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The dynamic Flory-Huggins-Zuo equation of state

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ABSTRACT

In recent years, the FHZ EoS (Flory-Huggins-Zuo equation of state) has been developed to model asphaltene gradients in reservoir crude oils. Resolution of the nanostructures of asphaltenes in crude as given by the Yen-Mullins model has enabled the explicit form of the gravity (and other) terms in the FHZ EoS. In addition, the recent development of accurate in-situ measurements of crude oil gradients in oil wells has motivated the need for thermodynamic modeling of asphaltene gradients. Many oil reservoirs exhibit thermodynamically equilibrated crude oils which are accurately represented by the FHZ EoS. Nevertheless, there are many reservoirs that are undergoing dynamic processes in geologic time. Consequently, time must be explicitly included in the FHZ EoS. The dynamic FHZ EoS is developed within a generalized formalism herein. Specific application of this formalism to diffusive dynamical processes is derived and corresponding simulations are shown. Extension of the dynamic FHZ EoS to other time-dependent processes of geologic importance is discussed.

1. Introduction

The thermodynamic modeling of reservoir crude oils can be very useful to understand fluid complexities as well as reservoir complexities [1,2]. Key fluid attributes that must be understood include the relative quantities of gas, liquid, and solids, the asphaltenes that can be expected in production. For example, in deepwater oil production, expensive seafloor facilities that process produced fluids must be designed with specific gas- and liquid-handling capabilities. Crude oil flow rates are strongly impacted by viscosity, and thus asphaltene content, of the oil. Various phase behavior properties of the reservoir crude oil define production constraints. For example, pressure reduction in production (thus flow rate) is generally limited by the bubble point of a crude oil. Production below the bubble point would cause production of the high-mobility gas and leave the valuable hydrocarbon liquids in the reservoir. In addition to fluid complexities, many complexities of reservoirs can be addressed by analysis of fluid gradients both vertical and lateral. One of the biggest concerns associated with oil reservoirs is their overall size. Some reservoirs are like a sponge, and fluid flow connectivity applies throughout the entire volume. Other reservoirs are like a spool of bubble wrap, and the flow units or compartments are very small and uneconomic. If reservoir fluids are established to be in thermodynamic equilibrium, then it is likely (but not definite) that these fluids reside in a single (potentially large) compartment [2,3].

For a myriad of major production concerns, it is imperative to obtain reservoir crude oil samples for analysis. Moreover, it is required to obtain fluid models to interpolate and extrapolate fluid characteristics of billion-barrel fields from small numbers of oil samples (e.g., 10 samples). Gas–liquid thermodynamic modeling of reservoir fluids has been successfully conducted with the cubic EoS (equation of state) for decades. For example, the Peng-Robinson EoS is used ubiquitously [4]. In addition, reservoir simulators often employ a cubic EoS for development and optimization of production plans for the oilfield.

However, until recently, there had not been any first-principles modeling of asphaltene gradients in reservoir crude oils. There had been no understanding of the structures of asphaltenes either in crude oils or in laboratory solvents. Even the molecular weight of asphaltenes had been debated over orders of magnitude [5]. Consequently, the negative buoyancy of dissolved asphaltene in crude oils remained unresolved and a first-principles model of asphaltene gradients was precluded. Fortunately, this limitation has been resolved. The molecular and stable nanocolloidal structures of asphaltenes in laboratory solvents and in crude oils have

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been codified in the Yen-Mullins model (Fig. 1) [6,7]. To build this model, a very broad array of results from many disciplines was employed for each of the three species of this model as described. Molecular weight and molecular architecture were obtained from TRFD (time-resolved fluorescence depolarization) [7,8] and from laser desorption, L2MS (laser ionization mass spectrometry) [9], and related measurements [10]. Alicyclic rings fused to aromatic rings as shown in Fig. 1 are consistent with the activity of asphaltene hydrogen in dehydrogenation studies [11]. Other mass spectral studies confirmed the molecular weight [12]. Polycyclic aromatic hydrocarbon size of asphaltenes was obtained from direct molecular imaging [13,14] and optical spectroscopy [15,16]. Nanoaggregates were observed using high-Q ultrasonics [17,18], NMR (nuclear magnetic resonance) [19], DC-conductivity [20,21], SANS (small-angle neutron scattering) and SAXS (small-angle X-ray scattering) [22], and centrifugation [23,24], along with related analysis of gravity gradients in oil reservoirs [25] among other techniques. Clusters were observed by flocculation kinetics [26,27], interfacial studies [28], and DC-conductivity [20].

Subsequent to the initial proposal of the Yen-Mullins model (then called the modified Yen model), all aspects of this model have been subjected to many stringent tests. For example, the proposed molecular weight and island molecular architecture have been strongly supported by L2MS studies [29]. Most importantly, L2MS studies have established the ability to disaggregate asphaltene nanoaggregates, [30] a known problem with some mass spectral techniques. Related mass spectral studies corroborate island molecular architecture [31,32]. In conceptually simple, robust, surface-tension studies, the PAH (polycyclic aromatic hydrocarbon) size for several asphaltene types has been confirmed [33,34]. NMR studies have also confirmed the asphaltene PAH sizes, [35,36] given the asphaltene orientation at the interface [37]. Alicyclic rings fused to aromatic rings have been confirmed by heteronuclear single quantum coherence NMR studies [36]. Nanoaggregate properties of aggregation number and critical nanoaggregation concentration have been confirmed by mass spectrometry [38–40]. Combined SANS and SAXS studies confirm the detailed structure of the nanoaggregate and cluster [41–43]. Powerful confirmation of asphaltene cluster size has been obtained in a gravitational gradient of an oil column with 50 m of height and with a 100-km circumference [44]. Related centrifugation along with DC-conductivity studies also obtained confirmation of cluster size and the critical clustering concentration [21]. NMR diffusion measurements have determined the cluster aggregation number (six), in close agreement with Fig. 1 [36].

In contrast to Fig. 1, some bulk decomposition studies of asphaltenes indicate the presence of some molecular populations with two or perhaps more aromatic ring systems [45]. Perhaps this fraction is relatively small, thereby not impacting molecular (not bulk) decomposition measurements, which clearly indicate the dominance of island architecture [29]. In addition, in bulk decomposition studies, asphaltenes are found to form structures with two or more aromatic ring systems; [46] thus, interpretation of these decomposition studies in terms of virgin asphaltene molecular structure is rendered very difficult.

The strong, diverse foundation studies behind the Yen-Mullins model coupled with the extensive, stringent confirmation studies combine to prove that this model is a sound basis for the thermodynamic treatment of asphaltene gradients in oil reservoirs. The Flory-Huggins equation has been used successfully to account for asphaltene phase instability [47,48]. The addition of a gravity term to this equation yields the so-called FHZ EoS (Flory-Huggins-Zuo equation of state), which can be used to model asphaltene gradients in oil reservoirs [3,49]. The FHZ EoS is given below:

$$\frac{OD(h_2)}{OD(h_1)} = \frac{\phi_a(h_2)}{\phi_a(h_1)} = \exp\left\{\frac{v_a g(\rho-\rho_a)(h_2-h_1)}{RT} + \frac{v_a}{RT}\left[(\delta_a-\delta)^2_{h_1} - (\delta_a-\delta)^2_{h_2}\right] + \left[\left(\frac{v_a}{v}\right)_{h_2} - \left(\frac{v_a}{v}\right)_{h_1}\right]\right\} \quad (1)$$

where OD, R, ϕ, v, δ, T, g, ρ, and h are the optical density, universal gas constant, volume fraction, molar volume, solubility parameter, temperature, gravitational acceleration, density, and depth, respectively. Subscript a denotes the properties of asphaltenes, symbols without subscript are the properties of the bulk fluid; subscripts h_1 and h_2 stand for the properties at depths h_1 and h_2, respectively. The solubility parameter, molar volume, and density of bulk fluids, temperature, pressure and compositions are dependent on depth. Therefore, the concentration (volume fraction) variations of asphaltenes with depth depend on three terms: gravity, solubility (enthalpy), and entropy.

From a practical standpoint, the FHZ EoS has properties that are particularly useful for oilfield application. For a given reservoir crude oil, the solubility term depends primarily on the GOR (gas-oil ratio) [3]. The GOR is almost always determined for reservoir crude oils and modeled using the cubic EoS. Moreover, there is a general understanding that gas addition to crude oils destabilizes asphaltene [7,50]. For example, it is common knowledge that using gas lift for heavy oils for high-pressure reservoirs will cause asphaltene deposition and flow assurance problems. (The high pressure ensures injected gas will cause dissolved gas to increase.) Such familiarity has led to rapid acceptance of the FHZ EoS, as is indicated by the large number of reservoir case studies employing the FHZ EoS [3,25].

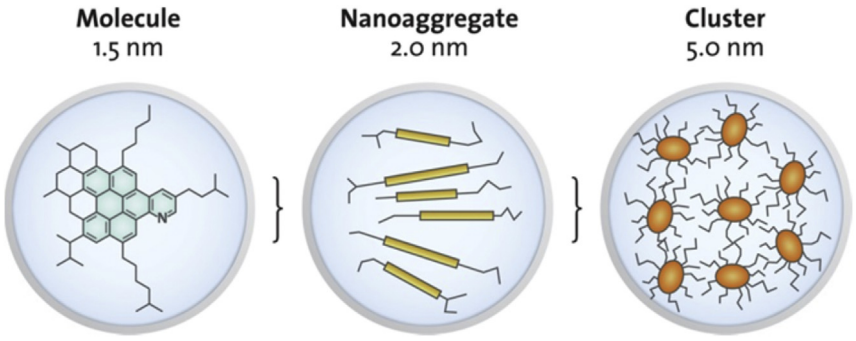

Fig. 1. Yen-Mullins model of asphaltenes. The predominant structures of asphaltene molecules (left), nanoaggregate consisting of six molecules (center), and cluster consisting of eight nanoaggregates (right) are shown. [6,7].