

Theory of Transport of Long Polymer Molecules through Carbon Nanotube Channels

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A theory of transport of long chain polymer molecules through carbon nanotube (CNT) channels is developed using the Fokker-Planck equation and direct molecular dynamics simulations. The mean transport or translocation time τ is found to depend on the chemical potential energy, the entropy, and the diffusion coefficient. A power law dependence $\tau \sim N^2$ is found, where N is the number of monomers in a molecule. For 10^5 -unit long polyethylene molecules, τ is estimated to be $\sim 1 \mu\text{s}$. The diffusion coefficient of long polymer molecules inside CNTs, like that of short ones, is found to be a few orders of magnitude larger than in ordinary silicate based zeolite systems.

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Long chain polymer molecules and nanometer sized channels or pores present a unique complex nanosystem, where the size of molecules and channels are comparable and the interactions between them may dominate the relative configurations and transport dynamics. Nanochannels have been found in various solid state or biological systems and were the subjects of previous studies, such as diffusions in microscopic zeolite channel [1], energies of polymer/molecule nanotube systems [2], and translocations of DNA through nanopores [3–5], for filtration, separation, and sequencing applications, respectively. Carbon nanotubes (CNTs), formed by rolling graphene planes into tubular structures, provide structurally perfect and stable nanochannels, with variable size. The potential applications of CNT channels therefore could be manifold. The transport phenomena, such as translocation and diffusion, of long chain polymer molecules through CNT, however, could be more complicated as compared with the transport of small gas [6,7] and water molecules [8] in CNTs due to the long length scale and entropy effects. The interaction between polymer molecules and CNTs and intrapolymer connectivities could also play a significant role in the dynamics of such systems.

There are two processes in the transport of long chain polymer molecules to pass through CNT channels. First is the transport from surrounding solutions into CNTs, which we refer to as translocation; second is the diffusion inside CNTs. In this Letter the translocation of polymers into CNTs is studied using the Fokker-Planck equation. An analytic expression for the mean translocation time τ is obtained, which is found to have a N^2 dependence on the number of monomers in the molecule. The calculated diffusion coefficient for linear polyethylene (PE) molecules, using molecule dynamics (MD) simulations, shows a significantly faster diffusion as compared with silicate based zeolite systems. A fast translocation for very long chain polymer molecules through CNTs is also found.

When a polymer molecule goes inside a nanotube channel, the total energy E and entropy S will change due to the interactions with channel walls and geometric

confinements. S is dependent on the conformation Ω of the molecule as $k_B \ln \Omega$, where $\Omega \sim N^{\xi-1} q_{\text{eff}}^N$ (N is the number of monomers in the molecule, q_{eff} is the effective coordination number for each unit, and ξ is an exponential parameter) [9]. Thus the entropy of a polymer molecule is $S = k_B(\xi - 1) \ln N + k_B N \ln q_{\text{eff}} + \text{const}$. In a general form the free energy $f = E - TS$ of a N -unit polymer molecule, partially inside (n units) and partially outside ($N - n$ units) of a nanotube, can be expressed as

$$\begin{aligned} f(n) &= f_1 + f_2 \\ &= k_B T \left[n \times \left(\frac{\Delta\mu}{k_B T} + \ln \frac{q_1}{q_2} \right) - (\xi_1 - 1) \ln(N - n) \right. \\ &\quad \left. - (\xi_2 - 1) \ln n \right] + \text{const}. \end{aligned} \quad (1)$$

Subscripts 1 and 2 are for the portions of the molecule outside and inside of the nanotube, respectively; we use this notation throughout the Letter. $\Delta\mu$ is the change in chemical potential per monomer between the two configurations.

At finite temperature the translocation time describing how fast a molecule can be pulled into a CNT is a statistical value. The probability function $P(n, t)$, with n segments of the molecule into CNT at time t , can be described by a one-variable Fokker-Planck (FP) equation, $\partial P(n, t)/\partial t = L_{\text{FP}} P(n, t)$. For cases with time-independent diffusion coefficients D , the operator $L_{\text{FP}} = \partial/\partial n [e^{-f/k_B T} (\partial/\partial n) D e^{f/k_B T}]$ [10]. Thus the mean translocation time τ , defined as $\int P(N, t) t dt$, for a N -unit polymer molecule into a CNT can be obtained by solving the above equation (assuming only the head unit of the molecule is inside the nanotube at $t = 0$) [4,5,10,11]:

$$\tau = l_0^2 \int_1^{N-1} e^{f(n)/k_B T} dn \int_1^n \frac{1}{D(n', N - n')} e^{-f(n')/k_B T} dn', \quad (2)$$

where l_0 is the length of a single monomer, $f(n)$ is the free energy as expressed in Eq. (1), and $D(n, N - n)$ is the diffusion coefficient for a polymer molecule with

$n/(N - n)$ units inside/outside the channel, with the general form

$$\frac{1}{D(n, N - n)} = \frac{(N - n)^{\nu_1}}{D_1} + \frac{n^{\nu_2}}{D_2}, \quad (3)$$

where D_1/D_2 is the diffusion coefficient for a single monomer outside/inside CNT, and ν_i is an exponential parameter, with a value of 0.5 in the Zimm model where hydrodynamics interactions are taken into account, or 1 in the Rouse model where hydrodynamics interactions are omitted [12], or 0 if only local friction at the end of CNT is considered. τ can be obtained by applying Eqs. (1) and (3) into Eq. (2). For cases of large N , by calculating the integrals in Eq. (3) through an integration by parts, an approximation for τ can be expressed as follows:

$$\tau = \frac{l_0^2}{|\frac{\Delta\mu}{k_B T} + \ln \frac{q_1}{q_2}|} \left[\frac{N^{\nu_1+1}}{(\nu_1 + 1)D_1} + \frac{N^{\nu_2+1}}{(\nu_2 + 1)D_2} \right] + O[(\xi_i - 1)N^{\nu_i}], \quad (4)$$

assuming that $N|\Delta\mu/k_B T| \gg 1$ and $\Delta\mu < 0$ (which is the case of interest here as discussed later). The second term in Eq. (4) can be omitted for large N . Equation (4) shows that τ directly depends on the entropy and diffusion of the polymer inside CNT, different from previous studies on polymer translocation through nanopores on cell membranes [13] (where pores were treated with zero length or polymer was treated as a straight line inside pores). To study the characteristic of D_i and ν_i , we use a system of PE and CNT, because of the representative linear structure of PE.

A polymer molecule adsorbed into a nanotube is energetically favorable through energy gain due to van der Waals (VDW) interactions. We study the PE-CNT system using MD simulations. Tersoff-Brenner potentials [14] are used for carbon-carbon and hydrogen-carbon interactions, and the VDW potential between PE and CNT is modeled as a 6-12-type truncated Lennard-Jones potential [15]. The VDW energy per monomer of a straight PE molecule is calculated as a function of distance from CNT walls in the radial direction, with the axis of its backbone parallel to the axis of CNTs. The length of CNTs is chosen long enough as compared to that of PE to avoid edge effects. Shown in Fig. 1 are results for cases of CNT(10,10), (20,20), and (40,40). As can be seen, PE molecules can be absorbed along the internal wall of CNTs, with the gain of VDW energy of up to 0.1 eV/unit [on CNT(10,10)]. The equilibrium distance of PE molecules from CNT walls is about 4 Å. For small radius CNT such as (5,5) (not shown in Fig. 1), the adsorption is not favorable due to the repulsive VDW interaction at small distance.

Although there is also a local energy minimum for PE molecules absorbed along the external walls of CNTs as seen from Fig. 1, it is energetically more favorable for the molecules to be absorbed inside CNTs due to the curva-

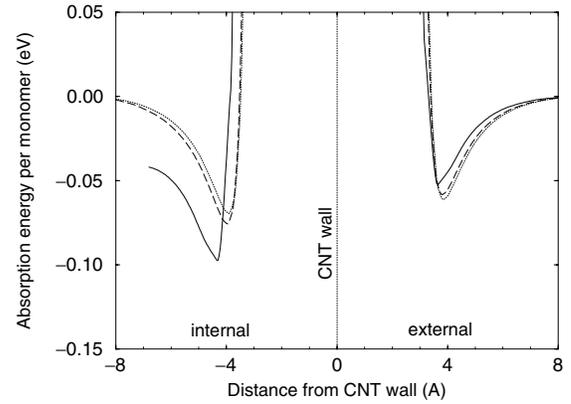


FIG. 1. The absorption energy (VDW) per monomer of a polyethylene molecule as a function of distance from CNT walls in the radial direction. The axis of the backbone of the molecule is parallel to the axis of CNTs. The left/right side is for the internal/external of CNTs, respectively. The two sides are separated by CNT walls. Solid, dashed, and dotted lines are for CNT(10,10), (20,20), and (40,40), respectively.

ture effects. The change in adsorption energies and barriers due to the registry of the molecules with CNT walls (moving along the CNT axis) are found to be negligible. More calculations show that the VDW energy is lower with the backbone structure of the PE molecules parallel to the CNT surface, compared to that with its backbone structure perpendicular to the surface. The difference is rather small (~ 0.001 eV), and the barrier separating the two local energy minimum is only 0.01 eV, small enough for PE molecules to switch freely between the two configurations at room temperature.

The energy gain through the VDW potential per monomer gives a driving force $\mathbf{F} = -\nabla E$ for molecules to be pulled into CNTs and the translocation time for an isolated PE molecule is estimated to be $t \sim N\sqrt{2m_0 l_0 / F}$, where m_0 and l_0 are the mass and length of a single unit, respectively. For general cases of polymers and CNTs in aqueous solutions at finite temperatures, the thermodynamic effects need to be considered and can be included through MD simulations.

The insertion of PE molecules into a CNT is demonstrated using MD simulations and snapshots of such a process are shown in Fig. 2. PE molecules are surrounded by a decane ($C_{10}H_{22}$) solution outside CNTs, the influence of which on the dynamics of molecules is modeled through Langevin equation $m\dot{\mathbf{v}}(t) = -m\gamma\mathbf{v} + \mathbf{R}(t)$, with friction coefficient $\gamma = 50 \text{ ps}^{-1}$ [16]. The random force $\mathbf{R}(t)$ is assumed to be white noise, obeying the fluctuation-dissipation theorem with $T = 300$ K. The wall of CNT is kept fixed. Decane molecules inside CNT are omitted. Such an approximation is justified as the interactions and collisions of long polymer molecules with a CNT wall would dominate the dynamics, due to their large contacting area, as compared to that with decane molecules. At $t = 0$ ps, a 40-unit PE molecule is

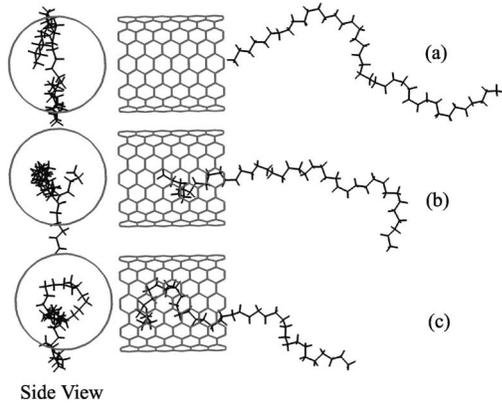


FIG. 2. The snapshots of a 40-unit PE molecule into CNT(10,10) (15 Å) from MD simulations (see the text for details). (a) $t = 0$ ps, the molecule is just outside the CNT; (b) $t = 600$ ps, the molecule is partially inside the CNT; (c) $t = 750$ ps, the molecule reaches the other end of the CNT.

outside a CNT(10,10) [Fig. 2(a)]; after $t = 500$ ps, the molecule begins to enter the CNT due to the VDW interaction. The configurations of the molecule partially inside the CNT and reaching the other end of the CNT are shown in Figs. 2(b) and 2(c), respectively. The side views show that the PE molecule is curved around the CNT wall to minimize the VDW energy. Note that the translocation time for molecules into the CNT is a statistical value, and as we mentioned above, τ is directly related to diffusion of molecules inside CNTs, which is discussed below.

We study the diffusion of molecules inside CNTs also using MD simulations. As an example system, we choose a 40-unit PE molecule inside a CNT(10,10) channel (63 Å long). The CNT is immersed in a heat bath controlled by a Langevin friction force scheme [17], and the PE molecule inside is not directly connected to the heat bath but reaches its thermal equilibrium through the VDW interaction with the CNT wall. The time step is 0.2 fs and a periodic boundary condition is used. The heat bath is controlled at a relatively high temperature $T = 600$ K [18] to shorten the times for simulations. Simulations for room temperature are similar and the corresponding diffusion coefficient D can be obtained easily as $D \sim T$.

The system is equilibrated for 1.2 ns till the end-to-end distance $\langle R_d \rangle$ of the PE molecule inside CNT reached a convergence. The molecule is found to be in an extended configuration ($\langle R_d \rangle \sim 28$ Å) as compared to the case in free space ($\langle R_d \rangle \sim 18$ Å [19]). This suggests a decrease of the effective coordination number for the inserted molecules. Similar simulations on PE molecules with 10 and 20 monomers show that $R_d \sim N$, rather than \sqrt{N} in free space. This agrees with the prediction from the scaling theory for polymers in confined space [9].

The self-diffusion coefficient D_{\parallel} of the center of mass (c.m.) of PE molecules along the CNT axis is related with the mean-squared displacement (MSD) function as follows:

$$D_{\parallel} = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle [r_{\parallel}(t + t_0) - r_{\parallel}(t_0)]^2 \rangle, \quad (5)$$

where $r_{\parallel}(t + t_0)$ is the coordinate of the c.m. of molecules along the CNT axis. Shown in Fig. 3 is the MSD of PE molecules as a function of time in a log-log scale at $T = 600$ K. The MSD is averaged from 12 independent simulation trajectories and also averaged over initial times. In the beginning time at $0 < t < 30$ ps, the collisions between molecules and CNT walls have not reduced the ballistic transport feature, with the slope of $\log(\text{MSD})$ to $\log t \sim 2$; for longer time $t > 40$ ps, the diffusion characteristics begin to show, with the slope of $\log(\text{MSD})$ to $\log t \sim 1$, which is the behavior described by Eq. (5). The ballistic transport could be important for short CNT channels. For the 40-unit PE molecule studied here, a critical length of CNTs ($\sim \bar{v}_{\text{c.m.}} t_c$), separating the two ranges, is estimated to be 35 Å, where $\bar{v}_{\text{c.m.}}$ is the mean velocity of the c.m. of the PE molecule at $T = 600$ K and $t_c \sim 40$ ps. The velocity autocorrelation function $C_{vv}(t)$, shown in the inset of Fig. 3, confirms that the correlations decrease with time and the critical time for $C_{vv}(t)$ approaching zero is about 40 ps. During the diffusion process, PE molecules mostly move along the CNT walls with a separation corresponding to the VDW energy minimum.

The diffusion coefficient D_{\parallel} of a 40-unit PE molecule inside CNT(10, 10) is found to be 25.4 ± 0.5 Å²/ps at $T = 600$ K, using Eq. (5) with MSD data in the time interval of [60 ps, 160 ps]. According to the reptation theory of a straight tube model for polymers [20], $D_{\parallel} \sim N^{-1}$. A modified Einstein relation for a N -unit polymer can be written as

$$D_{\parallel} = \frac{k_B T}{N m_0 \gamma_{\text{eff}}}, \quad (6)$$

where m_0 is the mass of a monomer and γ_{eff} is the effective friction coefficient for a monomer. For a PE

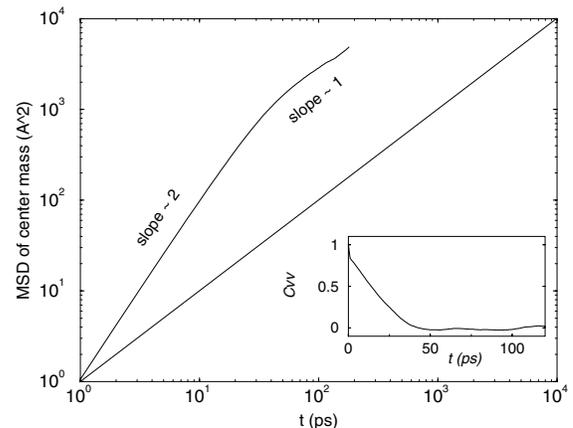


FIG. 3. The MSD of the c.m. of polyethylene molecules inside a CNT as a function of time in a log-log scale. At $0 \text{ ps} < t < 30$ ps, the slope of $\log(\text{MSD})$ to $\log t \sim 2$; at $t > 40$ ps, the slope ~ 1 . Inset: The velocity autocorrelation function (C_{vv}) as a function of time.

molecule, γ_{eff} is estimated to be $3.5 \times 10^{-2} \text{ ps}^{-1}$ from Eq. (6). An extrapolation value of D_{\parallel} for CH_4 ($N = 1$) gas molecules is found to be about $10^3 \text{ \AA}^2/\text{ps}$ ($10^{-1} \text{ cm}^2/\text{s}$) at $T = 300 \text{ K}$; it shows the faster diffusion of methane in CNTs compared with zeolite, such as silicalite ($D \sim 10^{-4} \text{ cm}^2/\text{s}$) [7], although the above estimated value is smaller than that from the direct simulation of methane ($D \sim 10^0 \text{ cm}^2/\text{s}$) [7]. The difference could be attributed to the energy transfers with CNT walls which was not considered in the direct simulation. The faster diffusion feature is expected to remain for long polymers in CNTs, compared with ordinary zeolite channels, considering the same dependence of D on N as expressed in Eq. (6). While a fast drop of self-diffusion with increased density was found for small gas molecules inside CNT due to the increasing molecule collisions [7], such collisions would be less frequent and less important in the case here as only the end units of a long polymer involve a collision and the change of momentum dissipates along the polymer chain.

Equation (6) suggests that $\nu_2 = 1$ in Eq. (3); thus the translocation time expressed in Eq. (4) has N^2 dependence from the contribution of diffusion inside the CNT. This feature is expected for other types of polymers, too, as it arises from the confinement of a nanotube. For diffusion outside CNT, the Zimm model is suitable for cases of aqueous solutions, where $\nu_1 \sim 0.5$, leading to a $N^{1.5}$ dependence. For large N , the contribution from diffusion inside a CNT dominates and an approximation for Eq. (4) is

$$\tau \approx \frac{l_0^2}{|\frac{\Delta\mu}{k_B T} + \ln\frac{q_1}{q_2}|} \frac{N^2}{3D_2} \quad (N \gg 1). \quad (7)$$

The change in chemical potential $\Delta\mu$ is dependent on the relative structure of polymers and CNTs, and properties of surrounding solutions. For a system of a PE molecule in its own solution, the VDW energy is about 0.05 eV/unit [19]; thus a negative change of $\Delta\mu = -0.1 \text{ eV} + 0.05 \text{ eV} = -0.05 \text{ eV}$ is found, as the gain of VDW energies into CNT is up to 0.1 eV/unit . For long PE molecules, condition $N|\Delta\mu/k_B T| \gg 1$ for Eqs. (4) and (7) is satisfied at room temperature. Thus τ is estimated as $N^2 \times 10^{-4} \text{ ps}$ (taking $l_0 \sim 1 \text{ \AA}$, $|\Delta\mu/k_B T| \sim 2$, $\ln(q_1/q_2) \sim 1$, and $D_2 \sim 10^3 \text{ \AA}^2/\text{ps}$) at $T = 300 \text{ K}$. For a $N \sim 10^5$ long PE molecule, a fast translocation is found with $\tau \sim 1 \text{ \mu s}$.

In summary, we have studied the transport of long polymer molecules through CNT channels. The expression for translocation time τ is obtained from the Fokker-Planck equation, which is found to be dependent on the chemical potential, entropy, and diffusion. For long N -unit polymers τ scales as N^2 . Calculations of VDW potential show that the absorption of PE molecules on the internal walls of CNT is energetically favorable, with absorption energy up to 0.1 eV/unit . The calculated diffusion coefficient from MD simulations suggests very fast

diffusions of polymer molecules inside CNT. The corresponding translocation time is estimated to be $\sim 1 \text{ \mu s}$ for a 10^5 -unit PE molecule.

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