

Investigation of Rotational Diffusion of a Carbon Nanotube by Molecular Dynamics

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The rotational diffusion coefficient of a single carbon nanotube in fluid is calculated by equilibrium and nonequilibrium molecular dynamics (MD). The validity and accuracy of the MD simulations are checked on plenty of data points by varying the length and diameter of the nanotube. The three-dimensional (3D) coefficients are larger than the two-dimensional (2D) ones, both having non-negligible deviations from the theoretical predictions [J. Chem. Phys. 1984, 81, 2047–2052]. By changing the parameter ε_{C-Ar} of Lennard-Jones potential, the interaction strength between carbon and argon atoms is also taken into account. A monotonic decrease of the coefficients for both 2D and 3D cases with the increase of ε_{C-Ar} can be observed. Our present work suggests that we must be cautious when using the literature theory in practical situations.

Keywords: Rotational Diffusion Coefficient, Carbon Nanotube, Molecular Dynamics.

1. INTRODUCTION

Due to the unique band gap structure, the single-walled carbon nanotubes can fluoresce in the near-infrared and thus can act as fluorescent probes of local environments in bioimaging and materials science.^{1–3} To establish quantitative description of its movement, the corresponding single-particle-tracking technique (SPT)^{4–6} can be utilized to provide the full image of the diffusion processes by recording the trajectory, analyzed later to identify modes of motion. For a non-spherical single particle like CNT, its movement at equilibrium may involve the coupling between translational and rotational diffusion.^{7,8} While the translational diffusion has been studied quite extensively, the rotational diffusion draws much less attention. From the above perspectives, getting a better understanding on the rotational diffusion of a CNT is an urgent task, to be accomplished not only through observation in the laboratory, but via theoretical and computational methods.

A theoretical equation was derived by Tirado et al.^{9,10} to calculate the rotational diffusion coefficient D_r of a cylindrical rod-shaped object and has been applied to various experimental studies a lot recently.^{11,12} In our previous work,¹³ the systematical calculation of this diffusivity has been conducted by molecular dynamics (MD) methods on

the two dimensional (2D) rotation of a carbon nanotube in fluid argon. In the present work, we aim to extend the discussion to the three dimensional (3D) problem, which is more realistic concerning the particle manipulation processes.^{1,2,14} We further consider the influence of interaction strength between carbon and argon atoms, which may serve as an indication of the slip of fluid on the solid surface of a rotating particle,¹⁵ not addressed in the Tirado's work.^{9,10}

2. COMPUTATIONAL DETAILS

In the MD simulations, the selected nanoparticle is a single carbon nanotube and the surrounding fluid is argon. Figure 1 shows the schematic diagram of the carbon nanotube in fluid for the initial configuration. The simulation system is established in the orthogonal coordinates labeled as x , y , z , with periodic boundary conditions applied in all three directions. Fluid argon is selected to simplify the MD simulation procedure. The simulation domain has a size of $L_x \times L_y \times L_z = 10.6 \times 10.6 \times 10.6 \text{ nm}^3$. The density ρ and temperature T of fluid argon is 1772 kg/m^3 and 300 K , respectively. To model a rodlike molecule, the nanotube is capped at both ends to prevent argon atoms from entering the nanotube. An MD package LAMMPS is used to perform the calculations.¹⁶ Lennard-Jones (LJ) pair potential,

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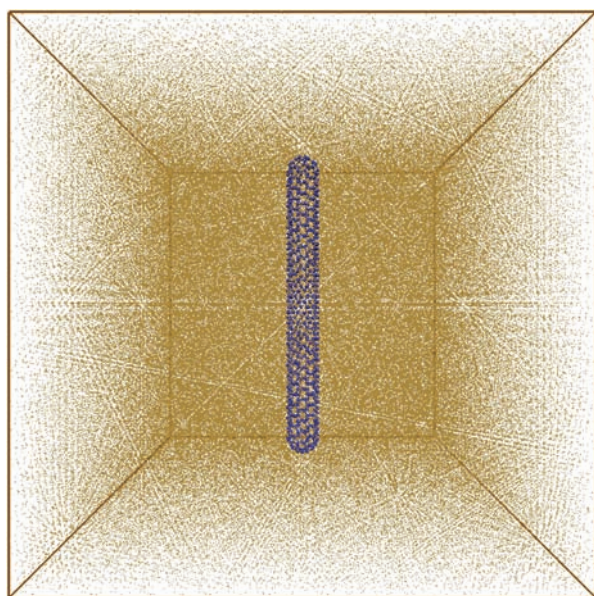


Figure 1. Schematic diagram of the initial configuration of the simulation system established in the orthogonal coordinates x, y, z .

in the form of Eq. (1), is considered between argon atoms and between argon and carbon atoms.

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

The basic parameters are listed as follows, $\sigma_{\text{Ar-Ar}} = 0.3405$ nm, $\varepsilon_{\text{Ar-Ar}} = 1.6546 \times 10^{-21}$ J, $\sigma_{\text{C-Ar}} = 0.3573$ nm, $\varepsilon_{\text{C-Ar}} = 1.9646 \times 10^{-21}$ J.^{17,18} The $\varepsilon_{\text{C-Ar}}$ will be altered in the latter sections to see its influences. The C-C interactions are not considered and instead the nanotube is treated as a rigid body,¹⁹ which allows direct comparison with the theoretical work.^{9,10} To reduce the time-consuming calculations of the inter-particle interactions, a cutoff distance of 0.77 nm is imposed. The canonical ensemble, i.e., NVT ensemble, is used accompanied with the Nose-Hoover thermostat.

3. RESULTS AND DISCUSSION

3.1. 2D Rotational Diffusion

In this section, the nanotube is confined to rotate on the $x-y$ plane. We use two methods to calculate the coefficient. The first is an equilibrium molecular dynamics (EMD) method. Fick's second law predicts how concentration changes with time due to rotational diffusion processes,

$$\frac{\partial C}{\partial t} = D_r \Delta_\varphi C \quad (2)$$

Here, the concentration C depends on the particle's directional angle in its own spherical coordinate frame and D_r is the rotational diffusion coefficient. The Einstein relation can be derived based on Eq. (2), in the final form of¹³

$$D_r = \frac{\langle (\Delta\varphi)^2 \rangle}{2t} \quad (3)$$

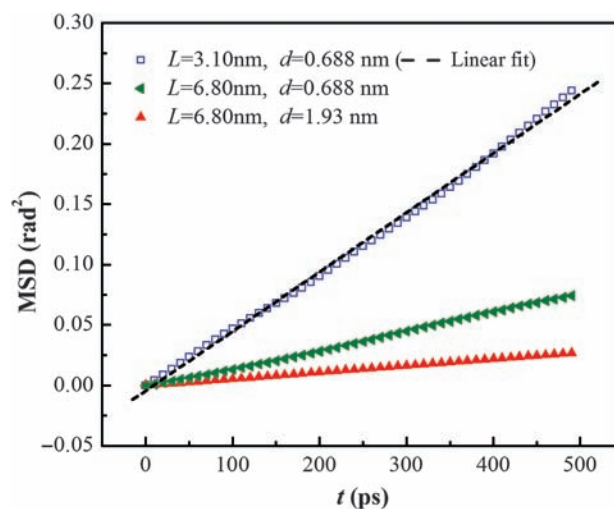


Figure 2. 2D rotational diffusion: Angular MSDs for three simulation cases, with different nanotube lengths L and diameters d .

Using EMD simulations, an ensemble of the nanotube trajectories, starting at different initial times τ and ending a time t later, is extracted. $\Delta\varphi$ is the angular displacement expressed as $\Delta\varphi(t) = \varphi(t+\tau) - \varphi(\tau)$. Figure 2 is the time-varying angular mean-squared displacement (MSD) for three simulation cases with different nanotube lengths L and diameters d at equilibrium. Diffusive behavior can be observed for all the selected cases and the curves can be fit by linear functions.

The second method is a nonequilibrium molecular dynamics (NEMD) method. Einstein (1905) noticed that the viscous friction of a Brownian particle must be related to the diffusion constant of the particle by the equation $D = 1/fk_B T$.²⁰ Here, k_B is the Boltzmann constant T is the temperature of the fluid and f is the friction coefficient, which is the inverse of mobility μ . For rotational diffusion, the above relation can be expressed as

$$D_r = \mu_r k_B T = \frac{\omega}{\Gamma_\theta} k_B T \quad (4)$$

In Eq. (4), μ_r denotes angular mobility and equals to the proportion of the nanotube's angular velocity and external force. To perform nonequilibrium simulations, a constant torque is applied to the nanotube, which will drive it to go through uniform circular motions at all times. Figure 3 shows change of angular velocity ω along with the imposed external torque Γ . The slope of the curve can be obtained via the linear fitting and by submitting the slope into Eq. (4), D_r is extracted.

The results calculated by the above methods are compared with the expected values as predicted by the Tirado model.¹⁰

$$D_r = \frac{3k_B T (\ln p + \delta)}{\pi \eta L^3} \quad (5)$$

where $p = L/d$, $\delta = -0.662 + 0.917/p - 0.05/p^2$

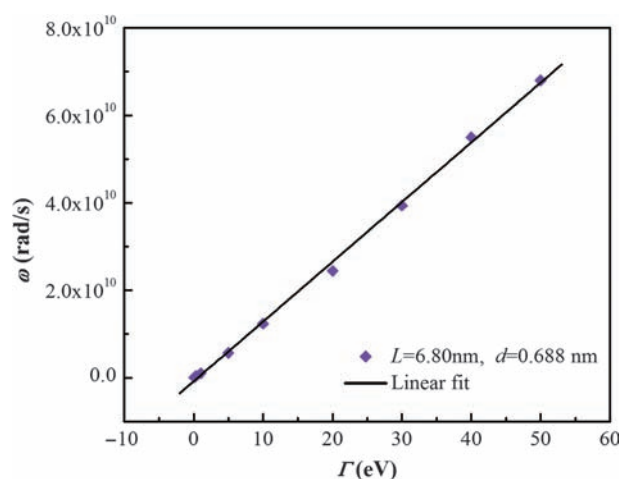


Figure 3. 2D rotational diffusion: Dependence of the angular velocity on the external torque along with the linear fitting ($L = 6.80$ nm, $d = 0.688$ nm).

Table I. Selected simulation cases with varying the nanotube's length L and diameter d .

L (nm)	3.10	5.61	6.80	8.10	6.80	6.80	6.80	6.80
d (nm)	0.688	0.688	0.688	0.688	1.10	1.38	1.65	1.93

The symbols of Eq. (5) share the same meaning as above along with η denoting the shear viscosity. This equation gives the theoretical D_r for a cylindrical rod-shaped object rotating around its perpendicular axis. The selected simulation cases are summarized in Table I and the results are shown in Figure 4. The calculated rotational diffusion coefficients are all lower than the predicted values by a factor ~ 2 , while the EMD and NEMD results agree relatively well with each other. The accuracy of the simulations is

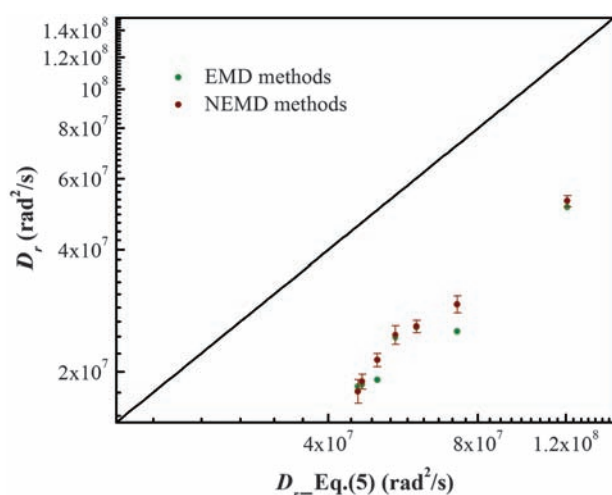


Figure 4. 2D rotational diffusion: The rotational diffusion coefficients D_r extracted from EMD and NEMD simulations as a function of the theoretical values calculated using Eq. (5). The selected simulation points are summarized in Table I.

thus checked and the great deviation from theory should be noticed.

3.2. 3D Rotational Diffusion

For the 2D rotation, the nanotube's rotation axis is oriented along the same direction, which is z direction in the present simulations. When the confinement is removed, the nanotube can rotate freely with the rotation axis pointing towards different directions, which is the 3D case. Figure 5 exhibits the time-varying nanotube's length projection ratio on plane $x-y$. For the 2D case, the ratio is always equal to unit; while for the 3D case, the nanotube rotates out of plane $x-y$ with the ratio becomes smaller than unit. Here to emphasize is that the rotational diffusion is actually discussed in the particle's own spherical coordinate frame. The 2D and 3D cases are only different by the orientation of the rotation axis which is fixed or not. This indicates that the above equations, i.e., Eqs. (2)~(4) still apply to the 3D rotational diffusion. Then, we utilize Eq. (3) at equilibrium and obtain the time-varying three-dimensional angular mean-squared displacements (MSD) in Figure 6. Here to note that $\Delta\varphi$ is a three-dimensional angular displacement instead of a two-dimensional one. Similar diffusive behavior as Figure 2 is again observed. To compare the results of D_r among the 2D, 3D and theoretical values of Eq. (5), Figure 7 is plotted. Two points are worth mentioning here. First, the 3D coefficients are larger than the 2D coefficients. This is actually expectable when the confinement is removed. Second, the deviation from theory is still not eliminated. The 3D coefficients can be smaller or larger than the theoretical values, and the relative differences between them approximately lie in the range of 15%~6%.

3.3. Influence of the C-Ar Interaction Strength

From the molecular point of view, the interaction strength between carbon and argon atoms should also be considered

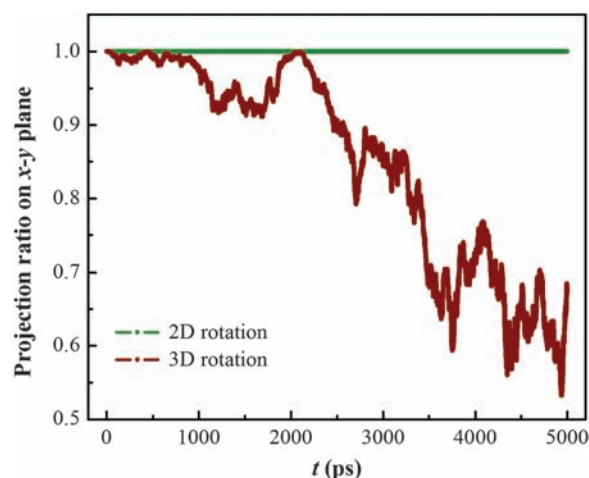


Figure 5. The nanotube's length projection ratio on plane $x-y$ varying with time, for 2D rotation and 3D rotation (The selected case is $L = 6.80$ nm, $d = 0.688$ nm).

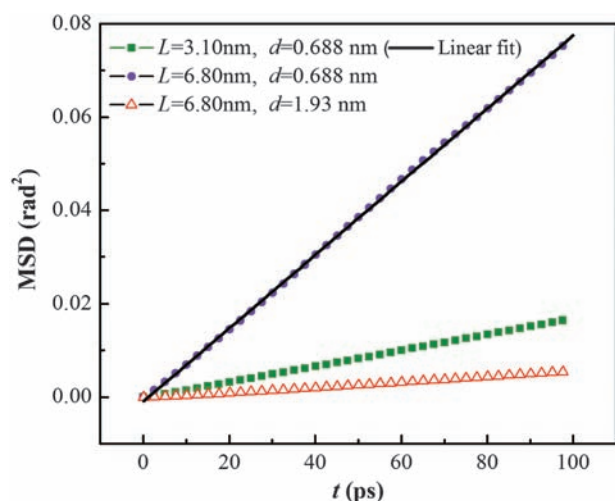


Figure 6. 3D rotational diffusion: Angular MSDs for three simulation cases, with different nanotube lengths L and diameters d .

on this issue, which is not presented in Tirado's model. The interaction can be tuned by varying the potential coefficient ε_{C-Ar} of LJ potential of Eq. (1). Figure 8 exhibits the dependences of 2D and 3D coefficient D_r on different ε_{C-Ar} , calculated via EMD simulations. Increase of ε_{C-Ar} brings about the decrease of D_r , for both 2D and 3D cases. This trend may come from that a more ordered solid-like structure is formed by argon atoms near the nanotube surface, due to a stronger argon-carbon interaction. It will result in a larger friction coefficient at larger ε_{C-Ar} and the rotation is thus hindered. A good qualitative agreement can be found between this observation and the results in literature work¹⁵ that D_r is larger under slip²¹ than stick boundary condition. It is important to note that Eq. (5) is established based on the stick boundary condition. And as D_r of the 2D cases are always smaller than the theoretical

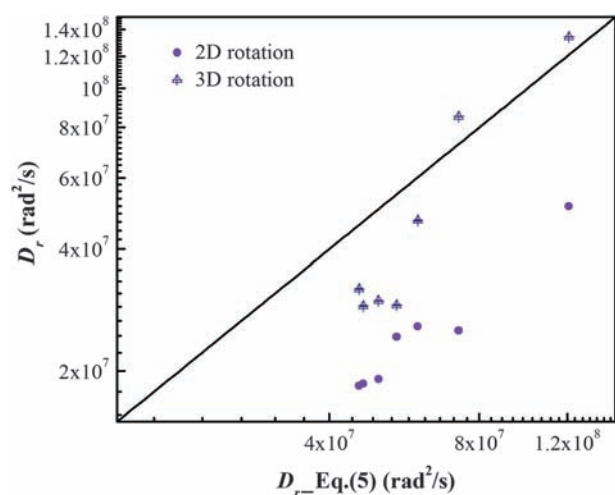


Figure 7. The 2D and 3D rotational diffusion coefficients D_r calculated using EMD methods as a function of the theoretical values calculated using Eq. (5). The selected simulation points are summarized in Table I.

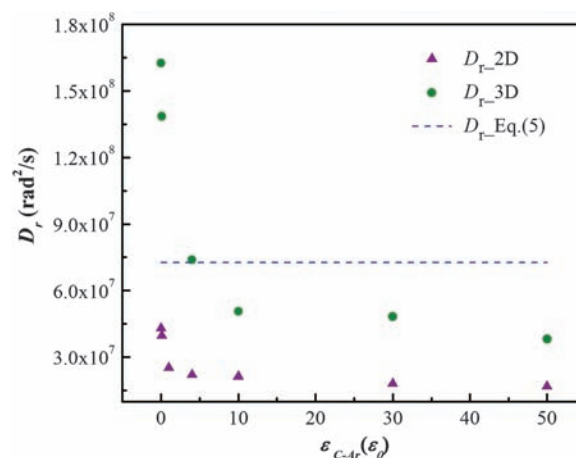


Figure 8. Dependence of the 2D and 3D rotational diffusion coefficient D_r on the potential parameter ε_{C-Ar} , obtained from the three methods. The unit of the horizontal axis is the default value $\varepsilon_0 = 1.9646 \times 10^{-21}$ J. (The selected case is $L = 6.80$ nm, $d = 0.688$ nm).

predictions, D_r of the 3D cases cross the theoretical line when ε_{C-Ar} changes. A perfect match with the theory can be observed for the 3D rotation when ε_{C-Ar} is four times as the referenced value.¹⁷ However, the deviation between theory and our molecular dynamics results, when considering 2D, 3D cases as well as the influence of ε_{C-Ar} , has not been appropriately accounted for. And some disagreements can also be spotted when using the theory to predict some experimental results.^{2,12} This suggests that we must be cautious when using the literature theory in practical situations.

4. CONCLUSION

Herein, we put forward equilibrium and nonequilibrium molecular dynamics methods to investigate the rotational diffusion of a single carbon nanotube in fluid. The validity and accuracy of the MD simulations are checked on plenty of data points by varying the length and diameter of the nanotube. For the two-dimensional rotation, the nanotube is confined to rotate on plane $x-y$ and the rotational diffusion coefficient D_r is found to be lower than the theoretical values by a factor ~ 2 . For the three-dimensional cases, the nanotube rotates freely and D_r is larger than the 2D cases. But the deviation compared with the theory is still not negligible. The influence of the interaction strength between carbon and argon is also taken into account by tuning the potential parameter ε_{C-Ar} of LJ potential. The 2D and 3D coefficients both decrease with the increase of ε_{C-Ar} , indicating a faster rotation at slip boundary condition. This implies that for practical situations, more factors should be considered when utilizing the literature theory. We hope this work will be a bridge to link the rotational diffusion between theoretical predictions and experimental observations. The proposed MD methods can be applied to more realistic circumstances.

Acknowledgments: This work is financially supported by National Natural Science Foundation of China (Nos. 51322603, 51356001, 51136001, 51321002), Program for New Century Excellent Talents in University and the Tsinghua National Laboratory for Information Science and Technology of China.

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Received: 24 September 2013. Accepted: 18 January 2014.