# Asphaltenes, Heavy Oils, and Petroleomics

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This book is dedicated to all those scientists and technologists who have and will become enthralled and enchanted by the wiles of the asphaltenes and heavy oils, and to the families and friends of our fold who at least feign enthusiasm when subjected to renderings of the mysterious objects of our study.

—OCM

# Preface

This book represents an amalgam of objectives related to the study of petroleum at many, diverse levels. The most important attribute any thriving technical field must have is an injection and infusion of dedicated, expert, young scientists who have absorbed from their elders the fascination of scientific mystery coupled with the fundamental satisfaction of revelation and providing contribution. And, of course, these youthful practitioners must also learn to challenge the authority of their elders. From experiences with my own students, this seems not to be a problem. Many chapters in this book are coauthored by young scientists yielding the prognosis of continued health of our scientific field. Indeed, I am quite proud that several of my own chapters in this book are coauthored with students and young engineers of enormous capability. It is a humbling honor to help delineate direction of this formidable talent. It is incumbent upon my generation of scientists to provide a vision of the future. In this book, we connect the scientific excellence of the past with a vision for petroleum science, Petroleomics. Medical science of the past has been of singular societal focus with scientific discoveries of enormous import. Nevertheless, Genomics is revolutionary in that causal relations in medical science are being established with scientific exactitude and fundamental understanding. Genomics is creating a predictive medical science that was but a dream for previous generations. In a similar way, scientific advances described in this book are laying the foundations for Petroleomics—the challenge and framework to agitate our youthful contributors. Petroleomics embodies the establishment of structure—function relations in petroleum science with particular focus on asphaltenes, the most enigmatic of petroleum components. Correlative phenomenology is giving way to proper predictive science based in detailed petroleum chemical composition. This book describes the nascent development of the Petroleome, the complete listing of all components in a crude oil. As is shown herein, causal scientific relations in petroleum and asphaltene science are now being established that were merely plausible conjectures in the recent past.

This book also serves the purpose to reinforce the seemless continuity in petroleum science of basic scientific discovery with application of technology in a major and growing economic sphere. Longer standing concerns such as flow assurance are treated herein within a much more rigorous setting. In addition, very recent advances in the use of Downhole Fluid Analysis to address the most important issues in deepwater production of oil motivate renewed vigor in detailed chemical investigations in petroleum science. Oil operating companies and oil services companies are at the forefront of many of these technologic developments of enormous import. The economic impact of these new directions mandates development of exacting scientific underpinnings from leading universities and national facilities. Research dollars are too scarce and the technological challenges too great to employ research models of redundant effort in different institutions or of moving directionless unaware of impact. The new model promulgated in this book is to have cohesive collegial, international teams across corporate and university boundaries, across scientific and technological disciplines with research portfolios consisting of basic science and applied technology with a mix of near term and long term objectives. Certainly, internecine scientific battles will rage, and proprietary knowledge must be managed. (This book attempts to settle several of the most fierce, long-standing battles.) Nevertheless, this new research model delivers efficient use of expert human capital to address concerns of major scientific and economic impact. Life's experiences are greatly broadened by participation in such endeavors. As Chief Editor of this book, I have tried to reflect in this book the spirit of my own experiences of visiting six continents recently to grow our new business segment which I had the good fortune to initiate, to visit universities around the world, to interact with our field engineers, reservoir engineers, university professors and their students, male and female, of so many interesting cultures and nationalities. Science and technology are truly enriching for those lucky enough to participate.

*Oliver C. Mullins*

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# 1

# Petroleomics and Structure–Function Relations of Crude Oils and Asphaltenes

**Oliver C. Mullins**

## 1. Introduction

Petroleum science and technology are advancing at a rapid pace due to a myriad of considerations. The efficient generation and utilization of energy are increasingly being recognized as a societal necessity from economic and environmental vantages. Increasing concerns regarding physical limits of total hydrocarbon resources are colliding with rapidly expanding economies in heavily populated regions of the world, that require plentiful, affordable transportation fuels to realize expectations of impatient populaces. Geopolitical instabilities are magnified by disparate distributions of hydrocarbons attracting attention of powerful hydrocarbon consuming nations commensurate with the perceived value of these resources. Exploitation of hydrocarbon resources in many cases is the best hope for lifting nations out of grinding poverty. However, in large measure, the "easy" hydrocarbon resources have already been drained, increasing the technical demand for exploitation of the remainder. Heavy oils and bitumens that were bypassed in favor of their lighter bedfellows constitute an increasing fraction of remaining hydrocarbon resources. Deepwater production of hydrocarbon resources involves tremendous costs, thereby mandating efficiencies that can be achieved only with proper understanding of petroleum chemistry. Exploitation of marginal reserves in mature markets rich in infrastructure, such as the North Sea, hinges on accurate prediction of production. The insightful characterization of reservoir architecture and of reservoir dynamics, very challenging tasks, rests in large part on the detailed understanding of the contained fluids.

The confluence of these diverse considerations has created a welcome challenge amongst those scientists and technologists who find crude oils and asphaltenes worthy subjects of study. At the same time, investigative methods are inexorably improving; new technology, greater sensitivity, higher resolution coupled with improved theoretical modeling and simplifying formalisms more clearly

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rooted in physical foundation are providing the scientist sharper, more powerful tools to prod, probe, inspect, and interrogate the carbonaceous materials of our concern. The petroleum technical community has been galvanized applying sophisticated new techniques and advanced application of mature methods; this focus is bearing fruit in all areas of petroleum science and technology. The most enigmatic component of crude oil, the asphaltenes are finally revealing their secrets; in particular, basic asphaltene molecular structure is now understood, an absolute necessity for development of predictive petroleum science. Simplifying governing principles of asphaltenes are being uncovered enabling development of structure–function relationships, one of the pillars of Petroleomics. Connection of molecular scale knowledge of asphaltenes is helping to provide the basis of the phase behavior of asphaltenes at the different length scales, thus vertically integrating diverse studies. Petroleomics, the establishment of structure–function relations for asphaltenes and crude oils, is being implemented. New mass spectral and other analytic techniques are of sufficient resolution that generation of the petroleome is in sight, the complete listing of every component even for heavy crude oil. For the first time, asphaltene science and petroleum science are poised to join the pantheon of scientific disciplines sufficiently developed that new phenomena can be treated within a framework of first principles. It is an exciting time to be involved in the study of asphaltenes and crude oils.

"If you want to understand function, study structure" advises Francis Crick.[1] To perform proper predictive science, the structure of the system under study must be known. This necessary step allows structure–function relations to be established. Further study then reveals detailed mechanistic processes and identifies broad, underlying governing principles. In a perfect scientific world, structure can be determined and these investigative precepts are followed without interruption. Results are questioned, but not the process. Consider the evolution of the understanding of a rather important liquid other than petroleum(!). Water has played a central role in all aspects of life since life started on the planet. It is certainly true that the use of water by sentient beings greatly preceded the understanding of this life enabling substance. Nevertheless, the concept of understanding and explaining properties of water is unimaginable without knowing its molecular structure and its intermolecular interactions. The water molecule is a bent triatomic with D2h symmetry. The oxygen in water is $sp^3$ hybridized and has two lone electron pairs; as such the H-O-H bond angle is close to that expected for a tetrahedron, $109.5^\circ$ but due to the increased repulsion of the unshared nonbonding electrons, the bond angle of water is $105.5^\circ$. The large electronegativity contrast of constituent water elements creates a large dipole moment and large dielectric constant of the bulk enabling water to dissolve a large number of ionic compounds. The lone pairs of electrons can engage in hydrogen bonding giving water an unusually high boiling point for a molecule of 18 amu, contrasted by methane and ethane for example. The very directional hydrogen bond structure in the solid (ice I) causes the lattice to open up, thereby creating a lower density of the solid than the liquid. Knowing the structure does not imply that the understanding all properties of water follows immediately. In fact, recent results are changing the understanding of the extent of H-bonding per molecule in liquid water.[2] Petroleum chemists are forgiven for not “solving” the multicomponent, complex object of their study since pure liquid water still retains controversy. It is important to recognize that asphaltene-rich materials, such as bitumen, are perhaps best described as composites. Composites such as bone, steel, and wood possess properties that are defined by the integration of their constituents.[3] Certain crude oils share this trait. Nevertheless, in the case of water, and every other substance, pure or otherwise, it is of paramount importance to realize function follows structure.

System complexity generally retards predictive science and of course the platitude “necessity is the mother of invention” continues to prevail. Advances in materials that portend the greatest distinctions from previous human eras identify archeological ages. The stone age, the bronze age, and the iron age all corresponded to fundamental advances in the mastery of the natural world, and always preceded detailed structural understanding. While samurai sword makers followed a ritualistic process to create the world’s best blades; the explanation of this process and of the metallurgy of steel followed much later.[3] Rubber was utilized long before polymer science matriculated to an academic discipline. Superconductivity was discovered long before it was understood at a fundamental level. Many advances proceed with an intriguing mix of some predictive conceptualization coupled with indefatigable Edisonian searches. In such cases, structure is not known a priori. History has taught that alert, perceptive minds can recognize patterns that yield valuable advances, even without knowing basic structure. There may even be a natural human aversion to alter processes known to yield phenomenological successes; we may all have a little of the samurai sword makers in us. Nevertheless, to *understand* function, structure simply must be known.

The endeavor of human medicine is exquisitely enshrouded in phenomenology. The subject is too important and the complexity too great to wait for scientific validation. Shamans embodied some of the earliest approaches to medicine mixing mysticism with natural curative agents perceptively discovered. Of course, medical science has made tremendous advances through the ages. Still much of the methodology has remained unchanged. The small pox vaccine developed by Edward Jenner rested upon the astute observation by that milk maidens (thus exposed to cow pox) did not develop small pox. Countless serendipitous advances in medical science have similarly occurred. Nevertheless, in many ways medicine is practiced by responding to symptoms. We collectively are individually in the wait-and-see mode regarding our health. It is true that diagnostic medical science continues to improve and will continue to be exploited in ever expanding ways. However, this approach is fundamentally flawed; the disease must develop to be detected. It is greatly preferred to predict and treat disease *prior* to the development of symptoms. Early detection of symptoms requires repeated, sensitive, thus costly testing; without prediction, the diagnostic search is not directed. But repeated Edisonian searches cannot be sensitive and cost effective. The deficiency of predictive medical science is not due to the lack of focus. Any physical scientist trying to acquire funding is well aware of the behemoth engine of medical research which must be sated first. And as a scientist who studies asphaltenes, it is hard for this author to argue against this priority. Beepers are not the norm for asphaltene emergencies. Of course, asphaltene science does directly impact the oil business, which is not inconsiderable. The biggest impediment to predictive medical science has been the lack of understanding structure, known to Crick when he expounded the guiding principle cited above.

Millennia after humans initiated medical science, Watson, Crick, Franklin, and Wilkins discovered the structure of the alphabet of human life in 1953. It took 50 years, but/and in 2003 the book of human life, the human genome has been read. This event is a turning point in human history—but there was some disappointment accompanying this great achievement. It was known that the *C. elegans* roundworm (a popular subject of study) has ~19,000 gene. Naturally, speculation was rife that we humans, so much better than the roundworm, must have perhaps 100,000 genes or more. (Some limits of human DNA were known at that time, or undoubtedly the estimates would have been much higher.) Well, humans only have about 30,000 genes. Now we are using this modest excess of our genes versus the roundworm in an exponent or as a factorial where it would clearly show our superiority again. Tautology notwithstanding, reading the book of human life is a monumental achievement.

Now that the structure of the human genome is known, structure–function relations can finally be established in medicine. Deleterious genes are being uncovered that relate to a variety of medical problems; major public health issues are being addressed. For instance, an article in the *New England Journal of Medicine*[4] (and on the front page of the *New York Times*) that a particular variant of a gene is associated with a factor of five increased risk of congestive heart failure. In the United States there are more people hospitalized with congestive heart failure than all cancers combined, thus is of enormous public policy concern. The initial application of genomics may be screening for particular deleterious genes for congestive heart failure, for stroke, for specific cancers. For those with the offending genes, specific sensitive diagnostic analyses can be performed searching for the corresponding symptoms, controlling costs while being sensitive.

In the longer term, genomics promises to change the way medical science is practiced. By knowing the deleterious genes, the hope and expectation is that one will know the proteins encoded by the normal and defective genes; one will know the biomedical pathways involving these proteins. One will know precisely the impact of the deleterious gene. Effective treatments can then be developed for those who possess the deleterious genes. In the future, the medical community will read *your* genome. (But the reader may have to live a considerable while for this to come to fruition.) A bar chart will be generated for the probability of your developing specific maladies. If the probability of a specific ailment is high, the treatment for this problem can be launched. One can treat the disease prior to the development of symptoms. In this way, genomics will revolutionize medicine. The absolute foundation and requirement for genomics are knowing the structure of DNA and reading the human genome. Without this structural foundation, we would revert back to phenomenology, the analysis of symptoms, as the predictive approach would be precluded.

In addition to improving the direct application of medical science, genomics has enormous public policy implications as well. It is known that black Americans have a congestive heart failure rate a factor of five greater than white Americans. Had one been asked to identify likely causality for this observation prior to the discovery of the deleterious gene for congestive heart failure, factors including socioeconomic differences, access to health care, and a myriad of other plausible origins would be listed. Solutions to problems of congestive heart failure in the black American community would then be based on these "likely" candidates. These solutions, ignoring the importance of genetics, would have little or no impact on the rate of congestive heart in the black American community. Understanding the importance of the genetics is critical to understanding the origins of congestive heart failure and developing the proper remedies. The origins of congestive heart failure in black and white Americans are linked in large measure to our genes.[4] Expenditure of public funds in the United States to address these genetic origins and corresponding curative measures is in fact unifying and effective for the population at large. One may also wish to address racial imbalances regarding access to and exploitation of societal resources; however, inaccurate identification of causality leads to ineffective and wasteful "solutions", engendering division and reduced allocation of resources.

There is always concern that application of first principles to complex systems may fail; the less adventurous path is to default to phenomenology when the complexity is perceived too formidable. One does not need an acute acoustic sense to hear such foreboding expressed about petroleum. One might choose a bold path. It is known that a broad array of factors have helped shaped human development including the shapes of continents and variations in natural flora and fuana.[5] Nevertheless, E.O. Wilson makes a strong case that various elements of human behavior, with its extreme complexity, can be understood from a genomics vantage.[6] A forceful point is that social scientists neglect genetics to their considerable detriment. For instance, Wilson describes in detail the Westermarck effect, named after a Finish anthropologist. The effect is simply that inbreeding amongst human siblings and between parents and children is very uncommon. Indeed, human societies envelop close kin mating in taboo. The Westermarck effect has been observed not only in most human societies but all primates studied.[6] A plausible cause for this effect is the documented destructive concentration of double recessive, deleterious genes with inbreeding. The suggestion is that the Westermarck effect is controlled in part by genetic impulse. However, note that major components of Freud's Oedipal complex run counter to the Westermark effect. At the least, plausible genetic influences on human behavior should be understood by social scientists in their endeavors. It behooves all scientists to understand the foundations to locate and decipher phenomenology.

## 2. Evolution of the Oil Patch

As currently practiced, petroleum science shares many traits with medical science. The analysis of crude oil for issues of economic concern is often rooted in phenomenology. For instance, in the upstream side of the petroleum business, crude oil phase transitions can be quite problematic. Figure 1.1 shows several

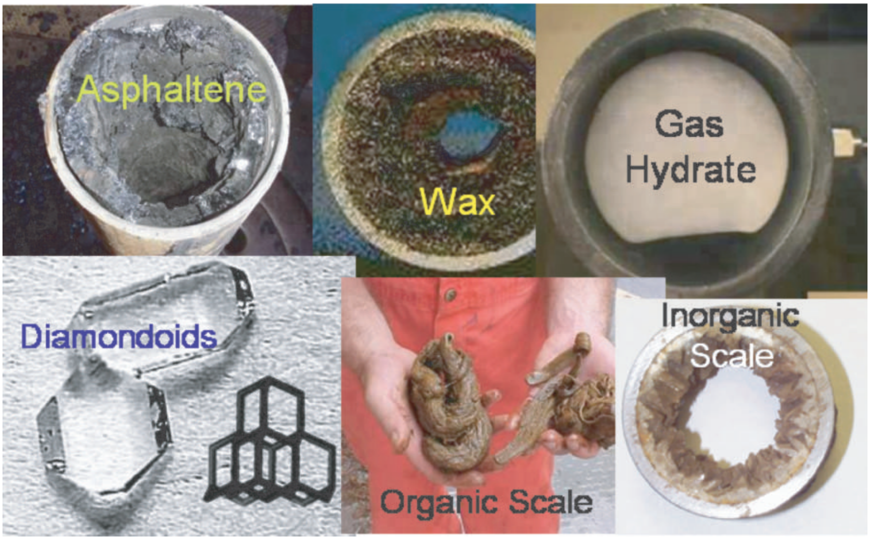

**Figure 1.1.** Various solids that obstruct oil pipelines.

solid phases that can form during the production of crude oil; all but one directly involve hydrocarbons. These phase transitions of crude oil include the formation of solid deposits of asphaltene, wax, gas hydrate, organic scale, and diamondoids, possibly in combination. The appearance of organic scale accurately reflects what production engineers think of it. For completeness, an inorganic scale is also shown.

The crude oil chemistry involving the formation of a solid precipitant or flocculant is complex. The factors that determine whether a newly precipitated solid phase actually forms a deposit which then grows and occludes tubulars, pipelines and production facilities involve not only the oil chemistry but are compounded by interfacial interactions of the organics with oil, water, gas, mineral, and metal surfaces, altered by natural corrosive and erosive interactions. As with biological systems, the complexities are significant, but not preclusive. As with medical science, the petroleum industry has had to develop operational solutions to the problems displayed in Figure 1.1 prior to development of proper scientific description of the problems; the approach has largely been phenomenological. “Does a crude oil have a wax problem?” stick it in the refrigerator and see if wax forms. “Does the live oil have an asphaltene deposition problem?” drop the pressure on the live oil and see if asphaltenes precipitate. Flocculation or asphaltene destabilization is a necessary but not sufficient condition for the formation of deposits. It is much harder to determine if deposits form under high shear and realistic conditions (cf. Chapter 23). Thus fairly basic and phenomenological methods have been employed to uncover problems associated with oil chemistry.

Petroleum science mandates establishing the first principles that govern the behavior of crude oil in all of its sundry manifestations. Utilizing a complete chemical description of crude oil to predict all properties is the ultimate objective of

Petroleomics. The Petroelome, the complete listing of all chemical constituents in a crude oil thus enables Petroleomics. Phase behavior (cf. Fig. 1.1), interfacial activity, viscoelasticity, and solubility, which is the defining characteristic of asphaltenes, are subsumed within this overarching agenda. Molecular structure of crude oil components and especially of their enigmatic constituents asphaltenes must be understood as the root source of all that follows. In addition, crude oils and asphaltenes exhibit hierarchical aggregation behavior in different physical length scales; for corresponding accurate characterization, petroleum science mandates establishment of causal relations between different hierarchical regimes. In the broadest sense, structure–function relations must be developed providing vertical integration of this hierarchy. Ultimately, petroleum science rests upon developing the complete listing of every component in a crude oil. Analogous to the genome, the complete representation of petroleum provides a clear and only path toward establishment of all structure–function relations in crude oil. In practice, it might be sufficient to determine the elemental composition of each component in a crude oil concatenated with bulk structural determination for the whole crude or important bulk fractions. Nevertheless, the objectives remain—full resolution of crude oil chemical constituents and full determination of structure-function relations in all crude oil hierarchies.

## 3. Phenomological Petroleum Analysis

The phenomenological approach to the analysis of oil chemistry issues has served the petroleum industry reasonably well for many years, but the efficacy of this approach has deteriorated substantially in recent years due to the dramatic changes in the petroleum market. According to the Minerals Management Service, the arm of the United States Government, which oversees oil production offshore, many experts believed as late as 1990 that formations in deepwater environments would contain no oil of economic value. Since that time, intrepid oil operating companies moved off the continental shelf and continued to find oil in deeper water. Either we have had very recent reservoir charging, or many experts were in error! The understanding of turbidity currents resulting in turbidites in river-fed marine basins has helped explain large discoveries in deepwater. Deepwater is now recognized as a global play and includes deepwater basins corresponding the Mississippi River, the Niger River, the Congo River, the Nile River, the Paraiba River, the Mahakam River. Other high cost markets such as the North Sea and offshore eastern Canada have also contributed substantially to the changing the oil market. Some estimates conclude that 50% of the world’s undiscovered oil is offshore. A sea change has taken place with regard to the location of new oil.

In addition to Flow Assurance issues, the efficient production of oil is now known to depend critically on petroleum analysis, but within an entirely new context (cf. Chapter 22), thereby providing new opportunities for scientific and technological contributions. The oil industry operating practices have routinely incorporated two large physics errors in reservoir exploitation. In spite of the concerns from knowledgeable technologists, the operations side of the oil industry has often been forced, not unreluctantly, to presume the most optimistic scenario for the production of crude oil. The erstwhile default scenario is that, unless proven otherwise, oil fields were considered to consist of giant tanks of homogeneous hydrocarbons. Of course, gas caps, oil columns and the occasional tar mat were recognized, as was gross compartmentalization. Nevertheless, the industry defaulted to an overly optimistic scenario for several reasons. First, there had been no cost effective means of acquiring accurate information on fluid compositional variation, and on compartmentalization prior to production. (A compartment is defined as a single flow unit that must be penetrated by a well to be drained.) Second, the identification of either fluid compositional variation or compartmentalization is "bad news", decreasing reserves and increasing costs. It is difficult to justify inclusion of costly complexity without the existence of corresponding established procedures for data acquisition and analysis.

The use of these reservoir descriptions, optimistic to a fault, has led to the commonplace occurrence that the prediction of production and the actual production are rarely in agreement, often with regard to both the quantity and type of fluids produced. In a low cost environment, one can tolerate large initial errors in prediction by updating prediction as more wells are drilled and put into production. It is illustrative to consider that the cost structure in the land production of crude oil is commensurate with the existence of many small oil companies. A relatively small amount of capital is needed to explore and, with luck produce oil. But beware, as the principal owner of the Harvard oil company told this author, "the oil business is not for the weak hearted".

However, in high cost markets such as deepwater, prediction of production is of paramount importance. Entire production projects must be forward modeled to justify requisite billion dollar sea floor installations. In this environment, errors in prediction have cost operating companies billions of dollars in individual fields. It is no longer tolerable nor economically viable in the oil industry to sustain enormous errors in prediction built on frequently invalidated optimism. The relatively recent arrival of deepwater has altered the landscape; proper technical solutions are now mandated. In fact, this represents a new, huge opportunity to hydrocarbon fluid experts around the world.

There is a dramatic revision in thinking taking place regarding the understanding of the distribution of hydrocarbons in subsurface formations. This revision is in fact for operating units. The technologists have been aware of the following issues; however, previously there had been no cost effective method to acquire requisite data prior to development of production facilities and strategies. There are two components to this dramatic revision in thinking; (1) hydrocarbon compositional grading and (2) compartmentalization. In the past, the normal presumption was that the hydrocarbons are present in the subsurface formations as a homogeneous fluid. That is, it was presumed that there was no spatial variation in hydrocarbon properties. Ironically, in the oil business, the formation rocks have been given due respect. It is recognized that rock mineralogy and petrophysical properties can easily change, laterally and vertically, on a centimeter length scale or less. Rock variations could include a change in mineralogy such as going from shale to sandstone, a change in cementation, grain size and/or shape, changes in clay content etc. But the liquid oil columns were presumed to be invariant unless otherwise proven. It turns out that the hydrocarbons are frequently highly graded compositionally in the subsurface formations. The new view is that "hydrocarbons in the formation are considered compositionally graded unless otherwise proven."[7] Contributing factors include gravity, thermal gradients, multiple reservoir charging, current reservoir charging, leaky seals possibly pressure dependent, biodegradation, water washing, and reservoir alteration during charging. All but the first two factors move the hydrocarbon column away from equilibrium.

A second component in understanding complexities of hydrocarbon fluids in the formation relate to compartmentalization. In the deepwater arena, it is very difficult to determine compartment size. Traditional methods of finding compartment size such as well testing (essentially a production test) are often precluded due to cost. A well test can cost nearly what a new well would cost in deepwater. Consequently, this expensive solution is not performed on a routine basis. For many years, the primary method used to find compartment size had been to determine hydraulic (pressure) communication. In a well, pressure communication is established by obtaining a single pressure gradient at different points in the fluid column. Pressure communication was then presumed to imply flow communication. However, pressure communication in geologic time is a necessary but insufficient condition to establish flow communication in a production time frame. Geologic to production time differs by 6 orders of magnitude; requisite permeabilities for flow versus pressure communication differ by several orders of magnitude. Thus, the standard industry method for identification of compartments is in error by up to 9 orders of magnitude. Given this gross technical failure to identify compartments, it is no wonder that compartmentalization is generally viewed as public enemy number one in the oil industry today, at least for deepwater production. For a technologist, discovery of such a gargantuan disconnect in the application of technology is fertile ground for revolutionary innovation.

Downhole Fluid Analysis (DFA) is a new technology that is enabling cost effective identification of fluid compositional variation and of compartmentalization. DFA (Chapter 22) enables important and different fluids to be identified at the point of sample acquisition in the subsurface. Thus, DFA is aiding the laboratories to get a proper representative sampling of the variation of fluids in the formation. Without DFA, requisite random sample acquisition and analysis had been too expensive to employ on a routine basis. In addition, DFA is identifying compartmentalization by virtue of identifying fluid density inversions in the hydrocarbon column.[7] That is, DFA is routinely identifying higher density fluids higher in the column. In general, the most likely explanation for such an occurrence is compartmentalization. This new technical solution to some of the industry's most important problems directly involves fluid complexities and places a new focus on understanding petroleum. It is important for the academic community that has a strong focus on fluids (e.g., all academic contributing authors in this book!) to understand this new use of fluid analysis to address the largest problems in the oil business.

## 4. Petroleomics

Again, we consider Francis Crick's axiom, "If you want to understand function, study structure." For the first time, the basic structural issues of asphaltene science are sufficiently well developed that Crick's axiom has become an achievable goal. It behooves the asphaltene scientist to place his/her own results within the context of structural information at adjacent length scales. In the past, the asphaltene literature had been rather contradictory. Consequently, structure–function relations had been largely precluded since the foundations were so uncertain. Often, measurements at a particular length scale were extrapolated to other length scales without regard to direct measurements from other laboratories at that length scale. A cynical characterization of this approach might be "if I didn't measure it, it doesn't exist." However, asphaltene science is too complex for a single laboratory to measure everything there is to know. This difficulty has been exacerbated by the existence of simple, low cost measurements that consistently generate the wrong answer. Improper asphaltene molecular weight determination via vapor pressure osmometry comes to mind. As this book demonstrates, there is now considerable consistency regarding the resolution of fundamental issues in asphaltene and petroleum science.

## 5. Building Up Petroleum Science—A Brief Outline

Low molecular weight components are treated within a proper chemical framework. For instance, if a subsurface hydrocarbon reservoir contains $H_2S$, all aspects of resource utilization will incorporate treatment of this pernicious chemical component. However, the fundamental chemical description of the most enigmatic components of crude oil, asphaltenes, has been the subject of debate for decades. The most fundamental question of any chemical compound, its elemental constituents, is easily determined for asphaltenes and agreement prevails here. Within this agreement, one never hears that the polydispersity of asphaltenes precludes determination of their elemental composition. The second most basic property of a chemical compound, its molecular weight, has been the subject of dispute by one or more orders of magnitude in asphaltene science for decades. It turns out that for molecules, size counts. This is also true for quantum mechanics, and bank accounts so the importance of size for asphaltene molecules should not be a surprise. In large measure, the debate regarding asphaltene molecular weight reduces to the question whether asphaltenes are monomeric or polymeric. Clearly, asphaltenes are polydisperse so there will be a molecular weight distribution with its various moments. It is important to understand not only the mean asphaltene molecular weight, but also the width of the distribution, and the (asymmetric) tails on the small and large mass sides. Nevertheless, the debate on asphaltene molecular weight has been one to several orders of magnitude, so resolving the mean is the first important task. More specifically, the asphaltenes are known to be interfacially active. Any question involving interfacial science of crude oils is likely to have a component, potentially critical, involving asphaltenes. Issues such as emulsion stability, deposition, and wettability all involve interfaces. Prediction of asphaltene phase behavior clearly necessitates proper understanding of asphaltenes at the molecular level. We believe chapters herein (Chapters 2 and 3) present compelling evidence that this longstanding controversy is resolved, asphaltenes are small molecules.

After molecular weight, the next question is to understand asphaltene molecular structure. There has been some convergence on this topic. Here it is important to acknowledge polydispersity at the outset. The chemistry of interest for a particular observable might be dominated by a component of the asphaltenes that is present in small mass fraction. While it is unlikely that this would prevail in the formation of asphaltene nanoaggregates, this situation plausibly applies in at least some cases of interfacial interactions. Nevertheless, in high concentrations, the highest energy asphaltene sites might be tightly complexed and thus unavailable for facile interfacial access. Regarding molecular structure, the asphaltene molecular weights are not high. This fortuitous circumstance limits possible candidate structures. A polymeric structure consisting of covalent linkages with many large fused aromatic ring systems is incompatible with measured asphaltene molecular weights. An issue of primary concern is the size of the average aromatic fused ring system in asphaltenes. There is convergence from several lines of investigation. Asphaltenes are deeply colored in the visible and extending into the near infrared spectral range. Small aromatic ring systems, even those containing heteroatoms, are nonabsorptive or of very low absorptivity in the visible (e.g. benzene, naphthalene, anthracene, dibenzothiophene, dibenzopyrrole, pyrene, phenanthrene, etc.). The smallest fused ring systems that are optically absortive such as pentacene are catacondensed while x-ray raman spectroscopy (Chapter 5) as well as energetic considerations (Chapter 4) clearly show that asphaltenes are pericondensed. Consequently, what one sees visually is evidence that asphaltene ring systems contain more than a few rings. Detailed molecular orbital calculations (Chapter 4) coupled with detailed optical studies confirm intuition. Direct molecular imaging studies of asphaltenes indicate the asphaltene ring systems contain on order 7 fused rings (Chapter 8). Measurement of rotational diffusion of asphaltene molecules is consistent with this mean number with a width of roughly 4 to 10 rings (Chapter 2). 13C NMR studies also indicate a ratio of interior to exterior carbon that is consistent with this assessment. Known asphaltene molecular weights coupled with these determinations of fused ring systems leads to the conclusion that generally asphaltene molecules are shaped "like your hand" with the palm representing the single aromatic fused ring system in the molecule (with possible alicyclic substituents) and the fingers, alkane substituents. This description is consistent with the very definition of asphaltenes. Aspahltenes are defined by a solubility classification. The intermolecular attraction of the polarizable $\pi$-bond ring systems is counterbalanced by steric repulsions of alkane substituents. Thus, asphaltenes exhibit a strong correlation between the size of their fused ring systems and the extent of alkyl substitution. Asphaltene sulfur and nitrogen chemistry have been elucidated by x-ray spectroscopy methods (Chapter 6).

Asphaltene molecules aggregate at low concentrations, for instance at ~150 mg per liter in toluene, to form nanoaggregates (Chapters 9, 10, and 11).