Mesoscopic Simulation of Aggregate Structure and Stability of Heavy Crude Oil by GPU Accelerated DPD

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The aggregate structure of heavy crude oil, influencing the rheology, dispersity, stability of water-in-oil emulsions, attracts much industrial attention. In this work, aggregate behavior of asphaltenes in heavy crude oil was explored by a DPD based mesoscale platform. GPU was used to accelerate the simulation, which gains over 20x speedup against the serial version DPD provided by Materials Studio and over 10x speedup against the parallel version of DPD provided by CULGI running on 5 CPU cores. Rigid body fragments, which represent the significant presence of fused aromatic rings structure in fractions such as asphaltenes and resins, were introduced into DPD.

During the simulation, face to face, offset and T-shaped asphaltene aggregate structures were observed. The interlayer distance in well-ordered structure obtained from simulation was near 0.36 nm no matter which kind of model molecules, which agreed with experimental data (Trejo et al, 2009) well. The cluster size of asphaltene molecules was used to represent the stability of crude oil, which show that the stability of crude oil was independent on the concentration of saturate or aromatic with enough resin; if there was not enough resin to disperse asphaltene clusters, the ratio of saturate/aromatic must be limited to low values to maintain the oil stable. The relationship between concentration and stability of crude oil was consistent with Shell's work (Stankiewicz, et al, 2002).

1. Introduction

The research interest on heavy crude oil is increasing as the reservoir of conventional crude oil decreased (Marshall and Rodgers, 2008). The recovery and refining of heavy crude oil encounters various physicochemical phenomena concerning with the aggregates formed by asphaltene molecules. Experimental investigating the microstructure of heavy crude oil was proved to be difficult, owning to the strong dependence on the experimental conditions and the absence of effective approaches (Kharrat et al, 2007). During the past decades, quantum chemistry (QM), molecular mechanics (MM), molecular dynamics (MD), were widely used to study the interaction energies between asphaletene and resin molecules (Rogel, 2000), the quantitative molecular representations (QMRs) of asphaltene (Boek, et al, 2009), the effect of

hydrogen bond on aromatic-aromatic stacking of asphaltene molecules (Takanohashi, et al, 2003), etc. However, due to the very small length and time scales associated with these methods, they are too computationally expensive to be applied to study the micro structure of heavy crude oil. Dissipative particle dynamics (DPD) (Groot and Warren, 1997), in which a part of model molecule or several molecules are represented by a bead, can process a larger spatial and temporal scale system than MD can do.

Though DPD can tackle time and space scales beyond those available with molecular dynamics (MD), the demand of computing power to study heavy crude oil is still beyond a desktop computer. Until recent few years, a fast growing hardware GPU offers an alternative. This paper presents an implementation of DPD on heavy crude oil running on GPU. To make use of the GPU as optimal as possible, the kernel code was built from very beginning instead of migrating from any CPU version. Then the aggregate structure of heavy crude oil was explored by this DPD simulation platform.

2. DPD simulation platform details

2.1 GPU accelerated DPD

For a given bead, all interaction partners are located in the neighboring cells. By choosing R_c as the cells' width, which is cut-off radius of forces, 27 neighboring cells need to be considered when calculating forces. We assigned a fixed sized array of placeholders to every cell and physically copy beads' IDs into this array. Updating the cell-list, involving looping through the N beads and placing them into N_{cell}, was done by invoking the serial algorithm running only 1 thread on GPU.

When calculating forces, each bead was assigned to one independent thread. The position and velocity of the bead were copied from global memory to local variables of the thread which the bead was assigned to. 27 neighboring cells are searched for beads within range of interaction, and then DPD forces were calculated.

The integrating forward to the next time step, involving updating the position and velocity of all beads, was similar as the force calculation, having an independent thread per bead. Verlet-velocity method was used to update the position and velocity to the next time step.
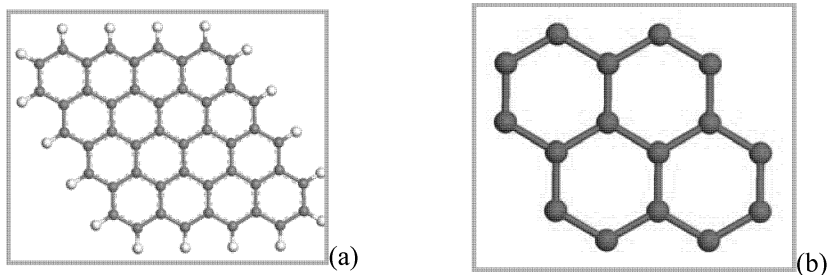
2.2 Model molecules

Figure 1: Coarse-graining the fused aromatic ring: (a) the fused aromatic rings in asphaltene molecules; (b) coarse-grained fused rings

Four average model molecules corresponding to SARA fractionation were constructed to represent heavy crude oil, since we still have no answer to how many compounds were in heavy crude oil or what their structures were exactly like. The fused aromatic rings, however, couldn't be exactly processed by grouping adjacent carbons as alkyl chains do for its complex topology. To maintain its topologic features, fused hexa-bead rings were chosen. Meanwhile, the rigidity of these aromatic rings was taken into account, seen in Figure 1. The alkyl chains are represented by DPD beads with spring force connecting them as many works did (Yamamoto, et al, 2002). We set the average length of side chains of asphaltenes to 1 or 2, and 2 to 3 for resin, 3 to 4 for aromatic, and 4 to 8 for saturate respectively.

Four types of DPD beads, A, B, C and D, representing aromatic rings bead, alkyl chain bead, functional group containing heteroatom and water respectively, were employed to construct model molecules. The physical units could be derived from the promissory coarse-graining level (Groot and Warren, 1997). The mass, length and time scales in physical units were $m = 8.97 \times 10{-20}$ kg, $R_c = 6.46 \times 10^{-10}$ m and $\tau = 8.8 \times 10{-11}$ s when we get the choice $N_m = 3$ and $\rho = 3$. It is easy to know the spatial and temporal range of DPD simulation could be in the range of nano-meter and micron.

2.3 Parameters in simulation

Table 1: Parameters of conservative force

	A	B	C	D
A	20	30	32	37
B	30	25	45	50
C	32	45	15	32
D	37	50	32	25

Table 1 presents the conservative force parameters obtained by Blends calculations at 298 K. According to Groot's theory (Groot and Warren, 1997), the conservative force parameters between beads of type A should be $a_{AA} = 25$ when $\rho = 3$. We roughly determined $a_{AA} = 20$ since the beads of type A were placed in the rigid sheets and the bead density of type A must be larger than even value of the system.

In this work, we set the noise parameter $\sigma = 3$, the dissipative parameter $\gamma = 4.5$, and the spring constant $C = 6.0$ to construct rather soft side chains in model molecules. The dimensionless temperature T was initialized as 1.0 and monitored at each step in our DPD simulations.

3. Results

3.1 Performance of GPU accelerated DPD compared with commercial software

The performance of our implementation was compared with Materials Studio® and CULGI. The DPD module of Materials Studio was only available in serial version, it was chosen as the baseline. The single CPU/GPU benchmarks of our implementation and Materials Studio were run on a desktop computer with an Intel® Core™ 2 Quad Q9400 CPU and a Nvidia® GTX285 graphics card manufactured by GigaByte®. The

multi CPUs benchmarks of CULGI were run on a workstation with 2 Intel Xeon 5320 CPUs and 4GB RAM. The DPD module of CULGI restricts the number of MPI process must be an aliquot part of the number of particles. So the number of process was set to 5. The density of simulation system was 3. Each benchmark runs for 10,000 time steps. Table 1 gives the benchmark results under different scale of simulation system of 20*20*20, 40*40*40 and 80*80*80. CULGI encountered a memory limitation on 80*80*80 for we only have 4GB RAM, so it is not listed in the table. Our GPU implementation shows more than 20x speedup compare with the serial version of DPD module of Material Studio and over 10x speedup against the parallel version of DPD provided by CULGI running on 5 CPU cores.

Table 2: the benchmark results under different scale of simulation system

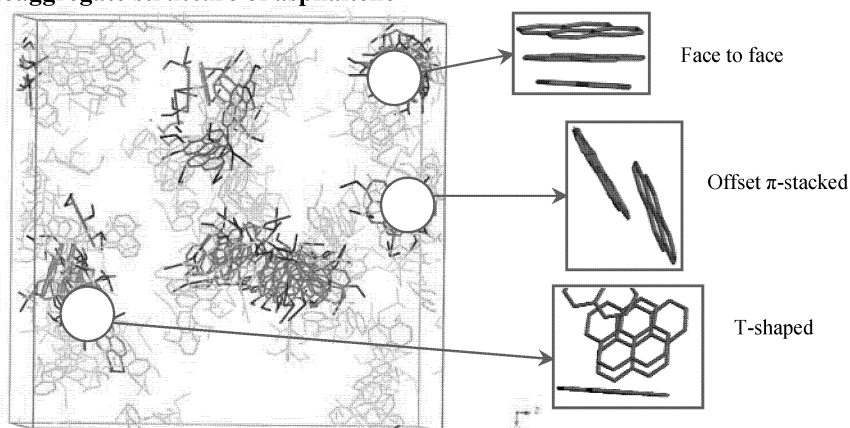| Box Length	Particles	Platform	Time/s	Improvement
20	24000	Material Studio	1513	-
20	24000	CULGI	650	2.3
20	24000	GPU	48	31.5
40	192000	Material Studio	12608	-
40	192000	CULGI	5792	2.18
40	192000	GPU	549	23.0
80	1536000	Material Studio	116546	-
80	1536000	CULGI	*	*
80	1536000	GPU	4486	26.0

3.2 Nanoaggregate structure of asphaltene

Figure 2: Snapshot of asphaltene nanoaggregates (aromatic and other light fractions concealed. the side chains in asphaltene molecules are highlighted by black color.)

As figure 2 shows, the fused aromatic rings (in red) of asphaltene molecules attract each other and form the cores of the nanoaggregates with surrounded resin molecules. The side chains (in black) act as the repulsive part to prevent further aggregation of

asphaltene molecules. On a larger scale, there are about 3 nanoaggregates (in the middle of Figure 2) combining to form a cluster of nanoaggregate. Moreover, three typical asphaltene aggregate structures can be observed in figure 2: face-to-face geometry attribute to π-π repulsion, T-shaped geometry attribute to π-σ attraction, and offset π-stacked geometry attribute to σ-σ attraction, which is the same with the rules summarized by Hunter and Saunders (1990). The reproduce of these three typical geometries certifies the capacity of mesoscale platform at integrating interaction mechanism among asphaltene molecules.

The calculated interlayer distance, the distance between the centroids of two fused aromatic rings, was in the range of 0.375~0.405 nm no matter which kind of model molecules, which was slightly larger than the experimental data 0.355nm (Trejo et al, 2009). The reason is that the rigid sheets in simulation tend to adopt offset π-stacked rather than face-to-face geometry in most situations, the distance between the centroids is larger than the real interlayer distance.

3.3 The effect of concentration on stability of crude oil

The stability of crude oil is assessed by various techniques such as SARA screens and titration tests using n-heptane in experiment. In our work, cluster size was taken as the parameter for judging the status of a crude oil. The crude oil was considered to be marginal when the maximum cluster size was 8 asphaltene molecules, be stable or unstable when less or more than 8 asphaltene molecules.
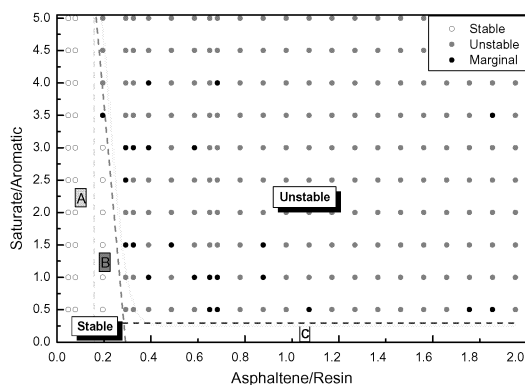

Figure3: A cross-plot of heavy crude oil from Simulations

The effect of concentration on stability of crude oil can be seen in figure 3. When the ratio of Asphaltene/Aromatic is set to 1:3, the stable area can be divided into 3 zones, marked as A, B and C. Zone A represents that the crude oil will keep stable among the whole range of ratio of saturate/aromatic, demonstrating the stability of crude oil could be independent on the amount of saturate or aromatic because of enough resin in oil. This phenomenon is pretty similar to the area marked "resin controlled" in Shell' work (Stankiewicz, et al, 2002). Resin molecules are able to produce a protective "wrapping" around the asphaltene clusters and prevent their aggregation by steric repulsion

mechanism. In zone B, however, there is not enough resin to disperse asphaltene clusters and thus the ratio of saturate/aromatic should be limited to low values to maintain the oil stable. Zone C is considered as a part of stable phase since the simulation systems tend to be stable as setting the ratio of saturate/aromatic to an exceedingly low value, though there is no stable sample oils appeared in Shell's cross-plot (Stankiewicz, et al, 2002).

4. Acknowledgement

References

Trejo F., Ancheyta J., Rana M.S., 2009, Structural Characterization of Asphaltenes Obtained from Hydroprocessed Crude Oils by SEM and TEM, Energy Fuels, 23, 429-439.

Stankiewicz A. B., Flannery M.D., Fuex N.A., Broze G., Couch J.L., Dubey S.T., Iyer S.D., Ratulowski J., Westerich J.T., Prediction of Asphaltene Deposition Risk in E&P Operations, 2002, AIChE 2002 Spring National Meeting: New Orleans, American, 47C, 410-416.

Marshall A.G., Rodgers R.P., 2008, Proceedings of the National Academy of Sciences of the United States of America, American, 105, 18090-18095.

Kharrat A.M., Zacharia J., Cherian V.J., Anyatonwu A, 2007, Issues with Comparing SARA Methodologies, Energy Fuels, 21, 3618-3621.

Rogel E., 2000, Simulation of Interactions in Asphaltene Aggregates, Energy Fuels, 14, 566-574.

Boek E.S., Yakovlev D.S., Headen T.F., 2009, Quantitative Molecular Representation of Asphaltenes and Molecular Dynamics Simulation of Their Aggregation, Energy Fuels, 23, 1209-1219.

Takanohashi T., Sato S., Saito I., Tanaka R., 2003, Molecular Dynamics Simulation of the Heat-Induced Relaxation of Asphaltene Aggregates, Energy Fuels, 17, 135-139.

Groot R.D., Warren P.B., 1997, Dissipative Particle Dynamics: Bridging the Gap between Atomistic and Mesoscopic Simulation, Journal of Chemical Physics, 107, 4423-4435.

Yamamoto S., Maruyama Y., Hyodo S., 2002, Dissipative Particle Dynamics Study of Spontaneous Vesicle Formation of Amphiphilic Molecules, Journal of Chemical Physics, 116, 5842-5849.

Hunter C.A., Sanders J.K.M., 1990, The Nature of .pi.-.pi. Interactions, Journal of the American Chemical Society, 112, 5525-5534.