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Study on the wax/asphaltene aggregation with diffusion limited aggregation model

Wenyuan Sun [a], Wei Wang [a,*], Yunqing Gu [a], Xiaoxuan Xu [b], Jing Gong [a,*]

[a] *National Engineering Laboratory for Pipeline Safety/MOE Key Laboratory of Petroleum Engineering/Beijing Key Laboratory of Urban Oil and Gas Distribution Technology, China University of Petroleum, Beijing, China*

[b] *The Petroleum Exploration & Production Research Institute, Sinopec, China*

HIGHLIGHTS

- Modified DLA model has been used to simulate the co-precipitation of wax/asphaltene particle.
- Fractal dimension is adopted to explore the geometric property of the aggregates.
- The changing law of fractal dimension with concentration and size ratio has been explored.

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ABSTRACT

Diffusion-limited aggregation (DLA) model has been widely used to simulate the aggregation processes. In this work, the aggregation of wax and asphaltene particles in crude oil is studied with a modified DLA model. Assuming both wax and asphaltene particles are sphere, the co-precipitating process could be regarded as a simple aggregation process containing two kinds of particles. Three important parameters are discussed, as the sticking coefficient between particles, the ratio of particle size, and the particle concentration. Via analyzing the fractal dimension of the formed aggregates, the aggregation mechanism of wax and asphaltene particles could be explained, and help to further reveal the nature of the disordered growth.

1. Introduction

Various aggregation mechanisms have been proposed to theoretically investigate the disordered growth under non-equilibrium conditions. Such as snowflake structure in nature [1] and magnetic α-Fe_2O_3 [2], among which the diffusion limited aggregation (DLA) has been intensively studied by many researchers.

The original DLA model was proposed by Witten and Sander [3], which is a stochastic model, and is suitable for the system of which the main mode of motion is diffusion. Such as dielectric breakdown [4], electrochemical deposition [5], viscous fingering, and Laplacian flow [6]. During the simulation, an original *seed* is placed in the center of the lattice, and the next particle is released from a certain distance to do Brownian motion. Power-law scaling of the two-point correlation function was discovered in the previous work by Witten and Sander [3]. It has been proved to be able to represent the aggregations of many kinds of nano-particles and colloids [7–11], and asphaltene aggregation is definitely one of them [12].

Asphaltene is a heavy component of crude oil, whose deposition would cause significant problems during the exploration of crude oil, such as reduced production rate, equipment fouling, and catalyst poisoning [13]. Additionally, another appreciable component in the oil, wax, is also sensitive to the change of pressure and temperature as asphaltene is. Reservoir conditions could keep them in solution [14]. When crude oil is brought to the surface, equilibriums will be broke and precipitations occur [15]. However, interactions between asphaltene and wax would make the problem even complex.

Experimental measurements as UV–visible Spectrophotometer helping to detect the precipitation of asphaltene in crude oil showed that asphaltene undergoes a gradual aggregation process from nanometer scale to micrometer length [16]. Asphaltene could self-associate at molecular level, where the driving force comes from the intermolecular forces. When asphaltenes precipitate as

* Corresponding authors.
E-mail addresses: w.wang@cup.edu.cn (W. Wang), ydgj@cup.edu.cn (J. Gong).

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Nomenclature

M	mass of the fractal cluster
Rg	gyration radius of the cluster
D_f	fractal dimension of the cluster
$D_f(i)$	fractal dimension of the current state of an aggregate
s	sticking coefficient
seed	initial particle of the aggregate
walker	particle which has not stuck on the clusters or moved out of the lattice
Rmax	outer radius of the cluster
δ	three times of the reduced diameter of the particle
dmin	distance from the *walker* to its closest particle in the cluster
l	sum of radius of two particles
ρ	a certain factor
L	side length of the lattice
σ_m	size ratio of asphaltene to wax particle
σ^*	reduced diameter of the '*walker*'
X_n	Concentration of asphaltene

the change of solvent, temperature, or pressure, they aggregated via hydrogen bonding from polar components or pi-pi bonds in aromatic rings [17]. While for wax precipitation, the long n-paraffin has the dominated impact on the crystal among the linear, branched, and cyclic alkane [18–20]. The interaction between wax and asphaltene particles is even more complicated.

The potential importance of such interaction is first seen in the study by Knox et al. [21], who found the deposition of wax in crude oil was inhibited by the additives containing asphaltene when he was trying to find an inhibitor for wax deposition. Yang and Kilpatrick [22] proposed there was little reciprocity of wax and asphaltene, but asphaltene particles could be trapped in the wax deposit. However, research of Tinsley [23], Wu [24] showed that the aggregated asphaltene particles provided nucleation sites, and accelerated the precipitation of wax, where the wax crystal morphology would be changed. Venkatesan et al. [25] held the view that compared to the former entangled rod-like structure, the wax crystals become more globular and less entangled after the addition of asphaltenes. Oliveira et al. [26], Oh and Deo [27] have similar findings.

From the aspect of growth dynamic, particles are driven by intermolecular forces to do Brownian motions and self-association. The aggregates absorb new particles while breaking down and finally reach an equilibrium state [28]. If there were different kinds of particles in the system as wax and asphaltene, the adhesion behavior would differ due to various attractions. Particles belonging to different kinds contribute dissimilarly to the aggregates due to their different size. It was difficult to express the unordered structure of aggregates until the concept of fractal dimension was introduced [29].

Fractal geometry is frequently related to diffusion-limited aggregation. It is used to describe intricate details under arbitrary small scales. These details are irregular at both global and local parts, and cannot be described by traditional Euclidean geometry. The fractal dimension is self-similar and is usually greater than the topological dimension. Researchers as Visintin et al. [30] proved that the wax crystal is fractal geometric by analyzing microscopic images of crude oil from Ferris and Cowles [31], Chang [32], Hénaut et al. [33] and Létoff [34]. Gao [35] explored the relationship between wax rheological character and its fractal structure. And fractal analysis is considered in asphaltene aggregation for the former scattering and viscosity investigation [29,36,37]. Also, the aggregates formed by wax and asphaltene co-precipitation have a fractal character.

In the present paper, DLA model is adopted to analyze the aggregation behavior between two kinds of particle, the original one, representing the asphaltene particle, and the later one, representing the wax particle. The effects of the particle size ratio and the concentration on the fractal dimension of the aggregates are particularly discussed.

2. Model and simulation

2.1. Theoretical background

2.1.1. Diffusion limited aggregation

The DLA model is based on two mechanisms, diffusion and aggregation.

- Diffusion

Diffusion is the macroscopic result of molecules' random thermal motions. If the distribution of particles in the solution is not uniform, there would be a net flux which is proportional to the concentration gradient.

$$\vec{j} = -D\vec{\nabla}n \tag{2.1}$$

where D is a diffusion constant, n is concentration

And

$$\vec{\nabla} \times \vec{j} = -\frac{\partial n}{\partial t} + q \tag{2.2}$$

where q stands for the sources. Thus the diffusion equation can be written as:

$$\frac{\partial n}{\partial t} = D\nabla^2 n - q \tag{2.3}$$

- Aggregation

If particles are likely to stick together, aggregates would be formed. The attractive force varies with the type and the size of particles. Aggregation is the preferred state of dispersed particles, and the aggregates are usually well-ordered.

- DLA clusters

DLA clusters are fractal aggregates obtained by diffusion-limited aggregation. The morphology of clusters is determined by the possibility of the particles to stick together by Brownian motion. The forming processes of the clusters comply with the Laplacian equation with a movable boundary, and particles would keep moving in clusters' external area until they adhere to the cluster. Clusters keep growing by having these moving particles adhered on them. As the self-association of wax and asphaltene could be considered as Brownian motion, the DLA process is appropriate to describe their aggregation process.

2.1.2. Fractal dimension

The fractal dimension has different definitions as box dimension [38], Hausdorff dimension [39], which is defined from the effectiveness to occupy the space. For a two-component DLA