

## **The direct simulation Monte-Carlo of clusters formation process in a magnetron-type generator**

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Formation and growth of clusters during diffusion of flow of metal atoms with energies of 1-100 eV towards a flat surface through slow flow of cold argon have been studied by the Direct Monte-Carlo Simulation method (DSMC). The problem approximately simulates processes in a magnetron-type generator of clusters [1].

The model of clusters formation for DSMC method describes a consecution of reactions leading to formation and growth of particles [2]. Both elastic and inelastic processes are considered. The simulation of elastic collisions is based on the variable hard sphere model. Inelastic processes include three body atomic recombination resulting in dimer formation, association processes at atom-cluster and cluster-cluster collisions, and processes of particles destruction. The cluster is characterized by the number of atoms in it, collision cross-section, binding energy, translational and internal energies.

Diffusion of niobium through argon and deposition on a flat cold surface have been considered. The main peculiarities of clusters growth under considered condition have been investigated.

This work was supported by the INTAS grant (N 03-51-5208)

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## Calculation of the electronic structure of carbon nanomaterials affected by pressure

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The unique properties of carbon nanomaterials, resulting from quantum dimensions, take the big attention of the researchers. Last experimental works on registration of changing of the electronic structure of carbon nanomaterials depending on values of the external pressure lead to necessity to carry out more careful theoretical researches in the given area.

In this paper, an ab initio calculations of the electronic structure for different geometries of single-wall carbon nanotubes and graphite nanoribbons of various width has been performed. The density functional theory with pseudo-potential method was used for the calculations. The electronic structure has been modelled for isolated nanotubes, nanotubes aggregated in rouples, isolated graphite nanoribbons and ribbons in the sample with interaction with neighbours. Also the computer modelling of the dependence the electronic structure upon varying pressure for nanotubes and nanoribbons has been performed.

The results of the calculations show that the pressure increase leads to the decrease of energy of allowed optical transitions in the nanomaterials. This result corresponds to the experimental data published [1]. It allows to consider carbon nanotubes and nanoribbons as nonlinear optical elements with characteristics precisely arranged in a small range.

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## Silicon nanowire junctions: a theoretical prediction of atomic structure and electronic properties

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At present a number of perfect 0D (quantum dots or QD) and 1D (nanowires or NW) silicon nanostructures are synthesized under high temperature conditions. Mostly the surface of such nanostructures is covered by hydrogen. All silicon nanostructures with saturated surface dangling bonds display pronounced semiconducting properties. The surface tension caused by different type of interfaces or formation of surface dimers can cause the closing of semiconducting band gap of *nc*-silicon. It was shown that nanostructures without saturation of surface dangling bonds demonstrate pronounced metallic conductivity.

Like heterojunctions of the nanotubes with different transport properties, a combination of metallic NWs with semiconducting ones with different band gap widths and types of conductivity caused by different surface saturation groups around central IQD in one SiNF can serve as a background in developing of big variety of nanoelectronic devices. To study the electronic structure of such complex SiNF structures we designed and calculated by semi-empirical method a set of small nanoflowers based on the Si<sub>20</sub> dodecahedron and 3 PP(1)s.

Combination of the different numbers of PPs with a single IQD produces a set of perfect pristine silicon nanostructures look like flowers (SiNFs) or stars. The atomic structure of the objects was optimized using empirical potential due to the large size (in order of thousand atoms) of even smallest SiNF structures.

The proposed 2D SiNW/SiIQD structures can be used as springs and other mechanic-electrical parts in the nanomechanical devices and micromachines. The SiNFs and SiNW/SiIQD structures can be used as a filling agent for increasing strength of different composites due to their structural features.

This work was partially supported by project “Materials Design with New Functions Employing Energetic Beams” and JAEA Research fellowship, by the Russian Foundation for Basic Research (project no. 05-02-17443) and Deutsche Forschungsgemeinschaft/ Russian Academy of Sciences (DFG/RAS, project no. 436 RUS 113/785).

## Carbon nanotube production from the waste of chemical industries and accessible reagents

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We succeeded in developing several new technologies of the multiwall nanotube (MWNT) production. The separation of MWNTs from the electrochemical alkali metal production waste (slum) and the self-propagating high temperature synthesis (SHS) from easily accessible chemical reagents are among them.

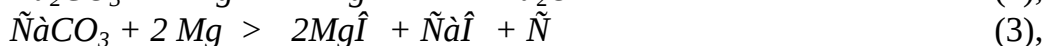
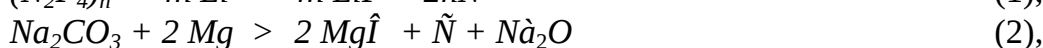
In the researched industrial alkali metal production by the electrolysis of melted salts the raw material was the lithium- and potassium chloride eutectics.

The size of the industrial electrochemical salt bath is larger than that of the laboratory electrochemical cell about two orders of magnitude. Together with the long "company period" of the bath (1-1.5 years) this fact enables to accumulate the MWNTs which are formed during the electrolysis. The total mass of carbon component of the slum reaches 300 kg during the "company period", the mass of nanotubes is about some tens of kg.

The analysis of the samples, obtained from different regions of the bath, showed the presence of MWNT of (10-40)nm in diameter and ~ (1-2) μm length. A substantial part of MWNT had opened ends. This fact points to the prospects of the investigation of these MWNTs as applied to the catalysis problems: as electrode material for lithium batteries and oxidation membranes of fuel elements.

The specific character of nanotubes stimulated the development of specific mechanism for their formation, different from the VLS-mechanism [1].

A different way for the nanotube production is SHS, i.e. the reaction, caused by a local heat impulse. Then the reaction is propagated farther owing to the heat discharge in the reaction zone. One of the initial products must be the carbon carrier, the second one must be the carbon reducing-agent, e.g.



The experiments showed that with the presence of catalysts (e.g. nickel in the form of NiO) the reactions (2), (3) generate the nanocarbon-containing material, which consisted of both MWNTs and carbon nanofibers of several μm length. The content of the MWNTs and the nanofibers was estimated of about 30% of the reduced carbon. Besides that, nanosize globular carbon structures, similar with the technical carbon black, were also observed.

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## Modelling of one-dimensional conjugated subsystems in single-walled carbon nanotubes

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Presence of conjugated  $\pi$ -electron system in single-walled carbon nanotubes (SWCNTs) is a physical base for display the unique properties. Creation of anisotropic environment in SWCNT by means of their modification can open novel perspectives of practical applications of such nanostructures. In [1] was shown that the fluorine atom adsorption on SWCNT surface leads to formation of isolated polyacetylene chains. Regular hydrogenation of SWCNTs initiates creation of quasi-independent  $\pi$ -conjugated subsystems which can be represented by polyphene or poly(*peri*-acene) macromolecules [2].

In the present paper different approaches to modelling of conjugated one-dimensional subsystems are applied to SWCNTs with chirality indexes (6,0) and (8,0) which consist of 132 (12) and 176 (16) carbon (terminal hydrogen) atoms, respectively. Calculations are performed in semiempirical AM1 scheme. The surface of SWCNTs is modified by regular adsorption of fluorine atoms. The various ways of decoration form carbon subsystems of different topology. A degree of conjugation in the formed subsystem estimated by means of Wiberg indexes [3]. The results obtained indicate that formation of isolated polyacetylene-like *cis*- and *trans*-chains, as well as polyacene and polyphene subsystems, are possible depending on fluorine atom arrangement on SWCNT surface.

Moreover, the influence of formed one-dimensional subsystems on energy properties of modified SWCNTs are investigated. Adsorption energy ( $E_{\text{ads}}$ ) per fluorine atom and change in band gap ( $E_{\text{gap}}$ ) of modified SWCNTs relatively to initial carbon nanotube are calculated. It is shown that adsorption energy  $E_{\text{ads}}$  and band gap width  $E_{\text{gap}}$  decrease with increasing of conjugation degree in formed one-dimensional subsystems.

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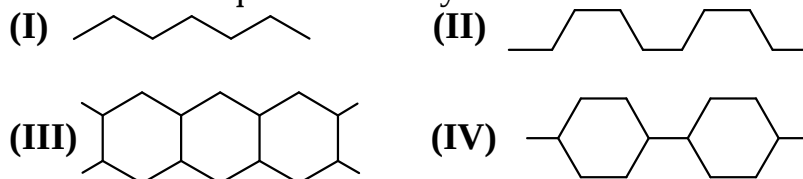
## Chemisorption modification of conjugated p-electron system of graphene

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The potential of practical applications of carbon 2D-allotrope, – graphene [1], – determined by regularities of its conjugated  $\pi$ -electron system structure. In view of this fact the problem of graphene modification takes on special significance with the purpose to generate 1D subsystem. An anisotropy of the graphene  $\pi$ -electron system can be achieved by creation of regular dislocations [2], and also by the regular doping atom chemisorption on graphene.

In the present paper we study the regularities of conjugated 1D subsystems generation caused by atomic chemisorption of fluorine and hydrogen on the graphene surface. The latter is modeled by molecular clusters consisting of  $\sim 200$  carbon atoms. The electronic structure calculations are performed in the framework of PM3 method with geometry optimization. The various manners of graphene surface decoration are considered in which the following detached 1D and quasi-1D subsystems exist:



To explore conjugation character in these subsystems the Wiberg indexes and the Mulliken population analysis was used. The results obtained demonstrate that decoration manners resulting in subsystems (I) and (II) generate 1D subsystems of *trans*- and *cis*-polyacetylene type, respectively. The subsystem (III) can be considered as pair of carbon chains of polyene type connected to each other by single C–C bonds, whereas (IV) has the main features of electronic structure of polyphenylene. Thus conjugation character in subsystems (I)–(IV) is sufficiently adequate to corresponding macromolecules.

It is found that conjugation properties depend on adsorbed atom concentration in considered types of the regular adsorption. It is shown that structure of the conjugated 1D subsystems formed by chemisorption control over band gap in electronic spectra that opens up possibilities for tuning the electronic transport properties.

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## Molecular dynamics study of fullerene behavior in different solutions

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The tendency for high aggregation of fullerene  $\tilde{N}_{60}$  molecules is well-known, even the introduction of substituents containing ionic groups into the fullerene core do not always hinder their association and formation of supramolecular clusters. At the same time physical, chemical and biological properties of isolated molecules and those in the aggregates can differ significantly.

It is possible to estimate the aggregation degree and the solubility of fullerenes in different media not only experimentally, but also by means of computer simulation methods, analyzing the changes in the mean force potential (PMF is the interaction energy of the solute molecules in the presence of the solvent) caused by the replacement of the solvent. The advantage of such approach is the possibility to predict the degree of solvation of different fullerene derivatives in different solvents even before the synthesis of such substances.

Second osmotic virial coefficients  $B_2$  and mean force potentials PMF are calculated in the present work using molecular dynamics method for fullerene  $\tilde{N}_{60}$  molecules in n-hexane, carbon disulphide and water – three solvents with quite different solvency for fullerene. The estimated values of  $B_2$  change in accordance with the experimentally defined regularities of fullerene solubility in the solvents under consideration. Peculiarities in PMF (mostly, the potential depth in comparison to the average energy of the thermal motion) allow us to define the states of fullerene molecules in the studied solutions and to explain the sensitivity of different fullerene solutions to such perturbation effects as shaking, stirring, the way of preparation, etc.

## ***Ab initio* molecular dynamics studies on the thermodynamics and cluster collision of fullerenes**

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Fullerenes are exciting new forms of carbon existence and subjected to intensive investigations since their discovery in 1985. The thermodynamic property and collision between fullerenes are among the most interested aspects in these investigations both from experimental and theoretical considerations. However, many questions in the field are still awaiting clarification including the exact formation mechanism of fullerenes.

There have been many research publications in the thermodynamic property of fullerenes by classical molecular dynamics simulation. Since the configuration variation of fullerenes involves bond change and orbit recombination of electrons, it is will be more informative to study the problem by the first-principles simulation in the base of quantum mechanics theory. In this work, we study the thermodynamic behavior and cluster collision of fullerenes by *ab initio* Car-Parrinello molecular dynamics simulation [1]. Our calculation is performed using the CPMD code [2]. The interaction between carbon nuclei and the core electrons is described by Vanderbilt ultra-soft pseudopotential [3] to speed up the calculation. The cluster temperature is increased from 1500K to 4500K. The variations in the bond's length and angle are inspected during the procedure to check the structure transformation and melting of fullerene clusters. The collisions of two or more fullerene clusters are simulated under different temperature, injecting angle and initial velocity. The patterns of melting and formation-by-collision of fullerenes are summarized.

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## Migration mechanism and thermodynamics of He atom dopant in the C<sub>60</sub> lattice

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Intercalation of C<sub>60</sub> with species that are not expected to form chemical bonds with fullerene molecules, such as rare gases and simpler close-shell light-mass molecules was extensively investigated. Helium in this respect presents a big advantage due to its high mobility and permeability into the C<sub>60</sub> lattice.

Our recent x-ray diffraction experiments revealed a few new unusual properties of this system. In order to properly understand the new findings, the thermodynamics of He intercalation into C<sub>60</sub> at room temperature has been constructed to show that the main thermodynamic force that at room temperature and low pressures drives He atoms into the fullerite C<sub>60</sub> interstitial sites is *entropy* rather than van-der-Waals binding. The potential energy profiles of a He atom in octahedral (O) and tetrahedral (T) cavities of C<sub>60</sub> were calculated to show that the energy barrier for the O-to-O path is prohibitively high and practically rules out direct migration of He atoms between O sites. On the other hand, the O-to-T and return pathways are easy to follow, thus, the passage of He atoms from an O-site to another O-site occurs via intermediate high-energy T-sites, while the T voids occupancy is temporary. When the occupancy of O-voids approaches completeness, T-sites start to get occupied. The calculated potential well of He atoms in O cavity is wide enough to treat the He atom in an O cavity as a “pea in a rattle toy”. In that model the internal pressure the helium atom exerts on the octahedral cage walls due to the kinetic energy was evaluated as 1 kbar. The value of lattice expansion calculated from this internal pressure and the fullerite compressibility is in good agreement with our room-temperature experiment.

## **Influence of bordering functional groups on processes of capillary filling of single-wall tubulenes with elemental hydrogen**

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The rates of hydrogen power engineering development are increasing dramatically. Hydrogen energy can be widely applied and used in different spheres starting with space exploration and ending with creation of environmentally friendly car fuel. That's why one should focused on the prospect and possibility of using single-wall nanotubes as reservoir for storing hydrogen.

In our research we examined molecular clusters of half-infinite single-wall carbon nanotubes type  $(n, n)$  and  $(n, 0)$ ,  $n = 6, 8$ . One end of a cluster was enclosed by pseudo-atoms, and the other end was enclosed by functional groups: oxygen atoms ( $-O-$ ); hydroxyl groups ( $-OH$ ); amides ( $-NH_2$ ). MNDO-based calculations of process of modified tubulenes filling with elemental hydrogen were carried out.

"Capillary" way of hydrogen atom penetration into nanotubes was examined. The process of filling of the chosen tubulenes with elemental hydrogen was modeled by moving H atom step-by-step towards the saturated with functional groups nanotube butt-end along its main longitudinal axis till the H atom would penetrate into nanotube.

The surface profiles of H atom potential energy of penetration into nanotube were drawn and potential barriers that H atom overpassed while penetrating were defined. It was revealed that the process of H penetration into tubes  $(6,0)$  enclosed by six amides ( $-NH_2$ ) and hydroxyl groups ( $-OH$ ) is going without any barrier. The formed complex is stable. So one can assert that these enclosing groups provide effective capillary filling of the tubulenes with hydrogen atoms because forces of electrostatic interaction arise. It is defined that H atom penetration into nanotubes saturated with three or six oxygen atoms is going on in a classical way and the potential barrier of  $\sim 2$  eV is overpassed. H atom penetration into tube enclosed with three amides  $3(NH_2)$  is going without barrier, although the formed system is metastable. H penetration into tubulenes  $(8,0)$  modified with amides and hydroxyl groups is going on without barrier, although the process is metastable.

It is found out that modified tubulenes  $(n, n)$  provide more effective filling of tubulenes with elemental hydrogen (the process is stable and goes without barrier).

Analysis of nanotubes modified with (O) atoms and these nanotubes length influence on the process of H penetration revealed the fact that the less the bordering saturation of the tubulene  $(8,0)$ , the more active the process of H penetration into tube cavity.

## On the stability 6,6- and 5,6 - closed and open adducts of fullerene $\tilde{N}_{60}$

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Reactions of cycloaddition of organic reagents with fullerenes can give hypothetically four types of adducts with preservation or breaking of single or double bonds (5,6-or 6,6-closed or open) on fullerene sphere, but structures of the obtained products are not so various. What of four types adduct can be obtained, what are not, what researches will be successful are not clear yet.

We are carried out theoretical research of stable isomers of fullerene  $\tilde{N}_{60}$  adducts with various reagents which can lead to formation of 3-, 4, 5-or 6-membered rings or acyclic structures on fullerene sphere. Cross-sections of potential energy surface (PES) of adducts are investigated by DFT/PBE method at a variation of 5,6- or 6,6- bonds lengths. Basis on the analysis of local minima on PES a conclusion is drawn, whether those or other structures are stable, unstable, or can not be obtained at all.

The 6,6-closed adducts of fullerenes with strained 3-member cycles (methano-, aziridinofullerenes and etc.) and their 5,6-opened isomers are found to be stable. Except for extreme cases 6,6-opened and 5,6-closed isomers have no local minima. Acyclic and the cyclic derivatives containing 4, 5-or 6-membered rings that fused to fullerene case are established to form only closed adducts. Thus the 6,6-closed structures are more stable then 5,6-closed (15-20 kcal/mole). Contrary, opened 5,6 and 6,6 isomers of these adducts have no minima on PES and, accordingly, don't synthesis else.

It is shown, that structures of four types adducts cardinaly differ, but different addends uniformly transform every type structures, the lengths 5,6- and 6,6- bonds of monoadducts are characterized stability of 6,6 and 5,6 bisadducts. The factors, influencing on relative stability and electron affinity of mono-and bisomers are investigated. Theoretical results are applied to an explanation of experimental dates and prognoses.

The calculations were performed on the Supercomputer Centre of KSC RAS. Financial support Department of Chemistry and Material Sciences of the RAS (Program 7) is gratefully acknowledged.