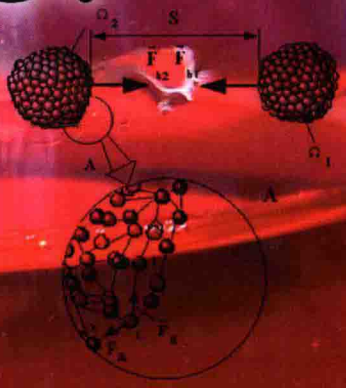
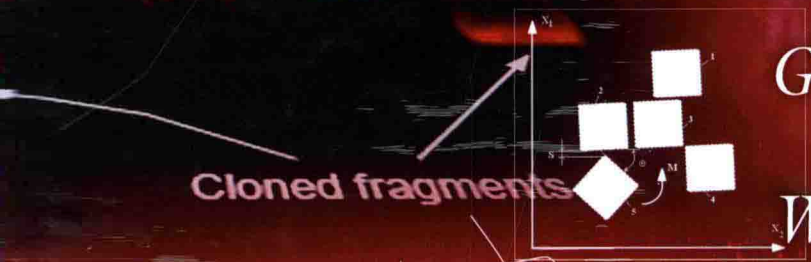
Quantitative Chemistry, Biochemistry and Biology

Steps Ahead





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Editors

Chemistry Research and Applications

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CHEMISTRY RESEARCH AND APPLICATIONS

QUANTITATIVE CHEMISTRY, BIOCHEMISTRY AND BIOLOGY

STEPS AHEAD

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STEPS AHEAD

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three winter months"
The proverb from
Perry, OH, US

"We live and enjoy ourselves"
Margarita Eskina

"Every person is born a genius"
J. Goethe

'The motivation of any scientific
discovery is craving for a flight.
It is enough to start a flight but for
the flight to be successful the recognition
of scientific authorities is absolutely inevitable"
Ahmed Zevile
Winner Noble Prize

PREFACE

The monk-Jesuit Escober proposed the slogan "The aim justifies the means". This slogan at large is not correct because it permits any action. However in our case this slogan is acceptable because our aim is to target a reader.

We collected the reviews and original papers about quantitative chemistry, biochemistry and biology. Special attention is given to new ideas in the fields of nanoelements formation and reactivity, synthesis of thermoplastic bio-based polyurethanes on the base of vegetable oils, carvacrol and thymol for fresh food packaging, polymer composites structure and electric properties, some properties of small water clusters in water-starch systems, solubility of aluminum polyhydroxochloride in the water-acetone solution, about diversified fenomena of entropy, quantitative calculation of spatial-energy interactions entropy, bacterial plasmids (cloning of multi-copy CpG motifs), using full-length diguanylate cyclase of Thermotoga Maritime for enzymatic synthesis of 3′,5′-cyclic diguanylate, nanocomposites polyethylene/organoclay on suprasegmental level (the reinforcement mechanism) and nanocomposites polypropylene/carbon nanotubes: fractal model and the crystallization kinetics. This volume also includes information about the segmental and translational movements of kinetic parameters, interaction of hydroxyorganocyclotetrasiloxanes with propyl butyrate side groups and polymer electrolyte membranes, UV-protective properties of nanocomposites films based on low density polyethylene, production, morphology, properties. Biodegradable compositions of starch with synthetic polymers and natural polysaccharides, kinetics and mechanism of the modificated starches during gelatinization, investigation of ethylene copolymers silanol modification, determining the surface free energy parameters, investigation of ethylene–vinylacetate copolymers binary mixtures

structure and investigation the kinetics and degradation mechanism of the tertiary hydroperoxides activated by the tetraethylammonium bromide.

We also decided to discuss the following topics: investigation of kinetics and mechanism of biologically awake antioxidants in reactions of esterification 2- (n-acetylamid)-3-(3 ', 5 '-*di-tert.butyl*-4 '-hydroxyphenyl)-propionic acid, the turbulent apparatus for oil neutralization, effect melaphen on a mitochondria of sprouts of peas under stressful influences by some methods, preparation of new antioxidants in reaction 2- (n-methylamide)-3- (3 ', 5 *'-di-tert.butyl*-4 '-hydroxyphenyl)-propionic acid and effect of external influences on the structural and dynamic parameters of polyhydroxybutyrate–hydroxyvalerate-based biocomposites.

Some chapters about quantum-chemical calculation of some molecules, the mechanism of protonation of isobutylene by method MNDO, geometrical and electronic structure of molecule 2-(2,2-dimethoxiethylsulfanil)-5-izopropyl-6-methyl pyrimidine-4(3h)-oh method MNDO, geometrical structure of some molecules aromatic olefins, composite materials based on LDPE with the addition of wood flour and rubbers of different nature, fungicidal influence of ions of Cu^{2+} on microorganisms as a way of biocorrosion protection of metal constructions, interfacial rheology of hen egg white lysozyme-5-methylresorcinol mixtures and their foaming properties, structure and thermophysical properties of blends based on isotactic polypropylene and low-density polyethylene, investigating the effect of fungies on thin films of polyethylene, polyethylene – poly-3-hydroxybutyrate and polyethylene – d_2w, determination of the identity of the signs of natural pomegranate juice, influence of carbon nanofibers on the structure and properties of vulcanized EPDM were included in this volume.

We also discuss the problems of determination diffusion coefficient of Brownian particles using velocity or force autocorrelation function in molecular dynamic simulations, in silico simulation of silver and copper ions interacting with fungal cell wall (in vitro antifungal activity of copper ions and silver ions) and the estimation of antioxidants as nuts quality index were included in this monograph as well, structure of soluble unlinked and cross-linked fibrin oligomers, kinetics and mechanism of the ozone reaction with alcohols, ketones, ethers and hydroxybenzenes, structure and antioxidative properties tert.butyl ester 3-(3 ', 5 '-di-tert.butyl-4 '-hydroxyphenyl)-propionic acid, comparative estimation of Kalanchoe juice antioxidant properties, the mechanism of the selective ethylbenzene oxidation, catalyzed with triple binuclear metallocomplex catalysts, including Ni and redox-inactive metal Na (or Li) (nanostructures {NiII(acac)2·NaSt(or LiSt)·(PhOH)}n formation due to intermolecular H-bonds) and quantum-chemical calculation studies the mechanism of protonation of 4-methylpentene-1, 4-methylhexene-1 and 4,4-dimethylpentene-1 by method MNDO.

The editors and contributors will be happy to receive some comments from the readers which we can take in account in our future research.

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CONTENTS

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Chapter 1

NEW IDEAS IN THE FIELD OF NANOELEMENTS FORMATION AND REACTIVITY

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INTRODUCTION

The properties of a nanocomposite are determined by the structure and properties of the nanoelements, which form it. One of the main tasks in making nanocomposites is building the dependence of the structure and shape of the nanoelements forming the basis of the composite on their sizes. This is because with an increase or a decrease in the specific size of nanoelements (nanofibers, nanotubes, nanoparticles, etc.), their physical-mechanical properties such as coefficient of elasticity, strength, deformation parameter, etc. are varying over one order [1 – 5].

The calculations and experiments show that this is primarily due to a significant rearrangement (which is not necessarily monotonous) of the atomic structure and the shape of the nanoelement. The experimental investigation of the above parameters of the nanoelements is technically complicated and laborious because of their small sizes. In addition, the experimental results are often inconsistent. In particular, some authors have pointed to an increase in the distance between the atoms adjacent to the surface in contrast to the atoms inside the nanoelement, while others observe a decrease in the aforementioned distance [6].

Thus, further detailed systematic investigations of the problem with the use of theoretical methods, i.e. mathematical modeling, are required.

The atomic structure and the shape of nanoelements depend both on their sizes and on the methods of obtaining which can be divided into two main groups:

1) Obtaining nanoelements in the atomic coalescence process by "assembling" the atoms and by stopping the process when the nanoparticles grow to a desired size (the

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so-called "bottom-up" processes). The process of the particle growth is stopped by the change of physical or chemical conditions of the particle formation, by cutting off supplies of the substances that are necessary to form particles, or because of the limitations of the space where nanoelements form.

2) Obtaining nanoelements by breaking or destruction of more massive (coarse) formations to the fragments of the desired size (the so-called "up down" processes).

In fact, there are many publications describing the modeling of the "bottom-up" processes [7-8], while the "up down" processes have been studied very little. Therefore, the objective of this work is the investigation of the regularities of the changes in the structure and shape of nanoparticles formed in the destruction ("up down") processes depending on the nanoparticle sizes, and building up theoretical dependences describing the above parameters of nanoparticles.

When the characteristics of powder nanocomposites are calculated it is also very important to take into account the interaction of the nanoelements since the changes in their original shapes and sizes in the interaction process and during the formation (or usage) of the nanocomposite can lead to a significant change in its properties and a cardinal structural rearrangement. In addition, the experimental investigations show the appearance of the processes of ordering and self-assembling leading to a more organized form of a nanosystem [9-15]. In general, three main processes can be distinguished: the first process is due to the regular structure formation at the interaction of the nanostructural elements with the surface where they are situated; the second one arises from the interaction of the nanostructural elements with one another; the third process takes place because of the influence of the ambient medium surrounding the nanostructural elements. The ambient medium influence can have "isotropic distribution" in the space or it can be presented by the action of separate active molecules connecting nanoelements to one another in a certain order. The external action significantly changes the original shape of the structures formed by the nanoelements. For example, the application of the external tensile stress leads to the "stretch" of the nanoelement system in the direction of the maximal tensile stress action; the rise in temperature, vice versa, promotes a decrease in the spatial anisotropy of the nanostructures [10]. Note that in the self-organizing process, parallel with the linear moving, the nanoelements are in rotary movement. The latter can be explained by the action of moment of forces caused by the asymmetry of the interaction force fields of the nanoelements, by the presence of the "attraction" and "repulsion" local regions on the nanoelement surface, and by the "non-isotropic" action of the ambient as well.

The above phenomena play an important role in nanotechnological processes. They allow developing nanotechnologies for the formation of nanostructures by the self-assembling method (which is based on self-organizing processes) and building up complex spatial nanostructures consisting of different nanoelements (nanoparticles, nanotubes, fullerenes, super-molecules, etc.) [15]. However, in a number of cases, the tendency towards self-organization interferes with the formation of a desired nanostructure. Thus, the nanostructure arising from the self-organizing process is, as a rule, "rigid" and stable against external actions. For example, the "adhesion" of nanoparticles interferes with the use of separate nanoparticles in various nanotechnological processes, the uniform mixing of the nanoparticles from different materials and the formation of nanocomposite with desired properties. In connection with this, it is important to model the processes of static and dynamic interaction

of the nanostructure elements. In this case, it is essential to take into consideration the interaction force moments of the nanostructure elements, which causes the mutual rotation of the nanoelements.

The investigation of the above dependences based on the mathematical modeling methods requires the solution of the aforementioned problem on the atomic level. This requires large computational aids and computational time, which makes the development of economical calculation methods urgent. The objective of this work was the development of such a technique.

This chapter gives results of the studies of problems of numeric modeling within the framework of molecular mechanics and dynamics for investigating the regularities of the amorphous phase formation and the nucleation and spread of the crystalline or hypocrystalline phases over the entire nanoparticle volume depending on the process parameters, nanoparticles sizes and thermodynamic conditions of the ambient. Also the method for calculating the interactions of nanostructural elements is offered, which is based on the potential built up with the help of the approximation of the numerical calculation results using the method of molecular dynamics of the pairwise static interaction of nanoparticles. Based on the potential of the pairwise interaction of the nanostructure elements, which takes into account forces and moments of forces, the method for calculating the ordering and self-organizing processes has been developed. The investigation results on the self-organization of the system consisting of two or more particles are presented and the analysis of the equilibrium stability of various types of nanostructures has been carried out. These results are a generalization of the authors' research in [16-24]. A more detailed description of the problem you can obtain in these works.

1. Problem Statement and Modelling Technique

The problem on calculating the internal structure and the equilibrium configuration (shape) of separate non-interacting nanoparticles by the molecular mechanics and dynamics methods has two main stages:

1) The "initiation" of the task, i.e., the determination of the conditions under which the process of the nanoparticle shape and structure formation begins.
2) The process of the nanoparticle formation.

Note that the original coordinates and initial velocities of the nanoparticle atoms should be determined from the calculation of the macroscopic parameters of the destructive processes at static and dynamic loadings taking place both on the nano-scale and on the macro-scale. Therefore, in the general case, the coordinates and velocities are the result of solving the problem of modeling physical-mechanical destruction processes at different structural levels. This problem due to its enormity and complexity is not considered in this paper. The detailed description of its statement and the numerical results of its solution are given in the works of the authors [16-19].

The problem of calculating the interaction of ordering and self-organization of the nanostructure elements includes three main stages: the first stage is building the internal

structure and the equilibrium configuration (shape) of each separate non-interacting nanostructure element; the second stage is calculating the pairwise interaction of two nanostructure elements; and the third stage is establishing the regularities of the spatial structure and evolution with time of the nanostructure as a whole.

Let us consider the above problems in sequence.

1.1. The Calculation of the Internal Structure and the Shape of the Non-Interacting Nanoelement

The initialization of the problem is in giving the initial coordinates and velocities of the nanoparticle atoms

$$\vec{\mathbf{x}}_i = \vec{\mathbf{x}}_{i0}, \vec{\mathbf{V}}_i = \vec{\mathbf{V}}_{i0}, t = 0, \vec{\mathbf{x}}_i \subset \Omega_k, \tag{1}$$

where $\vec{\mathbf{x}}_{i0}, \vec{\mathbf{x}}_i$ are original and current coordinates of the i-th atom; $\vec{\mathbf{V}}_{i0}$, $\vec{\mathbf{V}}_i$ are initial and current velocities of the i-th atom, respectively; Ω_k is an area occupied by the nanoelement.

The problem of calculating the structure and the equilibrium configuration of the nanoelement will be carried out with the use of the molecular dynamics method taking into consideration the interaction of all the atoms forming the nanoelement. Since, at the first stage of the solution, the nanoelement is not exposed to the action of external forces, it is taking the equilibrium configuration with time, which is further used for the next stage of calculations.

At the first stage, the movement of the atoms forming the nanoparticle is determined by the set of Langevin differential equations at the boundary conditions (1) [25]

$$\begin{aligned} m_i \cdot \frac{d\vec{\mathbf{V}}_i}{dt} &= \sum_{j=1}^{N_k} \vec{\mathbf{F}}_{ij} + \vec{\mathbf{F}}_i(t) - \alpha_i m_i \vec{\mathbf{V}}_i, \qquad i = 1,2,..,N_k, \\ \frac{d\vec{\mathbf{x}}_i}{dt} &= \vec{\mathbf{V}}_i, \end{aligned} \tag{2}$$

where N_k is the number of atoms forming each nanoparticle; m_i is the mass of the i-th atom; α_i is the "friction" coefficient in the atomic structure; $\vec{\mathbf{F}}_i(t)$ is a random set of forces at a given temperature which is given by Gaussian distribution.

The interatomic interaction forces usually are potential and determined by the relation

$$\vec{\mathbf{F}}_{ij} = -\sum_{1}^{n} \frac{\partial \Phi(\vec{\boldsymbol{\rho}}_{ij})}{\partial \vec{\boldsymbol{\rho}}_{ij}}, \; i = 1,2,...,N_k, \; j = 1,2,...,N_k, \tag{3}$$

where $\vec{\boldsymbol{\rho}}_{ij}$ is a radius-vector determining the position of the i-th atom relative to the j-th atom; $\Phi(\vec{\boldsymbol{\rho}}_{ij})$ is a potential depending on the mutual positions of all the atoms; n is the number of interatomic interaction types.

In the general case, the potential $\Phi(\vec{\rho}_{ij})$ is given in the form of the sum of several components corresponding to different interaction types:

$$\Phi(\vec{\rho}_{ij}) = \Phi_{cb} + \Phi_{va} + \Phi_{ta} + \Phi_{pg} + \Phi_{vv} + \Phi_{es} + \Phi_{hb}. \quad (4)$$

Here the following potentials are implied: Φ_{cb} - of chemical bonds; Φ_{va} - of valence angles; Φ_{ta} - of torsion angles; Φ_{pg} - of flat groups; Φ_{vv} - of Van der Waals contacts; Φ_{es} - of electrostatics; Φ_{hb} - of hydrogen bonds.

The above addends have different functional forms. The parameter values for the interaction potentials are determined based on the experiments (crystallography, spectral, calorimetric, etc.) and quantum calculations [25].

Giving original coordinates (and forces of atomic interactions) and velocities of all the atoms of each nanoparticle in accordance with equation (2), at the start time, we find the change of the coordinates and the velocities of each nanoparticle atoms with time from the equation of motion (1). Since the nanoparticles are not exposed to the action of external forces, they take some atomic equilibrium configuration with time that we will use for the next calculation stage.

1.2. The Calculation of the Pairwise Interaction of the Two Nanostructure Elements

At this stage of solving the problem, we consider two interacting nanoelements. First, let us consider the problem statement for symmetric nanoelements, and then for arbitrary shaped nanoelements.

First of all, let us consider two symmetric nanoelements situated at the distance S from one another (Figure 1) at the initial conditions

$$\vec{\mathbf{x}}_i = \vec{\mathbf{x}}_{i0}, \vec{\mathbf{V}}_i = 0, t = 0, \vec{\mathbf{x}}_i \subset \Omega_1 \bigcup \Omega_2 , \quad (5)$$

where Ω_1, Ω_2 are the areas occupied by the first and the second nanoparticle, respectively.

We obtain the coordinates $\vec{\mathbf{x}}_{i0}$ from equation (2) solution at initial conditions (1). It allows calculating the combined interaction forces of the nanoelements

$$\vec{\mathbf{F}}_{b1} = -\vec{\mathbf{F}}_{b2} = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \vec{\mathbf{F}}_{ij} , \quad (6)$$

where i, j are the atoms and N_1, N_2 are the numbers of atoms in the first and in the second nanoparticle, respectively.

Forces $\vec{\mathbf{F}}_{ij}$ are defined from equation (3).