

A SIMPLE MODEL OF DNA ADSORPTION ON CARBON NANOTUBE

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One of the major interaction mechanisms between carbon nanotubes (CNT) and DNA is π - π -stacking, which is a van der Waals type of interaction. Attraction between the polycyclic aromatic surface elements of CNTs and the aromatic nucleotides of DNA leads to reversible adsorption (physisorption) between them. We propose to describe the ssDNA adsorption on CNT using zipper model and address the connection between the thermodynamics of adsorption and the flexibility of ssDNA.

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Introduction. Deoxyribonucleic acid (DNA) is a biomolecule, composed of two polymer chains, stabilized by hydrogen bonds (H-bonds) in the perpendicular direction to its axis. If H-bonds are broken and two strands are separated, each single strand DNA (ssDNA) is still stabilized by π -stacking of neighbour nucleotides in the parallel direction to the axis. Since the longitudinal dimension of DNA exceeds the lateral one by at least several million times, we can think of the system as one-dimensional (1D) [1]. Another constituent of the hybrid under study, carbon nanotube (CNT), is the system with cylindrical symmetry, that has unique electronic properties due to the relevant size-quantization effects [2], as well as outstanding mechanical properties thanks to its amazing structure. Due to the large ratio of longitudinal and lateral dimensions, just as for DNA, CNTs can be considered as 1D objects.

There are several reasons, motivating the study the DNA–CNT complex. One is the insolubility or extremely poor solubility of CNTs that imposes a considerable challenge when it comes to applications. Different techniques have been developed to improve CNT dispersion including the use of surfactants, oligomers, biomolecules, polymer-wrapping, chemical functionalization. One of the most efficient dispersing agents for water solutions is ssDNA, which forms a stable (very) complex with CNTs [3].

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Recently, several phenomenological models have been applied to the problem, mainly through the modifications of adsorption theories, known from the past. Thus, to process the experimental data of a recent experimental study [4], the adsorption of ssDNA oligomers and dimers was interpreted as a simple chemical reaction [5, 6].

Zipper Model. In this paper we describe the CNT–ssDNA physisorption phenomenon using the zipper model [7] in spin Hamiltonian formulation and validate the theoretical results against the experimental data.

For this reason we will describe the process of adsorption (desorption) of DNA on the surface of CNT in terms of helix-coil transitions. In order to estimate the free energy of adsorption of nucleotides on SWCNT on the base of the experimental data we adopted the “Zipper” model suggested by Schellman in 1958, originally developed for description of helix-coil transitions in short biopolymers [7].

According to this model, in the context of adsorption each nucleotide of the chain can adopt one of the two possible states: bound (b) and unbound (u). And here all bound bases must be concentrated in the same region, i.e. only one region of bound residues is permitted (Fig. 1). The nucleus of bounded region can be formed in any point along the oligonucleotide and from this point will begin to propagate the bounded region.

The so-called stability parameter s has the meaning of a statistical weight, and is usually represented in terms of a (Gibbs or Helmholtz) free energy change between the helix and coil states, ΔG_{bind} :

$$s = \exp\left(-\frac{\Delta G_{bind}}{RT}\right). \quad (1)$$

The cooperativity parameter σ , by its definition, describes, how much the original probability of bounded region growth, s , is hindered by the fact that there is no preceding bounded repeated unit [8]:

$$\sigma = \exp\left(-\frac{\Delta G_{init}}{RT}\right), \quad (2)$$

where ΔG_{init} is the free energy of initialization of helical region. It has been shown that [7, 9]

$$s = \exp\left(-\frac{\Delta H - R \ln Q}{RT}\right), \quad (3)$$

$$\sigma = Q^{1-\ell},$$

where ΔH is the enthalpy of binding per nucleotide; ℓ is the persistent length of ssDNA; Q is the number of microscopic states of one nucleotide.

The partition function of the Zipper model is written [1] as

$$Z_N(\sigma, s) = 1 + \frac{\sigma s^2}{(s-1)^2} \left[s^N + \frac{N}{s} - (N+1) \right], \quad (4)$$

the degree adsorption is defined as a fraction of nucleotides bound to CNT and is written as

$$\theta = \frac{1}{N} \cdot \frac{\partial Z}{\partial \ln s}. \quad (5)$$

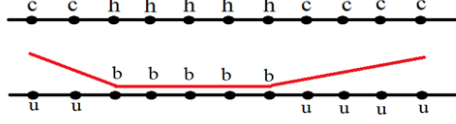


Fig. 1. Schematic illustration of the similarity between the mixture of helical and coil conformations at DNA melting (above) and bound-unbound conformations of DNA on CNT (below).

The dependence of the cooperativity parameter σ on the persistence length ℓ can be explained in terms of analogy between ssDNA adsorption on CNT and another well-studied phenomenon, the helix-to-coil transition or DNA melting. Indeed:

i) ssDNA adsorbs in pieces, having the scale of Kuhn length. DNA melting takes place in pieces of the order of the persistence length (Fig. 1). Thus, both phenomena require the account of strong cooperativity;

ii) on the level of each repeat unit, ssDNA has many possible free conformations, and the unique one, when adsorbed. In a similar way, when helical, repeat units are in a distinct conformation, as opposed to the molten DNA;

iii) short-range interactions (H-bonding between the strands of DNA and stacking between DNA and a nanotube) stabilize the association between the two 1D systems.

Using the above mentioned similarity, we make use of models we have suggested in the past [10–12]. We describe the adsorption of ssDNA on CNT with the energy function (Hamiltonian) that depends on coarse-grained variables of the system. The Potts-like Hamiltonian from [9, 13] is adopted to the problem of ssDNA–CNT association. We estimate the partition function and calculate experimentally measurable quantities, paving the way for a fitting procedure.

Employing nearest-neighbor approximation, we start with a Potts-like spin Hamiltonian formulation, equivalent to Zimm and Bragg model [13]:

$$\mathcal{H}(\{\gamma_i\}) = -U \sum_{i=1}^N \delta(\gamma_i, 1) \times \cdots \times \delta(\gamma_{i+\ell-1}, 1) \equiv -U \sum_{i=1}^N \delta_i^{(\ell)}, \quad (6)$$

where $\gamma_k = 1, 2, \dots, Q$ are spin variables, describing the conformations of each of $i = 1, 2, \dots, N$ repeat units (nucleotides), spin value $\gamma = 1$ corresponds to the ordered (bound) conformation, other $Q - 1$ values describe disordered (free) conformations.

The authors of [14] have investigated the DNA–CNT interactions experimentally. The solution of 12-base-long ssDNA homopolymers consisting of poly $d(A)_{12}$, poly $d(T)_{12}$, poly $d(C)_{12}$ and poly $d(G)_{12}$, as well as regular heteropolymers poly $d(AC)_6$ and poly $d(GT)_6$ was added to single walled carbon nanotubes (SWNT) at a DNA : SWNT = 1 : 1 mass ratio. From this article it follows that measuring quantity is close to an average degree of DNA/CNT association. In the Fig. 2 the experimental results, obtained in [14], are digitalized and reproduced.

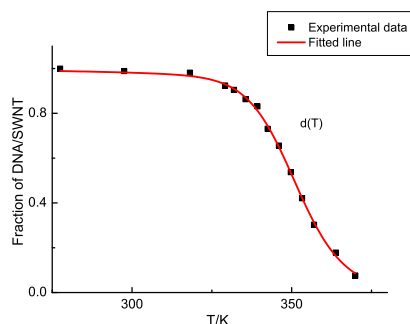


Fig. 2. The fraction of total initial DNA/SWNT as a function of temperature for poly $d(T)_{12}$.

The results presented in the Fig. 2 are very similar to the melting, curves describing DNA melting and the proposed Zipper model can be easily used to fit the experimental data and to estimate thermodynamics parameters of ssDNA adsorption on the surface of CNT.

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REFERENCES

1. Cantor C.R., Shimmel P.R. *Biophysical Chemistry*. Part 3. San-Francisco: Freeman and Co. (1980), 597 p.
2. Iijima S. Helical Microtubules of Graphitic Carbon. *Nature*, **354** (1991), 56–58.
3. Vogel S.R., Muller K., Plutowski U., Kappes M.M., Richert C. DNA-carbon Nanotube Interactions and Nanostructuring Based on DNA. *Phys. Stat. Sol. (b)*, **244** (2007), 4026–4029.
4. Brunecker F.K., Schoppler F., Hertel T. Interaction of Polymers with Single-Wall Carbon Nanotubes. *J. Phys. Chem. C*, **120** : 18 (2016), 10094–10103.
5. Kato Y., Inoue A., Niidome Y., Nakashima N. Thermodynamics on Soluble Carbon Nanotubes: How do DNA Molecules Replace Surfactants on Carbon Nanotubes? *Scientific Reports*, **2** (2012), 733(7) p.
6. Butyrskaya E.V., Zapryagaev S.A., Izmailova E.A. Cooperative Model of the Histidine and Alanine Adsorption on Single-walled Carbon Nanotubes. *Carbon*, **143** (2019), 276–287.
7. Schellman J.A. The Factors Affecting the Stability of Hydrogen-bonded Polypeptide Structures in Solution. *J. Phys. Chem.*, **62** (1958), 1485–1494.
8. Zimm B.H., Bragg J.K. Theory of the One-Dimensional Phase Transition in Polypeptide Chains. *J. Chem Phys.*, **2** (1958), 1246–1247.
9. Hairyan Sh.A., Mamasakhlisov E.Sh., Morozov V.F. Helix-coil Transition in Polypeptides. A Microscopic Approach II. *Biopolymers*, **35** (1995), 75–84.

10. Morozov V., Mamasakhlisov E., Hayryan Sh., Hu C.K. Microscopical Approach to the Helix- Coil Transition in DNA. *Physica A*, **281** (2000), 51–59.
11. Badasyan A., Tonoyan Sh.A., Giacometti A., Podgornik R., Mamasakhlisov Y.Sh., Morozov V.F. Osmotic Pressure Induced Coupling Between Cooperativity and Stability of a Helix-Coil Transition. *Phys. Rev. Lett.*, **109** (2012), 068101(5) p.
12. Badasyan A., Giacometti A., Podgornik R., et al. Helix-coil Transition in Terms of Potts-like Spins. *Eur. Phys. J. E*, **5** (2013), 46(9) p.
13. Badasyan A., Giacometti A., Mamasakhlisov Y.Sh., Morozov V.F. Benight A.S. Microscopic Formulation of the Zimm-Bragg Model for the Helix-coil Transition. *Phys. Rev. E*, **81** (2010), 021921(4) p.
14. Albertorio F., Hughes M.E., Golovchenko J.A., Branton D. Base Dependent DNA-carbon Nanotube Interactions: Activation Enthalpies and Assembly-disassembly Control. *Nanotechnology*, **20** : 39 (2009), 395101 (9) p.

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ԱԾԽԱԾՆԱՅԻՆ ՆԱՆՈՒՆՈՂՈՎԱԿՆԵՐԻ ՆԵՏ ԴՆԹ-Ի ՊԱՐԶ ԿԱՊՄԱՆ ՄՈՂԵԼ

Ածխածնային նանոխողովակների (ԱՆԽ) և դեզօքսիռիբոնուկլեինաթթվի (ԴՆԹ) միջև փոխազդեցության կարևոր մեխանիզմներից մեկը π - π սպեկինգն է, որն իրենից ներկայացնում է վան դեր Վաալսյան փոխազդեցություն: Ձգողությունը ԱՆԽ-ի պոլիցիկլիկ արոմատիկ մակերևույթի փարրերի և ԴՆԹ-ի արոմատիկ նուկլեոտիդների միջև հանգեցնում է միմյանց հեպ դարձելի կապման (ֆիզիկորբցիա): Մենք առաջարկում ենք ԱՆԽ-ի հեպ՝ մշ-ԴՆԹ-ի կապման եղանակի նկարագրություն զիպեր մոդելի օգնությամբ և ենթադրում ենք, որ փոխազդեցության թերմոդինամիկայի և մշ-ԴՆԹ-ի ճկունության միջև առկա է կապ:

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ПРОСТАЯ МОДЕЛЬ АДСОРБЦИИ ДНК НА УГЛЕРОДНЫХ НАНОТРУБКАХ

Одним из важных механизмов взаимодействия между углеродными нанотрубками (УНТ) и ДНК является π - π -стекинг-взаимодействие, которое само по себе является вандерваальсовым взаимодействием. Притяжение между элементами полициклической ароматической поверхности УНТ и ароматическими нуклеотидами ДНК приводит к обратимой адсорбции (физисорбция) между ними. Мы представляем способ описания адсорбции оц-ДНК на УНТ посредством зишпер-модели и полагаем, что существует связь между термодинамикой адсорбции и гибкостью оц-ДНК.