

Ab-initio investigation of thermoactivated directional transport of hydrogen molecules inside narrow carbon nanotubes

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Using the pseudopotential DFT and the empirical potential methods we calculate the potential acting to the hydrogen molecules in narrow single-wall carbon nanotubes (SWCNT) (6,0),(7,0) and (3,3). The 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. Taking into account that hydrogen density distribution inside nanotube is stationary and assuming the temperature is changed

linearly along the SWCNT length we show that the H₂ density is sufficiently varied, especially for the case of (6,0)SWCNT where the density on both SWCNT ends are different at ~ 30 times when the temperature is changed along the SWCNT from 300K to 1200K. Suppose that H₂ molecules can penetrate in the both open SWCNT ends, the molecules would move in the direction of the temperature decreasing. This effect may be used potentially to build up a molecular pump driven by the temperature gradient along narrow nanotube.

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1 Introduction Carbon nanotubes (CNT) and similar structures provide perfect and stable nanochannels of variable diameter. The potential applications of carbon nanotubes therefore could be manifold. In [1, 2] it were demonstrated they can be aligned in a polymer film to form a well-ordered nanoporous membrane structure that can be used as “nanopipes” for the controlled delivery of gases or liquids. Another interesting application were described in Reference [3, 4] where an artificial nanomotor was fabricated in which one short-carbon nanotube moves relative to another coaxial nanotube. A cargo was attached to an ablated outer wall of a multiwalled carbon nanotube that could rotate and/or translate along the inner nanotube. The motion was actuated by imposing a thermal gradient along the nanotube, which allowed for sub-nanometer displacements.

To regulate the molecular transport inside SWCNT, it is vital necessary to understand the diffusive behavior of molecules inside SWCNT [5–9]. It was observed by atomistic simulations [5] that the exceptionally high-transport rates of guest molecules in range of SWCNTs are the result of the inherent smoothness of the carbon nanotubes.

In series of publications by Bhatia and co-workers [7, 10, 11] 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 $V(r)$ acting across the pore and by diffuse boundary conditions. Under conditions of steady flow the transport coefficient may be determined from the travel mean duration between successive reflections of a molecule from nanopore walls. Inelastic collisions of molecules with thermal fluctuations of the wall atoms might be a source of diffusive transport of molecules in the flexible SWCNT [12].

Experimentally the molecular transport deals mostly with the wide SWCNT having diameters of one nanometer and more [2, 13]. The tubes (10,0), (10,10) and higher fall onto the case in which the only force which governs motion of the 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 limit begins when the tube diameter is comparable with the size and shape of the guest molecules. For that case the inner transversal potential profile may be interpolated $V(r) = \frac{1}{2}M\omega_r^2 r^2$, see Table 1.

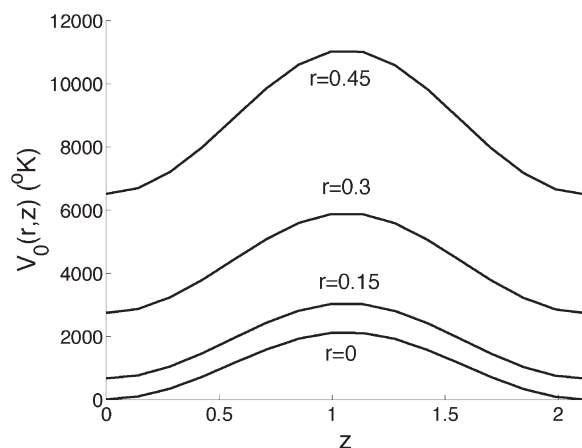
Table 1 Parameters of the SWCNTs and rates of H₂ self-diffusion at 300 K.

CNT	(3,3)	(6,0)	(7,0)
diameter (Å)	4.07	4.70	5.48
V ₀ (DFT) (K)	160	1025	365
V ₀ (L-J potential) (K)	215	1400	290
$\omega_0 = \frac{2\pi}{a} \sqrt{\frac{V_0}{m}}$ (Hz)	2.4×10^{13}	5.3×10^{13}	3.1×10^{13}
$\hbar\omega_r$ (K)	655	436	375
$-kT/2 \ln \Lambda$ (K)	6	113	49
Γ_0 (s ⁻¹) by (3)	4.2×10^{11}	5.7×10^{10}	1.4×10^{11}
Γ_0 (s ⁻¹)	4.0×10^{11}	2.7×10^{10}	10^{11}
D (cm ² s ⁻¹)	4.5×10^{-5}	1.6×10^{-5}	6×10^{-5}
$\tilde{\omega}_0(z=0)\Lambda$ (Hz)	3.4×10^{13}	2.9×10^{13}	3.4×10^{13}

Our DFT calculations show that the longitudinal potential acting to the H₂ molecule inside the narrow SWCNT forms a goffered surface and it can be described by the sinus potential along the tube axis. In the low H₂ density limit the self-diffusion mainly defined by the rate of thermoactivated jumps of the guest molecule through potential barrier between adjacent potential minima. It would be expected that the coefficient of self-diffusion D in the narrow SWCNTs is to be enormously suppressed compared to the case of the wide SWCNTs calculated in Reference [10, 11]. Surprisingly, we find that the D value for the hydrogen molecules diffusion 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 H₂ in SWCNT for $T=0$ To describe it 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, ϕ describe position of the H₂ molecule center of mass in cylindrical coordinates centered inside the SWCNT along the tube axis. We calculated the inner potential using the VASP package [14] on the base of density functional *ab-initio* total energy code using plane-wave basis set and the Vanderbilt ultrasoft pseudopotentials. Exchange-correlation effects were treated within GGA-PBE approximation.

The results of calculations for the potential $V(z, r, \phi)$ are shown in Fig. 1 and listed in the Table 1. It is well known that the DFT calculations disregard the long-range Van der Waals interaction between carbons and H₂. In order to evaluate to which extent that might be essential we also calculated the inner potential profiles for H₂ by use of the empirical exp-6 Lennard-Jones potential [15] which describes interaction of the H₂ molecule with a flat surface of graphite. This potential well describes both the strong repulsion for short distances $< 3 \text{ \AA}$ and long distance Van der Waals interaction with the bounding energy around 0.05 eV with the equilibrium distance $r_0 = 3.2 \text{ \AA}$. One can see from Table 1 that maximal distances between H₂ and carbon atoms of CNT walls less than 3 Å, and, therefore, only strong repulsive interaction between carbons and H₂ is important.

**Figure 1** The potential of SWCNT as dependent on the z -axis for different radial positions of the hydrogen molecule inside (6,0) SWCNT.

Indeed, one can see from Table 1 a reasonable agreement between empirical and DFT methods. The discrepancy between methods can be explained by the SWCNT surface curvature, so the discrepancy grows with decreasing of the CNT radius. As seen from Fig. 1 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 $r \leq 0.3 \text{ \AA}$. One can see from Fig. 1 that for the room temperature the molecule H₂ is strongly confined at $r=0$. Moreover, the angular dependence of the potential can be disregarded and the potential can be well described by the sinus one:

$$V(z, r, \phi) \approx V_0(z) + V(r); \quad V_0(z) = V_0 \sin\left(\frac{2\pi z}{a}\right). \quad (1)$$

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 [16]:

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

Here $\beta = 1/kT$, M is the H₂ mass, z_S is the z -position of molecules at which $V(z, r)$ achieves saddle point.

Because of separable potential (1) for the case $kT \ll V_0$ this formula can be reduced to the Arrhenius law of the thermoactivated transport

$$\Gamma_0 \approx \omega_0 \exp(-2\beta V_0) \quad (3)$$

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 (1) at $z=0$. The value $2V_0$ defines the migration barrier for the thermoactivated self-diffusion of the molecules H₂ in the SWCNT for the case $kT \ll V_0$. One-dimensional character of the guest molecule movement

inside such SWCNT lead to peculiar diffusion properties for single file system when long time mean squared displacement is proportional to $\sqrt{T_0 t}$, rather than $\Gamma_0 t$ as is generally observed for Fickian diffusion [17, 18].

3 Phonon assisted transport of H₂ 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, phonon thermal elastic fluctuations of CNT might affect the potential $V(z)$. Thermal fluctuations of the host CNT are also important in a molecular linear motors for motion of a capsule-like CNT [3, 4].

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 x_j , where $R_j = |x_j - z_a e_z|$ is the distance between the guest molecule and carbon ones, $j = 1, \dots, M$. Here e is a unit vector along the tube axis, M is the total number of carbon atoms. An expression $\rho(z, x_1 \dots x_M) = \frac{1}{Z_{3M+1}} \exp\left(-\frac{E_{CNT} + \sum_{j=1}^M U(|ze_z - x_j|)}{kT}\right)$ 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 [19]

$$\begin{aligned} \rho(z) &= \frac{1}{Z_{3M+1}} \int d^3 x_1 \dots d^3 x_M \rho(z, x_1 \dots x_M) \\ &= \frac{1}{Z_1} \exp(-\beta V(z, T)) \end{aligned} \quad (4)$$

where $Z_1 = \int dz \rho(z)$. Usually thermal displacements of carbon atoms are small enough, so we can expand both the energies in Eq. (4) over carbon displacement phonon modes in the harmonic approximation $E_{CNT} \approx \frac{m_C}{2} \sum_{\lambda\alpha} \omega_{\lambda\alpha}^2 \xi_{\lambda\alpha}^2$. Here m_C is the carbon atom mass, $\omega_{\lambda\alpha}$ and $\xi_{\lambda\alpha}$ are the phonon eigenvalues and the eigenvectors respectively in the pure CNT, $\alpha, \gamma = x, y, z$, $\xi_j^\alpha = x_j^\alpha - x_j^{\alpha 0}$. Obviously, the total energy of the SWCNT is the quadratic form over the carbon displacements whose eigenfrequencies $\tilde{\omega}_{\lambda\alpha}(z)$ can be found, at least, numerically for every position of the hydrogen molecule z . With help of Eq. (4) one can find the effective potential $V(z, T)$ as follows:

$$\begin{aligned} \tilde{V}(z, T) &= V_0(z) + kT \sum_{\lambda, \alpha} \ln \tilde{\omega}_{\lambda\alpha}(z) \\ &\quad - \left[\frac{\sum_j \frac{\partial U(z, x_j^0)}{\partial x_j^\alpha}(z)}{\tilde{\omega}_{\lambda\alpha}(z)} \right]^2. \end{aligned} \quad (5)$$

From (5) we have a simple expression for the reduced amplitude of the potential

$$\begin{aligned} \tilde{V}_0 &= V_0 - \frac{kT}{2} \ln \Lambda, \quad \text{where} \\ \Lambda &= \frac{\prod_{\lambda\alpha} \tilde{\omega}_{\lambda\alpha}(z=0)}{\prod_{\lambda\alpha} \tilde{\omega}_{\lambda\alpha}(z=a/2)}. \end{aligned} \quad (6)$$

Here $\tilde{\omega}_{\lambda\alpha}$ are the frequencies of vibrations of the total system SWCNT plus H₂ for H₂ located at the minimum of the SWCNT potential, while the frequencies $\tilde{\omega}_{\lambda\alpha}(z = a/2)$ are given for the position of H₂ at saddle point in the SWCNT potential.

As a result we obtain a similar formula for the rate of thermoactivated jumps of molecules interior the SWCNT with account of thermal fluctuations of carbon atoms of the SWCNT $\Gamma \approx \tilde{\omega}_0 \exp(-2\beta\tilde{V}_0) = \Lambda \Gamma_0$, where $\tilde{\omega}_0$ is the frequency of longitudinal molecule oscillations around the minimum of the renormalized potential Eq.(5) at $z = 0$. Note, at the stationary positions of molecule at $z = \{0, a/2\}$ the last term in Eqs. (5) do not contribute into the rate. One can verify this formula as just the Vineyard one [16]. As seen from Table 1, the effective potential $V(z, T)$ become more rigid for all examined SWCNT because of squeeze CNT walls under phonon influence. In order to evaluate the phonon contribution to the inner potential value we numerically calculated the phonon spectra in whole system SWCNT plus H₂ by the frozen phonon method [20]. The summation over λ in Eq. (6) included an integration over wave vector k_z and summation over all phonon branches. The frequency of the H₂ vibration mode at the stable position of H₂ at $z = 0$ gives us the frequency $\tilde{\omega}_0(z = 0)$. The results of calculation of this frequency and evaluation of Λ by different methods are collected in Table 1. Also the diffusion coefficient $D = \Gamma a^2$, where a is the distance between minima has been calculated for all examined SWCNT.

4 Thermoactivated directional transport

We consider here effect of the temperature gradient along SWCNT also. For that a simple model was proposed, where the basic values are Θ_i , T_i and Γ_i . Index i define the number of potential minimum for H₂ position along the CNT axis. Θ_i is the average occupation of site i by the molecule and Γ_i is H₂ hopping rate from site i to nearest ones. From Eq. (3) it is obvious that Γ_i is dependent on local temperature T_i . In the model it is assumed that H₂ distribution along the CNT is stationary, so the average H₂ stream is equal zero for any site i . Introducing the average streams $j_{i,i+1}$ and $j_{i+1,i}$ from site i to right and left directions for the stationary state, it is obvious that $j_{i,i+1} = j_{i+1,i}$. Introducing distance between adjacent sites Δz , using Eq. (3) it is easy to calculate variation of $j_{i,i\pm 1}$, Θ_i and Γ_i :

$$\begin{aligned} j_{i,i+1} &= \Theta_i \Gamma_i (1 - \Theta_{i+1}); \\ j_{i+1,i} &= \Theta_{i+1} \Gamma_{i+1} (1 - \Theta_i) \end{aligned} \quad (7)$$

$$\begin{aligned} \Theta_{i+1} &= \Theta_i + \frac{d\Theta_i}{dz} \Delta z; \\ \Gamma_{i+1} &= \Gamma_i + \frac{d\Gamma_i}{dz} \Delta z; \end{aligned} \quad (8)$$

$$\frac{d\Gamma_i}{dz} = \Gamma_i \frac{2V_0}{kT_i^2} \frac{dT_i}{dz}.$$

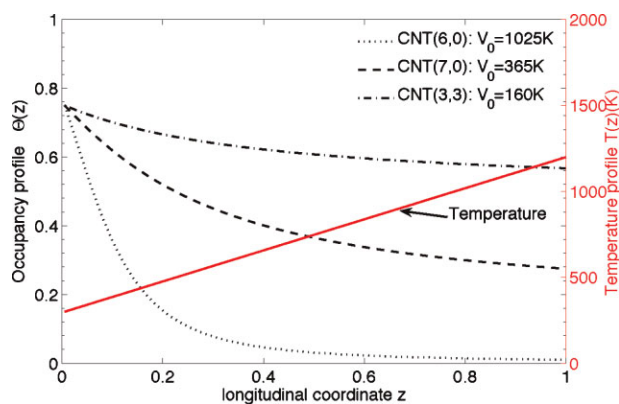


Figure 2 (online color at: www.pss-b.com). Equilibrium distribution of H_2 molecule occupancies $\Theta(z)$ along SWCNT and temperature profile $T(z)$.

Using Eq. (7) one can calculate

$$\frac{d\Theta_i}{\Theta_i} + (1 - \Theta_i) \frac{d\Gamma_i}{\Gamma_i} = 0. \quad (9)$$

It is significant that these formulas are correct even at high-occupation Θ_i . Integrating Eq. (9) over i from site 1 till site n and assuming the temperature is changed linearly along the tube it is easy to find distribution Θ_n :

$$\frac{\Theta_n^{-1} - 1}{\Theta_1^{-1} - 1} = \exp\left(\frac{2V_0}{k} \left(\frac{1}{T_1} - \frac{1}{T_n}\right)\right). \quad (10)$$

For example, assuming that the temperature is changed along the tube from 300 K to 900 K and fixing $\Theta_1 = 0.75$ we calculate the Θ_i distribution along NT, see Fig. 2.

5 Conclusions and discussion The influence of CNT diameter and temperature on self-diffusion of the hydrogen molecule inside three different narrow SWCNT has been analyzed. It was shown that the potential profile is essentially shallow inside (3,3) nanotube though it has diameter comparable to that for (6,0) CNT. That difference is caused by different arrangement of carbon atoms along CNT. From the Table 1 one can see that the hopping rate is strongly reduced for zigzag (7,0) and (6,0) CNT especially because of phonons. Physical origin of the effect is related to effective squeezing of tube because of thermal fluctuations of the tube walls. It might be thought that the diffusion of simple molecules in narrow SWCNT is orders of magnitude lower than in the wide SWCNTs which effect only as confined tube. However our calculations of the diffusion rate D for the SWCNT (7,0) which is the most wide CNT considered here qualitatively agrees with results obtained by Bhatia and co-workers for molecular transport in considerably wider nanopores [7, 10, 11]. It is surprisingly, because we used absolutely different model for describing of one-dimensional H_2 movement inside narrow CNT. At such movement the H_2 molecule feel the potential of all CNT walls

simultaneously, so the diffusion rate D might be decreased in comparison with that for movement inside wide CNT. But such unidirectional movement decrease the diffusive reflection from the CNT walls and thereby increase the diffusion rate value. Also the equilibrium hydrogen density inside examined nanotubes was analyzed at the temperature gradient along the CNT. From Fig. 2 one can see that H_2 density would be essentially varied if the potential barriers for H_2 movement are higher than the outer temperature, see curve for (6,0) CNT. At that H_2 molecules would move in the direction of temperature decreasing. We hope this effect is possible to use to build up a molecular pump driven by the temperature gradient along narrow nanotube.

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