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Abstract. – An approach is proposed to evaluate the average velocities of adsorbate molecules in one-dimensional nanopore, when quantum tunneling between neighboring potential minima leads to nonzero velocity. The approach is used to calculate the hydrogen isotope molecule (H_2, D_2, T_2) velocities in ultrathin carbon single-wall nanotubes (SWNT) $(3,3)$ and $(6,0)$. It is shown that the isotope mass difference leads to large differences of the quantum tunneling value and large differences of the average molecule velocities, especially inside the tube $(6,0)$. It is shown that different tube chirality leads to drastically different velocities of adsorbate molecules, even if the diameters of both nanotubes do not differ significantly.

Introduction. – The experimental finding in 1991 [1] of carbon nanotubes opened brand new possibilities both in technology and in fundamental physics. The nanoscale and one-dimensionality provided by these new materials led to the discovery of novel mechanical, chemical, and electrical properties [2], which suggested new exciting technological applications. One of the interesting phenomena is the adsorbate molecule movement inside nanotubes. There is a special interest regarding the description of isotopes molecules movement inside nanotubes. Difference in velocities of adsorbate isotope molecules can be used for isotope separation. The same chemical affinity of the isotopes does not allow one to use usual chemical methods of separation.

The quantum theory of molecular separation has been proposed by Beenakker *et al.* (see [3]) for absorption of hard spheres in square-well cylindrical tubes in the last decade. This theory and its further development [4] exploit the fact of transverse confinement of adsorbate molecules. According to this theory, the selectivity S (the equilibrium ratio of different isotope molecules densities inside the tube) is equal to $S = \frac{m_j}{m_i} \exp[-\frac{E_i - E_j}{kT}]$, where m_j, E_j, m_i, E_i are the mass and the lowest energy levels of the molecules of the different isotope species i and j, which move inside the nanotube in the transverse potential profile $V(r)$, where r is varied perpendicular to the tube axis direction.

If the difference between the lowest energy levels $\triangle E_1$ of different isotopes satisfies the condition $\triangle E_1 \gg k_\mathrm{B}T$ (hereinafter T is the temperature, k_B is Boltzmann constant), the ratio value S of the isotopes densities in the nanotube will be very large at equilibrium. It may be used for separation of isotopes by quantum sieving.

Unfortunately, this theory explains the transverse confinement effect only. A longitudinal adsorbate molecule movement along the nanopore axis is beyond the scope of this theory. Moreover, the theory operates with static-equilibrium densities only.

There are many works devoted to the description of diffusion in one-dimensional structures, where the mutual passage of particles is inhibited (single-file systems) [5–7]. In such systems a given order of particles within the system is strictly maintained. This extreme mutual hindrance of the diffusing particles inhibits counter-diffusion and drastically decreases the mobility of the particles. In the infinite single-file system the mean-square displacement of a tagged particle increases only proportionally to the square root of the observation time. Such unusual diffusion properties of the external molecules inside nanopores have been astonishingly confirmed by experiment [8]. Recently, single-file–structures monosized SWNT with extremely small diameters, (4–5 Å) have been successfully fabricated inside inert $AlPO_4$-5 zeolite channels [9, 10].

Theoretical analysis of single-file systems is considerably complicated by the fact that the diffusing particles are not able to pass each other, so their positions are correlated to the positions of all other particles and, therefore, to the past dynamical development of the whole system. Because of this difficulty, analytical results are mainly restricted or made by some approximations. The usual approaches are the diffusion Monte Carlo (DMC) method, the lattice gas model and the molecular-dynamics (MD) method. The DMC method [11] offers thermodynamic and equilibrium density properties, but it is very time consuming usually. The gas model [7] deals with a linear chain of N equidistant sites. These sites correspond to the troughs of a periodical potential describing the interactions of the particles and the channel walls. Each pair of adjacent troughs is separated by a potential barrier of height E_b. The rate of a particle jump from one site to the nearest neighbor is given by $P = P_0 e^{-\frac{E_\mathrm{b}}{k_\mathrm{B}T}}$, where the pre-exponential factor P_0 is a property of the activation mechanism. Unfortunately, any gas model is a statistical model and does not take into account the real molecule movements inside the nanopore. Furthermore, the P_0 value cannot be determined honestly in the framework of this model.

The MD method (both the *ab initio* MD approach [12, 13] or the approach with empirical potentials of interaction between atoms) allows one to calculate molecular dynamics via calculations of the forces influence on the atoms. The fundamental limitation of any MD method modification is that atoms obey the Newtonian equations of motion, rather than the quantum-mechanics equations. Zero point motion, quantum interference, quantized energy levels and tunneling phenomena are absent in classical mechanics, so any MD approach cannot even predict true qualitative results for a particle movement at low temperatures, when the particle kinetic energy E_kin is less than the potential barrier height $E_\mathrm{kin} < E_\mathrm{b}$. Unfortunately, a fully quantum-mechanical version of the molecular-dynamics scheme for complex systems is not likely to be practical in the nearest future, but a number of works involve the quantum effects in molecular-dynamic scheme already [14, 15].

Calculation details. – In this work we aim at elucidating the characteristic features of movements of a single adsorbate particle in one-dimensional channels inside SWNT on the basis of quantum-mechanical calculations. More precisely, the simple approach is proposed for the calculation of the average velocity of the molecule, which moves inside SWNT at nonzero temperatures. The approach is applied for the description of single-molecule (H_2, D_2, T_2)
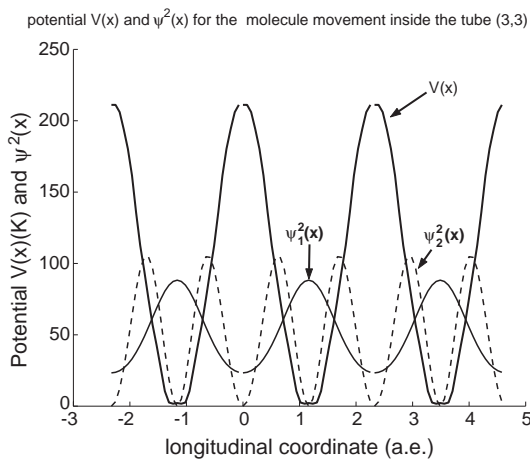
potential V(x) and ψ^2(x) for the molecule movement inside the tube (3,3)

potential V(x) and ψ^2(x) for the molecule movement inside the tube (6,0)

Fig. 1

Fig. 2

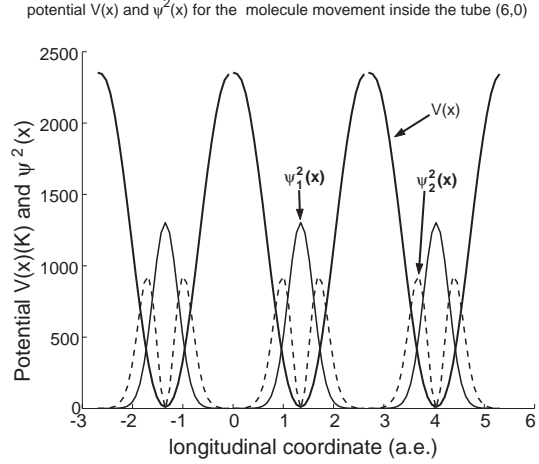Fig. 1 – The potential relief and lower ψ^2 for the $(3,3)$ tube.

Fig. 2 – Potential relief and lower ψ^2 for the $(6,0)$ tube.

movements. The proposed approach predicts that the average velocity of intruded molecule be $\langle V \rangle \neq 0$ at any temperature. The MD method cannot be used at low temperatures, when the particle energy E is less than $V_{\max}$. It has been shown that quantum tunneling leads to large differences in isotope molecule velocities.

The calculations are performed using the Vienna *ab initio* simulation package VASP [16, 17] which used the DFT approach and plane-wave decomposition. It is perfectly suited for the investigation of one-dimensional unrestricted systems like single-wall carbon nanotubes (SWCNT). Utilization of the Vanderbilt-type pseudopotentials [18] allows significant reduction of the number of basis plane waves in the calculations. The maximum kinetic energy (E_{cutoff}) value in our calculations has been put equal to $211\,\text{eV}$.

We have studied a hydrogen isotope molecule movement inside ultrathin SWCNT $(3,3)$ and $(6,0)$ with diameters $\sim 4.07\,\text{Å}$ and $4.70\,\text{Å}$, respectively. From the MD calculations for both systems it has been found the all isotopes molecules (H_2, D_2 and T_2) move along the tube axis in both tubes. Particularly, for the hydrogen molecule movement inside the $(3,3)$ tube the maximal angle between the molecule and the tube axes was $\cong 5°$ at $T = 200\,\text{K}$. At that, the molecule begins to reflect from the wall potential barriers below some critical temperature T_{c}. According to the classical laws of motion in the MD scheme, the average adsorbate molecule velocity is $\langle V \rangle \equiv 0$ below this temperature. T_{c} has been found to be equal to $155 \pm 5\,\text{K}$ for the H_2 molecule movement inside the $(3,3)$ tube. This value is in good agreement with the maximal height of the potential $V_{\max} = \max(V(r))$ along the tube axis, which is equal to $211\,\text{K}$. The discrepancy can be explained by temperature smoothing of the potential barriers due to atomic vibrations. For the $(6,0)$ tube, T_{c} has not been determined because the $V_{\max}$ value in this tube was too high ($V_{\max} \cong 2300\,\text{K}$).

The potential profile $V(r)$ for the adsorbate particle movement along the tube axis has been determined by calculations of the total energy of the joint system (tube + adsorbate molecule (H_2, D_2, T_2)). The particle coordinates have been fixed on the grid of points along the tube axis. The profiles $V(r)$ for the $(3,3)$ and $(6,0)$ tubes are shown in figs. 1, 2.

The validity of the assumption that the adsorbate molecule moves along the tube axis

only has been verified by the evaluation of the potential energy profile of the particle ϵ^i at its displacement transverse to the tube axis directions. Namely, molecule displacements at 0.1, 0.2 and 0.3 Å from the tube axis in both X and Y directions (the Z-axis was chosen along the tube axis) have been used for the energy profile calculation. The energy values in these points have confirmed that the transverse potential profile can be well approximated by a parabola. The potential gain $\triangle V_\perp$ was equal to 0.455 eV at a molecule shift of 0.3 Å from the $(3,3)$ tube axis. As $\triangle V_\perp$ is much higher than the amplitude of the potential at the molecule movement along the tube axis $V(r)$(0.019 eV), the conclusion that the adsorbate molecule moves along the tube axis only can be made.

Considering this transverse potential profile, averaged in X, Y directions, the energy level values ϵ^i of the hydrogen isotope molecules have been obtained. The large values of the two lowest energy level differences $\epsilon^2 - \epsilon^1$ (788, 557 and 455 K for H_2, D_2, T_2 molecules, respectively) also confirm that the hydrogen isotope molecules occupy mainly the first energy level in the $(3,3)$ tube, so the molecule movement is a 1-dimensional motion. Similar results have been obtained for case of the $(6,0)$ tube too.

Here we consider the adsorbate particle velocity distribution under interaction with atoms of the tube walls only. The following description of 1-dimensional adsorbate molecule movement is based on band theory. It describes a particle motion under the periodical potential influence. At that, the particle eigenstates form energy bands E_i. Hereinafter the index i includes wave vector $\overrightarrow{k}$ $i = \{\overrightarrow{k}, \nu\}$. Every particle state i is characterized by the velocity V_i and occupation number Θ_i. At that, temperature T causes smooth occupation numbers of the particle states. According to the Boltzmann distribution, the particle average velocity $\langle V \rangle$ can be calculated:

$$\langle V \rangle = \frac{1}{Z} \sum_I \langle V_i \rangle \exp\left[-\frac{E_i}{k_B T}\right]; \quad Z = \sum_I \exp\left[-\frac{E_i}{k_B T}\right]. \tag{1}$$

Here Z is the statistical sum, $\langle V_i \rangle$ and E_i are the average velocity and the particle energy in the state i, respectively.

The eigenstates are calculated by the plane-wave decomposition. Written in reciprocal space terms, the Hamiltonian is equal to

$$H_{ij} = \frac{\left(\overrightarrow{k} + \overrightarrow{G}_i\right)^2}{2m} \delta_{ij} + V\left(\overrightarrow{G}_i - \overrightarrow{G}j\right). \tag{2}$$

We have used $\overrightarrow{G}_i$ with the maximum module $G \leq G_{\max} = 32$ (in units $\frac{2\pi}{a}$) and 21 $\overrightarrow{k}$ uniformly located points within the first Brillouin zone.

The results of the calculations were not sensitive to the number of vectors G and $\overrightarrow{k}$ points because the Fourier transformation of the tube potential $V(\overrightarrow{G}_i - \overrightarrow{G}j)$ had only a few relevant harmonics.

An average particle velocity in state $\{\nu, k\} V^\nu(k)$ has been calculated with the help of the Hellmann-Feinmann theorem:

$$V^\nu(k) = \frac{\partial E^\nu(k)}{\partial k} = \left\langle \psi^{\nu,k} \left| \frac{\left(\overrightarrow{k} + \overrightarrow{G}_i\right)}{m} \right| \psi^{\nu,k} \right\rangle.$$

From the symmetry $(\overrightarrow{k} \longrightarrow -\overrightarrow{k})$ the average velocity $\langle V \rangle = \frac{1}{N_g N_k} \sum_{\nu,k} V^\nu(k)$ must be equal to zero. Since only the absolute velocity value is relevant, the average velocity should be calculated as $\langle V \rangle = \frac{1}{N_g N_k} \sum_{\nu,k} |V^\nu(k)|$.
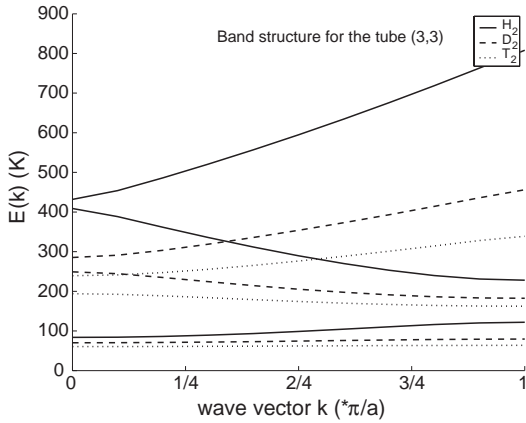
Fig. 3

Fig. 4

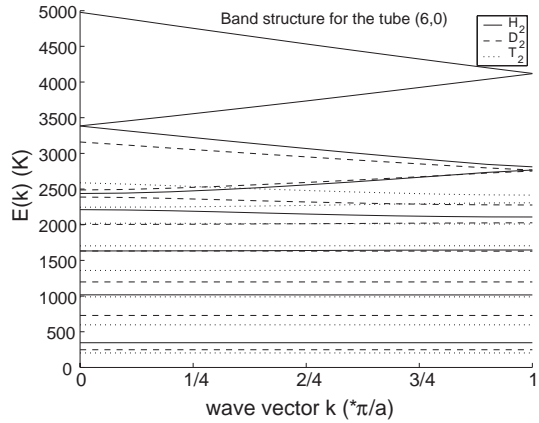Fig. 3 – Band structure for the $(3,3)$ tube.

Fig. 4 – Band structure for the $(6,0)$ tube.

Results. – The calculated potentials $V(x)$ (in kelvins) for the hydrogen molecules move-ment inside the tubes $(3,3)$ and $(6,0)$ are shown in figs. 1, 2. The probabilities ψ^2 (for $\vec{k} = 0$) (in arbitrary units) for the two lowest eigenstates are shown there too. One can see that the tunneling effect is negligible for the $(6,0)$ tube in comparison with the $(3,3)$ tube due to a significant overlapping of eigenfunctions in the last case.

There is a drastic difference between the potentials inside both tubes. Although the diameters do not differ significantly, the potentials differ by $\cong 12$ times. This is explained by the different chirality of these tubes.

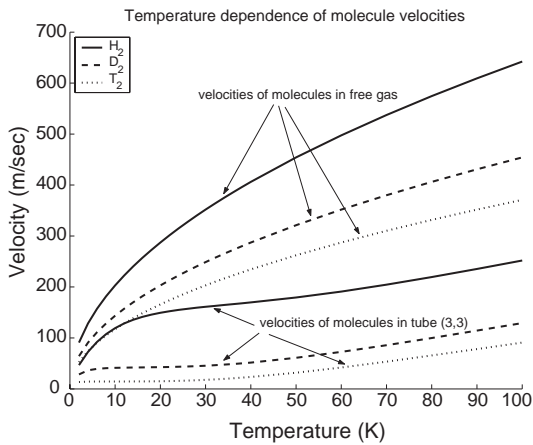In the case of the $(3,3)$ tube, having C_3 symmetry, any point lying on the tube axis has one

Fig. 5

Fig. 6

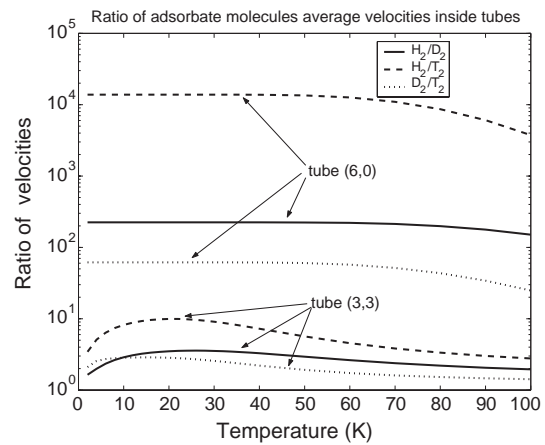Fig. 5 – Isotope velocities inside the $(3,3)$ tube and in a free gas.

Fig. 6 – Ratios of H_2 isotope velocity inside the $(3,3)$ and $(6,0)$ SWCNT.

nearest carbon atom of tube walls only. For the $(6,0)$ tube, having C_6 symmetry, there are two nearest wall atoms. So, along the $(6,0)$ tube axis points the potentials of the wall atoms sum up in-phase. For the tube $(3,3)$ the potentials do not sum up in-phase. This result in a very large difference between the potentials along both tube axes. Additionally, the distances between the potential minima along the tube axes are quite different in the two cases. The period of the potential for the $(6,0)$ tube is $\sqrt{3}$ times more than that for the $(3,3)$ tube.

The band structures $E^\nu(k)$ (in kelvins) of hydrogen isotope molecules are shown for both cases in figs. 3, 4. Solid, dashed and dotted lines correspond to the bands of H_2, D_2, T_2 molecules, respectively.

One can see significant dispersion of bands ($\triangle E^\nu = \max(E^\nu) - \min(E^\nu)$) for the $(3,3)$ case, so the tunneling effect is much more essential here. This may be proved by the comparison of this task and the task of particle quantization in the 2-minima potential hole. For the last one there is a formula which connects the tunneling frequency Ω^ν and the eigenstate energy dispersion: $\Omega^\nu = \frac{\triangle E^\nu}{\hbar}$. From the similarity of this task and the task of adsorbate molecule movement in the periodical potential of the nanotube one can assume that the average adsorbate velocity for any eigenstate ν is proportional to the tunneling frequency Ω^ν and therefore to the eigenstate dispersion $\triangle E^\nu$.

Keeping in mind that the tunneling is very sensitive to the potential barrier amplitude and the particle mass, the tunneling value and the average particle velocity inside the $(6,0)$ tube have stronger dependence on the particle mass than those inside the $(3,3)$ tube.

In fig. 5 one can see the temperature dependence of the isotope molecule average velocities inside the $(3,3)$ tube. For comparison, the temperature dependence of the average velocities of hydrogen isotope molecules in a free-gas phase are shown too. The velocities for the $(6,0)$ tube are negligible at this scale, so these values are not shown.

Figure 6 shows the dependencies of the isotope velocity ratio (for H_2/D_2, H_2/T_2, D_2/T_2 pairs) on temperature. There are the very large ratios of the isotope average velocities inside the $(6,0)$ tube, where the potential barriers are very high and the tunneling value is very small and very sensitive to the adsorbate particle mass.

In conclusion, the movement of single hydrogen isotope molecules inside ultrathin SWCNT $(3,3)$ and $(6,0)$ has been studied. It has been proved that the particle movement could be considered as 1-dimensional. It has been demonstrated that there are very large ratios of the isotope molecule average velocities inside SWCNT at low temperatures due to the tunneling effect. This effect may potentially be used for isotope separation purposes.

$$* * *$$

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