Manybody effects at low-energy ions channeling in carbon nanotubes

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Abstract. The molecular dynamics method has been used to consider manybody interactions at the channeling of the ion in a carbon nanotube, and the importance of their accounting has been shown. The effect of the wall elastic perturbation of a nanotube on a channeled particle is studied. It was confirmed that when ion with perturbation of the wall of the carbon nanotube interaction is taken into account, the ion energy loss is reduced by a factor of 1.5-3. It is shown that as the temperature of the nanotube decreases, the effect of ion interaction with wall perturbation acquires a more determinate character. Within the framework of the considered model, electronic stopping power on the electronic subsystem of a carbon nanotube is small compared to energy losses of an ion in elastic collisions on atoms of a nanotube wall.

1. Introduction

After the discovery of carbon nanotubes (CNTs) and the discovery of their unique properties, they found application in many areas of solid state physics. Interesting applications are 1) the use of carbon nanotubes as channels for ion transport [1-3]; 2) creation of nanocontainers from carbon nanotubes by means of ion implantation [4, 5]. On the one hand, both applications are applicable to chemistry and biology for the delivery of substances to the cell, to the chemical reaction zone. On the other hand, the first application is applicable for precise control of an ion beam during ionic modification of a solid surface [6, 7], and the second can be useful in the modification of the chemical and electronic properties of the nanotubes themselves. The ion modification of carbon nanotubes was studied in works of Nordlund [8-13], Shemukhin [14-16] both theoretically and experimentally. Transport of ions through the channels of nanotubes was studied mainly theoretically by computer simulation [17]. The author knows only one experimental work [18] on the transport of ions through an array of multi-walled carbon nanotubes grown in the pores of porous alumina. Theoretically, channeling of ions in carbon nanotubes was studied for three energy ranges: high (~1 GeV) [19-21], medium (~1 MeV) [22-30] and low (~1 keV) [31-35]. When channeling the ion, it interacts with the atoms of the wall of the carbon nanotube, collisions of ions and CNT wall atoms usually occur at sliding incident angles. Depending on the energy of the ion, it is possible to exhibit both elastic and inelastic scattering of the ion on CNT wall atoms. It should be noted that in the low-energy range, ion energy losses predominate over elastic collisions of an ion with CNT wall atoms. In the middle energy range, the energy losses associated with the stopping of CNT walls on an electron gas are more pronounced. In the high-energy range, there is a collective interaction of the ion with atoms and inelastic scattering by electrons of the nanotube wall.
Historically, the high energy range was first investigated. To control beams of high-energy ions as an alternative to cumbersome magnetic systems, it [36] has been proposed to use nanotubes. In the works [21, 37] it was shown that the fluxes of ions of high (ultra relativistic) energies can be controlled by CNT bundles or multiwalled CNTs better than curved crystals. Beams of medium-energy ions interact predominantly with the electron subsystem of the nanotube, which affects the nature of channeling in nanotubes and energy losses [26, 38, 39]. In the low-energy range, nuclear (elastic) inhibition predominates, and the interaction of ions with the atoms of the tube is due to manybody interactions [17, 31, 39]. Manybody collisions are collisions influenced by the position, type, and degree of hybridization of neighboring atoms. The channeled ions in this energy range are rapidly neutralized [31]. Earlier it was shown that it is important to take into account the motion of all atoms in the nanotube, and not only the nearest ion to the channeled one. Using the method of molecular dynamics, results were obtained on the passage of ions through carbon nanotubes with heterojunctions [40], which can be used as focusing apertures for low-energy particles.

In this paper, we demonstrate the effects observed when many-body interactions are taken into account in modeling the channeling of low-energy ions in carbon nanotubes.

2. Methods

For the calculations in this paper we used the molecular dynamics method. The LAMMPS code was used [41]. Carbon nanotubes were created using the VMD code [42], visualized using Ovito [43].

It is important to take into account the manybody interactions of the ion and the atoms of the nanotube. The use of the classical approach to describe such interactions is confirmed in [44], using the time-dependent density functional theory method.

For molecular dynamics calculations, carbon nanotubes were first prepared. The coordinates of the atoms were created using the VMD code, three models of nanotubes ["armchair" (10, 10), “zig-zag” (17, 0) and “chiral” (11, 9)] were constructed with approximately equal diameters (1.3 nm), the length of each of the tubes was 14.3 nm. To describe the interatomic interactions of carbon atoms the AIREBO potential was used [45]. Then, using the conjugate gradient method with the LAMMPS code, the energy of the carbon nanotube was minimized, and then the thermostat of Berendsen [46] for 5 ps and a relaxation time of 0.1 ps and Nose-Hoover [47] also for 5 ps and a relaxation time of 0.1 ps with an integration step of 1 fs.

To calculate the trajectories of channeled ions, the following initial conditions were applied: the ions were launched from the nanotube axis with incident energy 100 eV for all cases, the angle of incidence α varied from 10 to 30 °, the azimuth angle θ varied from -18 to +18°) and the initial position on the Z axis. The total number of spans per tube was 13689, that is, for each angle of entry α, 169 span.

\[ F = \frac{Z_1^2 \gamma \nu}{8 \omega_c^2 \rho^3} - 3 \frac{Z_1^2 \nu \ln(0.629 k_F \rho)}{2 \pi (k_T \rho)^4} \]

where \( Z_1 \) - ion atomic number, \( \nu \) - longitudinal velocity of an ion, \( \gamma = 3 \text{eV} \) - damping coefficient, \( \omega_c = 10 \text{eV} \) - surface plasmon frequency, \( \rho \) - distance between ion and nanotube wall, \( k_F = \frac{\nu_F}{\gamma k_F^2} / 4 \), where \( \nu_F = 10^6 \) - Fermi velocity (here we use Hartree units, unless otherwise indicated). All parameters listed here concise with metallic carbon nanotubes (‘arm-chair’ chirality).

The step of integrating the equations of motion 0.0005 fs as a result of the trajectories obtained was analyzed: ion collisions with the nanotube wall were tracked, changes in the total ion energy after each collision were calculated. Dependences of ion energy losses in collisions versus the angle of entry α were obtained, with the results at each angle of entry being averaged over the azimuthal angles and the initial position on the Z axis. The total number of spans per tube was 13689, that is, for each angle of entry α, 169 span.
3. Results and Discussion

The trajectory of the ion inside the carbon nanotube is shown in figure 1. The general view of the trajectory is shown in figure 1 a sections of the trajectory of the ion and the state of the atoms of the tube when the atom approaches the wall is shown in figure 1 b. When the ion collides with the wall, the carbon atoms move from the equilibrium position and the wall deforms.

![Figure 1](image)

**Figure 1.** a) The trajectory of Ar$^+$ in the CNT fragment (10, 10) with a length of 14.3 nm with the time points marked on it. (b) Instant "snapshots" at the instants indicated in Figure 3 (a) of CNT fragments with images of the trajectory sections at the appropriate instants of time. The current position of the particle is indicated by a circle.

Figure 2 shows the dependence of the relative displacement of the atoms of the wall of the tube as a function of time during the first collision of an ion with the nanotube wall. As can be seen from figure 2 there is a simultaneous displacement of several wall atoms. This proves the validity and validity of a more consistent method of molecular dynamics, in contrast to the approximation of pair collisions or models based on averaging the potential of the nanotube wall that does not take into account the atomic displacements. It should be noted that this statement is most true at relatively large ion channeling angles. The displacement of atoms generates the appearance of a perturbation on the wall of the nanotube and affects neighboring carbon atoms, including diametrically opposite to those encountered by the ion. The perturbation propagates along the axis of the nanotube, and the propagation velocity of the perturbation is approximately 16 km/s, which is close to the propagation velocity of phonons in a carbon nanotube [50, 51]. Simulation shows that the perturbation of the tube wall can propagate at a velocity close to the longitudinal velocity of ion motion, in this case the perturbation can interact with the ion. Earlier in the work [52] it was shown that the interaction of the ion with the perturbation caused by it leads to a decrease in the energy loss by the ion in a collision with the wall. If we compare the graphs of the dependence of the energy loss of an ion on the angle of entry, taking into account the perturbation of the nanotube wall and without taking into account
(figure 3), it turns out that for the second and third collisions in the model, taking into account the wall perturbation, the ion is lost by 1.5-3 times less energy than in model without taking into account the perturbation of the nanotube wall. This is explained by the exchange of energy between the perturbation of the wall and the moving ion - there is a gliding of the particle on the wave of perturbation of the nanotube wall [52]. Such a phenomenon becomes possible if the longitudinal velocity of the particle and the propagation velocity of the perturbation along the tube axis are close. This conclusion is also confirmed by the fact that when the longitudinal component of the ion velocity increases, the effect of energy exchange between the perturbation and the ion is not so significant. It was previously shown that for the Ar$^-$ ion the observation condition of the effect can be represented in the form of a range of angles (21-28 degrees) and energies (20 - 55 eV) of the ion.

![Figure 2](image_url)

**Figure 2.** Dependence of the deformation of the CNT wall (11, 9) on the time per atom for the first collision of the Ar$^-$ ion with the wall. The arrow indicates the direction of motion of the ion in the nanotube. Figures 1-6 denote the atoms of a nanotube, for which the deformation of a section of a CNT wall is calculated.

We have obtained data on the effect of temperature on the character of the ion energy losses as a function of the initial angle of entry, with and without electronic stopping. The dependences indicate a non-monotonic character of the dependence of the ion energy losses on the angle of flight. It was shown that the inclusion of electronic inhibition does not make a significant contribution to the character of the dependences of energy loss by an ion on the angle of entry (figure 4). But taking into account the temperature of the nanotube affects the energy loss vs incident angle dependencies. So nanotubes at low temperature are less subject to the influence of temperature fluctuations, and as a result, the curve of the dependence of ion energy loss as a function of the angle of entry looks more deterministic. Since nanotubes of various chiralities were investigated, but diameters for each of them were close, analogous dependences of ion energy losses on the angle of entry into the tube were constructed. For the second and third collisions with the wall, the form of the dependences (figure 5) differs somewhat especially for room temperature, but on average they are close, and the differences disappear at a temperature of 0.1 K (figure 6).
Figure 3. Dependence of the ion energy losses in the third collision with the wall of the (11, 9) nanotube versus the angle of entry, taking into account (curve 1) and disregarding the perturbation (curve 2) at a nanotube temperature of 300 K, as well as in the third collision, taking into account the perturbation at a temperature of 0.1 K (curve 3).

Figure 4. Dependence of ion energy losses in the third collision with the wall of the nanotube versus the angle of incidence, taking into account (curve 1) and disregarding stopping (curve 2) on an electron gas.
Figure 5. The loss of energy after the second (second to the left) and third (third to the right) collisions of the Ar^+ ion with the CNT wall (at a temperature of 300 K), depending on the initial channeling angle for the "armchair" (10, 10), "chiral" (11, 9) and "zig-zag" (17, 0) nanotubes.

Figure 6. The loss of energy after the second (second to the left) and third (third to the right) collisions of the Ar^+ ion with the wall of the CNT (at a temperature of 0.1 K), depending on the initial channeling angle for the "armchair" (10, 10), "chiral" (11, 9) and "zig-zag" (17, 0) nanotubes.

4. Conclusion

When approaching the CNT wall, the channeled particles experience an effective interaction simultaneously with several atoms, and an elastic deformation of the wall takes place. Hence, the incomplete adequacy of the approximation of the continuous potential, the binary collision model, and the need to use the molecular dynamics method in modeling the channeling process follow.

An elastic perturbation of the nanotube wall under the action of a channeled particle affects the motion of this particle if its velocity is close to the propagation velocity of the perturbation. At the same time, the particle loses less energy than in the case of motion in the unperturbed tube.

The temperature oscillations of the atoms of a carbon nanotube randomize the trajectory of the channeled particle. With decreasing temperature, the dependence of the ion energy loss on the angle of entry upon collision with the wall acquires a more determinate character.
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References

[1] Liu Y and Wang Q 2005 Transport behavior of water confined in carbon nanotubes Physical Review B 72 085420
[2] Shiomi J and Maruyama S 2009 Water transport inside a single-walled carbon nanotube driven by a temperature gradient Nanotechnology 20 055708
[3] Hanasaki I, Yonebayashi T and Kawano S 2009 Molecular dynamics of a water jet from a carbon nanotube Physical Review E 79 046307
[4] Mousavi S Z, Amjad-Iranagh S, Nademi Y and Modarress H 2013 Carbon Nanotube-Encapsulated Drug Penetration Through the Cell Membrane: An Investigation Based on Steered Molecular Dynamics Simulation The Journal of Membrane Biology 246 697-704
[5] Mejri A, Vardanega D, Tangour B, Gharbi T and Picaud F 2015 Encapsulation into Carbon Nanotubes and Release of Anticancer Cisplatin Drug Molecule The Journal of Physical Chemistry B 119 604-11
[6] Villanueva L G, Martin-Olmos C, Vazquez-Mena O, Montserrat J, Langlet P, Bausells J and Brugger J 2011 Localized Ion Implantation Through Micro/Nanostencil Masks IEEE Transactions on Nanotechnology 10 940-6
[7] Pang S W, Lyszczarz T M, Chen C L, Donnelly J P and Randall J N 1987 Masked ion beam lithography for submicrometer-gate-length transistors Journal of Vacuum Science & Technology B: Microelectronics Processing and Phenomena 5 215-8
[8] Krasheninnikov A V, Nordlund K, Sirviö M, Salonen E and Keinonen J 2001 Formation of ion-irradiation-induced atomic-scale defects on walls of carbon nanotubes Physical Review B 63 245405
[9] Krasheninnikov A V and Nordlund K 2010 Ion and electron irradiation-induced effects in nanostructured materials Journal of Applied Physics 107 071301
[10] Krasheninnikov A V and Nordlund K 2004 Irradiation effects in carbon nanotubes Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 216 355-66
[11] Pomoell J A V, Krasheninnikov A V, Nordlund K and Keinonen J 2004 Ion ranges and irradiation-induced defects in multiwalled carbon nanotubes Journal of Applied Physics 96 2864-71
[12] Krasheninnikov A V, Nordlund K and Keinonen J 2002 Production of defects in supported carbon nanotubes under ion irradiation Physical Review B 65 165423
[13] Krasheninnikov A V and Nordlund K 2002 Stability of irradiation-induced point defects on walls of carbon nanotubes Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures 20 728-33
[14] Elsehly E M, Chechenin N G, Makunin A V, Shemukhin A A and Motaweh H A 2017 He ion irradiation effects on multiwalled carbon nanotubes structure The European Physical Journal D 71 79
[15] Elsehly E M, Chechenin N G, Makunin A V, Shemukhin A A and Motaweh H A 2018 Enhancement of CNT-based filters efficiency by ion beam irradiation Radiation Physics and Chemistry 146 19-25
[16] Kushkina K D, Shemukhin A A, Vorobyeva E A, Bukunov K A, Evseev A P, Tatarintsev A A, Maslakov K I, Chechenin N G and Chernysh V S 2018 Evolution of the multi-walled carbon nanotubes structure with increasing fluence of He ion irradiation Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 430 11-7
[17] Mišković Z L 2007 Ion channeling through carbon nanotubes Radiation Effects and Defects in Solids 162 185-205
[18] Zhu Z, Zhu D, Lu R, Xu Z, Zhang W and Xia H 2005 The experimental progress in studying of channeling of charged particles along nanostructure Proceedings International Conference on Charged and Neutral Particles Channeling Phenomena 5974 597413-8
[19] Klimov V V and Letokhov V S 1996 Hard X-radiation emitted by a charged particle moving in a carbon nanotube Physics Letters A 222 424-8
[20] Zhevago N K and Glebov V I 1998 Channeling of fast charged and neutral particles in nanotubes Physics Letters A 250 360-8
[21] Zhevago N K and Glebov V I 2003 Computer simulations of fast particle propagation through straight and bent nanotubes Physics Letters A 310 301-10
[22] Mowbray D J, Chung S, Mišković Z L, Goodman F O and Wang Y-N 2005 Dynamic interactions of fast ions with carbon nanotubes Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 230 142-7
[23] Mowbray D J, Mišković Z L, Goodman F O and Wang Y-N 2004 Interactions of fast ions with carbon nanotubes: Two-fluid model Physical Review B 70 195418
[24] Borka D, Mowbray D, Mišković Z, Petrović S and Nešković N 2008 Dynamic polarization effects on the angular distributions of protons channeled through carbon nanotubes in dielectric media Physical Review A 77
[25] Borka D, Mowbray D J, Mišković Z L, Petrović S and Nešković N 2010 The donut and dynamic polarization effects in proton channeling through carbon nanotubes New Journal of Physics 12 043021
[26] Borka D, Petrović S, Nešković N, Mowbray D and Mišković Z 2006 Influence of the dynamical image potential on the rainbows in ion channeling through short carbon nanotubes Physical Review A 73
[27] Kramberger C, Roth F, Schuster R, Kraus R, Knupfer M, Einarsson E, Maruyama S, Mowbray D J, Rubio A and Pichler T 2012 Channeling of charge carrier plasmons in carbon nanotubes Physical Review B 85 085424
[28] Mowbray D J, Mišković Z L and Goodman F O 2006 Ion interactions with carbon nanotubes in dielectric media Physical Review B 74 195435
[29] Mowbray D J, Mišković Z L, Goodman F O and Wang Y-N 2004 Wake effect in interactions of fast ions with carbon nanotubes Physics Letters A 329 94-9
[30] Mowbray D J, Segui S, Gervasoni J, Mišković Z L and Arista N R 2010 Plasmon excitations on a single-wall carbon nanotube by external charges: Two-dimensional two-fluid hydrodynamic model Physical Review B 82 035405
[31] Dedkov G V 2002 Characterization of nanotubes as microscale beam manipulators: transmission of neutral atoms and low-energy ions Surface and Coatings Technology 158–159 75-80
[32] Moura C S and Amaral L 2005 Channeling on carbon nanotubes: a molecular dynamics approach The journal of physical chemistry B 109 13515-8
[33] Wei Z, Zhiyu Z, Zijian X, Zhenxia W and Fengshou Z 2005 Molecular dynamics study of a low energy carbon ion moving in a single-wall carbon nanotube Nanotechnology 16 2681
[34] Krasheninnikov A V and Nordlund K 2005 Channeling of heavy ions through multi-walled carbon nanotubes Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 228 21-5
[35] Aleksandrov V A, Lysova I V, Sabirov A S, Samsonov A M, Stepanov A V and Filippov G M 2012 Atomic particle channeling simulation in carbon nanotubes J. Synch. Investig. 6 172-5
[36] Gevorgyan L A, Ispiryan K A and Ispiryan R K 1997 Channeling in single-wall nanotubes: Possible applications Journal of Experimental and Theoretical Physics Letters 66 322-6
[37] Greenenko A A and Shul’ga N F 2003 Fast ion passing through straight and bent nanotubes  
Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with 
Materials and Atoms 205 765-72  
[38] Granger B E, Král P, Sadeghpour H R and Shapiro M 2002 Highly Extended Image States 
around Nanotubes Physical Review Letters 89 135506  
[39] Zamkov M, Woody N, Bing S, Chakraborty H S, Chang Z, Thumm U and Richard P 2004 
Time-Resolved Photoimaging of Image-Potential States in Carbon Nanotubes Physical Review Letters 93 156803  
[40] Stepanov A V and Filippov G M 2017 Channeling of low energy atomic particles in carbon 
nanotubes with heterojunctions Nucl. Instrum. Methods Phys. Res. B 402 263-6  
[41] Plimpton S 1995 Fast Parallel Algorithms for Short-Range Molecular Dynamics Journal of 
Computational Physics 117 1-19  
[42] Humphrey W, Dalke A and Schulten K 1996 VMD - Visual Molecular Dynamics Journal of 
Molecular Graphics 14 33-8  
[43] Stukowski A 2010 Visualization and analysis of atomistic simulation data with OVITO—the 
Open Visualization Tool Modelling and Simulation in Materials Science and Engineering 18 015012  
[44] Krasheninnikov A V, Miyamoto Y and Tománek D 2007 Role of Electronic Excitations in Ion 
Collisions with Carbon Nanostructures Physical Review Letters 99 016104  
[45] Stuart S J, Tutein A B and Harrison J A 2000 A reactive potential for hydrocarbons with 
intermolecular interactions The Journal of Chemical Physics 112 6472-86  
[46] Berendsen H J C, Postma J P M, Gunsteren W F v, DiNola A and Haak J R 1984 Molecular 
dynamics with coupling to an external bath The Journal of Chemical Physics 81 3684-90  
[47] Nosé S 1984 A unified formulation of the constant temperature molecular dynamics methods 
The Journal of Chemical Physics 81 511-9  
[48] Ziegler J F, Biersack J P and Littmark U 1985 The Stopping and Range of Ions in Matter, New 
York: Pergamon.  
[49] Nunez R, Echenique P M and Ritchie R H 1980 The energy loss of energetic ions moving near a 
solid surface Journal of Physics C: Solid State Physics 13 4229  
[50] Jishi R A, Venkataraman L, Dresselhaus M S and Dresselhaus G 1993 Phonon modes in carbon 
nanotubes Chemical Physics Letters 209 77-82  
[51] Dresselhaus M S, Dresselhaus G and Avouris P 2001 Carbon Nanotubes Synthesis, Structure, 
Properties, and Applications (Berlin: Springer Berlin Heidelberg)  
[52] Stepanov A V 2015 Influence of elastic perturbations of the wall of a carbon nanotube upon the 
channeling of slow atomic particles J. Synch. Investig. 9 789-98  
[53] Sadovnichy V, Tikhonravov A, Voevodin VI and Opanasenko V 2013 Contemporary High 
Performance Computing: From Petascale toward Exascale, ed J S Vetter (Boca Raton, 
USA: CRC Press) 283-307

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