Self diffusion of argon in flexible, single wall, carbon nanotubes

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The high-throughput Condor environment now allows many simulations to be performed on related systems, whether the focus is on improving the statistics or on broadening the range of conditions under which these simulations run. We illustrate the scope of the approach by using equilibrium molecular dynamics (EMD) to calculate self-diffusivities of argon atoms diffusing through single wall carbon nanotubes (SWNT). The diameters of the tubes and their helicities were varied and different argon loadings were studied. We also considered the effect of the rigidity/flexibility of the tube on the diffusivity. We found that the helicity and flexibility of the tubes have almost no noticeable influences. The size of the pore had a small effect, but the diffusivity depended essentially on the fluid loading.

Keywords: Self-diffusivity; Equilibrium molecular dynamics (EMD); Helicity; Nanotubes; Argon; Diffusion coefficient

1. Introduction

Microporous materials have many industrial applications, most of them based on their ability to condition the diffusion of fluids. Amongst these, single wall carbon nanotubes (SWNT) have a very regular structure and controllable geometry (size and helicity). Consequently they have very interesting properties and are prime candidates for applications such as molecular sieves or membranes and for hydrogen storage. In 1991, Iijima first identified carbon nanotubes as multi-walled structures consisting of concentric layers [1], but later, different groups isolated SWNT [2,3]. These have typical diameters of around 0.5–2 nm, and can assemble in bundles with an hexagonal lattice parameter of around 0.32 nm.

Although the diffusion of atoms or small molecules inside SWNT is starting to receive a good deal of attention from the computing modelling community, there are still very few simulations of diffusion in SWNT.

Mao and co-workers [4–6], simulated the diffusion of organic molecules in nanotube bundles, taking tube flexibility into account with a reactive bond order potential, and showing the influence of pore size on the self-diffusivity.

Two groups also calculated the macroscopically more relevant transport diffusivity, a quantity significantly more difficult to compute than the self-diffusivity.

Düren *et al.* [7] considered a large, rigid, multiwalled nanotube, but did not explicitly take into account the atomistic interaction between the particles and the walls.

Johnson and his group [8,9] produced the most up to date results, using a combination of Grand Canonical Monte Carlo (GCMC) and equilibrium molecular dynamics (EMD). They considered only a limited number of nanotubes, without flexibility, but the emphasis was in comparison with zeolites. It was clearly shown that the diffusion in SWNT can be order of magnitudes faster than in zeolites (silicalite) of similar pore size.

In this paper we use classical EMD to simulate the diffusion of argon at room temperature inside a range of SWNTs exhibiting various diameters and helicities as a way of demonstrating the potentialities of the high throughput environment provided by the Condor paradigm [10]. Different tube loadings are also considered. Furthermore, we test whether the fact that the SWNTs are rigid or flexible affects the self diffusivity. This study differs from preceding works by its focus on evaluating which parameters influence the diffusion coefficients, namely tube diameter, helicity

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and flexibility, and the density of argon. It is also the preliminary step to a more complete study in which the transport diffusivity is investigated.

2. Methodology

2.1 Condor

The simulation of many systems requires good statistics to obtain meaningful properties. One of the simplest approaches to improve the statistics of a given simulation consists in repeating it, with independent starting configurations. This straightforward albeit inelegant approach has been rendered especially attractive by a relatively novel type of resource, the Condor pool [10]. The Condor pool is simply a collection of machines, without any intercommunication, except with a master node. These machines can be modest library or student lab style PCs, which are idle most of the time. Thus, instead of running bigger, longer, more demanding simulations in order to reduce statistical errors, the alternative is to simply run a lot of smaller ones, on almost free resources.

The study described here was carried out on the UCL Condor pool [11,12], which at the time of writing contains more than a thousand PCs (1 GHz CPU speed and 256–512 Mb RAM) and is expanding. These machines function under Microsoft Windows operating systems, requiring specific compilation of the simulation and analysis codes.

The technical difficulties thus relate to the automatisation of the entire process and the problems caused by the submission of large numbers of individual simulation and their analysis. Scripts and procedures have been developed,[†] whose usefulness is not limited to statistical improvement, but more generally to "perfectly parallel" calculations, such as Monte-Carlo or phase space sampling to name a few.

2.2 Nanotubes

The geometry of a SWNT is described by the nanotube chiral indices, n:m [13] (n and m integers). They map how the SWNT may be formed from folding a graphene sheet onto the surface of a cylinder. In this study we consider only atomically smooth, defect free nanotubes. We used eight different nanotubes chosen to sample helicity and size related influences: 13:0, 10:5, 19:0, 16:5, 12:10, 19:10, 23:5 and 26:0. Two of these can be considered small with radii around 5 Å. Three others have radii around 10 Å, and the last three around 15 Å. Amongst these eight, two SWNTs are metallic (19:10 and 23:5), while the six others are semi conducting. Their characteristics are indicated in table 1 and the three

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Table 1. Physical properties of the SWNT considered in this study.

Indices	Radius (Å)	Length (Å)	Carbon numbers	Argon number (Higher load)
13:0	5.088	119.28	1456	12
10:5	5.178	112.70	1400	12
19:0	7.437	89.46	1596	90
16:5	7.437	80.94	1444	80
12:10	7.468	81.27	1456	82
19:10	9.987	108.69	2604	317
23:5	10.124	110.18	2676	330
26:0	10.177	119.28	2912	352

nanotubes with radii of approximately 10 Å are illustrated in figure 1.

2.3 Potential

Two different families of simulations were carried out: The first one taking into account the flexible nature of the SWNT, the second one, computationally less demanding with rigid SWNT.

The flexible tubes require a carbon–carbon interaction potential [14], consisting of four terms.

$$U(r, \theta, \phi) = E_0\left[(1 - e^{-k_1(r-r_0)})^2 - 1\right]$$
$$+ \frac{1}{2}k_2(\cos\theta - \cos\theta_0)^2$$
$$+ \left[\frac{1}{2}A_1(1 + \cos\phi)\right.$$
$$+ \frac{1}{2}A_2(1 - \cos(2\phi))\frac{1}{2}A_3(1 + \cos(3\phi))\right]$$
$$+ 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

The first term is a Morse potential to describe the interatomic bonding. The second term is a valence angle potential specifying deflections of the angles. Torsion along bonds is described by the third term, the dihedral angle potential. The final term is a Lennard–Jones potential to account for steric and van der Waals interactions. The parameters for this potential are given in table 2. Additionally, one carbon atom has to be fixed in space or the tube rotates, and in some cases translates, along the nanotube axis.

For the fixed tubes, each carbon atom is held in space.

The remaining interactions, between argon atoms and between argon and tube carbon atoms are essentially of a dispersion–repulsion nature and are represented in the form of the Lennard–Jones Potential (see table 3 for parameters).

It has to be noted that these potentials (Ar–C and C–C) are derived from graphite potentials, a planar, metallic
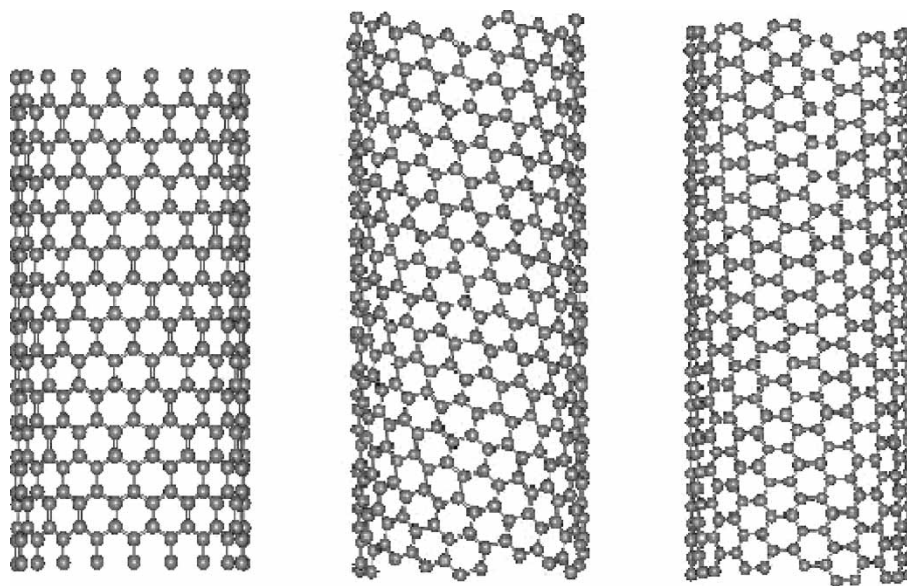
Figure 1.   Carbon nanotubes. From left to right:19:0, 16:5 and 12:10.

surface. The extent to which they can be applied to curved, semi conducting surfaces is not a simple issue. In the present work, we assume that the difference in polarisability between carbons in sheets of various curvature and electronic band structure are sufficiently small and that the resulting dispersion interactions with adsorbates are comparable.

2.4 Simulations

We used EMD simulation in the NVT ensemble, as implemented in the code DL_POLY [15].[‡] The equations of motion were solved using a leapfrog algorithm with a 2 fs time step. Temperature was constrained at 300 K with a Nosé-Hoover thermostat with a relaxation time of .5 ps.

For each SWNT, we considered 4 different loads. The higher load tubes were filled by superposing a simulation box containing the nanotube itself with an auxiliary argon simulation box and then removing these argon atoms which were outside the nanotubes or inside it but closer than $3.82\,\text{Å}$ ($\sqrt[6]{2}\sigma_{\text{C-Ar}}$) to a carbon atom. Randomly removing Ar atoms and re-equilibrating for 20 ps generated the three lower loading simulations (containing approximately 75, 50 and 25% of the amount of argon). The number of argon atoms for the higher load simulations can be found in table 1.

The simulations were conducted with equilibration time ranging from 20 to 40 ps, and production time ranging from 200 to 400 ps, depending on the amount of argon in the tubes. The resulting trajectories were then analysed to compute the self-diffusion coefficients along the direction of the axis of the nanotube.

2.5 Analysis

The self-diffusion D_{s} describes the diffusion of a molecule in a homogenous environment without an external gradient. We obtain D_{s} with the mean squared displacement approach, via the Einstein relation [16,17]. The analysis tool Polyview[¶] is used to calculate the mean square displacement of an argon atom along the axis of the tubes as a function of time, and to extract the diffusion coefficients from its slope between 2 and 10 ps.

The narrower tubes pose problems as far as the determination of the diffusion coefficient is concerned, as their essentially 1D nature only allows a very limited number of particles to be adsorbed (as little as three for the low loading simulation of the narrower tubes!). Therefore, even if using improvements, such as block-averaging, the statistics can be especially poor. This is illustrated in figure 2, which shows the distribution of the diffusion coefficient in a 13:0 tube (high load, 12 argon atoms), from one hundred independent simulations. One could increase the size of the simulation cell along the axis of the tube (at a steep increase in computational requirement, time and memory) but the alternative is to increase the number of independent simulations. The approach was then to run a preliminary simulation for each tube/loading, hereby generating a "parent" trajectory. One hundred different configurations were then extracted from this trajectory (every 2 ps) to generate different initial configurations. Each configuration was then run as an independent simulation. The corresponding diffusion coefficients were calculated and then averaged.

[‡] DL_POLY is a package of molecular simulation routines written by W. Smith and T.R. Forester, copyright The Council for the Central Laboratory of the Research Councils, Daresbury Laboratory at Daresbury, Nr. Warrington (1996)

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Table 2.   Parameters for the flexible carbon nanotube potential [11].

Parameter	Value
E_0	4.963466 eV
k_1	2.1867 Å^{-1}
r_0	1.418 Å
k_2	5.826812 eV
θ_0	120°
A_1, A_3	0
A_2	0.260351 eV
σ, ϵ	see table 3

Table 3.   Parameters for the dispersion–repulsion potential.

	ϵ *(eV)*	σ *(Å)*	*Reference*
C–Ar	0.005079	3.41	[9]
Ar–Ar	0.010690	3.42	
C–C	0.004556	3.85	[14]

3. Results and discussion

3.1 Rigid tubes

The results for the rigid tubes are presented in figure 3. The diffusion coefficients vary between 5×10^{-9} m^2 s^{-1}
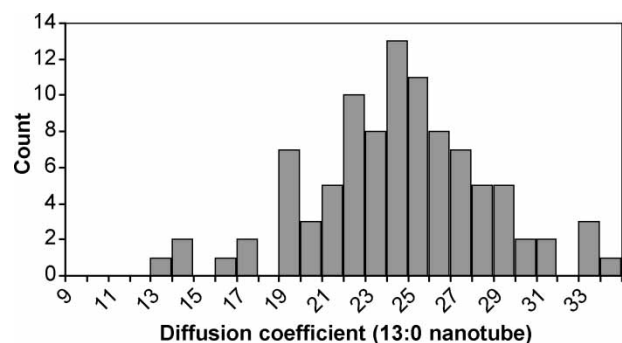
Figure 2.   Statistical distribution of the self-diffusity (in 10^{-9} m^2 s^{-1}) for argon at a density of 1.24×10^{-3} atom Å^{-3} in a 13:0 nanotube.
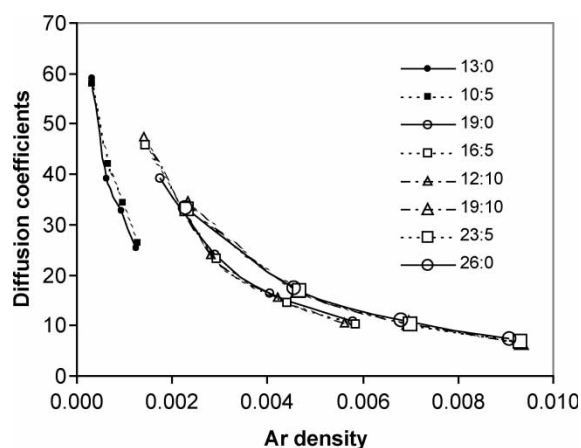
Figure 3.   Diffusion coefficients (in 10^{-9} m^2 s^{-1}) as a function of argon density (atom Å^{-3}) for the eight SWNTs considered.

Table 4.   Ar self-diffusivity (in 10^{-9} m^2 s^{-1}) in rigid/flexible tube frames, for a 19:0 SWNT.

Density (atom Å^{-3})	Rigid	Flexible
5.793×10^{-3}	10.86 ± 0.81	10.76 ± 0.79
4.055×10^{-3}	16.41 ± 1.33	16.96 ± 1.58
2.896×10^{-3}	24.24 ± 2.85	25.46 ± 3.19
1.738×10^{-3}	39.21 ± 4.58	41.20 ± 6.76

and 60×10^{-9} m^2 s^{-1}. The upper values are comparable to the results of a previous study [9].

It is clear that tubes of similar size lead to strongly related diffusion coefficients, whatever the argon density. The helicity of the tube seems to bear very little impact on the diffusivity of argon.

The influence of the tube size is more difficult to interpret and indeed Ackerman *et al.* [9] do not show any specific trend. Here, it seems that tubes of larger size lead to higher diffusivity, which can be attributed to the fact that in smaller tubes all atoms experience the tube corrugation while in larger tubes the more central atoms are subjected to almost free-fluid conditions. Nevertheless, care must be exercised, as the volume used to calculate the argon density uses the diameter from one carbon centre to another carbon centre. While this definition unambiguously defines a density, it fails to account for the reduced volume due to the C–Ar repulsive interaction. This excluded volume is obviously more important for small tubes than big ones. The correct quantity to plot the diffusivities against would be the pressure (or chemical potential) of a reservoir of particles in equilibrium with those in the tubes. While these quantities are accessible from GCMC calculations [18], they are out of reach of the EMD approach of this paper.

Finally, it is not surprising to note that the higher the loading, the lower the diffusivity, for all tube sizes and helicities, which confirms previous findings.

3.2 Flexible tubes

The results given in table 4 show that the diffusivities obtained from a flexible tube differ very little from those of a rigid tube. This leads us to think that the additional complexity required to set up such flexible systems with a very detailed potential is not required.

On the other hand, the shake algorithm used by DL_POLY to constrain the rigid carbon frame is time consuming, and those simulations where the nanotube is flexible are not excessively more expensive than those where it is rigid. The memory requirements are not significantly increased either. Choosing between flexible or rigid tubes is therefore probably a matter of personal choice.

4. Conclusion

We simulate the diffusion of argon in eight SWNTs of varying radii and helicity, at different loadings. Using

EMD with semi-empirical potentials, we compute the self-diffusivity of argon in these tubes, which are either kept rigid or allowed to relax. We observe that

- Helicity has no bearing on self-diffusion
- Self-diffusion coefficients are similar in flexible and rigid tubes
- The size of the pore conditions partially the diffusity, and argon diffuses less efficiently in smaller pore
- The most important parameter is the density of argon
- Condor pools are very adapted to the modelling of diffusion in nanoporous materials

Finally let us point out that it is the transport diffusivity (which appears in Fick's law) which is relevant for comparison with macroscopic experiments or to help with the design of membranes or nanopipes (virtual prototyping), not the self-diffusivity. The calculation of the transport diffusivity, following the method outlined by Theodorou [19,20] is especially well adapted to the Condor architecture, as it requires a set of EMD calculations and a GCMC calculations, both of which are perfectly parallel. The computation of the transport diffusivity in a high throughput, Condor environment will be presented in a companion paper.

Acknowledgements

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