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Space environment (natural and artificial) — Modelling of space environment impact on nanostructured materials — General principles

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Foreword

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Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

In the near future nanomaterials and nanoelements will be widely applied in spacecraft and space engineering. Nanomaterials superiority in mechanical, thermal, electrical and optical properties over conventional materials will evidently inspire a wide range of applications in the next generation spacecraft intended for the long-term (~15 to 20 years) operation in near-Earth orbits and the automatic and manned interplanetary missions as well as in the construction of inhabited bases on the Moon.

The near-Earth's space is described as an extreme environment for materials due to high vacuum, space radiation, hot and cold plasma, micrometeoroids and space debris, temperature differences, etc. Existing experimental and theoretical data demonstrate that nanomaterials response to various space environment effects can differ substantially from the one of conventional bulk spacecraft materials. Therefore, it is necessary to determine the space environment components, critical for nanomaterials, and to develop novel methods of the mathematical and experimental simulation of the space environment impact on nanomaterials.

Modelling is a very important scientific tool for explaining various phenomena and predicting the behaviour of existing and designing materials under different conditions. In the case of nanotechnologies, modelling and simulations become even a more significant method of studying nanomaterials and processes in the nanoscale due to difficulties of observing and measuring many nanoscale phenomena experimentally. In computational nanotechnology, it is necessary to develop new integrated approaches for different length and time scales that enable explaining mechanisms of mesoscale phenomena and predicting emerging material macro-properties.

The changes in the materials properties, caused by the space environment impact, are determined with structural parameters and processes that are related to different spatial scales: from the size of atoms and molecules to the size of macroobjects. There are a variety of simulation methods but most of them can be applied only for a special space and time range/scale because of underlying approximations. To estimate the durability of nanostructured materials to the space environment impact it is necessary to investigate both fundamental effects of incident atom/particle interaction with nanosized structures within very short time intervals and resulting effects of material damage and changes in their properties, that can be observed at micro- and macroscale within much longer periods. Thus, in general case to study the whole set of elementary processes and resulting effects it is necessary to apply the multiscale simulation approach.

The main concept of this document is:

— for main space environment components to choose the most important space and time scales;

— for every scale to choose the most important physical and chemical processes that occur in nanostructured materials under the influence of the given space environment component and can be considered as elementary for the chosen scale;

— for every process to determine a method (or a group of methods) that can be used for their simulations under space environment conditions;

— for every chosen method to describe necessary and possible approximations as well as its limitation when used for simulation of the given process.

Space environment (natural and artificial) — Modelling of space environment impact on nanostructured materials — General principles

1 Scope

The document considers peculiarities of the space environment impact on a special kind of materials: nanostructured materials (i.e. materials with structured objects which size in at least one dimension lies within 1 nm to 100 nm) and specifies the methods of mathematical simulation of such processes. It emphasizes the necessity of applying multiscale simulation approach and does not include any special details concerning concrete materials, elements of spacecraft construction and equipment, etc.

This document provides the general description of the methodology of applying computer simulation methods which relate to different space and time scales to modelling processes occurring in nanostructured materials under the space environment impact.

The document can be applied as a reference document in spacecraft designing, forecasting the spacecraft lifetime, conducting ground-based tests, and analysing changes of material properties during operation.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10795, *Space systems — Programme management and quality — Vocabulary*

ISO 17851, *Space systems — Space environment simulation for material tests — General principles and criteria*

ISO/TS 18110, *Nanotechnologies — Vocabularies for science, technology and innovation indicators*

ISO/TS 80004-1, *Nanotechnologies — Vocabulary — Part 1: Core terms*

ISO/TS 80004-2, *Nanotechnologies — Vocabulary — Part 2: Nano-objects*

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

3 Terms and definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 10795, ISO/TS 18110, ISO/TS 80004-1, ISO/TS 80004-2, ISO/TS 80004-6 and ISO 17851 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.2 Abbreviated terms

AMD	accelerated molecular dynamics
CC	coupled cluster
CI	configuration interaction
DFT	density functional theory
DFTB	density functional based tight-binding
ESD	electrostatic discharge
HF	Hartree–Fock method
kMC	kinetic Monte Carlo
MC	Monte Carlo
MD	molecular dynamics
MP	Møller-Plesset perturbation theory
QM/MM	quantum mechanics – molecular mechanics
UV	ultraviolet radiation
VUV	vacuum ultraviolet radiation

4 Nanostructured materials

The peculiar properties of nanomaterials are determined by the presence in their structure of nanoobjects – particles or grains, fibres, platelets, etc. with at least one linear dimension in nanoscale (size range from approximately 1 nm to 100 nm)[1]–[5]. The lower boundary of this range approaches the size of atoms and molecules; and its upper one separates nanoobjects from microobjects.

The strong influence of the material nanostructure on its properties is caused by the so-called nanometre length scale effects which can be of classical and quantum nature. The nanoscale effects appear when the size of structural objects becomes comparable with a certain parameter of material which has a considerable influence on some physical-chemical processes in the matter and consequently on the material properties[1],[2]. A mean free path of charged particles, a diffusion length, etc. may be regarded as such a parameter in the case of classical length scale effects; and for quantum ones its role is usually played by the de Broglie wavelength.

Another parameter of nanostructures is called dimensionality; it corresponds to the number of dimensions that lie within the nanometre range, and is used for analysing the quantum confinement effects[1],[2]. According to this parameter, all objects may be divided into four groups:

— 3D-objects – bulk materials;

— 2D-objects – nanofilms, nanoplatlets;

— 1D-objects – nanofibres, nanotubes, nanorods, etc.;

— 0D-objects – nanoparticles, nanopores, nanocrystals, quantum dots, etc.

In a 3D-object, electrons can move freely in all three dimensions. In a film whose width is comparable with the de Broglie wavelength (2D-object), electrons move without restrictions only in the film plane, but in the perpendicular direction they are in a deep potential well; that's why 2D-objects are usually called quantum well. In 1D-objects, or quantum wires, two dimensions are comparable with the de

Broglie wavelength. If the electron movement is limited in three directions, a nanostructure becomes a 0D-object, or a quantum dot with discrete electronic states.

Due to nanosized scale effects, nanostructured materials acquire novel mechanical, thermal, electrical, magnetic and optic properties, which can surpass the properties of conventional bulk materials[1],[2],[6],[7]. Nanocomposites with nanoclays, nanotubes and various nanoparticles as fillers are one of the most promising materials for space applications. They may be used as light-weighted and strong structural materials as well as multi-functional and smart materials of general and specific applications, e.g. thermal stabilization, radiation shielding, electrostatic charge mitigation, protection of atomic oxygen influence and space debris impact[8].

Therefore, the creation of polymer nanocomposites with fillers of various shape and composition may play the pivotal role in spacecraft development and implementation of challenging space projects. Among possible fillers, the main attention is paid to carbon nanostructures: fullerenes, carbon nanotubes (CNT), graphene that represent particular allotropic forms of carbon[6],[7]. Due to superior mechanical properties, high electric and thermal conductivity of these nanostructures, one may develop various light-weighted and strong multifunctional nanocomposites. Of special interest are CNT structural analogues, boron nitride nanotubes (BNNTs), that are electrical insulators and in addition to excellent mechanical properties and high thermal stability possess high resistivity to oxidation[9],[10].

5 Main space environment components and processes

5.1 General

The space environment has a significant damaging effect on many materials, including nanostructured materials. During the flight, the spacecraft is influenced by a set of space environment components: electrons and high-energy ions, cold and hot space plasma, solar electromagnetic radiation, meteoroids and space debris, vacuum and other factors[11]–[18]. As a result of this impact, various physical and chemical processes take place in the materials and elements of the spacecraft equipment, leading to deterioration of their operational parameters. Depending on the nature of the processes triggered by the impact of the space environment, the changes in the properties of materials and equipment elements can have different time scales, be reversible or irreversible, and present a different degree of danger for on-board systems. To evaluate the potential effects of the space environment on material properties and the characteristics of spacecraft equipment, it is important to determine the combinations of the most significant factors in various areas of outer space. In this case it should be regarded as effects caused by the impact of individual components of the space environment, and their combined effect[12].

5.2 Space radiation

5.2.1 General

Ionizing radiations of the Earth's radiation belts are electron and proton flows with energies from several hundred eV to several hundred MeV[11]–[15]. As a result of different penetrability and energy, ionizing particles exert influence on all materials independent of their location, both on the exterior of spacecraft (coatings, blankets) and inside it. The dominant degradation mechanism depends on type of material, LET, type of ray, etc. Ionizing radiation breaks chemical bonds but in other cases may lead to cross-linking in polymers. These processes cause decomposition, embrittlement, colour change and darkening, change in electrical resistivity, mechanical strength degradation, etc. Wire insulator indicates decrease in breakdown voltage or cracks.

5.2.2 Special features of nanostructured materials response

Existing experimental and theoretical data demonstrate that nanostructured materials response to space radiation can differ substantially from that of conventional bulk spacecraft materials[19]–[24]. When an electron or ion with high energy interacts with a nanostructure, only a small amount of energy of the incident particle is imparted to it. Therefore, a nanostructured object is characterized by a small number of additional charge carriers or structural defects that appear due to the irradiation;

and their number is reduced with increasing incident particle energy, which is opposite to the situation in conventional materials.

The migration of structural defects and charges in nanostructures and conventional materials also differ: already at the stage of the ballistic cascade, the displaced atoms have more opportunities to leave a nanoobject due to its higher surface area to volume ratio as compared to the bulk material, which leads to a cascade slowdown within the nanostructure[21],[24]. In the conventional bulk materials, displaced atoms can freely reach the surface, causing the material to swell while leaving the vacancies behind. These point defects can aggregate, forming larger obstacles to dislocation motion and causing hardening and embrittlement[7]. In nanostructured materials which contain a large number of nanoscale grains, the grain boundaries can capture interstitials and then fire them back into the lattice to destroy any vacancy that comes within a few nanometres of the grain boundary[20]. Therefore, in nanostructured materials, which are characterized by the presence of large number of grain boundaries, there exists an efficient mechanism which implies that boundaries act as sinks for defects and prevents accumulation of radiation-induced defects within the grain. Controlling radiation-induced-defects via interfaces is considered to be the key factor in reducing the damage and imparting stability in certain nanomaterials under conditions where bulk materials exhibit void swelling and/or embrittlement[22],[23].

Thus, processes of formation of structural defects and charge carriers due to the ionizing radiation, as well as subsequent processes of carriers and defects migration and recombination, differ substantially in conventional bulk materials and nanostructured materials. The influence of these processes on the radiation damage of nanomaterials is ambiguous[19]–[22]. In addition, it is necessary to take into account that the relationship between the stability of nanostructures to the formation and accumulation of radiation defects and the radiation resistance of nanomaterials, determined by a change in their performance characteristics, can be very complicated[20],[21]. By now, there is no sufficiently complete and generally accepted description of the specific radiation effects in nanostructures and their effect on the properties of nanomaterials and spacecraft elements built on them.

Special features of nanostructured materials response to the space radiation:

— presence of grain boundaries or interfaces (nanocrystalline materials, nanocomposites) acting as sinks for defects;

— possibility to use structures and substances possessing enhanced radiation tolerance as fillers in nanocomposites;

— ability of defect healing and enhanced sputtering due to high aspect ratio (nanostructures).

5.3 Atomic oxygen of the Earth's upper atmosphere

5.3.1 General

Atomic oxygen (AO) space environment in low Earth orbits is very dangerous for polymeric materials. High translational energy of O atoms due to the spacecraft orbital velocity enhances their reactivity, so atomic oxygen is capable to break bonds in polymeric materials and create a thin oxidized layer on the surface of some metallic materials, resulting in polymer erosion and severe structural and/or optical properties deterioration.

In general, AO affects near-surface layers of materials, and the ram facing surface of the spacecraft suffers the highest AO fluence. However, oxygen atoms can be reflected and penetrate into covered area via multiple reflections.

Some metals like silver and osmium are rapidly oxidized when exposed to AO. In the case of polymers, the hyperthermal oxygen flux causes fragmentation of the polymer chains and formation of volatile species. As a result, a typical carpet-like relief is grown on the surface (buried regions and profile peaks). Its topology is specific to polymer type.

There are two main approaches to improve the durability of conventional polymeric materials to AO:

— thin surface coatings or ion implantation;

— embedding AO resistant fillers into polymeric matrices.

5.3.2 Special features of nanostructured materials

Nanostructured materials (nanocomposites) can possess a higher durability to AO if they consist of AO resistant nanosized fillers (e.g. Si-containing and metal oxide nanoparticles). Under AO exposure, on the nanocomposite surface forms a layer consisting of nanofillers and protecting underlying polymer layers against AO attack.

5.4 Hot magnetosphere plasma

5.4.1 General

Hot magnetosphere plasma consists of particles with an average kinetic energy of 10 eV to 10^5 eV and is located mainly at heights measured by tens of thousands of kilometres[11]-[14],[16]. Main processes induced by hot magnetosphere plasma are as follows:

— surface and internal charging;

— surface defect formation and sputtering (see 5.2).

Charging of spacecraft materials in hot magnetosphere plasma is the accumulation of electric charge on the external spacecraft surface. This accumulated charge can be distributed unevenly on the surface due to its low conductivity (so-called differential charging of the spacecraft surface).

The main consequence of spacecraft charging is electrostatic discharges (ESD), which create electromagnetic interference to the performance of on-board devices, and in some cases damage and destroy construction and equipment elements.

The phenomenon of charging is related to three groups of processes:

— leakage of electron and ion plasma currents to the spacecraft surface;

— exchange of charged particles between the spacecraft surface and the environment;

— redistribution of electric charges on the spacecraft surface.

The processes of the first group do not depend on properties of spacecraft materials.

The processes of the second groups imply the consideration of all types of secondary emission due to impacts of plasma electrons and ions incident to the surface as well as photoelectron emission induced by solar radiation. However, charging can lead to the appearance of high negative potential (up to several tens of kilovolts) of a certain construction element on the spacecraft and thereby initiate field emission from its surface. The intensity of this emission is closely related to the form and size of edges.

The redistribution of electric charges on the spacecraft surface (the third group) is the most important factor which reduces gradients of electric potential: tangential ones between different elements on the surface and normal ones between the charged surface of dielectric materials and the metallic frame. So to describe the charging effects in spacecraft materials, it is necessary to take into account the electric conductivity of different objects which is related closely to their electronic structure.

5.4.2 Special features of nanostructured materials response

Nanostructured materials consisting of non-conductive polymeric or ceramic matrices with conductive nanofillers (nanotubes, nanoparticles, nanosheets, etc.) possess high surface and volume electric conductivity under certain conditions, namely, high enough concentration of fillers and their good dispersion[1],[2],[6],[7]. Due to this important feature, their usage on the spacecraft surface can minimize negative ESD effects. However, it should be taken into account that embedding nanosized fillers into the polymer and ceramic matrices can lead to the deterioration of other properties that can be important for spacecraft operation (e.g. optic transparency[8]). Additionally, some nanostructures (e.g. CNT) are

considered as very efficient field emitters that can be used for reducing the negative potential of the spacecraft due to the charging effects.

5.5 Heating, cooling and thermal cycling

5.5.1 General

The materials on the outer spacecraft surface are subjected to periodic heating and cooling by solar radiation in the temperature range of 180 K to 390 K, depending on the orientation of the spacecraft surface with respect to the Sun. Such a periodic change in the temperature of materials (thermal cycling) requires considering two distinct physical phenomena:

— heat transfer;

— repeated thermal expansion and compression.

The first phenomenon is closely related to thermal conductivity and ensures the efficiency of the performance of spacecraft thermal control systems. The second one causes mechanical stress within the materials and at their contacts, which can lead to material destruction.

5.5.2 Special features of nanostructured materials

Embedding nanofillers with a high thermal conductivity (e.g. CNTs) can lead to substantial improvement of thermal properties of materials[1],[2],[6]–[8] owing to:

— increasing thermal conductivity;

— reducing thermal expansion coefficient.

5.6 Meteoroids and space debris

5.6.1 General

Impacts of hypervelocity hard particles (micrometeoroids and space debris) cause erosion on the material surface due to the formation of craters and cracks[11]–[13]. The most serious changes happen in the uppermost layers of materials, but underlying layers can be damaged by heat.

5.6.2 Special features of nanostructured materials

Nanostructured materials can possess higher tolerance to hypervelocity particle impacts owing to the presence of hard nanofillers that are able to reduce the damage:

— reinforcement by incorporation hard nanosized fillers;

— enhanced fracture strength (or crack resistivity) by embedding flexible nanofillers.

5.7 Solar UV and VUV radiation

5.7.1 General

Short-wave solar UV and VUV electromagnetic radiation is one of the most important factors causing the degradation of materials on the outer spacecraft surface. Under its influence, the optical, mechanical, electrical, and thermal properties of materials can be altered substantially.

UV and VUV radiation can break chemical bonds, so this space component influences strongly polymeric materials located on the external spacecraft surface. UV and VUV can cause bond scissor (if the bond energy corresponds to the light wavelength) or induce cross-linking depending on polymer composition and structure. As a result of structural changes, UV and VUV can induce changes of polymer mechanical (brittleness) and optical (colour darkening) properties.

5.7.2 Special features of nanostructured materials

In general cases, UV and VUV radiation interacts with materials at atomic level and influence mainly chemical bonding, so important changes in mechanisms of its influence on nanostructured materials are not expected. However, solar radiation can cause changes in the interface between main matrices and nanofillers as well as in properties of nanofillers themselves. These processes can alter the interaction between the matrices and fillers, thereby leading to changes of macroscopic properties of nanocomposites.

In addition, UV and VUV solar radiation influences the secondary emission properties of materials, including photoelectron emission (see 5.3).

6 Multiscale approach to simulation of space components impact on nanostructured materials

6.1 Multiscale simulation methods

6.1.1 General

To estimate the durability of nanostructured materials to the space environment impact it is necessary to investigate both fundamental effects of incident particle interaction with nanosized structures within very short time intervals and resulting effects of material damage and changes in their properties, that can be observed at micro- and macroscale within much longer periods. Thus, in general case to study the whole set of elementary processes and resulting effects, it is necessary to apply the multiscale simulation approach[25]–[27].

Four most significant and fundamentally different groups of methods are usually considered:

— quantum mechanics (*ab initio*) and semi-empirical methods;

— molecular dynamics;

— mesoscale methods;

— continuum methods.

Quantum mechanical, or quantum chemistry methods are based on numerical solving of the Schrödinger's formula and do not require any empirical assumptions, so they are usually called *ab initio* methods ("*ab initio*" comes from the Latin phrase "from first principles"). These methods can be effective only for small size systems no more than 100 atoms and in the region of 10^{-10} m to 10^{-9} m.

Semi-empirical methods are a combination of *ab initio* methods coupled with data from empirical studies. Such methods are computationally much more efficient than the *ab initio* method and can be applied for systems consisting of 10^3 to 10^4 atoms, but they are limited to systems for which parameters exist. Methods of this group are particularly useful in the study of organic chemistry and the structure and reactions of organic molecules.

The molecular dynamics (MD) method enables enlarging the size of modelling objects to the upper border of the nanoscale range and increasing the number of particles up to 10^6 to 10^7. Within this approach, atoms are considered to be hard spheres that are connected to other atoms by a spring. An important feature of the method is the use of empirical potentials, or force fields that determine the forces acting between particles and can affect significantly results of calculations. This method enables predicting the time evolution of a system of interacting particles and determining the system parameters, from which the macroscopic properties can be derived. Sometimes for reducing calculation volume the various types of Monte Carlo technique are applied in this space and time range.

In the case of large systems, the accumulation of detailed information on the movement of each atom limits the capabilities of the MD method. Therefore, for time intervals of the order of microseconds and above, one should apply the methods that are developed for the mesoscale. However, before doing so, a

special coarse-graining procedure which enables transferring from molecular objects to mesosystems should be carried out. An important shortcoming of mesoscale approach is the absence of universal principles for this procedure which leads to an ambiguous interpretation of the results obtained.

The continuum methods are used to model processes and objects at the macro level: for objects and phenomena with characteristic dimensions of more than a few tens of micrometres at typical times of the processes from fractions of a second to hours and years. These methods are based on statistical regularities and suggest the possibility of averaging calculation parameters within the specified cell sizes. In this group of methods, the approximation of a homogeneous medium is applied, which is not valid for nanostructured materials.

To reduce the amount of computations both for quantum mechanical calculations and for meso- and macro-scale modelling, different versions of the Monte Carlo method are used, with the help of which numerical systems solve formulae and multidimensional integrals are calculated.

The main challenge for the multiscale simulation is to provide a seamless transitional mechanism from one space and time scale to another where they are used as input data. Currently there are the two approaches to solving this problem: hierarchical and hand-shaking (concurrent)[25]–[27]. The hierarchical, or sequential approach is currently the most universal and common. It involves step-by-step application of different level models, from quantum mechanical to macroscale. A series of computational methods is linked so that the results obtained with one of the methods on one scale can be used to define parameters for modelling on the upper size and time scale with the next method. Since the simulation is done from the lower to the upper levels, this approach assumes knowledge of the parameters of the main processes occurring at the lowest level. This concept is most effective for systems in which structures and processes occurring at different space-time scales are loosely related to each other.

The concurrent or parallel approach assumes building a combined model for which different models may be used simultaneously in its different parts. During the simulation the spatial domain in which a particular multiscale process is studied is divided into several parts, each for its own method. This approach attempts to “tie together” several methods for different scales and treat them as acting simultaneously and transmitting data to each other within a certain procedure. A simultaneous approach is necessary if the various space and time levels of the system are closely related to one another, and the processes occurring on one of them depend on the behaviour of the system on the other.

It should be noted that the implementation of the described multiscale approach can meet additional complications that arise due to the non-linear dependences of macroscopic properties of materials on their structure at lower dimensional levels and on the nature of the processes occurring at these levels[25]. The most important and reliable software codes for multiscale simulation are listed in Annex A.

6.1.2 Quantum (electronic) scale

6.1.2.1 *Ab initio* methods

Quantum mechanical methods are based on numerical solving of the Schrödinger’s formula which is a partial differential formula with 3*N* unknowns.

The existing quantum mechanical methods can be divided into two main parts[28]–[30]:

Hartree-Fock (HF) and post-HF methods (wavefunction-based electronic structure theory) include the density functional theory (DFT) method (electron density formalism).

The HF or self-consistent field (SCF) method enables reducing the many-particle problem to a set of single-particle problems in which each particle moves in an averaged field created by all the other

particles. The solution of HF formulae is determined by the variational technique, i.e. HF orbitals yield the lowest energy within the restriction applied. The one-electron HF formulae are as follows[28]–[30]:

$$\boldsymbol{f}\varphi_i = \varepsilon_i \varphi_i\,,\ i = 1,2...N$$

$$\boldsymbol{f} = \boldsymbol{h}_1 + \sum_j^N (\boldsymbol{J}_j - \boldsymbol{K}_j)$$

where

$\boldsymbol{f}$ is the Fock operator;

$\boldsymbol{h}_1$ is the one-electron Hamiltonian describing the motion of a chosen electron in the field of all the nuclei;

$\boldsymbol{J}_j$ is a Coulomb operator, representing the classical repulsion between the chosen electron and electron j;

$\boldsymbol{K}_j$ is an exchange operator.

Therefore, in the HF method all electron-electron interactions are accounted in an average fashion and the fast correlation between electrons are neglected. This limitation is being addressed with the development of advanced, post-HF methods, that include Møller-Plesset perturbation theory (MP), configuration interaction (CI), and coupled clusters (CC) methods and take into account static and dynamic electron correlation, thus providing much more reliable results, especially for excited states. The accuracy of the electronic correlation calculations is determined not only by the chosen method, but also by the quality of the used basic set.

Ab initio approach is the most accurate and precise of all of the currently available methods in molecular modelling. However, the post-HF methods are quite costly in terms of computing resources. The number of computational operations for the usual HF method is M^4, where M is the number of basis functions, M^5 and higher for the MP-based method, and M^6 and higher for the CC method.

6.1.2.2 Density functional theory method

Density functional theory (DFT) is based on the independent-particle model, as the HF method, but in general provides better results, so it can be considered as an improvement on HF theory, where the many-body effect of electron correlation is included via the concept of the electron density. Within the DFT formalism, the energy of a N-electron system is considered as a functional of the electron density, which depends only on 3 spatial coordinates and is independent of the number of electrons. The DFT method is scaled as M^3, so this method can be used for larger systems consisting of 200 to 300 atoms.

DFT energy expression can be written as[28]–[31]:

$$E^{\mathrm{DFT}}[n] = T_{\mathrm{s}}[n] + E_{\mathrm{H}}[n] + E_{\mathrm{eN}} + E_{\mathrm{NN}} + E_{\mathrm{XC}}[n]$$

where

$T_{\mathrm{s}}[n]$ is the kinetic energy of non-interacting electrons;

$E_{\mathrm{H}}[n]$ is the classical Coulomb energy of electron-electron interaction, considered as functional of the electron density $n(\boldsymbol{r})$;

E_{NN} is the energy of nuclear-nuclear repulsion;

E_{eN} is the energy of attraction between nuclei and electrons;

$E_{\mathrm{XC}}[n]$ is an exchange-correlation functional.

The minimization of the total energy $E^{\mathrm{DFT}}[n]$ with respect to the electron density yields one-electron Kohn–Sham formulae that are analogues of HF formulae:

$$\boldsymbol{H}_{\mathrm{KS}}\varphi_i = (\boldsymbol{T}_{\mathrm{s}} + \boldsymbol{V}_{\mathrm{KS}})\varphi_i = \varepsilon_i\varphi_i$$

where $\boldsymbol{V}_{\mathrm{KS}}$ is an effective Kohn–Sham potential for the electron system:

$$\boldsymbol{V}_{\mathrm{KS}} = \boldsymbol{V}_{\mathrm{ext}} + \boldsymbol{V}_{\mathrm{H}} + \boldsymbol{V}_{\mathrm{XC}} = \boldsymbol{V}_{\mathrm{ext}} + \int d\boldsymbol{r}' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{\mathrm{XC}}[n]}{\delta n}.$$

The exact form of an exchange-correlation functional is unknown, however, the corresponding exchange-correlation energy is a rather small fraction of the total energy; and even relatively crude approximations for this term provide quite accurate computational models for systems in their ground states. Currently, conventional functionals within local density approximation (LDA) or generalized gradient approximation (GGA) are local or semi-local. This leads to some limitations in DFT calculations, e.g. this method is unable to describe correctly van der Waals interactions[31]. To correct this deficiency, more elaborated functionals are developed (hybrid, meta, optimized effective potential, range-separated hybrid functionals, etc.).

DFT can use both localized orbitals and plane waves as basis functions. In the latter case, pseudopotentials are often applied to reduce the amount of calculations. The state-of-art pseudopotentials are developed on the basis of high-quality *ab initio* calculations; however, to model a given system, it is necessary to carefully analyse the applicability of the chosen pseudopotential.

The DFT method can be used to simulate a wide class of systems - from small molecules and clusters to periodic and amorphous polyatomic systems. At present, it is one of the most frequently used and universal quantum mechanical methods in atomic and nuclear physics, quantum chemistry, condensed matter and solid state physics. The main disadvantage of DFT is that there is no systematic approach to improving the results towards the exact solution. The DFT method was developed for the ground state of a system; so to study excited states, one should apply time-dependent density functional theory (TD-DFT) method[32].

Direct dynamic simulation within Born–Oppenheimer approximation is usually performed for relatively small molecules or periodic structures by means of DFT of semi-empirical methods with MD algorithms. This approach usually called Born–Oppenheimer molecular dynamics (BOMD) implies the calculation of forces acting on nuclei at each simulation step, the determination of the position of the nuclei in the next step, then the recalculation of forces, etc.[28]–[31]. The development of TD-DFT method makes it possible to analyze the evolution of quantum mechanical systems in cases when the Born-Oppenheimer approximation is not valid[32]. At present, TD-DFT calculations are carried out mainly in the linear response regime, according to which the external perturbation is a small value and, therefore, the change in the electron density, which describes the deviation of the system from the ground state, can be considered within the non-stationary perturbation theory. In most cases, an adiabatic approximation is also used, which implies that the time dependence of the exchange-correlation functional does not change with time. There two other approaches for simulating the dynamics of a quantum system. Within the Ehrenfest dynamics approach the nuclei are considered classical particles, but for electrons at each step the time-dependent Schrödinger formula is solved. In the case of the Car–Parinello molecular dynamics (CPMD), electrons are assumed to have a fictitious mass so their motion can be taken into account explicitly during the simulation. As a result, the calculation of the motion of nuclei and the determination of the ground state of the system occur simultaneously due to the use of the extended Lagrangian[28].

6.1.2.3 Quantum Monte Carlo

For a system with N electrons, the dimensionality of the problem is $3N$, and the integral can be estimated much more efficiently by sampling the function point-wise within the whole function space. Variational quantum Monte Carlo (QMC) method implies estimating the functional value by a random sampling of points within the integration limits, weighted by the probability factors. The generation of points is

done using a Metropolis algorithm; and the calculated energy is simply the average of the local energies over the sampling points[30].

The main problem with QMC methods is these methods require a trial wave function, for determining how to sample the huge phase space most efficiently and in agreement with the fermion nature of the electrons. The accuracy of the results is tightly coupled to the form of the trial wave function.

The scaling of QMC methods is N^3, but in practice these methods are roughly two orders of magnitude more expensive than independent-particle models such as HF and DFT. However, low-order scaling, makes QMC competitive with e.g. CC methods even for relatively small systems. The main disadvantage of QMC is the statistical error in the calculated results; and generating highly accurate results is thus computationally expensive.

6.1.2.4 Semi-empirical methods

Semi-empirical methods take into account the electron-electron interaction only partly. They use several large assumptions, including neglecting core (non-valence) electrons and replacing some integrals with parameters that are fitted to experimental data, especially molecular energies and geometries. This imposes respective constraints on the applicability of such methods and on the accuracy of the results that they yield. These methods make it possible to simulate systems involving 10^3 to 10^4 particles with size of about 10^{-9} m to 10^{-8} m. However, these methods were developed largely for complex organic compounds.

The existing semi-empirical methods can be divided into two groups:

— HF-based methods;

— DFT-based method – density functional based tight-binding (DFTB).

The central assumption of HF-based semi-empirical methods is the zero differential overlap approximation, which neglects all products of basis functions that depend on the same electron coordinates when located on different atoms. This approximation leads to reducing the overlap matrix S to a unit matrix, setting all three-centred one-electron integrals to zero, and neglecting all three- and four-centre two-electron integrals. To compensate for these approximations, some remaining integrals are turned into parameters; and their values are assigned based on calculations or experimental data. Exactly how many integrals are neglected, and how the parameterization is done, defines the various HF-based semi-empirical methods[30].

The density functional based tight binding (DFTB) method is based on a second-order expansion of the Kohn-Sham total energy in DFT with respect to charge density fluctuations[33]. The fundamental step of the DFTB derivation is to expand the total energy of the DFT representation to the second order in charge density and spin density fluctuations with a number of approximations. The total energy in the DFTB formulation contains a few terms that do not depend on the electron density fluctuations; and they are combined into a short-range repulsive energy consisting of atom-type specific pair potentials. This method offers a high degree of transferability and universality. Currently, DFTB method is able to be used in calculations of optical properties of materials and to model electron transport in molecular nanostructures.

6.1.2.5 Quantum mechanics – molecular mechanics

A special hybrid approach called quantum mechanics – molecular mechanics (QM/MM) is developed to simulate large systems in which there is a small region where atoms should be treated with electronic structure methods (usually semi-empirical, low-level *ab initio* or DFT), while the all remaining atoms

are simulated by means of force field[30]. The partition can be done by dividing the Hamiltonian and resulting energy into three parts:

$$\boldsymbol{H}=\boldsymbol{H}_{\mathrm{QM}}+\boldsymbol{H}_{\mathrm{MM}}+\boldsymbol{H}_{\mathrm{QM/MM}}$$

The main problem with QM/MM schemes is deciding how the two parts should interact. The lowest level of interaction is called mechanical embedding when QM atoms have additional forces generated by the MM framework, and vice versa, but there is no interaction between the electronic parts of the two regions. The next level of improvement is called electronic embedding, where the atoms in the MM regions are allowed to polarize the QM region. A further refinement, polarizable embedding, can be made by allowing the QM atoms also to polarize the MM region, so the electric field of the QM region influences atomic charges and dipoles of atoms in the MM area. The main deficiency of QM/MM methods is that there is no unique way of deciding which part should be treated by force field and which by quantum mechanics.

6.1.3 Atomistic scale (molecular dynamics and Monte Carlo)

In the general case, the evolution of the many-body system can be investigated in two fundamentally different ways: by means of MD (averaging over time) or by MC (ensemble averaging). For atomistic modelling, i.e. modelling at the level of individual atoms, the MD method is used more widely, since it allows one to obtain complete information on the dynamic behaviour of each atom.

MD methods generate a series of time-correlated points in phase space (a trajectory) by propagating a starting set of coordinates and velocities according to Newton's second formula by a series of finite time steps[34]. A typical time step is $\sim 10^{-15}$ s and a simulation involving 10^6 steps thus covers $\sim 10^{-9}$ s. The traditional MD method is based on the integration of the classical formulae of motion:

$$M_\alpha \frac{d^2\boldsymbol{R}_\alpha}{dt^2}=\boldsymbol{F}_\alpha=-\frac{\partial U(\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_N)}{\partial \boldsymbol{R}_\alpha},\quad \boldsymbol{F}_\alpha=\sum_{\beta\neq\alpha}\boldsymbol{F}_{\alpha\beta}+\boldsymbol{F}_\alpha^{\mathrm{ext}}$$

where

M_α is the mass of particle α;

$\boldsymbol{R}_\alpha$ is the position of particle α;

$\boldsymbol{F}_{\alpha\beta}$ is the force acting on particle α from particle β;

$\boldsymbol{F}_\alpha$ is the total force on particle α by all other particles;

$\boldsymbol{F}_\alpha^{\mathrm{ext}}$ is the external force on particle α;

$U(\boldsymbol{R})$ is the potential energy of the system at position $\boldsymbol{R}$.

The state of a system of N particles at any time is determined by a set of $3N$ coordinates and $3N$ particle velocities. At each time step, the acceleration shall be evaluated from the calculated forces, which then allows the atomic positions to be propagated in time and thus generate a trajectory. A standard MD simulation generates an NVE ensemble with the constant energy, i.e. the temperature and pressure will fluctuate. It is possible also to generate NVT or NPT ensembles by modifying the velocities or positions in each time step using the thermostat or barostat algorithms[34].

The potentials describing the interactions between atoms are parameterized on the basis of experimental data; therefore, they are usually called empirical potentials, or force fields[28]. To simulate complex systems, it is necessary to use many-body force fields, which include effects from the interaction of three or more particles with each other. For instance, to describe forces in metals, effective medium theory (EMT) and embedded atom method (EAM) are widely used, while for materials with strong covalent bonding, bond-order force fields are better choice[29],[30],[34],[35].

For systems in which the long-time dynamical evolution is characterized by a sequence of activated events, accelerated molecular dynamics (AMD) methods can extend the accessible time scale by orders of magnitude relative to direct MD, while retaining full atomistic detail[28]. In the AMD approach, the system is allowed to evolve according to the classical formulae of motion, as in a direct MD simulation, but during this evolution, state-to-state transitions are coaxed into occurring more rapidly. Three main AMD methods imply the parallelization of the state-to-state dynamics of such a system on some processors (parallel-replica dynamics), the acceleration of transitions from one state to another due to the modification of the potential surface (hyperdynamics) or by increasing the temperature (temperature accelerated dynamics).

In the MD method, periodic boundary conditions are often used to enable simulating the behaviour of infinitely extended systems with a limited number of particles. For various simulation tasks, especially in the case of nanostructured materials, special periodic boundary conditions should be applied.

6.1.4 Mesoscale

Among the existing methods of mesoscale modelling, the dynamic density functional theory (DDFT), mesoscale MD and the dissipative dynamics of particles (DPD) are most often used[28]. A large role in mesoscale modelling is also played by stochastic Monte Carlo methods, which are used in the so-called lattice models describing systems with discrete degrees of freedom, as well as in the modelling of rare processes with a high activation barrier.

The creation of mesoscale models is based on the coarse-graining procedure applied to the system under investigation. As a result of it, the system, initially consisting of many interacting atoms, turns into a collection of particles ("beads") that are agglomerates of certain functional groups or entire molecules. The motion of atoms inside the system, which is "fast" in comparison with the motion of the unified particle, is averaged, and the degrees of freedom associated with it disappear. However, the coarsening procedure applied to a particular system depends to a large extent on the physical phenomena under study, since certain degrees of freedom can be important for correctly taking into account the features of the processes. Therefore, the choice of those degrees of freedom that are coarsened is critical, but even for the same material it can differ depending on what properties will be studied in the simulation.

The DDFT method is a mesoscale generalization of the density functional theory. This approach does not consider the behaviour of individual particles (atoms, molecules, beads, etc.) but collective variables: distributions or fields. The state of the system at any time is characterized by functions of the 3D distribution of the concentration field $\rho_i(\boldsymbol{r})$ for a particle of i type. The evolution of the system is described by a formula analogous to the dynamic Langevin formula:

$$\frac{\partial \rho_i}{\partial t} T = D\nabla\left(\rho_i \nabla \mu_i\right) + \eta_i$$

where

D is the coefficient determining the particle mobility;

μ_i is the chemical potential of the the i-th species;

η_i characterizes a stochastic noise.

The DPD method[36], based on the particle formalism, analyses the behaviour of "beads" of the same size, which can be fragments of molecules, the molecules themselves or groups of molecules. The motion of beads obeys the Newton's laws. The interacting forces between pairs of beads are short-range and are divided into three categories: conservative, dissipative, characterizing the medium response to the motion of particles due to viscosity, and random, ensuring the energy supply to the system as opposed to the action of dissipative forces. The final force acting on the bead i by other particles can be written as the sum of these forces. The value of each force depends on distances between beads and some other parameters.

The main difference between the coarse-grained MD and conventional atomistic MD methods is that the interacting objects are not atoms, but beads; and forces between them are described by mesoscopic force fields. Such force fields can take into account a fairly wide range of parameters: the types of "beads", their structure, the number of nearest neighbours, etc.

For simulating the time evolution of systems with discrete degrees of freedom (lattice models) or with rare events (activation processes) whose time intervals are more typical for the mesoscale range, the Monte Carlo (MC) method is preferable. However, the conventional MC algorithms lack a time concept. Time scale can be included by introduction of a typical time step (e.g. an average time between transitions from one state to another), but if these transitions can be realized via several processes that have different time characteristics, the situation becomes more complicated.

Kinetic Monte Carlo (kMC) method attempts to overcome the limitation of MD by exploiting the fact that the long-time dynamics of this kind of system typically consists of diffusive jumps from state to state[28]. Rather than following the trajectory through every vibrational period, these state-to-state transitions are treated directly. The result is that kMC can reach vastly longer time scales, typically seconds and often well beyond.

The kMC approach makes it possible to give a physical meaning to the integration step. Within the framework of this method, the main processes causing transitions are chosen, and for each of them a corresponding rate constant is determined. The created model takes into account the features of the crystal lattice and the limitations in atom displacements while the probabilities of the processes are either determined in advance (e.g. by the DFT method or from experimental data) or calculated in on-fly during the simulation. The main difficulty in using this method is a reliable parameterization of the model.

6.1.5 Macroscale (continuum methods)

Methods of macroscale (finite element method, boundary element method and others) are used for the analysis of objects and phenomena with dimensions of more than few tens of micrometres at typical time intervals from fractions of a second to hours and years. These methods are based on statistical regularities and suggest the possibility of averaging parameters within the specified cell sizes[28]. At this level of modelling, the considered objects are considered homogeneous, i.e. their structure at the molecular level is not taken into account, as a result of which the macroscopic characteristics of objects (for example, density, electric resistance, etc.) are continuous.

Since in this group the homogeneous medium approximation which is not valid in the case of nanostructured materials is applied, it is necessary to average over the spatial characteristics when using them for such materials. An important role in this approach is played by the concept of a representative volume element, which corresponds to the minimum possible volume of the body, allowing one to investigate some of its properties. The use of such an approach makes it possible to apply traditional methods of solving boundary-value problems in the mechanics of continuous medium. In special cases of the 3D distributions of concentration, density, or some other quantities obtained in mesoscale calculations can be used as input data for simulation at the macro level.

To reduce the amount of computations both for quantum mechanical calculations and for meso- and macro-scale modelling, different versions of the Monte Carlo (MC) method are used. MC approach refers to techniques for obtaining the value of a multi-dimensional integral of a function by randomly probing its value within the whole variable space and estimating the integral by statistical averaging. In the limit of an infinite number of sampling points, the result is identical to that obtained from an analytical integration, but for a finite number of points, the calculated value is given as an average with an associated standard deviation. The standard deviation, the uncertainty, depends inversely on the square root of the number of sampling points.

6.2 Radiation damage modelling

6.2.1 General

Radiation-induced processes in matter are characterized by widely different spatial and time scales. When analysing a collision of an incident particle with atoms of a solid target and a further development of cascade processes, it is important to take into account atomic oscillations with periods of the order of 10^{-17} s to 10^{-15} s, while defect migration and recombination occur at significantly longer time intervals reaching micro- and milliseconds. A large role in the interaction of the incident particles with matter is played by ionization energy losses, i.e. energy lost for the excitation of atoms, so modelling of such effects in the general case requires a quantum mechanical description. An additional complication is the fact that the processes of defect migration are characterized by irregular transitions of the system from one state to another. Thus, when modelling the radiation effects on nanostructured materials, it is necessary to use methods related to different space-time scales, or their combinations.

The general guidelines to simulate the most important processes in nanostructured materials under the irradiation are given in Table 1.

Table 1 — General guidelines to simulate the most important processes in nanostructured materials under the irradiation

	Quantum scale: electrons and nucleus; atoms; molecules	Atomistic scale: complex molecules, nanoobjects	Mesoscale: grains, nanoobjects prolong processes	Macroscale: continuum
Important processes to be simulated	Defect formation and relaxation, atom excitations, nuclear reactions	Cascade processes, defect migration, sputtering, nanoobject/matrix interaction at interfaces	Atomic defect migration and accumulation, energy distribution, heat dissipation, dispersion of nanoobjects in a matrix	Material destruction, emissions, dose accumulation
Methods to be applied	*Ab initio* methods; semi-empirical methods	MD, MC	kMC, accelerated MD Mesoscale methods (dispersion processes)	Continuum methods; MC
Limitations	Excited states	Chemical sputtering only with specially developed force fields (with a great caution)	A precise description of all involved processes is needed	Homogeneous media approximation Some parameters of main processes are needed

6.2.2 Quantum scale

To model the processes of formation of defects and their relaxation at the atomic level, in the general case it is necessary to use *ab initio* or semi-empirical methods.

The main processes to be simulated are as follows:

— nuclear reactions;

— atom excitations;

— defect formation.

For nuclear reaction the main simulation method is nuclear HF method (in the case of heavy elements - nuclear DFT method).

For defect formation in periodic structures, the most widely used method is DFT. It can be applied to calculate formation energy of point defects, changes in electron structure of crystalline materials due to vacancies of interstitials[19]. In dynamic simulations (e.g. to study sputtering process), the DFT of DFTB methods can be applied for determination of surface binding energy or threshold displacement energy[21]. The data obtained can be used to calculate probabilities of defect migration and relaxation for kMC models as well as for development empirical potentials.

The limitations of the methods lie in the necessity to take into account the limitations of Born-Oppenheimer approximation (for H atom and ion in carbon target ~100 eV), so for high incident energies (high ionization losses), the account for excited states is needed (TD-DFT method or Ehrenfest dynamics should be applied)[21],[37].

6.2.3 Atomistic scale

For the next space-time range, which is characterized by cascade processes, defect migration, physical sputtering, it is possible to use MD. Simulation of cascade processes is also performed using MC models based on the independent binary collision approximation (MC-BCA), as well as with hybrid approaches that imply the simultaneous use of MD and MC-BCA methods[19],[28],[38],[39].

The main processes to be simulated are as follows:

— cascade processes;

— defect relaxation and migration;

— physical sputtering.

To apply MD methods for radiation induced process modelling, it is necessary to make some corrections[21] to standard MD codes including:

— specially developed force fields or short-range correction of conventional force fields;

— additional forces for describing the energy loss to ionization (for low v);

— adaptive time step to take into account the motion of particles with relatively high kinetic energy;

— account for reduced dimensions – intensive sputtering, limits for energy dissipation;

— computational supercells and special boundary conditions.

MD makes it possible to study the development of a cascade that arises when collisions of high-energy ions with nanostructure atoms, to investigate the mechanisms of formation and accumulation of defects. The main problem of such simulation is associated with the usage of empirical potentials so it is very important to test thoroughly the applicability of a chosen potential for the system under study[35].

To study cascade processes in materials, the MC approach based on the independent binary collision approximation (BCA) is also widely used. Within this approach all collisions between pairs of atoms are considered independent of each other; and between collisions particles move along rectilinear trajectories[38]. An incident particle interacts with the atom through a predetermined repulsive potential; and velocities of the particles after the collision are calculated on the basis of the scattering theory by the Monte Carlo method. The currently available MC-BCA software codes[40]–[42] simulate the motion of an incident particle in a homogeneous cell of a given size (up to tens of nanometres).

6.2.4 Mesoscale

For mesoscale processes (e.g. long-term migration of defects, energy redistribution in the target), the accelerated molecular dynamics and the kinetic Monte Carlo (in solid materials), as well as conventional mesoscale methods are applied.

The most important processes for this scale are as follows:

— atomic defect migration and accumulation;

— energy dissipation;

— structural changes;

— account for the electron–phonon coupling with specially developed models (e.g. a two-temperature model).

To simulate defect migration and relaxation kMC is often used. Special features of this method:

— prior calculation of rate constant with *ab initio* or MD methods;

— initial space distribution of defects within material.

Structural changes of materials can be simulated with accelerated MD or coarse-grained mesoscale methods (coarse-grained MD, DPD, DFFT). The main problem with the latter is the absence of universal principles describing the transition from molecular objects to mesosystems and the resulting ambiguous interpretation of the results obtained.

6.2.5 Macroscale

Processes of material destruction, effects of dose accumulation, etc. are simulated continuous methods.

The most important processes for this scale are as follows:

— dose accumulation;

— radiative emissions;

— material destruction.

To simulate these processes beam models and MC models are used.

Limitations of these approaches for nanostructured materials:

— homogeneous simulation cell approximation;

— BCA (MC models);

— experimental or calculation data on interaction cross-sections of incident particles with bulk materials (substances).

6.3 Modelling of atomic oxygen impact

6.3.1 General

Processes related to the AO interaction of with surface layers of the spacecraft materials proceed in completely different space and time scales. The dominant mechanism for the interaction of hyperthermal O atoms with the surface is chemical reactions, leading to the material erosion and mass losses[43]. Due to erosion, materials can lose not only their mechanical strength, but also many other physical and chemical properties. Polymeric materials are most severely affected by AO. In order to evaluate the resistance of polymer nanocomposites to the of AO influence, it is necessary to take into account both the fundamental effects of the interaction of an O atom with nanoscale structures for short periods of time, and the total damage and destruction of composites that can be observed in micro- and macroscale ranges over much longer time intervals.

For AO environment influence on nanostructured materials, one should consider the following space and time scale and related elementary processes:

— quantum scale:

  direct chemical reactions with hyperthermal O atoms, defect formation;

— atomistic scale:

  chemical sputtering, processes at interfaces due to nanoobject/matrix interaction;

— mesoscale:

  non-direct (thermal) reactions, defect relaxation and migration, dispersion of nanoobjects in a matrix;

— macroscale:

  mass losses, material erosion.

The general guidelines to simulate the most important processes in nanostructured materials due to the AO impact are given in Table 2.

Table 2 — General guidelines to simulate the most important processes in nanostructured materials due to the AO impact

Space environment component: **atomic oxygen**	Quantum scale: electrons and nucleus; atoms; molecules	Atomistic scale: complex molecules, nanoobjects	Mesoscale: grains, nanoobjects prolong processes	Macroscale: continuum
Important processes to be simulated	Direct chemical reactions with hyperthermal O atoms, defect formation	Nanoobject/matrix interaction at interfaces, chemical sputtering	Non-direct (thermal) reactions, defect relaxation and migration, dispersion of nanoobjects in a matrix	Mass losses, material erosion
Methods to be applied	*Ab initio* methods, semi-empirical methods	MD	kMC, accelerated MD (reactions, defect relaxation) Mesoscale methods (dispersion processes)	Continuum methods; MC
Limitations	Excited states	Chemical sputtering only with specially developed force fields (with a great caution)	A precise description of all involved processes is needed	Homogeneous media approximation Some parameters of main processes are needed

6.3.2 Quantum scale

To study direct chemical reactions, *ab initio* method or semi-empirical should be applied. In general, there are two approaches to investigate chemical reactions: static and dynamic.

The static approach involves the study of the most probable adsorption sites, calculation of the potential energy surface (PES), analysis of possible reaction paths, determination of reaction energies and activation barriers. Within this approach, high-precision *ab initio* methods are used for small molecules, but for larger objects, DFT and semi-empirical methods are usually applied[30]. At present, the DFT method is the main method for studying adsorption processes on the surface of periodic structures, including crystalline materials and nanostructures. For such calculations, the usage of plane wave basis is preferable.

The dynamic approach implies the simulation of the time evolution of the system under study. Direct dynamic simulation within Born–Oppenheimer approximation is usually performed for relatively small molecules or periodic structures by means of DFT or semi-empirical methods with MD algorithms (BOMD). Much more reliable is TD-DFT method which can correctly take into account excited states of the system. The Car–Parinello molecular dynamics (CPMD) can also be applied for simulation of chemical reactions.

6.3.3 Atomistic scale

In case of small molecules, the MD method is applied for so called direct dynamic simulation technique. It implies the generation of interatomic potentials on the base of the potential energy surface calculated with the *ab initio* methods, and then MD simulation of many trajectories to obtain reliable statistics for reactive channels. In addition, the state-of-art bond-order force fields can simulate more or less properly few chemical reactions in some systems for which they were parameterized[26],[30].

The MD method is the main method to simulate filler/matrix interaction at interfaces. Apart from the properties of individual components in a nanocomposite, interfaces play an essential role in enhancing or limiting the overall properties of the system[2],[6],[7]. Due to the high surface area of nanostructures, nanostructured materials possess many interfaces between the constituent intermixed phases; and some special properties of such materials often arise from interaction of its phases at the interfaces.

To analyse the interface features, it is necessary to take into account at least the interactions at the molecular level, and in some cases also at the quantum mechanical level, since the presence of defects on the surface of nanostructures can radically change the nature of its interaction with molecules and functional groups.

6.3.4 Mesoscale

The presence of nanosized fillers (nanoparticles, nanotubes, nanoplatlets) embedded in the polymer matrix complicates significantly the task of predicting the macroscopic properties of nanocomposites. To solve this task, it is of great importance to determine the equilibrium structure of the nanocomposite.

The MD method makes it possible to calculate the energy parameters of the "filler-polymer" system, which can then be transferred as initial parameters to the mesosystem. To model the equilibrium structure, it is necessary to use mesoscale methods that allow one to investigate the formation of agglomerates from filler particles over long enough (10^{-6} s or more) time intervals.

To simulate non-direct (thermal) reactions, the kMC method is widely used. It implies the detailed knowledge of all important elementary processes that occur in the system and the a priori calculation of their rates which is very difficult in many cases[28].

However, in the case of polymer nanocomposites, the application of the kMC method to simulate erosion processes in accordance with the approach presented above is difficult, since the structure of the polymers is very different from that of the crystalline materials. For such complex structures, coarse-graining procedures are used when the characteristic monomer fragments, the monomers themselves or their combinations are selected as an elementary object during the simulation (see 6.1.4).

6.3.5 Macroscale

Agglomerated fillers in polymer nanocomposites can be of hundreds of nanometres or even few micrometres in size, so when studying the erosion processes of such materials under the influence of atomic oxygen, a high degree of detailing of the model is not needed; and a traditional Monte Carlo method based on a model with sufficiently large cells can be used. The main task in the development of the physic and mathematical model of erosion of polymers and polymeric nanocomposites is the identification of the most important elementary processes and the determination of their probabilities. In the kMC method, necessary parameters of involved processes are determined on the basis of *ab initio* calculations, whereas for models with larger cells, they can be obtained from experimental data.

Currently there are several 2D and 3D MC models to simulate AO erosion in polymeric materials with complicated structure, including nanostructured materials.

6.4 Modelling of charging effects

6.4.1 General

The main task of studying charging effects in nanostructured materials is modelling of their electrical conductivity. This task is multiscale, too, and the following scales should be considered:

— quantum scale:

  electronic structure and electron transport, influence of defects and interfaces;

— atomistic scale:

  processes at interfaces due to nanoobject/matrix interaction;

— mesoscale:

  dispersion of nanosized fillers in a matrix to obtain the equilibrium structure of a nanocomposite;

— macroscale:

  electric current in the nanocomposite.

6.4.2 Quantum scale

Processes of electron transport are simulated for relatively small nanostructures with non-equilibrium Green function approach[44]. To determine the conductive properties of nanocomposites, it is important to take into account electron transport:

— within a nanostructure;

— between nanostructures in a close contact and at a given distance (tunnelling effects);

— between nanostructures within a non-conducting matrix.

Special features of electron transport modelling:

— usage of semi-empirical methods for simple homogeneous structures is possible but usage of the DFT is preferential;

— a simulation model should consist of a nanostructure and two semi-infinite electrodes (reservoirs).

The main approximations used within this approach are one-electron approximation, or the transport of many independent 'single' electrons, within linear response theory. This single-electron picture can turn out to be not valid in cases of strong electron-phonon scattering, screening and charging effects, or many particle interactions in magnetic systems, etc.[44].

6.4.3 Atomistic scale

The MD method is the main method to determine parameters of the filler/matrix interaction at interfaces and to use them for simulating equilibrium structure of nanocomposites at mesoscale (see 6.3.3).

MD modelling is useful to simulate crack formation in nanostructured materials caused by ESD.

6.4.4 Mesoscale

The mesoscale methods should be applied to determine the equilibrium structure of nanocomposites (see 6.3.4).

In general, two approaches are used:

— coarse-grained models (e.g. the DPD method) with the filler/matrix interaction parameters obtained with atomistic scale modelling (e.g. the MD method);

— MC models to determine the mutual arrangement of nanofillers within the material.

6.4.5 Macroscale

The methods of this group are used to simulate electric currents on the spacecraft surface (balance of currents), including electron and ion plasma, secondary emission and photo-induced currents.

The equilibrium structure of a nanocomposite obtained with mesoscale methods can be used for further calculations with continuum approaches (e.g. finite-difference method, boundary element method) which imply the homogeneous medium approximation within an integration cell. The mesoscale morphology is projected onto a finite-element grid; and the electrical conductivity of the nanostructured material is computed.

6.5 Modelling of heating/cooling and thermal cycling effects

6.5.1 General

The main task of studying heat transfer effects in nanostructured materials is modelling of their thermal conductivity. The thermal conductivity is mainly related to atomic vibrations (electronic part is important only under special conditions), so quantum scale is needed only for peculiar quantum effects, e.g. at very low temperatures of several Kelvins. Therefore, for spacecraft materials the following scales should be considered:

— atomistic scale:

  heat transfer through a nanostructure and a matrix, role of defects and interfaces, processes at interfaces due to nanoobject/matrix interaction;

— mesoscale:

  dispersion of nanosized fillers in a matrix to obtain the equilibrium structure of a nanocomposite;

— macroscale:

  heat transfer in the nanocomposite.

6.5.2 Atomistic scale

The MD method is the most important one to simulate heat transfer in nanostructures, matrices and nanostructured materials. It can be applied for different models, including models consisting of a nanostructure in a polymer/ceramic/metallic matrix to simulate directly process of heat transfer within such a model. In addition, this method is applied to calculate thermal expansion coefficients of different materials including nanostructured materials and to study destruction processes in contacting materials under thermal cycling.

The MD method is the main method to determine parameters of the filler/matrix interaction at interfaces and to use them for simulating equilibrium structure of nanocomposites at mesoscale (see 6.3.3).

MD modelling is useful to simulate crack formation in nanostructured materials caused by thermal cycling.

6.5.3 Mesoscale

The mesoscale methods should be applied to determine the equilibrium structure of nanocomposites (see 6.3.4).

In general, two approaches are used:

— coarse-grained models (e.g. the DPD method) with the filler/matrix interaction parameters obtained with atomistic scale modelling (e.g. the MD method);

— MC models to determine the mutual arrangement of nanofillers within the material.

6.5.4 Macroscale

The methods of this group are used to simulate heat transfer within materials of different composition.

The equilibrium structure of a nanocomposite obtained with mesoscale methods can be used for further calculations with continuum approaches (e.g. finite-difference method, boundary element method) which imply the homogeneous medium approximation within an integration cell. The mesoscale morphology is projected onto a finite-element grid; and the thermal conductivity of the nanostructured material is computed.

6.6 Modelling of meteoroids and space debris impact

6.6.1 General

Processes induced in nanostructured materials by hypervelocity hard particle impacts should be simulated at different spatial and temporal scales, too. Currently there are only a few examples of this approach since micrometeoroids and space debris particles are too large to be simulated with atomistic methods.

In this case the most important feature of nanostructured materials is special mechanisms of crater formation, crack propagation and heat transfer owing to the presence of nanosized objects inside the materials, so the following scales should be considered:

— atomistic scale:

  crater formation, crack propagation and heat transfer, role of defects and interfaces, processes at interfaces due to nanoobject/matrix interaction;

— mesoscale:

  crater evolution, crack propagation, dispersion of nanosized fillers in a matrix to obtain the equilibrium structure of a nanocomposite;

— macroscale:

  crater formation, destruction of material, heat transfer in the nanocomposite.

6.6.2 Atomistic scale

The MD method is the most important one to simulate crater formation, crack propagation, and heat transfer in nanostructures, matrices and nanostructured materials (see 6.5.2).

The MD method is the main method to determine parameters of the filler/matrix interaction at interfaces and to use them for simulating equilibrium structure of nanocomposites at mesoscale (see 6.3.3).