.0.

property	West Texas Asphaltenes	Louisiana Asphaltenes				
Elemental analysis (wt. %)						
С	85.78	86.24				
Н	7.16	6.78				
Ν	1.19	1.23				
S	2.71	0.65				
0	1.34	3.19				

Table 1. Elemental composition of exemplary oil samples¹¹

Metal content (ICP)(ppm)		
V	190	13
Ni	266	63
Fe	178	526

As the demand for energy continuously increases while the lack of crude oil sources becomes more compelling, the world's desire for crude oil and derived fuel product are being significant. Therefore, optimizing oil technologies and maximizing oil production are urgent issues. Before improving process industrially, a comprehensive understanding of the mechanism of asphaltenes aggregations should be stressed, since asphaltenes behavior is related to many difficulties in petroleum industry, including petroleum extraction, transportation and refining¹³. A number of modeling have been suggested, most of them can be referred to one of two major groups. The first group of models considers asphaltenes precipitation as a bulk phase (liquidliquid or solid-solid) separation process. They are mostly focused at the final (equilibrium) result: after all, the final products of asphaltenes precipitation are bulk (gel-state) bitumen and uniform solution of remaining oil components. However, the separation process can take hours, weeks, or even months and involves various colloidal structures where asphaltenes play a critical role. Therefore a number of colloidal models of asphaltenes were put forward. Among them, the Yen model is recognized as the cornerstone. Yen¹⁴ stressed a hierarchy of structures within heavy crude oil, asphalt and asphaltenes, in which micelle was the small stacks of fused aromatic compounds of asphaltenes and able to grow to a small limit cluster, and those cluster can be aggregated when the concentration is high. Mullins ^{15, 16} brought up a modified Yen model, also known as Yen-Mullins Model, in which the predominant asphaltenes molecular architecture has a single, large polyaromatic hydrocarbon with peripheral alkanes, those asphaltenes molecules stack to form nano-aggregates, and the nano-aggregates aggregate to form clusters. And integrated studies of asphaltenes and their fractions with solubility prove the coexistence of both the 'continental' and 'archipelago' type molecules^{4, 10}. A continental asphaltene molecule contains one polyaromatic hydrocarbon

sheet with alkane sidechains while an archipelago molecule contains more than one polyaromatic sheets and alkane chains link the centers into one.

Atomistic and mesoscale simulations have been also utilized in studies of asphaltene precipitation recently. Pacheco-Sanche el al.¹⁷ simulated asphaltenes under vacuum by molecular dynamics (MD) and observed 3 aggregating patterns (i) face to face geometry (ii) edge-on on T-shape geometry and (iii) offset π geometry. Kuznicki et al.¹ studies behaviors of both continental and archipelago asphaltenes in binary aqueous and toluene systems. Boek et al.¹⁸ developed a computer algorithm to create quantitative molecular representation (QMRs) of asphaltenes based on Monte Carlo method, and the results give good match with experimental data. The dissipative particle dynamics (DPD) simulations have also been employed for modeling of asphaltenes. Alvarez et al.¹⁹ simulated a system of polymer/crude oil/water (PCW) time evolution of the emulsion using DPD models of ASAR. They coarsely grained asphaltenes molecules based on fraction types regardless of volumes differences. But this models present rough similarity to real structures: the planar structures of polyaromatic hydrocarbon are missing and no parallel stacking features can be observed in simulations. Zhang et al.^{5, 20} chose fused hexa-particle rings to build asphaltenes planar structures in DPD simulations. And they observed stacking structures of asphaltenes under different circumstances. The existing DPD studies share one serious shortcoming: they lack a systematic parameterization. The "mismatch" in parameters assigned to beads of different types (say, aliphatic and aromatic) is basically assigned arbitrarily and in reality taken close to those in simulations of surfactant-like molecules in water⁵. In reality, the behavior of oil systems (that are almost entirely hydrophobic) is very subtle, and this work shown the importance of that. Ironically, arbitrary parameters⁵ worked even better than say, attempts to use "blend"²¹ method to parameterization of asphaltenes that lead to completely unphysical picture^{5, 19} (outright phase separation to multiple liquid phases in oil) that the authors did not even notice.

This study mainly focuses on creating comprehensive asphaltenes models that can well

represent the real molecules in DPD simulations. Several molecular models are discussed and parameterized, on both continental and archipelago categories. Resin model are also constructed using coarse-graining concept and deployed in asphaltenes-solvents system. The solvents chosen are hexane and toluene and binary mixture of both kinds in different proportions. Morphology are discussed and characterized by size distribution and asymmetry measures. The dilution of asphaltenes solution in binary solvents and structural properties are calculated and compared with experimental data.

Chapter 2 Dissipative Particle Dynamics Simulation Method

Dissipative Particle Dynamics (DPD) is an off-lattice, discrete method based on soft repulsion potential for modelling mesoscopic system. DPD method evolves from classical MD ²². In DPD, individual molecules are divided into quasi-particles (beads). The interacting particles' time evolution is governed by the Langeven equations of motion. The forces contain conservative soft short-range repulsion F_{ij}^{c} , random F_{ij}^{R} , drag forces F_{ij}^{D} all acting between particular beads that allows DPD conserve momentum. The geometry of molecules is controlled by bonds and angles connecting the beads, with corresponding forces F_{ij}^{B} and F_{ijk}^{A} .

$$f_{i} = \sum_{i \neq j} \left(F_{ij}^{C} + F_{ij}^{R} + F_{ij}^{D} + F_{ij}^{B} + F_{ijk}^{A} \right)$$
(1)

All beads are assigned an equal effective diameter. The soft short-range repulsion force acts along the line of centers and is given by

$$\boldsymbol{F_{ij}^{C}} = \begin{cases} a_{ij} \left(1 - \frac{r_{ij}}{R_{c}}\right) \left(\frac{r_{ij}}{r_{ij}}\right), \ r_{ij} < R_{c} \\ \boldsymbol{0}, \ r_{ij} \ge R_{c} \end{cases}$$
(2)

Where R_c is the effective geometric parameter, and a_{ij} is the energy parameter for the shortrange repulsive force. R_c and a_{ij} are specific to bead types *i* and *j* to which beads *i* and *j* belong. Note that the effective bead diameters R_c and intra-component repulsion parameters a_{ij} may differ for different bead types, subject to the given particle pair *i* and *j*.

Since the dominating interactions are repulsive, the beads in the system have to overlap. The densities typical in DPD simulations range from 3 to 5 beads by R_{c}^{3} .

The stochastic random forces take the form

$$F_{ij}^{R} = \sigma w^{R}(r_{ij})\theta_{ij}\Delta t^{-1/2}\frac{r_{ij}}{r_{ij}}$$
(3)

In which Δt is the time step and $w^{\mathbb{R}}(r_{ij})$ is a switching function that imposes a finite limit on the

range of the stochastic force. θ_{ij} is a random number with zero mean and unit variance, chosen independently for each pair of interacting particles and at each time step. And σ is a constant related to the temperature, as a role of the random force in representing a heat bath.

The particles also experience a drag force, which depends on the relative velocity between interacting pairs of particles

$$\boldsymbol{F_{ij}^{D}} = -\gamma w^{\mathrm{D}} (r_{ij}) (r_{ij} \cdot v_{ij}) \frac{r_{ij}}{r_{ij}^{2}}$$

$$\tag{4}$$

Where $w^{D}(r_{ij})$ is again a switching function and the γ is the drag coefficient, which follows the fluctuation-dissipation theorem. For thermodynamic equilibrium to result from this method, the following relations must be obeyed

$$\sigma_{ij}^2 = 2\gamma_{ij}k_{\rm B}T\tag{5}$$

$$w^{\mathrm{D}}(r_{ij}) = \left[w^{\mathrm{R}}(r_{ij})\right]^{2}$$
(6)

In practice, one of the two switching functions can be chosen arbitrarily and that this choice fixes the other weight function. Here, $w^{D}(r_{ij})$ is taken as

$$w^{\mathrm{D}}(r_{ij}) = \begin{cases} \left(1 - \frac{r_{ij}}{R_{\mathrm{c}}}\right)^2, \ r_{ij} < R_{\mathrm{c}} \\ 0, \ r_{ij} \ge R_{\mathrm{c}} \end{cases}$$
(7)

By defining so, all interactions are confined in range of cutoff R_c . The random and drag coefficients are usually constant for all interactions in many DPD simulations.

The bonds and angles controlling the shape of the molecules are harmonic, where

$$F_{ij}^{B} = -k_{\rm s} \left(r_{ij} - r_0 \right) \left(\frac{r_{ij}}{r_{ij}} \right) \tag{8}$$

$$U_{ijk}^{A} = \frac{k_{\theta}}{2} \left(\theta_{ijk} - \theta_{0} \right)^{2}, \boldsymbol{F}_{ijk}^{A} = -\boldsymbol{\nabla}_{ijk} U_{ijk}^{A}$$
(9)

Where k_s in equation 8 is a spring force constant, r_0 is an equilibrium bond length. And in

equation 9, k_{θ} is angle force constants and θ_0 is an equilibrium bond angle.

Chapter 3 DPD Models of Crude Oil Components

Due to the definition of asphaltenes as the oil fraction soluble in toluene and insoluble in aliphatic hydrocarbons, we considered 6 example molecules (1) single-core asphaltene with H/C ratio close to 1.0 and molecular mass of 810 Da denoted as model A-asphaltene (2) multicore asphaltene with molecular mass of 2475 Da and similar H/C ratio denoted as model S-asphaltene (3) single-core asphaltene with similar H/C ratio and molecular mass of 1965 Da denoted as model L-asphaltene (4) an example of a resin molecule (5) toluene (6) hexane. The last two solvents represent low molecular weight aliphatic and aromatic oil fractions. Section 3.1 extends on solvent modeling, Section 3.2 considers sub-model of aromatic cores, Section 3.3 describes sub-model of aliphatic chains, and Section 3.4 explains hetero functional models. Section 3.2, 3.3, 3.4 are fundamental descriptions to further asphaltenes and resins modeling and provide necessary parameterization methods for DPD simulations.

3.1 Solvents

Correlations between density, pressure and compressibility of single-component DPD systems were first obtained by Groot & Warren (GW)²³ The equations that relate pressure, density and compressibility of the systems are given by GW

$$\frac{3}{R_c^3} = \frac{\rho}{MW} N_A \tag{10}$$

GW determined the correlation between reduced dimensionless compressibility, density and the intracomponent repulsion parameter a

$$\kappa^{-1} = \frac{1}{nk_{\rm B}T\kappa_{\rm T}}, \ \kappa^{-1} = 1 + 0.2\alpha\rho/k_{\rm B}T \tag{11}$$

The pressure depends on the reduced density $(/R_c^3)$ and repulsion parameter as

$$P = \rho k_{\rm B} T + \alpha a \rho^2, (\alpha = 0.101 \pm 0.001)$$
(12)

Such soft repulsive systems are inherently supercritical (attractive interaction is necessary for modeling vapor-liquid equilibria). At bead densities most common in DPD simulations, the pressure reaches hundreds of atmospheres. That is, if the actual fluid density is reproduced, the pressure cannot be. Varying the *a* and *R*_c, one however can reproduce density and compressibility of a pure liquid, which has become a standard approach in DPD simulations. However, since the pressure and compressibility are almost proportional to each other (Equations 11-12), one cannot fit densities and compressibilities of 2 dissimilar liquids at the same pressure just by varying *a* and *R*_c. At a fixed density of DPD beads $\rho R_c^3=3$, Equations 10-12 would give different parameter sets for all solvents in this work (Table 2) and this would result in different pressures in systems of different pure components. If two immiscible phases are observed in the same simulation, the pressure in the both is the same due to the mechanical equilibrium, and therefore the densities (Equations 11-12) would strongly deviate from the experimental values.

Taken this into account, we decided to choose hexane (denoted using subscript H here and further on) as the "standard component". Namely, hexane was modeled as a standard DPD fluid at ρR_{c^3} =3, and $R_{c,H}$ and a_{HH} were fitted to the density (0.6548 g/mL at 298K) and compressibility (1.669×10⁻⁹ Pa⁻¹) of liquid hexane at ambient conditions.

Equations 10 and 11 yield $R_{c,H} = 0.87$ nm and $a_{HH} = 51.4 k_B T/R_{c,H}$. Simulations are performed at constant pressure equal to the pressure of the DPD model of liquid hexane. P=46 $k_B T/R_{c,H^3}$. The importance of keeping the same pressure in simulations with beads of different sizes was previously stressed by Kacar et al.²⁴. In Lee et al.²⁵, constant pressure simulations were applied to systems with short bonds, where standard GW EOS could not be used for predictions of pressure and compressibility dependence on density.

For simplicity, we described toluene (T) using beads with the effective size similar to that of hexane. Using the effective volumes of functional groups (so called Bondi tables used in group

contribution thermodynamic models like UNIFAC²⁶) we determined that the volume of toluene molecule is 13% less than that of hexane. Therefore one H bead models 1.15 toluene molecules.

The intra-component hexane-toluene parameters were determined in a fashion proposed in Vishnyakov et al.²⁷: $R_{c,HH}=R_{c,TT}=R_{c,HT}$; a_{HT} was calculated from the infinite dilution activity coefficients in toluene-hexane solutions. The correlation between a_{HT} and γ_{inf} obtained in Vishnyakov et al.²⁷ gives $\Delta a_{HT}=a_{HT}-a_{TT}=1.0 \ k_{B} T/R_{c,H}$, therefore $a_{HT}=52.4 \ k_{B} T/R_{c,H}$.

Table 2. solvents R_{\circ} and intracomponent repulsion parameters for different solvents that would have been obtained from densities and compressibilities of the pure solvents provided that $\rho R_{\circ}^3=3$

	toluene	water	hexane	heptane
				1
$R_{ m c}$ /Å	8.1	4.5	8.7	9.0
$a R_{\rm c}/k_{\rm B}T$	78.7	25.0	51.4	67.4

3.2 Describing asphaltenes in DPD: the poly-aromatic core

It is been widely acknowledged that asphaltenes are combination of aromatic cores to which aliphatic side chains and hydrophilic hetero-groups are attached, besides that, heteroelement would mostly occur on the periphery of the cores either on rings but may also found in sidechains. The first step is determining the size of the beads that is necessary for a reasonably accurate representation of the aromatic and aliphatic fragments. The necessary conditions for an adequate description of aromatic cores are

(1) A flat geometry;

(2) A reasonable agreement with the surface density of the graphene sheet;

(3) A reasonable agreement with the experimental distance between poly-aromatic cores in the "stack" (see section 3.2.1).

Since a typical core of an asphaltene molecule only contains several aromatic rings, we

decided to describe one aromatic ring with one DPD bead. A planar graphite sheet model provided a suitable zero approximations for the skeleton for later modeling of single asphaltenes core. The beads are arranged in the hexagonal simple lattice, similarly to the core centers in graphene. As graphite has a layered, planar structure and the carbon atoms are arranged in hexagonal fashion with bonds of 0.142 nm between the nearest neighbors. Therefore, the nearest neighbor beads were connected by harmonic bonds with the parameters of 0.246 nm. A harmonic angle potential was imposed on adjustment of co-linear bonds (κ_0 =40 k_BT). As a result, the asphaltenes core forms a flat sheet with rigidity approximately similar to those obtained in atomistic MD simulations. We therefore build aromatic core by replacing every aromatic ring as a single bead and connecting each other with DPD bonds. Figure 1 shows the bond connectivity scheme, each node represents one aromatic bead.

One can of course argue that the relative volumes of a ring located inside a PAC is much lower than that of a peripheral ring (at least, the effective Bondi volumes²⁸ of an aromatic CH group and an inside aromatic carbon (all 4 bonds connecting it to other carbons) are related as 0.53/0.35) and here each is described by the same bead. However, in our DPD model an addition of a peripheral core bead to a PAC (say, a bead connected to a PAC only by one bond) also adds more volume to a PAC than addition of an inside bead, because the bond length is way lower than a standard distance between 2 neighbor beads in a single-bead DPD fluid.

(a)





Figure 1. (a) Coarse-grained pyrene model (b) building the graphene sheets out of DPD beads (each node represents one aromatic bead): beads form a hexagonal structure and connected in a triangular fashion. The resulting models of polyaromatic fragments contain 14 beads.

3.2.1 Geometric considerations

From the surface density of carbon atoms in the graphene and the distance between the centers of benzene rings we have estimated the bond length between the beads in the triangular structure: 2.45 Å. We assigned the bond stiffness of κ_s = 500 $k_B T/R_c^2$ – the lowest value that sufficient to keep the structure rigid enough. The next step is estimating a and R_c paramters for C-C interactions. We decided to choose the parameters from the best match to experimental relative volumes of aromatic hydrocarbons and distance between the closest layers in a polyaromatic stack. For this purpose, we modelled bulk solutions of monomers, dimers, tetramers, and 14-mers of C beads. The corresponding physical systems would be bulk benzene, naphthalene and pyrene (Figure 1a; correspondingly, in the simulation of tetramers the beads were arranged in rhombic fashion), and the molecule composed of 14 carbon beads shown in Figure 1b (referred as 14-mer). Note that pure naphthalene and pyrene are crystalline at ambient conditions, while asphaltenes and the soft-core model systems considered here are liquid-like. Therefore, we did not straightforwardly match a and R_c to the densities of pure benzene, naphthalene and pyrene, but rather used the effective volumes they would occupy in a liquid hydrocarbon solution. The volumes were calculated from the "Bondi tables" ²⁸ – the tables of effective volumes and surface areas of different functional groups applied to group-contribution thermodynamic models such as UNIFAC²⁶.

The last component denoted here as 14-mer, was considered solely to obtain the distance between the nearest layers in a polyaromatic stack (that as we mentioned in Section 3.2 is crucially important in asphaltene modeling). Several estimates for this distance was found in the literature. Tetyana et al.¹ studied the resembling asphaltenes-like structures in water, toluene and heptane and they reported the mean separation between two consecutive polyaromatic rings are 0.4-0.45 nm in all three solvents. Tanaka et al.¹⁰ measured 3 crude oil samples using X-ray to get the layer distance of two aromatic sheets of asphaltenes are about 3.6Å. Pacheco-Sánchez et al.¹⁷ gave the asphaltenes sheet distance in a range of 3-4Å by observing 96 asphaltene molecules' behavior in MD simulations. Overall, the distance of 3.8 Å can be considered as the effective consensus.

The simulations of pure polyaromatic compounds (as all other simulations) were performed with DL_MESO²⁹ software at constant pressure of 46 $k_{\rm B}T/R_{\rm c}^3$. The monomers, dimers and trimers each were put into 10x10x10 $R_{\rm c}^3$ cubic box randomly and equilibrated over 2x10⁴ timesteps. The timestep was Δt = 0.01. Then averaging was performed for additional 5x10⁴ steps. As a result, the effective volume per single bead was calculated and compared to the targets. The simulations of the 14-mer were longer (5x10⁵ equilibration steps and 2x10⁵ averaging steps) because more time is needed to compact such a fluid in NPT simulation.

The distance between the sheets in the stack was obtained from the radial distribution function (RDF) between the beads. The intermolecular RDF ("intermolecular" means that the bead pairs which belong to the same 14-mer are excluded from consideration) is shown in Figure 2b. The first peak of the intermolecular RDF characterizes the pairs belonging to the adjustment layers in the stack. We assume that the most probable configuration is one where a bead of a 14-mer is spaced equally from three closest beads of the next 14-mer in the stack. Therefore, the location of the first peak and the actual distance between the 14-mers in a stack are related as:

$$h = \sqrt{r^2 - (0.142 \ nm)^2} \tag{13}$$



Figure 2. (a) Final frame of simulation of 14-mers at constant pressure showing a locally ordered stacked structure (b) intermolecular RDF for the same system. Now we need to vary a and R_c for C beads to achieve the best compromise between the relative volumes of the molecules and distance in the stack. We did this manually without any specific optimization procedure looking for the best overall match. Table 3 shows the results for four exemplary parameter sets. It is hardly possible to conform to all three target values: in particular, in DPD models the effective volume of the molecule rises steeper with the number of rings than in experiment. The reason is probably the spherical nature of the beads, which does not replicate the actual shape of the aromatic rings. The best compromise was reached with the parameter set that is denoted in Table 3 as "model D": the volume ratios overestimate the experiment by about 12% which is quite acceptable considering the crudeness of DPD. The distance between the benzene rings is in the range reported in the literature. "Model D" is what we decided to use in this work.

	Table	3. Exempla	ry param	eter	setti	ng of I	Model A	B, C and	d D	
Model		А		В			С		D	
$a R_{\rm c}/k_{\rm B}T$		50		20			30		56	
$R_{\rm c,C}/R_{\rm c,H}$		0.652		0.75			0.65		0.75	
	Table 4.	Effective	volumes	of Mo	del D	(<i>a</i> =56	$k_{\rm B}T/R_{\rm c}$,	<i>R</i> _{c, c} =0.75	δR_{c})	
Molecule		Benz	zene	naj	ohthal	ene	руг	ene	14-m	er
Effective Vo	lume	3.18	878		4.9808	3	7.5	042	18.693	34

Table 5. Effective volume ratios

Models	А	В	С	D	Bondi tables
Vnaph/Vbenz	1.779	1.828	1.689	1.78	1.562
$V_{\text{pyre}}/V_{\text{naph}}$	1.731	1.355	1.681	1.709	1.507
	Tabl	e 6. RDF layer	distance of	14-mer	
Models	А	В		С	D
$h_{14-\mathrm{mer}}/\mathrm{\AA}$	3.393	3.26	3	3.409	3.567

3.2.2 Parameters for PAC-solvent interaction

As we discussed earlier, compared to aqueous solutions of common surfactants, the interactions in the asphaltenes system are "subtle", all components have reasonable (several %) mutual solubility, while solubility of common hydrocarbons in water is negligible. Therefore accurate parameterization of pyrene-solvent interaction is important for DPD model of asphaltenes. We followed the standard approach of parameterization of DPD model form the thermodynamic properties of solutions of reference compounds. The choice of a reference compound for PAC is arbitrary but the main criterion is chemical similarity and simplicity. We chose pyrene as the reference compound for PAC beads (C) and model in as a rigid rhombic tetramer (Figure 1a). There is unfortunately no published data for infinite dilution activity coefficients of pyrene (to the best of our knowledge) but solubility of pyrene was reported in a number of solvents; the data was compiled by NIST³⁰. We follow the same way as earlier: build a correlation between the intercomponent parameters and the solubility of model tetramer (with intracomponent and bonded parameter of model pyrene) in a single-component solvent and then interpolate the experimental solubilities³⁰ only correlation to find the parameters for C-T and C-H interactions.

For each intercomponent interaction (that is an interaction between beads of different types) we need two parameters: $R_{c,ii}$ and a_{ij} . We followed the conventional calculation of the geometric parameter: $R_{c,ij} = (R_{c,ii} + R_{c,jj})/2$. Such a mixing rule commonly applied to very different models, both soft- and hard- core such as Lennard-Jones mixtures. The energy parameters were fitted

to the experimental data. Following GW²³ we performed a series of simulations, measuring the mutual solubilities as a function of a_{cx} (where X is a one-component solvent). The components at approximately 1:1 volume ratio were put in a box of $15 \times 15 \times 45 R_c^3$ size. The NPT DPD simulation was performed 10^6 steps with time steps equal to 0.01. As simulations starts, hexane and pyrene molecules incline to move and mix subject to hexane-pyrene repulsion potential. At low a_{cx} , pyrene and the solvent are miscible, and as it increases, the system separates. Figure 3a and 3b shows the initial and the final configurations of solvent-pyrene mixture as interaction repulsion parameter equal to $65 k_B T/R_c$. The target is to find the optimizing solvent-pyrene repulsion parameter a_{cx} , under which the solubility of pyrene in hexane and toluene matches the experiment. The solubility at each particular case was determined from the density profile along z axis (an example is shown in Figure 3c). A variety of a_{cx} from 36 $k_B T/R_c$ to 96 $k_B T/R_c$ were attempted.



Figure 3. (a) Initial simulation box distribution, blue for pyrene and yellow for

Table 7.	Densities of	pyrene and	solvents with	increasing repulsion	parameters	
$a_{\rm cx} R_{\rm c}/k_{\rm B}T$	$ ho_{ m pyre}R_{ m c}{}^3$	$ ho_{ m hexa} R_{ m c}{}^3$	χhexa	$ ho_{ m tolu} R_{ m c}^3$	χ tolu	_
57	1.217	1.999	0.777	2.299	0.801	
59	1.537	2.584	0.914	2.797	0.903	
60	1.585	2.739	0.946	2.972	0.924	
61	1.620	2.829	0.964	3.150	0.953	
62	1.642	2.886	0.975	3.254	0.969	
63	1.660	2.923	0.983	3.319	0.979	
64	1.670	2.944	0.987	3.361	0.985	
65	1.681	2.959	0.990	3.385	0.988	
66	1.683	2.972	0.992	3.402	0.991	
67	1.689	2.985	0.994	3.418	0.993	
68	1.690	2.989	0.995	3.429	0.995	

solvent; (b) last DPD frame of simulations, solvents beads are hidden; (c) density profile of pyrene in single-component solvent, $a_{cx}=65 k_{\rm B} T/R_{\rm c}$.

Table 7 shows the average densities of solvent and pyrene when interaction repulsion parameters increase, compared to designed densities $3/R_c^3$ for solvent and densities 1.70 $/R_c^3$ of pyrene from model D. And corresponding mole fractions are displayed as well.





parameters equal that of pyrene in single bead solvent on the intercomponent repulsion parameter- the parameter is obtained by interpolation of the experimental solubility onto this reference correlation. According to NIST³⁰, the solubility of hexane in pyrene is 0.99 at 293 K and 0.9896 at 298 K. Interpolation of this value on the reference curve (Figure 4) gives a_{CH} =65 $k_{B}T/R_{c}$ as the best match to the experimental data.

The same procedure is applied to the parameters for interaction of C bead with toluene (we need to take into account however that 1 bead represents more than one toluene molecule). According to NIST³⁰ data, the solubility in mole fraction of toluene is 0.9389 at 295.35 K and 0.9050 at 313.55 K. The best match between simulation and experiment is achieved as a_{cT} = 58 $k_{B}T/R_{c}$.

3.3 Aliphatic hydrocarbons of asphaltenes and resins

Aliphatic hydrocarbon fragments are not only found in the solvent, but also in asphaltenes and resins. Do not we already have a model for aliphatic hydrocarbon fragments? Yes, but it is not suitable for the asphaltene fragment, but rather for the solvent only. The reason is the length of aliphatic chains typically found in asphaltenes: if the beads of diameter we have applied to hexane were used, the aliphatic sidechains and junctions of asphaltenes would only contain one bead. Considering the quasi-micellar nature of asphaltene aggregates, the aliphatic are, essentially, the soluble tails of micelle; their entropy is crucial for a reasonable description of self-assembly and crude models are much less accurate in prediction of aggregation number ^{25, 31} Therefore, we decided to use smaller beads (B) for the aliphatic fragments of PAC, and each bead only contains 2 carbon atoms.

We parameterized the sidechains based on the properties of hexane and hexadecane, the longest alkane liquid at ambient conditions. Hexadecane has 16 aliphatic carbons and therefore is presented by 8 beads. The number of carbon in side chains is reported as 5-6 in literatures¹. Hence, 3 consecutive beads cropped from hexadecane model is the basic

sidechain model.

Although the beads for both aromatic cores and aliphatic chains have the same carbon number in one, the proper R_c of side chain beads in order to have density of 3 $/R_c^3$ is different. To reasonably evaluate the aliphatic chain R_c , we used several properties and sets of data. To firstly start with hexadecane, one molecule volume of hexadecane is estimated by hexadecane density and molecular weight. The hexadecane consists of 8 beads while 3bead chain is the proper sidechain model, hence sidechain model takes up 3 out of 8 volume of hexadecane and corresponding R_c of sidechain is 5.67 Å. Also, we can use other approach to calculate R_c of sidechain. If 8 beads in a row represent hexadecane, 3 beads in a row are well on behalf of hexane molecules. Similarly, the molecule volume of one hexane can be estimated in the same method and it gives R_c of sidechain as 6.02 Å. In addition, we can estimate R_c of sidechain starting from water molecules. In UNIFAC table, one water molecule has the similar effective volume of a CH_2 functional group, hereby two water altogether can be considered as an aliphatic bead. We use the same method to evaluate the molecule volume of a water and obtain R_c of sidechain as 5.63 Å. Overall, all 3 approaches give the value of sidechain R_c in a range of 5.6 to 6Å, we finally decide R_c of sidechain as 5.7Å.

The intra-component repulsion parameters a_{BB} and the bonded parameters- bond length and angle stiffness, were determined by matching the density at constant pressure and intramolecular RDFs obtained with the DPD model to that from atomistic MS simulations, similar to Lee et al.²⁵. The distribution of distances between the centers of mass of fragments described by certain beads characterize the average length and the rigidity of the sidechains. Here we selected the distribution of distances between the nearest neighbor beads (1-2 distance, 2.45 Å) and the terminal beads of the chain (1-8 distance, 15.5Å) as the primary targets.



Figure 5. Distributions of distances between the centers of two terminal beads in DPD simulation of hexadecane (modeled as a 8-mer with beads connected by harmonic bonds and angles with angle stiffness varied) and the distribution between centers of mass of the corresponding fragments obtained in an atomistic MD simulation ³² the best match is achieved with the stiffness of k_{e} =2.5 $k_{B}T$.

The repulsion parameters of side chains are varied from 1 to 90 $k_{\rm B}T/R_{\rm c}$, corresponding sidechain bead density are shown in Table 8.

$a_{\rm BB} R_{\rm c}/k_{\rm B}T$	$ ho_{ m sidechain} R_{ m c,B}{}^3$	$ ho_{ m sidechain} R_{ m c}^{3}$	
1	10.014	35.636	
10	4.348	15.473	
20	3.300	11.742	
30	2.835	10.089	
40	2.559	9.108	
41	2.537	9.029	
42	2.525	8.985	
43	2.496	8.883	
45	2.454	8.731	
50	2.372	8.442	
60	2.236	7.955	
70	2.129	7.578	

Table 8. Densities of side chains with increasing repulsion parameters



Figure 6. Linear dependence of squared density of aliphatic chains on its reciprocal repulsion parameters.

The best match to the experimental properties was found with the parameters shown in Table 8. Figure 5, 6 and Table 8 demonstrate the process of fitting: we first fixed the length and the rigidity of the nearest neighbor so that the MD nearest neighbor distance was reasonably reproduced. Then, we modeled flexible trimers of S beads (that is, with $k_{\theta}=0$ $k_{\rm B}T$) and determined the correlation between the density and *a* (Table 8). The shape of the correlation $(\rho^2 = \frac{2132.2}{\alpha} + 28.519)$ is essentially the same as for the DPD single-bead fluid. Interpolating the dependence onto liquid hexane bead density of 2.543 / $R_{c,B}$ ³ (or 9.043 / R_c ³), we obtained $a_{\rm BB}$ 41 $k_{\rm B}T/R_c$. Now, the angle rigidity k_{θ} in equation 9 can be determined from the best match of the DPD 1-8 distance distribution for hexadecane to the MD data. Demonstrated by Figure 6. An exact match between atomistic and mesoscale models could not be achieved. Yet, the overall agreement on the general rigidity of the sidechains is reasonable.

Repulsion parameters for the sidechain interactions with solvents were obtained from infinite dilution activity coefficients²⁵. In these simulations, hexane was chosen as the representative compound for the sidechain and presented as a trimer. The calibration dependence of $\gamma_{inf}(a)$

was calculated recently²⁵ and is not a part of the thesis work. By interpolating the activity coefficient on the calibration dependence, we obtained specify parameters presented in Table 10. The curious feature of this work is that hexane serves as the reference compound both for solvent and sidechains and is presented by a "fine model" (trimer, 2 carbons/bead) and a "crude model" (monomer, 6 carbons per bead) and the target value is $\gamma_{inf}=1$. The best fit achieve at the value $a_{HB}=44.5 k_B T/R_c$ for sidechain-hexane and $a_{TB}=45.5 k_B T/R_c$ for sidechain-toluene, surprisingly close to what the combination rule $a_{ij} = \sqrt{a_{ii}a_{jj}}$ would have given. Both values were used for PAC-sidechain interaction.

Pyrene and sidechain models at approximately 1:1 volume ratio were put in a box of $15 \times 15 \times 45$ R_c^3 size to simulate pyrene-hexane solubility subject to hexane-pyrene repulsion potential. Unfortunately, we could not reproduce the solubility of pyrene in hexane modelled with the fine model using reasonable parameter values for a reason still unknown to us. Table 9 gives the results of 3-bead hexane (side chain) with pyrene at a_{CB} is 68 $k_B T/R_c$. Linear regression of a_{CB} and solubility gives the optimal repulsion parameter of sidechain bead and pyrene bead as 69 $k_B T/R_c$. However, based on quantities of simulations and 69 $k_B T/R_c$ is proved not to be a favorable fit that enable asphaltenes molecules aggregates, meanwhile by decreasing the a_{CB} to 57 $k_B T/R_c$, models aggregate in a decent degree.

$a_{\rm CB}R_{\rm c}/k_{\rm B}T$	$ ho_{ m sidechain} R_{ m c} {}^3$	$ ho_{ m pyre} R_{ m c}^{3}$	Xsidechain
61	8.219	1.532	0.941
66	8.592	1.674	0.975
68	8.952	1.680	0.989
71	9.036	1.693	0.994
73	9.063	1.705	0.996
76	9.102	1.710	0.998

Table 9. Densities of side chains and pyrene with increasing repulsion parameters



Figure 7. Last DPD frame of simulation of pyrenes and side chains, (a) exhibiting pyrene and (b) for side chains.

3.4 hetero functional group

In order to mimic the formation of hydrogen bonds between the PACs, we also introduce a "hetero group" hydrophilic beads (O). Hetero groups in asphaltenes include carbonyl, carbonxyl, phenol and pyridine, among others. Some of them (alcohol, phenol, and carboxyl) can serve hydrogen bond donors, while other groups can only accept bonds. Here, we do not make such a distinction, but rather effectively introduce a hydrophilic component because asphaltenes form the most hydrophilic fraction of crude oil. Hetero groups are assumed to interact unfavorably with all beads but other hetero groups. We assumed parameters related hetero groups based on modified mixing rules shown in Table 10. Comparing the characteristic interaction energy between the "heterobeads", say, O-O bead interaction, to hydrogen bond energy, the effective bond energy is 2.77 kJ/mol, which is typical for a hydrogen bond. Hetero groups in this model always located at the periphery PACs.

Up to this point, we have discussed 5 types of beads that would be deployed in following simulations: hexane bead, toluene bead, pyrene bead, aliphatic bead and hetero function group bead. Pyrene bead is the fundamental element that forms aromatic cores for asphaltenes and resins. Aliphatic bead features side chains in both asphaltenes and resins. Hetero function group bead is attached to aromatic cores of asphaltenes. Table 10 displays reduced R_c of all bead kinds that taking hexane R_c as standard and table 11 gives both self-

repulsions and interactive repulsions.

Tab	ole 10. Bead types and reduced /	R
type	Representing element	Reduced R _c
Hexane bead	Н	1.0
Toluene bead	Т	1.0
Pyrene bead	C, P, N	0.75
Aliphatic bead	B, F, S	0.655
Hetero function group bead	0, Q	0.75

	Table 11. Repulsion parameters $(k_{\scriptscriptstyle B}T/R_{\scriptscriptstyle m c})$ of all bead types					
	Н	Т	С	В	0	
Н	51.4	52.4	65.0	44.5	61.6	
Т	52.4	51.4	58.0	45.5	61.6	
С	65.0	58.0	56.0	69.0(57.0)	64.0	
В	44.5	45.5	69.0(57.0)	41.0	56.0	
0	61.6	61.6	64.0	56.0	56.0	

Chapter 4 Aggregation in Asphaltenes Solutions Studied by DPD Simulations

Several models of asphaltenes, single core and archipelago, are designed based on the molecular weight distribution, H/C ratio and composition percentages. A resin model is designed using the same fundamental fractions of asphaltenes. We simulated systems of asphaltenes with and without resin in 1) toluene solvent, 2) hexane solvent and 3) mixture (toluene-hexane, 1:1 mass ratio) solvent.

4.1 models

The first asphaltene (S-asphaltene) we built has a molecular weight of 809.642 Da, in compliance with some literature reported 750 Da. 12 aromatic beads are knit into a single PAC, along with 3 side chains out of aliphatic beads, a functional group bead is attached to the core. Figure 8 shows the asphaltene structure and table 12 shows the basic features.



Figure 8. Molecular structure of S-asphaltenes

Beside small single-PAC asphaltenes, multi-core archipelago asphaltenes also present in oil.

The second model asphaltene molecule (A-asphaltene) has 3 cores that have similar

structure of that of S-asphaltene, except one of them is added one extra aromatic bead to meet structure requirement. The hetero functional group beads are linked to the same site in each core, and all three cores are connected by three 4-bead aliphatic chains to make a loop. Other aliphatic chains are attached to all three cores to increase the H/C ratio. We found that adding 5 more free aliphatic chains to cores are the optimized option. The PACs can actually stack on the top of each other due to the flexibility of the aliphatic chains or aggregate with S-asphaltenes if both kinds coexist. The model is shown in figure 9. And basic features are in Table 12.



Figure 9. Molecular structure of A-asphaltenes

The third asphaltene model (L-asphaltene) combines the single continental feature of the first model and the MW degree of the second model. Since the MW distributions of asphaltenes

are typically quite board, we presume that except asphaltenes aggregation and multi-core structure, big asphaltenes that has one large cores as a center and links several aliphatic chains might contribute to the board MW distribution as well. Hereby, we built a model that possesses 31 aromatic beads, 7 aliphatic chains (due to consideration of saturation, all chains possesses 4 aliphatic beads) and a hetero-group. Figure 10 shows L-asphaltene model. And basic features are in table 12.



Figure 10. Molecular structure of L-asphaltenes

We have built one resin model, which is assumed to have an aromatic core based on phenanthrene and a longer aliphatic chain compared to that of asphaltenes. The model is in figure 11 and basic features are in table 12.



Figure 11. Molecular structure of resin

Model	MW g/mol	H/C(n/n)	Composition percentages (w/w)		
Widder			С	Н	0
S-asphaltene	809.642	1.0	0.890	0.070	0.040
A-asphaltene	2474.969	1.0	0.893	0.068	0.039
L-asphaltene	1964.594	1.0	0.911	0.073	0.016
resin	346.278	1.3	0.902	0.098	0.000

Table 12. Properties of asphaltenes and resins models

4.2 Reproducing dilution experiments

To validate the forcefield, we reproduce experiments on dilution of asphaltene solution in toluene by hexane. Having developed the DPD models, we validate them against experiments on dilution of asphaltenes solutions in toluene by aliphatic solvents. In experiments, asphaltenes are first separated from crude oil by adding heptane, then the precipitate is filtered and re-dissolved in toluene. It should be noted that there is no reason to assume that the resulting solution of asphaltenes in toluene is a truly molecular uniform solution; it probably contains nano-size "stacked" aggregates. The heptane is gradually added to asphaltene solution in toluene. At some solvent composition, asphaltenes start to aggregate and precipitate; the amount precipitated is measured and reported in literature².

Similar process can be modeled by DPD: we create a box with a solution of asphaltenes in toluene and then start replacing the solvent by hexane. Of course, the amount precipitated cannot be compared with experimental data. But the concentration of remaining asphlatenes (in equilibrium with the precipitate) is an equilibrium property independent on that amount of

each phase, and comparison can be made. Such comparison is only semi-quantitative, as asphaltenes are not a particular compound but a broad group, and solvents also differ (hexane vs heptane)

The simulation box is $20 \times 20 \times 73 R_c^3$, and the DPD time are extended to 4 million steps with timestep equal to 0.01. The simulation boxes are initiated by paving a layer in one end $(20 \times 20 \times 13 R_c^3)$ with either S-asphaltenes or mixture of A-asphaltenes and S-asphaltenes with 1:1 mass ratio.

To examine the accuracy of our models to natural asphaltenes and crude oil, we decided to simulate dilution of asphaltene solution in toluene by hexane and compare which to literature records. The solubilities of asphaltenes are tentative studies since many literatures for asphaltenes solubility contradicts and a soundly convincing records is uncertain. We referred Spiecker et al.³³ for approximate comparison. Dilution studies are performed in simulations with sole S-asphaltenes and with both S-asphaltenes and A-asphaltenes. The principle of gaining dilution patterns inherits from parameterization of pyrene-hexane repulsion. The concentrations of asphaltenes under different type of solvents are averaged results after system reaches equilibrium balance.

The last DPD frames of selected simulation system are represent in Figure 12. After 2 million DPD steps, the system reaches balance hence the dilution data can be obtained. In pure toluene, we observe a quasi-uniform solution with most asphaltene molecules belong to various stacks of several PACs (detailed structural analysis of such solutions will be given later). As the hexane fraction increases, asphaltenes start precipitating and we extract the concentration of free asphaltenes (that is those that belong to small micellar aggregates or remain in the monomer form).



Figure 12. Final frame of S-asphaltenes solutions in (a) toluene, (b) hexane-toluene 1:1 (wt) mixture and (c) hexane. Bead P (Blue) presents aromatic beads of S-asphaltene, solvents not shown.

Intriguingly, the concentration of free S-asphaltenes are in a liner relationship with volume fraction of toluene in this concentration range. Precipitation starts at 25% fraction of hexane and reaches about 0.004 g/mL in pure hexane (Figure 13).



Figure 13. S-asphaltenes concentrations dependence on volume fractions of toluene. Similarly, we performed the dilution simulations to system that A-asphaltene and Sasphaltenes coexist. Noticing that the archipelago concentration in the solution is very close to zero, they all precipitate very quickly without resins involved. And the concentration to volume fractions of toluene in solvent is presented in a comparison with concentration curves of sole S-asphaltenes system and experimental records³³(Figure 14). CS, B6, HO and AH are different asphaltene samples obtained from different oil fields. To us the only matter is

that their solubilities are reasonably similar. The experimental concentrations are somewhat lower compared to DPD results. Considering the fact that the system is not exact, the agreement between the experiment and simulation (1.5-3 times) is very reasonable. An interesting takeaway is that concentration of S-asphaltene is not drastically affected by the presence of A-asphaltenes. Thus we may suppose that in general the partitioning of particular asphaltene show only weak dependence of bitumen composition.



Figure 14. S-asphaltenes concentrations dependence on volume fractions in binary system with A-asphaltenes (orange) and in single system (grey); experimental concentrations comparisons are CS, B6, H0 and AH.

4.3 Asphaltenes aggregation: the structure of asphaltenes solution

4.3.1 Small asphaltenes (S-asphaltenes)

The behavior of small asphaltenes presented by S-asphaltene model in multiple solvents under condition with/without resin is simulated. We use a system with $30\times30\times30$ R_c³, and all simulations are processed with 2 million time steps with Δ t equals to 0.001. Firstly, 5% wt of small asphaltenes and 95% wt of solvents, including hexane, toluene, mixture (47.5% wt of hexane and 47.5% wt of toluene) are simulated. Two parallel patches of simulations with different portions of resin, one 5% wt and the other 20% wt, replacing equivalent solvents are performed as well.



Figure 15. Final configurations of (a) 5% S-asphaltene and 95% toluene; (b) 5% S-asphaltene, 47.5% toluene, 47.5% hexane; (c) 5% S-asphaltene and 95% hexane; (d) 5% S-asphaltene, 5% resin and 90% toluene; (e) 5% S-asphaltene, 5% resin, 45% toluene and 45% hexane; (f) 5% S-asphaltene, 5% resin and 90% hexane; (g) 5% S-asphaltene, 20% resin and 75% toluene; (h) 5% S-asphaltene, 20% resin, 37.5% toluene and 37.5% hexane; (i) 5% S-asphaltene, 20% resin and 75% hexane. Bead P (tan) represents the aromatic cores of S-asphaltene, F (pink) the aliphatic chains and Q (cyan) the hetero-group, resins and solvents are not shown.

The final snapshots of DPD configurations of small asphaltenes are shown in Figure 15. In

pure toluene, asphaltenes can be found in monomeric form (about 17.4% of the total

asphaltene load) and in the form of small stack-type aggregates, consisting of 4 cores in

average. Basically, it is consistent with what we know of asphaltene solutions in toluene from

the literature³⁴. Replacement of half of the toluene by hexane decreases the monomer

concentration to 14.4% and increases the average aggregate size to 5 (Figure 16). It

appears that aggregate sizes are still much smaller than the box. Finally, Figure 15c simply demonstrates that care has to be taken in interpretation of DPD results, since compared to the aggregates box sizes may easily become insufficient. In pure hexane, asphaltenes form bigger and branching structures that can still be characterized by an equilibrium distribution. Yet, we know for certain that system phase separates both in simulation (section 4.2) and experiment. It is just the box size and shape that makes a difference. Still the snapshots demonstrate how the fractal structure of asphaltenes start forming: the stack "branches" with two asphaltenes stacking on the top of another.



Figure 16. Size distribution of small asphaltenes aggregates in hexane, toluene, toluenehexane 1:1 (wt) mixture, no resins involved.

Resins serve as surfactants and naturally increase the dispersity and reduce the aggregate size. The difference with a classic surfactant behavior is that the differences in interaction between lipophilic and lyophobic fragments are very subtle: resins are actually soluble in heptane and hexane. That is why most of the resins are in monomeric form and only a relatively small part (Figure 17) is adsorbed at the surfaces and participate in the aggregate formation. Yet, their influence is very significant. For example, addition of only 5% wt of resins decrease the average aggregate size in hexane from 9 to 8 aromatic cores. In pure

toluene, resins disrupt the branching structure, and with 20% wt of resin content asphaltenes appear soluble even in hexane.



Figure 17. Final configurations of (a) 5% S-asphaltene, 5% resin, 45% toluene and 45% hexane; (b) 5% S-asphaltene, 5% resin and 90% hexane. Bead P (tan) represents the aromatic cores of S-asphaltene and C (cyan) the aromatic cores of resins.

4.3.2 Effect of archipelago asphaltenes (A-asphaltenes)

Next, we performed similar simulations of solutions of asphaltene mixtures, where small asphaltenes were mixed with the archipelago structures in 1:1 mass ratio. The effect of resins was similarly considered, with 5% and 20% overall wt of resin content.

Addition of larger archipelago structures radically changes the aggregation pattern: such structures seem to be insoluble even in pure toluene and form a large aggregate with smaller asphaltenes located at the surface (they play the role of resins in this resinless system (Figure 18a-c); we should note that in practice there is no clear structural or mass distinction between resins and asphaltenes, polyaromatic fractions have a continuous distribution). Of course, here we consider an extreme example with 50% fraction of the heavy archipelago asphaltenes (average molecular weight of 2475 Da, heavier than typically found in oil). In systems with lighter asphaltenes and more continuous distributions, the tendency to separation will be less pronounced. Only the asphaltenes of the lighter fraction are found in small stacks or monomeric form. Since asphaltenes is separated from solvent even in

toluene, the same is observed in 1:1 toluene-hexane mixture and in pure hexane. Resins, however, drastically disperse the systems as shown in Figure 18d-i. It is however interesting that addition of resins in 5% wt fraction to hexane solution does not visibly affect (Figure 18d-f).



Figure 18. Final configurations of (a) 2.5% A-asphaltene, 2.5% S-asphaltene and 95% toluene; (b) 2.5% A-asphaltene, 2.5% S-asphaltene, 47.5% toluene, 47.5% hexane; (c) 2.5% A-asphaltene, 2.5% S-asphaltene and 95% hexane; (d) 2.5% A-asphaltene, 2.5% S-asphaltene, and 90% toluene; (e) 2.5% A-asphaltene, 2.5% S-asphaltene, 5% resin and 90% toluene; (e) 2.5% A-asphaltene, 2.5% S-asphaltene, 5% resin and 90% hexane; (f) 2.5% A-asphaltene, 2.5% S-asphaltene, 5% resin and 90% hexane; (g) 2.5% A-asphaltene, 2.5% S-asphaltene, 5% resin and 75% hexane; (i) 2.5% A-asphaltene, 2.5% S-asphaltene, 20% resin, 37.5% toluene and 37.5% hexane; (i) 2.5% A-asphaltene, 2.5% S-asphaltene, 20% resin and 75% hexane. Bead P (tan) represents the aromatic cores of S-asphaltene, bead F (pink) the sidechains of S-asphaltene, bead Q (cyan) the hetero group of S-asphaltene, bead N (blue) the aromatic

cores of A-asphaltene, bead B(purple) the sidechains of A-asphaltene and bead O (red) the hetero group of A-asphaltene.

In system with two different asphaltenes, notice that size distributions of each kind of asphaltenes are analyzed separately. We aim at finding the differences of asphaltenes aggregation size in toluene, toluene-hexane 1:1 (wt) mixture and hexanes, and in situations with or without resins. We assumed that the morphology can be explained by asphaltenes size distributions.

In system that archipelago A-asphaltenes and small S-asphaltenes coexist, we calculated number of A-asphaltenes in aggregates. The probability distributions of the number of A-asphaltenes in an aggregate are presented in Figure 19 at different resin content. The average number of A-asphaltenes in an aggregate decreases as the resin overall concentration increases. Without resins in hexane, the A-asphaltenes form one big aggregate that is not broken over the entire course of the simulation (Figure 19a), which probably means the system phase separates. As toluene concentration increases, the smaller aggregates appear, but reliable statistics is hard to obtain for very long time needed for aggregate formation and break-up. S-asphaltenes are mostly located at the aggregate surfaces. Addition of resins (as always) makes the system much more disperse, decreasing the number of A-asphaltenes per aggregate. At 20% resin content, the probability to observe an aggregate of a particular size decreases monotonically with the size, which means that in that case it is not even a colloidal system but rather a uniform solution³¹.



Figure 19. Size distribution of archipelago asphaltenes aggregates in toluene, toluenehexane 1:1 (wt) mixture and hexane with (a) no resin, (b) 5% wt of resins and (c) 20% wt of resins.

Figure 20 shows the distribution of numbers of small S-asphaltenes in the aggregates of the same system. One can note the distributions are very different from those in pure S-asphaltene system, because S-asphaltenes are able to aggregate with A-asphaltenes of much lower solubility. Even in pure toluene, the distribution of the number of S-asphaltenes in a cluster is clearly bimodal showing a characteristic cluster size of about 70 molecules. A substantial amount of S-asphaltenes are dissolved in the solvent bulk or form small stacks that do not include any A-asphaltenes. Addition of resins produces a dramatic effect on the distributions making the clusters smaller. 5% wt of resin in the simulation (Figure 20b) makes small asphaltenes less possibly to form big aggregate compared to simulations without resins. When 20% wt of resins in system, the number of S-asphaltenes are most possibly dissolved when large amount of resins are presented. And this analysis of small asphaltenes is in approval with corresponding simulation configurations.







The shape of the aggregates was characterized using the asymmetry factor ³¹. The asymmetry factor can be used to describe the associations and elongation between spherical aggregate. For an aggregate composed of N_g molecules beads, radius of gyration R_g is $R_g^2 = \frac{1}{N_g} \sum_{k=1}^{N_g} (\mathbf{r_k} - \mathbf{r_{mean}})^2$, where $\mathbf{r_{mean}}$ is the location of the center of mass of the aggregate. If the aggregate is composed of same number of beads at same density ($\rho R_c^3=3$) but in spherical shape, "spherical" radius gyration is $R_{Sg}^2 = \frac{3}{5} \left(\frac{N_g}{4\pi}\right)^{2/3}$. The asymmetry factor is defined as the ratio of the actual radius of gyration of the aggregate and the radius of gyration of a hypothetical spherical aggregate of the same size. The longer the aggregate, the larger the asymmetry

factor. They are presented in Figure 21.

Surprisingly, in all systems the anisotropy of the clusters is relatively low and their shape is close to spherical in almost all cases. That is, the clusters are, "stacks" and in this case non-spherical, but the anisotropy is not sufficient to speak of systematic formation, for example, of cylindrical or other particular shapes. While spherical aggregates were expected for relatively small clusters common for toluene solutions with higher resin concentrations (Figure 21c), the prevalence of spherical shapes in systems with larger aggregates (Figure 21a) are somewhat surprising. Judging from the snapshots (Figure 18a-c), the agglomerates in such systems are, "loose", carry substantial amounts of solvents and are formed by smaller quasi-micelles that connect and break-up. This phenomenon is, apparently, not so frequent, even though we do observe in 1:1 toluene-hexane mixture with very high asymmetry ratio (Figure 21a) belonging to such loose agglomerates.





Figure 21. Normalized asymmetry factor distributions of asphaltenes aggregates in toluene, toluene-hexane 1:1 (wt) mixture and hexane with (a) no resin and (b) 5% wt of resins and (c) 20% wt of resins.

4.3.3 Big asphaltenes and small asphaltenes system

Similarly, we performed simulations of mixtures of by small and big asphaltenes (Lasphaltene) with larger and flat PACs (The simulations are the same with that of Aasphaltene and S-asphaltene except here A-asphaltene is replaced by L-asphaltene). Those large flat PACs tend to stack extremely well and form elongated structures. Different stacks tend to orient in a parallel fashion and come close together, creating somewhat a nematic liquid-crystal structure (Figure 22). The solvent composition does not appear to influence their behavior, at least without presence of resins. Strictly speaking, such compounds no longer belong to the asphaltene fraction, but rather to the toluene-insoluble (TI) fraction of the crude oil, and TI behavior is quite different from asphaltenes in many aspects.

It is quite clear that the small asphaltenes make little effect on the TI fraction. Sometime asphaltenes do stack with the TI stack. But they mostly form stacks of their own. Those stacks are smaller in toluene and in toluene-hexane mixture and bigger since connected to the TI stacks in pure hexane; but they rather follow the behavioral pattern described above (Section 4.3.1). In these mixtures, small asphaltenes can be described by their own aggregate size distributions (Figure 24). The major probabilities of all nine parallel simulations are settled in a small aggregate number (5-7). However, the most possible aggregate number that under each resin conditions shows trends to decrease as more resins are included in the system. But the effect of solvents composition have barely influence on the size of clusters of small asphaltenes. Large aggregates are typical in hexane, and small stacks of 2-4 molecules and monomers prevail in toluene. Solvents influence on the TI fraction does not seem to be significant.

Addition of resins in 5% wt does not drastically change the aggregation pattern of TI despite larger fraction of relatively small aggregates that separate from the semi-solid TI precipitate. However, larger resins amount (20% wt) breaks up the liquid crystal structure: the average cluster size is much less than the total number of aromatic rings in the TI fraction, showing more or less an equilibrium size distribution.

Overall, the TI fraction forms very ordered and highly stacked structures that are mostly independent of the surrounding asphaltenes and even solvents. The structure also showed high tolerance to small amount of resins, however, larger amounts of resins tend to break the order.



Figure 22. Final configurations of (a) 2.5% L-asphaltene, 2.5% S-asphaltene and 95% toluene; (b) 2.5% L-asphaltene, 2.5% S-asphaltene, 47.5% toluene, 47.5% hexane; (c) 2.5% L-asphaltene, 2.5% S-asphaltene and 95% hexane; (d) 2.5% L-asphaltene, 2.5% S-asphaltene and 95% hexane; (d) 2.5% L-asphaltene, 2.5% S-asphaltene, 5% resin and 90% toluene; (e) 2.5% L-asphaltene, 2.5% S-asphaltene, 5% resin, 45% toluene and 45% hexane; (f) 2.5% L-asphaltene, 2.5% S-asphaltene, 5% resin and 90% hexane; (g) 2.5% L-asphaltene, 2.5% S-asphaltene, 2.5% S-asphaltene. Bead P (tan) presents the aromatic cores of S-asphaltene, and bead N (blue) the aromatic cores of L-asphaltene.



Figure 23. Size distribution of big asphaltenes aggregates in toluene and hexane with (a) no resin, (b) 5% wt of resins and (c) 20% wt of resins.



Figure 24. Size distribution of small asphaltenes aggregates (in system with big asphaltenes) in toluene, toluene-hexane 1:1 (wt) mixture and hexane with (a) no resin, (b) with 5% wt of resins and (c) with 20% wt of resins.

The asymmetric patterns for system that big and small asphaltenes coexist will be discussed in a different manner. We selected all simulations in hexane solvent, and analyze the asymmetric manner of big asphaltenes under conditions with different amounts of resins (Figure 25). Noticing small asphaltenes asymmetric patterns will not be discussed here. The asymmetry of big asphaltenes shows disparate features than that of archipelago and small asphaltenes. The asymmetric factor distribution of TI aggregates without resins in hexane are expanding from 1 to 9 and a distinct peak at higher values appear indicating strongly anisotropic structure, which means big asphaltenes apparently form rod-like clusters, combining morphology study of big asphaltenes, big asphaltenes actually have high ability to packing along an imaginary axis and the structure can be recognized as crystalline phase. At the same time, by increasing amount of resins, the asymmetry distribution starts showing reasonably spherical structure with a distinct peak about 1, although elongate aggregates still exist and can be seen visibly (Figure 22).



Figure 25. Normalized asymmetry factor distributions of big asphaltenes in hexane solutions with no resin, with 5% wt of resins and with 20% wt of resins.

Chapter 5 Conclusion

This work presents the first (to the best of our knowledge) experience in modeling of DPD model of a complex system with beads of different diameters. The need in beads of different sizes is dictated by the system geometry: PACs are flat and thin and thus require relatively small beads, while lion's share of volume is occupied by solvents which is better to be described in a cheaper fashion.

In building the DPD models for the components of crude oil we replied on the strategy developed earlier in the same group^{25, 32}: the geometry of the molecules is determined by "bonding terms": covalent bonds and angles, whose parameters are fitted to experimental structures or atomistic simulations. The intercomponent geometric and energy parameters are determined using the top down approach. For that purpose, we selected "reference compounds" for bead of each type and then fitted the intercomponent parameters to thermodynamic properties of the reference solutions. In particular, activity coefficients and mutual solubilities. The same strategy was applied earlier to the most standard DPD implementation, where all beads have the same effective diameter and all bead types share the same intracomponent repulsion parameter. The class of systems considered here presents a good test for parameterization strategy for complex geometry of molecules and subtle difference in interactions (all components of these systems are strongly hydrophobic- which means that with the approach conventionally applied to DPD simulation they would be described with beads of one single type with a possible exception for a hetero-group). The shortcoming of this system as a case study is lack of exact experimental data, because asphaltenes and resins are not particular compounds but solubility classes. With all that, our models derived with no arbitrarily assigned parameters produced a very reasonable qualitative and even quantitative picture of asphaltene solutions. In particular, dissolution experiments show good agreement with experimental data. The simulations of aggregation also provide

very reasonable picture, quite in agreement with what we know about the role of resins, asphaltene molecular mass and solvent composition.

An obvious problem with the parameterization strategy is its relative complexity, while the essence of DPD is easily justifiable, straightforwardly parameterizable forcefields that can produce qualitative results in computationally cheap way. In this work, fitting the parameters to the properties of reference compounds was much more difficult than in the original publication on that approach³¹ : it involved relatively complex basic models (including rhombic tetramer) and DPD simulations for calibration curves specific to these shapes (much less universal compared to the models of Lee et al.³¹. A decent alternative however is not exactly clear, not thinking of DPD only, but of mesoscale simulations in general. For example in a very recent publication by Wang and Fergusson³⁵, where asphaltenes were modeled by MARTINI coarse-grained MD, the authors chose not to use standard version of MARTINI bead types again making the forcefield arbitrarily assigned to produce a pre-determined picture compatible with the Yen-Mullins model¹⁵.

References

1. 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.

2. Angle, C. W.; Long, Y. C.; Hamza, H.; Lue, L., Precipitation of asphaltenes from solvent-diluted heavy oil and thermodynamic properties of solvent-diluted heavy oil solutions. *Fuel* 2006, 85, 492-506.

3. Wang, S. B.; Xu, J. B.; Wen, H., The aggregation and diffusion of asphaltenes studied by GPUaccelerated dissipative particle dynamics. *Computer Physics Communications* 2014, 185, 3069-3078.

4. Ganeeva, Y. M.; Yusupova, T. N.; Romanov, G. V., Asphaltene nano-aggregates: structure, phase transitions and effect on petroleum systems. *Russian Chemical Reviews* 2011, 80, 993-1008.

5. Zhang, S. F.; Sun, L. L.; Xu, J. B.; Wu, H.; Wen, H., Aggregate Structure in Heavy Crude Oil: Using a Dissipative Particle Dynamics Based Mesoscale Platform. *Energy & Fuels* 2010, 24, 4312-4326.

6. Barrera, D. M.; Ortiz, D. P.; Yarranton, H. W., Molecular Weight and Density Distributions of Asphaltenes from Crude Oils. *Energy & Fuels* 2013, 27, 2474-2487.

7. Speight, J. G., Petroleum asphaltenes - Part 1 - Asphaltenes, resins and the structure of petroleum. *Oil & Gas Science and Technology-Revue D Ifp Energies Nouvelles* 2004, 59, 467-477.

8. Hoepfner, M. P.; Favero, C. V. B.; Haji-Akbari, N.; Fogler, H. S., The Fractal Aggregation of Asphaltenes. *Langmuir* 2013, 29, 8799-8808.

9. Oh, K.; Ring, T. A.; Deo, M. D., Asphaltene aggregation in organic solvents. *Journal of Colloid and Interface Science* 2004, 271, 212-219.

10. Tanaka, R.; Sato, E.; Hunt, J. E.; Winans, R. E.; Sato, S.; Takanohashi, T., Characterization of asphaltene aggregates using X-ray diffraction and small-angle X-ray scattering. *Energy & Fuels* 2004, 18, 1118-1125.

11. Wang, J.; Opedal, N. V.; Lu, Q. Y.; Xu, Z. H.; Zeng, H. B.; Sjoblom, J., Probing Molecular Interactions of an Asphaltene Model Compound in Organic Solvents Using a Surface Forces Apparatus (SFA). *Energy & Fuels* 2012, 26, 2591-2599.

12. Fenistein, D.; Barre, L.; Broseta, D.; Espinat, D.; Livet, A.; Roux, J. N.; Scarsella, M., Viscosimetric and neutron scattering study of asphaltene aggregates in mixed toluene/heptane solvents. *Langmuir* 1998, 14, 1013-1020.

13. Mullins, O. C., The Asphaltenes. Annual Review of Analytical Chemistry, Vol 4 2011, 4, 393-418.

14. Mullins, O. C.; Sheu, E. Y.; Hammami, A.; Marshall, A. G., *Asphaltenes, heavy oils, and petroleomics*. Springer Science & Business Media: 2007.

15. Mullins, O. C.; Sabbah, H.; Eyssautier, J.; Pomerantz, A. E.; Barre, L.; Andrews, A. B.; Ruiz-Morales, Y.; Mostowfi, F.; McFarlane, R.; Goual, L.; Lepkowicz, R.; Cooper, T.; Orbulescu, J.; Leblanc, R. M.; Edwards, J.; Zare, R. N., Advances in Asphaltene Science and the Yen-Mullins Model. *Energy & Fuels* 2012, 26, 3986-4003.

16. Mullins, O. C., The Modified Yen Model. *Energy & Fuels* 2010, 24, 2179-2207.

17. Pacheco-Sanchez, J. H.; Zaragoza, I. P.; Martinez-Magadan, J. M., Asphaltene aggregation under vacuum at different temperatures by molecular dynamics. *Energy & Fuels* 2003, 17, 1346-1355.

18. 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.

19. Alvarez, F.; Flores, E. A.; Castro, L. V.; Hernandez, J. G.; Lopez, A.; Vazquez, F., Dissipative Particle Dynamics (DPD) Study of Crude Oil-Water Emulsions in the Presence of a Functionalized Co-polymer. *Energy* & *Fuels* 2011, 25, 562-567.

20. Zhang, S. F.; Xu, J. B.; Wen, H.; Bhattacharjee, S., Integration of rotational algorithms into dissipative particle dynamics: modeling polyaromatic hydrocarbons on the meso-scale. *Molecular Physics* 2011, 109, 1873-1888.

21. Akkermans, R. L., Mesoscale model parameters from molecular cluster calculations. *The Journal of chemical physics* 2008, 128, 244904.

22. Seaton, M.; Smith, W., DL MESO USER MANUAL. STFC Daresbury Laboratory: Cheshire, UK 2012.

23. Groot, R. D.; Warren, P. B., Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. *Journal of Chemical Physics* 1997, 107, 4423-4435.

24. Kacar, G.; Peters, E.; de With, G., A generalized method for parameterization of dissipative particle dynamics for variable bead volumes. *Epl* 2013, 102.

25. Lee, M. T.; Mao, R. F.; Vishnyakov, A.; Neimark, A. V., Parametrization of Chain Molecules in Dissipative Particle Dynamics. *Journal of Physical Chemistry B* 2016, 120, 4980-4991.

26. Magnussen, T.; Rasmussen, P.; Fredenslund, A., UNIFAC PARAMETER TABLE FOR PREDICTION OF LIQUID-LIQUID EQUILIBRIA. *Industrial & Engineering Chemistry Process Design and Development* 1981, 20, 331-339.

27. Vishnyakov, A.; Lee, M. T.; Neimark, A. V., Prediction of the Critical Micelle Concentration of Nonionic Surfactants by Dissipative Particle Dynamics Simulations. *Journal of Physical Chemistry Letters* 2013, 4, 797-802.

28. Bondi, A., van der Waals volumes and radii. *The Journal of physical chemistry* 1964, 68, 441-451.

29. Seaton, M. A.; Anderson, R. L.; Metz, S.; Smith, W., DL_MESO: highly scalable mesoscale simulations. *Molecular Simulation* 2013, 39, 796-821.

30. Acree, W. E., IUPAC-NIST Solubility Data Series. 98. Solubility of Polycyclic Aromatic Hydrocarbons in Pure and Organic Solvent Mixtures-Revised and Updated. Part 3. Neat Organic Solvents. *Journal of Physical and Chemical Reference Data* 2013, 42.

31. Lee, M.-T.; Vishnyakov, A.; Neimark, A. V., Calculations of critical micelle concentration by dissipative particle dynamics simulations: the role of chain rigidity. *The Journal of Physical Chemistry B* 2013, 117, 10304-10310.

32. Mao, R. F.; Lee, M. T.; Vishnyakov, A.; Neimark, A. V., Modeling Aggregation of Ionic Surfactants Using a Smeared Charge Approximation in Dissipative Particle Dynamics Simulations. *Journal of Physical Chemistry B* 2015, 119, 11673-11683.

33. Spiecker, P. M.; Gawrys, K. L.; Kilpatrick, P. K., Aggregation and solubility behavior of asphaltenes and their subfractions. *Journal of Colloid and Interface Science* 2003, 267, 178-193.

34. Frigerio, F.; Molinari, D., A multiscale approach to the simulation of asphaltenes. *Computational and Theoretical Chemistry* 2011, 975, 76-82.

35. Wang, J.; Ferguson, A. In *Mesoscale simulation of asphaltene aggregation*, APS Meeting Abstracts, 2016.