

# Clusterization and spontaneous polarization in thin Lengmuir – Blodgett films with modified multi-walled carbon nanotubes

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It was accomplished electron microscopy structural investigations of modified multi-walled carbon nanotube clusters formed by Lengmuir – Blodgett technology. It was revealed helical structure for these clusters and it was proposed a mechanism of its origin. A mathematical description of spontaneous polarization process in such structures was carried out.

**Keywords:** spontaneous polarization, Lengmuir – Blodgett monolayer, carbon nanotube

## 1. Introduction

The ordered arrays of carbon nanotubes (CNT) are perspective materials for nanoelectronic devices [1, 2]. In a given work high-ordered arrays of CNTs were fabricated by the Lengmuir – Blodgett (LB) technology.

At present time mathematical description of polarization of such structures was not carried out. To describe a process of redistribution of electronic density over nanotube, a theory developed in [3] will be used further. It was supposed that difference of energies of  $i$ -th and  $j$ -th sites of nanotube and difference of chemical potentials are small:  $E_{c,i} - E_{v,j} \ll 1$  and  $|\mu_i - \mu_j| \ll 1$ . Therefore to describe diffusion of particles we can utilize the expression for chemical diffusion coefficient in sites  $i$  and  $j$  [3]

$$D_{ij}^{ch} = \frac{1}{2} \lim_{i \rightarrow j} \left( \beta \epsilon - 1 \pm e^{\beta \mu_j} \right) e^{\beta \mu_i} \langle (1 - N_i) \rangle \frac{\beta}{[1 \mp \exp(\beta \mu_j)]^2}, \quad (1)$$

where  $\epsilon = E_{m,j} - E_{n,i} = E_m - E_n = \hbar \omega_{mn}$  is the energy of quasiparticle which lattice sites exchange in the interaction process. From here the integrated expression for chemical diffusion coefficient follows  $\overline{D}_{ch}$

$$\overline{D}_{ch} = \lim_{\vec{r}_j \rightarrow \vec{r}_i} \frac{z b^2}{2 d Z} \int Dq(t; \vec{r}_j) e^{\beta \mu_i} \left( \beta \epsilon - 1 \pm e^{\beta \mu_j} \right) \times (1 - N_i) e^{-\beta H(q(\vec{r}_j))} \beta / \left( 1 \mp e^{\beta \mu_j} \right)^2, \quad (2)$$

where  $\int Dq(t; \vec{r}_j)$  is the integral over trajectories on a lattice, physical meaning of  $q$  is a mean occupation number,  $d$  is a dimension,  $z$  is a number of nearest neighbors,  $b$  is a lattice constant,  $Z$  is a statistical sum.

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The displacement of Fermi sphere leads to a creation of negatively and positively charged quasi-particles (electron – hole pairs) simultaneously [4]. Therefore, by virtue of identity of atoms and also by virtue of translational invariance of the problem, a transfer of excitation having boson type can be described by the diffusion coefficient determined by the expression (2) at a choice of the top sign. Localization of a electron (hole) of a pair leads to that the atom without electron moves, and the transfer process should be described as a transfer of quasiparticle excitations having fermion type. In [3] it was shown that for fermion dynamics of transfer of quasiparticle excitations the diffusion coefficient can be negative. Physical sense of this is that owing to attraction of opposite charges the atom trends to locate in a vicinity of the localized charge.

The goal of the paper is to develop methods to form high-ordered LB-clusters of CNT, to make structural investigations and to carry out the mathematical description of the polarization processes in such structures.

## 2. Formation of LB-CNT-clusters

Clusters from multi-walled unmodified and modified carbon nanotubes being in a monolayer of stearic acid were fabricated by LB-technology. Diameter of multi-walled CNTs lays within the limits of 20 ÷ 50 nm. The carbon nanotubes have been modified hydroxyl and carboxyl groups and were dissolved in distilled water. In the obtained water suspension the carbon nanotubes were in a suspension state in concentration of 50 mg/ml. Before modification the lengths of CNTs were in the interval 50 ÷ 100 micron.

LB-monolayers have been formed under various thermodynamic conditions and speed regimes, and also on various subphases prepared by bidistilled water. Previously CNTs were dried and exposed to ultrasonic treatment in hexane.  $\pi - S_{mol}$ -isotherm which shows a state of stearic acid monolayer with unmodified carbon nanotubes changes at compression speed of barrier  $v = 3$  mm/min, at temperature  $T=17^\circ$  and equals to 2.0, is represented in fig. 1 a. Here  $\pi$  is a surface pressure,  $S_{mol}$  is an area per one molecule of stearic acid. In this case the limiting molecular area  $S_{mol}$  is  $35 \text{ \AA}^2$  /molecule, and a pressure of collapse for the monolayer is about 35 mN/m. It means, that the massive nanotubes have time to be reoriented and formation of LB-clusters with carbon nanotubes occurs.

Elastic properties of the stearic acid LB-monolayers with CNTs and with incorporated ions of metal from a subphase have been investigated. For this purpose, compressibility of the monolayers was estimated on their module of compression (elasticity) obtained from the data of  $\pi - S_{mol}$ -isotherms. The elasticity module for stearic acid LB-monolayers, equal on average to  $12 \text{ mN}/(\text{m} \cdot \text{\AA}^2)$  at  $v = 3$  mm/min, depends weakly on compression speed that is caused by large diffusion coefficient for relatively small molecules of a stearic acid. Opposite, the elasticity module for stearic acid LB-monolayers with CNTs depends on compression speed. It is stipulated by slow diffusion processes with participation of massive unmodified CNTs. At large speeds value of their elasticity module  $k$  (about  $9 \text{ mN}/(\text{m} \cdot \text{\AA}^2)$ ) comes near to the value for the stearic acid LB-monolayer. At small speeds, as a result of formation of LB-clusters from stearic acid molecules and unmodified CNTs the elasticity module of the monolayers sharply decreases (on average up to  $3.3 \text{ mN}/(\text{m} \cdot \text{\AA}^2)$ ). One reduced silver in a mixture from unmodified CNTs and salt  $\text{Ag}(\text{NO}_3)_3$  and then used a produced material to form LB-monolayers. Value of elasticity module  $k$  of these monolayers increases on average up to  $5.5 \text{ mN}/(\text{m} \cdot \text{\AA}^2)$  for medium  $\sim 6.0$ . Influence of subphase on parameters of LB-monolayer with modified CNTs has been studied. For a solution of salt  $\text{Ce}_2(\text{SO}_4)_3$ , the pressure of collapse for stearic acid LB-monolayer without CNTs was measured as 50 mN/m, and the limiting molecular area was  $S_{mol}=38 \text{ \AA}^2$  /molecule (fig. 1 b). At formation

of LB-monolayer from modified CNTs and molecules of stearic acid on the subphase with  $\text{Ce}_2(\text{SO}_4)_3$ , the pressure of collapse was 52 mN/m, and the limiting molecular area was  $S_{mol}=34 \text{ \AA}^2/\text{molecule}$  (fig. 1 c). Since the limiting molecular area has same order or less in comparison with unmodified CNTs, the modified by carboxyl groups carbon nanotubes interact with ions Ce.

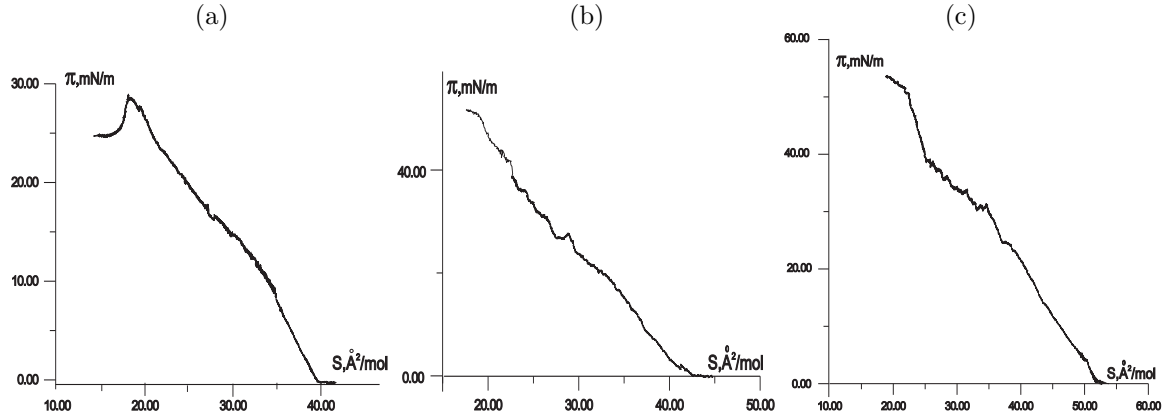


FIG. 1.  $\pi - S_{mol}$ -isotherms for stearic acid monolayer with CNTs and without CNTs at  $T=17^\circ$ : (a) =2.0, amount of nonmodified CNTs is equal to 0.004 mg in a monolayer,  $v = 3 \text{ mm/min}$ ; subphase is bidistilled water. (b) =6.3,  $v = 2.3 \text{ mm/min}$ , a monolayer does not contain CNTs, subphase is solution of salt  $\text{Ce}_2(\text{SO}_4)_3$ . (c) =6.3,  $v = 2.3 \text{ mm/min}$ , amount of modified by carboxyl groups carbon nanotubes is equal to  $5 - 7 \cdot 10^{-3} \text{ mg}$ , subphase is solution of salt  $\text{Ce}_2(\text{SO}_4)_3$ .

LB-monolayer which have been formed from a mixture of stearic acid and modified carboxyl groups CNTs, were deposited on a copper membrane with a polymeric coating to be investigated by a transmission electron microscope (TEM). Structure of the LB-monolayer is shown in fig. 2 a. LB-clusters of CNTs were deposited also on an interdigital capacitive sensor with a dielectric covering from nanoporous anodic alumina. Structural researches of the cluster have been carried out with the help of electronic scanning microscopy (SEM) too. Images made with the help of scanning electronic microscope demonstrate LB-clusters in a network (fig. 2 b). The length of these clusters bending around islands from anodic alumina can exceed 20 microns.

Thus, the obtained dependencies of thermodynamic parameters from fabrication conditions for monolayers from stearic acid and CNTs and the structural researches of these monolayers on various type substrates allow us to conclude that it is possible to incorporate CNTs into LB-monolayers with subsequent formation of LB-CNT-clusters.

### 3. Electron transport in zigzag CNT

Let us examine an structure of energy zones of  $(m, 0)$  CNT of zigzag type with open ends  
The Schrödinger equation in the circular cylindrical coordinates  $(\rho, \phi, z)$  [5] reads

$$\left(-\frac{1}{2\rho} \left(\rho \frac{\partial^2}{\partial z^2} + \frac{1}{\rho} \frac{\partial^2}{\partial \phi^2} + \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho}\right) + V(\rho, \phi, z)\right) \Psi = E\Psi, \quad \hbar = 1; \quad m_e = 1 \quad (3)$$

where  $\Psi$  is a wave function of an electron moving near macromolecular circumference chain. In the case of zigzag CN the variable  $\rho$ , being the cross-sectional radius of the zigzag CNT is a constant given

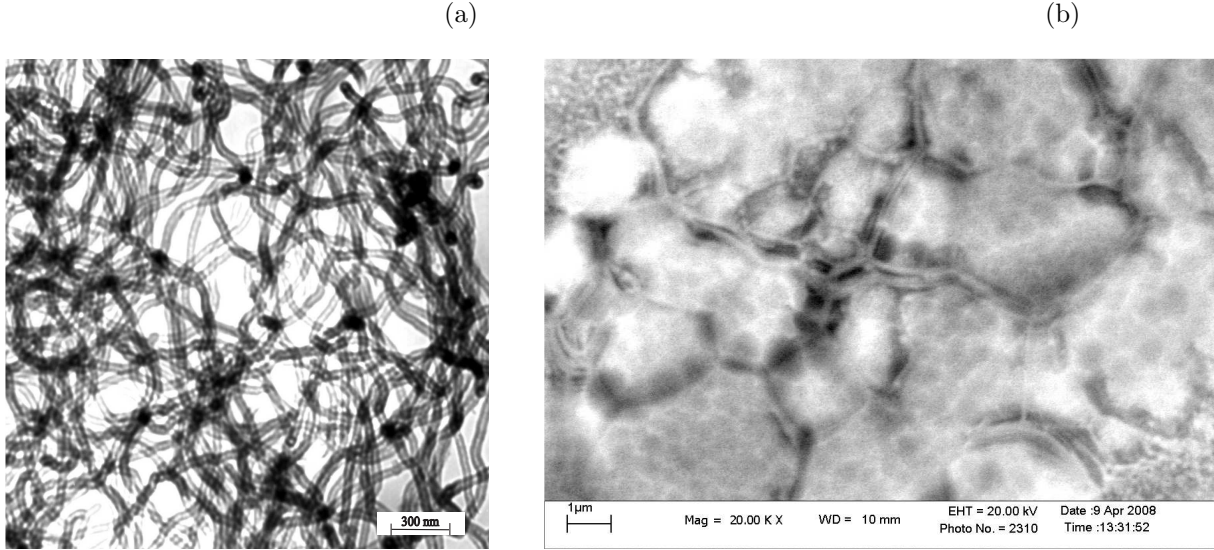


FIG. 2. Structure of film from three stearic acid LB-monolayers and one LB-monolayer formed from mixture of CNTs and stearic acid: (a) TEM-image, (b) SEM-image of LB-film deposited on anodic alumina with pore diameter 40 nm.

by

$$\rho = \frac{\sqrt{3}}{2\pi}bm = \text{const}, \quad (4)$$

where  $b$  is the interatomic distance in graphene,  $m$  is a number of hexagons disposed along the perimeter of the CNT. Let us introduce new variables

$$u = z - f(\phi) = z - \sin \nu\phi, \quad v = \phi, \quad (5)$$

where  $f(\phi)$  is a function approximating the configuration of linear macromolecule,  $\nu$  is a constant. Making the change (5) and taking into account the expression (4), we obtain the equation describing the quasi one-dimensional (Q-1-D) motion of electron along macromolecular circumference chain. Neglecting the electron deviation from the circular configuration of macromolecule we get

$$\left( -\frac{1}{2} \frac{\partial^2}{\partial v^2} + \tilde{V}(v) \right) \Psi = E\rho^2\Psi. \quad (6)$$

Factor  $E$  incoming into the expression (6) for problem eigenvalues, is chosen as

$$E = -\frac{1}{2n^2} + \frac{3}{2}g_{mol}n(n_2 - n_1). \quad (7)$$

Now, one finds the electron momentum  $k_{\perp}$  in transverse direction from the following equations which connect derivatives in Cartesian and cylindrical coordinates:

$$\begin{aligned} \frac{\partial \Psi}{\partial x} &= \cos v \frac{\partial \Psi(v)}{\partial \rho} - \frac{\sin v}{\rho} \frac{\partial \Psi(v)}{\partial v}, \\ \frac{\partial \Psi}{\partial y} &= \sin v \frac{\partial \Psi(v)}{\partial \rho} + \frac{\cos v}{\rho} \frac{\partial \Psi(v)}{\partial v}. \end{aligned} \quad (8)$$

From here it follows the expression for the square of electron momentum in transverse direction:

$$k_{\perp}^2 = p_x^2 + p_y^2 = p_v^2/\rho^2. \quad (9)$$

Hence, the transverse momentum is quantized in atomic units as

$$k_{\perp} = p_v/\rho = s/\rho, \quad s = 1, \dots, m. \quad (10)$$

Then taking into account the expression (4), Eq. (6) is transformed to the form

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial v^2} + \tilde{V}(v)\right)\Psi = \left(-\frac{1}{2n^2} + \frac{3}{2}g_{mol}n(n_2 - n_1)\right)\frac{3b^2}{4\pi^2}m^2\Psi, \quad (11)$$

where  $n, n_2, n_1$  are integers; the difference  $n_2 - n_1$  can have values in the interval from  $-(n-1)$  to  $n-1$ ,  $g_{mol}$  is a constant. If  $m = nq$ , then the Eq. (11) can be written as

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial v^2} + \tilde{V}(v)\right)\Psi = \left[-\frac{3b^2}{8\pi^2}q^2(1 - 3g_{mol}n^3(n_2 - n_1))\right]\Psi, \quad (12)$$

where  $q$  is an integer. Then, Eq. (12) describes one dimensional motion of a free electron (hole) in a periodic 1D-potential  $\tilde{V}(v)$  as a zone a lowest level of which is zero:  $E_0 = 0$  [4]. Low unoccupied  $\pi_0^*(d)$  symmetry states form the conduction band of CNT. Since for  $d$ -electrons we have a principal quantum number  $n$  equal to three:  $n = 3$  then we get the known condition of metallic zigzag CNT:  $m = 3q$  where  $q$  is arbitrary. Owing to cyclic symmetry,  $d$ -electrons can be also in  $m$ -th hexagon. Since the principal quantum number  $n$  for theirs is equal to  $n = m$ , then the energy of the electrons is determined by the following expression:

$$E = \frac{3b^2}{8\pi^2} [3g_{cnt}m^3(n_2 - n_1) - Q]. \quad (13)$$

From the condition that solutions at  $n = 3$  are a subset of solutions (13) one finds that:  $Q = m^2/9$ ,  $g_{cnt} = 3g_{mol}/m$ . If one assumes that  $g_{cnt}$  is an integer then due to the equality (10) for positive and equal to zero  $(n_2 - n_1)$  Eq. (13) gives an approximate law of dispersion for  $\pi^*$ -electrons:

$$\epsilon_c(p_v) = \frac{3b}{2}\gamma_0|p_{\perp} - p_F|\rho^2, \quad (14)$$

where  $g_{mol} = 2\pi\gamma_0/3\sqrt{3}m$ ,  $\gamma_0$  is an overlap integral. The expression (7) is nothing but the energy of hydrogen-like atom (in atomic units) in an external electric field  $g_{mol}$  directed along  $Z$ ,  $n_2, n_1$  are quantum numbers. The obtained result proves the following intuitively evident statement: circular conducting path of zigzag CNTs is the analog of hydrogen-like atoms in an external electric field. Hence, the energy  $E$  is the energy of  $\pi$ -electron in the field of effective charge  $Q$ , placed in the center of effective spherically symmetric orbital,  $g_{cnt}$  is an effective electric field of zigzag CNT, directed along axis  $Z$ .

#### 4. Chemical diffusion coefficient for electrons in CNT

Let us calculate chemical diffusion coefficient of electrons in zigzag  $(m, 0)$  type CNT nanotube in graphene approximation (approximation of graphite monolayer). In this approximation, electrons in conductivity zone of  $(c)$  and in valency zone  $(v)$  have the energies:

$$\epsilon_{c,v}(k_z, s) = \pm\gamma_0\sqrt{1 + 4\cos\left(\frac{\pi s}{m}\right)\cos(ak_z) + 4\cos^2\left(\frac{\pi s}{m}\right)} \quad (15)$$

where  $a = 3b/2\hbar$ . For CNTs it takes place  $z = 3$ , and the interaction energy  $\epsilon$  is equal to

$$\epsilon(k_z, s) = \epsilon_c(k_z, s) - \epsilon_v(k_z, s). \quad (16)$$

Since conductivity of the zigzag nanotubes is determined by the diffusion over the CNT circumferences then the circular paths give a dominating contribution into the integral (2):

$$\begin{aligned} \bar{D}_{ch} = \sum_{s=1}^m \frac{3a^2}{4Z} & \left( \beta(\epsilon_c(k_z, s) - \epsilon_v(k_z, s)) - 1 + e^{\beta\mu_s} \right) e^{\beta\mu_s} \\ & \times (1 - N_s) e^{-\beta H(q(\vec{r}_s))} \beta / \left( 1 - e^{\beta\mu_s} \right)^2. \end{aligned} \quad (17)$$

When tending  $k_z$  to zero one gets finally:

$$\begin{aligned} \bar{D}_{ch} = \sum_{s=1}^m \frac{3a^2}{4Z} & \left( \beta 2\gamma_0 \sqrt{1 + 4 \cos\left(\frac{\pi s}{m}\right) + 4 \cos^2\left(\frac{\pi s}{m}\right)} - 1 + e^{\beta\mu_s} \right) \\ & \times e^{\beta\mu_s} (1 - N_s) e^{-\beta H(q(\vec{r}_s))} \beta / \left( 1 - e^{\beta\mu_s} \right)^2. \end{aligned} \quad (18)$$

The formula (18) has a minimum when the radicand incoming in it equals to zero:

$$1 + 4 \cos\left(\frac{\pi s}{m}\right) + 4 \cos^2\left(\frac{\pi s}{m}\right) = 0. \quad (19)$$

The roots of the expression (19) have the following form:

$$\cos \frac{\pi s}{m} = -\frac{1}{2}$$

or

$$\frac{\pi s}{m} = \frac{\pi s}{3q} = \frac{2\pi}{3} + 2\pi n. \quad (20)$$

Hence, the difference  $\epsilon$  of energies for the conductivity and valence zones equals to zero for the metallic CNTs with  $(m = 3q)$  in separate points of Brillouin zone only as for graphene and graphite. It means that there is a null band gap, and since a volume of set from separate points is equal to zero then an electron state density at Fermi level is equal to zero too.

## 5. Model of helically deformed CNTs

Formation of nanocavities in CNTs at chemical modifying by carboxyl groups leads to an additional scattering of electrons on surface states of nanocavity. The reason of the fact that instantaneous dipoles  $\vec{d}_\uparrow$  and  $\vec{d}_\downarrow$ , arising at movement of an electron with spin "up" to the right and an electron with spin "down" to the left around of the effective charge  $Q$ ,  $Q > 0$  of nanotube do not compensate each other (fig. 3), and that a resulting dipole moment  $\vec{d}_{res} = \vec{d}_\uparrow + \vec{d}_\downarrow$  is not equal to zero, is a potential of interaction of electrons, moving over circle with the nanocavity electrons.

Electrochemical potential  $\zeta$  of such a system has an additional term as a scalar product  $eE_{bubble} \cos \alpha_{l(r)}$  of strength  $\vec{E}_{bubble}$  of the electric field which is created by the surface states of nanocavity, and the instant dipole  $e\vec{r}$ , arising at electron movement to the right (clockwise,  $\alpha_r = \pi$ ,  $e\vec{r} = \vec{d}_\uparrow$ )

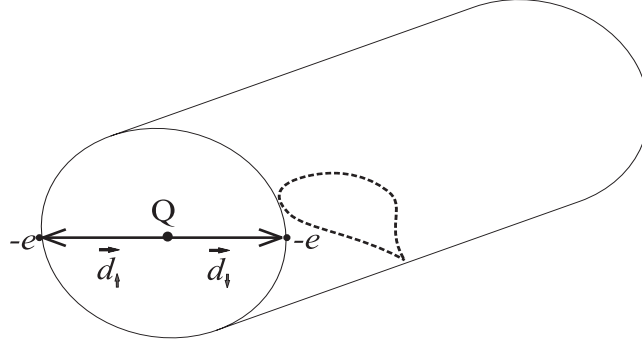


FIG. 3. Polarization of chemically modified zigzag – nanotube due to dipoles  $\vec{d}_{\uparrow(\downarrow)}$  which rotate with different velocity in nanocavity potential. A dotted line denotes the nanocavity which is formed by carboxyl or hydroxyl groups.

and to the left (counter-clockwise,  $\alpha_l = 0$ ,  $e\vec{r} = \vec{d}_{\downarrow}$ ) around of the effective charge  $Q$ . Then, we can find the chemical diffusion coefficient  $D_{ch}^{r(l)}$  of a free electron moving to the right (to the left) on carbon nanotube:

$$\begin{aligned} \bar{D}_{ch} &= \sum_{s=1}^m \frac{3a^2}{4Z} \\ &\times \left( \beta 2\gamma_0 \sqrt{1 + 4 \cos\left(\frac{\pi s}{m}\right) + 4 \cos^2\left(\left(\frac{\pi s}{m}\right)\right)} - 1 + e^{\beta(\mu_s - eE_{bubble}r_s \cos \alpha_{l(r)})} \right) \\ &\times e^{\beta(\mu_s - eE_{bubble}r_s \cos \alpha_{l(r)})} (1 - N_s) e^{-\beta H(q(\vec{r}_s))} \beta / \left( 1 - e^{\beta(\mu_s - eE_{bubble}r_s \cos \alpha_{l(r)})} \right)^2. \end{aligned} \quad (21)$$

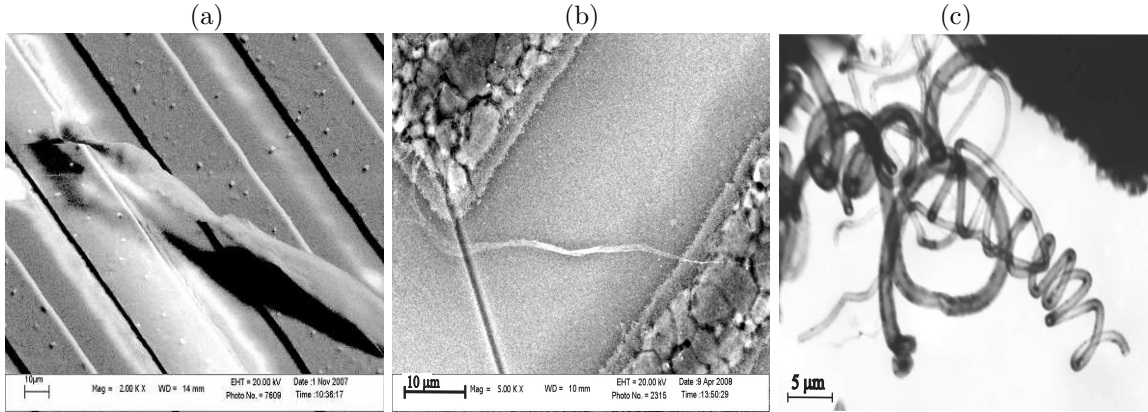


FIG. 4. SEM-images of helicoidal LB-cluster of CNTs modified by hydroxyl (a) and carboxyl (b) groups and deposited on anodic alumina with pore diameter 40 nm. (c) TEM-image of LB-cluster of CNTs modified by carboxyl groups

Let us find the resulting dipole moment  $\vec{d}_{res}$ . The physical sense of the particle's diffusion coefficient  $D_{ch}^{r(l)}$  is a root-mean-square displacement of a particle in time unit:  $D_{ch} = \langle \Delta r^2 \rangle / \Delta t$ . Therefore the displacement  $\Delta r(t_{p/4})$  of an electron on a Fermi surface with a momentum  $k_F$  for a quarter-period

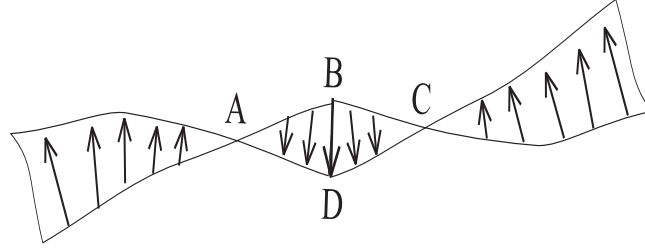


FIG. 5. Spontaneous dielectric polarization of LB-CNT-cluster having helicoidal structure

$t_p/4 = \pi\rho/2\hbar k_F$  has the order of magnitude  $\Delta r(t_p/4) = \frac{1}{2}\sqrt{D_{ch}t_p}$ . Now, we can find an angle  $\beta$  on which one of dipoles retards:

$$\beta = \frac{\pi^{1/2}}{\sqrt{2\hbar k_F \rho}} \left( \sqrt{D_{ch}^r} - \sqrt{D_{ch}^l} \right). \quad (22)$$

From here one gets the following formula for module  $\vec{d}_{res}$ :

$$\begin{aligned} d_{res} &= d\sqrt{\cos^2 \beta + (1 - \sin \beta)^2} = d\sqrt{2(1 - \sin \beta)} \\ &= \sqrt{2}d\sqrt{1 - \sin \left[ \frac{\pi^{1/2}}{\sqrt{2\hbar k_F \rho}} \left( \sqrt{D_{ch}^r} - \sqrt{D_{ch}^l} \right) \right]}, \end{aligned} \quad (23)$$

where  $d = |\vec{d}_\uparrow| = |\vec{d}_\downarrow|$ . The dipole – dipole repulsion leads to a twisting of one part relative to another part of carbon nanotube and to formation of helicoidal structure of CNT-cluster. At the same time the CNT-cluster structure loses the center of inversion.

## 6. Spontaneous polarization of modified CNTs

Lack of inversion center allows to assume that the spin-orbital interaction gives nonzero contribution in the energy of the modified CNT clusters. Spin-dependent scattering of electrons moving on a circumference is the cause of that an angular momentum  $\vec{J}$  associates with the dipole  $\vec{d}_{res}$ . Therefore, under action of an external electric field  $\vec{E}$ , the dipoles  $\vec{d}_{res}$  for various parts of CNT precess around of the equilibrium direction instead of reorientation along  $\vec{E}$ . Correspondingly, the structure of CNT-cluster undergoes oscillations.

Let us show that spontaneous polarization of CNT-clusters can be caused by this phenomenon of dipole  $\vec{d}_{res}$  precession in an external field  $\vec{E}$ . Uncompensated dipole moment of surrounding CNTs leads to that the dipole moments  $\vec{d}_{res}$  move in a self-consistent field  $\vec{E}_{sc}$  of the environment. When imposing of an external field  $\vec{E}$  the dipole  $\vec{d}_{res}$  begins to precess around of a direction  $\vec{E}_{sc}$  because of the presence of the moment  $\vec{J}$ . Therefore, reorientation of the vector  $\vec{d}_{res}$  is possible only in enough intensive external field  $\vec{E}$ . A vector  $P_c$  of possible residual polarization of samples gains an angular momentum finally too. If a temperature is that the vector  $P_c$  can exist long enough, then the phenomenon of spontaneous polarization  $P_c$  of samples (fig. 5) is observed.

Let us estimate a pitch of helix in fig. 5. Without spin-orbital interaction the helicoidal structure is distorted in external and self-consistent fields, and, hence, is unstable. Therefore, contribution of the spin-orbital interaction is expressed in stabilization of parameters of the spiral. It allows us to suppose



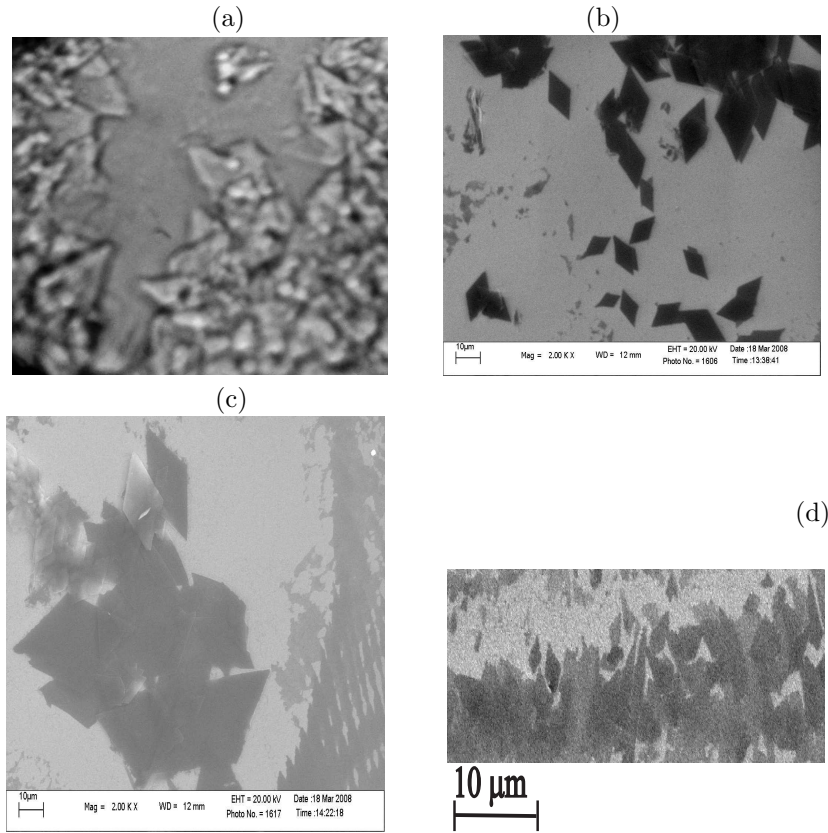


FIG. 6. Formation of diamond-shaped structures (a) on break of LB-film made from two stearic acid monolayers and one monolayer formed from a drop of a mixture of CNTs and stearic acid molecules which spreads on the surface of LB-monolayer in crystal state. Light-image, magnification is 600 times more. SEM-image of CNT-clusters modified by carboxyl groups. Formation of diamond-shaped structures on silicon Si by deposition of a drop of a mixture of CNTs and stearic acid (b), three LB-monolayers of stearic acid and one LB-monolayer formed from a mixture of CNTs and stearic acid (c), three LB-monolayers of stearic acid and one LB-monolayer formed from a drop of a mixture of CNTs and stearic acid molecules which spreads on the surface of the stearic acid LB-monolayer in crystal state (d).

that on average a quantity on which the energy of the system decreases by a transition of its form into the spiral one is determined by the spin-orbital interaction:

$$\langle \vec{s} \cdot \vec{l} \rangle \quad (24)$$

where  $\langle \rangle$  denotes a matrix element of scalar product of a spin operator  $\vec{s}$  and an orbital moment operator  $\vec{l}$ .

Now, one can write the free energy  $F_d$  of the LB-CNT-cluster deformation taking into account the lack of inversion center as [6]

$$F_d = \frac{K_1}{2} (\text{div } \vec{n})^2 + \frac{K_2}{2} (\vec{n} \cdot \text{rot } \vec{n} + q)^2 + \frac{K_3}{2} (\vec{n} \times \text{rot } \vec{n})^2, \quad (25)$$

where the coefficients  $K_1$ ,  $K_2$ ,  $K_3$  are modules of elasticity for transverse bending, twisting and longitudinal bending respectively;  $q$  is a parameter having a dimension of inverse length. The quantity  $F_d$

takes zero value in an equilibrium state:

$$F_d = 0. \quad (26)$$

From here it follows that configuration of directions  $\vec{n}$  which corresponds to the equilibrium state, is described by the following equations

$$\operatorname{div} \vec{n} = 0, \quad \vec{n} \cdot \operatorname{rot} \vec{n} = -q, \quad \vec{n} \times \operatorname{rot} \vec{n} = 0. \quad (27)$$

The solution of the system of equations (27) has a following form:

$$n_x = \cos qz, \quad n_y = \sin qz, \quad n_z = 0. \quad (28)$$

A structure described by the equations (28) is called a helicoidal one. The pseudoscalar contribution into  $F_d$  is equal to the work performed by spin-orbital interaction when twisting of cluster into the spiral. Therefore, we can rewrite the pseudoscalar contribution as proportional to the spin-orbital interaction (24) with minus sign ("−"):

$$qK_2 \vec{n} \cdot \operatorname{rot} \vec{n} = -2\alpha_2 \langle \vec{s} \cdot \vec{l} \rangle, \quad (29)$$

since  $\operatorname{rot} \vec{n}$  is proportional to the orbital moment  $\vec{l}$  of electron which moves over a circumference of nanotube, and  $\vec{n}$  is proportional to the spin  $\vec{s}$  of an electron. The coefficient "2" takes into account two states for electron ( spin "up" and spin "down"). Due to second formula in the system (27) it follows from the expression (29) the expression for the inverse pitch of the helix  $q$

$$q = \sqrt{2\alpha_2 \langle \vec{s} \cdot \vec{l} \rangle / K_2}, \quad (30)$$

## 7. Discussion of results and conclusions

The LB-CNT-clusters of the helicoidal form were observed by us in electron microscopy investigation of surface morphology for films (fig. 4 a, b) deposited on an interdigitated capacitor sensor having a dielectric coating from nanostructured anodic alumina and for films (fig. 4 c) on the membranes used in transmission electron microscope. The LB-CNT-clusters which are deposited on the porous surface alumina sag freely in a pore space and, therefore, an action of adhesion forces is reduced to a minimum.

Adhesion forces are very large for the CNT-monolayer formed on a solid surface, for example, on a silicon substrate or glass. One can see it from fig. 6 a where diamond-shaped clusters are formed under action of adhesive forces which violate entirety of the LB-film. It is possible to assume that the same origin of the diamond-shaped structures takes place on silicon (fig. 6 c – d). Because of the relation of these pieces width to their length is close to unit, the twisting puts on their projections into the diamond shape (rhomb ABCD in fig. 5). SEM-images of such diamond-shaped structures are shown in fig. 6 c – d. One can conclude from fig. 6 c– d that CNTs gain length mainly less than 2.5 microns during the modifying by carbogroups.

The above described phenomenon of spontaneous polarization in the thin LB-films with modified carbon nanotubes, apparently, was observed in electrophysical experiments which have been performed in [7].

So, it has been are mathematically examined localization effects which take place for diffusion of electrons in electric fields created by an effective charges of nanotubes and which lead to spontaneous

polarization of the ordered arrays of carbon nanotubes. The cause of spontaneous polarization of the samples is the spin-dependent scattering of electrons owing to nonzero spin-orbital interaction in the CNT-clusters of helicoidal shape for which the inversion symmetry center is absent. It was shown that LB-technology allows to form the helicoidal LB-CNT-clusters.

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