

# Carbon Nanotubes in Arrays: Competition of van-der-Waals and Elastic Forces

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**Abstract**—The van-der-Waals interaction between carbon nanotubes leads to the formation of agglomerates of bundles and strands. In such a self-assemblage, identical nanotubes are assembled into arrays with a high degree of ordering forming a crystalline structure. However, the van-der-Waals forces also result in a strain of the cross-section normal to their axes instead of only in the mutual attraction of nanotubes. This work presents an analysis of the nanotube strain and crystal-lattice parameters depending on the nanotube sizes and crystal symmetry.

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## 1. INTRODUCTION

Under the action of van-der-Waals forces, nanotubes of the same structure can form crystalline structures, which are quite stable even under the effect of external forces [1–4]. As is known [5], nanotubes of sufficiently large diameter tend to collapse under the action of van-der-Waals forces acting between carbon atoms belonging to the same nanotube. However, their stability increases with the agglomeration of nanotubes in an ordered array. In this case, generally speaking, the nanotubes experience polygonization determined by the symmetry of their environment [3, 4]. The interaction of carbon nanotubes with other carbon nanostructures, i.e., graphene sheets, nanotubes of various diameters and spatial orientations, and carbon fibers, has been studied many times [6–10] in the approximation of nondeformable nanotubes. An exception, perhaps, is [11] in which the contact problem for two nanotubes is considered. However, it is obvious that the strain mode of a nanotube interacting with its nearest neighbors should be determined by the symmetry of its environment. In [12], a semi-empirical model of a crystal of nanotubes was considered taking into account the strain of their cross section caused by the interaction with neighboring nanotubes for the case of a dense hexagonal (triangular) package. It is shown that the specific energy of the crystal has a nonmonotonic dependence on the diameter of nano-

tubes. Current paper presents an analysis of the effect of the diameter of nanotubes and the symmetry of the nearby environment on the strain of nanotubes and the lattice constant of the tube crystal.

## 2. GROUND-STATE ENERGY

We consider an ordered array of identical parallel nanotubes, each of which has  $n$  nearest neighbors. The nanotubes are assumed to be long enough so that the effect of the edges can be neglected. Each nanotube is considered as an elastic thin shell characterized by the radius  $R$  and the effective wall thickness  $\eta \ll R$  [13, 14]. In this case, the field of displacements of the points of the surface of the nanotube depends on the number  $n$  of nearest neighbors and can be written in the form

$$\{u, v, w\} = \{U_n \cos n\theta, V_n \sin n\theta, W_n \cos n\theta\}, \quad (1)$$

where  $u, v, w$  are the longitudinal, tangential, and radial displacement components, respectively;  $\theta$  is the azimuth angle in the cross section normal to the axis of the nanotube. The amplitudes  $V_n$  and  $W_n$  determine the deviation of the cross section from circular.

In a nanotube crystal, the elastic-strain energy together with the van-der-Waals energy determines the ground state and the parameters of the crystal. The potential energy of an ordered array of nanotubes can be represented as

$$E = U_{\text{el}} + U_{\text{in}} + U_{\text{out}}, \quad (2)$$

where  $U_{\text{el}}$  is the energy of elastic strain determined by the field of displacements  $\{u, v, w\}$ ;  $U_{\text{in}}$  and  $U_{\text{out}}$  are the interaction energy between carbon atoms belonging to the same and adjacent nanotubes, respectively. In the

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future, we consider the energy per unit length of a nanotube without specifying it every time.

The van-der-Waals energy is described by the Lennard-Jones potential, the parameters of which for carbon nanostructures are well defined:

$$V(x) = 4\epsilon \left[ \left( \frac{\sigma}{x} \right)^{12} - \left( \frac{\sigma}{x} \right)^6 \right], \quad (3)$$

where  $\epsilon = 2.84$  meV and  $\sigma = 3.403$  Å.

In accordance with the above assumption, we assume that carbon atoms are distributed over the nanotube surface with the density  $\rho_s = 4/3\sqrt{3}a^2$  ( $a$  is the length of the C–C bond in graphene). In this case, the van-der-Waals energy can be represented in the form of an integral over the surface of nanotubes:

$$U_{vdW} = (2\pi\rho_s)^2 \int_{-\infty}^{\infty} dz \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \tilde{R}(\theta_1) \tilde{R}(\theta_2) V(r), \quad (4)$$

where  $r$  is the distance between carbon atoms on the surface of nanotubes. The values of  $\tilde{R}$  describe the deviation of the contour of the nanotube cross section from the circumference.

For the self-action energy ( $U_{in}$ ), the value of  $r$  is written as

$$r^2 = z^2 + R^2[(1 + W_n \cos n\theta_1)^2 + (1 + W_n \cos n\theta_2)^2 - 2(1 + W_n \cos n\theta_1)(1 + W_n \cos n\theta_2) \cos(\theta_1 - \theta_2)], \quad (5)$$

where  $z$  is the coordinate along the nanotube axis. When calculating the interaction energy between adjacent nanotubes, the distance is written as

$$r^2 = z^2 + R^2[(h + (1 + W_n \cos n\theta_1) \cos \theta_1 - (1 + W_n \cos n\theta_2) \cos \theta_2)^2 + ((1 + W_n \cos n\theta_1) \sin \theta_1 - (1 + W_n \cos n\theta_2) \sin \theta_2)^2], \quad (6)$$

where  $h \gtrsim 2$  is the dimensionless distance between the axes of nanotubes (the lattice constant).

Calculation of the elastic-strain energy of a thin shell is, generally speaking, a very difficult problem. However, in this case, the strain of the nanotube is similar to the strain of the thin elastic ring in which the contour length of the cross section normal to the axis of the nanotube is preserved. It permits us to relate the amplitudes of the radial and tangential displacements of the surface [15]:

$$V_n = -\frac{1}{n} W_n. \quad (7)$$

Assuming that the longitudinal and shear strain  $s$  are negligibly small, we obtain for the elastic-strain energy [15]

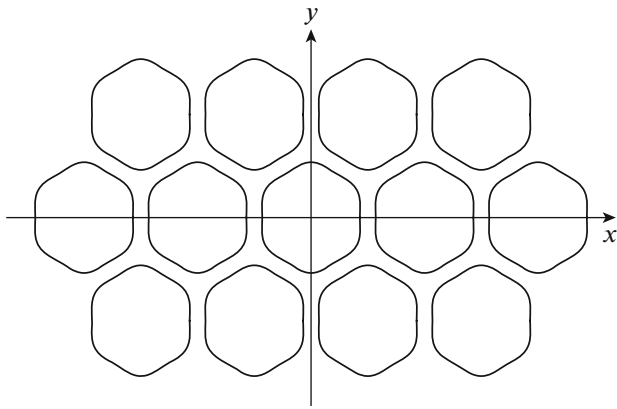
$$U_{el} = \frac{YR\eta}{1 - \nu^2} \frac{\beta^2}{24} (n^2 - 1) W_n^2, \quad (8)$$

where  $Y$  is Young's modulus of graphene,  $\nu \sim 0.2$  is the Poisson ratio of nanotubes;  $\beta = \eta/R$  ( $\eta \approx 0.67$  Å).

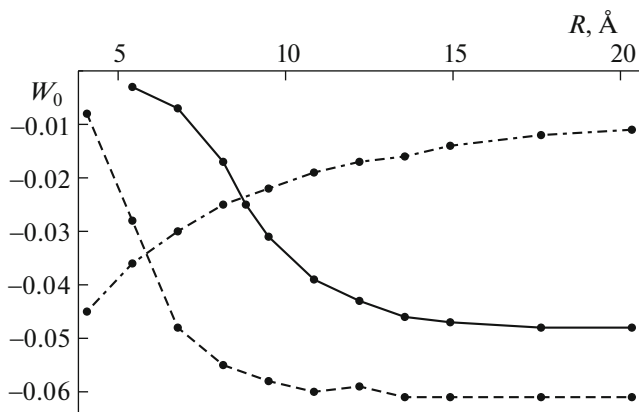
By minimizing energy (2) with respect to the amplitude  $W_n$  and distance  $h$  between the axes of the nanotubes, it is possible to find the equilibrium configuration and the crystal energy. Unfortunately, integrals (4) cannot be represented in analytical form; therefore, their estimates have to be performed by numerical methods. The spontaneous agglomeration of nanotubes leads to dense hexagonal (triangular) packing; however, bearing in mind the modern development of nanotechnology and for evaluating the effect of symmetry on the properties of such a crystal, we present below the results of calculations for the triangular, square, and one-dimensional lattices.

### 3. RESULTS AND DISCUSSION

Since the approach discussed above is based on description of a nanotube as a thin shell, the key parameter is its radius, while other parameters have an effect only through the elastic constants. Therefore, all calculations were performed for nonchiral nanotubes ( $m, m$ ). Figure 1 shows a fragment of the crystal of nanotubes with the radius  $R = 10.85$  Å with dense hexagonal packing. According to the data obtained, the dimensionless amplitude of the radial displacement amounts to  $W \approx -0.039$  and the lattice constant is  $h = 2.234$ . The figure clearly shows the polygonization of the nanotubes—the cross section resembles a hexagon with smooth vertices. In Fig. 2, we show the values of dimensionless amplitudes  $W_n$  and lattice constants  $h$  for nanotubes of various radii and different types of packings. It is noteworthy that the ratios between the amplitude and lattice constant for square and triangular lattices, although differing in value, are of uniform character, whereas the dependence of amplitude on the lattice constant is completely different for the one-dimensional lattice. This fact is confirmed by the analysis of Fig. 3, which shows the dependence of the amplitude of the radial shift on the nanotube radius. For triangular and square lattices, small radii correspond to smaller amplitudes, whereas, for a one-dimensional lattice, the opposite occurs. For nanotubes with the radius  $R \gtrsim 8$  Å in the cases of triangular and square lattices, the amplitude of the radial displacement exceeds the threshold value of  $w_* = -1/(n^2 + 1)$  above which the nanotube cross section ceases to be convex. Therefore, the points corresponding to the minimum distance between the walls do not lie on the straight line connecting the nanotube axes, which is clearly seen in Fig. 1. In this case, the minimum distance between carbon atoms belonging to adjacent nanotubes must be calculated by minimizing expression (6) with respect to azimuthal angles  $\theta_1$  and  $\theta_2$ . The corresponding dependences of the minimum distance between the walls of nanotubes for different



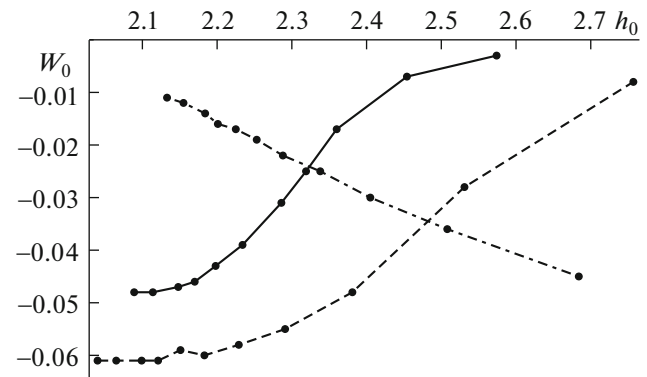
**Fig. 1.** Fragment of an ordered array of nanotubes (16,16) of radius  $R = 10.85 \text{ \AA}$  with hexagonal close packing. The lattice constant  $L = 2.234R$ .



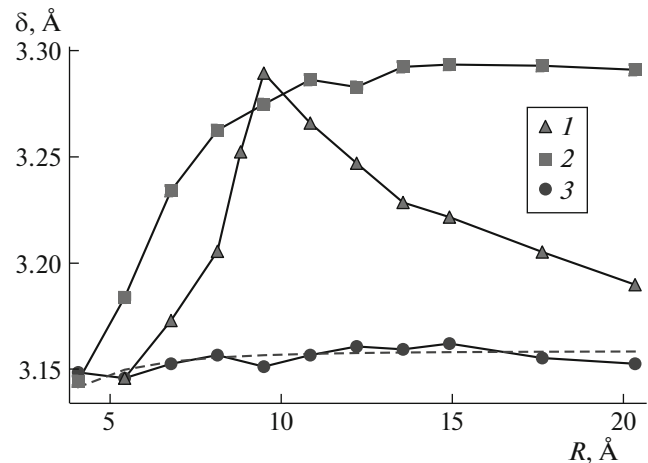
**Fig. 3.** Dimensionless amplitude of the radial displacement.

packings are shown in Fig. 4. It also shows the minimum distances between the walls calculated in the approximation of nondeformable nanotubes [10]. It can be seen that this approximation describes well the minimum distance only for the case of a one-dimensional lattice. The nanotubes of a small radius  $R \leq 6 \text{ \AA}$  in the case of square and triangular lattices turn out to be slightly deformed; therefore, they also correspond to the approximation [10].

Thus, systematic analysis of the ordered arrays of carbon nanotubes shows that it is both the diameter of the nanotubes and the lattice symmetry that affect significantly the strain of the nanotubes and the distance between them. At the same time, the one-dimensional array is closer in its characteristics to the crystal of nondeformable nanotubes. The nanotubes in quasi-two-dimensional lattices (triangular and square) have significantly greater strain as compared with the one-dimensional systems. Moreover, for the triangular lattice, a pronounced extreme character of the dependence of the minimum distance between the walls of



**Fig. 2.** Values of the amplitude of the radial displacement and the distance between the axes of nanotubes. Here and in Fig. 3, the solid, dashed, and dash-dotted curves correspond to the triangular, square, and one-dimensional lattices.



**Fig. 4.** Minimum distance between the walls of the nanotubes; 1, 2, and 3 correspond to triangular, square, and one-dimensional lattices. The dashed line shows the values in the approximation of undeformed nanotubes [10].

the nanotubes on their diameter is observed. This behavior, generally speaking, correlates with the extreme dependence of the specific energy of a crystal from nanotubes [12] and is explained by the fact that, for the small-diameter nanotubes, the van-der-Waals interaction is significant only for the relatively small part of the surface, whereas, for larger nanotubes, their strain leads to the fact that almost the entire surface of the nanotube interacts with its neighbors, which makes such a system similar to graphite. Stranger is the behavior of the minimum distance for the square lattice. In this case, the nanotube cross section resembles a square and the contribution to the bending energy of the shell at its vertices exceeds the gain from a closer distance between the walls. However, in any case, the presence of the initial strain of the nanotubes in an

ordered array should significantly affect the deformation and vibrational properties.

#### FUNDING

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