



# **Multi-Walled Nanotubes: Commensurate-Incommensurate Phase Transition and NEMS Applications**

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**Abstract:** Interaction of non-rigid walls of double-walled carbon nanotubes is studied within the Frenkel-Kontorova model. It reveals a clearly defined commensurate-incommensurate phase transition. Parameter which determines this phase is calculated for a set of double-walled nanotubes with non-chiral commensurate walls using ab initio interwall interaction energies and elastic properties. Possibility of formation of incommensurability defects in the commensurate phase is considered. The length of the defects and energy of their formation are calculated. Principal scheme of strain nanosensor based on the commensurate-incommensurate phase transition in double-walled nanotube is proposed.

**Keywords:** Carbon nanotubes, interwall interaction, incommensurability defects, electromechanical nanodevices

## **INTRODUCTION**

The discovery of carbon nanotubes is regarded as one of the most important advances in materials in the latter part of the 20th century. A wide range of

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applications in nanoscale electronic, optical and magnetic devices can be envisaged, ranging from logic elements to single-molecule sensing devices. Experimental studies of arbitrary (1) and controlled by a manipulator (2) relative motion of the walls in multi-walled carbon nanotubes (MWNTs) reveal that the weak interwall interaction gives an extremely smooth solid-solid interface. This unique property of MWNTs opens up the possibility of using relative motion of the walls in mechanical nanodevices. Possible nanodevices based on such motion have been proposed elsewhere: nanobearings (3), constant-force nanosprings and free sliding telescopic arms (2), nanogears (4), ultra-small switching devices (5) and gigahertz oscillator (6), variable nanoresistor (7–9) and perforating nanodrill (7–9). Theoretical modelling of the orientation and relative motion of the walls holds the key to the success of these applications.

The most commonly used convention employs the term “commensurate walls” for the walls which are commensurate with their structures obtained by graphene plane mapping on a cylindrical surface with the bond lengths kept constant. Otherwise, the walls are defined as incommensurate. However, as shown in (10), the bond lengths of the walls of nanotubes slightly differ from those in graphite, and for this reason the lengths of unit cells of isolated commensurate walls will also be slightly different. The interwall interaction in a double-walled carbon nanotube (DWNT) leads to the contraction (or expansion) of the walls and consequent change in the lengths of their unit cells. This phenomenon has been studied in this paper using the Frenkel-Kontorova (FK) model (11). It has been shown that the commensurate-incommensurate phase transition may occur in DWNTs with commensurate walls. In the commensurate phase of DWNT, the lengths of unit cells of constituent walls become equal due to the interwall interaction. In the incommensurate phase, the DWNT acquires a periodic structure of alternating long ‘near commensurate’ regions and short regions of incommensurability defects (*ID*). For the incommensurate phase of a DWNT, the length and energy of formation of the *ID* are estimated and the parameter which defines the phase of a DWNT is calculated. These estimations are based on Density Functional Theory (DFT) calculations of the structure, elastic properties and barriers to relative motion of the walls of DWNTs (10, 12).

The principal scheme of strain nanosensor based on the commensurate-incommensurate phase transition in DWNT is proposed.

## **COMMENSURATE-INCOMMENSURATE PHASE TRANSITION IN DWNTS: FRENKEL–KONTOROVA MODEL**

Recently, the possibility of expansion of a SWNT as a result of interaction with a graphite substrate has been suggested in (13). In this Section, we use the FK model to investigate expansion and contraction of the walls in a DWNT as a result of the interwall interaction. The ordinary one-dimensional

FK model comprises a harmonic chain which imitates particles moving in a spatially periodic potential. We extend the one-dimensional FK model to the case of two interacting harmonic chains which correspond to two walls of a DWNT.

If one of the interacting springs is expanded during the interaction causing a change in its length,  $\Delta x_a$ , and another is compressed with  $\Delta x_b$ , then the minimum elastic energy of the system with the combined change in the length of both springs  $\Delta x_a + \Delta x_b$  is given by

$$U_{el} = \frac{\mu_a \mu_b (\Delta x_a + \Delta x_b)^2}{2(\mu_a + \mu_b)} \quad (1)$$

where  $\mu_a$  and  $\mu_b$  are elastic constants of expanded and compressed spring, respectively. Potential energy of the system of two interacting chains of particles connected by a spring with a periodic potential can be defined as

$$U = \sum_n \left[ \frac{\mu_a \mu_b (x_{n+1}^a - x_n^a - l_a + l_b - x_{n+1}^b + x_n^b)^2}{2(\mu_a + \mu_b)} + \frac{1}{2} W \left( 1 - \cos \frac{2\pi}{c} (x_n^b - x_n^a) \right) \right] \quad (2)$$

where  $x_n^a$  and  $x_n^b$  are the coordinates of the  $n$ th particle in expanded and contracted chains, respectively;  $W$  and  $c$  are the amplitude and period of the interaction potential;  $l_a$  and  $l_b$  are natural lengths of two chains. In terms of dimensionless coordinate  $u_n = (x_n^a - x_n^b)/c$ , equation (2) can be re-written as

$$U = \sum_n \left[ \mu c^2 (u_{n+1} - u_n - l_d)^2 + W (1 - \cos 2\pi u_n) \right] \quad (3)$$

where

$$\mu = \frac{\mu_a \mu_b}{\mu_a + \mu_b} \quad l_d = \frac{l_b - l_a}{c} \quad (4)$$

Within the continuum approximation, summation over particles in equation (3) becomes an integration over  $n$ , and after having introduced a new variables  $u' = u/2\pi$  and  $n' = n/2\pi l_d$ , potential energy of the system (3) can be brought into the standard form

$$U = \frac{1}{2} \int_{-\infty}^{\infty} \left[ \mu (c l_d)^2 \left( \frac{\partial u'}{\partial n'} \right)^2 + W (1 - \cos 2\pi u') \right] \frac{dn'}{2\pi l_d} \quad (5)$$

In the systems, for which the interwall interaction energy can be described by potential (5), the commensurate-incommensurate phase transition

can occur (14–16). Namely, if we introduce the commensurability parameter  $h$  as

$$h = \sqrt{\frac{W}{2\mu(cl_d)^2}} \quad (6)$$

a system corresponds to the commensurate phase if  $h > h_c = \pi/4$ , and it is in the incommensurate phase if  $h < h_c$ .

For a DWNT, all quantities which define the parameter  $h$ , i.e., the barrier to relative sliding of the walls along the nanotube axis,  $W$ , the difference  $cl_d = l_b - l_a$  between natural lengths of non-interacting walls, and the elastic constants  $\mu_a$  and  $\mu_b$ , fall on the translational period  $\delta_z$  of the interwall interaction energy surface. As the parameter  $h$  does not depend on the period  $\delta_z$ , the translational length of the unit cell of a DWNT,  $t_d$ , can be conveniently taken as this length. As a result, the parameter  $h$  takes the form

$$h = \sqrt{\frac{\Delta U_{mz} N_m}{2\mu_d \Delta t^2}} \quad (7)$$

where  $\Delta U_{mz}$  is the barrier to relative motion of the walls along the nanotube axis per one carbon atom of the movable wall,  $N_m$  is the number of atoms in the unit cell of the movable wall,  $\Delta t = t_s^2 - t_s^1$  is the difference between the lengths of the unit cells of the walls, and  $\mu_d$  is defined in the same way as the elastic constant  $\mu$  of the interacting springs of equation (4) with the sole difference that  $\mu$  of (4) corresponds to the period of the interaction potential,  $c$ , whereas  $\mu_d$  corresponds to the translational length of the unit cell of a DWNT,  $t_d$ .

Let us consider the significance of the parameter  $h$ . The quantity  $U_{dif} = \Delta U_{mz} N_m / 2$  is the difference (per unit cell of an infinite DWNT) between the interwall interaction energy corresponding to the commensurate phase and the energy of the fully incommensurate state. Elastic energy of a DWNT (per unit cell) of the commensurate phase is

$$U_{el} = \frac{\mu_d \Delta t^2}{2} \quad (8)$$

Thus, the parameter  $h$  can be expressed in terms of the ratio of these energies,  $H = U_{dif} / U_{el}$ , which characterizes the commensurate and incommensurate phases of a DWNT

$$h = \sqrt{\frac{U_{dif}}{2U_{el}}} = \sqrt{\frac{H}{2}} \quad (9)$$

Now, the condition  $h > h_c$  defining the commensurate phase of a DWNT takes the form  $H > \pi^2/8 = 1.234 \dots$ . For all considered DWNTs, we calculate the ratio  $H$  and tabulate the results in Table 1.

**Table 1.** Characteristics of the incommensurability defect in DWNTs

Nanotube	$H$	$U^{ID}$	$l^{ID}$	$\varepsilon_c$
(4,4)@(10,10)	$0.010 \pm 0.004$		$87 \pm 27$	
(5,5)@(10,10)	$22.0 \pm 1.5$	$0.95 \pm 0.03$	$31.7 \pm 1.1$	$0.202 \pm 0.009$
(9,0)@(18,0)	$68.1 \pm 0.4$	$6.03 \pm 0.01$	$11.19 \pm 0.03$	$0.709 \pm 0.003$
(10,0)@(20,0)	$31.9 \pm 0.4$	$3.75 \pm 0.02$	$28.64 \pm 0.14$	$0.378 \pm 0.003$

Ratio  $H$  characterizes the incommensurate and commensurate phases of a DWNT and it is described in the text.  $U^{ID}$  (in eV) and  $l^{ID}$  (in nm) are the energy of formation and the length of the defect.  $\varepsilon_c$  (in %) is the minimum strain of the medium.

All DWNTs studied in this paper, with the exception of the (4, 4)@(10,10) DWNT, correspond to the commensurate phase. In general, DWNTs with commensurate walls have extremely small barrier to relative sliding of the walls if at least one of the walls is chiral (12, 17–20). For such DWNTs, the value of the ratio  $H$  is very small and we conclude that these DWNTs do not correspond to the commensurate phase. DWNTs with incommensurate walls also do not comply with the commensurate phase. In this case, the ratio  $H$  is very small due to a large difference in the lengths of the unit cells of the walls,  $\Delta t$ .

The main characteristics of the phases of systems described by the potential (5) are known (15, 16). Minimizing the energy  $\partial U/\partial u_n = 0$  for all  $n$  in equation (3), we find a solution with no forces on particles

$$u_{n+1} - 2u_n + u_{n-1} = -\frac{W\pi}{\mu c^2} \sin 2\pi u \quad (10)$$

In the continuum limit, equation (10) can be re-written as

$$\frac{d^2 u}{dn^2} = -\frac{W\pi}{\mu c^2} \sin 2\pi u \quad (11)$$

Solutions to equation (11) define the equilibrium configurations of the system. The solution  $u(n)=0$  corresponds to the commensurate phase. In the incommensurate phase, the structure of the system comprises a lattice of near-commensurate sectors separated by narrow incommensurability defects. When  $h \rightarrow h_c$ , only one  $ID$  remains in the system, namely the defect described by the following solution of equation (11)

$$u(n) = \frac{2}{\pi} \arctan \left( \exp \left( \pi n \sqrt{\frac{2W}{\mu c^2}} \right) \right) \quad (12)$$

Analytical solution  $du/dn$  of the FK model corresponding to equation (12) can be viewed as a single static soliton which represents a

distribution function of the strain in the system. In the case of DWNT, equation (12) takes form

$$u(x) = \frac{2}{\pi} \arctan \left( \exp \left( \frac{2\pi x}{t_d} \sqrt{\frac{\Delta U_{mz} N_m}{\mu_d t_d}} \right) \right) \quad (13)$$

Here,  $u(x)$  is a local relative shift of the walls in reference to the commensurate state (we take into consideration  $c = \delta_z = t_d/2$  (10, 20). If  $h > h_c$ , equation (12) describes the  $ID$  that can occur in the commensurate phase of the system. The occurrence of such  $ID$ s is analogous to the formation of dislocations in ideal crystals.

Reference to equation (12) shows that the length of the  $ID$  should exceed the effective value given by expression

$$l^{ID} = c \left( \left( \frac{du}{dn} \right)_{n=0} \right)^{-1} \quad (14)$$

or

$$l^{ID} = \frac{t_d}{2} \sqrt{\frac{\mu_d t_d^2}{2\Delta U_{mz} N_m}} \quad (15)$$

We calculate the effective length  $l^{ID}$  of the  $ID$  for a set of DWNTs and tabulate the results in Table 1.

We next estimate the minimum energy  $U^{ID}$  required to form the  $ID$  in the commensurate state. Generally, if  $l_a \neq l_b$ , numerical minimization of equation (5) is required for calculation of the formation energy of the  $ID$  (15). However, for all considered in this paper DWNTs in the commensurate phase, the length  $l_d$  is much less than unity (10). This suggests that for these DWNTs, the energy  $U^{ID}$  is close to the formation energy of the  $ID$  for  $l_a = l_b$ . In the case of  $l_a = l_b$ , the energy of the  $ID$  formation has been derived analytically (11)

$$U^{ID} = \frac{2\sqrt{2\mu^2 W}}{\pi} = \frac{\sqrt{2\mu_d t_d^2 \Delta U_{mz} N_m}}{\pi} \quad (16)$$

We use equation (16) to estimate the energies  $U^{ID}$  for DWNTs in commensurate phase and present the results in Table 1. The energy  $U^{ID}$  of the  $ID$  formation can be partitioned into two physically meaningful terms

$$U^{ID} = U_{el}^{ID} + U_{int}^{ID} \quad (17)$$

where  $U_{el}^{ID}$  is elastic strain energy of the chains and  $U_{int}^{ID}$  is the change in the interwall interaction energy as a result of the commensurability loss. Note that in the FK model,  $U_{el}^{ID} = U_{int}^{ID}$  if  $l_a = l_b$  for any periodic potential

describing the interaction energy of the system (21). The energy of the  $ID$  formation remains the same whether the inner wall of a DWNT is compressed and the outer wall is expanded or vice versa.

### POSSIBLE APPLICATIONS OF THE FRENKEL–KONTOROVA MODEL: STRAIN NANOSENSOR

The commensurate-incommensurate phase transition in DWNTs is defined and controlled by the parameter  $H$  which depends on the barrier  $\Delta U_{mz}$  to relative sliding of the walls and the difference  $\Delta t$  in the lengths of the unit cells of the walls. In principle, electromechanical nanodevices based on the change in the phase of a DWNT corresponding to this transition can be elaborated.

We propose a new electromechanical device, called here a strain nanosensor, in which a critical strain causes the commensurate-incommensurate phase transition. Successful operation of the strain nanosensor requires the parameter  $H$  to be close to the critical value of  $H_c$ . In the absence of any strain applied to a DWNT, this condition corresponds to a DWNT being near the commensurate-incommensurate phase transition, and as a result, having non-chiral commensurate walls. The principal scheme of such nanosensor is shown on Figure 1. Parameter controlling operation of the nanosensor is  $\Delta t$ . Nanosensor can be embedded into solid medium or mounted on solid surface. It consists of three parts: two side parts which provide the transfer of strain from the medium to the nanosensor, and the central part that registers the critical strain. The outer wall of a DWNT with defects of atomic structure on the side parts of the nanosensor provides a better adhesion between these parts and the medium. Central part of the nanosensor should have perfect structure. The inner wall of a DWNT with perfect structure is placed at the center of the nanosensor. The length of the inner wall should be less than the length of the central part of the nanosensor in order to avoid interactions with the side (defected) parts of the outer wall. The strain of the medium causes extension (or contraction) of the central part of the nanosensor and, as a result, the increase (or decrease) in the parameter  $\Delta t$ . At some value of  $\Delta t$  (critical strain), the commensurate-incommensurate phase transition takes place. Note that the difference  $\Delta t$  corresponding to the phase transition increases with decreasing length of the inner wall. Therefore, the nanosensor can be adjusted to a given critical strain by selecting the length of the inner wall. To study a strain distribution, a set of nanosensors adjusted to different critical values of strains can be produced and embedded into the sample.

Since the length of the outer wall is fixed by the strain of the medium, the commensurate-incommensurate phase transition takes place only in the inner wall. In this case,  $\mu_d$  in equation (7) is replaced by the elastic constant of the inner wall,  $\mu_l$ , corresponding to the length of the unit cell of the inner wall.

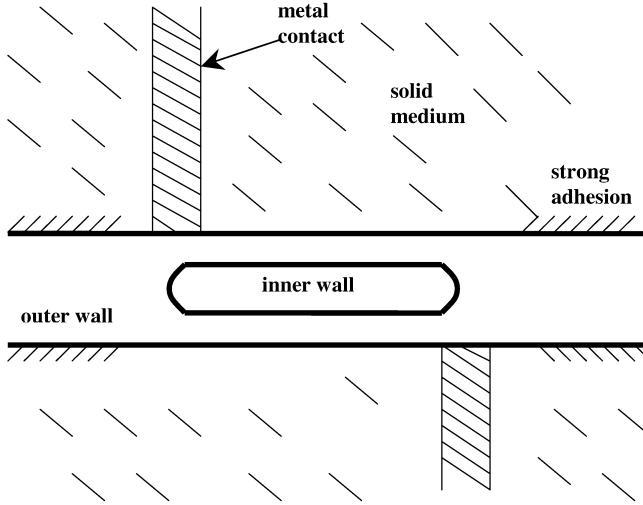


Figure 1. Principal scheme of strain nanosensor.

Equation (7) leads to the critical difference  $\Delta t_c$  corresponding to the commensurate-incommensurate phase transition in DWNTs defined as

$$\Delta t_c = \frac{2\sqrt{2}}{\pi} \sqrt{\frac{\Delta U_{mz} N_m}{\mu_1}} \quad (18)$$

We estimate the minimum strain of the medium as  $\varepsilon_c = \Delta t_c / t_d$ . The proposed nanosensor can measure values of strain of the medium which exceed the critical value  $\varepsilon_c$ . The calculated values of  $\varepsilon_c$  are listed in Table I.

We suggest a possible method of registration of the commensurate-incommensurate phase transition in DWNTs. At the phase transition, the sudden change in average relative displacement of the walls takes place (for example, see the calculations for 2D FK model (22)). The conductance of a DWNT with non-chiral commensurate walls is determined by the relative displacement of the walls (23). Thus, the conductance also exhibits the sudden change at the phase transition. This change can be registered with the use of the contacts shown on the Figure 1.

## DISCUSSION AND CONCLUSIONS

Possibility of the commensurate-incommensurate phase transition in DWNTs with non-chiral commensurate walls has been predicted. This phase transition has been described using the Frenkel–Kontorova model, which was modified for the case of a DWNT composed of two SWNTs with non-rigid walls and



with close values of the length of unit cell. Parameter  $H$ , which determines the commensurate phase of a DWNT, has been calculated using the DFT results of (10) for the interwall interaction energies and elastic properties of DWNTs. The value  $H_c = \pi^2/8$ , which defines the commensurate-incommensurate phase transition, has been obtained for infinite DWNTs. It has been shown that, if  $H$  is greater than the transition parameter  $H_c$ , DWNTs with non-chiral commensurate walls correspond to the commensurate phase for which the lengths of unit cells of constituent walls are equal.

This conclusion holds good for the DWNTs with relatively large radii, for example, the (5,5)@(10,10), (9,0)@(18,0) and (10,0)@(20,0) DWNTs and larger. DWNTs with non-chiral commensurate walls of small radii (the (4,4)@(10,10) DWNT) correspond to the incommensurate phase. In this case, the structure of a DWNT can be described as a lattice of near-commensurate sectors separated by narrow areas of incommensurability defects. Similarly to the formation of dislocations in ideal crystals, the incommensurability defects can occur in the system while it is in the commensurate phase. Recent high resolution transmission electron microscopy experiments on DWNTs produced by high temperature treatment of C<sub>60</sub>@SWNT peapods (24) show that the wall of nanotube can indeed elastically deform to produce short commensurate segments. However, in this case the IDs are not formed due to a large amount of defects of atomic structure occurred during annealing of the peapods.

One of the quantity which defines the parameter  $H$  and, therefore, controls the commensurate-incommensurate phase transition in DWNTs is the difference in the lengths of unit cells of the constituent walls. Thus if one of the walls is compressed or expanded by external forces, this phase transition can in principle occur. As a result, the average relative displacement of the walls can undergo a sudden change. This phenomenon can be used for developing a new electromechanical nanodevice, a strain nanosensor. The nanosensor is based on relative sliding of the walls along the DWNT axis. Attached to any object, it records its extension or contraction.

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