

# Thermoactivated transport of molecules H<sub>2</sub> in narrow single-wall carbon nanotubes

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**Abstract.** By use both of the plane wave DFT and the empirical exp-6 Lennard-Jones potential methods we calculate the inner potential in narrow single-wall carbon nanotubes (SWCNT) (6, 0), (7, 0) and (3, 3) which affects the hydrogen molecules. The inner potential forms a goffered potential surface and can be approximated as  $V(z, r, \phi) \approx V_0 \sin(2\pi z/a) + V(r)$ . We show that in these SWCNTs transport of molecules is given mainly by thermoactivated hoppings between minima of the periodic potential along the tube axis. The rate hoppings is substantially depends on temperature because of thermal fluctuations of tube wall.

**PACS.** 61.46.-w Structure of nanoscale materials – 66.30.Pa Diffusion in nanoscale solids – 63.20.dk First-principles theory

## 1 Introduction

Carbon nanotubes formed by rolling graphene plane into tubular structures provide structurally perfect and stable nanochannels with variable size. The potential applications of carbon nanotubes therefore could be manifold. They can be aligned in a polymer film to form a well-ordered nanoporous membrane structure [1,2] that can be used as “nanopipes” for the controlled delivery of gases or liquids [3]. As with all microporous materials, rates of molecular transport inside single-wall carbon nanotubes (SWCNT) may have a large impact on the usefulness of these materials [4]. If molecular transport through SWCNTs is slow, their usefulness may be severely constrained. It is therefore of practical interest to understand the diffusive behavior of molecules inside SWCNTs [5–9].

Molecular dynamics simulations were undertaken for wide range of transport molecules mostly inside (20, 0) and (10, 0) SWCNTs [10,11]. A particularly interesting observation is the remarkable increase of the diffusion coefficient of simple molecules like H<sub>2</sub> or CH<sub>4</sub> at low densities compared to molecular dynamics simulations as was observed by Skoulidas et al. by atomistic simulations [5]. The exceptionally high transport rates of these molecules in the range of SWCNTs are shown to be a result of the inherent smoothness of the nanotubes. The early theory pioneered by Knudsen [12] concentrated on gaseous flow where the interaction between the flowing molecules and the pore wall can be neglected. Classical kinetic theory was employed to determine the transport coefficient by considering trajectories of molecules following collision

with the tube wall or with other molecules [13]. These approaches were developed for systems where the molecular radius was typically much smaller than the tube one, and thus where hard wall (and often hard sphere approximations) are appropriate. However, when one considers transport in SWCNTs, where the molecular and tube dimensions are of similar orders of magnitude, the molecular-tube interactions becomes much more significant. In a series of publications by Bhatia and coworkers [7,14–19] the approach to describe transport in slit nanopores was developed in which the interaction between transport molecules and the pore was represented by a one-dimensional transverse potential  $V(r)$  across the pore and the diffuse boundary conditions. Under conditions of steady flow the transport coefficient may be determined from the travel mean duration between successive reflections. Inelastic collisions of molecules with thermal fluctuations of the wall atoms might be a source of diffusive transport of molecules in the flexible SWCNT [10,20].

Experimentally the molecular transport deals mostly with the wide SWCNT of one nanometer and more diameters [2,21]. The tubes (10, 10), (10, 0) and higher fall onto the case in which the only force on the part of CNT which governs motion of guest molecules is the radial one. However periodic potential profile along the tube axis might be important with reduction of the SWCNT diameter. Obviously, such a limit begins when the tube diameter is compared to the size and shape of the guest molecules. As demonstrated in [17] the potential profile of interaction of the molecule with CNT changes from double minima to a single minimum over the radius with the reduction of the SWCNT diameter. For the last case we can interpolate the potential profile  $V(r)$  as  $\frac{1}{2}M\omega_r^2 r^2$ . Then if the

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**Table 1.** Parameter sets of the SWCNTs and rates of H<sub>2</sub> self-diffusion at 300 K. All quantities are given on the basis of  $V_0$  calculated by DFT method.

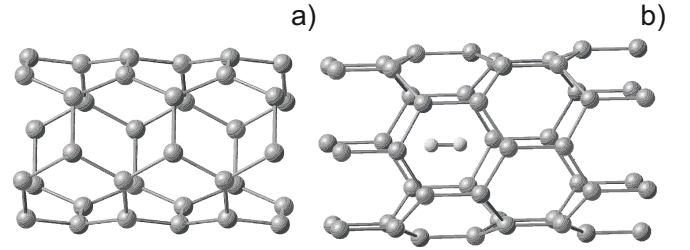
CNT	(3, 3)	(6, 0)	(7, 0)
diameter (Å)	4.07	4.70	5.48
period of potential (3) $a$ (Å)	1.05	2.44	2.44
$V_0$ (K) by use L-J potential (1)	215	1400	290
$V_0$ (K) DFT	160	1025	365
$\omega_0 = \frac{2\pi}{a} \sqrt{\frac{V_0}{m}}$ ( $10^{13}$ Hz)	2.40	5.28	3.14
$\tilde{\omega}_0 = \frac{2\pi}{a} \sqrt{\frac{\tilde{V}_0}{m}}$ ( $10^{13}$ Hz)	3.53	6.21	4.76
$\hbar\omega_r$ (K)	655	436	375
$A$ , by Eq. (13)	0.96	0.47	0.72
$-kT/2 \ln A$ (K)	6	113	49
$\Gamma_0$ ( $s^{-1}$ ) by (5)	$4.2 \times 10^{11}$	$5.7 \times 10^{10}$	$1.4 \times 10^{11}$
$\Gamma$ ( $s^{-1}$ )	$4.03 \times 10^{11}$	$2.7 \times 10^{10}$	$10^{11}$
$D$ ( $cm^2 s^{-1}$ )	$4.5 \times 10^{-5}$	$1.6 \times 10^{-5}$	$6 \times 10^{-5}$
$\tilde{\omega}_0 (z=0)A$ ( $10^{13}$ Hz)	3.38	2.92	3.42

characteristic energy of  $\hbar\omega_r$  exceeds the room temperature  $kT$  we can consider the SWCNTs as narrow ones. Our ab initio calculations (see Tab. 1) show the zig-zag SWCNTs (6, 0) and (7, 0), and the arm-chair one (3, 3) fall into this category of CNTs at room temperature. On the other hand, for example, the SWCNT (10, 0) has  $\hbar\omega_r = 53.7$  K. Then radial degrees of freedom of the guest molecule become important at the room temperature, and therefore the SWCNT (10, 0) can be classified as the wide one.

Our calculations show that the inner potential of the narrow SWCNT forms a goffered tube which can be described by the sinus potential along the tube-axis with an amplitude comparable to the room temperature. Then the low limit of the self-diffusion mainly defined by the rate of thermoactivated jumps of the guest molecule through potential barrier between potential minima of the sinus potential. It would be expected that the coefficient of self-diffusion in the narrow SWCNTs is to be enormously suppressed compared to the case of the wide SWCNTs calculated in [18,19]. Surprisingly, we find that the coefficient of self-diffusion of the hydrogen molecules in the narrow (7, 0) CNT is not so far from the results of Bhatia group irrespective to completely different approaches and different host systems.

## 2 Transport of H<sub>2</sub> in SWCNT for T = 0

In what follows we need the potential of the hydrogen molecule interior the SWCNT specified by  $V(z, r, \phi)$  in the cylindrical coordinate system. The coordinates  $z, r, \phi$  describe position of the center of mass of the molecule H<sub>2</sub> in cylindrical system of coordinates centered inside the SWCNT. General view of the system is shown in Figure 1. We calculated the inner potential using the VASP package [22] on the base of density functional ab-initio total energy code using plane-wave basis set and the Vanderbilt ultrasoft pseudopotentials [23]. The electron-electron interaction was treated within generalized gradient approximation using Perdew-Becke approach [24]. For performing

**Fig. 1.** (Color online) A view of the arm-chair (3, 3) (a) and the zig-zag (6, 0) SWCNT (b) consisted of a few periods along the tube axis with the hydrogen molecule inside.

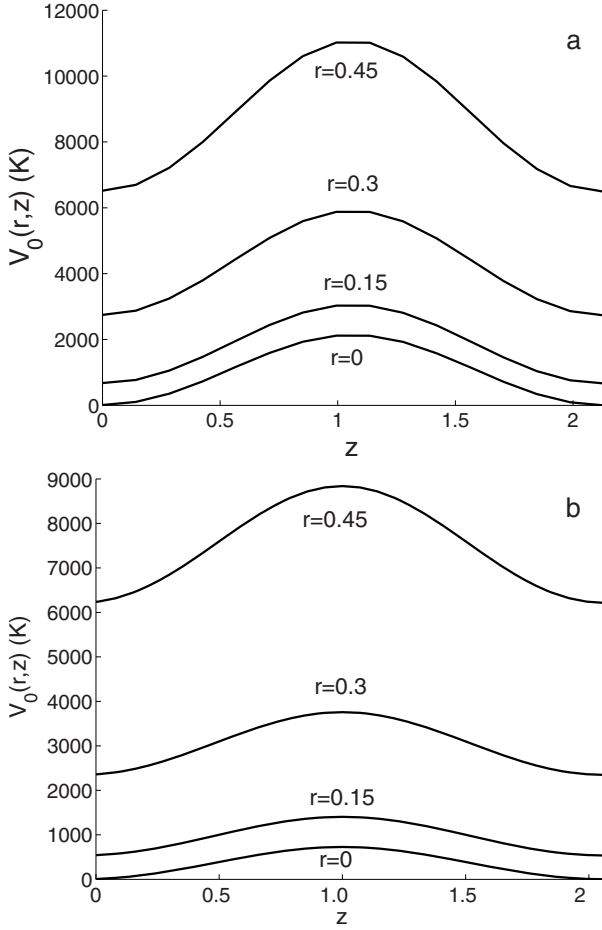
structural optimizations, we let coordinates of all atoms to relax until all forces became smaller 0.02 eV/Å. The kinetic-energy cutoff used for the plane-wave expansion of electronic wave functions was taken 286.7 eV. Because of large value of the SWCNT supercell (8.5 Å) the one-dimensional Brillouin zone was sampled on four k points.

The carbon equilibrium positions in the total system are defined as by the C–C interactions as by the carbon-hydrogen couplings both. Therefore a displacement of the hydrogen molecule through the narrow SWCNT complements by deformations of the carbon atoms in the vicinity of H<sub>2</sub>. The results of calculations for the potential  $V(z, r, \phi)$  are shown in Figure 2 and listed in the Table 1.

The DFT calculations disregard the long-range Van der Waals interaction between carbons and H<sub>2</sub>. In order to evaluate to which extend that might be essential we also calculated the inner potential profiles for H<sub>2</sub> by use of the empirical exp-6 Lennard-Jones potential [25]

$$U(R) = A \exp(-\lambda R) - \frac{B}{R^6}, \quad (1)$$

which describes interaction of the H<sub>2</sub> molecule with a flat surface of graphite. Here  $A = 1059.13$  eV,  $\lambda = 3.547 \text{ \AA}^{-1}$ ,  $B = 17.417 \text{ eV \AA}^6$ . This potential well describes as strong



**Fig. 2.** The potential of SWCNT as dependent on the  $z$ -axis for different radial positions of the hydrogen molecule. All distances are given in Å. (a) The case of (6, 0) SWCNT, and (b) the case of (7, 0) SWCNT.

repulsion for short distances below 3 Å and long distance attraction with the bounding energy around 0.05 eV with the equilibrium distance  $r_0 = 3.2$  Å. One can see from Table 1 that maximal distances between  $H_2$  and carbon atoms of the narrow CNTs less than 3 Å, and, therefore, only strong repulsive interaction between carbons and  $H_2$  is important. Indeed, one can see from Table 1 a reasonable agreement between empirical and DFT methods. Note, the exp-6 potential (1) was fitted for flat surface of graphite [25]. As a result we observe a discrepancy between methods grows with decreasing of the CNT's radius. As seen from Figure 2 the potential  $V$  affected the hydrogen molecule interior the SWCNT has remarkable feature:  $V(z, r, \phi) \approx V_0(z) + V(r, \phi)$ , at least, for  $r \leq 0.3$ . One can see from Figure 2 that for the room temperature the molecule  $H_2$  is strongly confined at  $r = 0$ . Moreover our calculations reveal that for the room temperature we can disregard the angular dependence of the potential, at least, for the SWCNTs (6, 0) and (7, 0) and approximate for room temperatures

$$V(z, r, \phi) \approx V_0(z) + V(r) \quad (2)$$

where the potential responsible for a motion of hydrogen molecules along the SWCNT axis is well described by the sinus one

$$V_0(z) = V_0 \sin(2\pi z/a). \quad (3)$$

The molecular transport in narrow tubes is mostly determined by thermoactivated processes of hopping of molecules through the potential formed by carbon atoms interior the SWCNT. The rate of these processes is given by the Vineyard formula [26]

$$\Gamma_0 = \sqrt{\frac{1}{2\pi\beta M}} \frac{\int_0^\infty r dr \exp(-\beta V(z_S = a/2, r))}{\int_0^{a/2} dz \int r dr \exp(-\beta V(z, r))}. \quad (4)$$

Here  $\beta = 1/kT$ ,  $M$  is the  $H_2$  mass,  $z_S$  is the  $z$ -position of molecules at which  $V(z, r)$  achieves saddle point. Because of separable potential (2) formula (4) can be calculated analytically to give

$$\begin{aligned} \Gamma_0 &= \sqrt{\frac{1}{2\pi\beta M}} \frac{\exp(-\beta V(z_S))}{\int_0^{a/2} \exp(-\beta V(z)) dz} \\ &= \frac{2\pi e^{-\beta V_0}}{a I_0(\beta V_0)} \sqrt{\frac{1}{2\pi\beta M}}, \end{aligned} \quad (5)$$

where  $I_0(x)$  is the modified Bessel function. For the case  $kT \ll V_0$  formula (5) reduces to the Arrhenius law of the thermoactivated transport

$$\Gamma_0 \approx \omega_0 \exp(-2\beta V_0), \quad (6)$$

where  $\omega_0 = \frac{2\pi}{a} \sqrt{\frac{V_0}{M}}$  is the frequency of longitudinal molecule oscillations around the minimum of the SWCNT potential (3) at  $z = 0$ . As seen from (6), the value  $2V_0$  defines the migration barrier for the thermoactivated self-diffusion of the molecules  $H_2$  in the SWCNT for the case  $kT \ll V_0$ . With growth of the density of  $H_2$  the effect of molecular confinement of the guest molecules lead to peculiar diffusion properties. For example in one dimensional narrow channels, particles are forced to move in a sequential order such that they are unable to pass each other. This leads to single file diffusion where the long time mean squared displacement is proportional to  $\sqrt{T_0 t}$ , rather than  $\Gamma_0 t$  as is generally observed for Fickian diffusion [27–30].

### 3 Phonon assisted transport of $H_2$ in SWCNT

For thermoactivated jump processes a value of potential barrier  $2V_0$  plays a key role. Thereby, account of any processes which modify the potential relief  $V(z)$  is very important. In particular, thermal elastic fluctuations of carbon atoms in the flexible CNT might affect the potential  $V(z)$  similar to that as the surface phonons reduce the potential barrier for thermal desorption of molecules from the surface [31]. These effect is expected to be especially important for narrow CNTs with simple molecules as well as for wider CNTs but with larger molecules. Thermal fluctuations of the host CNT have a key importance

in a molecular linear motors for motion of a capsule-like CNT [32,33] or water nanodroplets [34,35].

Let  $U(R)$  be a potential of interaction between the guest molecule specified by the coordinate  $(0, 0, z)$  and carbon atoms of the host CNT specified by the coordinates  $\mathbf{x}_j$ , where  $R_j = |\mathbf{x}_j - z_a \mathbf{e}_z|$  is the distance between the guest molecule and carbon ones,  $j = 1, \dots, M$ . Here  $\mathbf{n}$  is a unit vector along the tube axis,  $M$  is the total number of carbon atoms. An expression

$$\rho(z, \mathbf{x}_1 \dots \mathbf{x}_M) = \frac{1}{Z_{3M+1}} \times \exp \left\{ -\beta \left[ E_{CNT} + \sum_{j=1}^M U(|z\mathbf{e}_z - \mathbf{x}_j|) \right] \right\}$$

defines the probability density in the  $3M+1$  configuration space of the total system of the host CNT plus the guest molecule. Here  $Z_{3M+1}$  is the configuration integral over whole  $3M+1$  space. Hence the probability distribution to find the guest molecule at position  $z$  is [31]

$$\begin{aligned} \rho(z) &= \frac{1}{Z_{3M+1}} \int d^3 \mathbf{x}_1 \dots d^3 \mathbf{x}_M \rho(z, \mathbf{x}_1 \dots \mathbf{x}_M) \\ &= \frac{1}{Z_{3M+1}} \int d^3 \mathbf{x}_1 \dots d^3 \mathbf{x}_M \\ &\quad \times \exp \left\{ -\beta \left[ E_{CNT} + \sum_{j=1}^M U(|z\mathbf{e}_z - \mathbf{x}_j|) \right] \right\} \\ &= \frac{1}{Z_1} \exp(-\beta V(z, T)), \end{aligned} \quad (7)$$

where  $Z_1 = \int dz \rho(z)$ . Even numerically it is hardly possible to perform  $3M$  integrations over all carbon atoms. However if thermal displacements of carbon atoms are small compared to the characteristic distances of the SWCNT we can expand both energies in (7) over carbon displacements in the harmonic approximation

$$E_{CNT} \approx \frac{m_C}{2} \sum_{\lambda\alpha} \omega_{\lambda\alpha}^2 \xi_{\lambda\alpha}^2, \quad (8)$$

$$\begin{aligned} \sum_j U(|z\mathbf{k} - \mathbf{x}_j|) &\approx V_0(z) + \sum_j \frac{\partial U(z, \mathbf{x}_j^0)}{\partial x_j^\alpha} \xi_j^\alpha \\ &\quad + \frac{1}{2} \sum_j \frac{\partial^2 U(z, \mathbf{x}_j^0)}{\partial x_j^\alpha \partial x_j^\gamma} \xi_j^\alpha \xi_j^\gamma. \end{aligned} \quad (9)$$

Here  $m_C$  is the carbon atom mass,  $x_j^{\alpha 0}$  are equilibrium positions of the carbon atoms,  $\omega_{\lambda\alpha}$  and  $\xi_{\lambda\alpha}$  are the phonon eigen frequencies and the eigen vectors respectively in the pure CNT,  $\alpha, \gamma = x, y, z$ ,  $\xi_j^\alpha = x_j^\alpha - x_j^{\alpha 0}$ .  $V_0(z) = \sum_j U(|z\mathbf{k} - \mathbf{x}_j^0|)$  is the potential subjected the  $H_2$  at equilibrium carbon's positions. The total energy of the SWCNT presented by equations (8) and (9) is the quadratic form over the carbon displacements whose eigen

frequencies  $\tilde{\omega}_{\lambda\alpha}(z)$  can be found, at least, numerically, or by the perturbation theory for every position of the hydrogen molecule  $z$ . Then the integration over all carbon displacements  $\xi_j^\alpha$  gives us the following formula for (7)

$$\rho(z) = \frac{1}{Z_1} \frac{Z_1}{Z_{3M+1}} \prod_{\lambda\alpha} \sqrt{\frac{2\pi}{\beta m_C \tilde{\omega}_{\lambda\alpha}^2(z)}} \times \exp \left\{ -\beta V_0(z) - \left[ \frac{\sum_j \frac{\partial U(z, \mathbf{x}_j^0)}{\partial x_j^\alpha}(z)}{\tilde{\omega}_{\lambda\alpha}(z)} \right]^2 \right\}, \quad (10)$$

and find the effective potential  $V(z, T)$  via equation (7) as follows

$$\begin{aligned} \tilde{V}(z, T) &= V_0(z) + kT \sum_{\lambda, \alpha} \ln \tilde{\omega}_{\lambda\alpha}(z) \\ &\quad - \left[ \frac{\sum_j \frac{\partial U(z, \mathbf{x}_j^0)}{\partial x_j^\alpha}(z)}{\tilde{\omega}_{\lambda\alpha}(z)} \right]^2 + \text{const.} \end{aligned} \quad (11)$$

At least, numerically a profile of this renormalized potential can be found to obtain the same form as a former potential (3)  $\tilde{V}(z, T) = \tilde{V}_0 \sin \frac{2\pi z}{a}$ . From (11) we have a simple expression for the reduced amplitude of the potential

$$\tilde{V}_0 = V_0 - \frac{kT}{2} \ln \Lambda, \quad (12)$$

where

$$\Lambda = \frac{\prod_{\lambda\alpha} \tilde{\omega}_{\lambda\alpha}(z=0)}{\prod_{\lambda\alpha} \tilde{\omega}_{\lambda\alpha}(z=a/2)}. \quad (13)$$

Here  $\tilde{\omega}_{\lambda\alpha}$  are the frequencies of vibrations of the total system SWCNT plus  $H_2$  for  $H_2$  located at the minimum of the SWCNT potential, while the frequencies  $\tilde{\omega}_{\lambda\alpha}(z=a/2)$  are given for the position of  $H_2$  at saddle point in the SWCNT potential.

As a result we obtain a similar formula for the rate of thermoactivated jumps of molecules (atoms) interior the SWCNT with account of thermal fluctuations of carbon atoms of the SWCNT

$$\Gamma \approx \tilde{\omega}_0 \exp(-2\beta \tilde{V}_0) = \Lambda \Gamma_0. \quad (14)$$

$\tilde{\omega}_0$  is the frequency of longitudinal molecule oscillations around the minimum of the renormalized potential (11) at  $z=0$ . Note, at the stationary positions of molecule at  $z=0, a/2$  the first derivatives  $\frac{\partial U(z, \mathbf{x}_j^0)}{\partial x_j^\alpha} = 0$ , and therefore the last term in equations (10) and (11) do not contribute into the rate. One can verify that formula (14) is just the Vineyard one [26] for the rate processes in the total complex system SWCNT plus  $H_2$ .

The sign of the value  $\ln \Lambda$  is not obvious. In order to clarify physical origin of the phonon renormalization of potential  $V(z)$  let us consider the second term in (9) as a perturbation. Expanding the last term in (10) over this

perturbation one can easily obtain for the effective potential

$$V(z, T) \approx V_0(z) + \frac{1}{2} \sum_j V''_{\alpha\gamma}(z, \mathbf{x}_j^0) \langle \xi_j^\alpha \xi_j^\gamma \rangle. \quad (15)$$

The last contribution is result of thermal fluctuations of the CNT which are proportional  $kT$ . There are two distinctive types of the fluctuations. The first one originates from the transverse radial fluctuations of the SWCNT which effectively squeeze the cross-section of the CNT, and therefore enhance the amplitude of the periodic potential along the  $z$ -axis. The second contribution to the potential originates from longitudinal fluctuations, carbon displacements along the tube axis, which smooth this potential. As seen from Table 1, the first contribution dominates in the listed narrow tubes to make the effective potential  $V(z, T)$  more rigid.

In order to evaluate the factor (13) we numerically calculated the spectra of all vibrational modes of supercell consisted of two periods along the tube axis with use of the frozen phonon method [36]. This spectra ranges from 0 till  $\pi/2a$  for  $k_z$  and includes 141 distinct phonon branches for the (6, 0) SWCNT, 165 for the (7, 0) one and 105 for the (3, 3) SWCNT correspondingly. Then the phonon spectra are presented by three points  $k_z$  points  $k_z = 0, \pi/2a, \pi/a$ . Therefore, for integration over  $k_z$  this approach corresponds to parabolic interpolation. This evaluation is justified by that the supercell period 8.52 Å along the tube axis much exceeds a distance between carbons 1.41 Å to give rather flat phonon dispersion curves. Although, the procedure is rough in summation over  $k_z$ , all modes which change a cross-section of the tube were included. For the stable position of  $H_2$  at  $z = 0$  there are three acoustic modes with zero frequency at  $k_z = 0$  which leads to logarithmic divergence. This divergence signals of thermal instability of the one-dimensional infinite tube [37]. However these modes correspond to movement of the system as a whole while we are interested in movement of the hydrogen molecule relative to CNT. Therefore the acoustic modes with  $k_z = 0$  are to be excluded from summation in (13). In fact, their contribution is compensated by the contribution of acoustic modes for  $H_2$  position at saddle point  $z = a/2$ . Moreover at this point one frequency becomes imaginary which obviously related to an instability of  $H_2$  at the saddle point. The frequency of the corresponding mode at the stable position of  $H_2$  at  $z = 0$  gives us the frequency  $\tilde{\omega}_0(z = 0)$ . The results of calculation of this frequency and evaluation of  $\Lambda$  by different methods are collected in Table 1.

If there are no interactions between hydrogen molecules (the low density of  $H_2$ ), we have standard master equation for the probabilities to occupy the  $j$ -th minimum of the periodic potential (3)  $\dot{p}_j = \Gamma(p_{j+1} + p_{j-1} - 2p_j)$ . Therefore we have the diffusion coefficient  $D = \Gamma a^2$ , where  $a$  is the distance between minima. Substituting expressions for the rate constant (14) we can evaluate the diffusion coefficient for the SWCNTs

## 4 Conclusions and discussion

Although the arm-chair SWCNT (3, 3) has diameter comparable to the diameters of the zig-zag ones (6, 0) and (7, 0) its potential profile is essentially more smooth. That difference is caused by arrangement of carbon atoms along CNT. In the (3, 3) SWCNT at the position of minimum potential  $V(z)$  each hexagon of carbon atoms meets at opposite side of SWCNT single carbon atom as shown in Figure 1a. As a result the gain in potential energy at the position of minimum turns out much weaker compared to the case of the SWCNTs (6, 0) and (7, 0) where each hexagon stands opposite to the same hexagon as shown in Figure 1b. By the same reason we have a noticeable difference between the frequencies  $\omega_0$  in the arm-chair and zig-zag CNTs.

As a result the phonon renormalization of the rate of  $H_2$  hopping in the arm-chair CNT can be neglected at room temperature. However that is not the case in the zig-zag SWCNT (7, 0) and (6, 0) especially. One can see from Table 1 that the hopping rate is strongly reduced because of phonons. Physical origin of the effect is related to effective squeezing of tube because of thermal fluctuations of wall of the tube. Since the guest molecule is confined in the tube the effect of the wall potential enhances resulting in effective growth of amplitude  $V_0$  of the longitudinal potential (3). If the diameter of CNT was infinitely large the phonon renormalization would have opposite effect because of longitudinal fluctuations of the CNT wall similar to adsorbate atoms on the crystal surface [31]. Thereby the effect of thermal squeezing of the CNT is different from that considered in papers [10,11] where the role of thermal fluctuations of the CNT wall was to provide a thermal reservoir in wide CNT. For each event of collision of the guest molecule with the CNT tube the molecule irreversibly loses its longitudinal momentum.

In this article, we focused on the zero-loading limit and examine the influence of CNT diameter and temperature on self-diffusion of the simplest hydrogen molecule in the narrow SWCNTs. It might be thought that the diffusion of simple molecules in them is orders of magnitude lower than in the wide SWCNTs which effect only as confined tube. However even in wide CNTs the molecular dynamics simulations show that the intermolecular and molecule-nanotube interactions strongly affect both dynamic molecular flow and molecular diffusion [30]. The calculation of diffusion rate  $D$  for the SWCNT (7, 0) which is the most wide considered in the present paper qualitatively agrees with results obtained by Bhatia and coworkers for transport in molecularly confined spaces [7,19]. Although this theory was applied for transport of molecules in slit and cylindrical nanopores versus the pore diameter [14,15,17,18] the theory is general and can be used for the wide SWCNTs provided we can disregard by  $V_0(z)$  in (2).

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