Nanostructure, Nanosystems, and Nanostructured Materials

Theory, Production, and Development

P. M. Sivakumar, PhD
Vladimir I. Kodolov, DSc
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Editors

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Edited by

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LIST OF ABBREVIATIONS

AA	Acetylacetone
Adv-hBMP-2	Adenovirus-mediated human BMP-2 gene
AEM	Aryl ethynylene macrocycle
AES	Auger-electron spectroscopy
AFM	Atomic force microscopy
AP	Ammonium perchlorate
APP	Ammonium polyphosphate
APPh	Ammonium polyphosphate
ARDB	Aeronautical Research and Development Board
AcAc	Acetylacetone
bFGF	Basic fibroblast growth factor
BHK	Baby-hamster kidney
BMP	Bone morphogenic protein
BMSC	Bone marrow stromal cell
BSSE	Basis sets of complex molecules
CHEC	Cold-hardened epoxy composition
CTAB	Cetyltrimethyl ammonium bromide
CVs	Cyclic voltammograms
DAcA	Diacetonealcohol
DRDO	Defence Research and Development Organisation
DSSC	Dye sensitized solar cells
EC	Endothelial cell
ECM	Extracellular matrix
ED	Electron diffraction
EDAX	Energy Dispersive Analysis by X-Rays
EDR	Epoxy diane resin
EGF	Epidermal growth factors
ER	Epoxy resin
eV	Electron-volts
FDA	Food and Drug Administration
FET	Field-effect transistor
FGF	Fibroblast growth factor
FN	Fibronectin
FS	Fine suspensions
GATET	Gas Turbine Enabling Technology Initiative

GN	Gadolinium nitrate
GTRE	Gas Turbine Research and Establishment
HA	Hydrogen bonding agent
HBBA	2-(4′-Hydroxybenzeneazo) benzoic acid
hES	Human embryonic stem cells
IEP	Isoelectric point
IR MDCIR	Infrared microscopy of multiply disturbed complete inner reflection
KGF	Keratinocyte growth factor
LED	Light-emitting diode
LFE	Linear dependencies of free energies
LMMA	Laser microprobe mass-analysis
MPC	Monolayer protected cluster
MRI	Magnetic resonance imaging
MRSA	Methicillin-resistant S. aureus
MSs	Mesenchymal stem cell
nAl	Nano Al particle
NGF	Nerve growth factors
NS	Nanostructures
OFET	Organic field effect transistors
OLED	Organic light-emitting diode
P3HT	Poly (3-hexylthiophene)
PAGA	Poly (-[4-aminobutyl]-l-glycolic acid)
PAMAM	Poly (amido amine)
PAP	Polyammonium-phosphate
PC	Polycarbonate
PCM	Polymeric composite materials
PEG	Polyethylene glycol
PEPA	Polyethylene polyamine
PFR	Phenol-formaldehyde resins
PGA	Polyglycolic acid
PHA	Polyhydroxyalkanoate
PHB	Polyhydroxybutyrate
PHBV	Polyhydroxy-co-valerate
PLA	Poly-lactic acid
PLGA	Polyglycolic-co-lactic acid
PMMA	Polymethyl methacrylate
PPF	Polypropylene fumarate
PPI	Poly(propylene-imine)
PPy	Polypyrrole
PS-PVP	Polystyrene-b-polyvinylpyridine
PTCDI	Perylene tetracarboxylic diimide

PV	Photovoltaic
PVA	Polyvinyl alcohol
PVAc	Polyvinyl acetate
PVC	Polyvinyl chloride
rhVEGF	Recombinant human vascular endothelial growth factor
RS	Raman spectroscopy
SAM	Self-assembled monolayer
Sc	Coked surface
SC	Schwann cell
SCD	Spectroscopy of combination dissipation
SED	Spectroscopy of ionic dissipation
SEM	Scanning electron microscopy
SEP	Spatial-energy parameter
SFD	Squeeze Film Damper
SIMS	Secondary ionic mass-spectrometry
siRNA	Small interference RNA
SMD	Sauter mean diameter
SREM	Scanning raster electron microscopy
TEM	Tunnel electron microscopy
TEMEMD	Transmission electron microscopy with electron microdiffraction
TG-DTA	Thermo-gravimetric and differential thermal analyze
TGF	Transforming growth factor
TiO2	Titanium dioxide
TU	Technical condition
UPS	Ultraviolet photoelectron spectroscopy
UPSIO	Ultra small particulars of iron oxide
UVES	Ultraviolet electron spectroscopy
WF	Work function
XPS	X-Ray photoelectron spectroscopy
ZN	Zirconyl nitrate
ZPVE	Zero-point vibration energy

PREFACE

This volume accumulates the most important information about new trends in nanochemistry and also in the science about materials modified by nanostructures.

The editors selected papers, including reviewed articles, in the field of chemical physics of metal/carbon nanocomposites.

The book includes information on the new classes of metal/carbon nanocomposites and their new production methods in the nanoreactors of polymeric matrixes. In recent years, the chemistry in nanoreactors of polymeric matrixes has successfully been developed. For synthesis of metal containing nanophases in carbon or polymeric shells, it is expedient to evaluate the possibilities of redox reactions with the participation of metal containing phases and organic (or polymeric) compounds (matrixes).

The book raises discussion of the following topics:

1. The place of metal/carbon nanocomposites besides other nanostructures.
2. Main notions and characteristics of metal/carbon nanocomposites and nanosystems including them.
3. Nanochemistry principles for nanostructures synthesis in nanoreactors of polymeric matrixes.
4. Modeling of processes for obtaining nanocomposites, nanosystems and nanostructured materials.
5. Dependence of nanocomposites activity on their composition, sizes, forms and synthesis methods.
6. Experimental features of metal/carbon nanocomposite redox synthesis.
7. Types of fine dispersed suspensions and the interaction of metal/carbon nanocomposites with different media.
8. Material modification methods by super small quantities of metal/carbon nanocomposites.
9. The investigation of properties of materials modified by fine dispersed suspensions of metal/carbon nanocomposites.

The specific features of this book include:

- Computer prognosis, including quantum chemical modeling, for metal/carbon nanocomposites synthesis processes as well as fine dispersed suspensions obtaining processes and material modification processes
- Determination of new notions for metal/carbon nanocomposites and estimation of their activity
- Redox synthesis of metal/carbon nanocomposites in nanoreactors of polymeric matrixes
- Application of Avrami equations to determine the conditions for processes of metal/carbon nanocomposites synthesis and material modification
- Mechanic-chemical functionalization methods for increasing nanocomposite surface energy electronic component
- Modification methods for changing different materials properties

This book is unique and important because the new trends in nanochemistry and new objects of nanostructures are discussed. Its appeal to potential readers consists of its full information about new perspective nanostructures, new methods of synthesis in nanoreactors of polymeric matrixes and also different material modification by super small quantities of metal/carbon nanocomposites. Researchers, professors, post and undergraduates, students and other readers will find a lot of interesting information and obtain new knowledge in chemical physics of metal/carbon nanocomposites.

The editors and contributors will be happy to receive comments from readers, which we can use in our research and studies in future.

— P. M. Sivakumar, Vladimir I. Kodolov,
Gennady E. Zaikov, and A. K. Haghi

INTRODUCTION

A lot of scientific information in the field of nanotechnology and nanomaterial science has appeared recently. Since the Nobel prize winner R. Smalley [1] defined the range from 1 to 1,000 nm as the interval of nanostructures with the control of self-organization processes as the main feature, papers appeared [2-4] in which the upper value of nanostructures was limited by the size of 100 nm. At the same time, there was definitely insufficient substantiation taken from [5]. But nanostructures differing in size and shape found in the range given by Smalley are rather active in self-organization processes and differ by a special set of properties. In some papers [6-8] the problems of nanostructure activity and the influence of their supersmall quantities on active media structuring were discussed.

The present time can be defined as the time of quiet revolution in the concepts of matter and substance due to the discoveries in the field of nanotechnology. A lot of nanoparticles (nanostructures) of various shapes, sizes and element composition are known. Such terms as "fullerenes", "nanotubes", "graphene" have become widely known in popular scientific literature, though the shapes of nanostructures found are not limited by them and their names grow in number exponentially but not in arithmetic progression.

Carbon, silicide, metal, metal oxide, boron nitride and metal/carbon nanostructures are distinguished by composition but this list of classes is far from being complete. Carbon nanostructures have the most of shapes, though such nanostructures with peculiar shapes as nanorotors, nanonails, nanowalls and nanowires are known for zinc oxide nanostructures.

Naturally, shapes and sizes of nanostructures are stipulated by their composition and formation conditions. In turn, the nanostructure characteristics mentioned define the originality of nanostructure properties and possible fields of their application.

As usual, when new phenomena and new investigation objects appear, breakthrough in certain fields is expected. Such expectation "to obtain superconductors" was felt when conductive single nanotubes were discovered; however the corresponding result has not been obtained so far on nanotubes filled with metals. Despite recent developments and achievements in nanoelectronics and nanopower engineering, the center of attention for nanostructure application is shifting to

nanomedicine and is becoming most widely represented in nanomaterial science. However, although "the fashion" on carbon nanostructures of different shapes still remains, the preferences in investigations depending on nanostructure shape are changing. First, there was a rush and everybody wrote about fullerenes. Then there was a turn of carbon singlewall nanotubes. Some time later it was found out that multiwall nanotubes were the most convenient to give definite properties to the materials. Finally it was the turn of graphene. However there was information [9] on obtaining hydrocarbon polymeric films (graphane) by reducing graphene.

The main feature of all nanostructures obtained is a considerable excess of a number of surface atoms over the atom number in volume. This excess increases with the nanostructure size decrease. Therefore the nanoparticle size is its main feature.

In the majority of nanotechnology standards and programs [10] the range of nanostructure existence is defined by sizes 0.1– 100 nm. The authors of [11] demonstrated that the interval in which the nanostructure activity changes depends on nanostructure nature and shape. However, if the energy of nanoparticle field is comparable with the energy of electromagnetic radiation, when significant changes take place due to chemical reactions in substances under the action of radiation upon them in the wavelength interval indicated, the nanoparticle activity in size interval up to 100 nm will be considerable.

It should be pointed out that atoms on the surface of nanostructures are in energy non-compensated state. In general, this results in the growth of nanoparticle energy which can be presented as the total of atom energies on the particle surface. It is quite obvious that the freedom of movement of surface atoms is limited except for the possibilities of oscillatory motion and movement of electrons. Both these movement forms are interconnected since the shifts of electron clouds in atoms inevitably result in changes of oscillation frequencies of corresponding bonds with the atom participation. In turn, the changes in the position of valence electrons in bonds result in the change of bond polarity and the so-called "supramolecule" [12]. Here the electron shift to higher energy levels is possible.

In this regard, metal/carbon nanostructures are the most interesting objects of investigation. Since metal clusters in these nanostructures are associated with the carbon envelope protecting them from the environment, they were called metal/carbon nanocomposites.

In contrast with carbon nanostructures, metal and metal oxide clusters, metal/carbon nanocomposites, apart from metal and covalent bonds, have a significant share of coordination bonds contributing to their self-organization. At the same time, the bonds indicated can arise changes in the electron structure of d metals contributing to the increase in the number of unpaired electrons and growth of the number of atom magnetic momentum.

Metal/carbon nanocomposites are interesting for the investigation with the help of X-ray electron spectroscopy and electron paramagnetic resonance.

It is amazing that such informatively powerful method as X-ray electron spectroscopy is envisaged for the investigation of the electron structure of atoms in surface layers is insufficiently applied in the investigation of nanostructures and nanostructurized materials, especially polymers.

Therefore, the editors put down the discussions of the investigation results of metal/carbon nanocomposites with the application of X-ray photoelectron spectrometers with magnetic focusing in certain chapters of the book. A special place is provided for computer modeling of processes with the participation of metal/carbon nanocomposites. The development of prognosticating methods for the obtaining of nanocomposites is very important for the assessment of their activity in different media and modification of polymeric materials.

The authors and editors pay much attention to the application of metal/carbon nanocomposites in the form of fine suspensions and sols in the corresponding media for the modification of polymeric organic and inorganic materials.

Since, despite of a large number of theoretical and experimental works, there is no unified concept of the formation of nanostructures and nanocomposites, as well as nanostructurized materials with predetermined properties, there have been attempts in a number of papers to close this gap or, at least, to come closer to solving the problem.

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FUNDAMENTAL DEFINITIONS FOR DOMAIN OF NANOSTRUCTURES AND METAL/CARBON NANOCOMPOSITES

V. I. KODOLOV and V. V. TRINEEVA

CONTENTS

1.1   DETERMINATION OF EXISTENCE AREA OF NANOSTRUCTURES AND NANOSYSTEMS BASIC NOTIONS IN NANOCHEMISTRY AND NANOTECHNOLOGY NANOSIZED INTER VAL

In every new field of knowledge specific notions and terms or "language" are created limiting and isolating this field. However, first existence boundaries of new notions and ideas corresponding to the above field of knowledge are determined.

The appearance of "nanoscience" and "nanotechnology" stimulated the burst of terms with "nano-" prefix. Historically the term "nanotechnology" appeared before and it was connected with the appearance of possibilities to determine measurable values up to 10^{-9} of known parameters: 10^{-9}m–nm (nanometer), 10^{-9}s–ns (nanosecond), 10^{-9} degree (nanodegree, shift condition). Nanotechnology and molecular nanotechnology comprise the set of technologies [1] connected with transport of atoms and other chemical particles (ions, molecules) at distances contributing the interactions between them with the formation of nanostructures with different nature. Although Nobel laureate Richard Feyman (1959) showed the possibility to develop technologies on nanometer level, Eric Drexler due to his emotional book "Future without boundaries—revolution of nanotechnology" is considered [1] to be the founder and ideologist of nanotechnology. When scanning tunnel microscope was invented by Nobel laureates Rorer and Binig (1981) there was an opportunity to influence atoms of a substance thus stimulating the work in the field of probe technology, which resulted in substantiation and practical application of nanotechnological methods in 1994. With the help of this technique it is possible to handle single atoms and collect molecules or aggregates of molecules, construct various structures from atoms on a certain substrate (base). Naturally, such a possibility cannot be implemented without preliminary computer designing of so-called "nanostructures architecture". Nanostructures architecture assumes a certain given location of atoms and molecules in space that can be designed on computer and afterwards transferred into technological program of nanotechnological facility.

The term "chemical assembly" appeared together with the development of chemistry and physics of surface after the birth of "electron spectroscopy for chemical analysis" founded by Nobel laureate K. Zigban [2].

In Russia, chemical assembly comprising the interaction of chemical particles with the surface and "grafting" of functional groups to the surface or interface boundary "gas–solid" has been developed by the school of V. B. Aleskovsky [3].

The paper with the participation of Nobel laureates (Nobel Prize in 1995) Croto, Smalley and Carl on synthesis of fullerenes by graphite evaporation was published in 1985. At the same time in nanoproduct obtained fullerene C_{60} predominates by

its content, which represents an enclosed cluster of 60 carbon atoms. This cluster had a stable and symmetrical structure. Further, a specialist in electron microscopy Iijima discovered nanotubes in 1991. Afterwards, the investigations in the field of nanoparticles and nanosystems started spreading all over the world.

The development of these trends predetermined the appearance and development of so-called "nanoscience". In the same way as "nanotechnology" and "nanoscience" is determined as a combination of scientific knowledge from various disciplines, such as physics, chemistry, biology, mathematics, programming, and so on, adapted to nanostructures and nanosystems. Nanoscience comprises fundamental and applied scientific knowledge. Therefore, it is possible to speak about nanochemistry, nanometallurgy, nanoelectronics, nanomachine-building, science of nanomaterials, and similar disciplines. If we think of the world from the point that the nature is unified and different disciplines in the science were created by people for the convenience of perception and understanding of the world around, the appearing areas of nanoscience closely connected with nanotechnology represent a vast aggregation of disciplines the list of which will still be incomplete analogously too [4]. Let us be restricted to definitions connected with science of nanomaterials.

The notion "science of nanomaterials" assumes scientific knowledge for obtaining, composition, properties and possibilities to apply nanostructures, nanosystems and nanomaterials. A simplified definition of this term can be as follows: material science dealing with materials comprising particles and phases with nanometer dimensions. To determine the existence area for nanostructures and nanosystems it is advisable to find out the difference of these formations from analogous material objects.

From the analysis of literature the following can be summarized: the existence area of nanosystems and nanoparticles with any structure is between the particles of molecular and atomic level determined in picometers and aggregates of molecules or permolecular formations over micron units. Here, it should be mentioned that in polymer chemistry particles with nanometer dimensions belong to the class of permolecular structures, such as globules and fibrils by one of parameters, for example, by diameter or thickness. In chemistry of complex compounds clusters with nanometer dimensions are also known.

The notion "cluster" assumes energy-wise compensated nucleus with a shell, the surface energy of which is rather small, as a result under given conditions the cluster represents a stable formation.

In chemical literature a cluster is equated with a complex compound containing a nucleus and a shell. Usually a nucleus consists of metal atoms combined with metallic bond, and a shell of ligands. Manganese carbonyls $[(Co)_5MnMn(Co)_5]$

and cobalt carbonyls [$Co_6(Co)_{18}$], nickel pentadienyls [$Ni_6(C_5H_6)_6$] belong to elementary clusters.

In recent years, the notion "cluster" has got an extended meaning. At the same time the nucleus can contain not only metals or not even contain metals. In some clusters, for instance, carbon ones there is no nucleus at all. In this case their shape can be characterized as a sphere (icosahedron, to be precise)—fullerenes, or as a cylinder—fullerene tubules. Surely a certain force field is formed by atoms on internal walls inside such particles. It can be assumed that electrostatic, electromagnetic, and gravitation fields conditioned by corresponding properties of atoms contained in particle shells can be formed inside tubules and fullerenes. If analyze papers recently published, it should be noted that a considerable exceeding of surface size over the volume and, consequently, a relative growth of the surface energy in comparison with the growth of volume and potential energy is the main feature of clusters. If particle dimensions (diameters of "tubes" and "spheres") change from 1 up to several hundred nanometers, they would be called nanoparticles. In some papers, the area of nanoclusters existence is within 1–10 nm [5].

Based on classical definitions, in given paper, metal nanoparticles and nanocrystals are referred to as nanoclusters. Apparently, the difference of nanoparticles from other particles (smaller or larger) is determined by their specific characteristics. The search of nanoworld distinctions from atomic-molecular, micro- and macroworld can lead to finding analogies and coincidences in colloid chemistry, chemistry of polymers, and coordination compounds. Firstly, it should be noted that nanoparticles usually represent a small collective aggregation of atoms being within the action of adjacent atoms, thus conditioning the shape of nanoparticles. A nanoparticle shape can vary depending upon the nature of adjacent atoms and character of formation medium. Obviously, the properties of separate atoms and molecules (of small size) are determined by their energy and geometry characteristics, the determinative role being played by electron properties. In particular, electron interactions determine the geometry of molecules and atomic structures of small size and mobility of these chemical particles in media, as well as their activity or reactivity.

When the number of atoms in chemical particle exceeds 30, a certain stabilization of its shape being also conditioned by collective influence of atoms constituting the particle is observed. Simultaneously, the activity of such a particle remains high but the processes with its participation have a directional character. The character of interactions with the surroundings of such structures is determined by their formation mechanism.

During polymerization or co-polymerization the influence of macromolecule growth parameters changes with the increase of the number of elementary acts of its growth. According to [6], after 7–10 acts the shape or geometry of nanoparticles

formed becomes the main determinative factor providing the further growth of macromolecule (chain development). A nanoparticle shape is usually determined not only by its structural elements but also by its interactions with surrounding chemical particles.

From the aforesaid, it can be concluded that the possibility of self-organization of nanoparticles with the formation of corresponding nanosystems and nanomaterials is the main distinction of nanoworld from pico-, micro-, and macroworld. Recently, much attention has been paid to synergetics or the branch of science dealing with self-organization processes since these processes, in many cases, proceeds with small energy consumption and, consequently, is more ecologically clear in comparison with existing technological processes.

In turn, nanoparticle dimensions are determined by its formation conditions. When the energy consumed for macroparticle destruction or dispersion over the surface increases, the dimensions of nanomaterials are more likely to decrease. The notion "nanomaterial" is not strictly defined. Several researchers consider nanomaterials to be aggregations of nanocrystals, nanotubes, or fullerenes. Simultaneously, there is a lot of information available that nanomaterials can represent materials containing various nanostructures. The most attention researchers pay to metallic nanocrystals. Special attention is paid to metallic nanowires and nanofibers with different compositions.

Here are some names of nanostructures:

1) fullerenes, 2) gigantic fullerenes, 3) fullerenes filled with metal ions, 4) fullerenes containing metallic nucleus and carbon (or mineral) shell, 5) one-layer nanotubes, 6) multi-layer nanotubes, 7) fullerene tubules, 8) "scrolls", 9) conic nanotubes, 10) metal-containing tubules, 11) "onions", 12) "Russian dolls", 13) bamboo-like tubules, 14) "beads", 15) welded nanotubes, 16) bunches of nanotubes, 17) nanowires, 18) nanofibers, 19) nanoropes, 20) nanosemi-spheres (nanocups), 21) nanobands and similar nanostructures, as well as various derivatives from enlisted structures. It is quite possible that a set of such structures and notions will be enriched.

In most cases nanoparticles obtained are bodies of rotation or contain parts of bodies of rotation. In natural environment there are minerals containing fullerenes or representing thread-like formations comprising nanometer pores or structures. In the first case, it is talked about schungite that is available in quartz rock in unique deposit in Prionezhje. Similar mineral can also be found in the river Lena basin, but it consists of micro- and macro-dimensional cones, spheroids, and complex fibers [7]. In the second case, it is talked about kerite from pegmatite on Volyn (Ukraine) that consists of polycrystalline fibers, spheres, and spirals mostly of micron dimensions, or fibrous vetcillite from the state of Utah (USA); globular anthraxolite and asphaltite.

Diameters of some internal channels are up to 20–50nm. Such channels can be of interest as nanoreactors for the synthesis of organic, carbon, and polymeric substances with relatively low energy consumption. In case of directed location of internal channels in such matrixes and their inner-combinations the spatial structures of certain purpose can be created. Terminology in the field of nanosystems existence is still being developed, but it is already clear that nanoscience obtains qualitatively new knowledge that can find wide application in various areas of human practice thus, significantly decreasing the danger of people's activities for themselves and environment.

The system classification by dimensional factor is known [1], based on which we consider the following:

- Microobjects and microparticles 10^{-6}–10^{-3}m in size;
- Nanoobjects and nanoparticles 10^{-9}–10^{-6}m in size;
- Picoobjects and picoparticles 10^{-12}–10^{-9}m in size.

Assuming that nanoparticle vibration energies correlate with their dimensions and comparing this energy with the corresponding region of electromagnetic waves, we can assert that energy action of nanostructures is within the energy region of chemical reactions. System self-organization refers to synergetics [4]. Quite often, especially recently, the papers are published, for example, by Malinetsky [8], in which it is considered that nanotechnology is based on self-organization of metastable systems. As assumed [9], self-organization can proceed by dissipative (synergetic) and continual (conservative) mechanisms. Simultaneously, the system can be arranged due to the formation of new stable ("strengthening") phases or due to the growth provision of the existing basic phase. This phenomenon underlies the arising nanochemistry. Below is one of the possible definitions of nanochemistry.

Nanochemistry is a science investigating nanostructures and nanosystems in metastable ("transition") states and processes flowing with them in near-"transition" state or in "transition" state with low activation energies.

To carry out the processes based on the notions of nanochemistry, the directed energy action on the system is required, with the help of chemical particle field as well, for the transition from the prepared near-"transition" state into the process product state (in our case–into nanostructures or nanocomposites). The perspective area of nanochemistry is the chemistry in nanoreactors. Nanoreactors can be compared with specific nanostructures representing limited space regions in which chemical particles orientate creating "transition state" prior to the formation of the desired nanoproduct. Nanoreactors have a definite activity which predetermines the creation of the corresponding product. When nanosized particles are formed in nanoreactors, their shape and dimensions can be the reflection of shape and dimensions of the nanoreactor [10].

In the last years a lot of scientific information in the field of nanotechnology and science of nanomaterials appeared. Nobel laureate R. Smalley [11] defined the interval from 1 to 1000nm as the area of nanostructure existence, the main feature of which is to regulate the system self-organization processes. However, later some scientists [12–14] limited the upper threshold at 100nm. At the same time, it was not well-substantiated and taken from [15]. Now many nanostructures varying in shapes and sizes are known. These nanostructures have sizes that fit into the interval, determined by Smally, and are active in the processes of self-organization, and also demonstrate specific properties.

Problems of nanostructure activity and the influence of nanostructure super small quantities on the active media structural changes are explained [16–18].

The molecular nanotechnology ideology is analyzed [19]. In accordance with the development tendencies in self-organizing systems under the influence of nanosized excitations the reasons for the generation of self-organization in the range 10^{-6}–10^{-9}m should be determined.

Based on the law of energy conservation the energy of nanoparticle field and electromagnetic waves in the range 1–1,000nm can transfer, thus corresponding to the range of energy change from soft X-ray to near IR radiation. This is the range of energies of chemical reactions and self-organization (structuring) of systems connected with them.

Apparently the wavelengths of nanoparticle oscillations near the equilibrium state are close or correspond to their sizes. Then based on the concepts of ideologists of nanotechnology in material science the definition of nanotechnology can be as follows:

- Nanotechnology is a combination of knowledge in the ways and means of conducting processes based on the phenomenon of nano-sized system self-organization and utilization of internal capabilities of the systems that results in decreasing the energy consumption required for obtaining the targeted product while preserving the ecological cleanness of the process.

1.1.1   Theoretical substantiation of the approaches proposed

The activity of nanostructures in self-organization processes is defined by their surface energy thus corresponding to the energy of their interaction with the surroundings. It is known [10] that when the size of particles decreases, their surface energy and particle activity increase. The following ratio is proposed to evaluate their activity:

$$a = \varepsilon_S / \varepsilon_V \qquad\qquad (1.1)$$

where, ε_S—nanoparticle surface energy, ε_V—nanoparticle volume energy. Naturally in this case $\varepsilon_S \gg \varepsilon_V$ conditioned by the greater surface "defectiveness" in comparison with nanoparticle volume. To reveal the dependence of activity upon the size and shape we take ε_S as $\varepsilon_S^0 \cdot S$, and $\varepsilon_V = \varepsilon_V^0 \cdot V$, where, ε_S^0—average energy of surface unit, S—surface, ε_V^0—average energy of volume unit, V—volume, then the equation (1) is converted to:

$$a = d \cdot \varepsilon_S^0 / \varepsilon_V^0 \ S/V \qquad (1.2)$$

Substituting the values of S and V for different shapes of nanostructures, we see that in general form the ratio S/V is the ratio of the number whose value is defined by the nanostructure shape to the linear size connected with the nanostructure radius or thickness. The equation (2) can be given as

$$a = d \cdot \varepsilon_S^0 / \varepsilon_V^0 \ N/r(h) = \varepsilon_S^0 / \varepsilon_V^0 \ 1/B \qquad (1.3)$$

where, B equals r(h)/N, r—radius of bodies of revolution including hollow ones, h—film thickness depending upon its "distortion from plane", N—number varying depending upon the nanostructure shape. Parameter d characterizes the nanostructure surface layer thickness, and corresponding energies of surface unit and volume unit are defined by the nanostructure composition. For the corresponding bodies of revolution the parameter B represents an effective value of the interval of nanostructure linear size influencing the activity at the given interval r from 1 to 1,000nm (Table 1.1). The table shows spherical and cylindrical bodies of revolution. For nanofilms the surface and volume are determined by the defectiveness and shape of changes in conformations of film nanostructures depending upon its crystallinity degree. However, the possibilities of changes in nanofilm shapes at the changes in the medium activity are higher in comparison with nanostructures already formed. At the same time, the sizes of nanofilms formed and their defectiveness (disruptions and cracks on the surface of nanofilms) play are important.

TABLE 1.1   Changes in interval B depending upon the nanoparticle shape.

Nanostructure shape	Internal radius as related to the external radius	Interval of changes B, nm
Solid sphere	–	0.33(3)–333.(3)
Solid cylinder	–	0.5–500
Hollow sphere	8/9	0.099–99

TABLE 1.1   *(Continued)*

Hollow sphere	9/10	0.091–91
Hollow cylinder	8/9	0.105–105
Hollow cylinder	9/10	0.095–95

Proposed the parameter called the nanosized interval (B) may be used to demonstrate the nanostructures activity. Depending on the structure and composition of nanoreactor internal walls, distance between them, shape and size of nanoreactor, the nanostructures differing in activity are formed. The correlation between surface energy, taking into account the thickness of surface layer, and volume energy was proposed as a measure of the activity of nanostructures, nanoreactors and nanosystems [1].

It is possible to evaluate the relative dimensionless activity value (A) of nanostructures and nanoreactors through relative values of difference between the modules of surface and volume energies to their sum:

$$A = (\varepsilon_S - \varepsilon_V)/(\varepsilon_S + \varepsilon_V) = [(\varepsilon_S^0 d)S - \varepsilon_V^0 V]/[(\varepsilon_S^0 d)S + \varepsilon_V^0 V]$$

$$= [(\varepsilon_S^0/\varepsilon_V^0)S - V]/[(\varepsilon_S^0 d/\varepsilon_V^0)S + V] \qquad (1.4)$$

If $\varepsilon_S \gg \varepsilon_V$, A tends to 1.

If $\varepsilon_S^0 d/\varepsilon_V^0 \approx 1$, the equation for relative activity value is simplified as follows:

$$A \approx [(S - V)/(S + V)] = [(1 - B)/(1 + B)] \qquad (1.5)$$

If we accept the same condition for *a*, the relative activity can be expressed via the absolute activity:

$$A = (a - 1)/(a + 1) \qquad (1.6)$$

At the same time, if $a \gg 1$, the relative activity tends to 1.

Nanoreactors represent nanosized cavities, in some cases nanopores in different matrixes that can be used as nanoreactors to obtain desired nanoproducts. The main task for nanoreactors is to contribute to the formation of "transition state" of activated complex being transformed into a nanoproduct practically without any losses for activation energy. In such case, the main influence on the process progress and direction is caused by the entropic member of Arrhenius equation

connected either with the statistic sums or the activity of nanoreactor walls and components participating in the process.

The surface energy of nanostructures represents the sum of parts assigned forward motion (ε_{fm}), rotation (ε_{rot}), vibration (ε_{vib}), and electron motion (ε_{em}) in the nanostructure surface layer:

$$\varepsilon_S = \Sigma(\varepsilon_{fm} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{em}) \qquad (1.7)$$

The assignment of these parts on values depends on nature of nanostructure and medium. The decreasing of nanostructure sizes and their quantity usually leads to the increasing of the surface energy vibration part, if the medium viscosity is great. When the nanostructure size is small, the stabilization of electron motion takes place and the energy of electron motion is decreased. Also the possibility of coordination reaction with medium molecules is decreased. In this case the vibration part of surface energy corresponds to the total surface energy.

The nanostructures formed in nanoreactors of polymeric matrixes can be presented as oscillators with rather high oscillation frequency. It should be pointed out that according to references [1] for nanostructures (fullerenes and nanotubes) the absorption in the range of wave numbers 1,300–1,450cm^{-1} is indicative. These values of wave numbers correspond to the frequencies in the range 3.9–4.35·10^{13}Hz, i.e. in the range of ultrasound frequencies.

If the medium into which the nanostructure is placed blocks its translational or rotational motion giving the possibility only for the oscillatory motion, the nanostructure surface energy can be identified with the vibration energy:

$$\varepsilon_S \approx \varepsilon_v = m v_v^{2}/2, \qquad (1.8)$$

where, m—nanostructure mass, a $v_к$—velocity of nanostructure vibrations. Knowing the nanostructure mass, its specific surface and having identified the surface energy, it is easy to find the velocity of nanostructure vibrations:

$$v_v = \sqrt{2\varepsilon_v/m} \qquad (1.9)$$

If only the nanostructure vibrations are preserved, it can be logically assumed that the amplitude of nanostructure oscillations should not exceed its linear nanosize, that is $\lambda < r$. Then the frequency of nanostructure oscillations can be found as follows:

$$v_v = v_v/\lambda \qquad (1.10)$$

Therefore, the wave number can be calculated and compared with the experimental results obtained from IR spectra.

However with the increasing of nanostructures numbers in medium the action of nanostructures field on the medium is increased by the inductive effect.

The reactivity of nanostructure or the energy of coordination interaction may be represented as:

$$\Sigma\varepsilon_{coord} = \Sigma[(\mu_{ns}\cdot\mu_{m})/r^3] \tag{1.11}$$

and thus, the activity of nanostructure:

$$a = \{[\varepsilon_{vib} + \Sigma[(\mu_{ns}\cdot\mu_{m})/r^3]\}/\varepsilon_{V} \tag{1.12}$$

When, $\varepsilon_{vib} \rightarrow 0$, the activity of nanostructures is proportional product $\mu_{ns}\cdot\mu_{m}$, where μ_{ns}—dipole moment of nanostructure, μ_{m}—dipole moment of medium molecule.

1.2   NANOCOMPOSITES AND NANOMATERIALS. WHAT IS NANO-COMPOSITE AND IT'S UNLIKE NANOMATERIAL NANOSTRUCTURED MATERIALS (MATERIALS MODIFIED BY NANOSTRUCTURES)

At present the precise definition of nanomaterials and nanocomposites creates certain difficulties. Prefix "nano-" assumes small-dimensional characteristics of materials, and the notion "material" has a macroscopic meaning. In accordance with [20], material is a common substance used to produce objects and articles. Unlike substance, material has heterogeneous or heterophase composition. What is nanomaterial? Formally, it is a nanoparticle or aggregation of nanoparticles with properties necessary to produce several articles, for instance, in nanoelectronics or nanomachine–building. It is been assumed that obtained rather active nanoparticles, which can be interconnected in certain succession with the help of UV-laser radiation to produce spatial articles. Naturally, the swarm of nanoparticles in certain surroundings should be compacted accordingly in pulse electrostatic or electromagnetic field to afterwards treat the "phantom" formed with several laser beams successively connecting nanoparticles in accordance with computer software. In this case, the corresponding nanoparticles can actually be called nanomaterial further used to produce articles. Truly, the material formed from nanoparticles will not completely repeat the characteristics of nanoparticles constituting it. The material obtained from nanoparticles is also called [21] nanomaterial or nanocomposite if nanoparticles differ by their nature. Simultaneously, the notion nanocomposite or composition material has a wider meaning, under composites

[20], any macroheterophase materials consisting of two or more heterogeneous components with different physical or mechanical properties. In general case, composition material [22] represents multi-component and multi-phase material formed from the composition hardened when simultaneously obtaining material or article and containing mineral and organic, often polymeric materials, as a rule, with predominance of one of the components, for instance, a mineral one, thus allowing obtaining unique properties of composite formed. The definition of nanocomposites represents similar complexity as the definition of nanomaterials. In the paper by A. L. Ivanovsky [23], it is mentioned that fullerenes and tubules filled with various materials got to be called nanocomposites. At the same time, it was mentioned that effects for filling nanotubes with various substances are also interesting from the point of studying capillar properties of tubules.

Intercalated nanotubes or threads-like bunches of nanotubes, ordered layers of nanotubes in combination with different matrixes are referred to nanotubular composites. The notion "nanocomposite" in classical variant should also contain heterogeneous nanostructures or nanostructures with encapsulated nanoparticles or nanocrystals. At the same time under nanoparticles we understand nanoformations of different character without strict internal order. For gigantic tubules and fullerenes consisting of several spheres or tubes filled with other microphases and with various shapes, the corresponding verbal designations or terms, for instance "onions" or "beads", can appear. In case of formation of extensive structures, such as tubules or nanofibers their mutual interlacing with the formation of nets or braids is possible, between which particles of other components and other phases are located. Here, it should be mentioned that the mixture of phases with different shapes and structures can be referred to nanocomposites, although their composition remains the same. However, when the shape and ordering system change, the properties of nanoparticle change as well. Its surface energy and, consequently, interaction potentials between the particles of different shapes will be different in comparison with corresponding interaction potentials of nanoparticles homogeneous in composition, dimensions and shape. To some extent such conclusions follow from well-known definition of regularities for polymeric, ceramic, and metallic composites. It is known that multi-phase material with unique properties can be created under mechanical-chemical effect (monoaxial pulling from polymer melt), in which crystalline regions with different crystallization degree and amorphous regions will alternate. At the same time, in such material the formation of self-organizing reinforcing phases is possible. The availability of other component in the material, which can also form different nanophases, increases the abilities of nanocomposite formed.

What is nanophase?

By analogy with common definition of the phase it can be said that nanophase is a homogeneous part of nanosystem, which is isolated by physical boundaries on nanometer level from other similar parts. However, the difference in properties of nanophases can be insignificant. This is conditioned by the tendency to decrease total energy of nanosystem.

A considerable number of recent researches are dedicated to nanocrystals. When we extend the notion "cluster" adding particles with nuclei, substances consisting of non metallic components and shells different in energy and composition to this class, there appeared papers [24, 25] where the stability of clusters, nanoclusters to be more exact, is provided by their shape or surface on which these particles are located. Besides, in several cases nanoclusters identify with nanocrystals for which there are no corresponding protective shells, therefore nanoclusters and nanocrystals can be classified based on the type of crystalline structure, composition, sizes, and form of cluster structure, if a certain crystalline structure is preserved. At the same time, it should not be forgotten that cluster is translated as a group or bunch, and with nanoclusters this notion transforms into a group of chemical particles. Now, it is possible to produce clusters with a precisely determined number of atoms. Due to final sizes these small particles have structures and properties differing from "volumetric" characteristics of crystals of bigger sizes. At the same time, properties of nanoclusters change considerably even when one atom is removed from the cluster. It should be mentioned that a cluster can contain aggregates or groups of 2 up to 10^4 atoms. Therefore, aggregates of weakly bound condensed molecules can be presented as clusters. Thus nanocrystals or quasicrystals can be classified based on their sizes. Is there any difference between nanoclusters and nanocrystals? From the aforesaid translation of the word "cluster", it can be seen that a group or bunch of atoms or molecules in this chemical formation differs from the corresponding nanocrystals or crystals by weaker bonds. At the same time, the availability of crystalline lattice in nanocrystals assumes stronger organization of the system and increase in the strength of chemical bonds between the particles constituting nanocrystals. By their composition nanoclusters with a certain order, that can be an element of crystalline structure, can consist of the element of one type, for instance, carbon, metallic, silicon, and so on particles. It is interesting to note that nanoclusters of "noble" metals have fewer atoms in comparison with the clusters formed from more active elements. In Figure 1.1 there are three nanostructures of elements differing by electronegativity and electrochemical potentials.
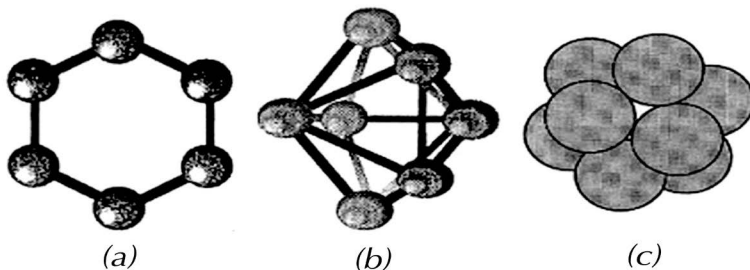
FIGURE 1.1   Nanoclusters of elements given according to the decrease of electronegativity of metals: (a) gold, (b) silicon, (c) aluminum.

Based on the increase of their activity in redox processes these elements can be arranged as follows: Au < Si < Al. The least number of atoms is in nanocluster of gold—6 (χ_{Au} = 2.54, by Polling), in nanocluster of silicon—7 atoms ($_{Si}$ = 1.9), and in nanocluster of aluminum—13 atoms ($_{Al}$ = 1.61). Atoms of gold form six-term ring, atoms of silicon—pentagonal pyramid, and nanocluster of aluminum has a shape of icosahedron. However, the least amount of atoms in a nanocluster is also determined, apparently, by the sizes of components and possibilities of their aggregation into certain initial geometrical formations. Let us point out that the structures given in the Figure refer to the third and sixth periods. The activity of elements of the second period is higher therefore the least number of particles in clusters of these elements can be expected to increase. For example, for carbon a six-term ring with π-electrons distributed between the atoms is initially the most stable, and the least number of atoms in carbon clusters is determined as 32 [26–28], that was obtained. However, in fullerenes with the shape of icosahedron five-term rings are also found. Silicon being an analog of carbon in chemical properties can form relatively stable nanostructures from three-term rings, and phosphorus atom can form four-term rings. Clusters are classified by the number of atoms or valence electrons participating in cluster formation. For instance, for atoms of group 1 in the Periodic Table it is pointed out [29] that an even number of valence electrons always participate in their cluster formation, starting from 2 and further 8, 18, 20, and 40. The stability of clusters, on the one hand, is conditioned by the stability of their electron composition, and, on the other hand, by the corresponding external potential of the medium surrounding particles. To increase the stability neutral clusters can be transferred into ionic form. Therefore, clusters and nanocrystals can also be classified by their charge. Apart from neutral clusters, clusters-anions and clusters-cations are known. Such clusters are investigated with the help of photoelectron spectroscopy [30, 31].

For metallic cluster-anions stable electron shells appear at odd number of atoms in a cluster. For example, for Cu_7^- p-orbital of the cluster is completely filled, similar situation of complete filling of d-orbitals is noted for cluster Cu_{17}^-. For clusters-cations the increase in stability at odd number of atoms in a cluster is seen [32]. For instance, spherically asymmetrical particles of single-charged

silver cations have the following numbers of atoms 9, 11, 15, and 21. The stability of nanoclusters and nanocrystals increases when the changes decreasing the cluster surface energy are introduced into the electron structure, this can be done when other atoms interacting with atoms-"hosts" are introduced into the cluster, or the protective shell is formed on the cluster*, or the cluster is precipitated on a certain substrate that stabilizes the cluster. Thus, clusters and nanocrystals can be classified by the stabilization method. Formation of clusters and nanocrystals on different surfaces is of great interest for researches. There is the phenomenon of epitaxy was mentioned, when the formation of or change in the structure of clusters proceed under the influence of active centers of surface layer located in certain order, thus contributing to the minimization of surface energy. The introduction of a certain structure of nanocrystals into the substrate surface layer results in the changes of nanoparticle electron structure and energy of corresponding active centers of surface layer providing the decrease of surface energy of the system being formed. As nanocrytsals have a rather active surface, their application to the substrate should proceed under definite conditions that could not considerably change their energy and shape.

However, depending upon the energy accumulated by a nanocrystal (nanocluster), even at identical element composition different results in morphology are achieved. The influence of substrate increases due to the dissipation energy brought by the cluster onto the substrate surface (Figure 1.2, [33]).
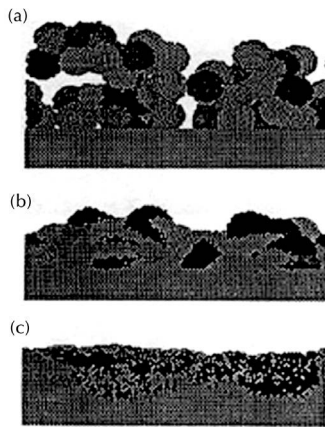
FIGURE 1.2   Morphology of cluster-assembled films created on Mo (100) surface as a function of the cluster energy: (a) 0.1eV/atom; (b) 1eV/atom; (c) 10eV/atom.

As seen from the Figure the elevation of nanoparticle energy from 0.1 eV up to 10 eV results in considerable changes in thin films being formed. The elevation

of energy up to 10 eV leads to finer mixing of structures of Mo cluster on molybdenum surface (100). The given type of morphology is observed on many other systems, such as manganese clusters on clean and covered with fullerenes C_{60} silicon surface (111) [34], кластеры железа на поверхности кремния (111) [35], clusters of gold on gold surface (111) [36], as well as clusters of cobalt and nickel on glass surface. In some cases, nanocrystals applied or formed on the surface are joined with the formation of relatively stable dendrite or star-like structures comprising hundreds of atoms. In Figure 1.3, there are pictures of such nanostructures of antimony on graphite surface [37].
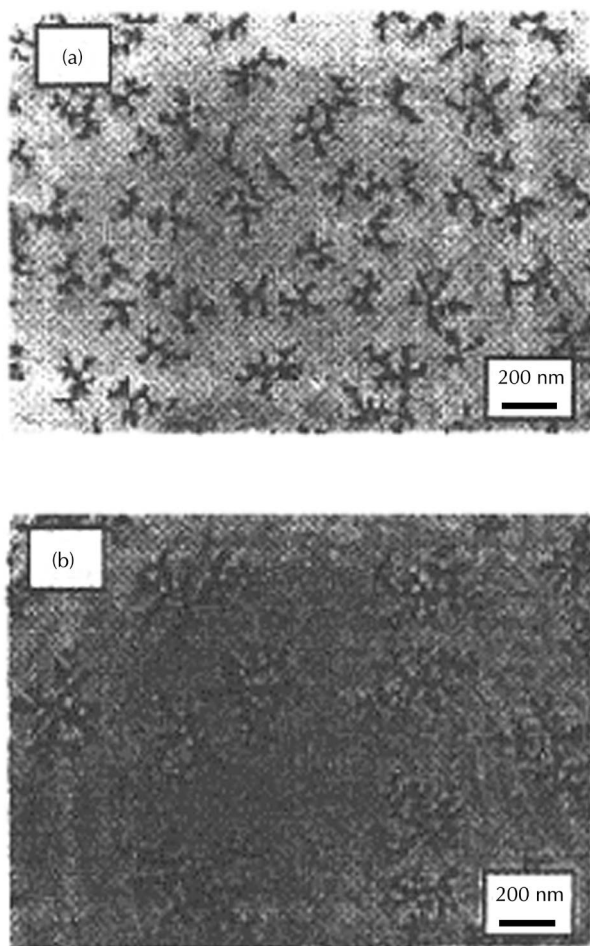
FIGURE 1.3   TEM images of islands formed by similar doses of Sb clusters on HOPG at 298K (a), 373K (b).

"Island" structure is produced. The clusters antimony formed contain 2,300 atoms [38]. Such nanostructures are less expressed on amorphous carbon and depend upon the substrate material and number of atoms in the cluster.

When the number of atoms in antimony cluster goes down [39], the nanostructures formed join to a lesser extent and represent "drop-like" formations.
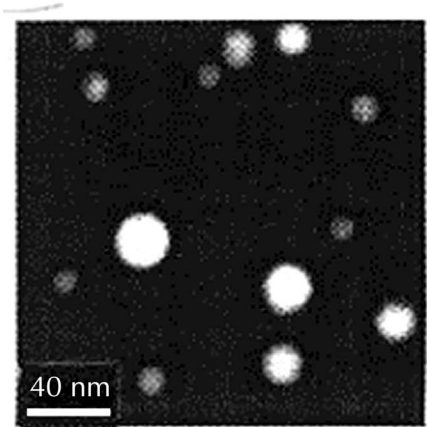
(a)
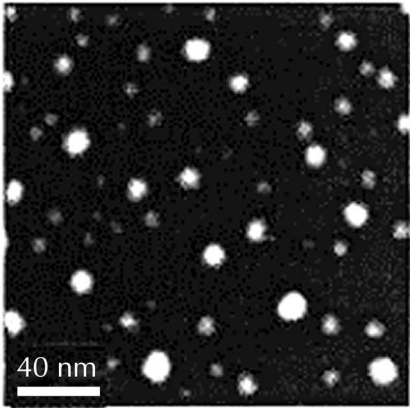
(b)

FIGURE 1.4   *(Continued)*
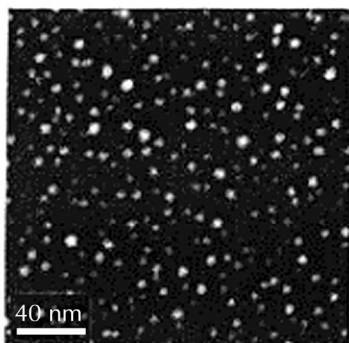
(c)
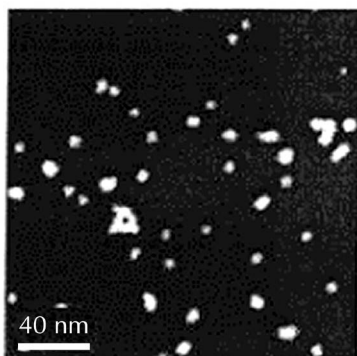
(d)

FIGURE 1.4   STEM images of islands formed by the deposition of different-sized Sb clusters on amorphous carbon (a) Sb4; (b) Sb60; (c) Sb150; (d) Sb2200.

"Island" morphology changes from spherical to the aforesaid shapes for the sizes from 4 up to 2,200 atoms. For transition metals the critical size for the formation of branched nanostructures is much less than for alkaline metals. Thin films from clusters of silver containing less than 200 atoms also have certain joints.

The morphology of structures formed can keep on changing in comparison with the initial one. This is explained, by the analogy with terminology from polymeric chemistry, by Ostwald's maturation when nanoparticles "merge" into larger formations.

The investigations of metallic or shifted nanocrystals are closely connected with the studies on carbon and carbon-containing (metal carbides) nanoclusters (nanocrystals). Therefore, nanocrystals are split into one-, two-, and multi-element structures. The stability of nanocrystals and nanoclusters increases if they comprise two or more elements. Simultaneously, the combination of elements active and passive by redox potentials contributes to the stabilization of multi-element clusters being formed. Clusters containing Co/Cu, (Fe-Co)/Ag, Fe/Au, Co/Pt are known [7]. Several clusters have a stabilizing shell in the form of oxides, carbides or hydrides, for example, Al_2O_3, Sm_2O_3, SiO_2, CO, Met_xC_y, $B_{2n}H_{2n}$ [24, 25, 40, 41].

Thus, clusters and nanocrystals can be classified based on the composition of the shell and nucleus, alongside with their evaluation based on size and shape.

In turn, nanocrystals are classified by the type of "superlattice" [42]. Overview [40] contains the classification of nanoclusters and nanosystems based on their production method. This paper describes the ways for organizing nanostructures from nanoclusters and mentions the new properties appearing during the merge of nanoclusters into a nanosystem.

Classification of carbon clusters (fullerenes and tubules) with metals or their compounds intercalated in them has a special position. The most complete idea was obtained during theoretical and experimental investigations of fullerene C_{60} filled with alkaline metals [29].

The shape of nanocluster or nanocrystal and their sizes are determined by the size and shape of the shell that often consists of ligands of different nature. Here, metal carbonyls are studied best of all, although some factors have to be explained. For instance, the nucleus of cluster Ni_4 is surrounded by the shell of ten ligands CO [43] and the nucleus of cluster Pt_4—only eight ligands CO. This is probably connected with the stabilization of electron shells and transition into a "neutral" cluster.

By their definition nanoreactors are energetically saturated nanosized regions (from 10 nm up to 1 cm), intended for conducting directed chemical processes, in which nanostructures or chemical nanoproducts of certain application are formed. The term "nanoreactor" is applied when considering nanotechnological probe devices. In these devices a nanoreactor is the main unit and is formed between the probe apex and substrate under the directed stream of active chemical particles into the clearance "probe—substrate" [44]. Therefore, nanoreactors are classified by energy and geometrical characteristics, by shape and origin of the matrix in which nanoreactors are formed, possibilities to apply for definite reactions. One of the types of reactions in nanoreactors are topochemical ones proceeding with the participation of solids and localized on the surface of splitting of solid phases of reagent and product. Gaseous and liquid phases can participate in these reactions. Here belong topotaxic polymerization that consists in obtaining macromolecules

under low temperatures from monomers located in crystal channels under the radiation and thermal action [45, 46].

Thus, the reactions for producing nanostructures—macromolecules in the channels being nanoreactors were proposed long time ago. The classical example is the topotaxic polymerization of butadiene and its derivatives in the crystals of thiourea and urea. Brown and White [38], as well as Chatani et al [39, 40] studied the polymerization of 2,3-dimethylbutadiene and 2,3-dichlorbutadiene in clathrate complexes of thiourea. The molecules of these substances are arranges in the complexes as shown in Figure 1.5.
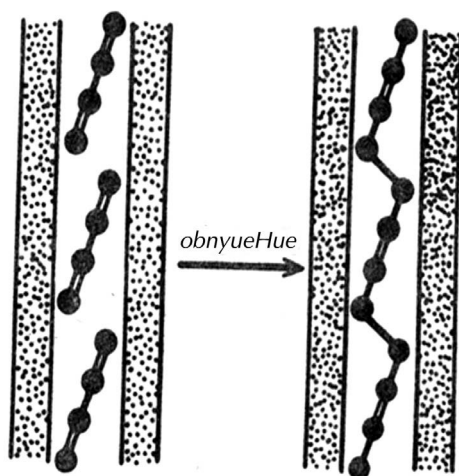
FIGURE 1.5   Polymerization scheme of dienes in the channel of thiourea molecules of included butadiene (a); Macromolecule of polybutadiene (b).

Molecules of butadiene—flat and fill the rectangle 0.76×0.5 nm (Figure 1.5). In a complex crystal the distance between the centers of molecules of butadiene derivatives mentioned equals 0.625 nm. Molecules are arranged obliquely that allows optimizing the interaction. At the same time, inner diameters of the channel (nanoreactor) in thiourea crystals (or clathrate complexes of thiourea and urea) are a little bit bigger than transverse size of butadiene molecule and equal 0.7 nm. The temperature of monomer polymerization reaction under radioactive impact equals approximately -80^0C. Since the monomer polymerization process flows in a condensed state, these reactions can be referred to topochemical reactions. However, stereoregulator macromolecules or nanostructures of certain regularity are rarely obtained, in other words, there are only a few topotaxic processes among topochemical reactions. The corresponding orientation of nanoparticles obtained in nanoreactors is determined, based on the results of topotaxic polymerization,

by the interaction level of reacting chemical particles with the walls of nanore-actor. Depending upon the value of the interaction energy of chemical particles located inside the nanoreactors with the walls of corresponding containers, it is advisable to separate nanoadsorbers and so-called nanocontainers from nanoreac-tors. Nanoadsorbers are applied to adsorb different substances, mainly toxic, but nanocontainers—to store certain products. However, the same nanostructures can be nanoadsorbers, nanocontainers, and nanoreactors. For instance, carbon nano-tubes are applied to remove dioxins [41]. These nanostructures are used to clean industrial wastes from sulfurous gas [42]. Nanotubes are also applied to adsorb hydrogen as nanocontainers or hydrogen storage [43]. All these containers should have active atoms in their walls to adsorb the corresponding chemical particles.

Nanoadsorbers and nanoreactors are evaluated and classified by the adsorp-tion value that, in turn, means the number of particles (N) or volume (v*) of adsorbed particles absorbed by the unit of adsorption space (w) of nanoadsorber.

Nanoreactors can have cavities dimensionally corresponding to the pores from 0.7 nm up to hundreds of nanometers. The pores are classified by their radii [44]: micropores (under 0.7 nm), supermicropores (from 0.7 up to 1.5 nm), meso-pores (from 1.5 up to 100nm), macropores (over 100nm). If we limit the size of the pores by the radius of 1cm, all the pores in porous adsorbers can be considered potential nanoadsorbers and nanoreactors.

Mono- and polymolecular layers are formed in nanoadsorbers with equiva-lent radius over 1.5nm during the sorption process, thus making the conditions to conduct condensation or chemical transformations. If the equivalent radius is less and when nanoadsorbers are filled completely, the equation by M. M. Dubinin written down in accordance with the theory of volumetric filling of micropores [53] is proposed:

$$a = (w_0/v^*) \exp[-(A/\beta E_0)^n], \qquad (1.13)$$

where, a—value of equilibrium adsorption, w_0—ultimate volume of adsorp-tion space, E_0—characteristic adsorption energy (or interaction energy); v*—vol-ume of adsorbed particles; β—similarity coefficient approximated by the ratio of parachors of the substance adsorbed to the substance taken as a standard (e.g., benzene); n—equation parameter (for the majority of coals equals 2); A—differ-ential work of. Work of adsorption equals

$$A = RT\ln(p_s/p); \qquad (1.14)$$

where, T—adsorption temperature; p_s and p—pressure of the substance satu-rated steam, approximately, this ratio equals n_s/n, in which n_s—number of parti-cles participating in the interaction, n—equilibrium number of adsorbed particles.

The sense of "a" for nanoadsorbers means an ultimate number of chemical particles adsorbed in nanoadsorber till the equilibrium is reached under the given conditions of the process. The dimensionalities of corresponding parameters will differ from classical Dubinin's equation but the external form of the equation will be preserved.

As mentioned before, materials modified with introduced nanoparticles or substances in which due to the formation conditions self-organizing processes with the formation of certain nanostructures are initiated can be referred to nanocomposites, in this variants for the formation of nanostructures the appearance of nanoparticles in the form of separate fragments of bodies of rotation. Images of bodies of rotation and their separate fragments realized in nanostructures as cones, cylinders, spheres, ellipsoids, slit ellipsoids, slit spheres, hyperboloids, paraboloids, sphere, and elliptical segments and sectors, barrel-like nanostructures. These nanostructures can be described by the formulas of analytical geometry using the corresponding terms.

The diversity of shapes of nanoparticles of one component results in the response reaction of another. If corresponding capillaries are available and caps closing the ends of nanotubes are absent, it is possible to fill them with atoms and ions of another component. An increased activity of one component leads to the dispersion and activity growth of another one with the formation of new nanophases.

Since, a considerable number of interface layers can be found in nanocomposites, the production of composites to be destructed with the formation of corresponding nanophases in certain media at given local pulse impacts, for instance, laser beam can be perspective. Such materials are of interest for their further utilization after the exploitation resource or functional depreciation of articles produced from these composites. The production of nanocomposites of such level is perspective and contributes to the ecological purity of the environment. However, to solve the tasks connected with the problem of environmental pollution by the products of human vital activity it is necessary to change engineering psychology and education of manufacturers of materials, articles, various structures, machines and mechanisms. At present any engineer after getting the task to produce the corresponding article does not think as for the destiny of this product after its life span. This is already resulted in "littering" the Earth and space around it. To clean the environment from the garbage having been produced by the people for many years the task of present and further generations of mankind.

In nanocomposite and nanomaterial terminology the terms taken from adjacent disciplines, such as coordination chemistry, play an important role. Since nanoparticles and nanoclusters are stabilized in particular surroundings, their transition into different medium results in decreasing their stability and changing

their "architecture". This increases interactions in the composition consisting of nanostructures (nanoparticles) and can be equated with "re-coordination" reactions. The possibility of such processes can be characterized by corresponding constants of instability or stability of nanoparticles in the medium or composite. If certain nanoparticles obtained in different medium are introduced into the composition, the change in their surface energy results in the particle shape distortion or its destruction with the formation of new bonds and shapes.

When nanoparticles (clusters) are stabilized in the surroundings, such notions as "conformation" and "conformation energy" can be applied. In this case conformation reflects spatial location of separate components of nanosystem. Since any nanoparticles in nanosystems or nanocomposites are highly effective "traps" of energy coming from their habitat, this energy can be conditionally divided into energy consumption connected with reactions of polycoordination or re-co-ordination (self-organizing energy) and consumption conditioned by orientation processes in the habitat (conformation energy). The increase in the number of nanoparticles can result in the destruction of their shells, changes in the nanoparticle shapes and sizes with the transition to micron level, thus finally leading to coagulation and separation of phases. Let us mention that coagulation means the adhesion of particles of disperse phase in colloid systems and it is conditioned by the system tendency to decrease its free energy. Mainly the process of phase separation in nanocompositions or nanosystems composed of a mixture of particles of different components (nanocomponents) depends upon the "architecture" of nanostructures and physical structure of nanocomposites. In turn, the decrease in concentration of nanoparticles in nanosystem can result in destruction (depending upon the medium activity) or decrease of nanoparticle dimensions, that is, dissolution of nanoparticles in the medium. Since the stability of nanosystems in different media is connected with dissolution processes of physical-chemical nature, such parameters as the degree of nanocomposite filling with nanoparticles, nanocomposite density in general and interface layers in comparison with nanophase density, nanocomposition effective viscosity require great importance. The determination of dissolution phase diagrams is of interest for investigating nanosystems and nanocomposites. In this regard the terminology widely used when studying polymeric systems and compositions seems appropriate.

Why is it possible to use this terminology and notions of polymer chemistry but not chemistry of metals with more advanced study of phase diagrams? It can be explained that nanocomponents are more active due to increasing their surface energy. This, in turn, contributes to the increase of interactions between nanocomponents and their mutual solubility with the formation of new strengthening nanophases.

Such notions as compatibility and operational stability of systems are applied. Interaction parameters (critical on nanophase boundaries, enthalpy, and entropy)

are calculated based on experimental data. Upper and lower critical mixing points are determined and phase diagrams with nodes, coexistence curves and spinodals are drawn. Such notions as spinodal decay and critical embryo are used in phase separation [54]. Such notion as "compatibility" defines the ability to form in certain conditions a stable system comprising dispersed (fine) components or phases. In case of nanomaterials or nanocomposites the compatibility is determined by the interaction energy of nanophases and, consequently, the density of interface layer being formed between them. The time period during which the changes in material characteristics are within the values permissible by operational conditions is defined as operational stability. When this time period is exceeded the changes in phase energy are possible, this can result in their destruction, coagulation, and, finally, phase separation and material destruction. The nanocomposite stability and compatibility of nanophases are conditioned by the values of interaction parameters ($\chi^{\text{кр}}$) or forces (energies) of interactions.

Many notions and terms in the field under consideration are taken from chemistry and physics of surface.

1.3   PHYSICS AND CHEMISTRY OF SURFACE: DEFINITIONS AND NOTIONS

1.3.1   The Comparison of Surface Energies of Carbon Nanostructures with Corresponding Energies of Metal or Carbon Nanocomposites

In physics and chemistry of surface of materials the basic notions still raising debates are the following: "surface," "interface layers", "surface", "boundary" layers. Round-table discussions, workshops, and conferences are dedicated to estimating these notions and assessing the rationality of their use.

First, when studying the surface, what surface do we mean? There is purely mathematical notion of the surface as geometrical space of points dividing the phases. A geometrical surface is simplistically shown as a line. However, everyone understands that this is an abstract conception and a surface cannot be presented as a line. Irregularities are always observed on the boundary of gas and liquid separation, liquid and solid separation, gas and solid separation caused by energy fluctuations. Physics of surface indicates that chemical particles on the surface are, on the one hand, in the action field of the particles of solid or liquid, and, on the other hand, in the action field of molecules of gas or liquid being in the contact with this body. Therefore, it is better to estimate properties, structure and composition of surface layers, the dimensions of which change in thickness from 1 nm up to 10 nm depending upon the nature of material being investigated (conductor or dielectric) and depth of surface influence on material inner layers. The relief of surface layer or morphology of material surface is determined by particular features of its formation and nature (composition and structure) of material.

Energy characteristics of surface of solids are usually estimated by curved angles of wetting. In turn, in authors' opinion [55], molecules from the layer about 1nm thick (from the side of solid or liquid phase volume) contribute to the surface energy, and then the influence of deeper layers decreases. Changes in the surface layer energy are determined by its chemical composition and structure, as well as the aggregate of chemical particles surrounding this surface layer and belonging to material and medium in which this material is placed. We are going to consider a surface layer of any body as a boundary separating the body and surroundings. At the same time, surface energy always tends to get balanced with the energy of surroundings (liquid or gas medium).

The notion "interface layer" has a wider interpretation and can refer to "surface layer", and "boundary layer". The notion "surface layer" is used to determine the boundaries: gas–solid, liquid–gas; liquid–solid. The notion "boundary layer" is used when phase boundaries in a solid, suspension and emulsion are considered.

However, interface layers are more often considered in complex compositions or composites containing a big number of components. The notion "boundary layer" is more often used for multilayer materials with a clearly lamellar structure, or for coatings, materials of solids and liquids located on a certain substrate. At the same time "boundary layers" can define the boundaries between phases in solid materials. Naturally, it is difficult to imagine quick jumps when transferring from one phase to another. As was already mentioned, surface energy tends to get balanced with chemical particles surrounding it. Here the notion "surface energy" will be used both for surface and interface and boundary layers of materials.

When investigating polymer films on different substrates (metal substrates), it is mentioned [56] that intermolecular interactions on the boundary of phase separation results in the appearance of structural heterogeneity on molecular and permolecular levels in polymer films. Simultaneously, the structure defective and heterogeneous by its film thickness is formed. The influence of nature and structure of substrate spreads to over 400cm. The more intermolecular interactions in a polymer or on a substrate boundary are revealed, the greater distance the substrate influences to film structure changes [57].

The surface characteristics determine many practicable macroscopic properties of materials. Such characteristics are revealed in the surface chemical and physical structure and morphology, that is, are immediately connected with surface chemical functional composition, crystallinity degree, shape, and roughness. Chemical composition of material surface represents complex characteristics determining their properties and reactivity expressed via the rate of chemical interaction of the surface of material being considered with other adjoining materials or media. Under the material surface chemical composition we understand its chemical composition and availability of molecule fragments or separate atoms

on the surface that enhance the surface activity or, on the contrary, passivate the surface. The surface of solids always contains the layers of gases physically and chemically sorbed [53]. The layer of adsorbed gases or impurities (usually hydrocarbonaceous) is about several monolayers thick. The layer of chemisorbed molecules can be found under the layer of molecules physically adsorbed. The thickness of such layer depends upon chemical activity of centers on the material surface. The material surface layer can be represented as adsorbed particles and the layer of surface atoms and molecules of material itself. Not only chemical composition but also surface geometry influence gas and impurity adsorption. It is possible to present the models reflecting the influence of surface geometry and various roughnesses of the surface in a simple way, when the active center or heteroatom is surrounded by different numbers of surface layer atoms (Figure 1.6).
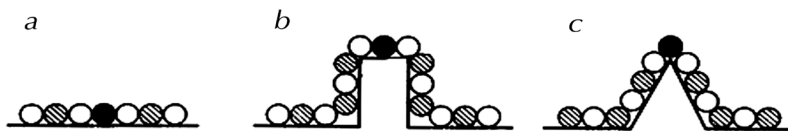

FIGURE 1.6   Model of various surface roughness (a–c heteroatom × is surrounded by different numbers of other atoms).

At the same time, on ledges the activity of heteroatoms on roughnesses increases in comparison with other surrounding atoms. The activity of neighboring atoms with chemical particles of environment increases. The surface peculiarities result in local elevations of surface energy or surface potential and influence the formation of adsorbed layers and their thickness on the surface.

It is known that [53] on the surface of monocrystals active centers are located on crystallographic steps or at the points where dislocations intersect the surface. Then an adsorbed particle can interact with several lattice atoms, as a result, the total interaction increases. For instance, the "adhesion" of oxygen molecule to silicon stepped surface is 500 times more probable than to the smooth surface.

Surface layers can also be found in the volume of material with defective regions such as micro- and macro-cracks, pores. Here it is possible that surface layers in one and the same material have different chemical composition. For instance, for cellular plastics chemical composition of such layers is practically the same (surfaces of material and pore), since pores are channels connected with material surface. For foam plastics, in which there are basically closed pores not connected with material surface, the surfaces of material and pore differ in chemical composition since gaseous medium in foam plastics bubble is considerably different from the gaseous medium surrounding the material.

As the majority of permolecular structures in polymers can be referred to nanostructures being investigated and polymeric materials to nanocomposites, in our opinion, several notions from the science of polymers can be referred to chemical physics of nanostructures. The main stage of polymer and nanoparticle formation is the formation of closed shape or their surface determining the existence area of polymeric molecule or nanoparticle. The particle surface formed in non-equilibrium conditions tends to transfer into the state of thermodynamic equilibrium. The rates of relaxation processes mainly depend on the surroundings ("habitat"), temperature and nature of the particle or polymeric material. However, we can distinguish two most important factors influencing the formation of properties and structure (chemical and physical) of the surface of polymers and nanoparticles—mobility of constituent groups of atoms and molecules (taking into account the conformation energy) and surface energy. In equilibrium conditions the surface energy is usually minimal and this minimum is provided by the mobility of chemical particles migrating from the volume to the surface and vice versa or adsorption and hemisorption of chemical particles from the environment onto the surface. This takes place even when "artificial pairs" are formed, for instance, polystyrene covered with polyethylene-oxide. The surface energy of polystyrene is lower the corresponding energy of polyethylene-oxide ($\gamma_{ps} = \gamma_{peo}$) [58]. Therefore, when this material is kept under the temperature above the vitrification temperature of both polymers, the outer layer is enriched with polystyrene. Polystyrene nanoformations in polyethylene-oxide film are 5nm thick. Depending upon the substrate surface energy that can be connected with its polarity, the chemical composition and structure of surface and boundary layers of static and graft copolymers change as well, for example, depending upon substrate material the polarity of boundary layers of vinylchloride and vinylacetate copolymers changes due to the decreased number of polar groups in boundary region copolymer-substrate. The changes in surface energies γ of copolymer and some materials of substrates are given below:

Substrate material	AuNi Al **PTFE***
Surface energy, γ, mN/m of	
substrate material	4337.3319
copolymer	5148.4638

*PTFE—polytetrafluorine ethylene film (sheet)

Based on X-ray photoelectron spectroscopy (XPS) the greatest number of polar acetate groups are present in the layer boundary to substrate of gold that is characterized by the highest surface energy. Depending upon the formation con-

ditions and substrate types the surface energy of polymers changes as well. The change in the surface energy (γ, mN/m) of some copolymers in comparison with polyethylene depending upon their formation conditions are given in Table 1.2.

TABLE 1.2   Values of surface energy for sheets and films obtained on the boundary of different media [58].

Polymer	Surface energy, γ, mN/m		
	Sheets of polyester film obtained by hot pressing	Sheets of PTFE obtained by die casting	Film of PTFE obtained by bulge formation
Non-polar polymers: Low-density polyethylene	32	31 (32)	32
Copolymer of vinylacetate ethylene (86:14)	33	32 (33)	33
Polar polymers:			
Statistic copolymer of ethylene and methacrylic acid (85:15)	44	37	38
Graft copolymer of maleic anhydride (2.1%) to high-density polyethylene	50	33 (33)	-
Graft copolymer of vinyltrime toxisilane (1.1%) to co-polymer of ethylene and vinylacetate (72:28)	39	36	33

Values of surface energy during the mold water-cooling are given in brackets

The results given above were obtained with the help of X-ray photoelectron spectroscopy (XPS) methods and infrared microscopy of multiply disturbed complete inner reflection (IR MDCIR). The essence of investigation methods is given below together with currently widely known nanoscale methods for examining nanostructures, nanosystems, and nanocomposites. To determine the morphology

of surface and shape of nanoparticles and nanosystems, various types of electron microscopy, such as scanning, transmission, tunnel, and atom force are widely applied. Diffractometric and spectroscopic methods are used to determine the structure and composition. Table 1.3 contains methods for investigating the surface of materials, boundary layers and nanostructures.

TABLE 1.3   Methods for investigating surface and boundary layers, nanostructures

Method	Information	Depth	Sensitivity, profiling, nm %
X-ray photoelectron spectroscopy (XPS)	Element composition Chemical surroundings Conformation analysis	<10	10^{-1}
Auger-electron spectroscopy (AES)	Element composition	<5	10^{-1}
Ultraviolet electron spectroscopy (UVES)	Chemical surroundings Conformation analysis	~1	10^{-2}
Spectroscopy of ionic dissipation (SED)	Element analysis	<1	10^{-2}
Secondary ionic mass-spectrometry (SIMS)	Element analysis	<1	10^{-3}
Laser microprobe mass-analysis (LMMA)	Element analysis	10	3×10^{-7}
Infrared microscopy of multiply disturbed complete inner reflection (IR MDCIR)	Chemical surroundings Conformation analysis	>1,000	monolayer portions
Spectroscopy of combination dissipation (SCD)	Chemical surroundings	~1000	monolayer portions
Raman spectroscopy (RS)	Conformation analysis Nanostructural analysis	~100	
Atom force microscopy (AFM)	Surface morphology and polarity	<100	monolayer portions

TABLE 1.3   *(Continued)*

Scanning raster electron microscopy (SREM)	Surface morphology	<10	10^{-1}
Transmission electron microscopy with electron microdiffraction (TEMEMD)	Chemical composition and structure Surface morphology	~1	10^{-1}
Tunnel electron microscopy (TEM)	Surface morphology	0.1	10^{-2}

1.4 BASIC NOTIONS IN MODELING NANOSTRUCTURES AND METAL OR CARBON NANOCOMPOSITES

To determine the possibility of nanostructure existence and forecasting the formation of different nanosystems it is necessary to develop the corresponding theoretical and computation apparatus. The creation of such an apparatus is possible based on corresponding ideas of quantum chemistry, molecular mechanics and thermodynamics. Apparently, in developing the overall theory of nanosystems the symbiosis of similar theoretical trends in physics, chemistry, biology, and computer modeling will be found.

The processes of nanostructure formation, the subject investigated by chemical physics, are of great interest. Therefore, apparently, it is more appropriate to discuss the creation of computational apparatus of chemical physics of nanostructure formation processes. In recent years, a lot of investigations connected with the development of different software products have been carried out in quantum chemistry, molecular dynamics and molecular mechanics of cluster and nanosystems. These investigations are fulfilled using semi-empirical and *ab initio* methods. Basically, "paired" interactions were used in all the methods, although there are works discussing "collective" interactions on atomic and molecular levels.

It is advisable to arrange a hierarchical scheme for predicting nanostructure formation. First, the stability of interacting particles and reaction centers should be determined. Under reaction center we understand the group of atoms being changed during the reaction. Potential reactivity centers, that is, groups of atoms able to participate in reactions, are usually called functional groups. This terminology can mainly be found in organic and polymer chemistry. The stability of particles and interaction energy are

evaluated with methods of quantum chemistry. After reactivity centers are selected possible reactions with their participation are assumed, this operation for finding reaction options is similar to the isolation of so-called "reaction series" in physical organic chemistry. Here, under reaction series we understand the directivity of processes in reactivity centers or similar nanosystems with the formation of nanoparticles of certain structure and composition. The advantage of one or another reaction series when compared with the others is determined based on energy consumption for performing successive acts of the process and the rate with which these acts are performed. Computational experiment can be carried out using apparatuses of quantum chemistry and molecular dynamics, in some cases in combination with semi-empirical methods of thermodynamics in the frameworks of activated complex theory or spatial-energy concept. At previous two stages of nanosystem modeling and formation single chemical particles, reaction centers or fragments of complex nanocomponents of the systems were discussed. The changes of nanostructures during the action of various fields, such as thermal, electrical, magnetic, field of particles, gravitation upon nanosystems, and nanoparticles are also determined at the aforesaid stages. Therefore, at third and the following stages collective interactions of nanoparticles with the help of apparatuses of molecular mechanics and thermodynamics are discussed. The transitions from one method of computational experiment to another one represent certain terminological and conceptual difficulties. This can be explained not only by the time frames when the corresponding notions, ideas and definitions appeared. In our opinion, the complete positive material accumulated in reactivity theory and reactions of chemical particles with the formation of nanosystems should be used in a new nanoscience. Therefore, modular construction should be introduced into the scheme of basic notions of nanosystem and nanostructure modeling together with hierarchical structure (Figure 1.7).
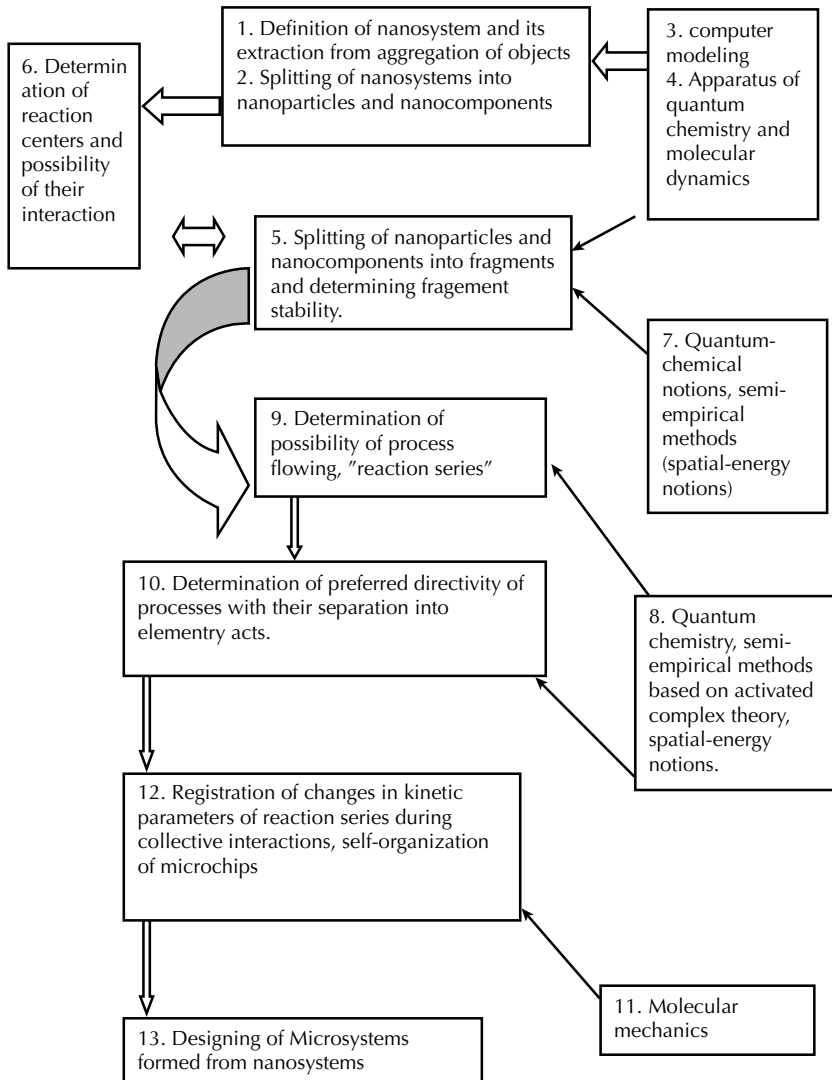
FIGURE 1.7   Scheme of nanosystem consideration.

Assumptions used for computational experiments, especially for transition from one theoretical and computational apparatus are discussed in Part 2.

Therefore, the transition to any trend in thermodynamics—nanothermodynamics—appears natural. The approaches can only be by developing Prigozhin's theorem [60] and synergetics theory. The key term here is entropy production.

The entropy production means the rate of entropy change during the process and is usually marked as $\sigma = ds/d\tau$. At the same time any system (dynamic and isolated) has certain accumulated information being in corresponding structure. If the system is stationary, the total of amount of entropies S and information I is constant [61], equaled to one. It is more correct to consider the changes of these values (ΔS и ΔI). Therefore, it can be written as follows: $\Delta I + \Delta S = 1$. At the same time, when structuring and self-organizing the substances: $\Delta I \rightarrow 1$, $\Delta S \rightarrow 0$. Actually ΔI mean the change in the record of "information" in the structure determined by structuring energy that consists of the energy of genetic and structural information, according to [61].

Here under genetic information, we understand the energy input of "embryo", substrate or walls of "nanocontainer" into structuring process that proceed with "inheriting" several features of the aforesaid information sources.

In turn, under the energy of structural information, we understand the energy input necessary to form a certain rank of structural formation in accordance with structural hierarchy. In this case, if the dynamic dissipative structure decays, $\Delta I \rightarrow 0$, that is, the substance structure decays, for example, into simple components, then $\Delta S \rightarrow 1$. The change in entropy grows together with the increase in the number of equiprobable states. The energy dissipates into the environment. The substance self-organizing process is possible, based on Prigozhin's theory, due to the action of energy flow onto the substance. The flow energy is consumed for structuring, but the flow itself is disordered and when the system is removed from equilibrium the system loses stability in flow separation point. Then Prigozhin's theorem can be expressed as follows: under external conditions preventing the system to reach stability, the stationary state corresponds to the production of minimal amount of entropy and maximum amount of information.

Any multi-atom nanoformations with repetitive fragments refer to so-called "permolecules". Academician Rusanov, by analogy with organic compounds, determines the aggregation of such permolecules of one nature and increasing size as homologies, and nanoparticles of one size but different composition as isomers.

Chemical potential is the characteristics of permolecules as well as of the majority of such molecules and their derivatives:

$$\mu_{\{n\}} = G^0_{\{n\}} + kT\ln(C_{\{n\}}\lambda_{\{n\}}^3), \qquad (1.15)$$

Where, μ—chemical potential, $\{n\}$—aggregate of structural units n_i of permolecule, $G^0_{\{n\}}$—Gibbs energy of permolecule taking into account the interactions of permolecule with surroundings and other permolecules present in the system, k—Boltzmann constant, T—temperature, $C_{\{n\}}$—concentration n_i of permolecule in the system, $\lambda_{\{n\}}$—average de Broil wavelength of permolecule [62].