

DISSERTATION

THE EFFECT OF RESINS ON THE AGGREGATION BEHAVIOR OF ASPHALTENES

Submitted by

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ABSTRACT

THE EFFECT OF RESINS ON THE AGGREGATION BEHAVIOR OF ASPHALTENES

Millions of barrels of crude oil are extracted on a daily basis. Crude oil has four main components separated by the SARA fractionation method.¹ Asphaltenes are the heaviest component of the cured oil. They are known to be responsible for clogging oil wellbores and pipelines, which bedevils the oil industry financially. Additionally, the cleaning chemicals and the clogging waste has a huge negative impact on our environment. The majority of the research on understanding the clogging problem is focused on the asphaltenes as a fraction of crude oil without much consideration for the effects of specific chemical structure. Moreover, the role of other components of the crude oil such as resins is not clear. Here, we have performed structure specific studies of asphaltenes by performing all-atom molecular dynamics (MD) simulations to quantify the aggregation behavior of asphaltenes in the absence and presence of resins.

In this research, we have studied the aggregation tendency of asphaltenes in connection with their molecular properties. Systems with 20 counts of model asphaltene molecules were studied for nanoaggregation behavior of eight model asphaltenes in their neat state. We have quantified the aggregation tendency of asphaltene molecules in n-heptane with isodesmic free energy of aggregation, ΔG_{iso} , as well as a quantity called aggregation propensity (AP).

Using ΔG_{iso} and AP value, we have classified model asphaltene molecules to three main category of non-aggregating, mildly-aggregating, and readily-aggregating asphaltenes. Each category of asphaltene have different aggregation behavior. They differ in their molecular features that ultimately is related to their aggregation propensity.

Subsequently, we have studied the aggregation tendency of asphaltene in the presence of resin with total of 48 systems comprising 8 model asphaltene molecules in the presence of 6 model resins. We wanted to determine the role of resins in the aggregation behavior of asphaltenes by

observing the effect of presence of resin on the ΔG_{iso} and AP values. Additional to ΔG_{iso} , we have defined a normalized quantity called aggregation propensity ratio (APR) to compare the effect of resin on the aggregation of asphaltenes. Resins studied in this work had no promoting effect on the aggregation tendency of asphaltenes. In general, both ΔG_{iso} and APR metrics suggest that aggregation of asphaltene in presence of resin is either not affected or is prevented to different degrees. We have studied the aggregation behavior of asphaltenes in nanoaggregation, clustering and flocculation stages proposed by Yen-Mullins model. Resins have from minimal disruptive to highly disruptive effect on the nanoaggregation of asphaltenes.

We investigated the further aggregation of stable nanoaggregates into clustering and flocculation with 500 counts of mildly-aggregating and readily-aggregating asphaltene molecules. We found that both clustering and flocculation stages occur for the readily-aggregating asphaltenes and do not occur for the mildly-aggregating asphaltenes. Readily-aggregating asphaltene molecules with large negative ΔG_{iso} and large AP values lead to clustering and flocculation whereas the mildly-aggregating asphaltenes stay in the form of nanoaggregates. Our results show that in order for asphaltenes to flocculate, there is a threshold for existence of adequate favorable molecular features. Asphaltenes containing large enough aromatic cores and/or heteroatom reach clustering and flocculation stages.

Furthermore, we found that in the presence of a highly disruptive resin, clustering and flocculation does not occur. For the readily-aggregating asphaltenes the aggregation stops in the nanoaggregation stage and for the mildly-aggregating asphaltenes the size of the nanoaggregates decreases. Our results explain what kind of resins are capable of potentially solving the deposition problem with providing insight on the molecular features of both asphaltene and resin molecules. Such molecular insights paves the road to explore more natural based solutions in preventing the clogging problem in the oil industry by informed characterization of each oil reservoir and its capability to form aggregate or prevent aggregates within itself and in another reservoir.

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DEDICATION

*I would like to dedicate this dissertation to my younger sister
for her courage to stand up for herself.
Her outstanding courage will always be inspiring for me.*

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Chapter 1

Introduction

1.1 Crude Oil Composition (SARA) and Crude Types

Crude oil is a complex mixture of classes of chemicals, the ratio of which vary from one crude type to another. Depending on the percentage of each class, and their corresponding molecular mass, the types of crude oil range from light to medium to heavy crude and lastly a particular type of crude called Bitumen. The chemical composition of crude oil is determined by a method called SARA fractionation.¹ Based on the SARA fractionation method, the main components of crude oil are Saturates, Aromatics, Resins, and Asphaltenes, each of which are a classes of chemicals varying in shape and weight.² Going from light crude toward heavier crudes the ratio of asphaltene and resin fractions increases while the ratio of saturates decreases.³ In Figure 1.1 the ratio of these components in four different crude types is demonstrated.

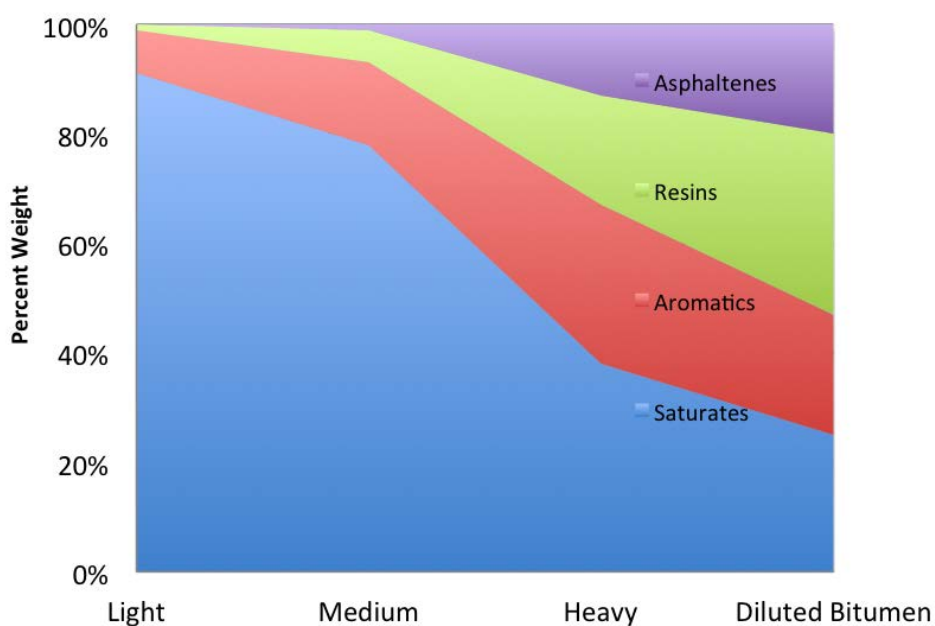


Figure 1.1: The ratio of SARA fractions in different types of crude oil. Heavier crudes contain more asphaltene and resins compared to lighter crude. They contain smaller fraction of saturates.³

1.1.1 Saturates

Saturates are alkane molecules with general formula of C_nH_{2n+2} . Gas chromatography analyses show that depending on the oil type the n value could vary between 3-55.³ The average n could vary from crude to crude based on their reservoir of extraction, which itself depends on the geographical location of the reservoir. Pentane (C_5H_{12}), Hexane (C_6H_{14}), and Heptane (C_7H_{16}) are common examples of these molecules. Saturates come in linear and branched shapes. Figure 1.2 shows examples of linear and branched saturates.

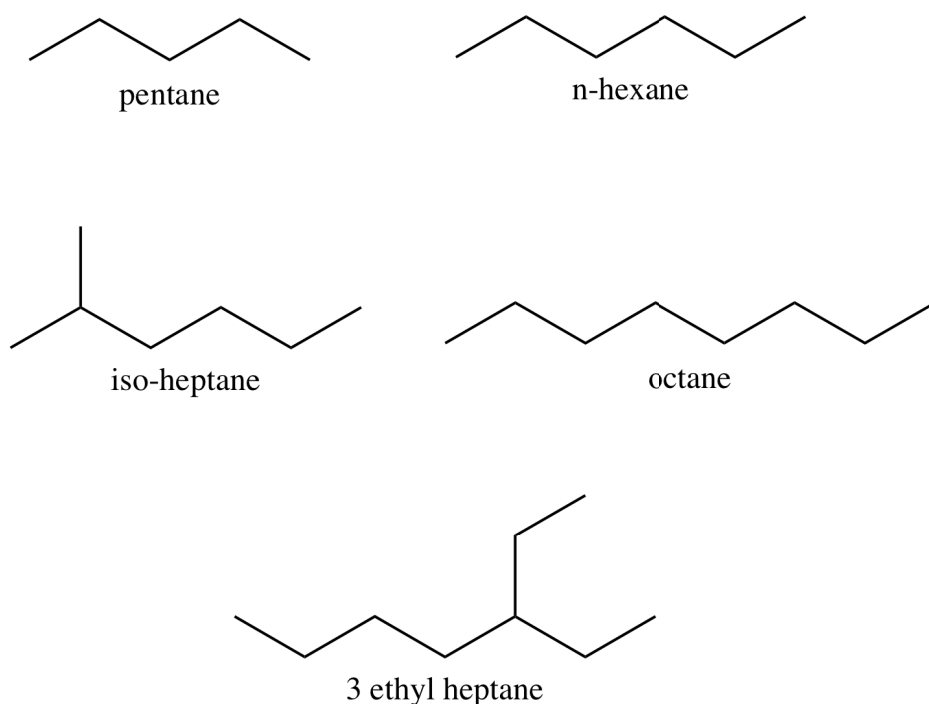


Figure 1.2: Representative examples of linear and branched saturates. Saturates are the most abundant fraction in light crude oil.

1.1.2 Aromatics

Aromatics are derivatives of benzene (C_6H_6) ring. Toluene, and Xylenes are examples of the aromatics. Depending on the oil type, aromatics could make up 10-35% of the crude.³ Figure 1.3 shows representative examples of three aromatic molecules.

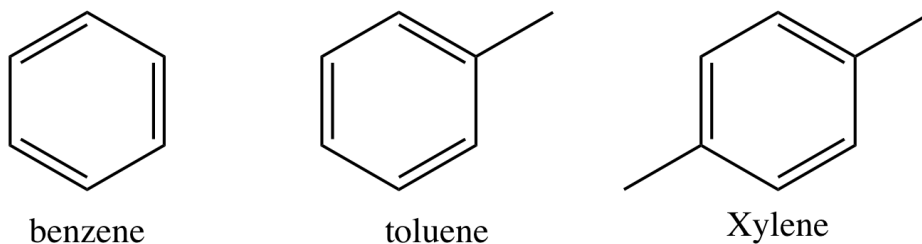


Figure 1.3: Representative examples of aromatic molecules

1.1.3 Resins

Resins are a class of molecules, and there is not a general or specific molecular formula for resins. Resins are made of an aromatic core with aliphatic chain(s), and they may or may not contain heteroatom(s). They are considered to be the second heaviest component of the crude oil.⁴ Figure 1.4 shows examples of two resin molecules.

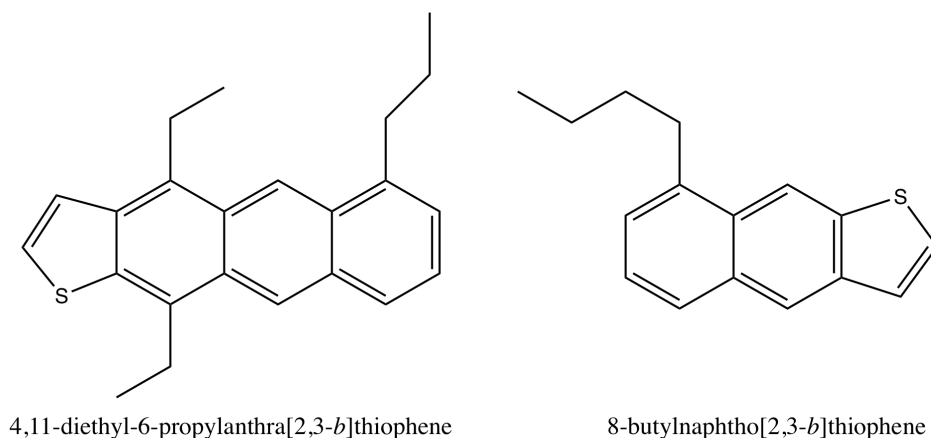


Figure 1.4: Representative examples of two resin molecules

1.1.4 Asphaltenes

Asphaltene are solubility class of molecules and their solubility has been studied in various non-polar, and semi-polar to polar solvents.⁵ They are defined as heptane insoluble and toluene soluble. In other words, they are insoluble in saturates and soluble in aromatics. Asphaltenes are the heaviest component of the crude oil. Structurally, these molecules are composed of aromatic

cores as well as aliphatic cycles and aliphatic carbon chains. Asphaltenes are mainly made of hydrogen and carbon and may or may not contain heteroatom. Sulfur, and oxygen are two of the most abundant heteroatoms in crude oil. The average weight of an asphaltene molecule is about 750 g/mol.⁶ The typical H/C ratio of asphaltenes is 1.2.⁷⁻⁹ Geometrically, there are two primary types of asphaltene molecules: Continental and Archipelago. In Figure 1.5 these two types of asphaltenes are demonstrated. Continental asphaltenes (*a*) include a large aromatic plane, to which aliphatic chains are attached, while archipelago asphaltenes (*b*) are composed of multiple small aromatic planes connected to each other by aliphatic chains.

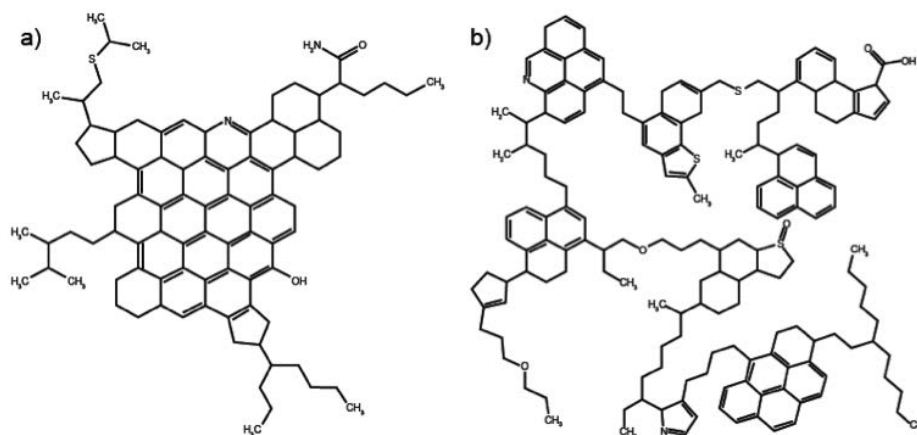


Figure 1.5: Continental and archipelago asphaltenes as two types of a typical asphaltene molecule. Continental asphaltenes (*a*) are made of a large central aromatic core and archipelago asphaltenes (*b*) are made of smaller aromatic cores connected via aliphatic chains.¹⁰

1.2 Asphaltene Deposition

Asphaltenes are known to be responsible for forming deposits in wellbore, pipelines and other petroleum industry equipment via aggregation. Aggregation of asphaltenes negatively impacts the extraction of oil and its transport through the pipelines. According to the US energy information administration, over 100 million barrels of crude oil have been produced on a daily basis in the first quarter of the year 2020. Clogged wellbore requires a shutdown of the oil well due to the pressure drop in production.¹¹ Loss of production or waste of asphaltenes as valuable chemicals has a nega-

tive economical and environmental impact.¹²⁻¹⁴ Cleaning up the asphaltene-clogged pipelines and other petroleum industry equipment is a very costly process.¹⁵ Currently, there are various methods of cleaning asphaltene depositions in clogged pipelines such as replacing the equipment, pulse pressurizing the pipelines and chemical treatments. These methods are either costly or harmful to the environment.^{16,17} Furthermore, these methods are treatments rather than prevention, which inherently adds to the cost of the problem. Understanding the aggregation process will lead to modified oil extraction and production processes that will minimize asphaltene deposition and subsequently can minimize economic and environmental consequences.

Like any other molecule, asphaltenes have a tendency to non-covalently bind together. However, the large size of these molecules cause them to have stronger attractions and could grow in size to form higher order aggregates.¹⁸ Numerous research attempted to alleviate this problem with various methods. For example, Seki, *et. al.* investigated the hydrodematallization of petroleum asphaltene in an attempt to decrease the molecular weight of these species.¹⁹ However, from literature it seems that this tendency is largely due to π - π interactions between their sizable aromatic cores.²⁰ π - π stacking are relatively strong intermolecular forces that can hold these large aromatic molecules together.²¹

1.2.1 Yen-Mullins Model

The Yen-Mullins model is a well-known and widely accepted model for the aggregation of asphaltenes. Based on this model there are three stages for asphaltenes aggregation. In the first step, approximately 5-7 individual asphaltene molecules stack and form nanoaggregates, which have approximately diameter of 2 nm. In the second stage, in high concentration of nanoaggregates, further aggregation leads to formation of clusters of nanoaggregates. Clusters of asphaltenes have diameter of approximately up to 5 nm. Lastly, in flocculation stage, clusters continue to aggregate further and form macroscopic aggregates that lead to the phase separation and troublesome deposition.^{9,12}

1.2.2 Previous Studies

Experimental Research

The asphaltene deposition problem has been studied experimentally toluene, n-heptane, and mixed environments. Although, most studies are done on the mixture of these molecules and not with a systematic set of asphaltene molecules.^{22–24} Fractionation methods are used to extract the mixture of asphaltenes from crude oil samples.²⁵ As expected, the resulting extract is the mixture of asphaltene molecules in a range of weights and shapes. Thus, aggregation behavior could not be attributed to specific molecular characteristics.

Additionally, there are studies on the effect of the various factors such as concentrations, temperature, and pressure on the aggregation behavior of the mixture of asphaltenes.^{26–33} In general, temperature inversely affects the aggregation of asphaltenes. At low temperatures, the deposition of asphaltenes intensifies, and at high temperatures, it slightly alleviates. A study showed that asphaltene aggregates' stability is governed by equilibrium thermodynamics. Thus, aggregation is considered reversible with temperature.²⁹ However, this study did not discuss the practicality and economic viability of the method. Another study found that, under the isothermal condition, asphaltene's deposition increases when the pressure decreases.²⁷ Several studies have been performed on mixtures of asphaltenes with no molecular description and without much consideration to the effect of specific molecular features.^{34–38} One main issue with these studies is that the oil industry deals with asphaltene deposition by pressurizing, temperature treatment, and other chemical treatment methods after clogging rather than preventing it.³⁹

Similar to asphaltenes the effect of resins on the aggregation of asphaltenes has been studied as a mixture of molecules with convoluted results. Soorghali *et. al.* found that when they inject resins from a crude with low tendency to aggregate, to another crude with a high tendency to aggregate, the amount of asphaltene aggregation decreases⁴⁰, which clearly shows that some crude oil with native resins have deposition problem and another resin alleviates this problem. In another study the resins are introduced as species causing asphaltene deposition.⁴¹ However, no molecular structure-specific investigations were performed. In general, previous experimental work on resin

as amphiphiles affecting aggregation in either promoting or demoting way is without molecular insight and does not provide atomistic or molecular detail on why resins have such effects.^{42–49}

Computational Research

A handful of computational studies have been done on the effect of certain molecular aspects of asphaltene molecules on their aggregation behavior. In earlier computational studies Rodriuez *et. al.* studied dimerization and tetramerization of coronene, an eight-membered aromatic plane.⁵⁰ More recently, the aggregation of asphaltenes has been studied with the molecular dynamics (MD) method. Most of these MD studies have used a few molecules instead of a systematic set of asphaltene to investigate the aggregation.^{51–58} For example, Sedgi *et al.*⁵⁸ semi-quantitatively showed that the size of the aromatic core is positively correlated with aggregation tendency of asphaltene molecules. However, they did not quantified the effect of size of aromatic core on the tendency of particular asphaltene to aggregate. Also, their study reveals that presence of an aliphatic chain has a negative effect on aggregation through steric hindrance. Sodero *et. al.* studied the effect of presence of a heteroatom with mixture of asphaltenes with up to 5 asphaltene molecules and concluded that heteroatom increases the tendency of asphaltenes to dimerize and form aggregates.⁵⁹ Despite this research on asphaltene, no structurally systematic study has been performed to quantitatively link the role of molecular features of resin and asphaltene molecules in the aggregation of asphaltenes. Systematic molecular structure-specific insight into the role of resins on the aggregation behavior of asphaltenes has been achieved neither through experimental research nor through computational studies.

1.3 Objectives

Below are the thesis's objectives that address an existing gap in the knowledge of the relationship between molecular characteristics and the aggregation behavior of asphaltenes in the presence of resins.

1. Classify the aggregation tendency of a set of model asphaltenes.
2. Find a quantitative relationship between molecular characteristics of asphaltenes and their aggregation behavior.
3. Identify dominant molecular features in aiding the aggregation.
4. Determine the role of resins in the aggregation process from a molecular perspective.
5. Find a quantitative relationship between resins' molecular components and their effect on the aggregation behavior of asphaltenes.
6. Develop computational predicting tools for aggregation behavior from molecular characteristics of asphaltenes and resins.

1.4 Organization of Thesis

The lack of molecular specific studies has handicapped the oil industry in finding or designing harmless and effective deterrent-based preventative methods for the problem of asphaltene deposition. Here we have elucidate the effect of molecular features of asphaltenes and resins both qualitatively and quantitatively. We provide a structural-specific results and a predictive model that can quantitatively predict aggregation tendency of asphaltenes and the effect of resins on the aggregation of asphaltenes based on their molecular features.

This thesis is organized in three chapters. In Chapter 2 we investigated the molecular features that are paramount to the nanoaggregation of asphaltenes qualitatively as well as quantitatively. We identified the molecular features that enable us to quantitatively distinguish asphaltenes by their aggregation tendencies. Furthermore, we present the results of the effect of resins in the nanoaggregation behavior of asphaltenes. We discuss the nanoaggregation of eight model asphaltene molecules in the absence and presence of six resins. Aggregation behavior of each asphaltene is investigated with metrics such as aggregate number and size, ΔG_{iso} , and aggregation propensity. Chapter 3 focuses on the aggregation behavior of asphaltenes past nanoaggregation stages. In this chapter larger systems of asphaltenes were studied in the absence and presence of deterring resin and their clustering and flocculation behaviors were investigated. Chapter 4 is composed of final conclusion and proposed future directions.

Chapter 2

Detering Effect of Resin on the Nanoaggregation of Asphaltenes in n-Heptane ¹

2.1 Overview

Deposition of asphaltenes bedevils the oil industry financially and environmentally. Asphaltenes are diverse set of macromolecules native to crude oil and are classified by their lack of solubility in light alkanes such as heptane. The diverse set of molecular features of asphaltenes leads to a diverse set of precipitation criteria. Resins are another native component of crude oil that have been implicated in both deterring and promoting asphaltene aggregation. Here we design a systematic set of model asphaltenes and resins to investigate the molecular features that lead to asphaltene precipitation in crude oil. We utilize extensive all-atom molecular dynamics simulations to quantify aggregation behavior. This behavior is then fit to a linear model based on asphaltene and resin molecular features. We find that all resins either deter or do not affect asphaltene aggregation in a light crude environment. It is also possible to match asphaltene and resin molecular features to best deter asphaltene aggregation behavior. These findings and models represent a possible framework for utilizing select resins to prevent asphaltene precipitation.

2.2 Introduction

The precipitation of asphaltenes in the extraction and transportation process cost the oil industry billions of dollars per year.¹³ The precipitation process occurs as a result of pressure change, temperature change and/or specific chemical composition of the crude oil.²⁶ Crude oil is a complex mixture of four main classes of molecules: saturates, aromatics, resins and asphaltenes.⁶⁰ Medium

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and heavy crude have higher content of asphaltene and lower content of saturates and aromatics. However, they have less deposition problem than light crude: the high saturate content of light crude tends to lead to instability and asphaltene precipitation⁶¹. Resins are amphiphiles present in both heavy and light crude that have been implicated in preventing⁴⁶ and aiding in⁶² asphaltene precipitation.^{4,62} It is thus of great interest to understand asphaltene precipitation and the role of resins in the process to predict and alleviate asphaltene precipitation problems.

Asphaltenes are the heaviest native component of crude oil and are classified by a solubility regime: they are insoluble in light alkanes and soluble in aromatic hydrocarbons.^{6,7,9,15,16,63} This classification leads to a diverse set of chemical structures with an average molecular weight of 750 Da (range of 400-1000).⁹ The modified Yen model of asphaltenes⁹ narrowed the structural scope of these molecules to be a core of 4-10 fused aromatic rings and peripheral hydrocarbon tails.⁹ Much of the research leading up to this structural description has been done using techniques such as time-resolved fluorescence correlation spectroscopy^{64,65}, nuclear magnetic resonance⁶⁶, laser desorption mass spectrometry⁶⁷, and small-angle neutron (SANS) and x-ray (SAXS) scattering⁶⁸. The results from these techniques have opened doors to the use of more structurally specific techniques including molecular dynamics.

Asphaltene precipitation is thought to follow the Yen-Mullins mechanism in which initial, π - π stacked, nanoaggregates are formed followed by subsequent clustering and flocculation and ultimately precipitation.⁶⁹ In this paper we focus on the initial aggregation process. Additionally, we consider the aggregation of asphaltenes in a light crude like solvent. Light crude is chosen because it promotes asphaltene aggregation and ultimately we would like to know what causes aggregation and how to stop it. The Yen-Mullins model, as well as many other previous studies of asphaltenes, ignore the effect of resins on asphaltene precipitation.

The role that resins play in the precipitation of asphaltenes is still debated;^{62,70-72} these molecules have been implicated in both preventing⁴⁶ and aiding in⁶² asphaltene precipitation. Resins are native to crude oil and are defined as the most polar aromatic species in deasphalted oil.^{4,46,62} Although resins are smaller than asphaltenes, resins and asphaltenes both derive from same parent

molecules and thus contain similar molecular features.⁴ The effect of resins on asphaltene aggregation has been studied by SANS⁴⁶, dynamic light scattering⁷², and microscopy⁴⁰ in addition to molecular mechanics^{73–76}. For instance, Soorghali et. al reported that resins extracted from one type of crude oil with low tendency to form an aggregate decrease amount of aggregation if added to another type of crude with a high tendency to form aggregates.⁴⁰ Similar studies suggest that resins with specific molecular features play a key role in affecting aggregation behavior of asphaltene molecules.^{44,45} Despite these studies, the thermodynamics of asphaltene-resin interactions and the structure of these aggregates is still poorly understood.

Molecular dynamics (MD) is a powerful tool that has been used to gain insight into a wide variety of processes including the assembly of asphaltenes.^{52–54,56,57,77–80} Early MD studies focused on the association of asphaltenes in vacuum or implicit solvents.^{52,73–76,79} More recently, studies have looked at asphaltene assembly in solvents^{14,53,54,56,57,77,78} including the computation of thermodynamic properties of asphaltene association.⁷⁷ An explicit representation of solvent is important to accurately capture the behavior of molecules in their solvated environment. To date, there has not been a large-scale systematic MD study of asphaltene aggregation and the role that resins play in this process.

We hypothesize that the large variability in the molecular structure of asphaltenes and resins causes the conflicting behavior observed for asphaltene-resin precipitation. A systematic all-atom explicit solvent MD study is proposed that will probe this hypothesis. Specifically, we (1) design a set of model asphaltene-like and resin-like molecules to probe the role of specific molecular features, (2) determine aggregation classes of neat asphaltenes in light crude and (3) determine classes of asphaltene aggregation inhibition by resins.

2.3 Methods

2.3.1 Choice of Model Asphaltenes and Resins

Shown in Figure 2.1A, a set of representative model asphaltene molecules (A1-A8) was chosen to study. These model asphaltenes were inspired by previous experimental and computational

studies^{25,55,58,81} and recent atomic force microscopy (AFM) studies of asphaltene structures.⁸² The core size of the model asphaltene molecules here are composed of 4-10 aromatic benzene fused rings, as suggested by Mullins et al.⁶. We note that not all of these model asphaltenes conform to the C/H criteria for asphaltenes rather the set was chosen to systematically test certain molecular features. A set of model resin molecules (R1-R6) was also chosen for a systematic study of the effect of resins on the aggregation of asphaltene molecules (Figure 2.1B). Both model asphaltene and resin molecules differ in size of aromatic core, presence and length of aliphatic chain, and presence of heteroatom(s).

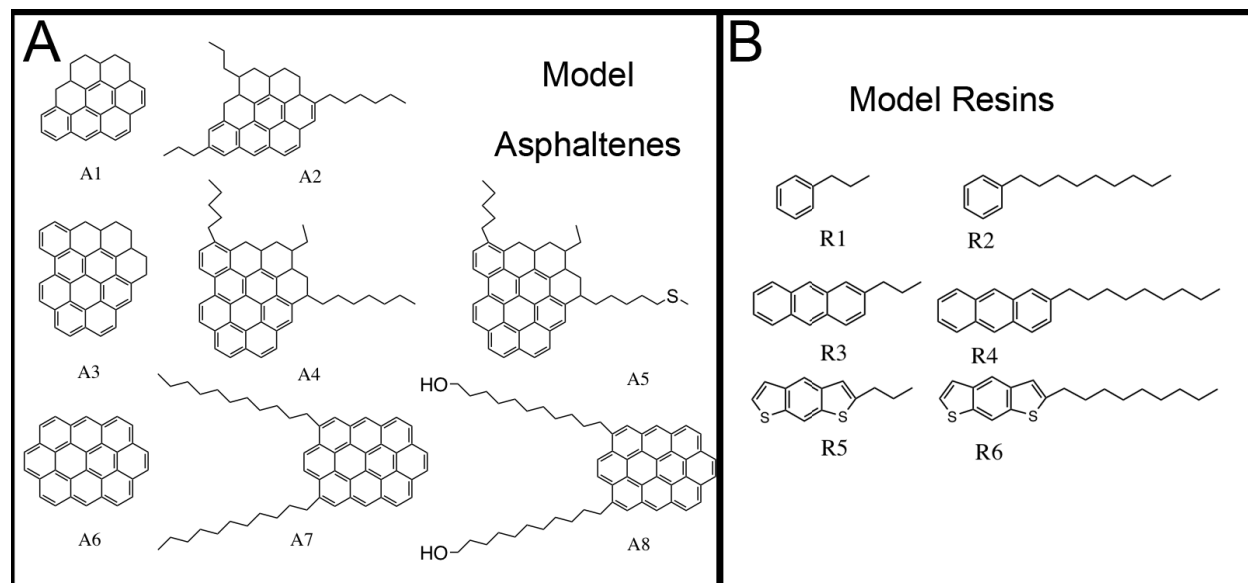


Figure 2.1: Model asphaltenes and resins used for this study.⁸³ These sets were chosen to systematically test the effect of size of aromatic core, presence of heteroatoms and presence of aliphatic groups for both asphaltenes and resins on the aggregation propensity of the asphaltene. A) Set of eight model asphaltenes used for this study. B) Set of six model resins.

2.3.2 Force Field Verification

OPLS-AA was chosen as the force field for all simulations. This force field is known to reproduce physical properties of organic molecules and in particular aromatic molecules.⁸⁴ Furthermore, prior to this research, an asphaltene model molecule, Violanthrone-79, was parameterized with OPLS-AA force field and simulated in chloroform and toluene. Orientational analysis of the

Violanthrone-79 simulation replicates antiparallel dimer structure supported by 2D-IR results. (See SI)⁸⁵ Cyran *et. al.* determined that the stacking geometry of Violanthrone-79 at formed nanoaggregates have strictly antiparallel stacking behavior with a twist angle of 180 ± 28 , which is in a good agreement with our molecular dynamics (MD) results. (See SI)

2.3.3 Simulation Procedure

All of the individual asphaltene and resin structures were built in GaussView V.5.0.⁸⁶ and Gaussian09⁸⁷ was used to geometry optimize all structures. The B3LYP exchange-correlation functional and basis set of 6-31+G(d) were used. The restricted electrostatic potential (RESP) procedure was utilized to find partial charges on individual atoms of each structure.⁸⁸ The GROMACS package (version 5.0.4) was utilized for all molecular dynamics (MD) simulations.⁸⁹ The VMD package was used for visualization of all trajectories.⁹⁰

In each of the fifty-six systems, 20 asphaltene molecules were randomly dispersed in a box with explicit n-heptane. The concentration of asphaltene in each system was 0.1 M. Figure 2.2 and Figure 2.3 show schematic of a simulation box with A6 before and after aggregation.

To investigate the effect of resins on the aggregation behavior of asphaltenes, each type of resin was paired with each type of asphaltene. A typical resin to asphaltene mass ratio in a medium crude is about five which was used in all paired systems.

Nose-Hoover^{91,92} and Parrinello-Rahman⁹³ algorithms were used to keep average temperature and pressure constant at 300K and 1 bar. Cubic periodic boundary conditions were applied for all of the systems to simulate infinite bulk behavior. For all systems the integration time step was 2 fs with a write frequency of 2 ps. Long-range electrostatic interactions were treated by Particle Mesh Ewald (PME).⁹⁴ Initial configuration of each system was energy minimized by using the steepest descent method to remove any existing high-energy structures. The minimization step was followed by 5 ns of equilibration and following that 250 ns of production run was performed for each system. Triplicate system were run to estimate ensemble error.

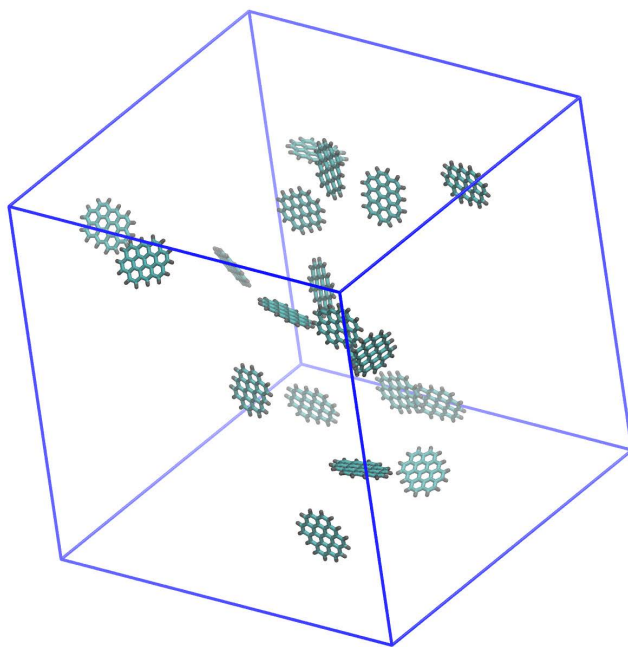


Figure 2.2: A representative snapshot of simulation box of 20 count of A6 asphaltene molecules in n-heptane. Solvent molecules were excluded for clarity. Solvated state of A6 molecules.

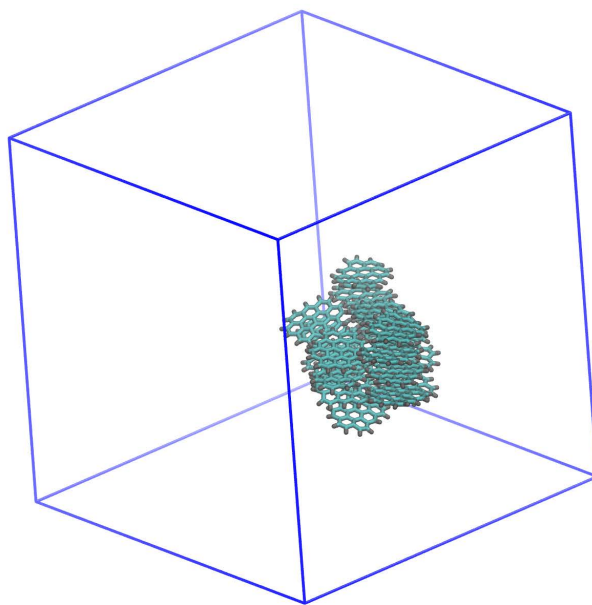


Figure 2.3: A representative snapshot of 20 count of aggregated A6 asphaltene molecules in n-heptane. Solvent molecules were excluded for clarity. Aggregated state of A6 molecules.

2.3.4 Data Analysis

Other than standard molecular dynamics analyses, we use the isodesmic model of aggregation, which we have derived from statistical mechanical principles for simulation purposes. (See SI) In an isodesmic mechanism of aggregation, which is commonly used to describe covalent polymerizations, monomers are added to small oligomers or other monomers. In this linear aggregation model, the free energy of binding for each additional step is equal and is not dependent on the aggregate size. Within this model, it can be shown that the average number of aggregates is given as

$$\langle N_n \rangle = \frac{\sum_{Partitions} N_n e^{N_{clu} \frac{\Delta G_{iso}}{T}}}{\sum_{Partitions} e^{N_{clu} \frac{\Delta G_{iso}}{T}}} \quad (2.1)$$

where ΔG_{iso} is the isodesmic free energy of aggregation, N_n is the number of aggregates of size n , N_{clu} is the number of aggregates and T is temperature in units of energy. We have fit aggregate number distributions to the isodesmic model to calculate the ΔG_{iso} for each system.

To calculate the number of aggregates in each time step, we measure the pairwise atomic distance between heavy atoms of model asphaltenes. We use the cutoff distance of 0.37 nm to include both face-to-face $\pi - \pi$ stacks as well as edge-to-edge aggregates. We compute the distribution of the number of aggregates by normalized histogramming of the number of aggregates in each time step over last 60 ns of the trajectory. Shown in Figure A.21, there are three distribution patterns for the number of aggregates of asphaltenes that qualitatively distinguishes asphaltenes with different aggregation behavior. (See SI)

The isodesmic model quantitatively captures the aggregation behavior of our model asphaltene systems. To demonstrate this, we fit the measured aggregate number distributions to the isodesmic model in Equation 2.1 and provided all fits in Figure A.22. (See SI) The fits demonstrate that the isodesmic model can accurately capture non-aggregating and easily-aggregating systems. For example, isodesmic fits can differentiate between non-aggregating A1 and easily-aggregating A5. The intermediate aggregation regime, such as A4, does not demonstrate a good fit between the observed aggregate number distribution and the isodesmic model. Despite this lack of fit, we still use ΔG_{iso} to measure aggregation because these values are between non-aggregating systems and

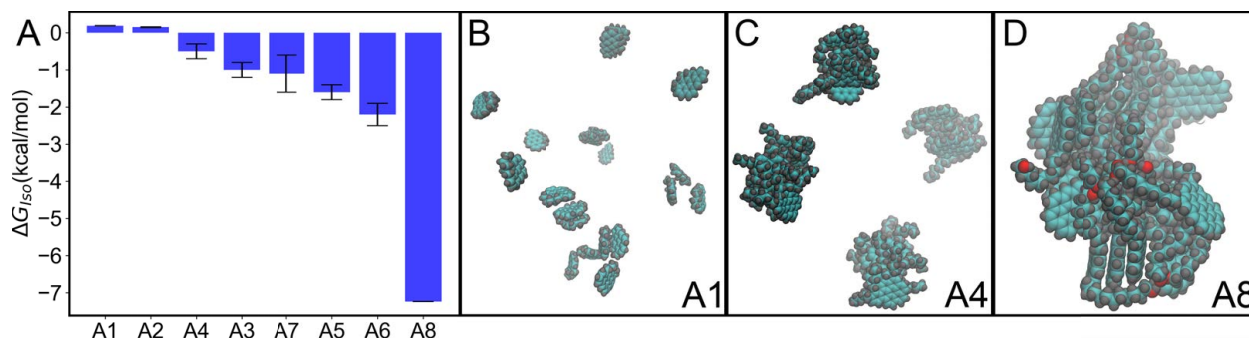


Figure 2.4: Aggregation classes of neat model asphaltenes. (A) The ΔG_{iso} values of all eight model asphaltenes simulated for this study in descending order of ΔG_{iso} . (B) Representative snapshot from the simulation of non-aggregating model asphaltene A1. (C) Representative snapshot from the simulation of mildly-aggregating model asphaltene A4. (D) Representative snapshot of readily aggregating model asphaltene A8.

easily-aggregating systems. Therefore, the isodesmic model holds merit to differentiate between aggregating systems quantitatively. Additionally, we have demonstrated a strong correlation between ΔG_{iso} and a different aggregation propensity metric (AP) in Figure A.4. (See SI) Thus, ΔG_{iso} can quantitatively distinguish between asphaltene systems that have different aggregation behavior.

2.4 Results and Discussion

2.4.1 Aggregation Behavior of Neat Model Asphaltenes

While it is known that larger, aromatic asphaltenes readily aggregate in light crude, the contribution to the ΔG_{iso} from different molecular features is not known. The set of neat model asphaltenes depicted in Figure 2.1A was chosen to systematically probe the role of certain molecular features on the aggregation propensity of the model asphaltene. Namely, we probe the role of aromatic core size, inclusion of aliphatic tails and the inclusion of heteroatoms on the aggregation of model asphaltenes.

Three Aggregation Classes

Aggregation of the eight model asphaltenes in n-heptane can be classified into three categories: non-aggregating, mildly-aggregating and readily-aggregating. Aggregation was monitored in all-

atom molecular dynamics simulations of each model asphaltene at a concentration of 0.1 M solvated in n-heptane. Aggregates size distributions were measured as described in Methods and ΔG_{iso} was fit to these distributions. (See SI) The results from this procedure are provided in Figure 2.4A in descending order of ΔG_{iso} . Non-aggregating asphaltenes are composed of A1 and A2 as with criteria that $\Delta G_{iso} > 0$ indicating effective solvation between asphaltenes. Mildly-aggregating asphaltenes are composed of A3, A4 and A7 with criteria $0 > \Delta G_{iso} > -1.5$ kcal/mol indicating mild attraction between asphaltenes. Readily-aggregating asphaltenes are composed of A5, A6 and A8 with $\Delta G_{iso} \leq -1.5$ kcal/mol indicating large attractive interactions and thus a strong propensity to aggregate. The molecular interaction was also investigated by radial distribution function. Furthermore, a consistent classification of asphaltenes were obtained by aggregation propensity metric. (See SI)

Non-aggregating asphaltenes are characterized by small aromatic cores and a lack of heteroatoms. $\Delta G_{iso} = 0.187 \pm 0.003$ kcal/mol for A1 and $\Delta G_{iso} = 0.15 \pm 0.01$ for A2 indicate an effective solvation of these asphaltenes in n-heptane. This effective solvation can also be observed in a representative snapshot near the end of the simulation of A1 in Figure 2.4. The lack of any type of stable aggregate is characteristic of both A1 and A2 and suggests that the dominant species is the monomer. Aggregates such as dimers and trimers are observed but only transiently. Model asphaltenes A1 and A2 have small aromatic cores (five fused benzene rings) and no heteroatoms. Thus we can conclude that simply the presence of a small aromatic core is insufficient to cause precipitation of asphaltenes in light crude.

Mildly-aggregating asphaltenes are characterized by medium to large aromatic cores and a lack of heteroatoms. Species A3, A4 and A7 have $0 > \Delta G_{iso} > -1.5$ kcal/mol which is achieved by forming long-lived aggregates of 4-5 asphaltenes. A representative snapshot from the simulation of A4 demonstrating such a set of clusters is depicted in Figure 2.4C. The smaller aggregates form but never fuse together to form larger stable aggregates. Model asphaltenes A3 and A4 have fused aromatic cores of eight benzene rings. The addition of three fused benzene rings convert A1 to A3 and lead to a dramatic increase in the aggregation behavior of A3 as compared to A1. The addition

of aliphatic tails to A3 yields A4 and leads to an increase in ΔG_{iso} from -1.0 ± 0.2 kcal/mol for A3 to -0.5 ± 0.1 kcal/mol for A4. Interestingly, increasing the fused aromatic core to 10 rings (A6, A7, A8) leads to increased aggregation behavior but this can be decreased by again adding aliphatic chains (A7) to make the asphaltene more soluble in n-heptane. Overall, mildly-aggregating asphaltenes form clusters of 4-5 asphaltene molecules that, under the simulation conditions tested here, do not further aggregate.

Readily-aggregating asphaltenes are characterized by large aromatic cores and/or inclusion of heteroatoms. Species A5, A6 and A8 all have $\Delta G_{iso} < -1.5$ kcal/mol indicating a strong effective attraction between asphaltene molecules. This strong effective attraction leads to the formation of a single aggregate in our simulation of 20 molecules as depicted for A8 in Figure 2.4D. A5 has an aromatic core identical to A3 and A4 which would place it in the mildly-aggregating category but the addition of a single heteroatom (sulfur) increases the aggregation propensity of this model asphaltene. A6 and A8 both have the ovalene fused aromatic core (10 rings) and readily aggregate because of it. The aliphatic chains of A8 are capped with alcohol groups, which lead to extreme aggregation due to both solvophobic and hydrogen-bonding behaviors. Since these aggregates are composed of all 20 molecules in our simulation box, we only say they are the nanoaggregates in the first step of the Yen-Mullins precipitation mechanism. However, this is the maximum possible size of aggregate we can observe due to system size constraints.

Molecular Features Predict Aggregation Behavior

The behavior of different molecular features such as size of aromatic core, presence of heteroatoms and presence of aliphatic tails distinguish the aggregation classes discussed in the previous section. We quantify this behavior by fitting the ΔG_{iso} values of the eight neat asphaltenes to a linear equation with respect to number of heteroatoms (N_{Ah}), number of aromatic carbons (N_{Aar}), and number of aliphatic carbons (N_{Aal}),

$$\Delta G_{iso} = A_h N_{Ah} + A_{ar} N_{Aar} + A_{al} N_{Aal} + C \quad (2.2)$$

where A_h represents the contribution to ΔG_{iso} per heteroatom, A_{ar} represents the contribution to ΔG_{iso} per aromatic carbon, A_{al} represents the contribution to ΔG_{iso} per aliphatic carbon and C the offset in ΔG_{iso} . The results of the linear regression to determine A coefficients are presented in Figure 2.5. We have performed a weighted regression and correlation coefficient evaluation in order to account for error in the measured values.

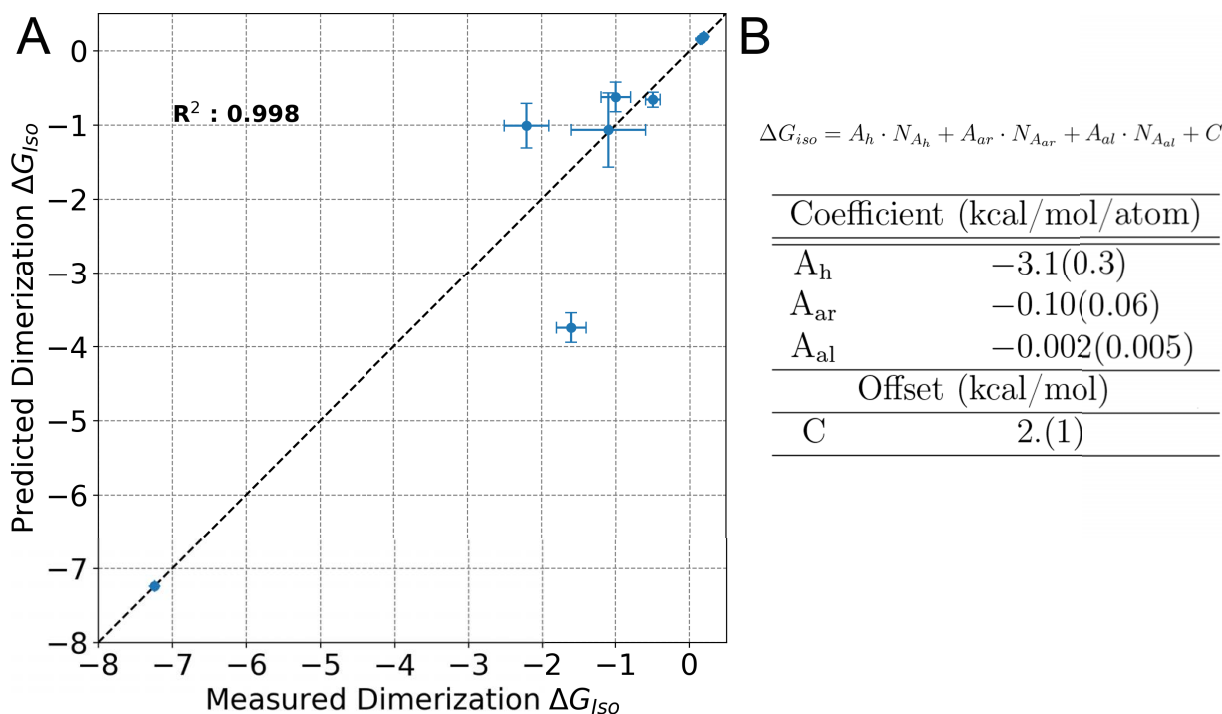


Figure 2.5: Linear regression for ΔG_{iso} to asphaltene molecular features in their neat state. A) The linear fit for all eight asphaltenes. B) The coefficients for the fit showing the importance of each molecular feature in the aggregation tendency. The presence of heteroatom heteroatom is the most favorable molecular feature for aggregation.

Molecular features of asphaltenes can be used to predict their aggregation behavior in n-heptane. The correlation coefficient of $R^2 = 0.998$ demonstrates that strong linear behavior of ΔG_{iso} with respect to molecular features in n-heptane. The values of the A coefficients suggest that the presence of a heteroatom has the largest per-atom effect on ΔG_{iso} as each heteroatom contributes -3.1 kcal/mol towards the binding free energy. This is mainly due to the extremely large negative ΔG_{iso} observed for A8. Aromatic carbons contribute -0.10 kcal/mol towards aggregation behavior. Addition of a fused aromatic ring to an aromatic core will contribute an additional

Table 2.1: ΔG_{iso} in kcal/mol for asphaltene-resin mixtures in n-heptane computed using isodesmic fitting of cluster size distributions measured from all-atom molecular dynamics simulations. Error estimates provided in parentheses are estimated from three separate 20 ns chunks of simulations.

R/A	A1	A2	A3	A4	A5	A6	A7	A8
NR	0.187(3)	0.15(1)	-1.0(2)	-0.5(1)	-1.6(2)	-2.2(3)	-1.1(5)	-7.239(1)
R1	0.20(1)	0.20(1)	-0.54(1)	-0.191(4)	-0.9(3)	-0.73(3)	-0.5609(4)	-4.9(4)
R2	0.21(1)	0.21(3)	-0.07(2)	-0.1(1)	-0.11(4)	-0.02(1)	0.08(1)	-3.0(4)
R3	0.20(1)	0.17(2)	0.04(1)	0.047(4)	0.08(1)	0.012(2)	0.08(1)	-1.5(1)
R4	0.242(1)	0.20(1)	-0.36(9)	0.08(1)	0.03(1)	0.05(2)	0.176(2)	-1.404(1)
R5	0.252(1)	0.26(1)	-0.03(3)	0.149(3)	0.022(3)	-0.001(4)	0.0(1)	-1.3(1)
R6	0.22(1)	0.25(2)	-0.5(1)	-0.002(3)	0.08(2)	-0.3(1)	0.14(1)	-5.4(1)

3-4 aromatic carbons thus contribute $-0.30 - 0.40$ kcal/mol towards aggregation behavior. Interestingly, addition of aliphatic carbons is found to have a negligible effect on isodesmic free energy of aggregation (-0.002 ± 0.005 kcal/mol/atom).

2.4.2 Aggregation Behavior of Model Asphaltenes in the Presence of Model Resins

The role that resins play in the aggregation of asphaltenes is debated. Here we investigate how a model set of resins affect the aggregation of our model set of asphaltenes. The aromatic core size, length of aliphatic chains and presence of heteroatoms are systematically varied in the set of model resins. We consider only the homo-aggregation of asphaltenes and the effect of a single type of resin. Resins are added in amounts to maintain a 5 % mass ratio of asphaltenes and resins as is typically found in medium crude.

Isodesmic Aggregation Free Energy for all Asphaltene-Resin Combinations

The isodesmic free energy of asphaltene aggregation can be used to assess the role of resins in promoting or preventing asphaltene aggregation. To measure this quantity, we again monitor the number of asphaltene clusters formed in our simulations using an asphaltene-asphaltene clustering procedure. The cluster distributions are then fit to an isodesmic aggregation model to obtain an effective aggregation free energy for the asphaltenes in the presence of resins. These values are presented for all asphaltene resin pairs studied here in Table 2.1.

All model resins either deter or have little effect on the aggregation of all model asphaltenes studied here. The isodesmic aggregation free energy of all asphaltene-resin mixtures tabulated in Table 2.1 are greater than the respective neat asphaltene (NR) value. Thus resins are preventing aggregation of the asphaltene molecules. This is due to the fact that even the base resin, R1, has an aromatic component that is not present in the solvent. Thus the resins will be attracted to the asphaltenes. The specific behavior of asphaltenes and resins are broken up into the asphaltene aggregation groups discussed in the previous section.

Resins do not affect the aggregation propensity of non-aggregating asphaltenes. While both A1 and A2, the non-aggregating asphaltenes, demonstrate slight increases in ΔG_{iso} in the presence of resins (Table 2.1), the increases are small and some are within error of the neat asphaltene values. Model asphaltenes A1 and A2 do not aggregate in n-heptane and none of the model resins we investigated cause them to aggregate.

Resins prevent the aggregation behavior of mildly-aggregating asphaltenes. Focusing on A3, A4 and A7, we observe a mild effect on the isodesmic binding free energy due to the presence of R1. This resin is small and has little measurable effect on the aggregation of any model asphaltene tested. The remaining resins significantly increase the solubility of the mildly aggregating asphaltenes. The lone exception is A3/R6 in which we see a muted effect similar to A3/R1. In the rest of the cases, the resins interact with the asphaltenes to help solubilize them in n-heptane leading to an increase in the ΔG_{iso} values for these mixtures as compared to the corresponding neat asphaltene. For A3, A3/R3 has largest effect; R3 has similar molecular features to A3: large aromatic core and small aliphatic tails. For A4, any resin with more than one aromatic ring solubilizes this asphaltene. For A7, even R2, with a small aromatic core but large aliphatic tail, solubilizes this asphaltene. It is possible to tune the resin to best suit the asphaltene but, in general, resins stop the aggregation of mildly aggregating asphaltenes.

The aggregation of asphaltenes designated as readily aggregating (A5, A6 and A8) is deterred by the presence of resins. Again, all values of ΔG_{iso} for A5, A6 and A8 in the presence of resins are larger than the corresponding neat value (Table 2.1). Exactly how deterred this behavior is depends

on the asphaltene. A5 and A6 are readily converted into non-aggregating or mildly-aggregating by any resin other than R1. A8, on the other hand, has ΔG_{iso} values below -1.0 kcal/mol in the presence of all resins. Thus while resins do deter the aggregation of A8, they do not completely prevent it.

Molecular Features Predict Aggregation Behavior

The molecular features of asphaltenes and resins can be used to estimate the aggregation propensity of a given asphaltene in the presence of a given resin. Following a procedure similar to the linear model for the neat asphaltenes, we consider six molecular features of a given system: number of heteroatoms in the asphaltene, number of aromatic carbon atoms in the asphaltene, number of aliphatic carbon atoms in the asphaltene, number of heteroatoms in the resin, number of aromatic carbon atoms in the resin and number of aliphatic carbon atoms in the resin. The isodesmic free energy of aggregation is then set equal to a linear function of these features as written out in Figure 2.6B. A linear fitting procedure is followed inversely weighted by the error of the measured ΔG_{iso} values. The results are provided in Figure 2.6.

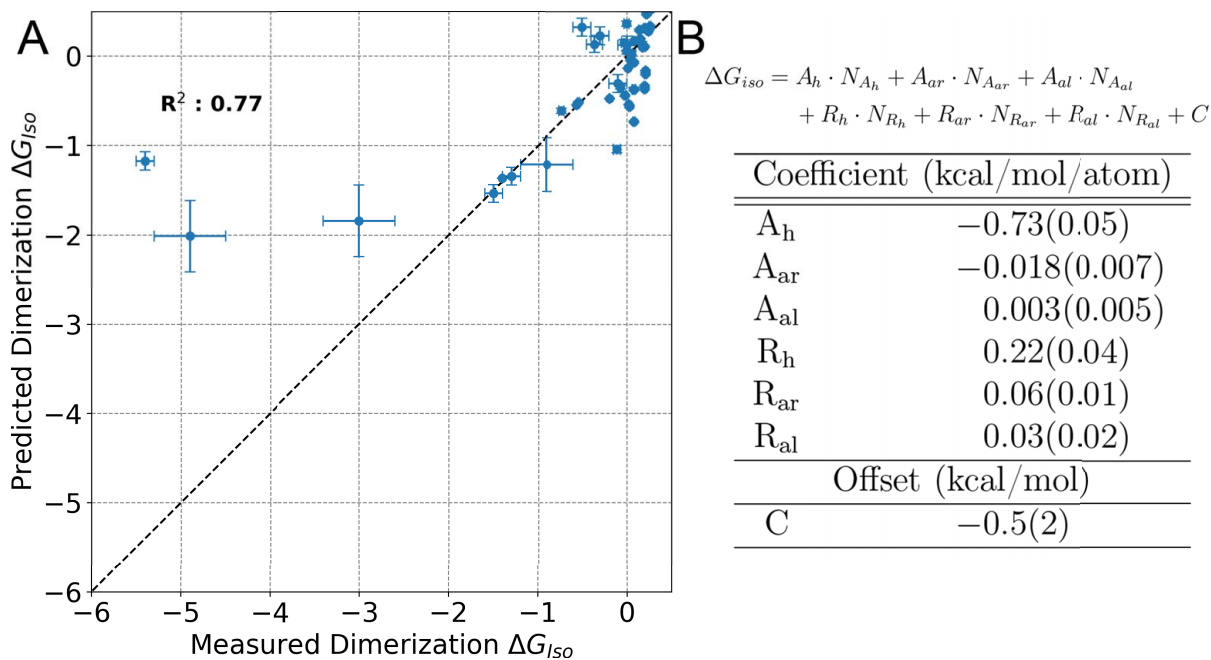


Figure 2.6: Linear regression for ΔG_{iso} to asphaltene and resin molecular features.

The asphaltene feature coefficients as expected are similar in the asphaltene-resin model and the neat asphaltene model. The most dominant component is the number of heteroatoms with an effective aggregation free energy of -0.73 kcal/mol/atom in the asphaltene-resin model. This is an increase as compared to the -3.1 kcal/mol/atom found in the neat asphaltene system indicating that resins, overall, reduce the effect of asphaltene heteroatoms on the aggregation of asphaltenes. The presence of aromatic carbon atoms in the asphaltenes also drive them to aggregate as is indicated by the -0.018 kcal/mol/atom found in this model. The presence of aliphatic carbon atoms on the resins has minimal effect.

All resin molecular features have a deterring effect on the aggregation of asphaltenes. The largest is the presence of heteroatoms in the resins, which provide an increase in ΔG_{iso} of 0.22 kcal/mol/atom. Aromatic carbon atoms on the resins provide 0.06 kcal/mol/atom increase in ΔG_{iso} of the asphaltene.

2.5 Conclusions

Asphaltene precipitation is an expensive problem for the oil industry. The molecular mechanisms behind this behavior remain enigmatic. In this manuscript we utilized large-scale all-atom molecular dynamics to investigate the molecular features of asphaltenes and resins that promote and deter asphaltene aggregation. Using an isodesmic fitting to our simulation data, the isodesmic free energy of aggregation was computed for all asphaltene systems. These results were then fit to linear models using asphaltene and resin molecular features. It was found that asphaltene heteroatom is the largest contributor to the aggregation propensity of asphaltenes in n-heptane.

Resins play a deterring role in asphaltene aggregation in n-heptane. The presence of heteroatoms and large aromatic cores of the resins, specifically significantly impact the resins ability to deter asphaltene aggregation.

The linear models built in this study represent possible predictive tools for asphaltene precipitation. One could envision using the coefficients here to compute the likeliness of asphaltenes observed in a particular well sample to precipitate. Additionally, one could predict the type of

resin to best deter the precipitation process. Additional data is needed to see how transferrable these models are to other types of crude and other asphaltene and resin systems.

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Chapter 3

The Effect of Resin on the Clustering and Flocculation of Asphaltenes in n-Heptane²

3.1 Overview

We investigated the flocculation of mildly-aggregating and readily-aggregating asphaltenes. Subsequently, we studied the effect of a stabilizing resin on the large-scale aggregation behavior of asphaltenes in n-heptane. Molecular dynamics simulations were used to gain atomistic resolution and insight into the dynamics of the flocculation process in relation to the asphaltenes and resin's molecular features. Asphaltenes are known to be responsible for forming deposition in extraction and transportation equipment in the oil industry. The deposition problem imposes an immense cost to the industry in the form of cleaning expenses and loss of production due to the shutdowns. Such shutdowns happen due to the severe clogging of the equipment caused by macroscopic depositions. This work tests all the pre-macroscopic stages of asphaltene deposition, which happen beyond the initial Yen-Mullins nanoaggregation stage.

We examine the effectiveness of resins at deterring aggregation in large scale systems with explicit solvent simulations. We show that the extent of assembly of readily-aggregating asphaltenes is not limited in the absence of a resin. In contrast, in the presence of a stabilizing resin, which contains favorable molecular characteristics as deterring factors, the aggregation is limited to the formation of only nanoaggregates. This work's results show the effectiveness of resin on disrupting the aggregation of asphaltenes in clustering and flocculation stages, providing confidence in applying metrics from nanoaggregation studies for predicting larger scale behaviors. Metrics such as the isodesmic binding energy and the aggregation propensity are computationally less expen-

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sive compared to the flocculation studies and can be used to identify critical molecular factors in the flocculation process. The results provide evidence for the direct applicability of dominant molecular factors for predicting the severity of aggregation by asphaltenes and the effectiveness of inhibition by resins.

3.2 Introduction

Asphaltene precipitation is a major problem for the oil industry.⁶ The precipitation of asphaltene causes clogging of equipment in the oil extraction and transportation sectors. This clogging problem economically taxes the industry due to the loss of production and cleaning costs.^{12,13,95,96} Minimizing the clogging issue or preventing it helps the industry avoid such expenses. One potential approach that can remarkably decrease the oil production and transportation expenses is using natural molecular species with an inhibiting effect.

Resins are a natural component of crude oil⁴, that have been implicated in both promoting⁶² and preventing⁴⁶ asphaltene precipitation. Thus, the role of resins in the precipitation of asphaltenes is still debated.^{62,70–72} The ratio of resins and asphaltenes increases, moving from lighter toward heavier oil types.^{3,16,60,97} Despite this increase in the ratio of asphaltenes in heavier crude oil, light crude has more precipitation problems.⁶¹ Hence, understanding the interaction between asphaltene and resin fractions is of great interest. These interactions can potentially act as an inhibiting factor in preventing asphaltenes' precipitation.

Asphaltene precipitation is a multiscale process proposed by Yen-Mullins model to follow nanoaggregation, clustering, flocculation, and phase separation mechanism.^{6,9} In the first stage, approximately 5-7 single molecules form nanoaggregates of stacked asphaltenes with an approximate size of 2 nm. In the second stage, nanoaggregates assemble and form clusters of nanoaggregates with an approximate size of 5 nm. In the third stage, in a high concentration of clusters, flocculation, a prerequisite of macroscopic precipitation, occurs.⁶

The molecular-level understanding of the factors promoting nanoaggregation and flocculation of asphaltenes is lacking. Asphaltenes, as the heaviest fraction of crude oil, are classified as a

solubility class: they are soluble in aromatics such as benzene and insoluble in n-heptane. Thus, the research in the last decades has treated asphaltenes as a class of molecules.^{6,7,9,15,16,63} Despite the proposed stepwise mechanism, the Yen-Mullins model does not provide a quantitative measure that links asphaltene's molecular characteristics to precipitation behavior. To efficiently prevent asphaltenes' precipitation, we need a qualitative and quantitative molecular understanding of the interaction between different crude oil components. Several molecular dynamics (MD) studies have investigated the aggregation of asphaltene molecules in implicit and explicit solvents.^{52–54,56,57,77–80} However, these studies only investigate nanoaggregation with a nonsystematic approach where they do not connect their molecules' molecular aspects to their aggregation behavior. For instance, there are medium-scale MD studies^{56,57,77}, with a limited number of asphaltene, which is only suitable for investigating the nanoaggregation stage. The current explicit-solvent studies are not large enough to test clustering and flocculation stages. One mesoscale coarse-grained (CG) study¹⁴ investigated all the three stages of the Yen-Mullins model with only asphaltenes. Also, using a CG approach could overlook the effect of critical atomistic details, such as hydrogen bonding.

The molecular-level understanding of the role of resins in affecting asphaltene precipitation is lacking. The effect of resins on the aggregation of asphaltene has been studied experimentally.^{4,40,46,62,70–72} For example, Soorghali et. al. found that resin from one oil decrease the severity of precipitation in another oil. However, they did not investigate this effect from a molecular perspective. All the past studies on resin's effect on asphaltenes aggregation have treated both as a class of molecules without considering their specific characteristics. Moreover, no flocculation scale simulation has investigated the effect of resin on flocculation. Thus, it is necessary to investigate resin's effect in the context of all Yen-Mullins stages of the aggregation.

This treatment of resins and asphaltenes as a class of molecules negatively affects investigators' capability in providing molecular insights. In this paper, we address two open questions in the field: 1. How do molecular-level features of asphaltenes affect nanoaggregation and flocculation of these molecules? 2. Do resins that deter nanoaggregation of asphaltenes also prevent further flocculation of these asphaltenes?

3.3 Computational Materials and Methods

3.3.1 Materials and System Setup

From the asphaltene set (A1–A8), shown in Figure 2.1A, some form nanoaggregates more intensely than the other ones due to the presence of certain molecular features such as large aromatic core and heteroatom(s). The set of asphaltene molecules were designed to study nanoaggregation and the effect of resins on the nanoaggregation.⁹⁸ This set was designed based on a number of previous experimental and computational studies, which provided insight on the structural scope of these chemical entities.^{25,55,77,81,82} Among the set in Figure 2.1A, the clustering and flocculation behavior of one mildly-aggregation and two readily-aggregation asphaltenes were investigated.

All of the individual asphaltene and resin structures were built in GaussView V.5.0.⁸⁶ and Avogadro⁹⁹. The Gaussian09 software⁸⁷ was used to optimize the geometry of all the structures. The B3LYP exchange-correlation functional in conjunction with the 6-31+G(d) basis set was used. We constructed six all-atom explicit solvent MD simulation systems from A4, A6, and A8, each containing 500 model asphaltene molecules. Three of the systems lacked the deterring resin, R3, to study clustering and flocculation of the asphaltenes in their neat state, and the other three contained R3 with the mass ratio of $R_w/A_w = 5$ to study the effect of a highly interrupting resin with three aromatic rings on clustering and flocculation of all three asphaltene molecules.

We randomly dispersed 500 counts of asphaltene molecules in simulation boxes. We chose n-heptane as the explicit solvent as it best differentiates the aggregation propensity of asphaltenes. The concentration of the asphaltenes was 0.1M in each experiment. In our previous study⁹⁸ we found that the size of the aromatic core and the presence of heteroatom(s) are two key molecular features in the aggregation process of asphaltenes. Also, heteroatom(s) and the size of the aromatic core are the dominant molecular feature of resin in interrupting the aggregation. These six systems test the effect of these molecular features in the clustering and flocculation of asphaltenes in the absence and the presence of an effective resin. We picked R3 for the clustering studies as it has the most abundant and yet effective molecular feature (the sizable aromatic ring) among resins we previously studied.

We used molecular dynamics (MD), which is the method of choice to study processes that are either very difficult for experimental methods or currently impossible. MD provides atomistic resolution as well as insight into the dynamics of the process of interest. We performed all-atom explicit solvent simulations for all of the above systems. Model asphaltenes and resin molecules were parameterized using the OPLS-AA force field. OPLS-AA force field is known to reproduce experimental thermodynamics observables for organic and, in particular aromatic molecules.⁸⁴ We also showed that OPLS-AA replicates the experimental 2D-IR orientational parameters for a model asphaltene molecule called Violanthrone-79⁸⁵ (See SI in Chapter 2). The RESP method⁸⁸ was used for calculating partial charges on individual atoms. Each system’s initial configuration was energy minimized by using the steepest descent method to remove any existing high-energy structures. The time step for each simulation was 2 fs , and we recorded the positions and energies every 2 ps . For all systems of study, the simulations were performed in the isothermal-isobaric ensemble (NPT). Nose-Hoover^{91,92} and Parrinello-Rahman⁹³ algorithms were used to keep average temperature and pressure constant at $T = 300\text{ K}$ and $P = 1\text{ bar}$ respectively. A cubic periodic boundary was applied for all of the systems to simulate infinite bulk behavior. Long-range electrostatic interactions were treated by Particle Mesh Ewald (PME).⁹⁴

We simulated the aggregation of the neat A4 and neat A6 for 300 ns and A8 for 200 ns. We simulated aggregation of the other three systems of A4, A6, and A8 in the presence of R3 for 150 ns. We also investigated the clustering of 100 counts of A8 in order of magnitude more dilute (0.01M) system to ensure that clustering happens in lower concentrations of the readily-aggregating asphaltene (See SI). However, it is noted that the formation of a single cluster aggregate takes a significantly longer time (600 ns). The system size is about 1.8 million atoms, which makes it substantially more expensive to study systems in very dilute concentration. Hence we only studied the aggregation behavior of asphaltenes in higher concentration to both reduce the simulation times and study the flocculation, which happens in a high concentration of clusters.

Due to the large size of the computations, we used several supercomputers for the simulation of the above systems. The computational resources in this work were of size 60 to 72 Intel’s Xeon

cores located on cluster computers. All the molecular dynamics simulations were run using the Gromacs 5.0.4 software.^{89,100} To visualize the molecular systems we used VMD 1.9 package.⁹⁰ Both Gnuplot¹⁰¹, and Matplotlib¹⁰² were used for generating plotted figures.

3.3.2 Analysis Methods

Aggregation Number

The number of aggregates on each experiment was calculated to compare the aggregation behavior of asphaltenes and the effect of resin on the aggregation. To calculate the number of aggregates as well as aggregate sizes (by count), we used a distance-based clustering algorithm, which uses a cutoff distance to count an individual asphaltene as part of an aggregate. As depicted in Figure B.1 in SI, a range of cutoff distances were scanned to find the appropriate distance. We used a cutoff distance of 0.37 *nm* between heavy atoms of the asphaltenes, which captures both face-to-face stacking as well as edge-to-edge stacking of asphaltenes. The result of the clustering algorithm is consistent with the visual analysis of the trajectories.

Aggregation Propensity

Aggregation propensity (AP) was measured in every time step by calculating the Solvent Accessible Surface Area for the individual asphaltenes and the aggregate. We used AP as a single scalar value to measure the tendency of asphaltene for the formation of aggregate in the absence and in the presence of resin. In this analysis, we calculated the ratio of the sum of solvent accessible surface area (SASA) values of the individual monomers to the SASA of entire aggregate(s) as AP in each time step along the trajectory.

Equation A.1 was used for calculation of AP every 2 ps. In this equation, SASA represents the surface area of asphaltenes accessible for solvent molecules. In the dispersed state of asphaltene molecules, SASA is expected to be at its maximum. If the SASA does not change during the simulation, the AP value will be close to unity; however, if SASA decreases due to the aggregation process in which the surface area accessible to the solvent decreases, the AP value will increase. A larger AP value is indicative of a higher aggregation tendency for that particular asphaltene.

The readily-aggregating asphaltenes have larger AP values compared to the mildly-aggregating asphaltenes. In the presence of a deterring resin, the AP value decreases.

$$AP = \frac{\overline{\text{SASA}}_{\text{monomer}}}{\text{SASA}_{\text{Aggregate}}} \quad (3.1)$$

Radius of Gyration

The radius of gyration (R_g) was used to estimate the size of the final aggregates in readily-aggregating asphaltenes. R_g is the root mean square of the distance between individual atoms of the aggregate and its center of mass. R_g of the asphaltenes in the absence of the resin gives us information about the overall dimension of the aggregate, where we can measure if the aggregate has surpassed the nanoaggregation and clustering stages. R_g was used in combination with the distribution of the number of aggregates to probe the physical dimensions as well as aggregate contents.

Equation 3.2 shows how the R_g is calculated for a single large aggregate where m is the mass of individual atoms, and r is the distance of each atom from the center of mass of the aggregate.

$$R_g = \left(\frac{\sum_i |\mathbf{r}_i|^2 m_i}{\sum_i m_i} \right)^{1/2} \quad (3.2)$$

Based on the Yen-Mullins model⁶, the size of an asphaltene cluster is about 5 nm. Considering the cluster's volume, it is about 16 fold larger than the volume of a typical nanoaggregate, which is 2 nm in diameter.⁶ This value is calculated from the ratio of their volume ($4/3R^3$) with the assumption that both nanoaggregate and cluster are spherical in shape. Hence, for clustering, the count of asphaltenes should be approximately 16 times the count of a nanoaggregate. Considering the low end of 5-7 asphaltene criteria from the Yen-Mullins model, it would be around 80 asphaltene molecules. With 500 counts of asphaltene molecules, both clustering and flocculation can be studied from molecular level resolution.

3.4 Results and Discussion

3.4.1 Flocculation of Neat Asphaltenes

From Single Molecules to Flocculation

In this work, we identified distinct species from single molecules up to a single massive aggregate. Based on the Yen-Mullins model⁶, aggregation of asphaltenes starts with the nanoaggregation of several single asphaltene molecules. In the second stage, clusters are formed with the aggregation of several nanoaggregates. In high concentrations, clusters further aggregate to flocculation. Flocculation is an essential step for the macroscopic deposition of asphaltenes. Clustering and flocculation do not occur for all of the asphaltenes in this study. However, for the asphaltenes that show such proceeding aggregation behavior, the aggregation starts from its first steps by nanoaggregation of single molecules up to flocculation. Nanoaggregates and clusters have approximately one order of magnitude size difference. As depicted in (Figure 3.1), the relative size of a nanoaggregate, a cluster, and a flocculate of clusters is distinguishable in 100 ns of the simulation in the aggregation of a readily-aggregating asphaltene. The aromatic cores of the asphaltene are highlighted in red, and the hydrogen bonds are shown with blue lines. Such distinction between stages of aggregation allowed us to determine the status of aggregation for each category of asphaltenes in the absence and presence of a resin.

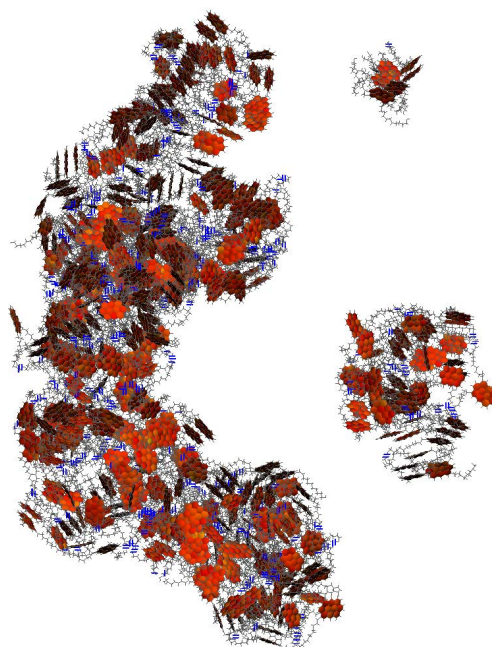


Figure 3.1: From nanoaggregates of readily-aggregating asphaltene, A8, to clustering and flocculation stages. Small aggregate made of 7 single A8 molecules, with a diameter of approximately 2 nm in top right corner to larger clusters of nanoaggregates in the bottom right and finally accumulation of clusters of A8, all are detectable in this snapshot half-way through the simulation of 500 A8 molecules in the light crude environment.

Mildly-aggregating Asphaltene Does not Flocculate

The aggregation behavior of a mildly-aggregating asphaltene, A4, was investigated in the absence of resin to probe the dynamics and the extent of its aggregation. As shown in Figure 3.2A, first 10 ns, aggregation started with the formation of primary aggregates, such as dimers and trimers, where the total numbers of aggregates dropped from 500 (only monomers) to 250 aggregates. Over the next 40 ns, further addition of molecules to the primary aggregates generated nanoaggregates. No additional aggregation was observed with the mildly aggregating A4, despite continuing the simulation for 300 ns and using such a high concentration (0.1M). As shown in Figure 3.2A, the steady value of 100 indicates that the average aggregate had 5 monomers of A4 in it, which is a typical number for a Yen-Mullins nanoaggregate (5-7). Figure 3.2B shows a representative snapshot of A4 nanoaggregates. The nanoaggregates do not grow and form clusters

out of nanoaggregates. They are in the process of forming and falling apart. This behavior from a mildly-aggregating asphaltene suggests that even in the presence of a large number of asphaltenes, a mildly-aggregating asphaltene does not proceed to the clustering and flocculation stages. The mildly-aggregating A4 does not contain proper molecular characteristics to grow beyond nanoaggregation. Due to the lack of a heteroatom and insufficient size of its aromatic core, this asphaltene does not flocculate. We can predict the clustering and flocculation behavior of a mildly-aggregating asphaltene such as A4 indirectly from their molecular features and directly from their AP values and also from ΔG_{iso} values obtained from nanoaggregation studies. Here we showed that with $AP = 1.9$ and $\Delta G_{iso} = -0.5 \text{ kcal/mol}$, A4 does not reach a large enough aggregate size to form clusters. We can conclude that an $AP > 1.9$ and a $\Delta G_{iso} < -0.5 \text{ kcal/mol}$ is required in order to form clusters. (See Chapter 2 for the table of AP and ΔG_{iso} values.)

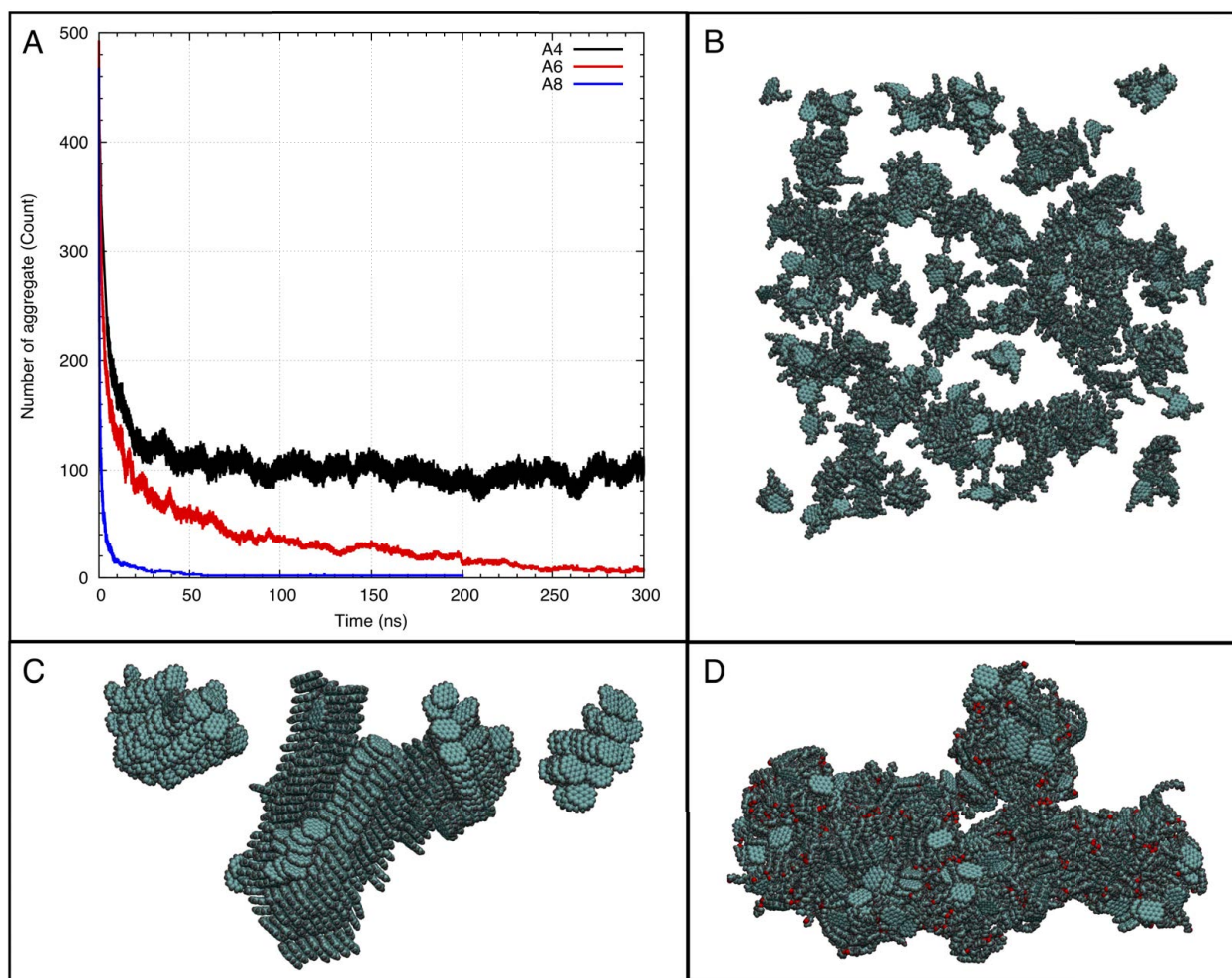


Figure 3.2: Aggregation behavior of asphaltenes in the absence of a resin. A) Number of aggregates of neat asphaltenes vs. simulation time where we can see the average aggregate size (the ratio of 500 to the number of aggregates). For example, for the mildly-aggregating A4, beyond 50 ns this number is 5 monomers, which is the size of a typical nanoaggregate. We can see the mildly-aggregating A4, in black, does not form clusters and is stagnant in the nanoaggregation stage, whereas readily-aggregating asphaltenes A6 and A8, in blue and red, proceed beyond the nanoaggregation stage and form clusters that later flocculate. B) A representative snapshot from nanoaggregates of A4 toward the end of the simulation shows despite a high concentration of A4 nanoaggregates, they do not further grow to clusters. C) A representative snapshot of A6 toward the end of the simulation shows rod-shaped grown flocculate out of clusters. D) A representative snapshot from A8 toward the end of the simulation shows more globular shape A8 flocculation due to its aliphatic tails with the capability of forming a hydrogen bond. In all molecular images above n-heptane, molecules are removed for clarity.

Readily-aggregating Asphaltenes Flocculate

The large scale aggregation of readily-aggregating asphaltenes, A6 and A8, was investigated in the absence of resin to probe their aggregation extent. Through nanoaggregation studies, A6 and A8 were classified as readily-aggregating asphaltenes by both AP and ΔG_{iso} metrics. As depicted in Figure 3.2A, unlike the mildly-aggregating asphaltene, both A6 and A8 formed stable nanoaggregates early in the simulation. After the first 10 ns, A6 and A8 quickly proceeded to form clusters. A6, with only one favorable to aggregation molecular feature (a large aromatic core), had a slower pace in developing clusters compared to A8, with two favorable to aggregation features (a large aromatic core and heteroatoms). As shown in Figure 3.2A, after nanoaggregation, both A6 and A8 quickly grew to clusters before growing more slowly to flocculates.

However, there was a difference in the slope of the curves for A6 and A8 in all three stages of aggregation shown in Figure 3.2A, which is due to the difference in their AP and ΔG_{iso} values. With larger AP and smaller ΔG_{iso} values, A8 is more prone to flocculation than A6. The higher AP value of A8 and more negative ΔG_{iso} resulted in reaching the flocculation stage in an earlier time scale compared to A6 at the same condition.

Flocculation of A6, with the $AP = 2.23$ and $\Delta G_{iso} = -2.2 \text{ kcal/mol}$, suggests that the critical criteria for a successful clustering and flocculation is near these values. Based on the criteria from the classification of readily-aggregating asphaltenes ($AP \geq 2.1$ and $\Delta G_{iso} < -1.5 \text{ kcal/mol}$), these values can be set as critical criteria for clustering and flocculation. Both $AP = 2.8$ for A8 and $\Delta G_{iso} = -7.2 \text{ kcal/mol}$ satisfy the critical criteria for clustering and flocculation.

The readily-aggregating A6 and A8 have features favorable to aggregation that support their further aggregation, and therefore these characteristics directly predict their aggregation extent according to their flocculation simulation. A6 has a large enough aromatic core with 10 benzene fused rings. However, even though A6 lacks any favorable to aggregation heteroatoms, it does eventually flocculate. This suggests that the existence of heteroatom is not necessary for clustering and flocculation. Similarly, A8 has both a sizeable aromatic core and two heteroatoms, proceeded to flocculation.

Both AP and ΔG_{iso} values, which were calculated from nanoaggregation studies, show predicting capacity. We showed in Chapter 2 that these metrics can be calculated using the diverse molecular features of asphaltenes and the linear equations obtained from nanoaggregation studies. Hence, in addition to the calculation of AP and ΔG_{iso} , we can use the molecular features of any new asphaltene molecule to directly predict its clustering and flocculation behavior.

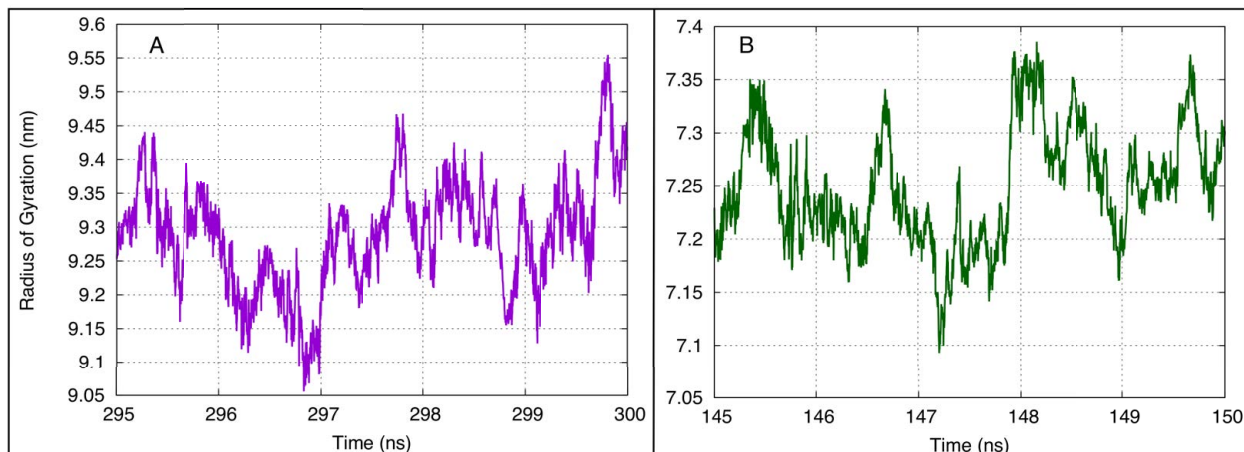


Figure 3.3: Radius of gyration of readily-aggregating A6 (A) and A8 (B) in last 5 ns of simulations show that they both form large clusters (Cluster size > 5 nm) that proceed to flocculation by aggregation of clusters of nanoaggregates.

Dynamics of the Yen-Mullins Stages with Molecular Details

The three stages of the proposed Yen-Mullins model for the flocculation of asphaltene was simulated for the first time with all-atom MD. Asphaltenes started from their single-molecule solvated state and assembled all the way up to flocculation. In the first stage of the Yen-Mullins model, single molecules dimerized by stacking and then continued to combine until nanoaggregates were formed. In the next stage, adjacent nanoaggregates are assembled to form clusters, and these clusters are assembled to flocculates via diffusion. Figure 3.2A shows these stepwise aggregation for A6 and A8 molecules. The general change in pace between stages, shown in Figure 3.2 is due to the slower diffusion of large clusters compared to smaller nanoaggregates in the flocculation and clustering steps, respectively. Moreover, as shown in Figure 3.3, the radius of gyration (R_g) off

final aggregate oscillates around 7.3 nm for A8 and approximately 9.5 nm for A6. These aggregate sizes are above the cluster size criteria of 5 nm and indicate flocculation, which is beyond the clustering stage. Our results verify the molecular mechanism proposed in the Yen-Mullins model⁶ by demonstrating all three distinct species within an all-atom MD simulation.

The shape of the large aggregates depends on the molecular characteristics of the asphaltenes. Figure 3.2C and Figure 3.2D depicts the flocculation of clusters of A6 and A8 asphaltenes. A8 formed a more globularly shaped aggregate, whereas A6 formed a rod-shaped aggregate. A8 with tangling aliphatic tails aggregates in a less organized fashion and is more prone to form a globularly shaped aggregate. On the contrary, A6 is less flexible in aggregation due to the lack of aliphatic tails, and its aggregates need to be more organized to have an effective $\pi - \pi$ stacking and hence forms rod-shaped like aggregates. This observation suggests that the microscopic shape of the aggregates depends on the shape of the individual asphaltene molecules.

3.4.2 Flocculation of Asphaltene Classes in the Presence of Resin

Nanoaggregates of Mildly-aggregating Asphaltenes are Downsized by Resin

The aggregation of the mildly-aggregating A4 was investigated in the presence of resin to probe the effect of resin on the aggregation behavior with 500 A4 molecules. As expected from nanoaggregation studies, introducing R3 did not promote the aggregation of the mildly-aggregating A4. As shown in Figure 3.4A, in the presence of R3, which is one of the most deterring resins based on the nanoaggregation simulations in Chapter 2, the initial stacking of A4 molecules are inhibited such that even dimerization happens more slowly compared to the neat state where there was no resin. Due to the deterring effect of R3, the nanoaggregation step was very slow, and the nanoaggregates of A4 were further destabilized. The slower formation of primary aggregates and destabilized nanoaggregates is due to the competition between asphaltene-asphaltene and asphaltene-resin attractions forces. (see Appendix II) Figure 3.4B shows R3 molecules in red in direct interaction with the A4 molecules preventing them from forming Yen-Mullins nanoaggregates (5 asphaltenes). It appears that A4 nanoaggregates are further destabilized in the presence of the resin.

The average size of nanoaggregates for A4 is smaller than its neat state in the presence of resin. The average size of aggregates decreased drastically in the presence of R3 and dropped from nanoaggregates with 5 asphaltene to smaller nanoaggregates and even pre-aggregates such as dimers and trimers. As shown in Figure 3.4, the average size of the nanoaggregates dropped from 5 asphaltene per nanoaggregate to 2.5 asphaltene per nanoaggregate. As depicted in Figure 3.5, the resin disrupted the nanoaggregation of the A4 and shifted the distribution of the number of aggregates to the right, where there is a larger number of nanoaggregates of smaller size compared to the neat state of this mildly-aggregating asphaltene. This distribution was calculated for the last 100 ns of the simulation, where the slope of the line in Figure 3.4A is about zero.

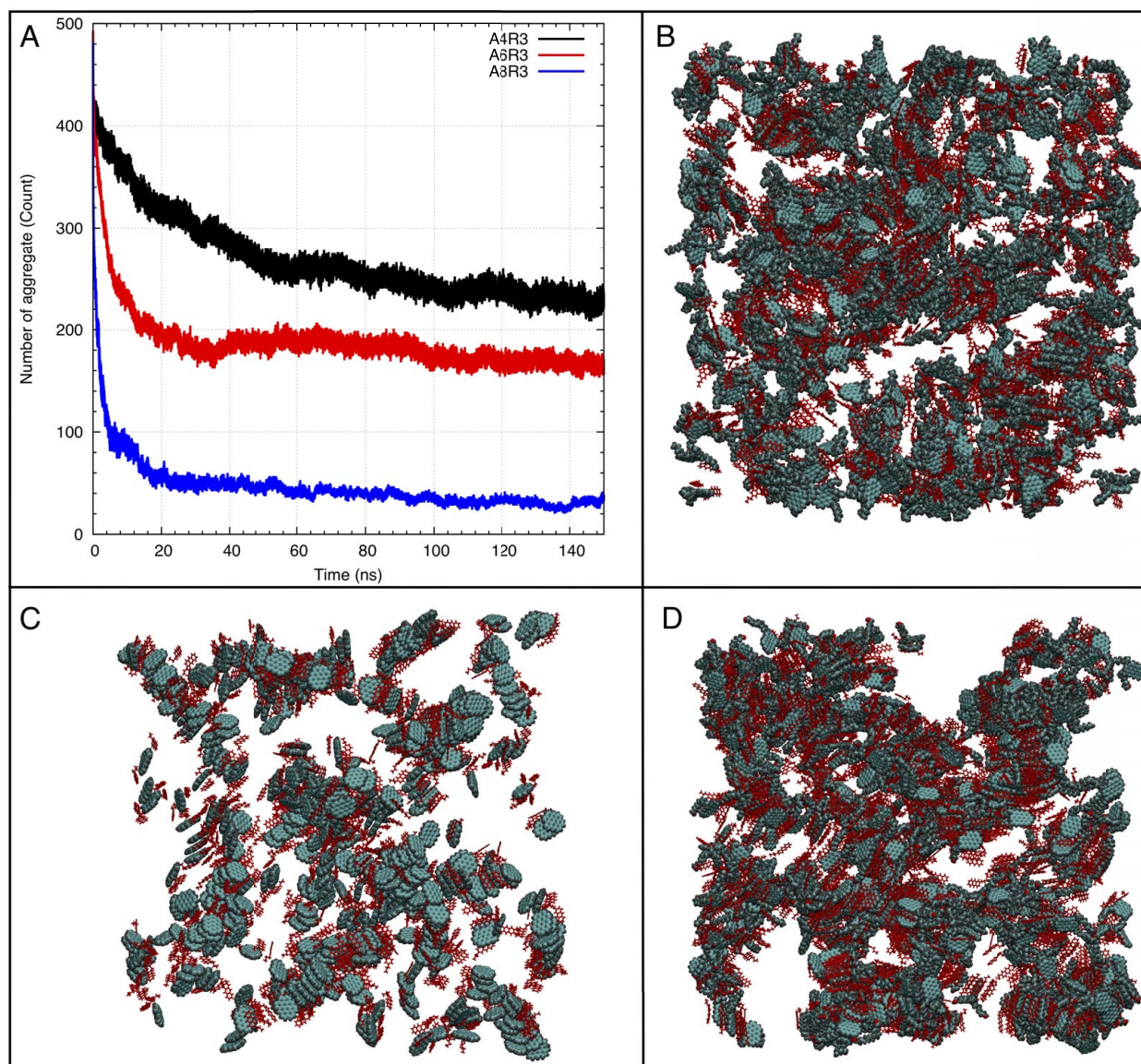


Figure 3.4: Aggregation behavior of asphaltenes in the presence of a stabilizing resin (R3). A) Number of aggregates of asphaltenes vs. time where the total number of aggregates for mildly-aggregating A4, in black, has decreased in comparison to its neat state in the absence of resin. Also, readily-aggregating asphaltenes A6 and A8, in blue and red, do not proceed beyond the nanoaggregation stage and do not form large clusters that would form a single aggregate of 500 asphaltenes. B) A representative snapshot from A4 nanoaggregates toward the end of the simulation where resins in red directly interact with the nanoaggregates and pre-aggregates of the asphaltenes. C) A representative image from A6 nanoaggregates toward the end of the simulation with resin molecules, in red, interacting with asphaltenes. D) A representative snapshot from A8 nanoaggregates toward the end of the simulation with resin molecules, in red, interacting with nanoaggregates of A8. In representative snapshots, A, B, and C, n-heptane molecules are removed for clarity.

Readily-aggregating Asphaltenes Do not Form Clusters in the Presence of Resin

We studied the aggregation behavior of two readily-aggregating asphaltenes, A6 and A8, in the presence of a deterring resin to probe the effect of resin in clustering and flocculation stages. Shown in Figure 3.4A, A6 with a favorably large aromatic core behaves like a mildly-aggregating asphaltene in the presence of R3. As shown in Figure 3.4C in the presence of the resin, A6 did not further aggregate to form large clusters, and hence flocculation did not occur; this is in contrast to its neat state, where both of these behaviors were observed. Similarly, R3 stops the aggregation of the readily-aggregating asphaltene A8 in the nanoaggregation stage. The statistical distributions observed in the number of aggregates is the signature of mildly- versus readily-aggregating asphaltenes. A normal distribution denotes a mildly-aggregating asphaltene, while an exponential decay denotes a readily-aggregating asphaltene. As shown in Figure 3.5, the distribution of the number of aggregates was shifted from exponential decay to normal distribution for both A6 and A8, where there are no clusters formed, and the only stable form of aggregate is nanoaggregate. The average number of molecules in the nanoaggregates based on the Figure 3.4 is 3 for A6 and 10 for A8. This shows that A8 is less affected by R3 than A6 is.

The readily-aggregating asphaltenes were inhibited by resin with different degrees due to the difference in their molecular features. Readily-aggregating A6 and A8 with $AP > 2.1$ and $\Delta G_{iso} < -1.5$ did not form clusters in the presence of R3. However, R3 is more effective in inhibiting the flocculation of A6 with only one favorable molecular factor compared to A8 with two favorable molecular factors in aiding aggregation. The difference in inhibiting efficiencies demonstrates the critical role of the dominant molecular features on asphaltene and resin molecules both in the flocculation and inhibition of deposition.

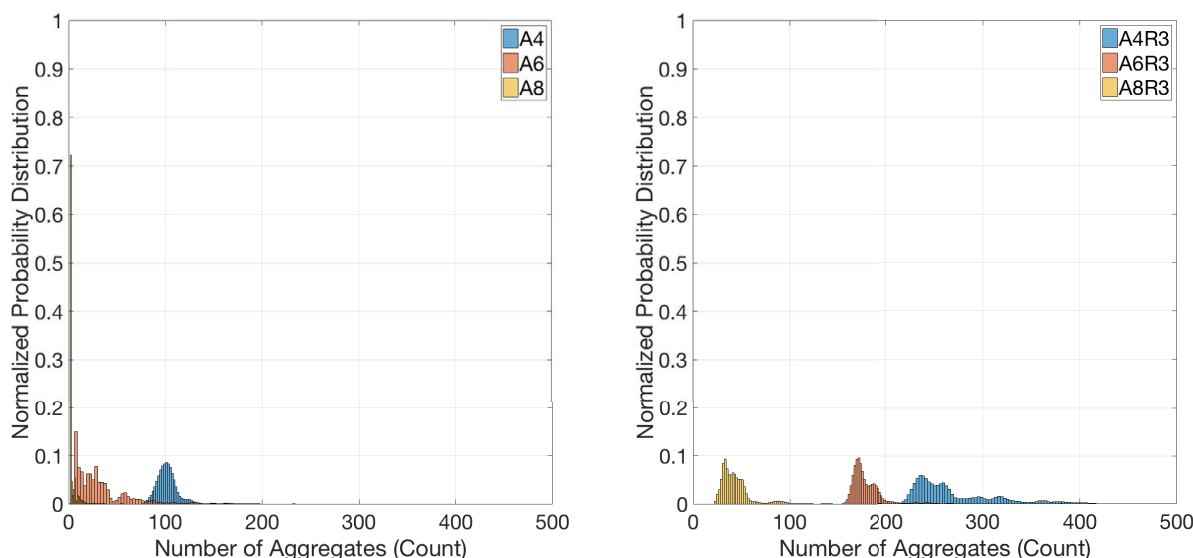


Figure 3.5: The normalized probability distribution of number of aggregates in the last 100 *ns* of simulation for asphaltenes in the absence of resin (left) presence of resin (right). These histograms show that resin shifts the distribution toward a larger number of aggregates, bringing down the average size of nanoaggregates for mildly-aggregating A4 and allowing readily-aggregating A6 and A8 to form only nanoaggregates by preventing further aggregation of their nanoaggregates.

3.5 Conclusion

The deposition of asphaltene is a substantial economic burden on the oil industry. Understanding the pre-deposition aggregation behavior of asphaltene in the absence and presence of resin in relation to their molecular features is an essential step in finding suitable natural resins as stabilizing agents. We previously showed that resins with three aromatic rings and resin with sulfur heteroatom as their effective molecular features could inhibit the formation of stable asphaltene nanoaggregates. In this work, we used all-atom molecular dynamics simulations to investigate three stages of the Yen-Mullins model and the possibility of inhibiting the aggregation of asphaltene with an effective resin with three aromatic rings.

In the absence of resin, mildly-aggregating asphaltenes only reached the first stage of the Yen-Mullins model and remained stable in their nanoaggregate form. However, the readily-aggregating asphaltenes were observed to first form nanoaggregates, then clusters, then flocculate. We demon-

strated that even though both readily-aggregating asphaltenes obeyed the Yen-Mullins model, there were still observable differences based on the number of molecular features favorable to aggregation.

We learned that only the readily-aggregating asphaltenes contain an adequate number of favorable molecular features supporting them to proceed into clustering and flocculation. We also showed that resins could inhibit the formation of aggregates beyond simply destabilizing the nanoaggregate structures. In the presence of R3, with three aromatic rings, the formation of all three intermediate structures predicted in the Yen-Mullins model was interrupted. We conclude that a resin with a large enough aromatic core can inhibit further aggregation of nanoaggregates and prevent them from forming clusters and flocculates. This, in turn, prevents the macroscopic precipitation of the asphaltenes.

The results of this work give the predictive potential to the AP and ΔG_{iso} metrics beyond the nanoaggregation stage and validates the application of molecular features to predict the ultimate extent of aggregation as well as inhibition. In short, it is possible to inhibit the readily-aggregating class's precipitation by a stabilizing resin and to keep it in the stable nanoaggregate stage where they do not clog the oil wells and pipelines.

To date, no molecule specific study has tested all the three stages of the Yen-Mullins model with all-atom MD or the effect of resin on the clustering and flocculation of asphaltenes. Our results show that the AP and ΔG_{iso} metrics obtained from nanoaggregation studies are very useful tools and are applicable to predicting clustering and macroscopic deposition behavior. Hence, One could use the results of this work to screen and separate similar resins from natural resources like medium and heavy crude. Crudes containing a relatively high amount of resin with three aromatic rings can be used to prevent the precipitation of asphaltenes in light crude oil. Our results provide a detailed molecular explanation for the experimental research by Soorghali *et. al.*⁴⁰ and explains why some crude's resins are effective at stopping precipitation of asphaltenes while other crude's resins are not.

This study has only been done for standard temperature and pressure. The effectiveness of the results needs to be investigated in other conditions as well. Furthermore, in our study, the resin to asphaltene mass ratio is 5. Further investigations are needed on the effect of concentration of resin. Such a study could determine the minimum effective concentration of resin required in order to prevent the deposition of asphaltenes.

Understanding the molecular-level dynamics of aggregation of asphaltenes is essential for understanding the deposition problem. This understanding of dynamics and the knowledge of critical molecular features in flocculation and inhibition establishes a rational design to recognize or develop highly effective deterrents.

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Chapter 4

Conclusions

4.1 The Role of Resins in the Nanoaggregation of Asphaltenes

Due to vast differences in their molecular features, asphaltenes have various degrees of tendency to self-assemble and form aggregates of different sizes and shapes. Hence, the aggregation behavior of asphaltenes highly depends on their molecular characteristics. Asphaltenes are most likely to form deposit in lighter crude where there is an abundance of saturates, the fraction in which asphaltenes are considered an insoluble class of molecules. Use of n-heptane as solvent medium allowed us to determine the aggregation tendency of asphaltenes. In Chapter 2 we categorized asphaltenes into three categories of non-aggregating, mildly-aggregating and readily-aggregating asphaltenes based on their isodesmic free energy of binding values. These values were calculated by an isodesmic fit to the aggregate number distribution of asphaltenes in their neat state. A linear fit was achieved with the main molecular features as fit parameters. The size of the aromatic core, the number of heteroatoms present in the structure of asphaltene, as well as the size of aliphatic chain were directly linked to the aggregation tendency of asphaltenes. Using these molecular features as fit parameters, the isodesmic free energy of bindings were computed for each asphaltene. The comparison of coefficients for molecular parameters showed that the presence and number of heteroatoms as well as the size of the aromatic core are favorable features in nanoaggregation of asphaltenes. These results are also in accord with the aggregation propensity (AP) values that we calculated using SASA analysis where the same categories of aggregation of asphaltenes were obtained by AP values and isodesmic free energy of binding.

The role of in the aggregation of asphaltenes resins has not been clear in the literature. There have been a number of studies citing them as either factors causing aggregation or as agents preventing aggregation. However, these studies have looked at the resins as either a class of molecules or a fraction of crude oil, none have provided atomistic insight on why or how resins have any ef-

fect on the aggregation. Our results show that resins do not cause aggregation of asphaltenes. Even though some resins do not affect aggregation remarkably, most resins in our study interrupted the asphaltene nanoaggregation through different molecular features depending on the resin and asphaltene type. Similar to the neat asphaltenes, the isodesmic fit with six molecular parameters helped us to find the dominant molecular feature of resins responsible for deterring the aggregation of asphaltenes. Using ΔG_{iso} , we showed that the size of aromatic core and number of heteroatoms are two dominant features in deterring aggregation. Hence, resins with large enough aromatic cores and also resin with sulfur heteroatoms are capable of deterring nanoaggregation of mildly-aggregating and readily-aggregating asphaltenes. Our results provide molecular and atomistic detail on how resins from certain crudes can prevent aggregation in light and other types of aggregation prone crude oils, and suggest that the resins that do not prevent asphaltene deposition lack these sufficient molecular characteristics required for deterring aggregation.^{44,103}

4.2 The Role of Resins in the Clustering and Flocculation of Asphaltenes

The systems with 20 asphaltene molecules were not adequate for studying clustering and flocculation so we used massive systems with 500 asphaltene molecules to study the aggregation stages of clustering and flocculation. By metrics of SASA, radius of gyration R_g and aggregation size analyses, we investigated clustering and flocculation behavior of mildly-aggregating as well as readily-aggregating asphaltenes. We showed that the mildly-aggregating asphaltenes such as A4 do not proceed to the clustering and flocculation stage where asphaltenes can proceed to a macroscopic deposit. On the contrary, they remain in the form of small nanoaggregates despite high concentration. On the other hand, readily-aggregating asphaltenes such as A6 and A8 proceed to form large clusters that form flocculates, which ultimately lead to macroscopic deposits. The clustering and flocculation results are consistent with the predictions made by ΔG_{iso} and AP from nanoaggregation studies. Hence the predictive measures from nanoaggregation studies are extendable to macroscopic behavior.

We also showed that resin with three aromatic rings prevents clustering and flocculation of nanoaggregates for readily-aggregating asphaltenes A6 and A8. Not surprisingly, the same resin destabilizes the nanoaggregation of mildly-aggregating A4 and decreases the average aggregate sizes. Ultimately, our results in this work could be used in two ways:

First: To identify reservoirs with large capacities for deterring aggregation based on the molecular structures of their resin contents (This is the best-case scenario because it uses naturally occurring molecules to solve the problem rather than creating new molecules).

Second: Knowing the dominant molecular features for deterring aggregation opens the door for targeted synthesis of a new generation aggregation-preventing agents. Also, the screening of existing harmless inhibitors among vastly produced chemicals in the industry would be an option given the knowledge of dominant molecular features for preventing aggregation.

4.3 Summary

We studied the aggregation of asphaltenes in the context of Yen-Mullins stages of assembly. We classified asphaltenes into three categories via their isodesmic free energies of binding. The class of non-aggregating, mildly-aggregating, and readily-aggregating asphaltenes have distinct molecular characteristics. Using linear regression, we linked the molecular features of asphaltenes to their aggregation behavior metrics and qualitative aggregation behavior. We identified dominant molecular features of asphaltene in aiding aggregation. We found that resins, in general, deter the aggregation of asphaltenes, and we did not observe any promoting behavior from the resin set that we studied. An increase in the isodesmic free energies of binding indicates this inhibitive behavior of resins. Observations from flocculation studies showed that the insights from nanoaggregation studies apply to macroscopic deposition behavior. Linear regression of free energies of binding to molecular features on both asphaltenes and resin revealed the resin's critical molecular characteristics for their inhibiting action. One can use these computational tools to predict macroscopic deposition from molecular fabric. These molecular and atomistic insights pave the way to choose

appropriate resins with molecular features favorable to inhibition. Such resins can effectively deter the deposition of asphaltenes in problematic oil wells.

4.4 Future Directions

We investigated the effect of two of the most abundant heteroatoms in asphaltene and resins, sulfur and oxygen. Hence, we propose to investigate the effect of other heteroatoms and the effect of their location within the molecule on the AP and ΔG_{iso} of asphaltenes. Furthermore, we learned that heteroatoms are the dominant factor for causing or deterring asphaltene aggregation. More specifically, the heteroatoms capable of hydrogen bonding have a large effect on ΔG_{iso} . We propose to further study the asphaltene aggregation effects of resins with hydrogen bonding capable heteroatoms. Our preliminary results on this subject show great potential for resins with these functional groups. By modifying R1, the resin without a significant effect on deterring aggregation of A8 (a readily-aggregating asphaltene), we designed R7 shown in Figure 4.1. We observe that the number of hydrogen bonds between A8 molecules in a nanoaggregation study of 20 A8 molecules significantly drop in the presence of R7 (shown in Figure 4.2).

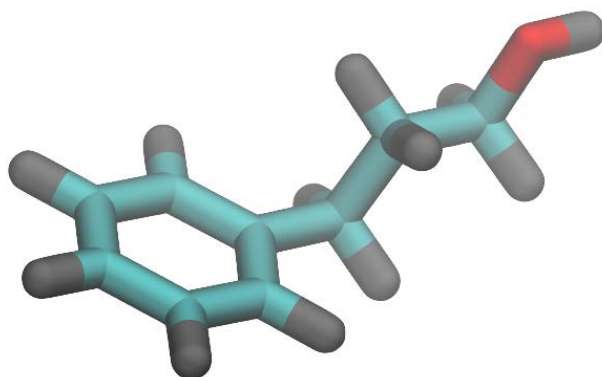


Figure 4.1: The schematic of a new proposed resin with hydrogen bonding capability. It is similar to R1 with an added hydroxyl group attached to the end of the aliphatic tail.

Since we learned that the results of nanoaggregation apply to clustering and flocculation, we can perform more diverse investigations into the effect of molecular structure on the aggregation

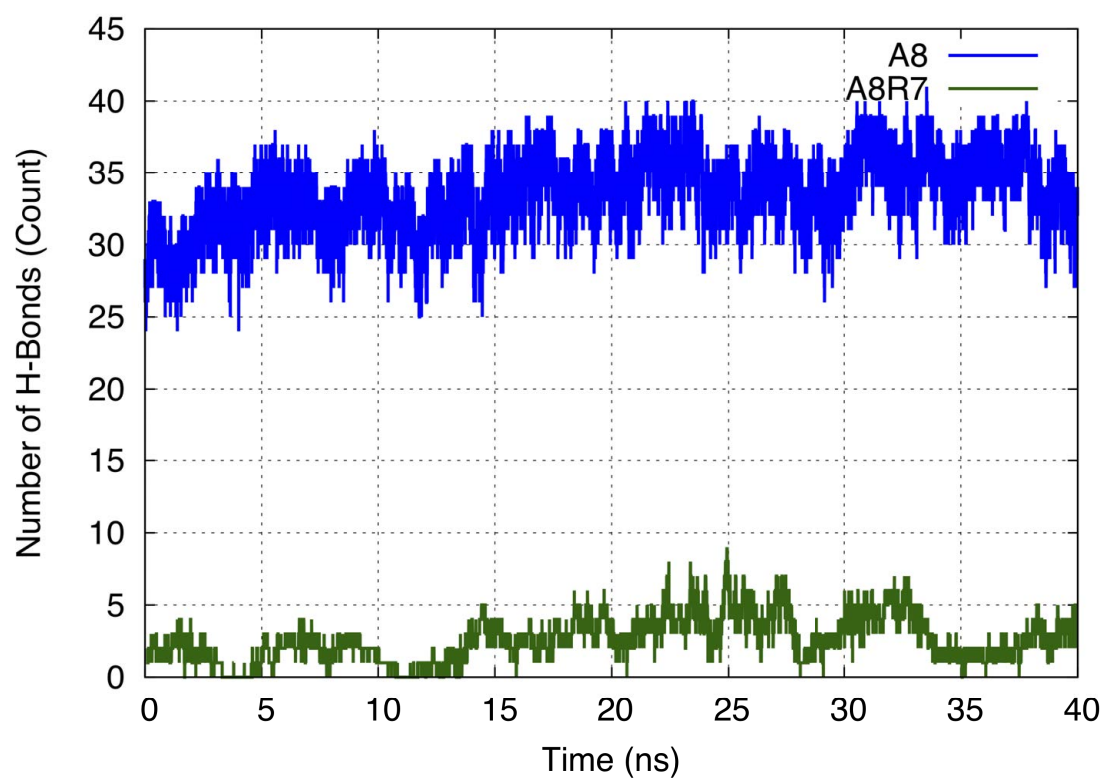


Figure 4.2: The effect of R7 on the number of hydrogen bonds A8 makes in the presence of the resin. Blocking hydroxyl groups by R7 molecules decreases the ability of A8 to aggregate.

behavior of asphaltenes by only performing nanoaggregation scale studies. We propose studying the effect of other heteroatoms such as Nitrogen. Also, investigation of other molecular features such as presence and type of heavy metals on the aggregation behavior can be performed.

The protocol of MD study we used in this work can be applied to more diverse asphaltenes and resins with an automated simulation workflow to fine-tune the model and improve its accuracy. Specifically, the use of slightly larger and more diverse resins with two, and four aromatic rings will help in finding the optimum size of aromatic core as well as number kind of heteroatoms on resins. These resin would be highly effective in deterring aggregation of readily-aggregating asphaltenes.

Ultimately, since we found that the resin to asphaltene mass ratio of 5 is effective in deterring aggregation, given resins contain the necessary molecular features, we speculate that smaller concentration of resins can be effective. Hence, we propose to study the effect of concentration of resin to find the minimum effective resin to asphaltene mass ratio required for deterring aggregation.

4.4.1 A Broad Perspective

Obtaining more detailed and accurate molecular insight into the aggregation process allows us to move from the treatment to the prevention strategy in dealing with asphaltene deposition problems. By fulfilling this goal, newer and more effective oil extraction processes can be developed to preserve maximum content of our natural crude oil resources. By preserving molecules such as asphaltenes, which have been seen more as a problem than an asset, we could use these valuable chemicals in producing smart materials, much needed for the ever-growing population. Furthermore, from an environmental viewpoint, their use in various areas of modern industries would be a much better approach than having them end up in wastelands.

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Appendix A

Supporting Information for Chapter 2

A.0.1 Isodesmic Model Derivation

Isodesmic model of aggregation assumes that each step of aggregation has the same K_{eq} value of association and hence same free energy of association. Assuming isodesmic behavior we worked out the below derivation that calculates number of aggregates for each asphaltene from isodesmic free energy of binding.

Definition of some terms:

Partitions: All the partitions of total number of initial monomers (20 for this case)

N_n : The number of clusters of size n

N_{clu} : Number of cluster

N : Total number of particles

G_{sys} : Free energy of the system

G_n : Free energy of a cluster size n

G_1 : Free energy of a monomer

ΔG_{iso} : Isodesmic free energy of binding

T : Temperature

We start by expressing G_{sys} as a function of cluster distribution.

For a given cluster partition we have.

$$G_{sys} = \sum_{n=1}^N N_n G_n$$

Assuming isodesmic behavior we have:

$$G_n = (n - 1)\Delta G_{iso} + nG_1$$

So,

$$G_{sys} = \sum N_n [(n-1)\Delta G_{iso} + nG_1]$$

Rearranging we have:

$$G_{sys} = (\Delta G_{iso} + G_1) \sum nN_n - \Delta G_{iso} \sum N_n$$

N is number of particles in the system.

$$N = \sum nN_n$$

N_{clu} is the number of clusters in the system.

$$N_{clu} = \sum N_n$$

Substituting we have:

$$G_{sys} = (\Delta G_{iso} + G_1)N - \Delta G_{iso}N_{clu}$$

So, total free energy for constant number of the particles can be obtained by summing over all cluster partitions. There are 627 total number of partitions for N=20.

Free energies do not add up but partitions do!

$$G_{tot} = -T \ln \left[\sum_{partition} \exp\left[-\frac{G_{sys}}{T}\right] \right]$$

Or, equivalently we can write:

$$Q_{tot} = \sum_{partition} Q_{sys}$$

$$Q_{tot} = \exp \left[-\frac{\Delta G_{iso} + G_1}{T} N \right] \sum_{partition} \exp \left[\frac{\Delta G_{iso} N_{clu}}{T} \right]$$

For N_1 we have:

$$\langle N_1 \rangle = \frac{\sum N_1 Q_{sys}}{\sum Q_{sys}} = \frac{\exp \left[-\frac{\Delta G_{iso} + G_1}{T} N \right] \sum_{partition} N_1 \exp \left[\frac{\Delta G_{iso} N_{clu}}{T} \right]}{\exp \left[-\frac{\Delta G_{iso} + G_1}{T} N \right] \sum_{partition} \exp \left[\frac{\Delta G_{iso} N_{clu}}{T} \right]}$$

Crossing off the first term:

$$\langle N_1 \rangle = \frac{\sum_{partition} N_1 \exp \left[\frac{\Delta G_{iso} N_{clu}}{T} \right]}{\sum_{partition} \exp \left[\frac{\Delta G_{iso} N_{clu}}{T} \right]}$$

Similarly for N_n

$$\langle N_n \rangle = \frac{\sum_{partitions} N_n e^{N_{clu} \frac{\Delta G_{iso}}{T}}}{\sum_{partitions} e^{N_{clu} \frac{\Delta G_{iso}}{T}}}$$

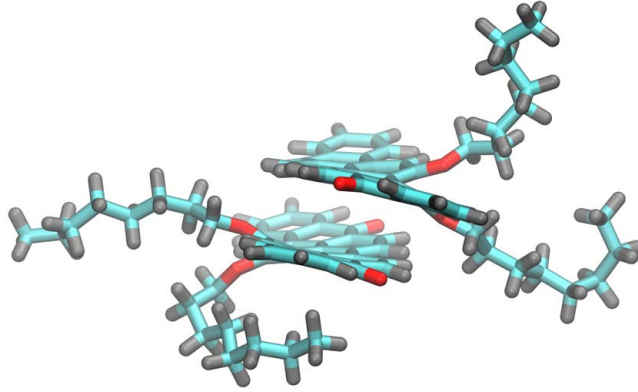


Figure A.1: Antiparallel orientation of Violanthrone-79 molecules.

Table A.1: Average and standard deviations for 6 helical parameters computed for dimer of Violanthrone-79 from MD simulations.

	Slide	Shift	Rise	Roll	Tilt	Twist
Average	-0.053	0.931	3.721	-4.504	5.319	187.567
STDEV	1.941	1.175	0.322	7.536	7.022	20.902

A.0.2 Aggregation Propensity (AP)

In order to measure aggregation status of asphaltenes along a simulation trajectory, quantities of solvent accessible surface area (SASA), and aggregation propensity (AP) were computed. SASA is the total area exposed to solvent by solute, where a decrease of the SASA value along a simulation trajectory is indicative of aggregation. Aggregation propensity (AP),¹⁰⁴, as a single scalar quantity, were calculated for each system by using SASA values. In simple definition, AP is the ratio of SASA of the asphaltenes in their initial non-aggregated configuration to their cumulative SASA in each time step. Aggregation propensity (AP) was calculated instantaneously at each time step and final singular AP value for each system was calculated by averaging instantaneous AP over last 50 ns. The SASA value was computed for each 20 individual asphaltene molecules (20 monomer) while ignoring all the other molecules. Individual SASA values were summated into one final value to get the initial non-aggregated SASA value. The total SASA of asphaltene computed for all 20 asphaltene ignoring other molecules which were not asphaltenes. Equation A.1 show the relationship between SASA and AP value.

$$AP = \frac{\sum_{i=1}^{20} SASA_{monomer(i)}}{SASA_{aggregate}} \quad (A.1)$$

At the beginning of the simulation where all the asphaltene molecules are dispersed, SASA has its highest value and aggregation propensity is unity by definition. Asphaltene molecules with a large AP value have a lower relative value of SASA toward the end of the simulation compared to the initial SASA value of the spread out configuration.

A.0.3 Aggregation Classes by AP

Figure A.2 shows the AP value for all eight types of asphaltene. Based on their AP value which is a measure of their different tendency to form aggregates, asphaltene molecules were categorized to three categories of: non-aggregating ($AP < 1.40$), mildly-aggregating ($1.40 \leq AP < 2.10$) and readily-aggregating ($AP \geq 2.10$). For example, A1 and A2 with AP value of

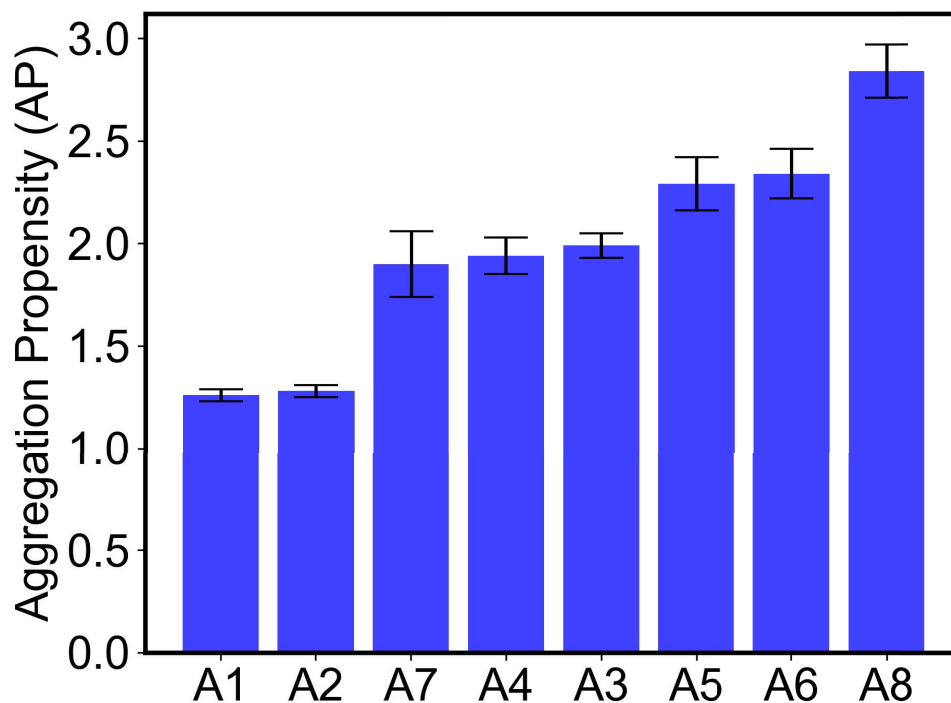


Figure A.2: Three classes of asphaltenes by aggregation propensity (AP) values is consistent with the three categories obtained from ΔG_{iso} value classifications.

1.26 and 1.28 respectively fall into the category of non-aggregating asphaltenes. On the other hand, A5, A6, and A8 belong to the category of readily-aggregating asphaltenes, which can make large and stable nanoaggregates with an aggregate size of equal to the total number of asphaltene molecules in the system meaning 20. Mildly-aggregating asphaltenes A3, A4, A7 do not form stable nanoaggregates. The classification by AP is consistent with classification by ΔG_{iso} values. Figure A.3 depicts the linear regression for AP values to the the number of benzene fused rings and number of heteroatoms on model asphaltenes.

As shown in Figure A.4, there is a strong correlation between AP values and ΔG_{iso} metric (Pearson correlation coefficient of -0.87 with $R^2 = 0.8$), which suggests that these two metrics contain similar information and both can be used for identifying dominant molecular features in aggregation and inhibition of aggregation. Both metrics can be used to classify aggregation behavior of asphaltenes. However, ΔG_{iso} provides a model for aggregation, which is related to thermo-

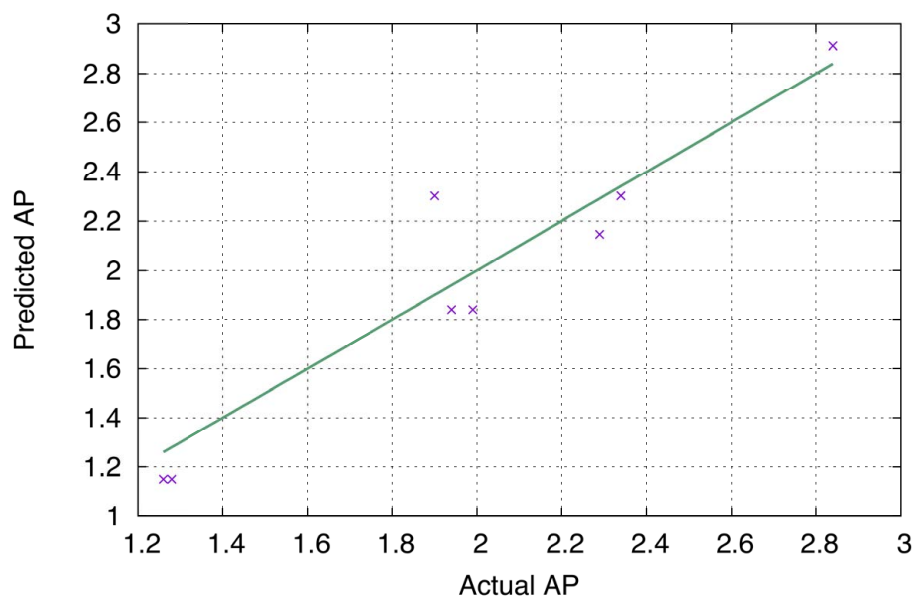


Figure A.3: Linear regression for AP value to asphaltene molecular features.

dynamical observables and the behavior of individual molecules rather than the final symptoms of these effect which are projected in forms of SASA and AP.

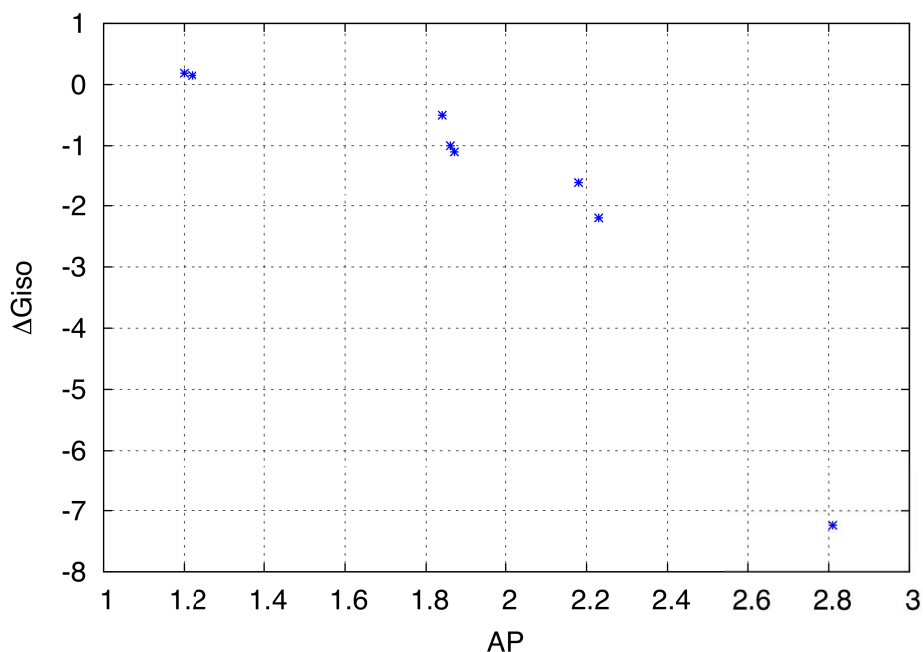


Figure A.4: The correlation between AP values and the isodesmic free energy of binding (in kcal/mol) for neat asphaltenes (A1-A8). Pearson correlation coefficient of -0.87 indicates that there is a strong correlation between ΔG_{iso} and AP values, which suggest they have similar information about the aggregation tendency of asphaltenes.

A.0.4 Dimerization Free Energies

We calculated the free energy of dimerization for our model asphaltene molecules in kJ/mol. However, as shown in Figure A.5, we did not find a very strong correlation between the free energy of dimerization and AP values as indicators of nanoaggregation behavior of asphaltenes. Furthermore, in order to extract dominant molecular features in probing the effect of resins on the asphaltenes, we would have needed to perform 56 expensive enhanced sampling calculations. With our resources, it would have taken approximately about 14 month of computation time with each system taking eight days to complete, which we avoided by using AP and ΔG_{iso} analyses. Appendix I contains the graphs of free energy of dimerization for A1 – A8.

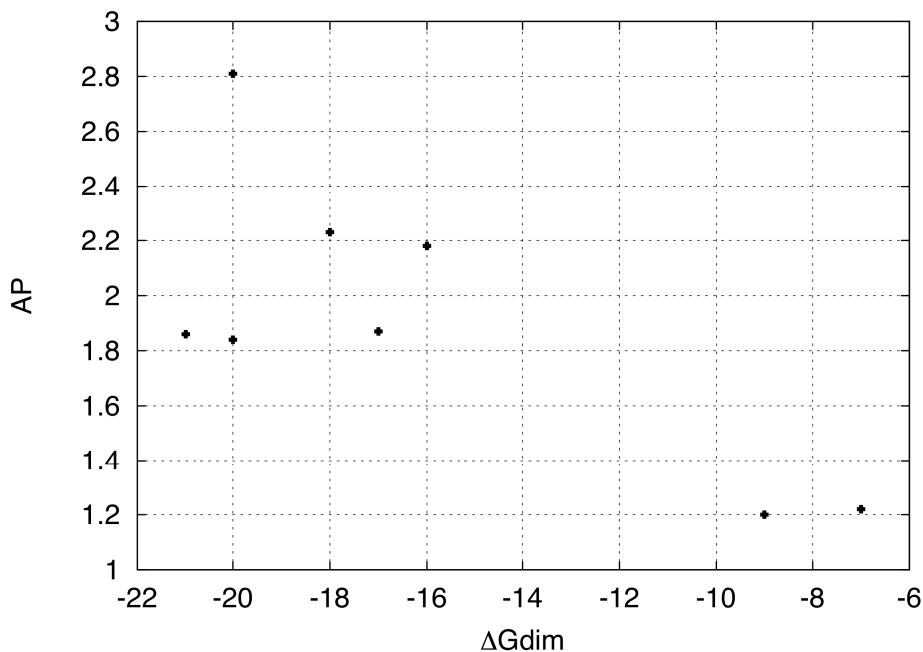


Figure A.5: The correlation between AP values and the free energy of dimerization for neat asphaltenes (A1-A8). There is not a very strong correlation between free energy of dimerizations and AP values (Pearson correlation coefficient of -0.76 with $R^2 = 0.58$) that could justify 56 expensive enhanced sampling simulations in order to identify dominant molecular features.

A.0.5 Interaction Metrics

Radial Distribution Function (RDF)

Radial distribution function (RDF) analysis was performed for asphaltene–asphaltene interactions both in the absence of resin (neat asphaltene) systems and asphaltene in the presence of resin systems to observe the change in the RDF due to the presence of resin. Also, the RDF of resin–asphaltene interactions was computed in order to study the strength of asphaltene–resin interaction and to study the relationship to the change in asphaltene–asphaltene RDF. Appendix (II) contains complete set of RDF plots for all of 56 systems. The complete collection of all RDFs can be found in appendix II.

Asphaltene-Asphaltene RDF

Asphaltene-Asphaltene RDF plots show the distribution of asphaltenes around each other. The first peak of RDF is indicative of immediate stacking of asphaltenes aromatic planes on top of each other. The second peak is indicative of second nearest neighbor of asphaltenes and similarly, the third peak belongs to the second nearest neighbor of asphaltenes. Figure A.6 shows the RDF of neat asphaltenes where the readily-aggregating ones such as A6 have consecutive peaks due to their structure and non-aggregating ones such as A1 only have one short peak, which is due to their lack of aggregate structure.

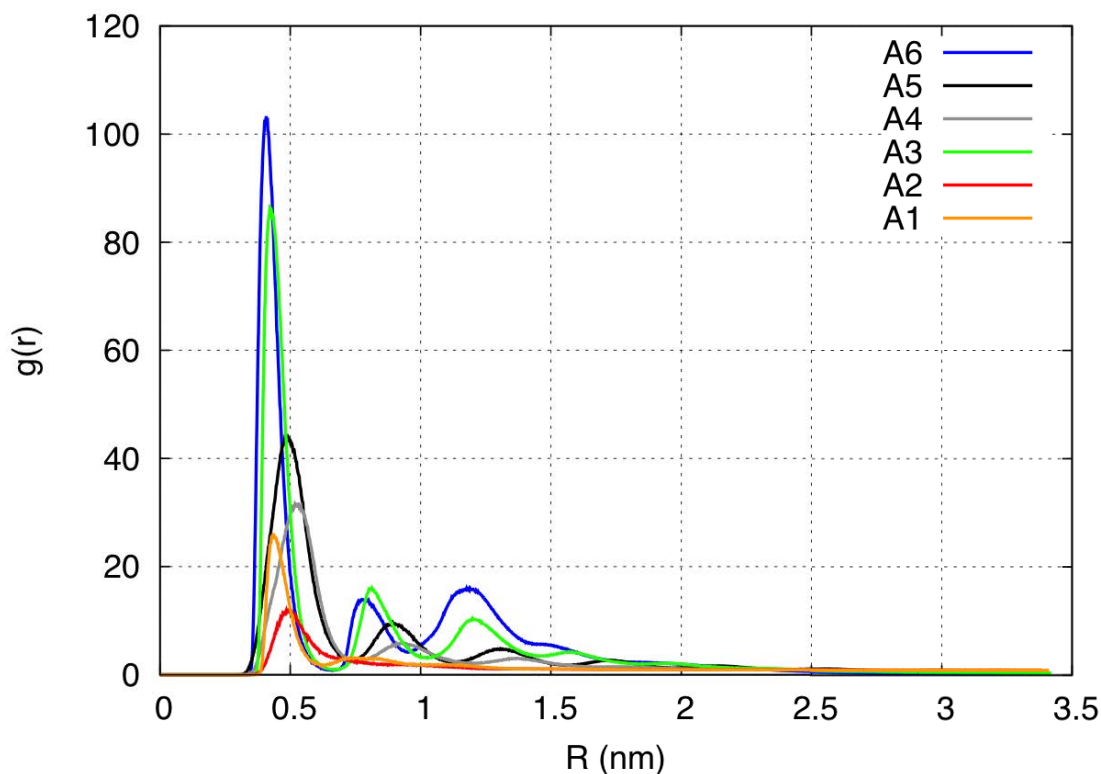


Figure A.6: Radial distribution function for neat asphaltene aggregation. Mildly-aggregating and readily-aggregating asphaltene show defined aggregate structures whereas non-aggregating asphaltenes show no structure.

Asphaltene-Resin RDF

Asphaltene-resin RDF shows the distribution of resins around asphaltenes. If there is a peak for asphaltene-resin RDF that is indicative of resin surrounding asphaltene molecules. If there is asphaltene–resin peak in the same distance as the first asphaltene–asphaltene RDF peak, it means that presence of resin interrupts an aggregation in dimerization stage. The peak of RDF beyond this point is indicative of interruption in higher order aggregates such as dimers, tetramers and nanoaggregation stage.

A.0.6 Effect of Resins on Nanoaggregation

We examined the general effect of resins in the aggregation behavior of asphaltenes via change in AP value for individual asphaltenes in presence of each type of resin. Aggregation propensity ratio (APR) is the ratio of AP value in the presence of resin to the AP value in the absence of resin. Table A.2 shows AP value of each asphaltene in presence of each resin, with the numbers in parentheses being APR values. For the resins studied here, APR value is generally smaller than unity, which means resins diminish aggregation propensity of asphaltenes. Comparing APR values in Table A.2 reveals that besides the general interruption of asphaltene aggregation there is different level of disruption by resins. According to the Table A.2, resins with either a sizable aromatic core and resins with heteroatom effectively interrupt aggregation of mildly-aggregating and readily-aggregating asphaltenes. Based on the APR values, asphaltene–resin interactions can be categorized into three main types. 1) Weak interaction ($APR < 0.9$): resins do not interact strongly in a direct or indirect form with the asphaltene molecules to interrupt its dimerization and further stacking. 2) Medium interaction ($0.70 < APR < 0.9$): Resins interact with the edge of stacked asphaltenes preventing them from forming stable stacks and nanoaggregates. 3) Strong interaction ($APR < 0.70$): there is a direct interaction between asphaltene and resin so that it can even disrupt asphaltene’s dimerization in some asphaltene–resin pairs. This categorization is semi-quantitative and its predictive capacity is limited. As shown in Figure A.7 the correlation between

APR and the area under RDF curves is not great. Also, RDF plots in Figure A.9 and Figure A.10 visually depicts strong and weak interactions by examples.

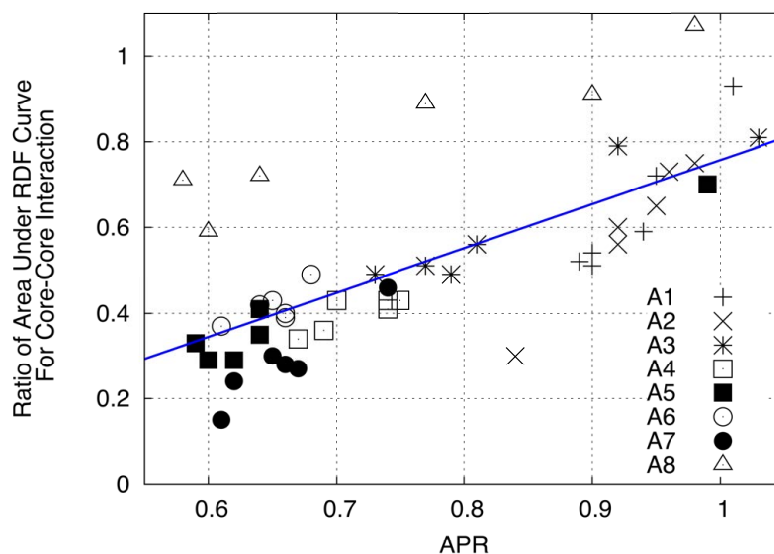


Figure A.7: Correlation between APR and ratio of area under asphaltene–asphaltene RDF curve for core–core interactions. As APR values approach unity the ratio of area under RDF curves do so as well. The unity means there is no difference in aggregation behavior in the absence and presence of resin. This area (upper right) is vastly occupied by A1 and A2 and the cases with weak interaction by resin such as A8 and R1.

Table A.2: Aggregation propensity (AP) for asphaltene molecules in the absence and presence of resin. Numbers in parentheses demonstrate APR values. The larger AP value is indicative of higher tendency for aggregation of asphaltene. The smaller value of APR are indicative of very effective interruption by resin.

R/A	A1	A2	A3	A4	A5	A6	A7	A8
NR	1.20 (1.00)	1.22 (1.00)	1.86 (1.00)	1.84 (1.00)	2.18 (1.00)	2.23 (1.00)	1.87 (1.00)	2.81 (1.00)
R1	1.12 (0.93)	1.16 (0.95)	1.94 (1.04)	1.36 (0.74)	2.16 (0.99)	1.46 (0.66)	1.37 (0.73)	2.77 (0.99)
R2	1.22 (1.01)	1.02 (0.84)	1.54 (0.82)	1.38 (0.75)	1.40 (0.64)	1.47 (0.66)	1.15 (0.61)	2.54 (0.90)
R3	1.10 (0.91)	1.16 (0.95)	1.49 (0.80)	1.36 (0.74)	1.33 (0.61)	1.40 (0.62)	1.24 (0.67)	1.64 (0.58)
R4	1.14 (0.95)	1.19 (0.97)	1.71 (0.92)	1.29 (0.70)	1.30 (0.60)	1.46 (0.65)	1.14 (0.61)	1.78 (0.63)
R5	1.08 (0.89)	1.12 (0.92)	1.38 (0.74)	1.24 (0.67)	1.39 (0.64)	1.44 (0.64)	1.21 (0.65)	1.60 (0.57)
R6	1.07 (0.89)	1.12 (0.92)	1.46 (0.78)	1.27 (0.69)	1.28 (0.59)	1.51 (0.68)	1.22 (0.65)	2.20 (0.78)

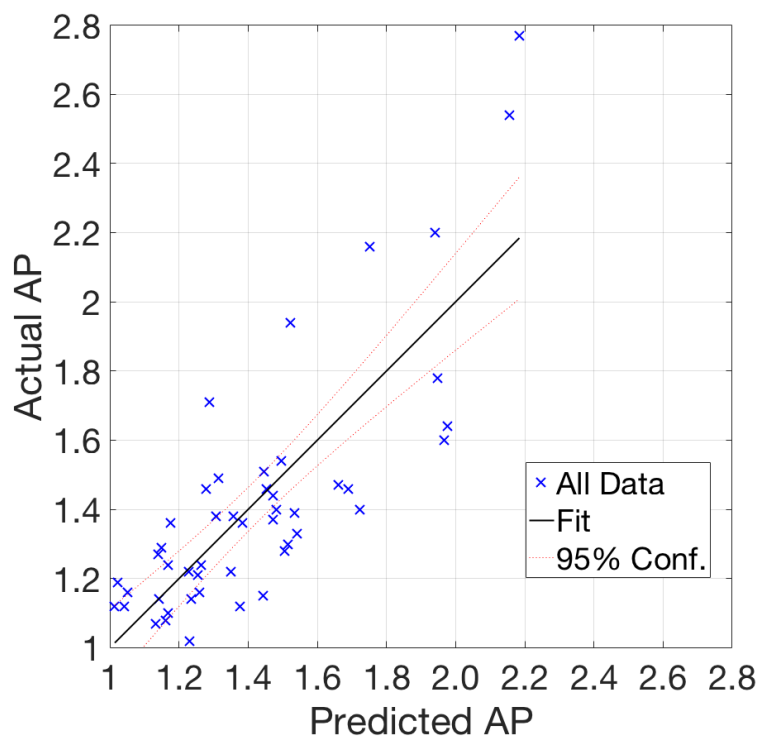


Figure A.8: Linear regression for AP to asphaltene and resin molecular features for 48 asphaltene-resin pair systems.

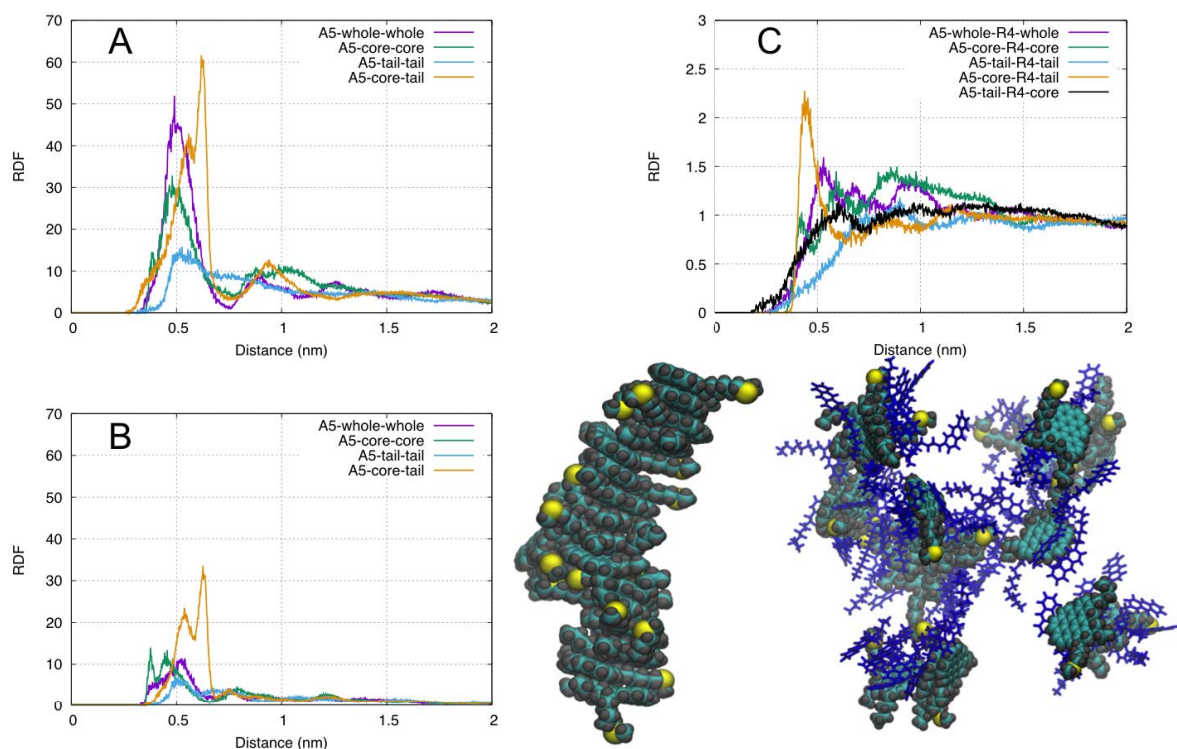


Figure A.9: Resin R4 interrupt aggregation of A5 via strong interaction with A5 and limits nanoaggregation of A5. Resins are shown in blue and asphaltenes are shown in green with gray being hydrogen atom. A) Asphaltene-asphaltene RDF in the absence of resin. B) Asphaltene-asphaltene RDF in the presence of resin. C) asphaltene-resin RDF.

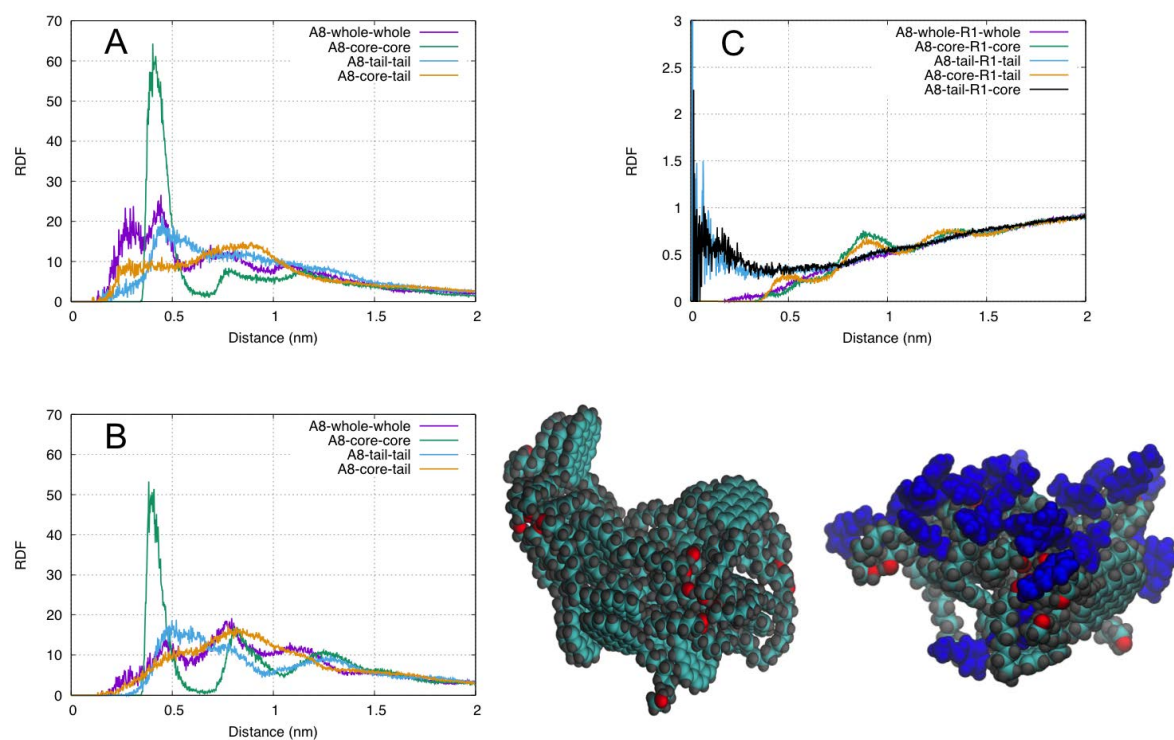


Figure A.10: Resin R1 has no effect on the aggregation of A8 due to weak interaction between them. Resins are shown in blue and asphaltenes are shown in green with gray and red being hydrogen and oxygen atoms. A) Asphaltene-asphaltene RDF in the absence of resin. B) Asphaltene-asphaltene RDF in the presence of resin. C) asphaltene-resin RDF.

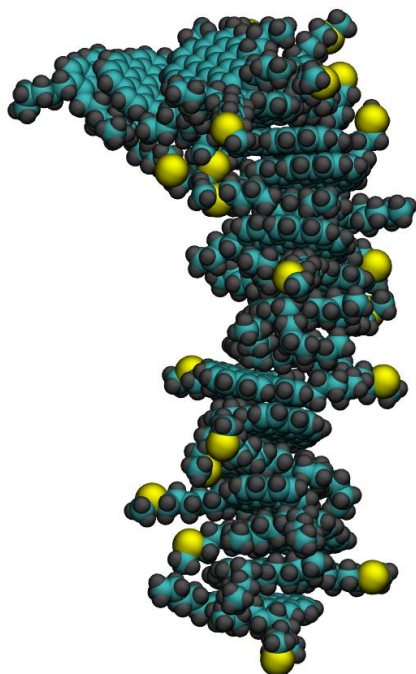


Figure A.11: Nanoaggregate of A5 in its neat state. The readily-aggregating A5 forms stable nanoaggregate by stacking individual A5 molecules with the aid of large aromatic core and presence of sulfur heteroatom as favorable molecular features for aggregation.

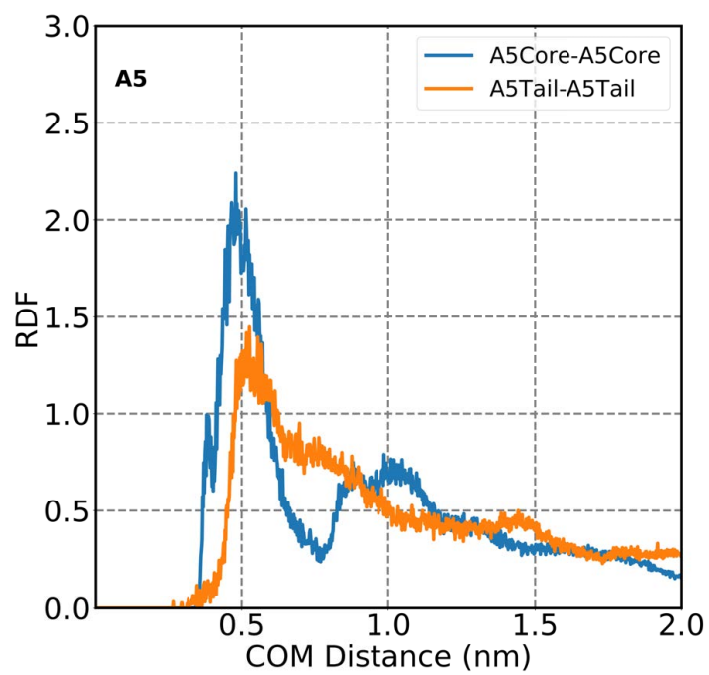


Figure A.12: Radial distribution function for A5 - A5 interactions in the absence of resin.

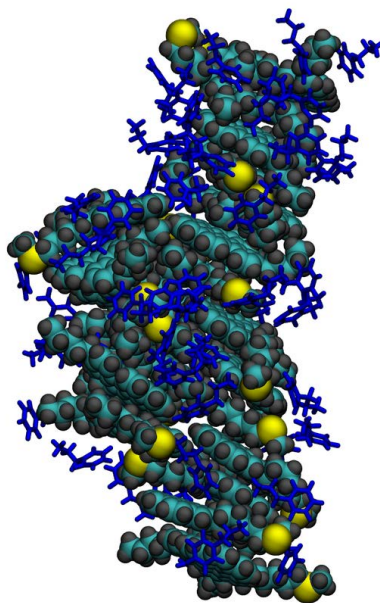


Figure A.13: Nanoaggregate of A5 in the presence of R1. The readily-aggregating A5 forms nanoaggregate by stacking individual A5 molecules with the aid of large aromatic core and presence of sulfur heteroatom as favorable molecular features for aggregation and the presence of R1 with only one aromatic ring as the favorable deterring effect does not have substantial effect on the aggregation tendency of A5.

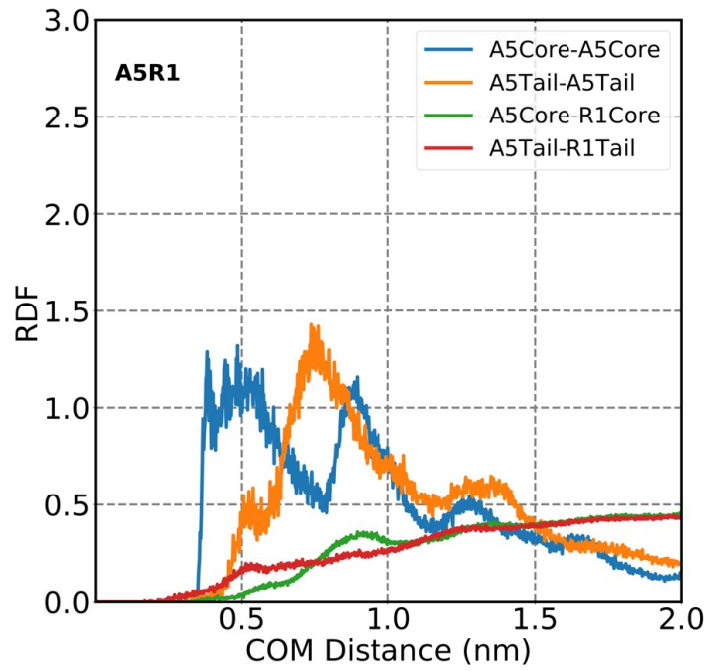


Figure A.14: Radial distribution function for A5 - A5 and A5 - R1 interactions. The interaction of A5 - A5 are slightly loosened but not substantially due to the lack of strong direct interaction between A5 - R1 in small distances.

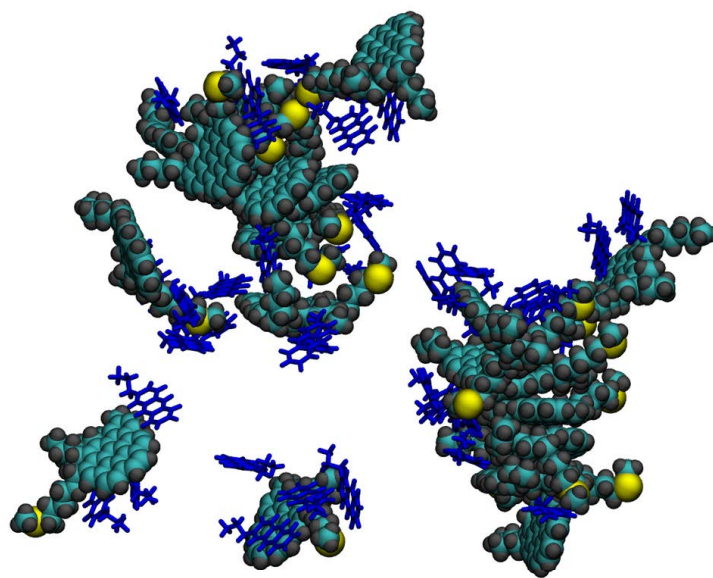


Figure A.15: Aggregate of A5 in the presence of R3. The readily-aggregating A5 does not form stable nanoaggregate. R3 with three aromatic rings as favorable deterring feature have substantial negative effect on the aggregation ability of A5 and brings the size of aggregates to smaller unstable stacks and dimers and even monomers.

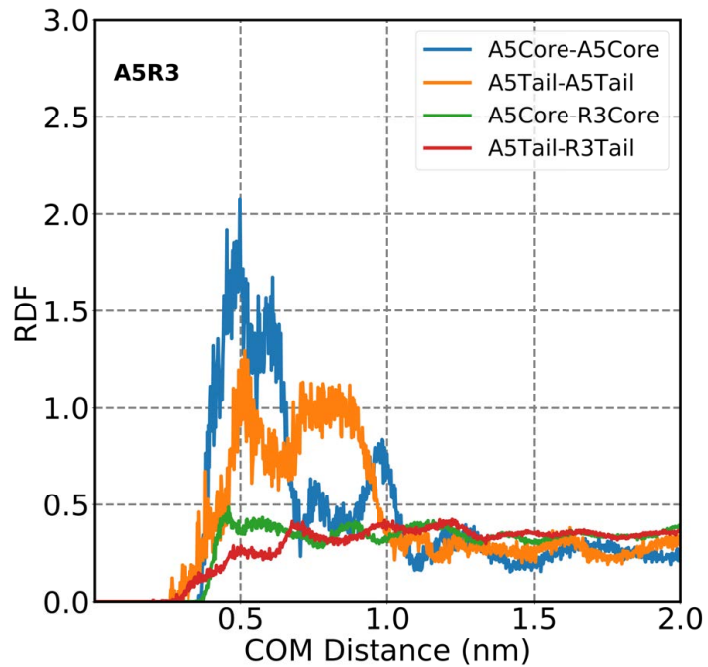


Figure A.16: Radial distribution function for A5 - A5 and A5 - R3 interactions. The interaction of A5 - A5 are loosened considerably due to the strong direct interaction between A5 - R3 in small distances and in the form of face-to-face interaction between aromatic cores of asphaltene and resin.

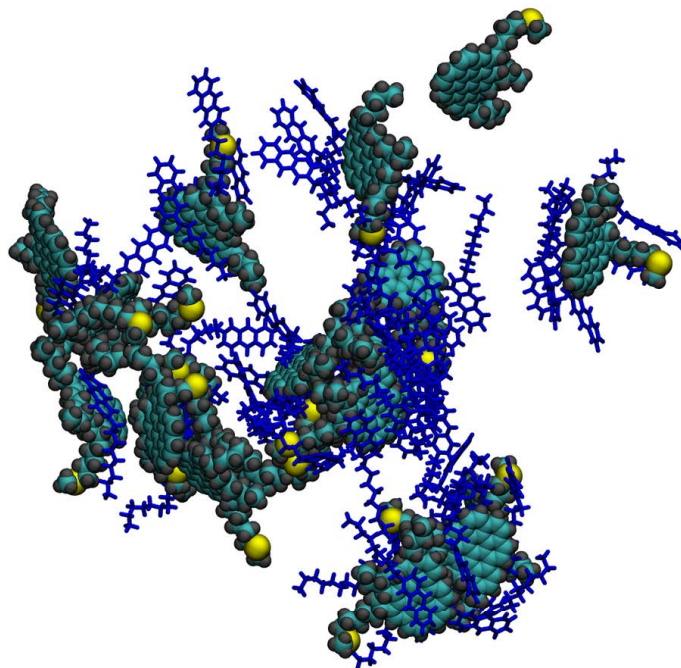


Figure A.17: Aggregate of A5 in the presence of R4. The readily-aggregating A5 does not form stable nanoaggregate. R4 with three aromatic rings as favorable deterring feature have substantial negative effect on the aggregation ability of A5 and brings the size of aggregates to smaller unstable stacks and dimers and even monomers.

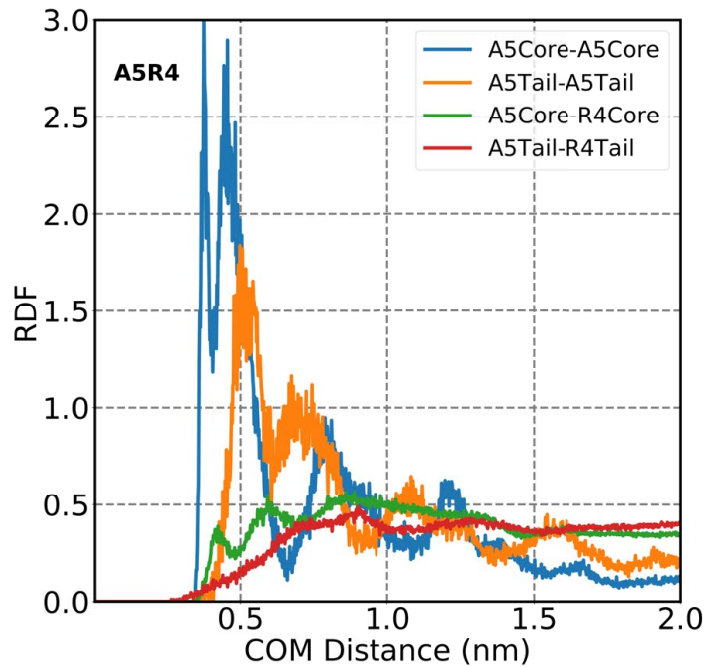


Figure A.18: Radial distribution function for A5 - A5 and A5 - R4 interactions. The interaction of A5 - A5 are loosened considerably due to the strong direct interaction between A5 - R4 in small distances and in the form of face-to-face interaction between aromatic cores of asphaltene and resin. The aliphatic tail of R4 has interactions with aliphatic tail of A5 in close distances which makes A5 - R4 interaction even stronger.

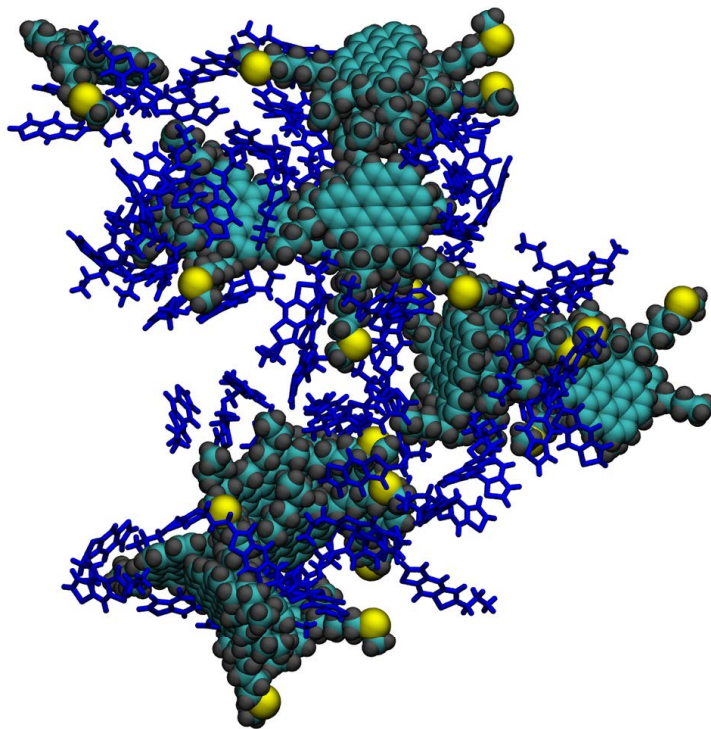


Figure A.19: Aggregate of A5 in the presence of R5. The readily-aggregating A5 does not form stable nanoaggregate. R5 with three aromatic rings and two sulfur heteroatoms as favorable deterring features have substantial negative effect on the aggregation ability of A5 and brings the size of aggregates to smaller unstable stacks like trimers, dimers, and even monomers.

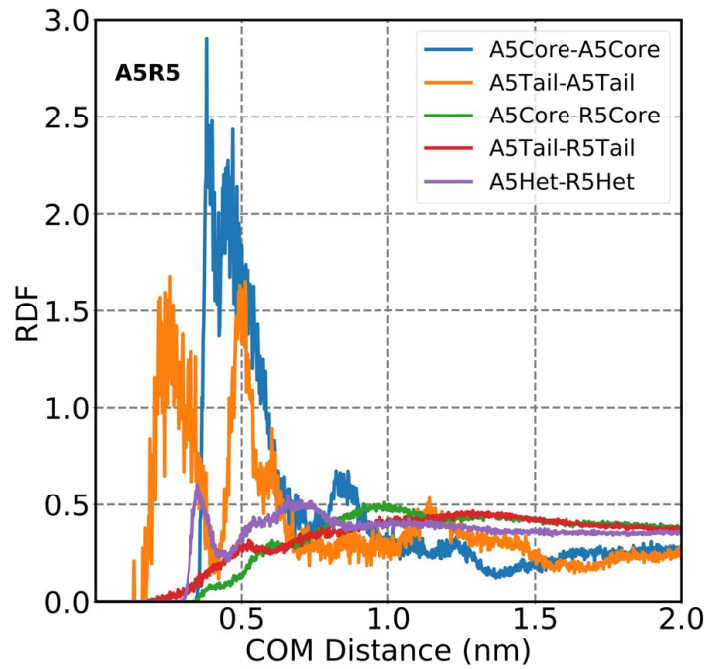


Figure A.20: Radial distribution function for A5 - A5 and A5 - R5 interactions. The interaction of A5 - A5 are loosened considerably (narrowing the curve of A5-A5) due to strong direct interaction between A5 - R5 in small distances.

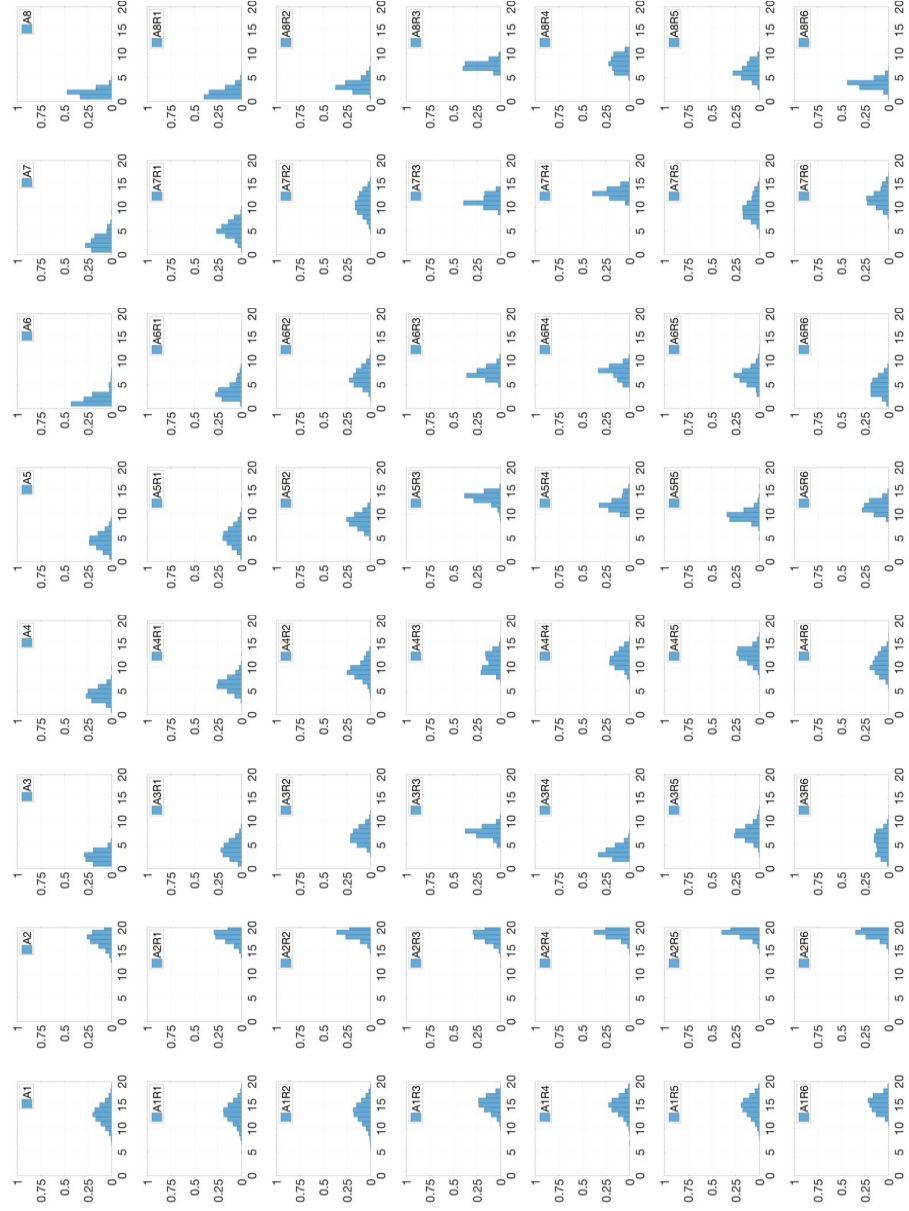


Figure A.21: Normalized Distribution of Number of Aggregates for all 56 systems.

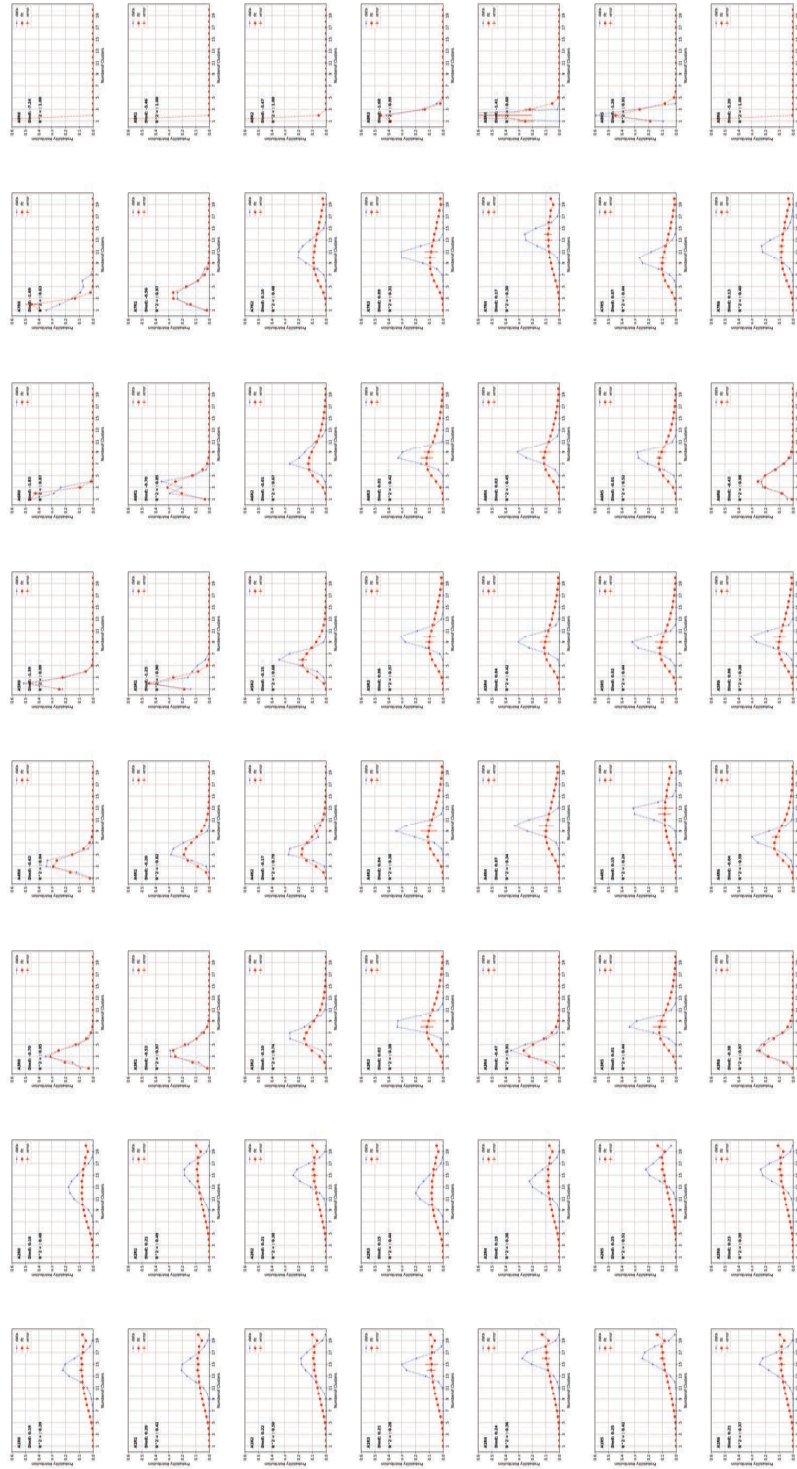


Figure A.22: Isodesmic fit for all 56 systems.

Appendix B

Supporting Information for Chapter 3

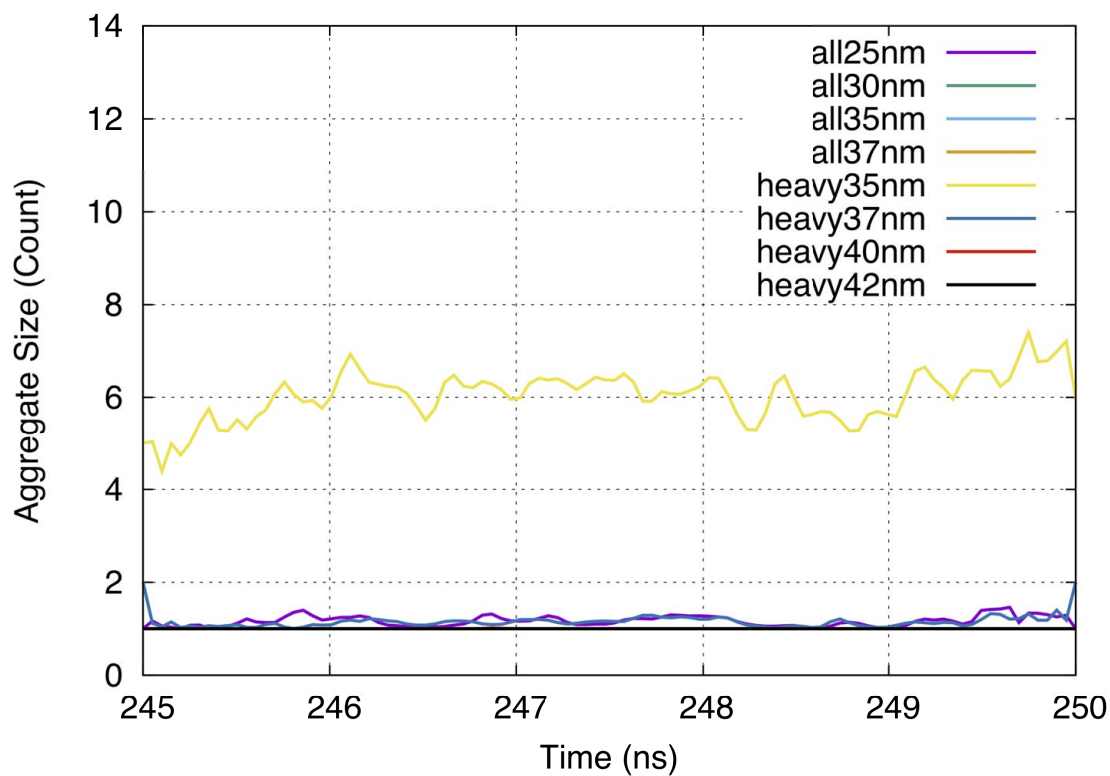


Figure B.1: Scan of different cutoffs to capture both edge-to-edge and face-to-face stacking.

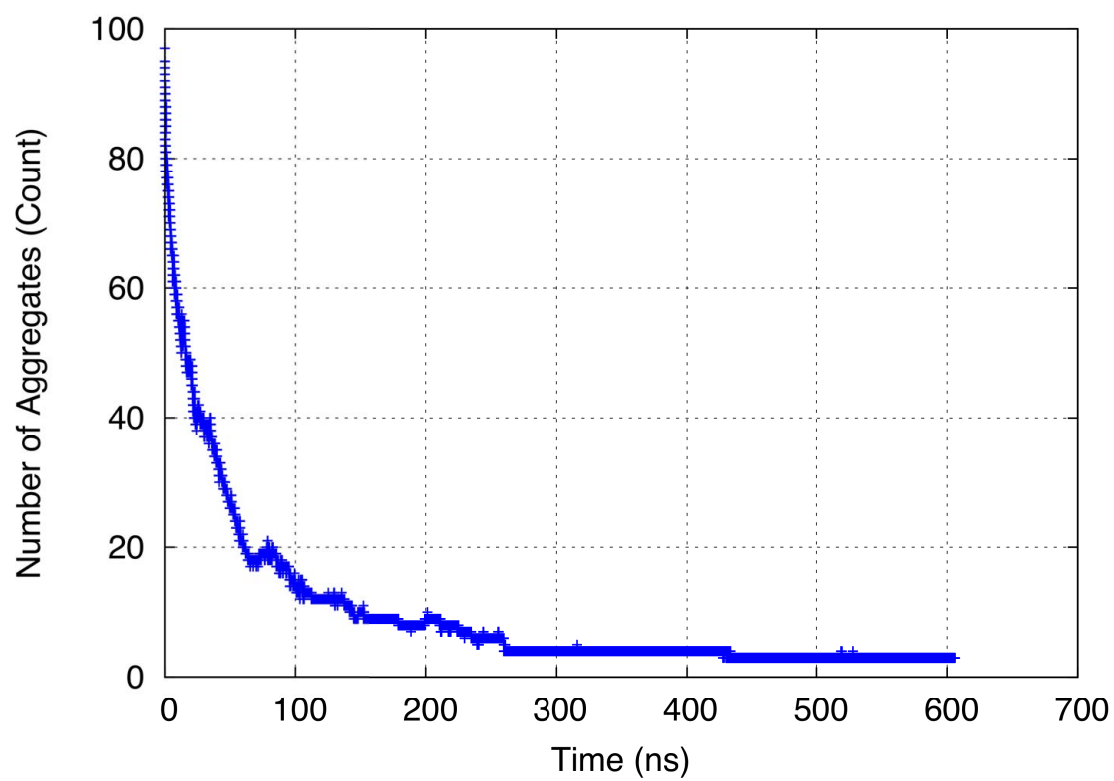


Figure B.2: Aggregation of 100 count of A8 molecule in dilution of 0.01 M. Even in low concentration, the readily-aggregating asphaltene proceeds to clustering and flocculation.

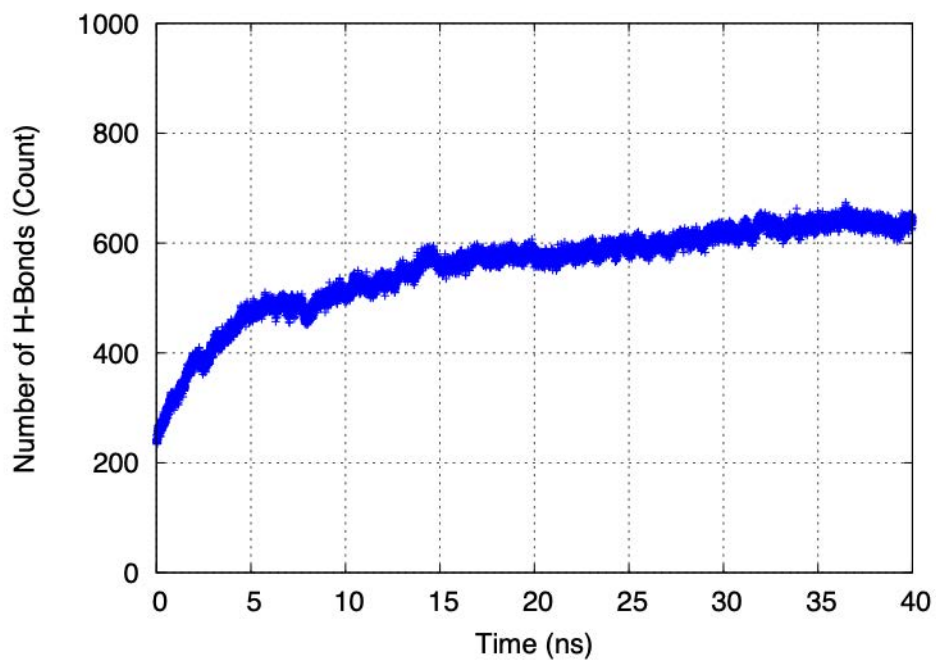
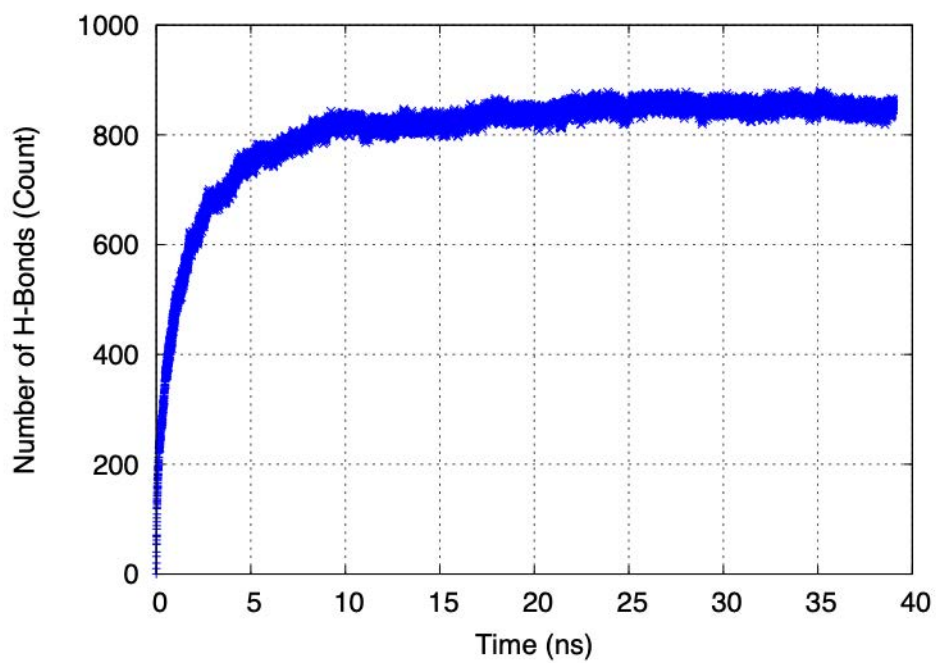


Figure B.3: Decrease in the number of hydrogen bond in the presence of the deterring resin R3 (Bottom graph) compared to neat A8 (Top graph).

Appendix C

Free Energies of Dimerization

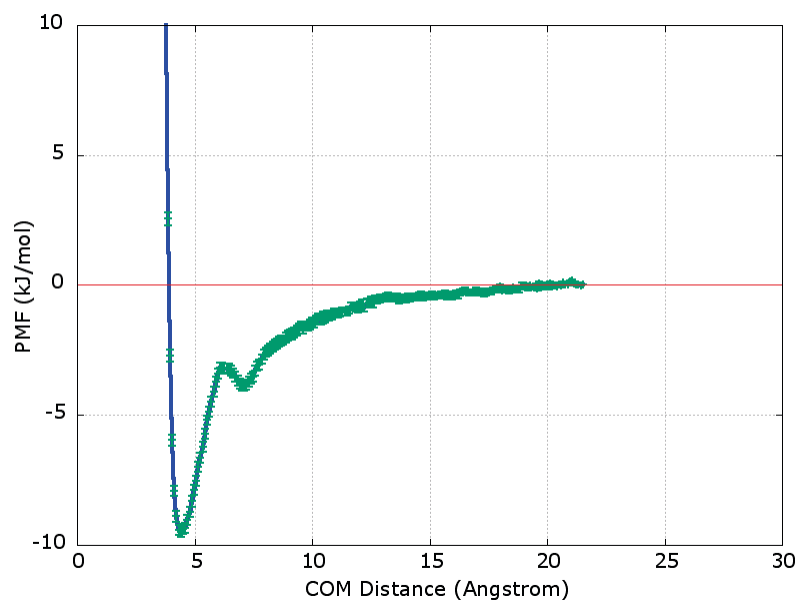


Figure C.1: Free energy of dimerization for A1 molecules.

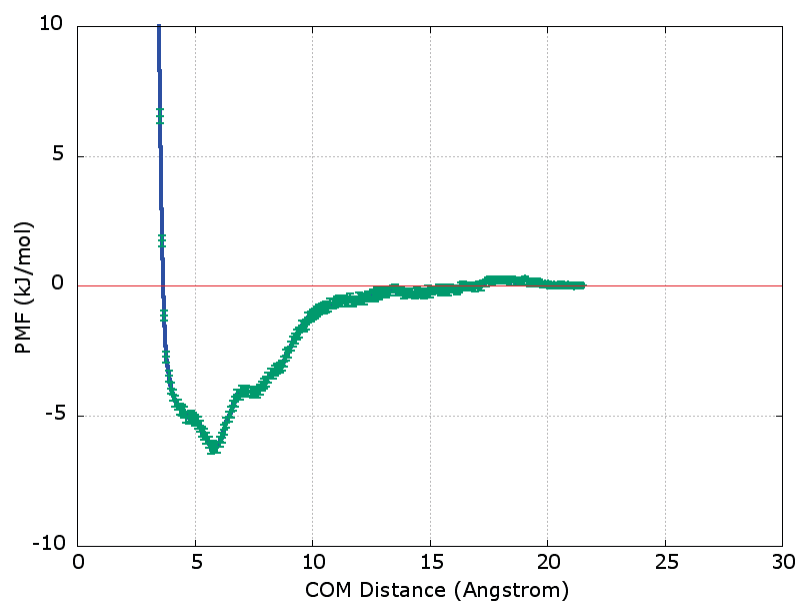


Figure C.2: Free energy of dimerization for A2 molecules.

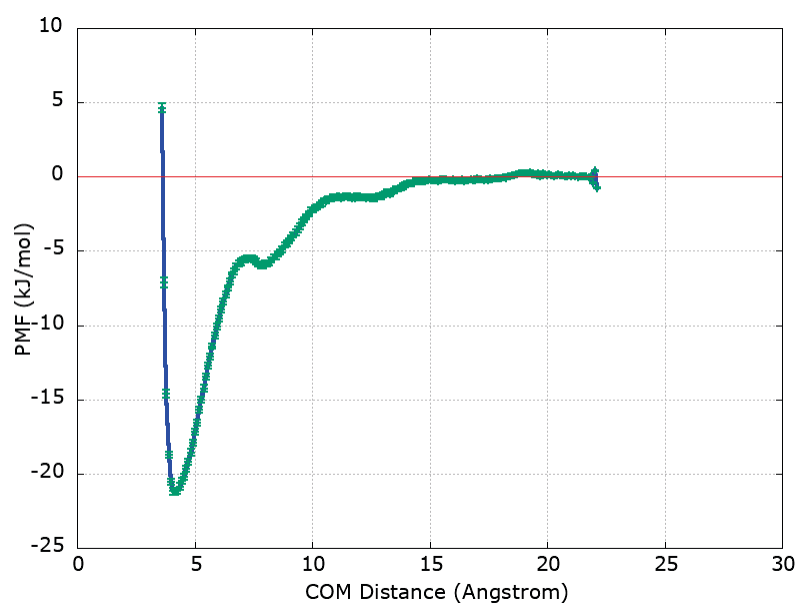


Figure C.3: Free energy of dimerization for A3 molecules.

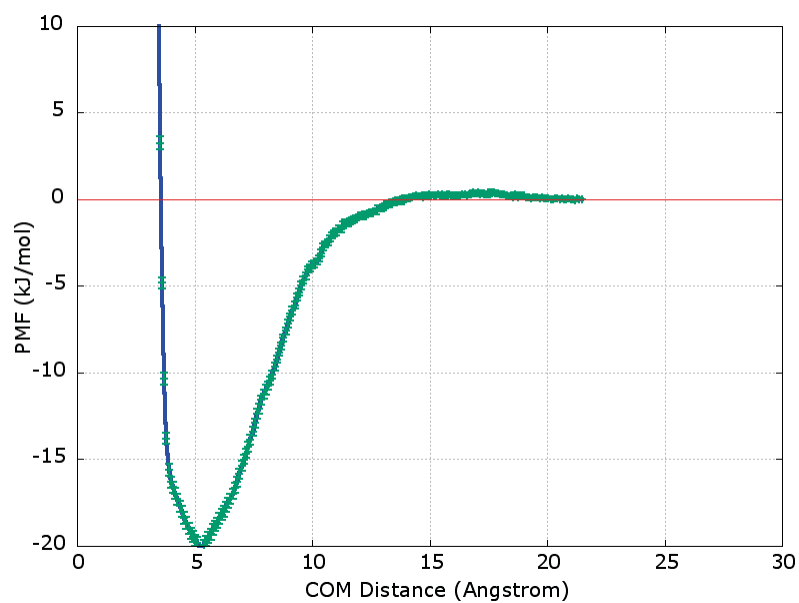


Figure C.4: Free energy of dimerization for A4 molecules.

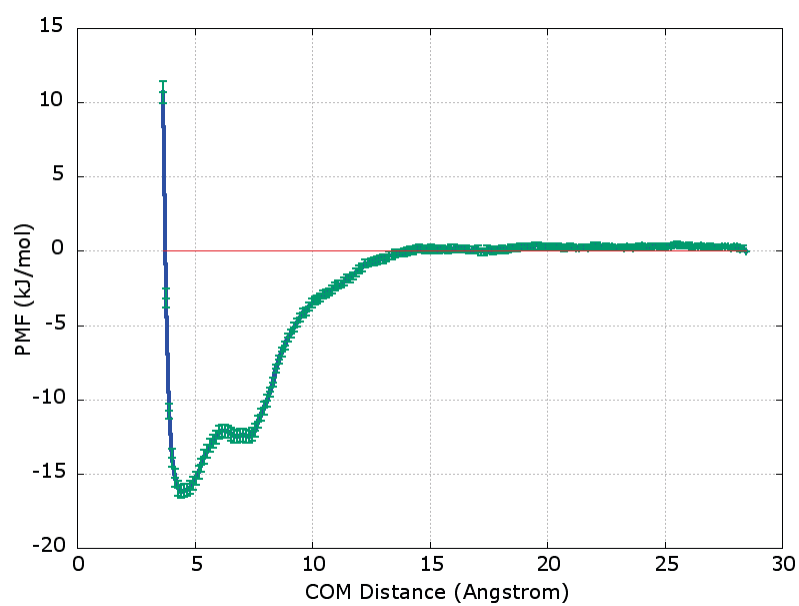


Figure C.5: Free energy of dimerization for A5 molecules.

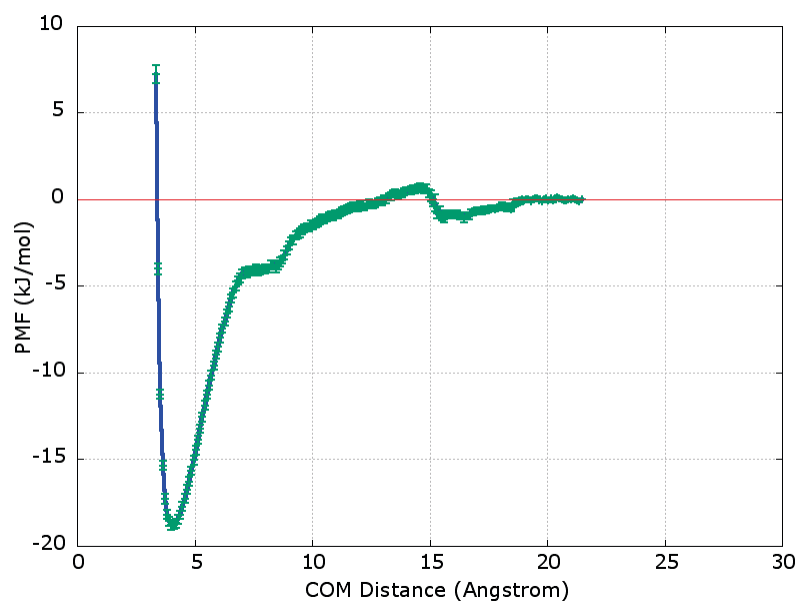


Figure C.6: Free energy of dimerization for A6 molecules.

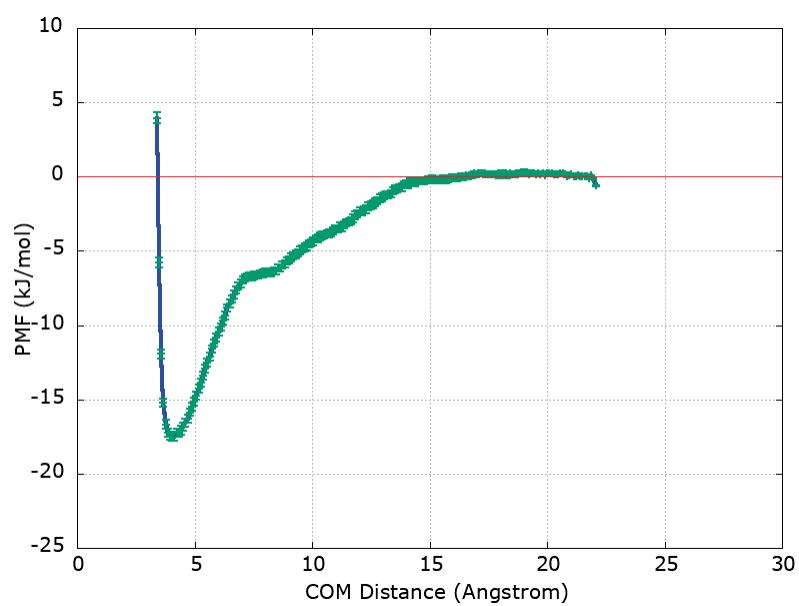


Figure C.7: Free energy of dimerization for A7 molecules.

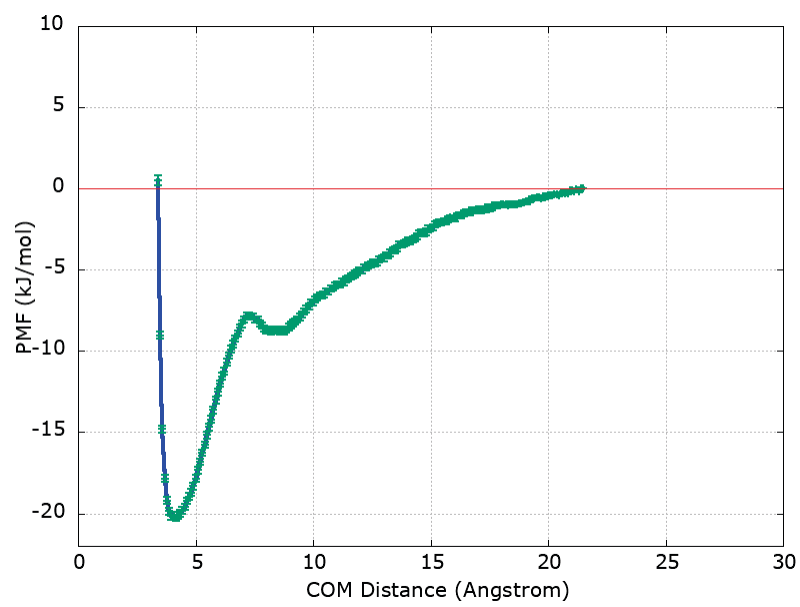


Figure C.8: Free energy of dimerization for A8 molecules.

Appendix D

Radial Distribution Function Curves

This appendix contains the radial distribution function (RDF) for all 56 systems of asphaltenes and resins. Asphaltene-Asphaltene RDFs in the absence and in the presence of resin, as well as Asphaltene-Resin RDFs for all systems have been computed and plotted to present interaction of asphaltene-asphaltene as well as asphaltene-resin molecules.

Guide to the following plots

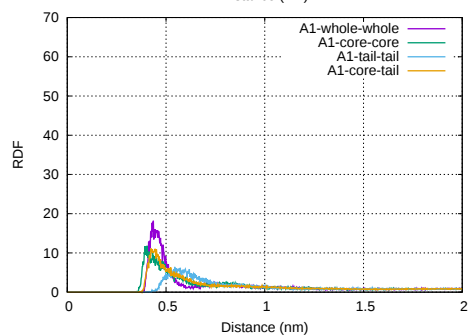
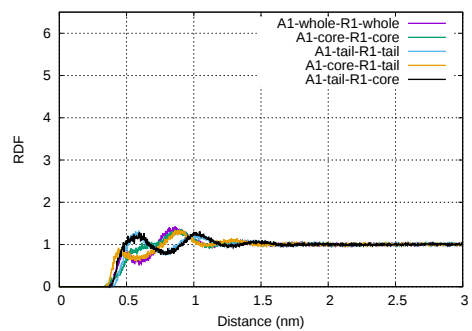
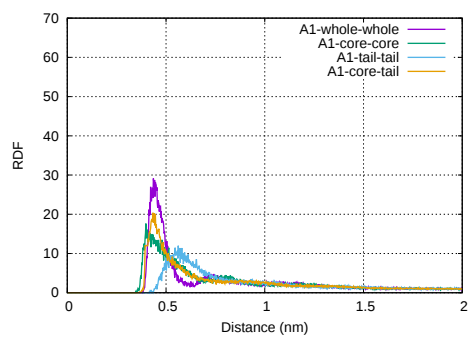
**RDF plot of Asphaltenes
in the absence of Resin**

RDF plot of Asphaltene-Resin

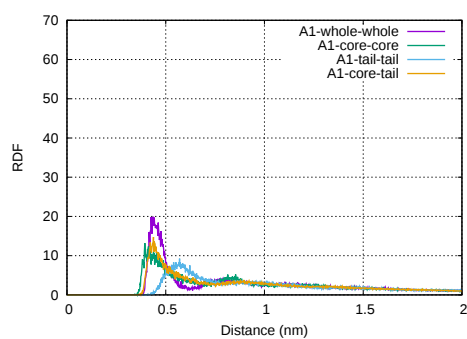
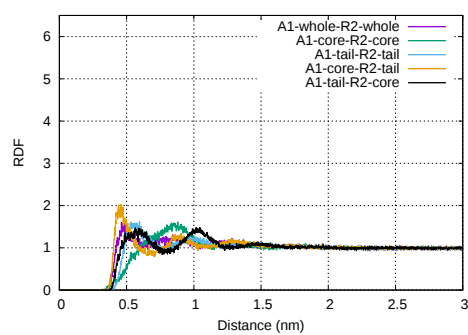
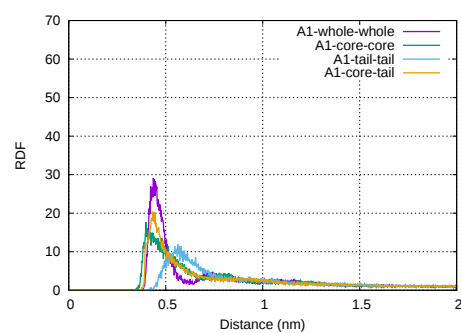
**RDF plot of Asphaltenes
in the presence of Resin**

A1 and Resins

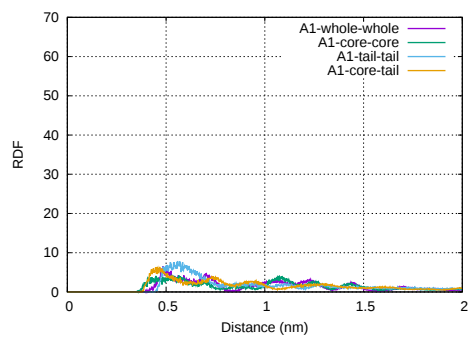
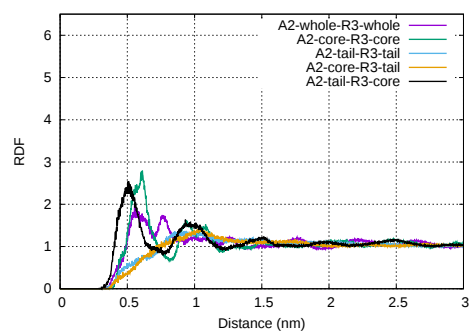
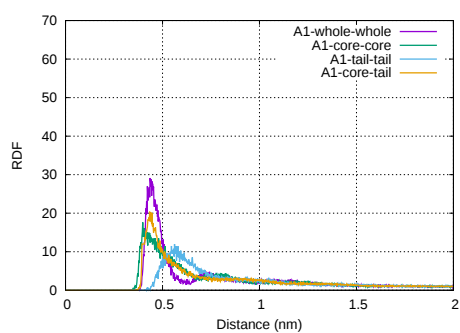
R1 and A1



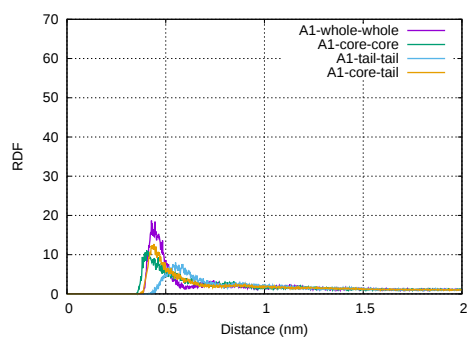
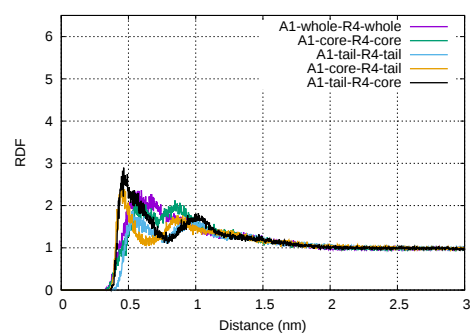
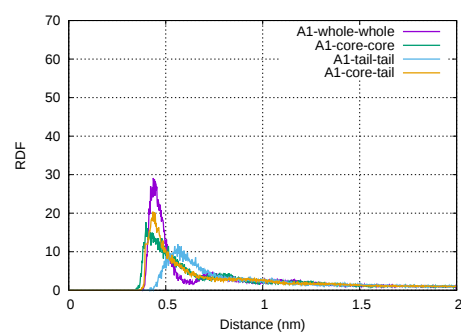
R2 and A1



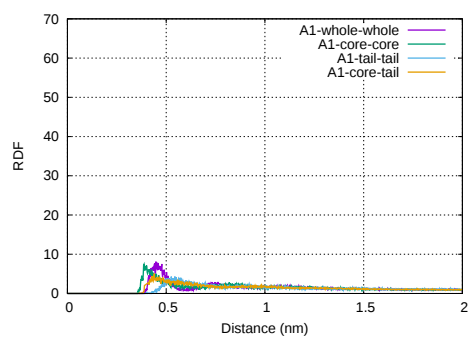
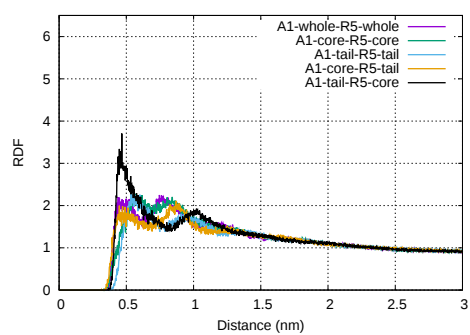
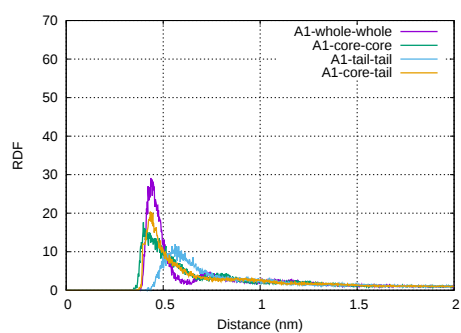
R3 and A1



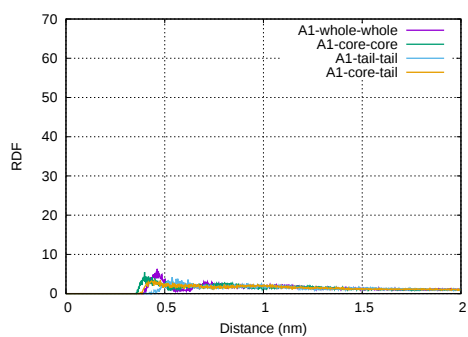
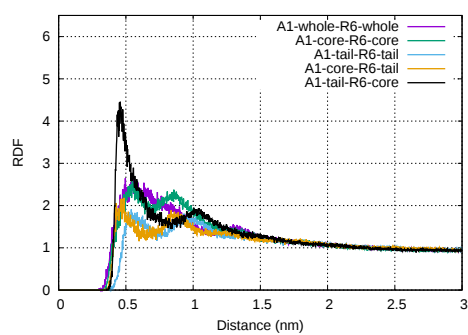
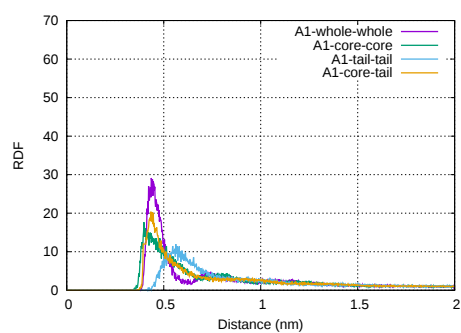
R4 and A1



R5 and A1

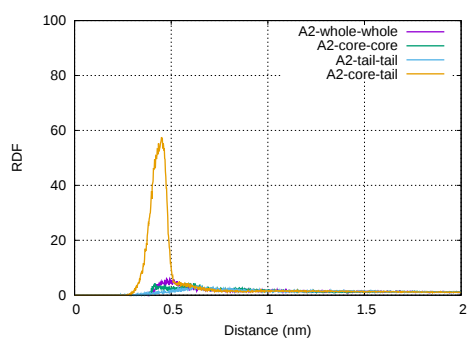
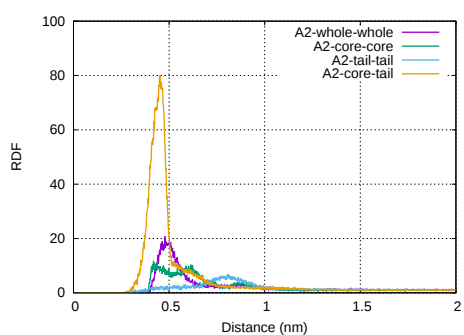


R6 and A1

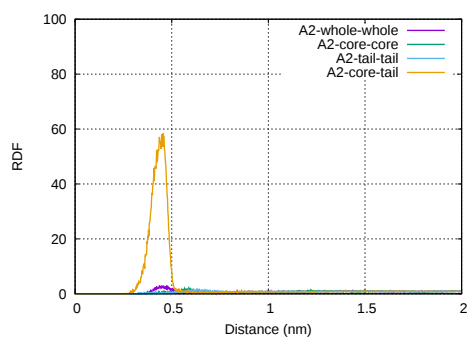
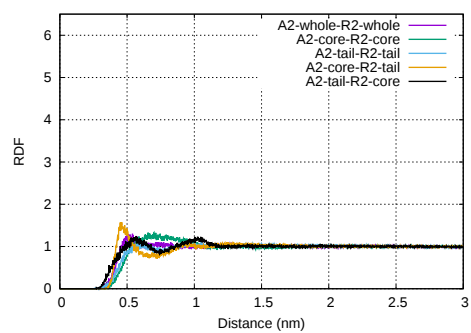
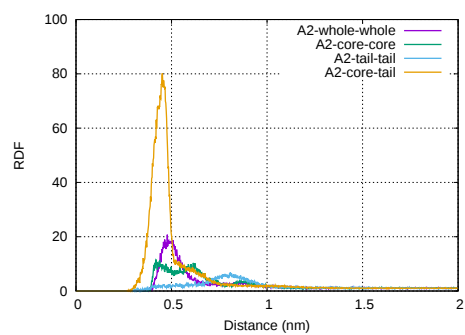


A2 and Resins

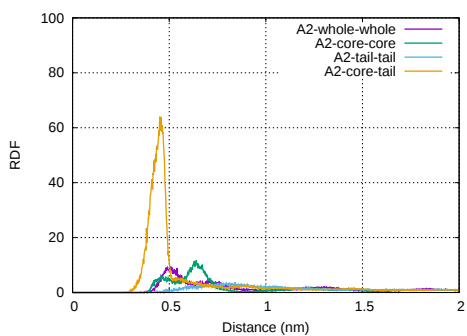
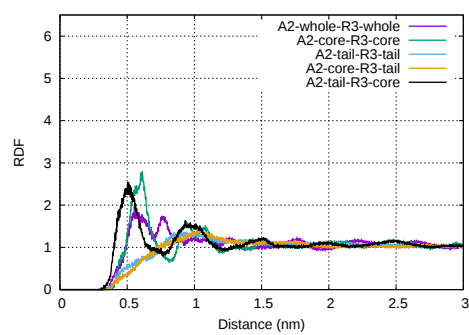
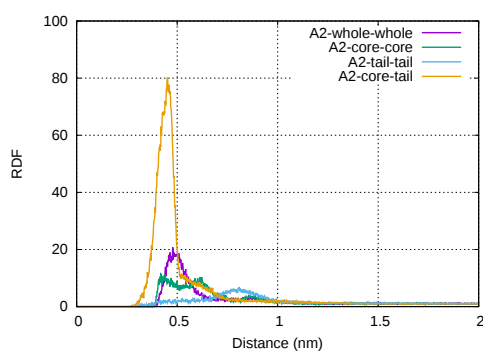
R1 and A2



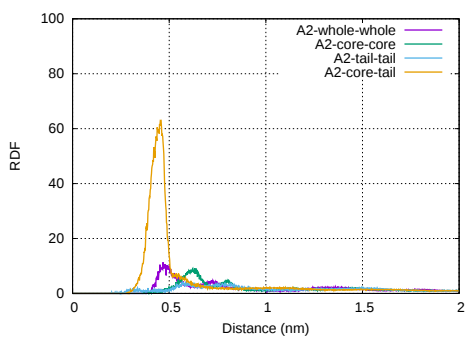
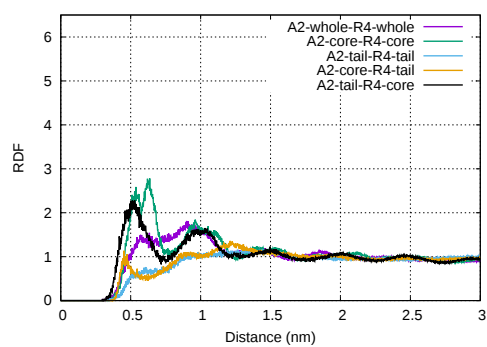
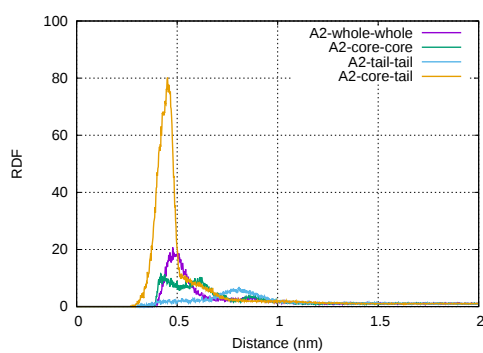
R2 and A2



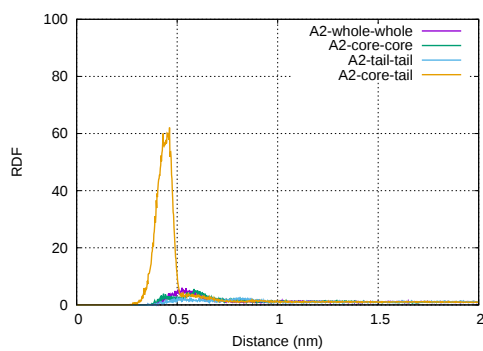
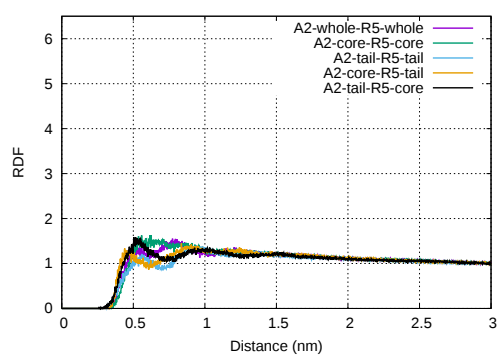
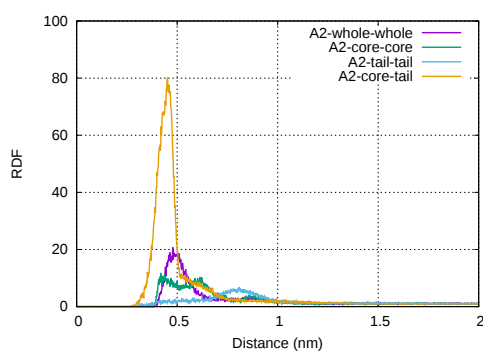
R3 and A2



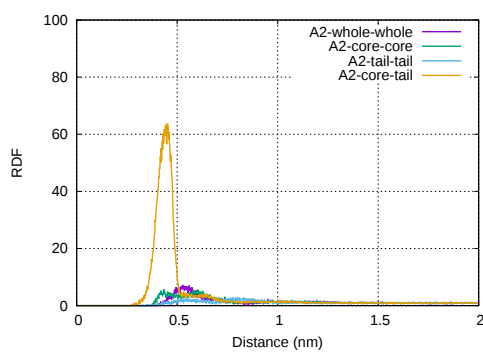
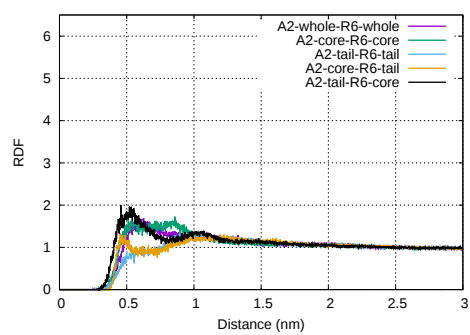
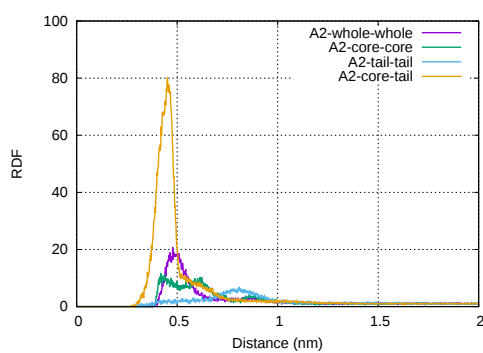
R4 and A2



R5 and A2

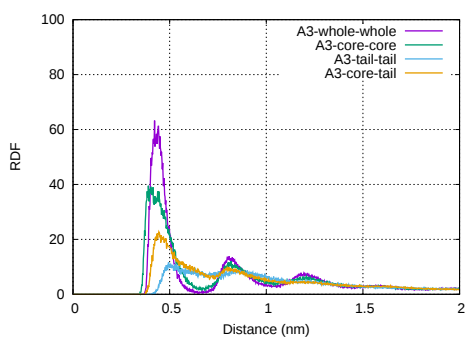
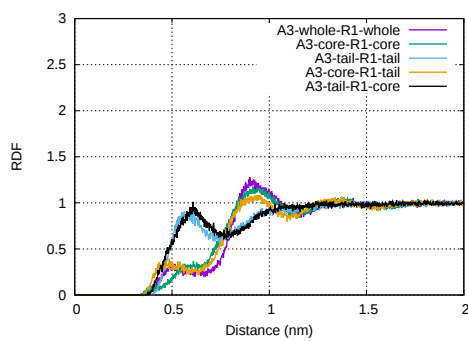
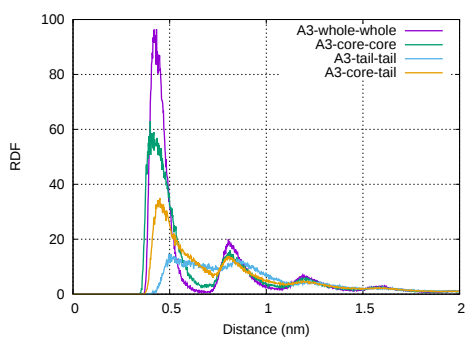


R6 and A2

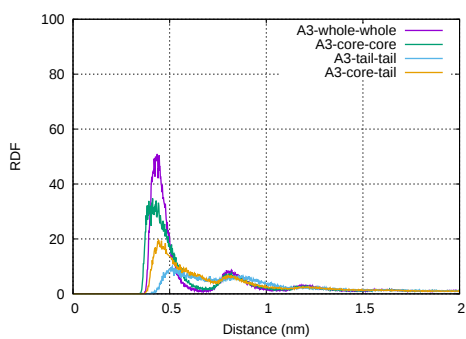
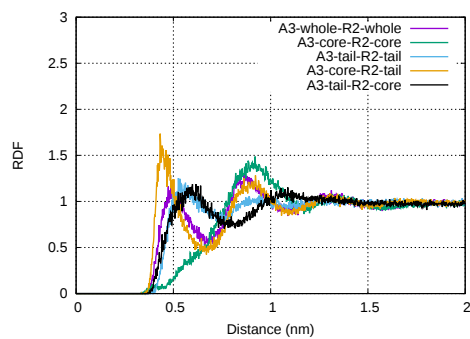
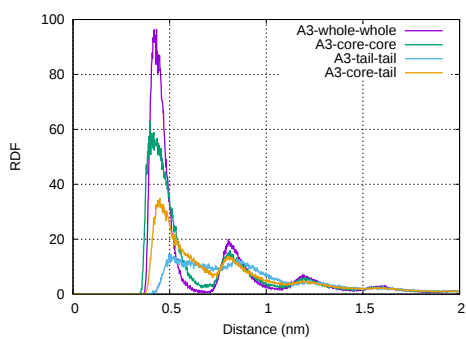


A3 and Resins

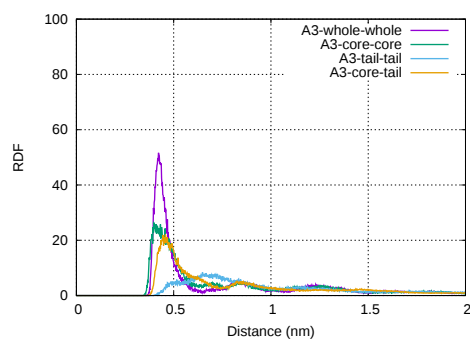
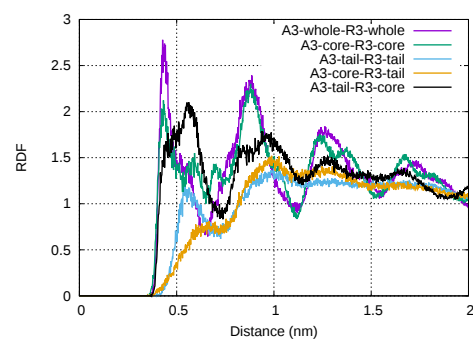
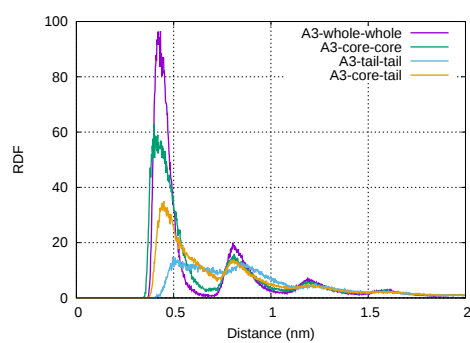
R1 and A3



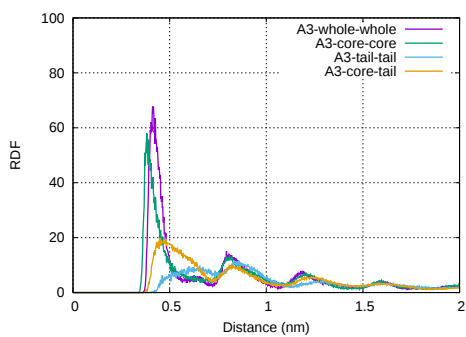
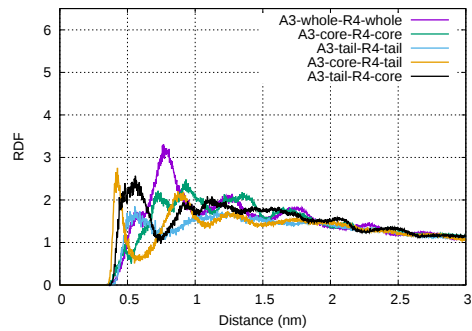
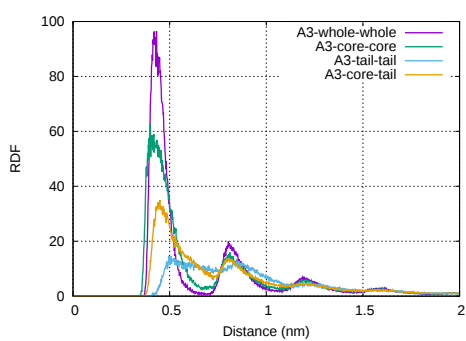
R2 and A3



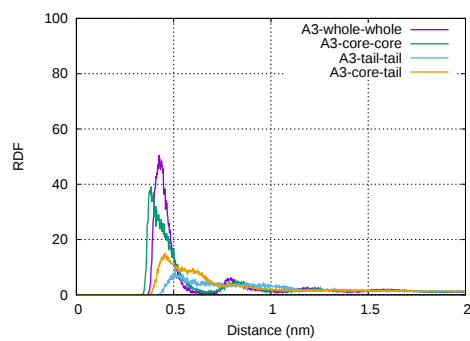
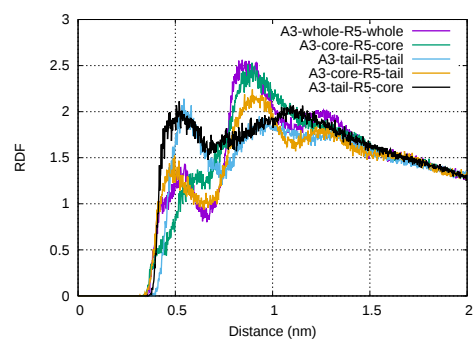
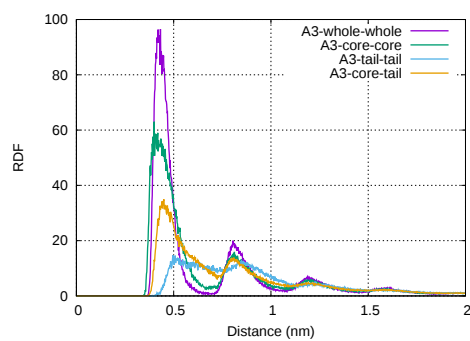
R3 and A3



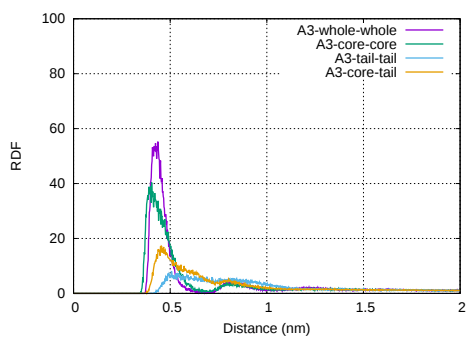
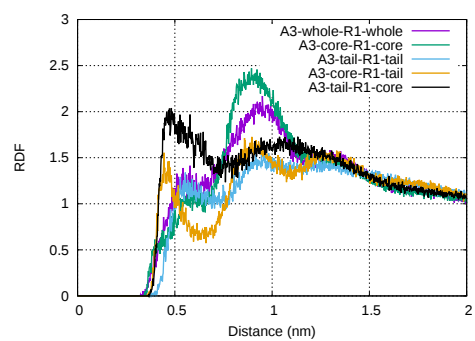
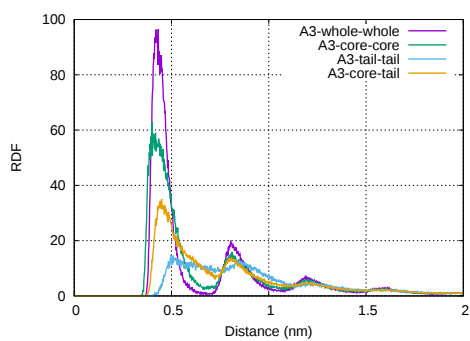
R4 and A3



R5 and A3

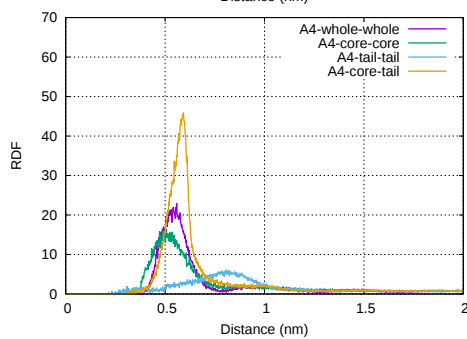
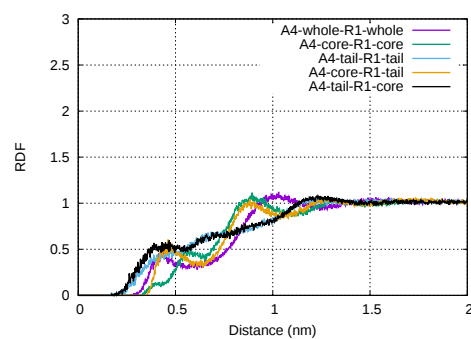
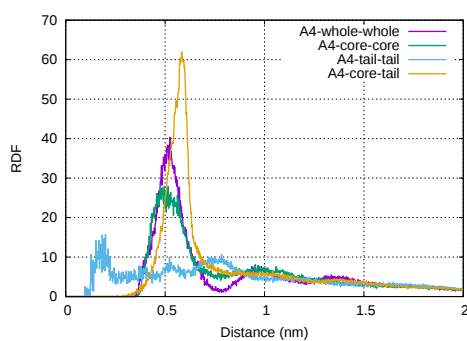


R6 and A3

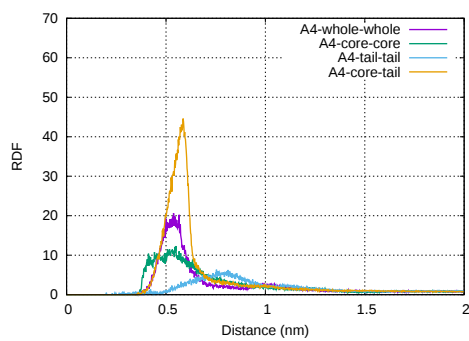
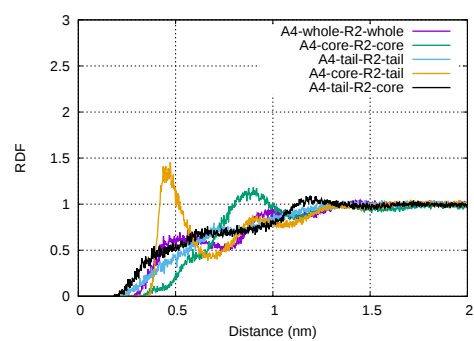
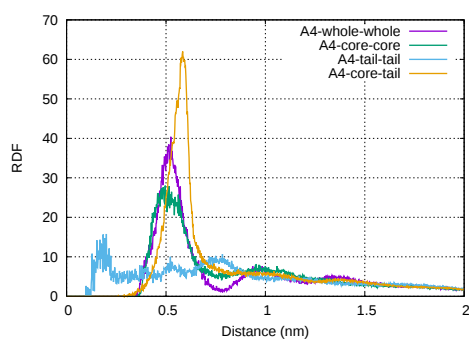


A4 and Resins

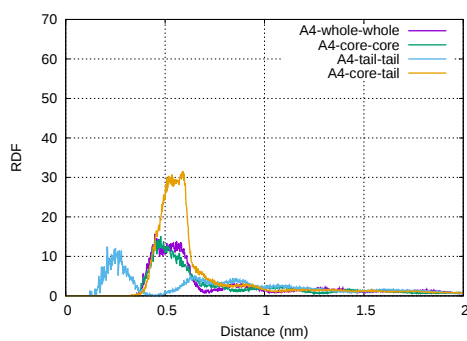
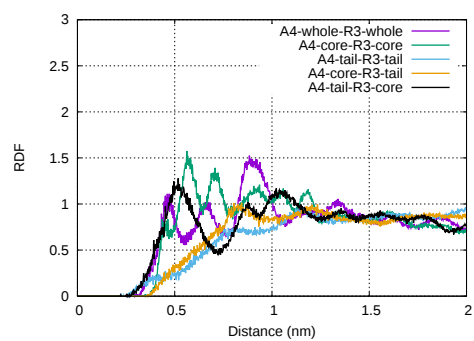
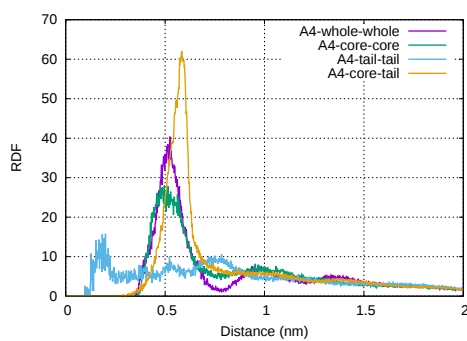
R1 and A4



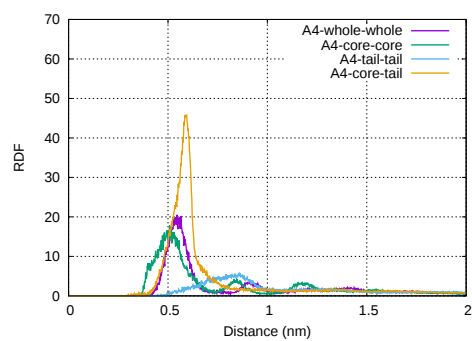
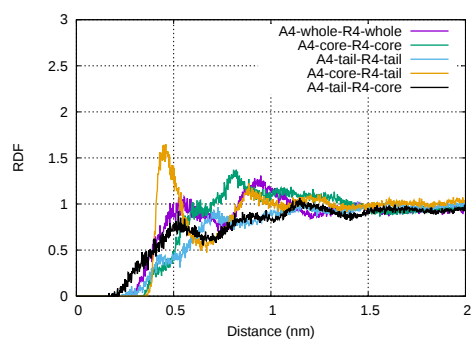
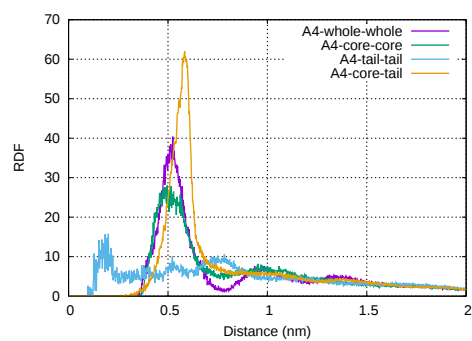
R2 and A4



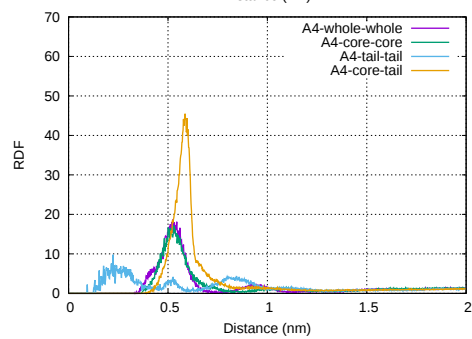
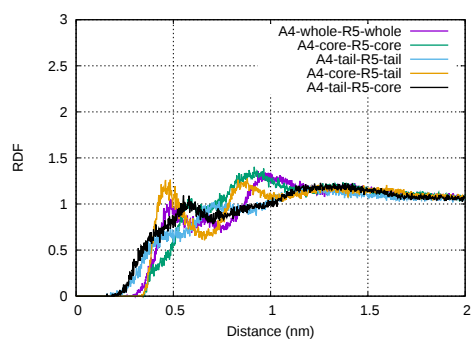
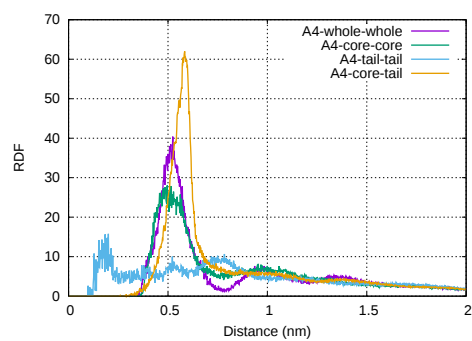
R3 and A4



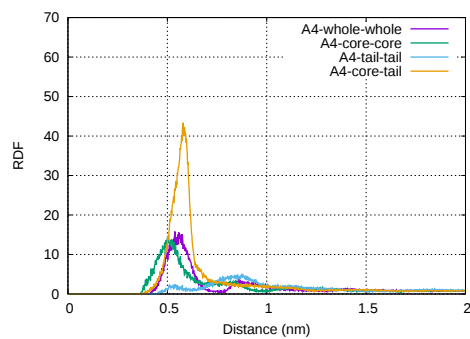
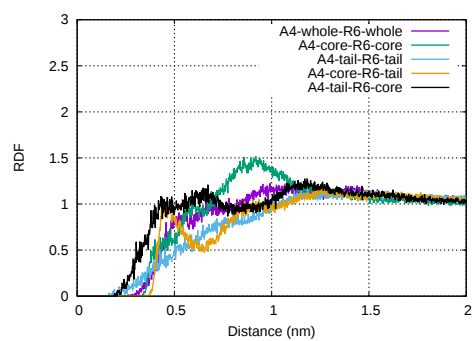
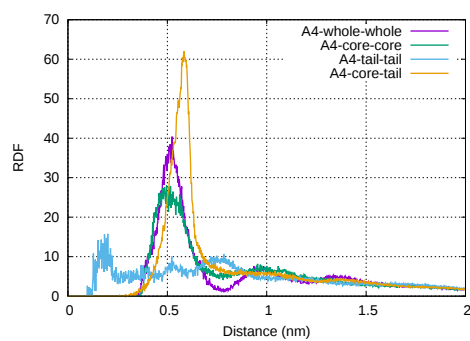
R4 and A4



R5 and A4



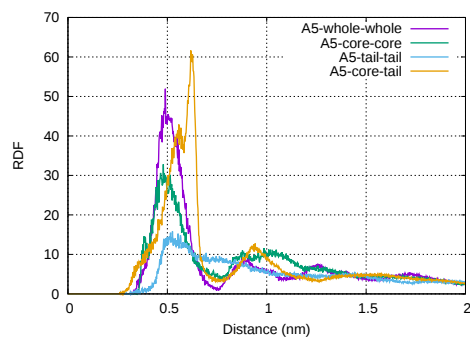
R6 and A4



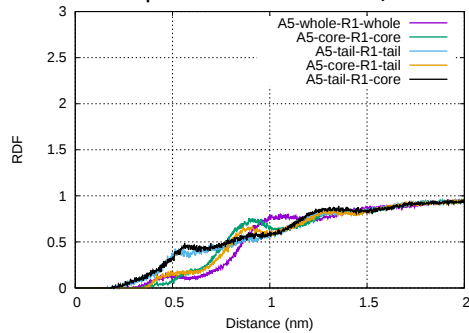
A5 and Resins

R1 and A5

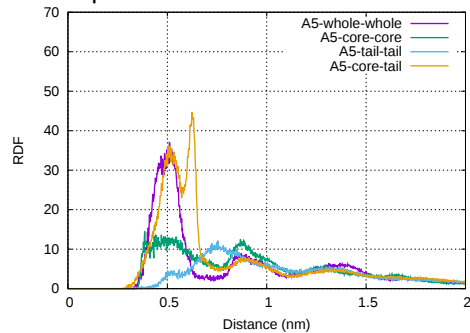
Neat A5 – A5 RDF



A5 in presence of R1 – A5/R1 RDF

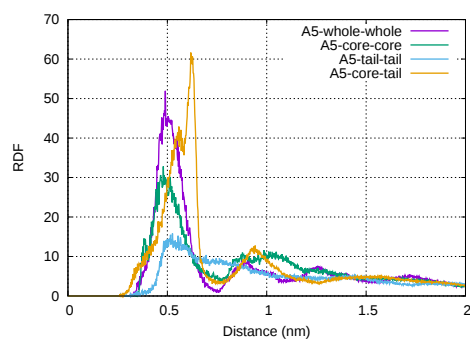


A5 in presence of R1 – A5 RDF

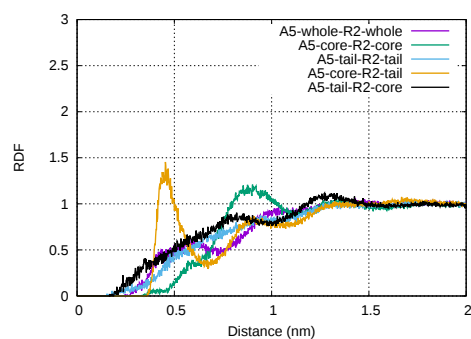


R2 and A5

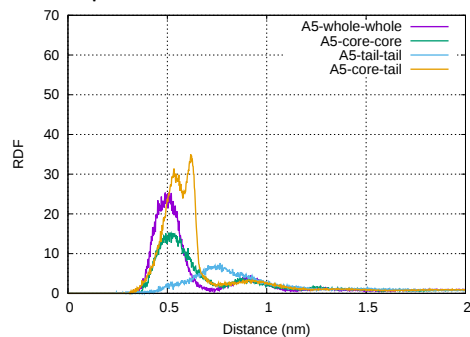
Neat A5 – A5 RDF



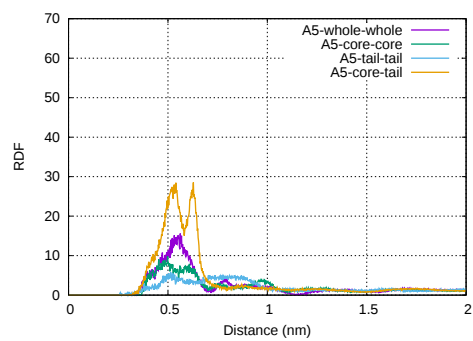
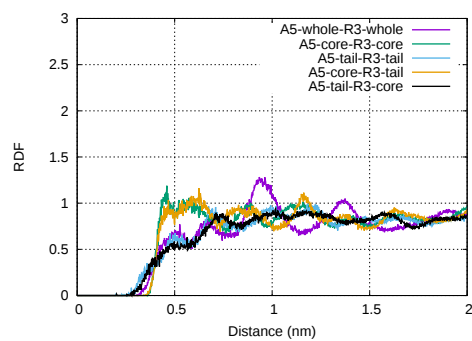
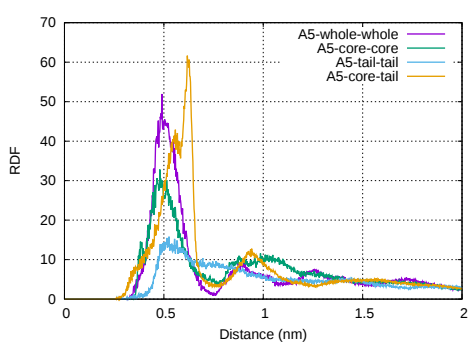
A5 in presence of R2 – A5/R2 RDF



A5 in presence of R2 – A5 RDF

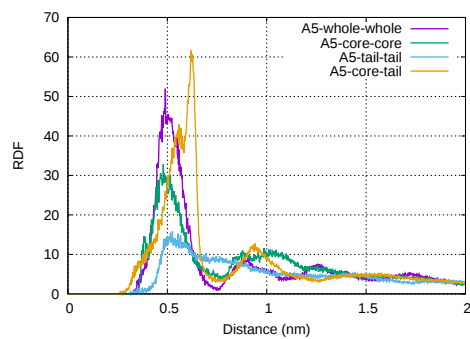


R3 and A5

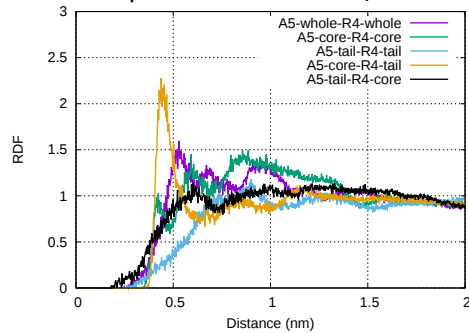


R4 and A5

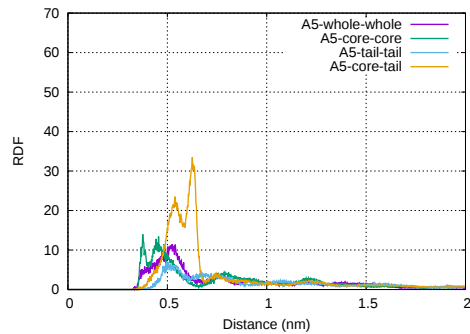
Neat A5 – A5 RDF



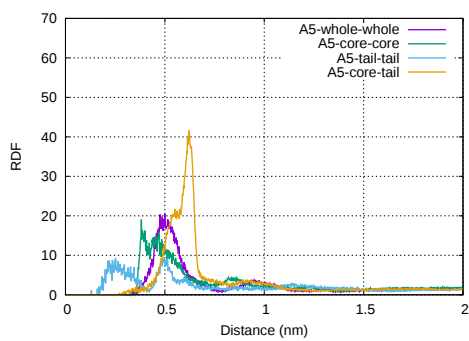
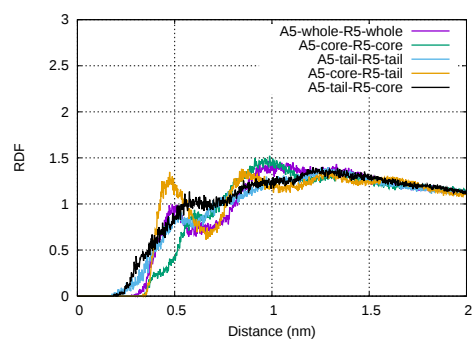
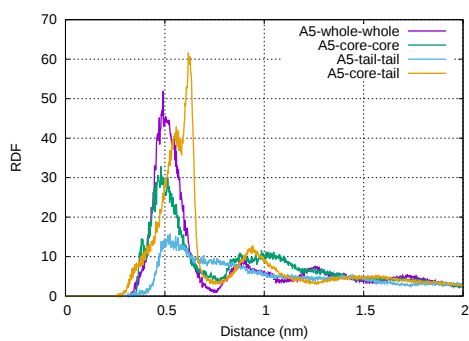
A5 in presence of R4 – A5/R4 RDF



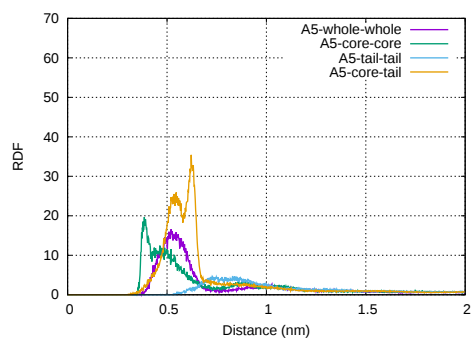
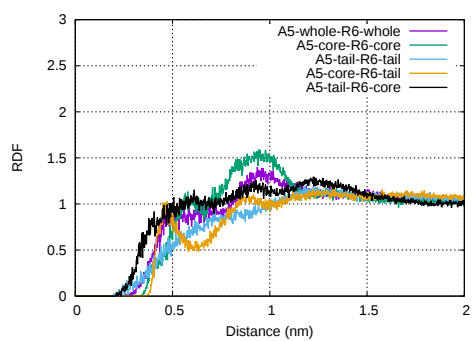
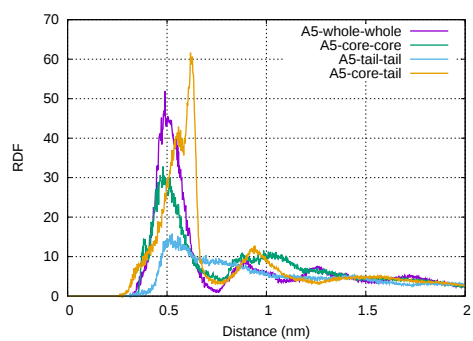
A5 in presence of R4 – A5 RDF



R5 and A5

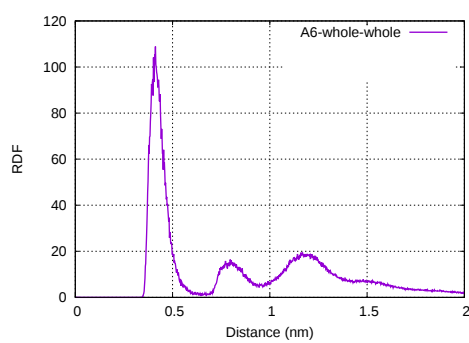


R6 and A5

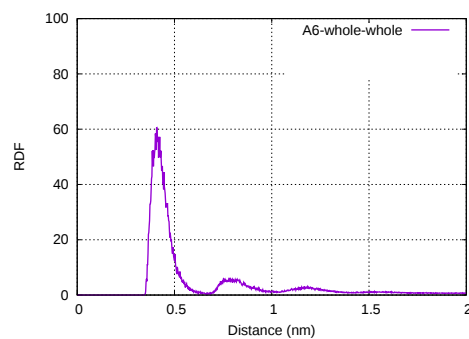
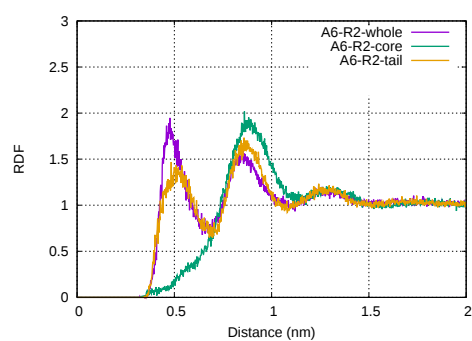
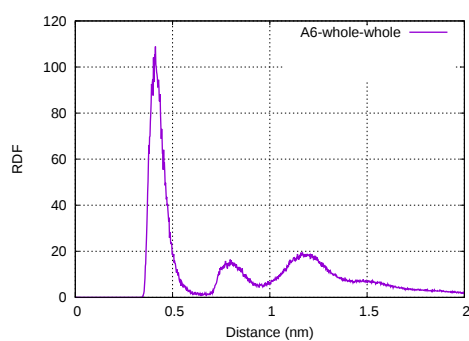


A6 and Resins

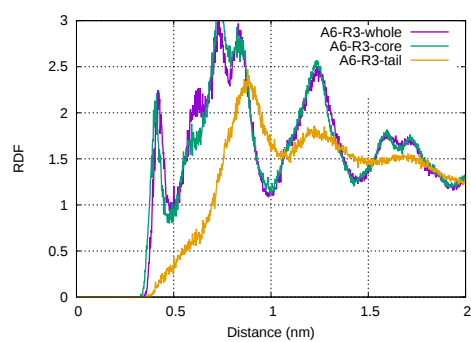
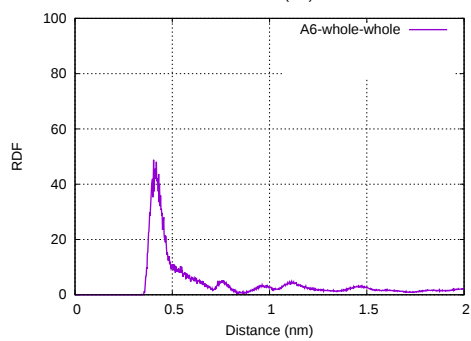
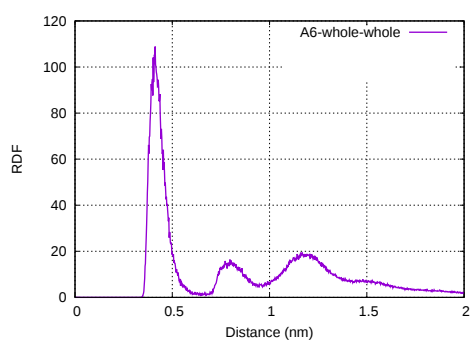
R1 and A6



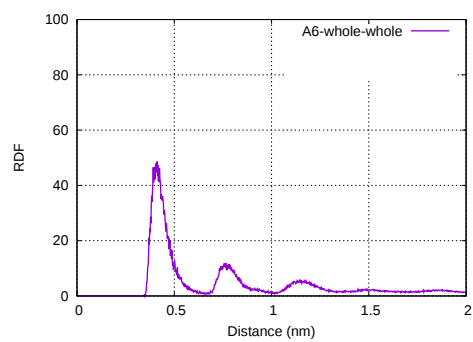
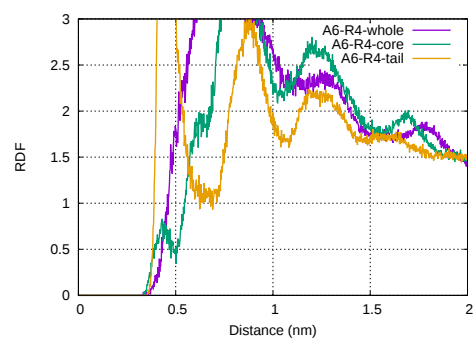
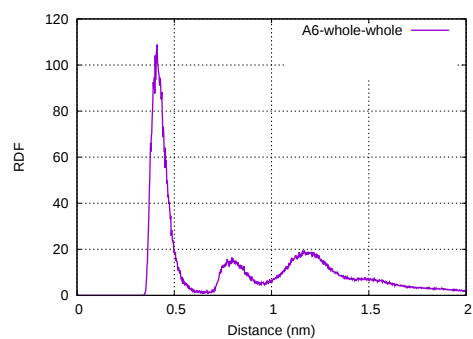
R2 and A6



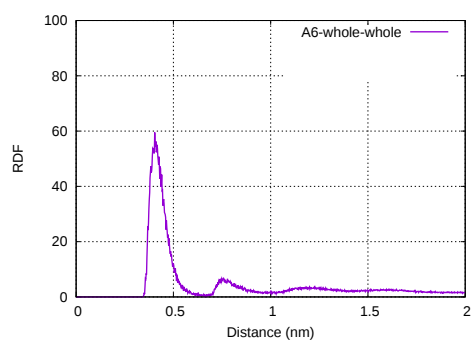
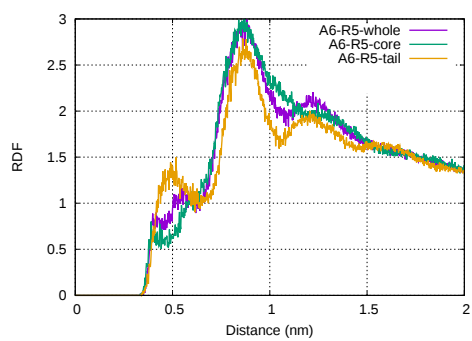
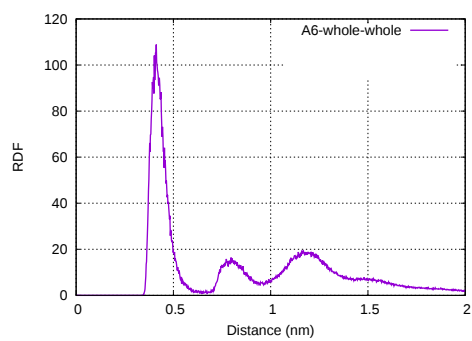
R3 and A6



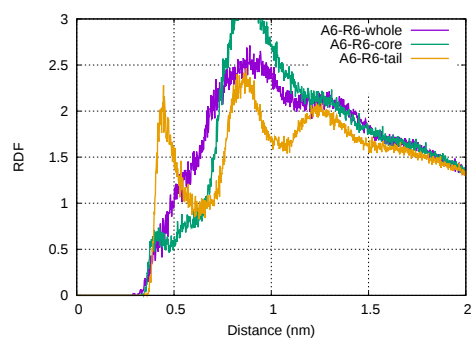
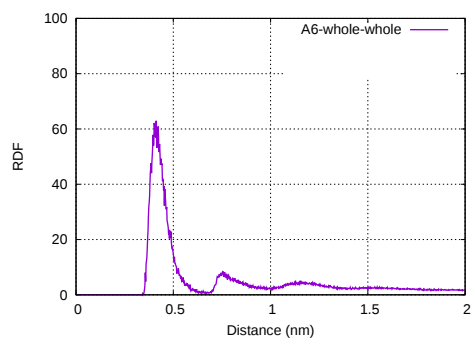
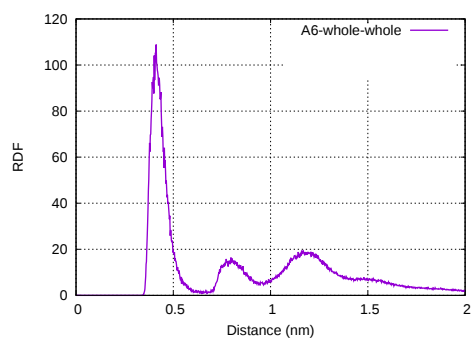
R4 and A6



R5 and A6

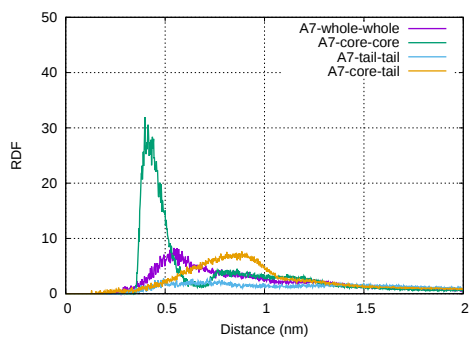
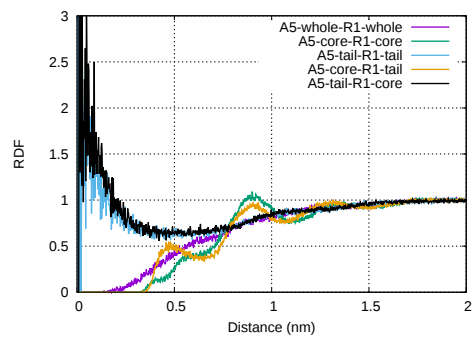
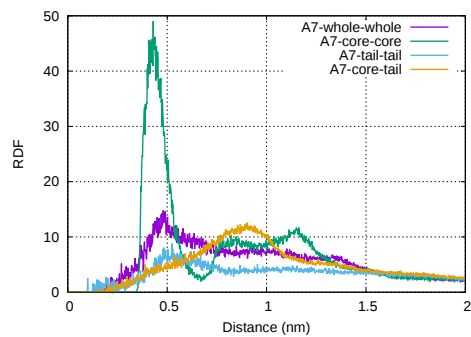


R6 and A6

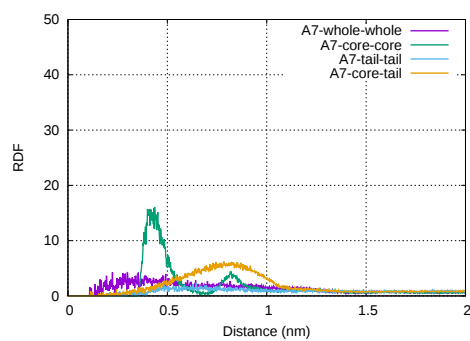
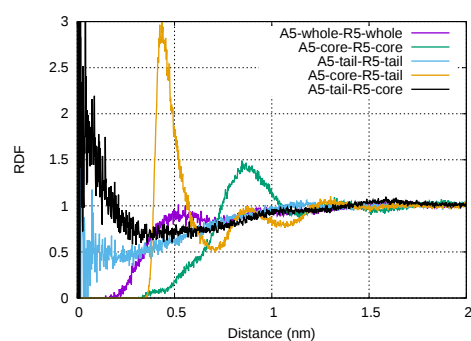
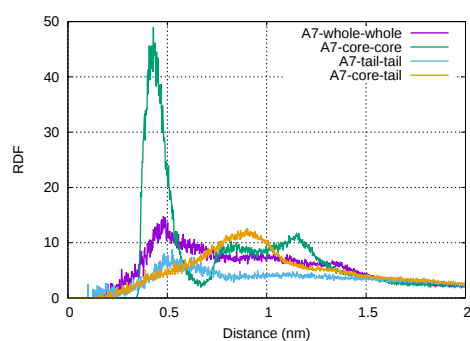


A7 and Resins

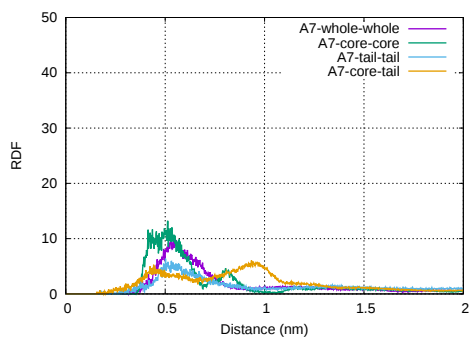
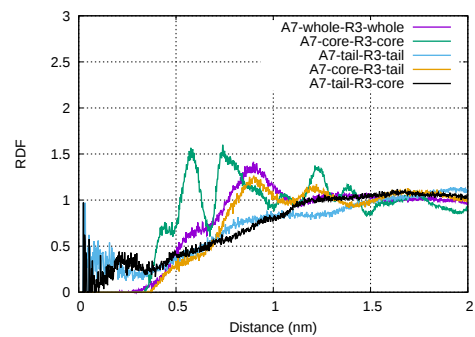
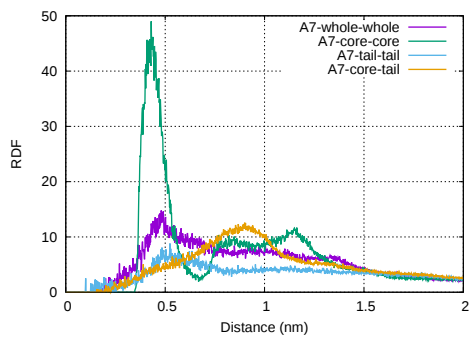
R1 and A7



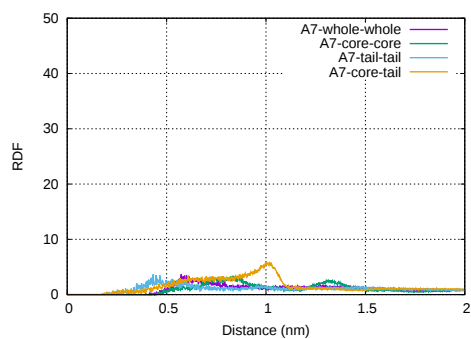
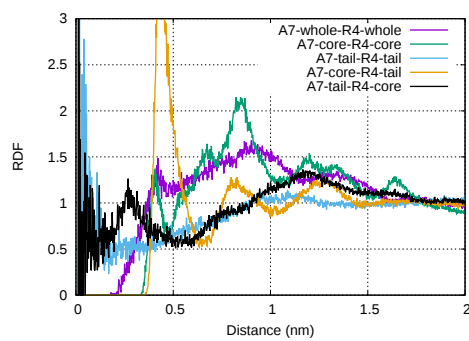
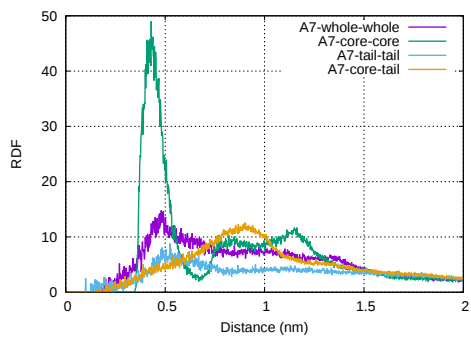
R2 and A7



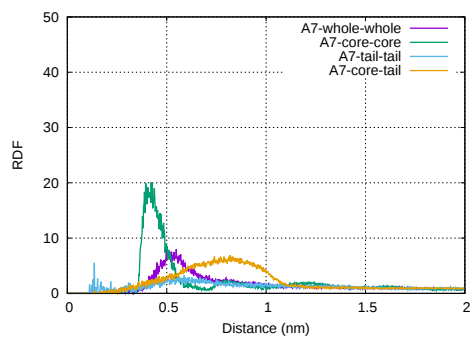
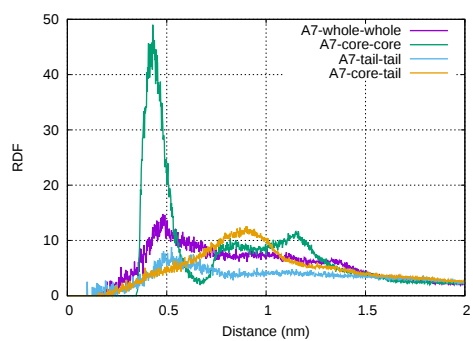
R3 and A7



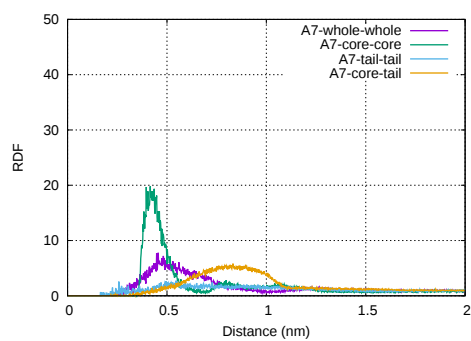
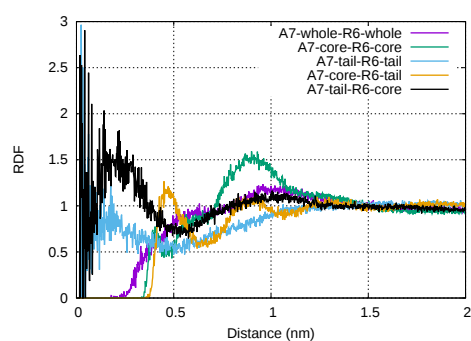
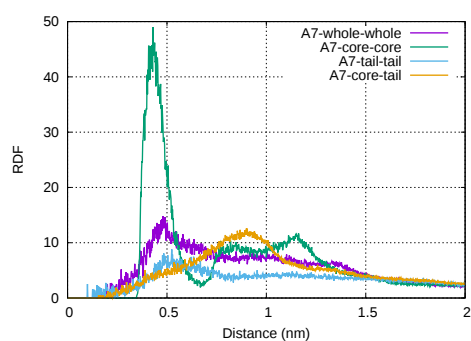
R4 and A7



R5 and A7

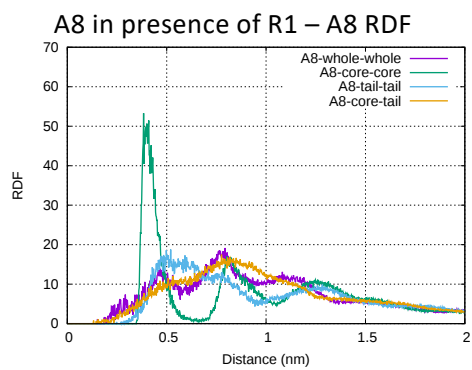
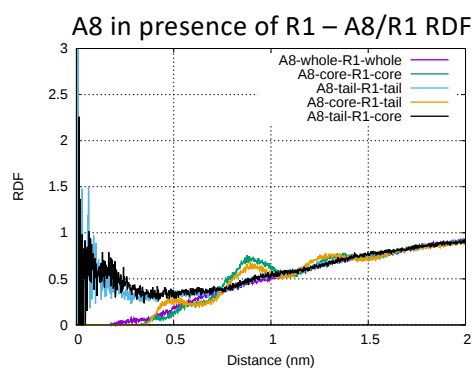
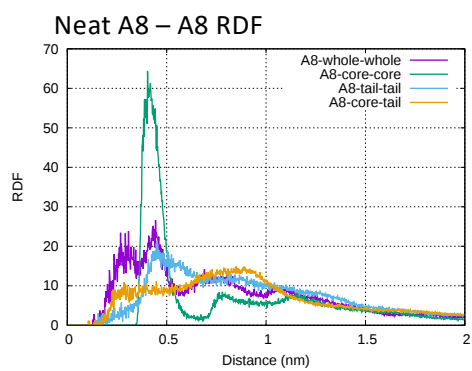


R6 and A7

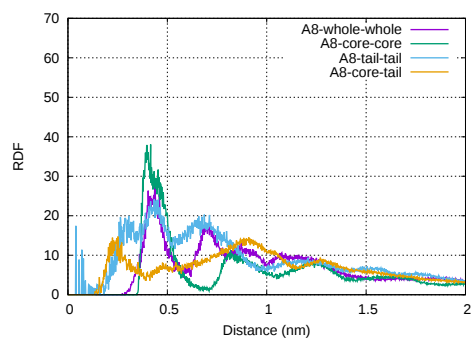
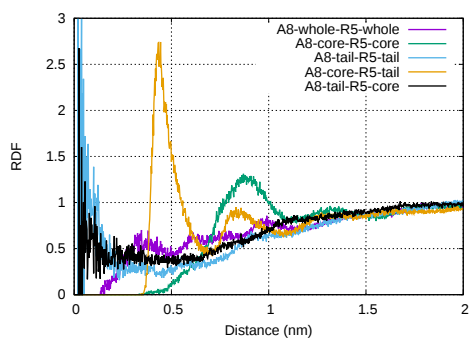
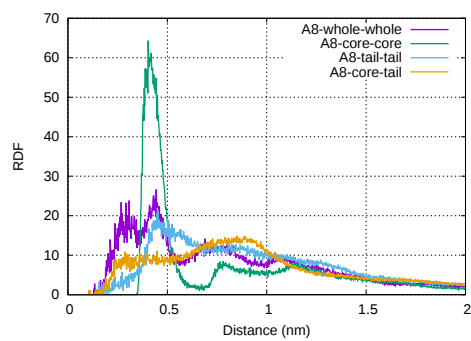


A8 and Resins

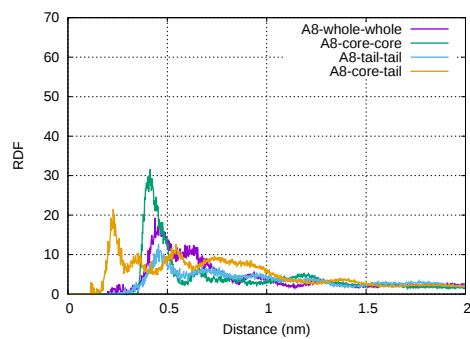
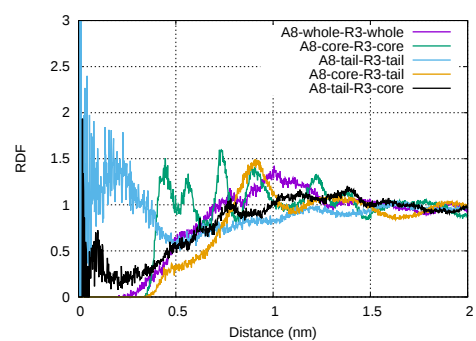
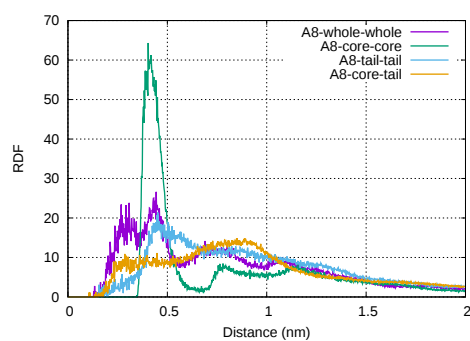
R1 and A8



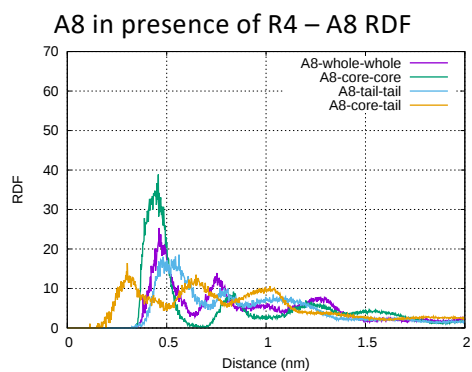
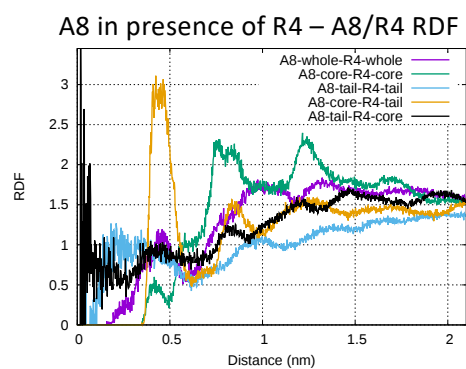
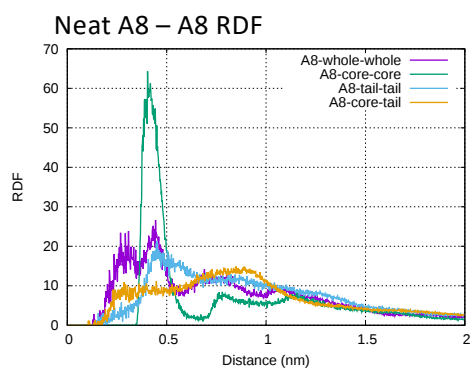
R2 and A8



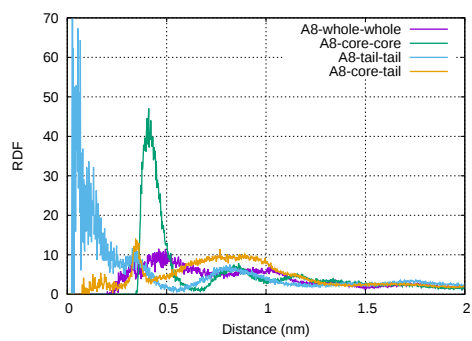
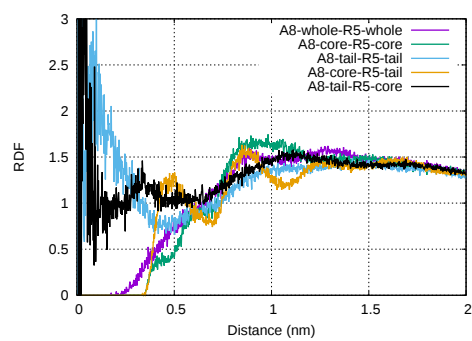
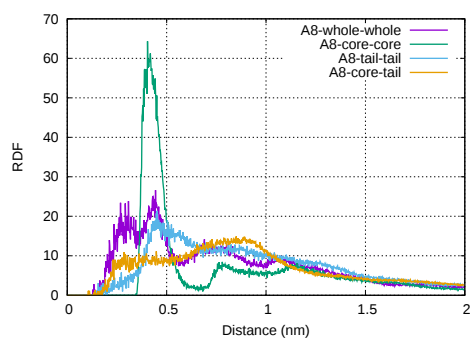
R3 and A8



R4 and A8



R5 and A8



R6 and A8

