

Chapter 2

General Approach to the Description of Fundamental Properties of Disordered Nanosized Media

2.1 Introduction

Non-regularities characterize surface nanointeractions (surface area, interaction quality, distribution of nanoagents of influence) and various nanointerconnects when essentially expected and unexpected effects of nanophenomena, nanosensing and nanomaterials' functionality take place. As a result, these effects will define prospective qualities of future consumer nanoproducts and nanodevices.

A special class of non-regular nanophenomena concerns the interaction of large carbon-based macromolecule assemblies of different chemical qualities, where the interaction boundaries of which are sporadically changed. A utilitarian interest to nanocarbon systems is explained by their suitability to become pertinent materials that are beneficial for the integration with biomaterials or biological systems since carbon is the chemical basis of all known living *systems* on Earth.

Regular nanosystems – are systems with morphologically ordered structures characterized by any type of spatial symmetry and at least one nanosized dimension (parameter).

Non-regular nanosystems – are systems comprising nanoscale morphological traits (characteristics) when there is no spatial symmetry of characteristics for the nano-, micro- and meso-levels in a steady state, or their spatial symmetry is broken by transients (nonsteady processes), or the systems are intensely functionalized at the nano- and micro-levels. Non-regular systems should also comprise technologically defective nanostructures (bending, vacancies, doping and various types of disordering), both organic and inorganic.

Nanophysics is a part of physics that combines experimental and theoretical methods of material and radiation studies at the nanoscale level. It also describes major physical approaches to the study of nanoobjects and their behaviours, which are important for the consideration of nanophenomena. Nanoobjects and

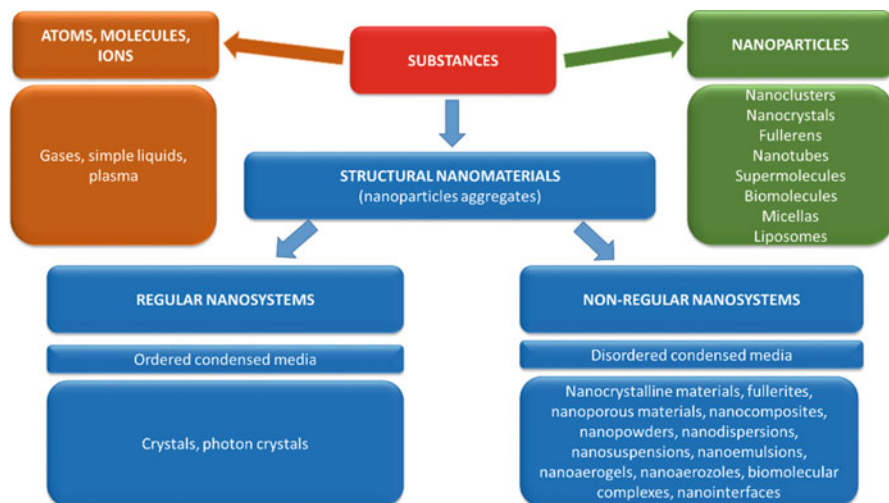


Fig. 2.1 Structural classification of nanomaterials

nanosystems being a combination of nano-, micro-, meso- and macrostructures demand a thorough description using classical and quantum approaches.

It is reasonable to start the classification of nanoobjects from the concept of ‘matter’ which is presented systematically in the periodic table. Properties of matter determine functional peculiarities of created materials for practical tasks. (see Fig. 2.1). Materials serve to carry out production activities or other activities, for example, related to the solution of health problems or environmental problems.

It is generally believed that objects of the nanoworld are objects whose characteristic dimensions lie in the range of 1–100 nm, i.e. characterized by nm scale (1–100 nm) at least in one dimension. The main feature of nanoobjects is that, due to their small size, they exhibit special properties.

In many cases, these special properties can also be manifested when the size of nanoobjects exceeds the conventionally established limit of 100 nm by 10 times, which forms functional mesostructures. Nanomaterials, as well as ordinary materials, can be in various aggregate states. Thus, ‘nano’ means usually the scale of nanophenomena, but not simply the characteristic sizes of functionalized nanodevices.

In practice, the most common are solid-state nanomaterials. Well-known features of nanomaterials are structural synergetics, new structural symmetries, new types of phase interfaces, high surface catalytic activity and dimensional effects in nanoparticle aggregates.

Our comments in Fig. 2.1 start with the definition of *nanoparticles* [1] as atomic and molecular aggregates – nanoclusters – particles between 1 and 100 nm in size. Morphologically ordered *nanoclusters* create *nanocrystals*. *Fullerenes* are carbon molecules formations in the form of a hollow sphere, ellipsoid, tube and many other

shapes. Spherical fullerenes are also referred to as buckminsterfullerenes (buckyballs) [2].

Nanotubes are nanometer-scale tube-like structures. Nanotubes are kinds of nanoparticles and can serve as pipes through which other nanoparticles can be channelled [3]. *Supermolecules* are host molecules with functional molecules – inclusions, e.g. hydrogen-bonded acetic acid dimers [4].

Biomolecules are molecules that are presented in living organisms, including large macromolecules, such as proteins, carbohydrates, lipids and nucleic acids, as well as small molecules such as primary metabolites, secondary metabolites and natural products [5, 6]. *Micelles* are aggregates of surfactant molecules dispersed in a liquid colloid [7]. *Liposomes* are spherical vesicles having at least one lipid bilayer. The liposome can be used as a vehicle for administration of nutrients and pharmaceutical drugs [8].

Talking about structural nanomaterials, we should regard classical crystals as a ‘marginal’ form of ideally composed and fully identical ordered nanoclusters. This definition will allow us to treat all structures in key terms of nanosystems. First of all, we note the concepts of regular and non-regular systems that include structural and physical regularity extents and then ordered and disordered condensed media that include topological and morphological aspects.

The next candidates into this group are *photonic crystals* (1D,2D,3D) being periodic optical nanostructures that affect the motion of photons in much the same way that ionic lattices affect electrons in solids [9].

Talking about non-regular nanosystems, we can mention *nanocrystalline materials* – the general class of materials consisting of nanocrystals [10]. *Fullerites* are the solid-state manifestation of fullerenes and related compounds and materials [11].

Ceramic-matrix nanocomposites (CNC) are the group of composites where the main part of the volume is occupied by a ceramic, i.e. a chemical compound from the group of oxides, nitrides, borides, silicides, etc. In most cases, ceramic-matrix nanocomposites encompass a metal as the second component [12]. *Metal matrix nanocomposites* (MNC) can also be defined as reinforced metal matrix composites. This type of composites can be classified as continuous and noncontinuous reinforced materials [13]. *Polymer nanocomposites* (PNC) consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. These may be of different shapes (e.g. platelets, fibres, spheroids), but at least one dimension must be in the range of 1–50 nm [14, 15].

Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. The size of the pores is generally 100 nm or smaller [16]. *Nanoaerogels* are nanoporous materials with nanosized walls [17]. *Nanopowders* are solid powders of nanoparticles, often containing micron-sized nanoparticle agglomerates. These agglomerates can be redispersed using, for example, ultrasonic processing. Nanoparticle dispersions – *nanodispersions* – are suspensions of nanoparticles in water or organic solvents. These dispersions can be diluted with suitable (compatible) solvents [18, 19]. *Nanosuspensions* are colloidal dispersions of nanosized drug particles stabilized by surfactants

[20]. *Nanoemulsions* consist of liquid nanodrops distributed within the other liquid [21].

Nanoaerosols consist of nanoparticles and nanodroplets that freely propagate in a gas medium [22]. *Biomolecular complex*, also called macromolecular complex or biomacromolecular complex, is any biological complex made of more than one molecule of protein, RNA, DNA, lipids and carbohydrates. The interactions between these biomolecules are non-covalent [23]. Various *nanointerfaces* for nanotechnology and nanodevices play an essential role in growing nanotubes, catalytic activities and nanointerconnect fundamental properties [24–26].

2.2 Correlation of Atomic and Electronic Structures

Disordered condensed matter is a general case of non-regular condensed nanosystems. This is an extremely wide class of materials, including amorphous substances, glasses, crystals with a high concentration of defects or spin disordering (spin glasses), composites, porous materials, gels, etc.

As a rule, they are united by a strong atomic-electron correlation at the nanoscale level. Using the term ‘disordered condensed medium (or system)’, most often we have in mind structural ‘nano-faults’ compared to crystals that are accepted as a standard of perfection and full order. The state of a disordered condensed medium is considered to be metastable, which does not correspond to the minimum of the total energy, which in time will be transformed into a stable crystalline state.

However, the relaxation time of such a process can be very large. General ideas about disordered condensed media almost immediately reveal difficulties in describing of their fundamental properties. Non-regularities of qualitative and quantitative nature do not allow the active use of periodic functions, periodic boundary conditions and the group theory.

Thus, many theoretical concepts used in the theory of crystalline solids are ineffective. In particular, the inability to apply the Bloch theorem and to establish boundary conditions of the Born-Karman type forces us to seek alternative approaches that somehow reduce to the concept of an effective medium as a boundary condition simulating the absence of long-range order in a disordered system.

The features of the short- and medium-range orders, as a rule, can be taken into account accurately, because they are reduced to the calculation of finite sums. However, the variety of realizations of these scale orders in specific local atomic configurations nullifies this certainty. Here, a statistical approach is required to describe macroscopic characteristics. The notions of short-, medium- and long-range orders also require a clarification in view of the noticeable progress in the development of new classes of nanomaterials.

As to the general direction in the study and modelling of fundamental properties of non-regular condensed media, such as characteristics of atomic and electronic structures, vibrational spectra and conductivity, usually it is based on a cluster

approach. The essence of the latter is as follows: non-regular condensed solids are mentally divided into elementary fragments of the atomic structure – *nanoclusters*.

The statistical characteristics of this set determine the integral properties of the entire substance as a whole. Based on this approach, it is possible to formulate various versions of the effective medium method, which differs only in the way of averaging the local characteristics by the volume of matter. The genesis of the cluster approach is based on a number of fundamental experiments, for example, on the electronic properties of disordered chalcogenides, performed in the 1950–1960s at the Leningrad Physical and Technical Institute.

To explain these properties Ioffe and Regel [27] have formulated a hypothesis about the decisive role of short-range order, which corresponds to the nanoscale effect. Further investigations are shown in the topological similarity of crystalline and noncrystalline materials. This quality leads to closeness of their physical and chemical characteristics. This quality also outlines nanoscale responsibility for all fundamental properties.

For the first time the theory fundamentals of disordered condensed state of matter were consequently described by Gubanov [28]. The next essential steps of conception development were made by Mott and Davis [29], Lifshitz et al. [30], Ziman [31], Feltz [32] (1983), Bonch-Bruевич et al. [33], Zvyagin [34], Cutler [35], Regel and Glazov [36], Shklovski and Efros [37], Ehrenreich and Schwartz [38], Klinger [39]) and Marshall [40]. Certainly, this is not an exhaustive list of the scientific works of 1960–1990, when we can review and consider as nanoscale physics and nanotechnology elements.

Comprehensive experimental studies of photo- and radiation-stimulated changes in optical properties in amorphous chalcogenides make it possible to speak of a completely determined correlation of the features of the atomic structure and the electronic spectrum. In addition, it is known that various external influences (radiation, light, pressure, heating, etc.) lead to a change in the short-range order in these and other amorphous semiconductor materials [29]. The analysis of published data in [42, 43] allows revealing one more side of the qualitative picture of the correlation being discussed.

For a significant part of the covalent compounds, the dependence of the band gap E_g on their density ρ_m , which is the integral parameter of the atomic structure, is described by an empirical relationship $E_g \approx 5.36 - 0.79\rho_m$, where ρ_m is the material density in g/cm³. This dependence is a manifestation of the known quantum-mechanical result of removing the degeneracy when the electronic subsystem is compacted. A similar tendency is demonstrated by many covalent compounds under high-pressure compressions [44], when metallization of properties (decrease of E_g) is observed.

The above-mentioned considerations allow formulating a semi-quantitative model of structurally optical correlations for the explanation of the interrelated photoinduced changes in the atomic structure and electronic spectrum in the region of the fundamental absorption edge in chalcogenide materials.

Note

Photoinduced changes in the atomic structure in the context of the foregoing are due to the thermal heating of the structure of the supposed ‘pixel’ of optical recording. This leads to a change in the local nanoscale properties in the density of electronic states and the refractive index due to a change in the local mass density. It is known that in the case of such traditional nanoobjects as, for example, nanotubes, their bending leads to a change in the local electronic density of states [46]. This effect can be used for the development of pressure nanosensors.

It is noteworthy that among a number of theoretical models that explain the features of the edge of fundamental absorption in the materials, Urbach’s empirical rule occupies a prominent place:

$$\kappa(\omega) = \kappa_0 \exp[-\gamma(E_g - \hbar\omega)/kT], \quad (2.1)$$

which is valid for $\kappa \approx 10^2 - 10^4 \text{ cm}^{-1}$, and a power-law dependence of the type:

$$k(\omega)\hbar\omega = B(\hbar\omega - E_g), \quad (2.2)$$

for $k > 10^4 \text{ cm}^{-1}$. The deviations from (2.1) and (2.2) in chalcogenides are noted in [29, 32].

However, the relations (2.1) and (2.2) serve as the basis for determining E_g from the frequency dependences of the absorption curves. The analysis (2.1) and (2.2) shows that the relative change in the absorption coefficient will be determined by the relations:

$$\frac{\delta\kappa}{\kappa} = -\left(\frac{\gamma}{kT}\right)\delta E_g, \quad (2.3)$$

and

$$\frac{\delta\kappa}{\kappa} = -\left[\frac{2}{\hbar\omega(\hbar\omega - E_g)}\right]\delta E_g. \quad (2.4)$$

On the other hand, as it was already indicated, decreasing E_g via the hydrostatic compression P takes place (typical dependence of E_g via pressure P looks as follows: $E_g = E_g(0) + \alpha P$, where for many chalcogenides $\alpha < 0$ [47]).

Assuming that an increase in pressure leads to a decrease in the average interatomic distances in matter, it is possible to relate the width of the energy gap E_g and the distance d between the adjacent neighbours in the linear approximation by the relation:

$$E_g = E_{g0} + b(d - d_0), \quad (2.5)$$

where E_{g0} and d_0 are the width of the energy gap and the interatomic distance before the action on the substance, respectively. In the case of photoinduced processes, the changes in δE_g and δd are usually small, which makes the approximation acceptable in the vicinity of any d_0 . Further we obtain:

$$\frac{\delta\kappa}{\kappa} = -\left(\frac{\gamma b}{kT}\right)\delta d, \quad (2.6)$$

or

$$\frac{\delta\kappa}{\kappa} = -\left[\frac{2b}{\hbar\omega(\hbar\omega - E_g)}\right]\delta d, \quad (2.7)$$

where δd is the interatomic distance change. This model allows explaining the mechanism of structural-optical correlations in amorphous chalcogenide films [41].

In [45], particularly, it has been demonstrated that a change in the width of the energy gap of a chalcogenide film ΔE_g and a change in the refractive index are stipulated by a change of its thickness Δd . It is assumed that Δd is proportional to δd . A more general analysis of the effect of external influences on the optical properties of amorphous semiconductors is possible with the aid of:

$$\left(\frac{\partial E_g}{\partial P}\right) = \left(\frac{\partial E_g}{\partial T}\right)_P \bigg/ \left[\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial p}{\partial v}\right)_T\right], \quad (2.8)$$

where the typical temperature dependence is usually described by a linear law $E_g = E_g(0) - \beta T$ [48]. However, in this case, it is necessary to know the thermodynamic properties of materials, which require a separate study of complex computer modelling [49]. Topological and morphological character is absolutely required.

The basic achievement of nanotechnology refers not only to the development of traditional nanosized and non-regular structures but also to the creation of new short-range structures such as nanotubes, fullerenes and thin-film nanoribbons, which should be considered more regular. This also applies to nanostructured chalcogenide glasses discussed here in connection with photoinduced processes (see also, Tanaka [50]).

2.3 Order and Disorder

Of course, one should determine the place of non-regular nanosystems within the general concepts of disordered condensed media. These concepts in the scientific literature are ambiguous, namely, (1) nanoobjects can be considered taking into account only their nanosized parameters for which the conditional boundaries of possible changes are established; and (2) nanoobjects are characterized by special properties, which are manifested by the nanodimensions inherent in them.

Nanomaterials should be divided into two main groups: (1) nanoparticles as self-sufficient nanoobjects and (2) nanostructured materials as complex structural objects saturated with various embedded (included also by technological processes) nanoparticles. We consider non-regular nanostructured materials from the point

of view of their internal structural correlation, which ultimately determines their local and integral fundamental properties. Moreover, determining the correlation lengths is decisive. The correlation length acts as the base scaling factor of a nanomaterial.

It is reasonable to connect the characteristic lengths of the correlation L_{cor} of the fundamental properties with the concepts of a short-range order L_{SRO} , medium-range order L_{MRO} and long-range order L_{LRO} . In many cases, the degree of ordering of atomic structures can be estimated from the thin structure of the radial distribution curves. In the case of liquids and many glasses, we can observe one really pronounced peak.

For ideal crystals L_{LRO} will be close to the characteristic size of a crystalline sample. We can find cases of different types of ordering, for example, a total magnetic spin disorder in perfectly ordered regular structures. We define disorder as a certain violation of the order of a fully ordered system, expressed in the absence of correlation of the physical quantity describing this system at distances that determine the scale of the disorder.

It is necessary to consider in more detail the degrees of ordering.

Short-Range Order SRO is the order due to the correlation function of local physical quantities $f(\mathbf{r})$, which is noticeably manifested at distances of $|\mathbf{r}_2 - \mathbf{r}_1| \approx L_{\text{SRO}} - 0.1 - 0.5$ nm and becomes insignificant when $|\mathbf{r}_2 - \mathbf{r}_1| > L_{\text{SRO}}$. In the scales of a solid, the distance L_{SRO} is of order of 1–3 coordination spheres radii magnitude. A correlation of local physical quantities (parameters) of a disordered material $f(\mathbf{r})$ means a noticeable difference from zero of the mean values of the type $\langle f(\mathbf{r}_1)f(\mathbf{r}_2) \rangle$. Talking about SRO, we have in mind only a structural SRO. Namely, the talk is about the identity of the positions of atoms in the material in the neighbourhood of an arbitrarily chosen atom in the region of L_{SRO} size. However, some more subtle characteristics (for example, spin orientation) are ignored and cannot be obtained by traditional methods of structure research. Correlation of fluctuations in the density of material $\Delta\rho_m(\mathbf{r})$ on a scale L_{SRO} determines the identity of atoms arrangement. However, according to another parameter, the correlation can be absent.

Medium-Range Order MRO is the order, due to the correlation of physical parameters, which is noticeably manifested at distances $|\mathbf{r}_2 - \mathbf{r}_1| \approx L_{\text{MRO}} - 0.5 - 5.0$ nm and becomes insignificant when $|\mathbf{r}_2 - \mathbf{r}_1| > L_{\text{MRO}}$ does not necessarily indicate the presence of SRO. For example, in complex amorphous compounds of the type $A_xB_{1-x-y}C_y$, the structural MRO characteristic for them does not allow judging about their SRO.

Long-Range Order LRO is the order due to the correlation of parameters, which manifests itself at distances $|\mathbf{r}_2 - \mathbf{r}_1| \approx L_{\text{LRO}} \rightarrow \infty$, where L_{LRO} is the characteristic size of the system. SRO and MRO can be absent. LRO is a characteristic, for example, for the electron subsystem of superconductors, where long-range correlations exist.

Thus, the quantities L_{SRO} , L_{MRO} , L_{LRO} are the scales (radii, lengths) of the correlation of physical parameters, characterizing the degree of order of the

material. In this case, the correlation can take place for one of any physical quantity and be absent for another.

Perfect Order PO is the order caused by a noticeable non-vanishing correlation of all physical quantities, which manifests itself at any distances within the system.

The correlation function is a measure of the order in a system, as characterized by a mathematical correlation function. Correlation functions describe how microscopic variables, such as spin and density, at different positions are related. More specifically, correlation functions quantify how microscopic variables covariate with one another across space and time. A classic example of such spatial correlations is in ferro- and antiferromagnetic materials, where the spins prefer to align parallel and antiparallel with their nearest neighbours, respectively.

The general definition of a correlation function is the canonical ensemble (thermal) average of the scalar product of two random variables, x_1 and x_2 , at positions R and $R+r$ and times t and $t+\tau$ [51]:

$$G(r, \tau) = \langle x_1(R, t) \cdot x_2(R+r, t+\tau) \rangle - \langle x_1(R, t) \rangle \cdot \langle x_2(R+r, t+\tau) \rangle.$$

Here, the brackets $\langle \dots \rangle$ indicate the above-mentioned thermal average. The main idea is to evaluate the characteristic correlation length L_{cor} , when the correlation function begins the essential decline. For example, in magnetic spin systems in the case of time-equal correlation function $G(r) = \langle x_1(R) \cdot x_2(R+r) \rangle - \langle x_1(R) \rangle \cdot \langle x_2(R+r) \rangle$.

Even in a magnetically disordered phase, spins at different positions are correlated, i.e. if the distance r is very small (compared to a certain length scale L_{cor}), the interaction between the spins will cause them to be correlated. The alignment that would naturally arise as a result of the interaction between spins is destroyed by thermal effects. At high temperatures, exponentially decaying correlations are observed with the increasing distance, with the correlation function being given asymptotically by $G(r) \approx \frac{1}{r^{d-2+\eta}} \exp\left(\frac{-r}{L_{\text{cor}}}\right)$, where r is the distance between spins, d is the dimension of the system and η is the critical exponent. At high temperatures, the correlation decays to zero exponentially with the distance between the spins.

One of the important directions in the study of the atomic structure of amorphous materials is a quantitative evaluation of the degree of order. In practice, the criteria based on comparing the disordered structure with its crystal analogue are often used. But not always such an analogue exists. In some cases, we can use the general Stevels criterion [32, 52, 64, 65], which is free from this drawback. In particular, the repeatability number represents the probability of finding an atom in an atomic structure similar to the initial atom in a certain direction and through a predetermined interval. The repeatability number is calculated as follows:

$$(\text{RN})_{r_0} = \frac{3}{4\pi r_0^3} \int_0^{r_0} \text{CRS}(r) 4\pi r^2 dr, \quad (2.9)$$

characterizing the structure as a whole, where $\text{CRS}(r) = (\sum_i N_i \text{ACR}_i) / (\sum_i N_i)$ is the coefficient of repeatability in space within a sphere of radius r , $\text{ACR} = (\sum_i n_i \text{CLR}_i) /$

$(\sum_i n_i)$ is the average weighted repeatability factor, CLR_i is the coefficient of linear repetition, equal to the number of atoms in the i -th direction on the n_i -th step, related to the number of steps n . For ideal crystals $\text{RN} = 1$ and for amorphous and non-regular solids $\text{RN} = 0$ [64].

It should also be noted that in itself the arrangement of atoms does not characterize the degree of ordering. In this sense, the knowledge of the exact coordinates of atoms in the structure $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_i \dots$ is useless. The use of the apparatus of many-particle distribution functions $g(1, 2, \dots, s) = n(1, 2, \dots, s)n^3$ is more productive. Here $n(1, 2, \dots, s)$ is the multiple-particle probability density, and n is the average particle density [31, 53].

Further we introduce the pair correlation function (the ‘pairs’ distribution function):

$$g(1, 2) = g(\mathbf{R}_{12})n^{-1}\delta(\mathbf{R}_{12} - \mathbf{l}), \quad (2.10)$$

which in the case of an isotropic medium looks like:

$$g(\mathbf{R}_{12}) = g(R) = n^{-1}N(l)\delta(R - l), \quad (2.11)$$

where $\mathbf{l}$ is the lattice vector and $N(l)$ is the number of lattice vectors of the same length l .

To describe simple liquids, we introduce a three-particle correlation function (the distribution of ‘triangles’):

$$g(1, 2, 3) = n^{-2}\delta(\mathbf{R}_{12} - \mathbf{l})\delta(\mathbf{R}_{13} - \mathbf{l}'). \quad (2.12)$$

In this case, the superposition approximation of Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) is usually used [53]:

$$g(1, 2, 3) \approx g(1, 2)g(2, 3)g(3, 1), \quad (2.13)$$

which allows us to close the chain of Bogoliubov equations for equilibrium distribution functions of the type:

$$\begin{aligned} \frac{1}{kT} \nabla_1 \ln(g(1, 2, \dots, s)) &= \nabla_1 g(1, 2, \dots, s) + \\ \frac{n}{g(1, 2, \dots, s)} \int_{V_s} g(1, 2, \dots, s+1) \Phi(1, s+1) dV_s. \end{aligned} \quad (2.14)$$

However, to describe an amorphous solid or non-regular disordered system, three-point distribution functions are not sufficient. Moreover, the technical difficulties of the next stage significantly increased. In particular, to calculate four-point distribution functions, we can use the so-called ‘over-superposition’ approximation [54]:

$$g(1, 2, 3, 4) = \frac{g(1, 2, 3)g(1, 2, 4)g(1, 3, 4)g(2, 3, 4)}{g(1, 2)g(1, 3)g(1, 4)g(2, 3)g(2, 4)g(3, 4)}. \quad (2.15)$$

Using the representation of many-particle functions developed in statistical physics through many-particle interaction potentials:

$$g(1, 2, \dots, N) = \exp\left(-\frac{1}{kT}\Phi(1, 2, \dots, N)\right), \quad (2.16)$$

we come to the necessity to reproduce the latter. Most practical, from the point of view of practical modelling, many-particle potentials are represented in the pair interaction approximation:

$$\Phi(1, 2, \dots, N) \cong \frac{1}{2} \sum_{i,j} \Phi(i, j). \quad (2.17)$$

As it has been mentioned earlier, the pair distribution function, which is calculated by the formula:

$$g(1, 2) \cong C \int_{V_3} \dots \int_{V_N} \exp\left(-\frac{1}{2kT} \sum_{i,j} \Phi(i, j)\right) dV_3 \dots dV_N, \quad (2.18)$$

is practically measurable.

The approximation of the pair interaction is satisfactory for gases, wherein:

$$g(1, 2) = C \exp\left(-\frac{1}{kT}\Phi(1, 2)\right). \quad (2.19)$$

However, if we assume that the averaged interaction energy $\overline{\Phi}(1, 2)$, which takes into account the interaction with other atoms of the system, is known, then:

$$g(1, 2) \equiv \exp\left(-\frac{1}{kT}\overline{\Phi}(1, 2)\right). \quad (2.20)$$

and the scope of such a ratio is greatly expanded.

The function $\overline{\Phi}(1, 2)$ is analogous to one electronic crystal potential in the problem of the electronic spectrum in the one-electron approximation (see Chap. 3). Based on the pair distribution function, the total correlation function $h(R) \equiv g(R) - 1$ is determined. Then the order parameter of the system (the characteristic scale of the system) can be defined as the correlation length L , when for some $R > Lh(R) = 0$. In more details, such an approach to the estimation of the degree of ordering is analysed in [32, 34], where, particularly, the characteristic scale of a disordered system of $A_x B_{1-x}$ type, depending on the composition of "x", is investigated. The system is regarded as a superposition of statistically independent sublattices A and B . The corresponding mass densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ are approximated by step

functions of different intensities. In this case, the effective correlation length of the system is given by the ratio $L_{AB}(x) = C(x^{1/3} + (1-x)^{1/3})^{-1}$, where C is the structure constant.

Further modelling efforts should be directed, first of all, to the reproduction of pair distribution functions and comparison of the latter with the experiment and, secondly, to the evaluation of the macroparameters of the material. For example, an entropy evaluation can be presented by the equation:

$$\begin{aligned} \frac{S}{Nk} = & -\frac{1}{2}n \int g(1,2) \ln(g(1,2)) dV_2 \\ & -\frac{1}{6}n^2 \iint g(1,2,3) \ln \left\{ \frac{g(1,2,3)}{g(1,2)g(1,3)g(2,3)} \right\} dV_2 dV_3. \end{aligned} \quad (2.21)$$

It is essential to calculate also the total energy, free energy, pressure, compressibility, etc. Really, this direction is connected with the construction of the material thermodynamics.

It should also be noted that the small correlation radii of the distribution functions of low order $g(1,2)$, $g(1,2,3)$ and $g(1,2,3,4)$, which can actually be taken into account, restrict the integration regions in (2.21) by small cluster volumes. Then, the cluster integrals only sum up and give the entropy evaluation of the entire material. This is especially important for the modelling of non-regular nanoscale structures.

2.4 Concepts of Modelling Atomic Nanostructures

The main theoretical efforts in modelling atomic structures of non-regular condensed materials are directed toward the construction of structural models, the study of their topological properties and evaluation of their nano-, micro- and macrophysical properties. Simulation of properties of a non-regular disordered material usually begins with a probable model of the atomic structure. At the first stage, purely qualitative and speculative views are usually used. Figure 2.2 summarizes the classification of condensed materials by the type of spatial disorder, from the point of view of topology and morphology as well as topological structures.

In this sense, a disorder is imposed on a spatial structure (ordered or disordered) on any parameter. For example, a magnetic disorder means a spin disorder in a spatially regular lattice (spin glasses of spin glasses – magnetic nanosystems). Such a disorder can also be represented in a non-regular lattice. However, in this case we will also have to consider the non-regularity factor. Small distortions of a regular atomic structure, as a rule, preserve the topology of a crystal (or rather, a regular object). This is a fairly common idea of disorder.

But it should be noted that such lattices are not physically stable and should quickly relax to a regular structure corresponding to a minimum of the total energy.

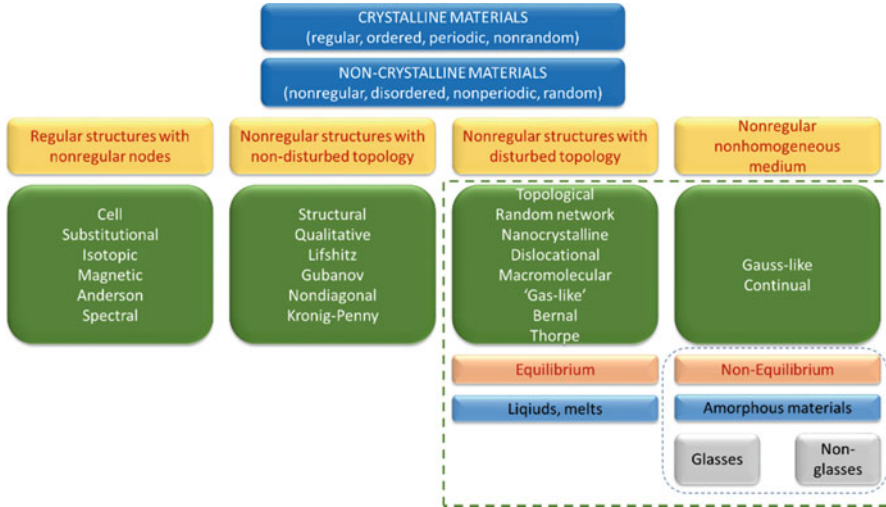


Fig. 2.2 Classification of condensed materials based on spatial disorder criterion

However, there are non-regular structures with a higher degree of disorder, which cannot be transformed into a regular analogue by a continuous topological transformation.

Restoring the broken topology of the structure requires significant energy costs, since this requires the breaking of atomic bonds. Such structures essentially remain nanosystems. In addition, non-regular lattices with broken topology are very stable and can exist for a long time. In this sense, they can be considered as a certain phase state of matter. Typical classic examples are glasses, which can crystallize. However, the times of crystallization (relaxation) are great. There are also models of disorder, which generally ignore any structure and develop the concept of a continuous medium. They are based on some special random distributions of mass densities (for example, Gaussian) or potential energy.

Using the concept of perfect order, the concepts of disorder can be divided into four classes: (1) disorder in spatially regular lattices, (2) disorder of spatially non-regular lattices with the topology of the crystal, (3) disorder of spatially non-regular lattices with broken topology and (4) disorder of the ‘continuous medium’ type without a lattice. Some types of disorder are presented in Fig. 2.3. *The disorder in regular lattices* can be considered as a cell disorder when the physical properties of the unit cells of the structural matrix are not identical and vary randomly (Fig. 2.3a). *The disorder in non-regular lattices* with the preserved topology of the crystal in comparison with the first class is characterized by a small displacement of the lattice sites relatively to the ‘correct’ positions, which leads to translational non-periodicity of the physical characteristics (Fig. 2.3b). *The disorder in non-regular lattices* with broken topology is associated with irreversible structural changes (in comparison with reversible structures of the second class), which may be accompanied by other violations of local physical characteristics.

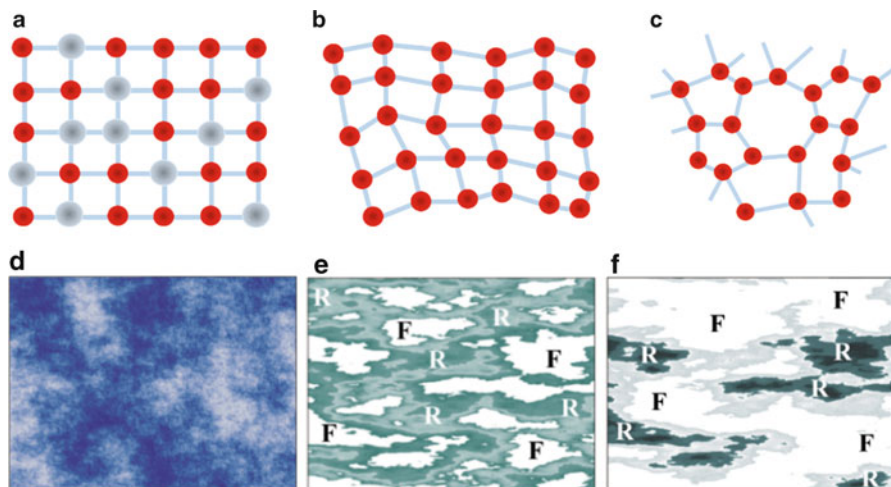


Fig. 2.3 Types of disorder: (a) quantitative; (b) positional; (c) topological; (d) continual; (e) Thorpe-amorphous solid; (f) Thorpe-polymer glass

The topological disorder (Fig. 2.3c) is the most characteristic. It refers to disordered systems, when the perfect order cannot be restored by a continuous topological transformation. Thus, the topological disorder in this sense is topologically irreversible, since it is characterized by a random structure. The most constructive content has the model of Thorpe disorder [55] (Fig. 2.3e, f). Thorpe model declares topologically disordered networks, containing, for example, large and small rings, which, in turn, cause the presence of rigid (rigid, R) and non-rigid (floppy, F) regions in the structure. The ratio of these areas defines a disordered material either (1) as a *polymeric glass* – with a lack of hardness regions – or (2) as an *amorphous solid*, with their excess. *The disorder of an inhomogeneous continuous medium* is based on the structureless concept of matter, where the distribution functions of mass or potential energy are random and continuous. For example, continual disorder (Fig. 2.3d) considers a disordered system as a *continuous medium* (*continuum approximation*). The microstructure of the medium is ignored because it is assumed that the wavelengths of the perturbations considered in the medium are greater than the characteristic detail sizes.

It is essentially relevant to analyse the order level for nanoporous and nanocomposite materials and control their technological repeatability, which normally consist of nanoparticles (e.g. CNTs, GRNs, fullerenes). A special attention should be paid to various interfaces and interconnects in the host material space. At present, the range of nanoparticles has significantly expanded (BN nanotubes, TiO₂-based nanotubes, etc.).

It would seem that the perfect experimental methods of visualization and detection of properties of nanomaterials should give full information on their atomic and nanostructure. However, the information, as a rule, is indirect and in many cases describes the properties of the surface.

Table 2.1 Basic methods of structural and chemical analysis of nanostructures

Method	Resolution
High-resolution transmission electron microscopy (HRTEM)	High resolution till 0.1 nm
Scanning electron microscopy (SEM)	Resolution (probe diameter) – 5...1000 nm
Auger electron spectroscopy (AES)	Electronic beam – 0.1...3 кэВ, scanning depth 0.5...3.0 nm, resolution – till 50 nm
Secondary ion mass spectrometry	Scattered secondary ions analysis, resolution depth 1–10 nm
Laser microprobe analysis	Laser pulse radiation, evaporation of tested nanomaterial, pulse duration – <30 ns diameter of laser beam 100...500 nm. Low accuracy of detection of composition of tested nanomaterial (~30%)
X-ray methods: X-ray structural analysis and X-ray phase analysis	Nanocrystals, nanocrystallites, study of orientations and distances of crystalline planes distributions
Scanning probe methods	Metrological precise 3D information (distribution map) about surface properties of tested nanosample, resolution – 1–10 nm
Scanning tunnelling microscopy (STM)	Voltage between a probe and a sample электрического (1–10 V). Tunnelling current is about 1–10 nA and, resolution along (x,y)-plane is about 0.1 nm, along the z-axis till 0.001 nm. However the tested material should be a good conductor. Conditions: vacuum and low temperatures (about 50...100 K). For resolution about 1 nm, these conditions are not obligatory
Scanning probe microscopy (SPM)	Visualization of nanostructures, wide range of external operation conditions: high and low temperature, vacuum, liquid and controlled gas medium. It is possible to observe surface processes dynamics. Surface resolution is about 1 nm
Atomic force microscopy (AFM)	The detection of the surface is based on controlled changes of interaction force of probe needle with the sample surface. Resolution on (x,y)-plane is about 1 nm, along the z-axis till 0.1 nm
Magnetic force microscope (MFM)	A variant of (AFM), however, a probe needle is prepared from ferromagnetic material. Resolution is about 10...50 nm
Near-field scanning optical microscopy (NFSOM)	NFSOM use as a probe detector a light waveguide. Resolution is about 10 nm
Photoacoustic spectroscopy (PA)	PA use in combination of a laser photoacoustic spectroscopy and methods of indentation for detection of internal stresses in nanostructural materials
Surface control of nanosurfaces	Control of properties of functionalized nanosurfaces, nanostructural covers, control of nanohardness

For the experimental study of nanoscale materials, the same methods can be used, practically the same as for the study of crystalline materials. Still, it is necessary to take into account the resolution of the methods, since surfaces with

dimensions smaller than 200 nm are subjected to the study. The main methods of structural and chemical analysis are presented in Table 2.1 [56].

Thus, experimental structural studies of non-regular condensed materials do not provide detailed information about the local atomic structure (exact coordinates of atoms, lengths and bond angles) and the structure of nanoclusters. Reliably, in the averaged form, it is possible to obtain structural information in the form of *radial distribution curves of atoms* (RDCA). Comparing the intensity and position of the RDCA peaks can give information about the conservation of short-range order and average order and to estimate the necessary correlation lengths. Perhaps, this is the only criterion for the technological comparison of serial nanomaterials. At the same time, obtaining probable local characteristics of the atomic and nanocluster structures is inevitably connected with its modelling. In this case, each version of the model is built on the structural units and relationships that are specific to particular classes of nanomaterials. Among the models of structures grouped by the method of their production, we can distinguish:

1. Obtained by introducing any structural perturbations into ideally ordered structures (crystals), for example, models of ‘*nanocrystallites*’, ‘*hot solid*’ disorder, dislocations and random packing [31, 57]
2. Obtained by randomly located ‘*hard*’ spheres or other structural units including *models of tight packing of hard spheres* (*Bernal liquid models*) [31, 58, 59] and *models of random close-packed structural units*, taking into account the features of the short-range order of the simulated structures [58]
3. Constructed from the ‘*ball and spoke models*’ [60, 61], in which fluctuations in the parameters of the structure for a given coordination (viz. fluctuations of lengths and bond angles) are within a few percent of the equilibrium values (*Polk models*)
4. Constructed from the ‘first principles’ using numerical simulation and, e.g. the theoretical apparatus of molecular dynamics [62] in the pair interaction approximation (as a rule) using the model potentials which are selected from physical considerations
5. Obtained by topological mapping onto a three-dimensional Euclidean space of a set of close-packed polyhedra completely filling a space with a higher dimension and a given coordination of the modelled structure [57]

2.5 Concepts of Nanoporous and Nanocomposite Materials

Special attention of technologists and manufacturers attract nanoporous and nanocomposite materials.

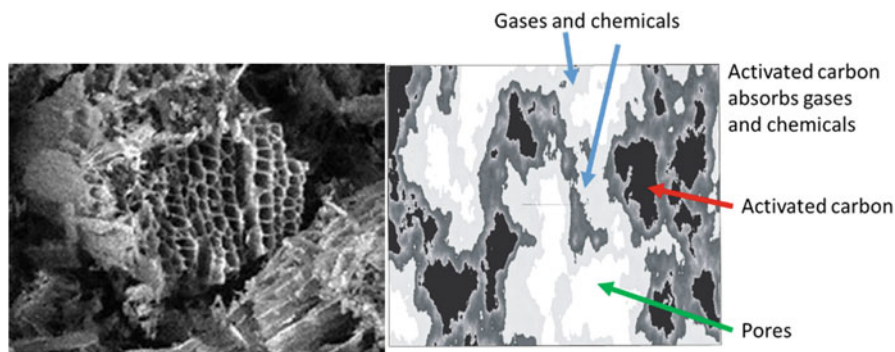


Fig. 2.4 Activated carbon and sorbent model

2.5.1 Nanoporous Materials

Nanoporous materials consist of a regular organic or inorganic network supporting a regular, porous structure. The size of the pores is generally 1–100 nanometers. Most nanoporous materials can be classified as bulk materials or membranes. Activated carbon (see Fig. 2.4) and large group of various zeolites (e.g. see Fig. 2.5) are bulk nanoporous materials. The reduction of pore sizes in nanomaterials leads to new capabilities for filtering and sorption of various chemical elements.

Cell membranes can be thought of as nanoporous membranes. There are many natural nanoporous materials, but artificial materials can also be manufactured. One method of doing so is to combine polymers with different melting points, so that upon heating one polymer degrades. A nanoporous material with consistently sized pores has the property of letting only certain substances pass through while blocking others. Nanoporous materials, in accordance with *IUPAC* (International Union of Pure and Applied Chemistry), are subdivided into three categories [63]: *microporous materials* (0.2–2 nm), *mesoporous materials* (2–50 nm) and *macroporous materials* (50–1000 nm).

The zeolites present a popular group of minerals for collectors and an important group of minerals for industrial and other purposes (see Table 2.2). They combine rarity, beauty, complexity and unique crystal habits. Typically forming in the cavities (or vesicles) of volcanic rocks, zeolites are the result of very low-grade metamorphism. The zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4 . In order to be a zeolite, the ratio $(\text{Si} + \text{Al})/\text{O}$ must equal to 1/2. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within.

Zeolites are characterized by their ability to lose and absorb water without damage to their crystal structures. The large channels explain the consistent low specific gravity of these minerals. Zeolites have many useful purposes. They can perform ion exchange, filtering, odour removal, chemical sieve and gas absorption



Clinoptilolite functionalities:

- ✓ Removal of ammonia
- ✓ Removal of iron
- ✓ Removal of manganese
- ✓ Mechanical filtration down to particle size of 5 micron
- ✓ Removal of odour in water

Fig. 2.5 Natural zeolite (clinoptilolite) granulated mineral

Table 2.2 Zeolites groups

Sample zeolite formulas	Mineral name general formula
Analcime	$\text{Na}_{16}[\text{Al}_{16}\text{Si}_{32}\text{O}_{96}] \cdot 16\text{H}_2\text{O}$
Chabazite	$(\text{Ca}_{0.5}, \text{Na}, \text{K})_4[\text{Al}_4\text{Si}_8\text{O}_{24}] \cdot 12\text{H}_2\text{O}$
Clinoptilolite	$(\text{Na}, \text{K})_6[\text{Al}_6\text{Si}_{30}\text{O}_{72}] \cdot 20\text{H}_2\text{O}$
Erionite	$\text{K}_2(\text{Na}, \text{Ca}_{0.5})_8[\text{Al}_{10}\text{Si}_{26}\text{O}_{72}] \cdot 28\text{H}_2\text{O}$
Heulandite	$(\text{Na}, \text{K})\text{Ca}_4[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot 24\text{H}_2\text{O}$
Laumontite	$\text{Ca}_4[\text{Al}_8\text{Si}_{16}\text{O}_{48}] \cdot 18\text{H}_2\text{O}$
Mesolite	$\text{Na}_{16}\text{Ca}_{16}[\text{Al}_{48}\text{Si}_{72}\text{O}_{240}] \cdot 64\text{H}_2\text{O}$
Scolecite	$\text{Ca}_8[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}] \cdot 24\text{H}_2\text{O}$
Stilbite	$\text{NaCa}_4[\text{Al}_{19}\text{Si}_{27}\text{O}_{72}] \cdot 30\text{H}_2\text{O}$

tasks. The most well-known use of zeolites is as water softeners. Calcium in water can cause it to be 'hard' and capable of forming stable salts, contamination and other problems. Zeolites charged with much less destructive sodium ions can allow hard water to pass through its structure and exchange calcium for sodium ions. This process is reversible. In a similar way, zeolites can absorb ions and molecules and thus act as a filter for odour control, toxin removal and chemical sieve.

Zeolites can have water in their structures removed by heat with the basic structure left intact. Then other solutions can be pushed through the structure, and zeolites can act as a delivery system for a new fluid. This process has applications in medicine, livestock feeds and other types of research. Zeolites added to livestock feed have been shown to absorb toxins that are harmful and even fatal to the growth of animals, while the basic structure of zeolites is biologically neutral (see Fig. 2.5 and Table 2.3).

Generally, we can consider one component porous material as a mixture of substance and emptiness. In the case of porous metals, we deal with the percolation matrix. However, one component system cannot include finite metal clusters. Really it is the infinite cluster, and we cannot talk about the percolation threshold x . Considering a two-component mixture, we can observe two percolation transitions at different values of x , which corresponds to the formation of an infinite cluster for each of the two components.

Table 2.3 Main uses for zeolites in industry

Function	Description
Catalysis	Catalysts for several important reactions involving organic molecules. The reactions can take place within the pores of the zeolite, which allows a greater degree of product control
Gas separation	The porous structure of zeolites can be used to ‘sieve’ molecules having certain dimensions and allow them to enter the pores. The porous structure provides polymerization of semiconducting materials and conducting polymers to produce materials having unusual physical and electrical attributes
Ion exchange	Hydrated cations within the zeolite pores are bound loosely to the zeolite framework and can readily exchange with other cations when in aqueous media. It is possible to remove radioactive ions from contaminated water

Pores are important for capacitive energy storage as, in general terms, more pores mean a larger surface area for *physical adsorption*, which, in turn, leads to higher storage capacity. Traditional porous carbon, once made, has a set volume with fixed pores randomly scattered inside and outside. It is not really possible to readjust the structure and jam more porous carbon in the same amount of space without crumpling a fraction of the pores that are especially crucial for capacitive energy storage. Nanofoams are a class of nanostructured, porous materials, foams, containing a significant population of pores with diameters less than 100 nm. Bryce Tappan at Los Alamos National Laboratory discovered a technique for producing *metal nanofoams* by igniting pellets of energetic metal bis(tetrazolato)amine complexes in 2006. Nanofoams of iron, cobalt, nickel, copper, silver and palladium have been prepared through this technique.

2.5.2 Aerogels

Aerogel is a synthetic porous ultralight material derived from a gel, in which the liquid component of the gel has been replaced by a gas. Aerogels are one example of nanofoams.

The result is a solid with extremely low density and low thermal conductivity. Nicknames include ‘frozen smoke’, ‘solid smoke’, ‘solid air’ or ‘blue smoke’ owing to its *translucent* nature and the way light scatters in the material. It feels like fragile expanded polystyrene (Styrofoam) to touch. Aerogel was first created by Samuel Stephens Kistler in 1931. Aerogels are produced by extracting the liquid component of a gel through supercritical drying. This allows the liquid to be slowly dried off without causing the solid matrix in the gel to collapse from capillary action, as would happen with conventional evaporation. The first aerogels were produced from silica gels. Kistler’s later work involved aerogels based on alumina, chromia and tin dioxide. Carbon aerogels were first developed in the late 1980s.

Table 2.4 Functionality of nanocomposites via nanoscale

Scale	Functionality
<5 nm	Catalytic activity
<20 nm	Making a hard magnetic material soft
<50 nm	Refractive index changes
<100 nm	Achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement

2.5.3 Nanocomposites

Nanocomposite is defined as a multiphase material with inclusions of 1D, 2D or 3D nanoscale (about 10–100 nm) component. Nanoinclusions can be nanolayers divided by distances about tens of nm within the host matrix of nanocomposite.

The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Nanoscale limits for these functionality effects presented in Table 2.4.

There are three basic morphological groups of nanocomposites as presented in Table 2.5.

2.6 Scaling in Functional Nanomedia

Many nanodevices using the advantages of nanophenomena are highly integrated structures called mesostructures (100–1000 nm), e.g. nanomemory and nanosensor systems. This provides an opportunity for human health correction and enhancement by using adequate dimensions of the corresponding nanodevices (See Fig. 2.6). Thus, ‘nano’ means usually the scale of nanophenomena, but not simply the characteristic sizes of functionalized nanodevices.

Analysing Fig. 2.6, we should point out the *top-down approach*, when nanocomponents are obtained using larger, externally controlled tools from the microscale, microcontact printing, imprint lithography or direct-write dip-pen nanolithography. This approach is able to obtain nanoscale components with atomic precision.

The *bottom-up approach* builds up smaller components into more complex assemblies. Molecular manufacturing, i.e. the process of assembling nanodevices molecule by molecule, exemplifies a bottom-up approach.

The *bio-hybrid approach* uses biological components as building blocks of integrated nanodevices for the creation of biosensors, nanoactuators, etc.

2.7 Concluding Remarks

Nanomaterials are fundamental to the creation of nanosystems for specific functional purposes (see Fig. 2.7 and Table 2.6). According to the principle of their functioning, they can be divided into electronic, optical and mechanical.

The functioning of electronic nanosystems is based on the transformation of optical signals, magnetic signals and chemical signals to electrical signals and vice versa, as well as mechanical ones to the transformation of mechanical motion. Nanosystems of certain types constitute the corresponding branches of nanosystems engineering, namely, nanoelectronics, nanooptics and nanomechanics. The development of various types of nanosystems is closely interlinked, which leads to the creation of more complex integrated nanosystems, such as nano-optoelectronic, nanoelectromechanical, nano-optomechanical and nano-optoelectromechanical systems.

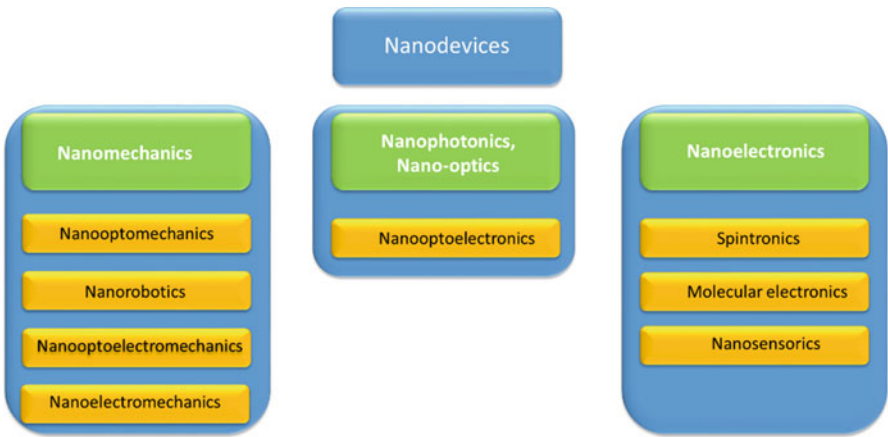


Fig. 2.7 Classification of functionalized nanosystems

Table 2.6 Functional groups of integrated nanodevices

Functionality	Properties
Nanophotonics or nanooptics	Light impact on the nm-scale materials, interaction of nanometer-scale objects with light (wavelengths from 300 to 1200 nm)
Nanomechanics	Mechanical (elastic, thermal and kinetic) properties of physical systems at the nm scale
Nanoelectronics	Nanoelectronic component development, in particular, for actual recent CMOS technology generations (10–20 nm nodes), development of spintronics, molecular electronics and nanosensorics

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