

## PETROLEUM ENGINEERING - DOWNSTREAM

# PHASE BEHAVIOR IN PETROLEUM FLUIDS

*(A Detailed Descriptive and Illustrative Account)*

**G.Ali Mansoori**

University of Illinois at Chicago, Chicago, IL 60607-7052 USA; email: [mansoori@uic.edu](mailto:mansoori@uic.edu)

**Keywords:** Aggregation; Alkane; Aromatic hydrocarbon; Asphaltene; Cloud point; Gas-condensate, Deposition; Diamondoid; Dynamic pour point; First order phase transition; Flocculation, Gas-condensate; Heavy oil; Heavy organic; Hydrocarbon; Infinite-order phase transition; Intermediate crude; Light crude; Natural gas; NGL, Oil; Oil shale; Onset of deposition; Paraffin; Petroleum fluid; Phase behavior; Phase-transition; Phase transition points, Polydisperse fluid; Polymer solution; Precipitation; Resin; Second order phase transition; Solid formation; Static pour point; Tar sand; Thermodynamics; Wax.

### Contents

1. Introduction
    - 1.1. Naturally Occurring Petroleum Fluids
  2. Components of Petroleum Fluids
    - 2.2. Impurities in Petroleum Fluids
    - 2.3. Heavy Fractions in Petroleum Fluids
      - 2.3.1. Petroleum Wax
      - 2.3.2. Diamondoids
      - 2.3.3. Asphaltenes
      - 2.3.4. Petroleum Resins
  3. Phase Behaviors in Petroleum Fluids
    - 3.1. Temperature Effect on Petroleum Fluids Phase Separation
    - 3.2. Pressure Effect on Petroleum Fluids Phase Separation
    - 3.3. Theory of Phase-Transitions
    - 3.4. Phase-Transition Points
  4. Discussion
- Glossary  
Bibliography

### Summary

This chapter presents a descriptive and illustrative account of phase behavior in the seven naturally occurring petroleum fluids and ties all the known eleven phase-transition concepts in a unified narrative. The figures and tables contained in this report are designed so that they could effectively support the discussion about molecular make-up of petroleum fluids, P- and T-effects on phase behavior and phase transition points.





























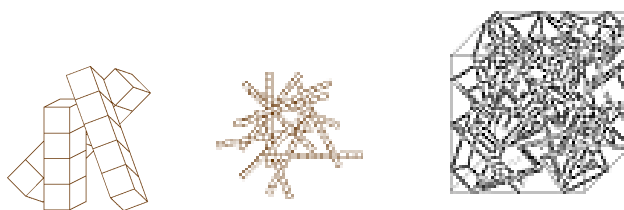




**Figure 13** - Pipeline petroleum transport plugging due to wax and other heavy organics depositions (Courtesy of Phillips Petroleum Company)

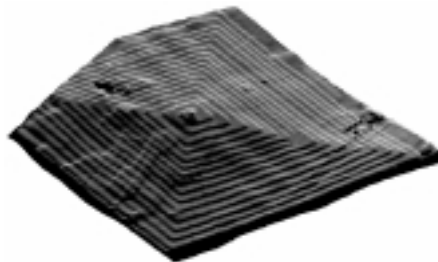
Waxy crude is a petroleum fluid in which there exist only hydrocarbons including paraffins, aromatics and wax as its constituents. Solidification of heavy paraffins in wax and their crystallization will occur because of lowering the temperature of a petroleum fluid below its cloud point. Such fluid-solid transitions are generally reversible and the Gibbs equilibrium criteria apply to such transitions provided there are no other compounds like asphaltenes and resins present in the petroleum fluid. Presence of such other heavy organics could enhance or delay solidification of paraffins / wax depending on the form (molecular, aggregate, steric colloid, floc or micelle) of the asphaltene and resins and their molecular structures.

As a waxy crude flows through a cold pipe or conduit (with a wall temperature below the cloud point of the crude), crystals of wax may be formed on the wall (see Figures 14 and 15). Wax crystals could then grow in size until completely wax deposits cover the inner wall.



**Figure 14** - Macrocrystalline, Microcrystalline, and Crystal Deposit Network of Wax





**Figure 15** - An atomic force microscope image of the spiral growth of paraffin crystal (measuring approximately 15 microns across). Inset shows orthorhombic arrangement (0.49nm x 0.84nm) of chain ends of one of the crystal terraces. (Courtesy of Professor M.J. Miles, Bristol University, GB).

As the wax crystal thickness increases, pressure drop across the pipe needs to be increased to maintain a constant flow rate. As a result, the power requirement for the crude transport will increase. When the temperature of a waxy crude oil is lowered to its cloud point, first the heavier fractions of its wax content start to freeze out. Upon lowering of the temperature to the crude pour point almost all the fractions of its wax content will freeze out. Presently, a waxy crude is characterized by its cloud point and its static pour point, which are measured according to the ASTM Test Methods D-2500 and D-97, respectively.

As with regard to the other petroleum fluids their heavy organics deposition problem is not just crystallization of their wax content at lower temperatures, but the formation of deposits which do not disappear upon heating and will not be completely removed by mechanical means. Petroleum fluids, generally, in addition to wax, contain other heavy organics such as asphaltenes and resins. Asphaltenes do not crystallize upon cooling and, for the most part, do not have a definite freezing point. Depending on their nature, the other heavy organics will have different interactions with wax, which could either prevent wax crystal formation or enhance it.

### 3.2. Pressure Effect on Petroleum Fluids Phase Separation:

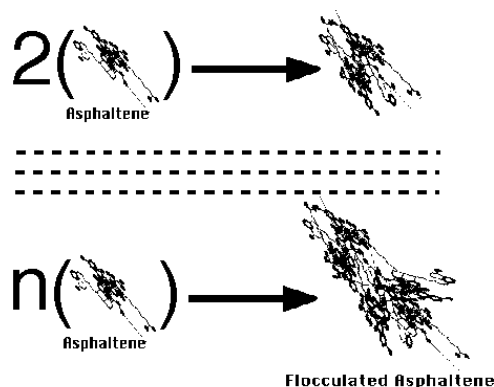
When we start with a petroleum fluid in liquid state by decreasing its pressure, at constant temperature, we will observe the bubble point, which is the start of evaporation of the volatile components of the petroleum. Upon further decrease of petroleum fluid pressure we will observe the dew point after which all the volatile components of petroleum will go to the vapor phase. By reversing this process the petroleum fluid will go back to its original liquid state. It must be pointed out that for some petroleum fluids, like the ones with a typical PT diagram as shown on Figure 12, if we change the pressure of the fluid at a temperature above the critical temperature we will also experience retrograde condensation [64].

By variations of pressure and / or composition of a petroleum fluid, we may cause the deposition of its polar heavy end content known as asphaltene. A petroleum fluid is a mixture of various polydispersed compounds. A mutual solubility balance among all such components makes a

petroleum fluid stable. Changes in that balance can cause phase separations in a petroleum fluid and, as a result, formation of various other phases.

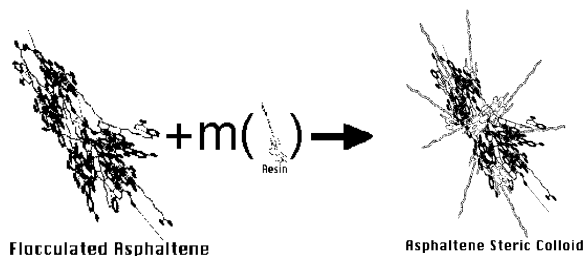
For example, dilution of petroleum fluids with low molecular weight alkanes could cause asphaltene precipitation, aggregation / flocculation and eventually deposition (see Figure 16) [65].

However, a paraffinic and asphaltenic petroleum fluid at low temperatures may not experience any solid formation due to the possible role that paraffin nanocrystals may play in peptization of asphaltene aggregates and formation of relatively stable steric colloids in the oil. For this kind of physical aggregation / flocculation, we have considered a polymerization chemical reaction mechanism along with the FRACTAL growth of aggregates [60,65,66] with an appropriate non-Euclidian dimensionality. In the absence of any peptizing agent, like petroleum resins, this aggregation will continue towards formation of a sticky non-crystalline solid phase. We have used the kinetic theories of aggregation and flocculation to predict solid formation of this nature.



**Figure 16 - Aggregation / flocculation of asphaltene molecule [53]**

Asphaltene flocs (random aggregates) can form steric–colloids in the presence of petroleum resins [60,65,66], as shown in Figure 17.



**Figure 17 - Steric colloid formation of asphaltene aggregate plus resins [53]**

The concept that asphaltene molecules could be present as a colloidal system is credited to Nellensteyn [67]. He proposed that asphaltenic compounds were made of flocs or aggregates of asphaltene molecules protected by adsorbed resin and hydrocarbon materials, all dispersed in a hydrocarbon medium. He also found that the peptizing or precipitating properties of different common solvents with respect to asphaltenic compounds are closely related to the surface tension.

We have modeled and predicted the conditions for colloidal effect such as the formation of asphaltene steric colloids formed because of a combination of asphaltenes aggregates / flocs and resins in petroleum fluids through consideration of resins balance / equilibrium between the oil phase and asphaltene-floc-surface phase [33,60,65,66,68].

Colloids are generally unstable and they could deposit. Of course, due to further dilution of a petroleum fluid with light paraffin hydrocarbons, colloids could grow further in size and their deposition will be enhanced (see Figure 18).

Knowing the properties of the fluid and colloids, or suspended solids, we can develop limit-of-Brownian-particle models to predict deposition of colloids from the liquids phase to form a deposited solid phase.

Flocculation and deposition of asphaltene in petroleum fluids can be either reversible or irreversible depending on the nature of asphaltene and resin involved and how far the aggregation and colloid formation and growth has progressed [33,62,68]. Certain experimental observation have indicated a hysteresis when a petroleum fluid conditions are returned to pre-flocculation point of its asphaltene contents. Due to their large size and their adsorption affinity to solid surfaces, asphaltene flocs (random aggregates) can cause quite stable deposits, which may not wash away by current remediation techniques. One of the effective and routine methods of remediation of fresh heavy organic deposits is the use of strong light aromatic solvents, such as xylene, that could dissolve such asphaltene deposits [69]. However, aging of such deposits may prevent it from complete dissolution [54,70].

In order to relate the observed phase transitions in petroleum fluids to the known theory of phase transitions we present the following section.

### 3.3. Theory of Phase-Transitions

From the thermodynamic point of view, phase transitions happen when the free energy of a system is non-analytic for some choice of thermodynamic variables. The distinguishing characteristic of a phase transition is an abrupt change in one or more physical properties, with a small or no change in the intensive thermodynamic variables such as the temperature and pressure. Phase transitions are generally categorized in the first order transitions, the second order transitions and the infinite-order phase-transitions [71].

The first-order phase transitions are those that are associated with an appreciable latent heat. In another words, during a first-order phase transition, a pure compound, as an example, exchanges a fixed and rather large amount of energy in the form of heat. During a first-order phase

transition the temperature and pressure of a pure compound will remain constant. Because the latent heat cannot be instantaneously transferred between the compound and its environment, the first-order transitions are associated with "mixed-phase regimes" in which some parts of the system have completed the transition and others have not. Those petroleum fluids phase transitions, which fall into the first-order category, include gas separation from petroleum fluids and crystalline wax formation. It must be pointed out that the first-order gas-liquid transitions in petroleum fluids and other mixtures occur at constant temperature over a range of pressures, as discussed elsewhere in this report.

The second-order phase transitions, also known as the continuous phase transitions are not associated with any latent heat exchange with the surroundings. The classical examples of the second order phase transitions are the ferromagnetic transition, superconductor and the superfluid transition. Examples of the second-order phase transitions in petroleum fluids are asphaltene precipitation from a petroleum fluid due to composition change, asphaltene steric colloid formation, asphaltene deposition from a petroleum fluid due to the limit of Brownian particle size limit and asphaltene micellization [72].

A third category of phase transitions is known as the infinite-order phase transitions. They are known to be continuous but breaking no symmetries. The classical example is the Kosterlitz-Thouless transition [73] in the many quantum phase transitions in two-dimensional electron gases. In the case of petroleum fluids phase transition from asphaltene to asphaltene micelles-coacervates belong to this category of phase transitions.

In Figure 12 we report a qualitative PT diagram of a petroleum fluid, which may experience variety of phase transitions. This diagram as a whole may not apply to all the seven petroleum fluids, but it gives a general picture of how various phase transitions may be distinguished from one another.

To specify all the possible phase-transitions in petroleum fluids we present below the general concept of phase-transitions points.

### **3.4. Phase-Transition Points:**

Because of the variety of phase-transitions, which may be occurring in petroleum fluids due to variations in temperature, pressure and composition, we observe a number of specific phase-transition points. Specifically there are up to eleven different and well-defined phase-transition points, which could occur in a petroleum fluid.

These eleven points are either observable directly by the naked eye or they can be distinguished by indirect property change indicators. In Table 2 we list these known and well-defined phase-transition points. Obviously not every petroleum fluid will possess all these eleven phase-transition points. The mere fact that a petroleum fluid will exhibit certain of these phase-transition points will distinguish it from the other kinds of petroleum fluids. In what follows we give a brief description of the eleven phase-transition points (PTP's) and the kind of petroleum fluid in which they may appear.

**PTP # 1.** The critical solution point is where the vapor and liquid phases separated from a petroleum fluid possess the same compositions, pressures, temperatures and densities. Generally, all liquid mixtures possess a critical solution point.

**PTP # 2.** Bubble point is the onset point of phase-transition from a liquid to a vapor phase upon increase of the temperature and/or lowering the pressure of the liquid phase.

**PTP # 3.** Dew point is the onset point of phase-transition from a vapor to a liquid phase upon decrease of the temperature and/or increasing the pressure of the vapor phase.

**PTP # 4.** Cloud point is the onset point of crystalline solid formation in petroleum fluids upon lowering its temperature. This phase-transition point is an indicator of the wax content of the petroleum fluid.

**Table 2 – Known and well-defined phase-transition points in petroleum fluids**

PTP #	Phase-Transition Point	Phases involved	Components involved	Major variables	Indicator	Ref. #
1	Critical solution point	Vapor-Liquid	Hydrocarbons	Pressure, Temperature	Visual	[10]
2	Dew point	Vapor-Liquid	Hydrocarbons	Pressure, Temperature	Visual	[10]
3	Bubble point	Vapor-Liquid	Hydrocarbons	Pressure, Temperature	Visual	[10]
4	Cloud point	Liquid-Solid	Paraffins / Wax	Temperature	Viscosity, etc.	[34]
5	Static Pour point	Liquid-Solid	Paraffins / Wax	Temperature, viscosity	Viscosity, Velocity	[34]
6	Dynamic Pour point	Liquid-Solid	Paraffins / Wax	Temperature	Visual, Viscosity	[34,74]
7	Onset of asphaltene precipitation	Liquid-Solid	Asphaltene	Paraffins, Pressure	Oil-Water IFT	[57]
8	Onset of asphaltene steric colloid formation	Liquid-Liquid	Asphaltene, Resin	Paraffins, Pressure	Viscosity	[75]
9	Onset of asphaltene deposition	Liquid-Solid	Asphaltene, Resin	Paraffins, Pressure	Visual, Microscopy	[74]
10	Onset of asphaltene micellization	Liquid- Liquid	Asphaltene	Aromatics	Viscosity, Surface tension	[53,55]
11	Onset of asphaltene micelle coacervation	Liquid-Liquid	Asphaltene micelles	Aromatics	Viscosity, Surface tension	[53,55]

**PTP # 5.** The static pour point is the lowest temperature at which a petroleum fluid will cease to flow out of a tilted test jar. Pour point is predominantly known to be due to the crystal growth and connectivity of wax crystals, which then increases the viscosity of the petroleum fluid extremely high preventing the flow of the oil.

**PTP # 6.** Dynamic pour point is the lowest temperature at which a petroleum fluid will cease to flow out of a tilted, but continuously agitated, test jar. It occurs at a lower temperature than the static pour point. The difference of the static and dynamic pour point temperatures is a measure of the nature of the paraffin wax present in a petroleum fluid. There is not much data available yet for petroleum fluids dynamics pour point and its measurement procedure is not yet standardized.

Petroleum fluids containing asphaltenes and resins could have five additional phase-transition points depending on their percentages of paraffins, aromatics, asphaltenes, resins as well as the nature and molecular weights of these compounds. These five additional phase-transition points, as described in Table 2 are:

**PTP # 7.** Onset of asphaltene precipitation

**PTP # 8.** Onset of asphaltene steric colloid formation

**PTP # 9.** Onset of asphaltene deposition

**PTP # 10.** Onset of asphaltene micellization

**PTP # 11.** Onset of asphaltene micelle coacervation

We have discussed the details of the latter five phase-transition points in our earlier publications [72]. While these five phase-transition points may not be visually observable, they define the behavior of petroleum fluids in regard to the solid phase formation and separation.

Except for the critical point, bubble point line and dew point line, which belong to light hydrocarbon components of petroleum fluids, the other eight phase-transition points are due to the heavy components. The latter eight phase-transition points represent the onset of heavy organics (wax, asphaltene, resin, etc.) transformations and separations from petroleum fluids. The knowledge about all these phase-transition points will allow us to understand and quantify the nature of petroleum fluids and develop models to predict and strategies to control various phase separations including the deposition of heavy organics from petroleum fluids. In Figure 12 we report the locations of phase-transition points 1-9 as discussed above and reported in Table 2.

#### 4. Discussion

There is a great deal of interest and need in the petroleum and natural gas industries to develop computational packages to predict the phase behaviors of petroleum fluids. This is because the knowledge about petroleum fluids phase behavior will allow us to design the production, transportation and utilization systems efficiently and will help us to prevent problems associated with fouling in petroleum fluids arteries due to untimely heavy organics deposition.

Our knowledge about phase behavior occurring in natural gas, gas-condensate and light crude is quite complete thanks to the extensive amount of database and computational packages which have been developed in the past century. However, worldwide shortage of such light petroleum fluids has caused the need to use not only intermediate crudes, which are also rather scares, but heavy oil, tar sand and oil shale. For efficient utilization of such heavy petroleum fluids we need to understand and quantify their phase behavior.

In this report we have identified all the phase transitions, which could occur in the seven naturally occurring hydrocarbon fluids known as petroleum fluids. We have also specified eleven phase transition points, which are responsible for all such phase transitions. Also in this report the nature of every petroleum fluid is presented and their constituents including their non-hydrocarbon components, known as impurities, are identified and categorized. It is shown that the heavy fractions in petroleum fluids are generally made of continuous families of constituents. Their major components, which have a strong role in their phase behavior, include wax, diamondoids, asphaltenes, heavy aromatics and petroleum resins.

We have introduced the generalized petroleum fluids phase behavior in light of the known theory of first-order, second-order and infinite-order phase transitions. We have also discussed about

the effects of variations of composition, temperature and pressure on the phase behavior of petroleum fluids. We have suggested eleven distinct phase-transition points of petroleum fluids, which are related to various state variables, and constituents of petroleum fluids. The aim of this report is to generalize and relate phase behaviors of all the seven naturally occurring petroleum fluids into a unified perspective. The major requirement in the efficient design of production, transportation and processes dealing with petroleum fluids is the accurate and efficient prediction of their phase behavior and other properties as they change phases between vapor, liquid and solid.

The concepts introduced in this report will be necessary for development of a comprehensive package to predict various seven petroleum fluids behavior as well as the behavior of their blends, which is of major interest in the petroleum industry. The challenges ahead in terms of generating such unified modelling are the following:

i. To relate all the eleven phase transition points to microscopic phenomena and come up with predictive methods for each.

ii. To produce a unified theory of phase transitions which will take into account changes of phases of molecules and their assembly between, not only liquids and vapour phases, but also solid crystalline, solid aggregates, colloid and micelle formations and micelle and colloid coacervation or self assembly.

iii. To develop a multi-scale model of phase behavior predictions for a multi-component / multi-family polydisperse mixture which will have its input certain compositions and/or sets of data from the eleven phase transition points.

iv. Equations of state are useful to predict phase equilibrium between fluid phases. However, for prediction of solid phase formation, aggregations (micelles, colloids and coacervates) other theories will be necessary. A combination of such phase transitions may be of reversible or irreversible nature as discussed above.

It is with no doubt that the techniques and facilities being developed for nanotechnology [76] can be quite useful to provide us a better understanding of the molecular interactions and self-assemblies, which are occurring during in petroleum fluids during various phase transitions.

## Glossary

*aggregation*: Attachment due to attraction between particles (polymers, macromolecules, etc.) due to non-covalent or covalent forces.

*atomic force microscope*: a microscope with extreme high resolution measuring intermolecular forces and producing nano-scale images.

*bubble point*: The onset point of phase-transition from a liquid to a vapor phase upon increase of the temperature and/or lowering the pressure of the liquid phase.

*cloud point*: the onset point of crystalline solid formation in petroleum fluids upon lowering its temperature. This phase-transition point is an indicator of the wax content of the petroleum fluid.

*coacervate*: self-assembly of micelles

*colloid*: a collection of particles of a substance aggregated and suspended in a fluid media.

*gas condensate*: a mixture of low to intermediate molecular weight hydrocarbons which is in liquid state at normal conditions and is in gas phase at high pressures due to dissolution in supercritical natural gas.

*critical solution point*: Where the vapor and liquid phases separated from a petroleum fluid possess the same compositions, pressures, temperatures and densities. Generally, all liquid mixtures possess a critical solution point.

*dew point*: the onset point of phase-transition from a vapor to a liquid phase upon decrease of the temperature and/or increasing the pressure of the vapor phase.

*diamonoids*: cage-shape saturated hydrocarbons as presented in Section 2.3.2 of this chapter.

*dynamic pour point*: the lowest temperature at which a petroleum fluid will cease to flow out of a tilted, but continuously agitated, test jar. It occurs at a lower temperature than the static pour point. The difference of the static and dynamic pour point temperatures is a measure of the nature of the paraffin wax present in a petroleum fluid. There is not much data available yet for petroleum fluids dynamics pour point and its measurement procedure is not yet standardized.

*first order phase transition*: a phase transition during which appreciable latent heat is exchanged between the substance and its surroundings.

*flocculation*: The same as aggregation.

*FRACTAL*: an object, shape or quantity is considered a FRACTAL if it exhibits self-similarity in various sizes and/or quantities. A FRACTAL entity is said to have a dimension which is not necessarily an integer as are Euclidean dimensions.

*infinite-order phase transition*: continuous phase transitions which break no symmetries.

*micelle*: self-assembly of surfactant molecules dispersed in a liquid medium.

*phase transition points*: a point on the phase diagram bordering the two phases.

*polydisperse fluid*: a fluid containing various families of molecules, each with a size distribution.

*retrograde condensation*: separation of a liquid phase from a high pressure gaseous mixture upon expansion.

*second order phase transition*: a phase transition during which little or no latent heat is exchanged between the substance and its surroundings.



*static pour point*: the lowest temperature at which a petroleum fluid will cease to flow out of a tilted test jar. Pour point is predominantly known to be due to the crystal growth and connectivity of wax crystals, which then increases the viscosity of the petroleum fluid extremely high preventing the flow of the oil.

*Steric colloid*: an aggregate of a macromolecular substance (asphaltene in the present case) peptized and suspended in a fluid media by a polar but smaller molecule (petroleum resins in the present case).

## Nomenclature

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## Biographical Sketch of the author

**G.Ali Mansoori** received BSc-*ChE* degree from University of Tehran, MSc-*ChE* degree from University of Minnesota, PhD from the University of Oklahoma and his postdoctoral training at Rice University, the latter in 1970. He is a professor of bioengineering, chemical engineering and physics at the University of Illinois at Chicago. He has been a visiting professor at University of Pisa, ITB, University of Kashan, Sharif University of Technology; and a visiting scientist at the Argonne National Laboratory, National Institute of Standards and Technology and CNR-Pisa. He has been a consultant to ARCO, BJ Services, British Petroleum (BP), C3 Int'l-LLC, Chevron Oil Field Services, DuPont, Exxon, Eng. Research Corp., Federation of American Scientists, Harza Eng. Co., Hitachi, Ltd., Hydrotech, IMP, Institute of Catalysis of Novosibirsk-Russia, Mitsubishi Chemicals, Motorola, MUCIA, NIGC, NIOC, Norsk Hydro, PEMEX, PETROBRAS, PetroStat Laboratories, Science Applications., Shell Int'l B.V., Synthetic/Johnson-Matthey, Technology International., The Anián Community (Reuters), United Nations

(UNDP; TOKTEN Project), UOP-LLC, Vista Research. Dr. Mansoori's academic and professional honors include: Academician of the International Academy of Creative Endeavors (science, arts, social issues); Algorithm scientific international award; diploma of honor from Pi Epsilon Tau National Petroleum Engineering Honor Society; honorary academician of the International Eco Energy Academy; Kapitsa gold medal from the Russian Academy of Natural Sciences; medal of fundamental science from UNESCO; recognition of dedicated service award from the fuels & petrochemicals division of AIChE, science medal from *Vezerat a Farhang va Aamozesh Aali*, honorary member of the IRI National Academy of Sciences, undergraduate instructional award from UIC. His research and educational activities include arterial blockage / fouling in petroleum and natural gas industries, atomic and molecular nanotechnology, molecular based study of condensed matter, disease diagnostic methods and therapeutic agents, nanostructures design (nanoclusters, nanoconjugates, nanoparticles), phase transitions, *ab initio* methods, density functional and molecular dynamics simulations, statistical mechanics, thermodynamics. Prof. Mansoori has published over 350 technical papers including seven books.



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