

# Molecular dynamics calculation of rotational diffusion coefficient of a carbon nanotube in fluid

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Rotational diffusion processes are correlated with nanoparticle visualization and manipulation techniques, widely used in nanocomposites, nanofluids, bioscience, and so on. However, a systematic methodology of deriving this diffusivity is still lacking. In the current work, three molecular dynamics (MD) schemes, including equilibrium (Green-Kubo formula and Einstein relation) and nonequilibrium (Einstein–Smoluchowski relation) methods, are developed to calculate the rotational diffusion coefficient, taking a single rigid carbon nanotube in fluid argon as a case. We can conclude that the three methods produce same results on the basis of plenty of data with variation of the calculation parameters (tube length, diameter, fluid temperature, density, and viscosity), indicative of the validity and accuracy of the MD simulations. However, these results have a non-negligible deviation from the theoretical predictions of Tirado *et al.* [J. Chem. Phys. **81**, 2047 (1984)], which may come from several unrevealed factors of the theory. The three MD methods proposed in this paper can also be applied to other situations of calculating rotational diffusion coefficient. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4861661>]

## I. INTRODUCTION

In fluid systems, nanoparticle manipulation and visualization techniques have drawn much attention due to its potential applications in the design of novel hydrodynamic nanodevices, e.g., sensors, probes for various areas, especially biotechnology. When the target object is a non-spherical single particle, its movement may involve the coupling between translational and rotational diffusion, increasing substantial complications for dynamics analyses.<sup>1,2</sup> While the translational diffusion has been studied quite extensively, the rotational diffusion draws much less attention. But under various nonequilibrium conditions, like shear flow,<sup>3</sup> electric fields,<sup>4</sup> or magnetic fields,<sup>5</sup> some rather interesting phenomena, like the nanoparticle's orientation and alignment can be observed, which are related to rotational diffusion and have a great impact on the physical properties of the nanocomposites<sup>6</sup> or nanofluids.<sup>7</sup> From the above perspectives, getting a better understanding on the rotational diffusion of a nanoparticle is an urgent task.

A theoretical equation was derived by Tirado *et al.*<sup>8,9</sup> to calculate the rotational diffusion coefficient  $D_r$  of a cylindrical rod-shaped object (CRSO). It has been applied to various experimental studies a lot recently, serving as a fundamental tool to analyze the diffusion processes.<sup>10–12</sup> However, as stated in Ref. 13, the slip of the fluid on the solid surface of the rotating particle may have a non-negligible effect on  $D_r$ , which is not considered in Refs. 8 and 9. Therefore, the validity of applying the literature theory to the nanoparticles may

be questioned. To address this issue, the solution points to the molecular dynamics (MD) calculation. The MD method is preferred for its simplicity in modeling the atom-atom interactions and directly monitoring the nanoparticle's Brownian motion. It has been successfully applied to the calculation of other transport coefficients, including thermal conductivity,<sup>14</sup> shear viscosity,<sup>15</sup> and translational diffusion coefficient.<sup>16</sup> But unfortunately, few reports on MD simulation methods of calculating the rotational diffusion coefficient exist, which requires further studies.

Thus, the objective of the present work is to propose MD methods to systematically calculate the rotational diffusion coefficient of a nanoparticle in fluid and compare the results with the theoretical predictions. Three MD methods include equilibrium molecular dynamics (EMD) based on Einstein relation, Green-Kubo (GK) formula, and nonequilibrium molecular dynamics (NEMD) based on the Einstein–Smoluchowski (ES) relation. The nanoparticle is confined to rotate two-dimensionally, in order to meet the hot topics of anisotropic particle diffusion in membranes in bioscience.<sup>1,17</sup> Here, the chosen nanoparticle is a capped carbon nanotube (CNT). Mathematically, it can be modeled as a CRSO, by treating it as a rigid particle, which allows direct comparison with Refs. 12 and 13. Compared with a flexible one, the effects of deformation and atom oscillation are not taken into account for the rigid case. Practically, CNT's rotational diffusion should attract special focus of attention due to its role as fluorescent probes in bioimaging,<sup>18,19</sup> or imparting its various great features to nanocomposites.<sup>20,21</sup> It is not surprising to find out that the theory may not coincide with the present cases any more, for the lack of consideration of some basic factors.

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## II. METHODOLOGY

### A. EMD based on Einstein relation

In the canonical ensemble, assume an  $N$ -nanotubes system and the rotational diffusion equation can be written as

$$\frac{\partial C}{\partial t} = D_r \Delta_\varphi C. \quad (1)$$

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. For the two-dimensional rotation, assume that at initial time  $t = 0$ , all the nanotubes locate at  $\varphi = 0$ , i.e.,  $C(\varphi, 0) = N\delta(\varphi)$ . Then, the solution of Eq. (1) is

$$C(\varphi, t) = \frac{N}{2\sqrt{\pi D_r t}} e^{-\frac{\varphi^2}{4D_r t}}. \quad (2)$$

Equation (2) implies that the concentration is actually a time related Gaussian distribution. And from Eq. (2), the angular mean-squared displacement (MSD)  $\langle \Delta\varphi^2 \rangle$  can be obtained,

$$\langle \Delta\varphi^2 \rangle = \frac{1}{N} \int_{-\infty}^{+\infty} \varphi^2 C(\varphi, t) d\varphi = 2D_r t. \quad (3)$$

Here,  $\langle \dots \rangle$  denotes ensemble average and  $\Delta\varphi$  is the angular displacement expressed as  $\Delta\varphi(t) = \varphi(t + \tau_0) - \varphi(\tau_0)$ . Finally, the Einstein relation describing the rotational diffusion for a single nanotube can be expressed as

$$D_r = \frac{\langle \Delta\varphi^2 \rangle}{2t}. \quad (4)$$

For EMD simulations,  $\overline{\dots}$  denotes the time average for a single nanotube. As ergodic hypothesis holds for our simulations, the time average is equivalent to the ensemble average.

### B. EMD based on Green-Kubo formula

The Green-Kubo formulas relate equilibrium fluctuations of the fluxes to the corresponding phenomenological (or Onsager) coefficients  $L_{ij}$  and give the exact mathematical expression in terms of integrals of time correlation functions:<sup>22</sup>

$$L_{ij} = \frac{V}{3k_B} \int_0^\infty \langle J_i(t) \cdot J_j(t_0) \rangle dt. \quad (5)$$

Given a microscopic and instantaneous expression for the fluxes  $J_i(t)$ , one can compute the  $L_{ij}$ , which can be connected with the transport coefficients within the framework of irreversible processes. The equivalence of GK formula to Einstein relation has been proven and for the present case of rotational diffusion coefficient, the GK formula can be directly deduced,

$$D_r = \int_0^\infty \overline{\omega(t) \cdot \omega(t_0)} dt. \quad (6)$$

Here,  $\omega$  is the angular velocity of the nanotube. The time integration of the angular autocorrelation function (AACF)  $\overline{\omega(t) \cdot \omega(t_0)}$  gives the final results of  $D_r$  from Eq. (6).

### C. NEMD based on Einstein–Smoluchowski relation

For the two dimensional rotation, suppose some potential energy  $U$  creates a torque  $\langle \Gamma \rangle = -dU/d\langle \varphi \rangle$  on the nanotubes, which would respond by rotating with angular velocity  $\langle \omega \rangle = \mu_r \cdot \langle \Gamma \rangle$ . Here,  $\mu_r$  denotes mobility. After some time, equilibrium will be established when there is no net flow and the nanotubes are located around the direction with the lowest  $U$ . The flow of particles due to drift and diffusion current can be separately expressed as

$$J_{\text{drift}}(\varphi) = \mu_r \langle \Gamma \rangle C(\varphi) = -C(\varphi) \mu_r \frac{dU}{dK \langle \varphi \rangle}, \quad (7)$$

$$J_{\text{diffusion}}(\varphi) = -D_r \frac{dC}{d\langle \varphi \rangle}. \quad (8)$$

At equilibrium, Boltzmann statistics infer that

$$C(\varphi) \propto e^{-U/(k_B T)}, \quad (9)$$

in which  $k_B$  is the Boltzmann constant and  $T$  is the temperature of the fluid. Equilibrium requires:

$$\begin{aligned} J_{\text{drift}} + J_{\text{diffusion}} &= -C(\varphi) \mu_r \frac{dU}{d\langle \varphi \rangle} + \frac{D_r}{k_B T} \frac{dU}{d\langle \varphi \rangle} C(\varphi) \\ &= -C(\varphi) \frac{dU}{d\langle \varphi \rangle} \left( \mu_r - \frac{D_r}{k_B T} \right) = 0. \end{aligned} \quad (10)$$

Finally, for the single nanotube, the Einstein–Smoluchowski relation can be expressed as

$$D_r = \mu_r k_B T = (\overline{\omega/\Gamma}) k_B T. \quad (11)$$

In Eq. (11),  $\mu_r$  is equal to the proportion of the nanotube's angular velocity and external torque. For nonequilibrium simulations, a constant torque  $\Gamma$  is applied to the nanotube, which will drive it to go through uniform circular motions at all times. Then, based on Eq. (11),  $D_r$  can be derived.

## III. COMPUTATIONAL DETAILS

The calculation of the rotational diffusion coefficient via molecular dynamics is investigated by taking a carbon nanotube in fluid argon as a case. 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. To model a rodlike molecule, the nanotube is capped at both ends to prevent argon atoms from entering the nanotube. A MD package LAMMPS is used to perform the calculations.<sup>23</sup> Lennard-Jones (LJ) pair potential, in the form of Eq. (12), is considered

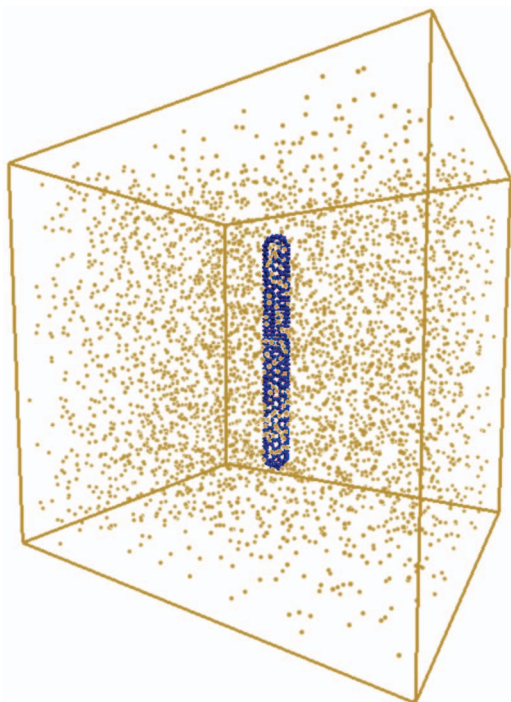


FIG. 1. Schematic diagrams of the initial configuration of the simulation system established in the orthogonal coordinates  $x$ ,  $y$ ,  $z$ .

between argon atoms and between argon and carbon atoms,

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

The basic parameters are listed as follows,  $\sigma_{\text{Ar-Ar}} = 0.3405$  nm,  $\epsilon_{\text{Ar-Ar}} = 1.6546 \times 10^{-21}$  J,  $\sigma_{\text{C-Ar}} = 0.3573$  nm,  $\epsilon_{\text{C-Ar}} = 1.9646 \times 10^{-21}$  J.<sup>24</sup> The C-C interactions are not considered and instead the nanotube is treated as a rigid body,<sup>25</sup> which ensures a larger time unit to be used, to be precise, 10 fs. The EMD simulations based on Green-Kubo formula and Einstein relation are run for 100 ns, while the total time for one NEMD case equals 5 ns. 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 whose isothermal relaxation time is selected as 0.1 ps. To calculate the rotational diffusion coefficient, the nanotube is confined only to rotate on the  $x$ - $y$  plane.

For convenience, a sample case should be defined here: The capped nanotube has the armchair (5, 5) configuration with a diameter  $d$  of 0.688 nm and length  $L$  of 6.80 nm. The density  $\rho$  and temperature  $T$  of fluid argon are 1763 kg/m<sup>3</sup> and 300 K, respectively. The simulation domain has a size of  $L_x \times L_y \times L_z = 10.6 \times 10.6 \times 10.6$  nm<sup>3</sup>. In the rest of the paper, the factors listed above will be changed in turn resulting in multiple sets of data of the nanotube's rotational diffusion coefficients.

#### IV. RESULTS AND DISCUSSION

Figure 2 is the time-varying MSDs for the sample case along with the cases of changing the length  $L$ , diameter  $d$ ,

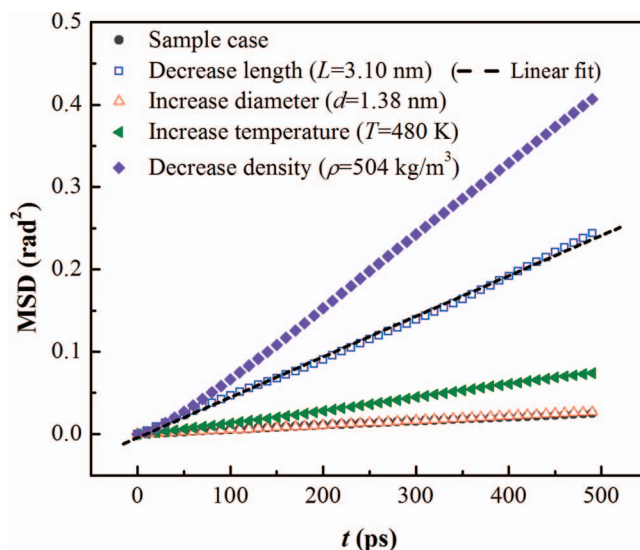


FIG. 2. Angular MSDs for the sample case and the cases of changing various factors including length  $L$  and diameter  $d$  of the nanotube, temperature  $T$ , and density  $\rho$  of the fluid argon.

temperature  $T$ , and density  $\rho$ , respectively. Diffusive behavior can be observed for all the selected cases and the curves can be fit by linear functions. As can be seen, the change of a particular factor brings about different slopes of the MSDs.  $D_r$  can be extracted therefrom based on Einstein relation of Eq. (4) with the uncertainties obtained from the standard error of the linear fitting. Figure 3 is the time-varying AACF and the convergence of the calculated rotational diffusion coefficient in terms of the AACF (the inset) for the sample case at equilibrium. The AACF rapidly converges to around zero from the initial value. The integration of the AACF, which is  $D_r$  according to the Green-Kubo formula of Eq. (6), increases rapidly at first, and then gradually becomes stable. The uncertainty is calculated by estimating the fluctuation of the plateau of the integrated curve.

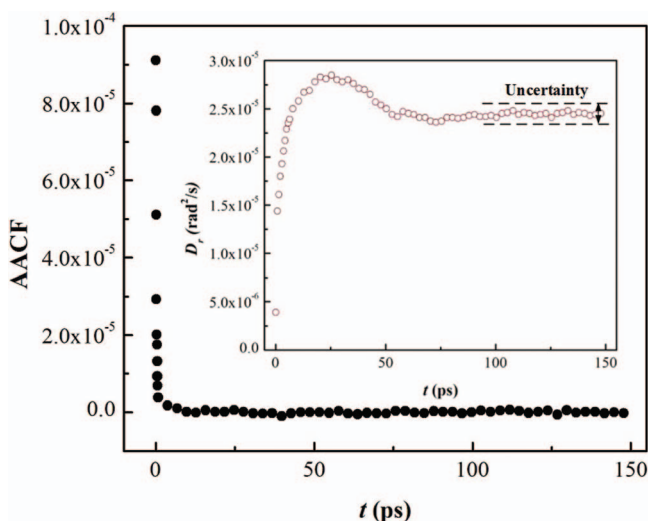


FIG. 3. Time-varying angular autocorrelation function (AACF) for the sample case. The inset shows the converging rotational diffusion coefficient  $D_r$  found by integrating AACF.

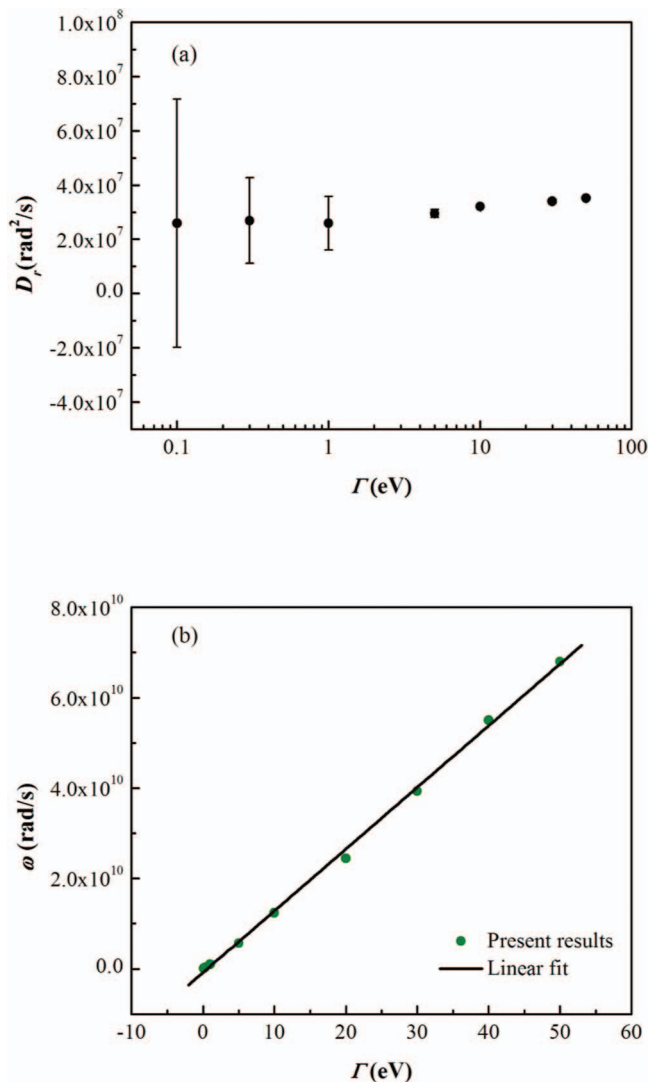


FIG. 4. (a) Dependence of the rotational diffusion coefficient  $D_r$  on the external torque; (b) dependence of the angular velocity on the external torque along with the linear fitting.

Figure 4(a) exhibits  $D_r$ , for the sample case, calculated from each imposed external torque  $\Gamma$ , respectively. From the statistical error of the  $D_r$  fluctuation along with time, the uncertainty of the results can be acquired. As can be observed, an almost monotonic decrease of the relative uncertainty exists with changing  $\Gamma$ . And for the first two points, the large error bars indicate the unreliability of the results at small torque. However, with the increasing of  $\Gamma$ ,  $D_r$  has a slight increase. This may come from that the fast rotation disturbs the local fluid flow around the nanotube, causing the friction coefficient (inverse of the mobility  $\mu_r$ ) to decrease at the same time. Thus, to get more reliable results, the linear response theory should be utilized. Figure 4(b) shows change of angular velocity  $\omega$  along with the imposed external torque  $\Gamma$ . The slope of the curve can be obtained via the linear fitting and by submitting the slope into Eq. (11),  $D_r$  is extracted. For the rest of the simulations,  $D_r$  will be calculated this way and the uncertainties are also gathered from standard error of the linear fitting.

Multiple groups of data are calculated by the above three MD methods, along with the uncertainty of each data point,

summarized in Table I. Theoretical values are also included for comparison, which are calculated from the equation of Tirado *et al.*,<sup>9</sup>

$$D_r = \frac{3k_B T (\ln p + \delta)}{\pi \eta L^3}, \quad (13)$$

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

The symbols of Eq. (13) share the same meaning as in Secs. II and III, along with  $\eta$  denoting the three-dimensional shear viscosity. First, increasing the length  $L$  or diameter  $d$  of the nanotube will both bring about a smaller  $D_r$ . Mathematically, by assuming  $L > d$ , at fixed diameter of  $d = 0.688$  nm, the change of  $D_r$  along with the length is strictly monotonic via differentiating Eq. (13) by  $L$ , and the case of changing  $d$  at fixed  $L = 6.80$  nm is the same. Second, increasing temperature  $T$  or decreasing density  $\rho$  of the fluid argon results in the increase of  $D_r$ . These two factors will cause viscosity of the fluid to change at the same time. From Eq. (13), at the fixed  $\rho = 1763$  kg/m<sup>3</sup>, viscosity decreases due to the increase of  $T$ , which both lead to a larger  $D_r$ . Although density is not explicitly involved in Eq. (13), its influence on  $D_r$  can be reflected by the viscosity as well. The maximum relative difference between the three MD results is within 15%, indicating a good agreement between the methods and accuracy of the simulations. And qualitatively, the simulation results show the same trend as the theoretical predictions, as illustrated by the above analyses. However, compared with Eq. (13), the relative differences approximately lie in the range of 45%–65%, which is a great deviation. This implies that there exist other unrevealed factors, such as inertia of the rotating nanotube and velocity slip,<sup>13</sup> affecting the rotational diffusion coefficient.

Accompanying with the above simulation results, three points are worthy to be discussed. First, the CNT is selected as a representative of various nanorods studied in experiments. The experimental results of nickel nanorods in colloidal dispersions<sup>11</sup> also show that values of  $D_r$  are systematically reduced by a factor of  $\sim 2$  as compared to the Tirado model, in perfect coincidence with our observations. Although the authors put forward three possible qualitative reasons to account for the discrepancy, it still suggests that we must be cautious when using the literature theory in practical situations. Second, the flexibility of CNT is not considered in the present simulations. This simplification is quite reasonable when our aim is to develop simulation methods to calculate  $D_r$  and compare it with the theoretical work of a rigid rod model. However, we need to note that the flexibility may affect the results in several ways. For instance, the energy used for the CNT to rotate may be partly stored as deformation energy, resulting in the decrease of  $D_r$ ; the deformation will also cause the decrease in the apparent length and then  $D_r$  may be increased. This is a non-trivial issue, worthy to be addressed in the future work. Third, the rotational diffusion coefficient is related to the rotary mobility by Eq. (11). Then, the current work can be further used as a guide to control the orientation of nanoparticles or macromolecules, which would find potential applications in the design of high mechanical,<sup>3</sup> electrical,<sup>4</sup> optical,<sup>26</sup> or thermal<sup>27,28</sup> performance systems.

TABLE I. Rotational diffusion coefficients  $D_r$  obtained from MD results and from Eq. (13).

$L$ (nm)	$d$ (nm)	$T$ (K)	$\rho$ (kg/m <sup>3</sup> )	$\eta$ (cP)	$D_{r\_Eq. (13)}$ ( $\times 10^7$ rad <sup>2</sup> /s)	$D_{r\_Einstein}$ ( $\times 10^7$ rad <sup>2</sup> /s)	$D_{r\_GK}$ ( $\times 10^7$ rad <sup>2</sup> /s)	$D_{r\_ES}$ ( $\times 10^7$ rad <sup>2</sup> /s)	MRD1 (%) <sup>a</sup>	MRD2 (%) <sup>b</sup>
3.10	0.688	300	1763	0.49	55.20	24.61 $\pm$ 0.19	21.01 $\pm$ 1.09	23.72 $\pm$ 0.97	14.6	62.0
5.61	0.688	300	1763	0.49	12.1	5.10 $\pm$ 0.02	4.83 $\pm$ 0.19	5.28 $\pm$ 0.17	7.7	60.0
6.80	0.688	300	1763	0.49	7.27	2.52 $\pm$ 0.01	2.63 $\pm$ 0.15	2.94 $\pm$ 0.14	13.8	65.7
8.10	0.688	300	1763	0.49	4.59	1.84 $\pm$ 0.01	1.61 $\pm$ 0.03	1.79 $\pm$ 0.12	11.1	64.9
6.80	0.688	300	1763	0.49	7.27	2.52 $\pm$ 0.01	2.63 $\pm$ 0.15	2.94 $\pm$ 0.14	13.8	65.7
6.80	1.10	300	1763	0.49	6.02	2.58 $\pm$ 0.02	2.60 $\pm$ 0.18	2.59 $\pm$ 0.09	1.0	57.1
6.80	1.38	300	1763	0.49	5.46	2.43 $\pm$ 0.01	2.49 $\pm$ 0.15	2.47 $\pm$ 0.13	2.4	54.8
6.80	1.65	300	1763	0.49	5.02	1.91 $\pm$ 0.01	1.89 $\pm$ 0.15	2.14 $\pm$ 0.08	9.5	62.4
6.80	1.93	300	1763	0.49	4.68	1.86 $\pm$ 0.01	1.88 $\pm$ 0.06	2.09 $\pm$ 0.08	9.5	60.3
6.80	0.688	240	1763	0.61	5.38	1.95 $\pm$ 0.01	1.73 $\pm$ 0.09	2.01 $\pm$ 0.07	15.0	67.8
6.80	0.688	300	1763	0.49	7.27	2.52 $\pm$ 0.01	2.63 $\pm$ 0.15	2.94 $\pm$ 0.14	13.8	65.7
6.80	0.688	480	1763	0.34	13.81	7.50 $\pm$ 0.03	6.40 $\pm$ 0.36	6.76 $\pm$ 0.25	14.7	53.6
6.80	0.688	720	1763	0.32	21.92	11.53 $\pm$ 0.01	10.42 $\pm$ 0.56	11.50 $\pm$ 0.32	9.6	52.5
6.80	0.688	300	168	0.026	115.8	61.03 $\pm$ 0.05	68.52 $\pm$ 4.32	61.69 $\pm$ 2.59	10.9	47.0
6.80	0.688	300	504	0.036	81.74	43.14 $\pm$ 0.03	42.55 $\pm$ 2.13	37.09 $\pm$ 1.70	14.2	54.7
6.80	0.688	300	840	0.054	47.26	26.91 $\pm$ 0.01	24.35 $\pm$ 0.83	23.72 $\pm$ 0.33	11.9	49.8
6.80	0.688	300	1344	0.16	18.22	11.18 $\pm$ 0.02	10.38 $\pm$ 0.54	9.37 $\pm$ 0.21	15.3	48.5
6.80	0.688	300	1763	0.49	7.27	2.52 $\pm$ 0.01	2.63 $\pm$ 0.15	2.94 $\pm$ 0.14	13.8	65.7

<sup>a</sup>MRD1: Max relative difference between the three MD results.<sup>b</sup>MRD2: Max relative difference between MD results and predictions of Eq. (13).

## V. CONCLUSIONS

Herein, we have successfully put forward three molecular dynamics simulation methods, i.e., two EMD methods, which are Einstein relation and Green-Kubo formula, one NEMD method, which is Einstein–Smoluchowski relation, and utilized them to calculate the rotational diffusion coefficient of a carbon nanotube in fluid. Multiple sets of data points are obtained by the above three methods and the maximum relative difference is well within 15%, which indicates the accuracy of the simulations. Remarkable deviation exists between MD results and the theoretical values and the maximum relative difference locates within 45%–65%. Some unrevealed factors should account for the inadequacy of the theory applied to practical cases. As characterization of the rotational diffusion of a single particle has become a key step to analyze many complex nanoparticle-diffusion processes, this work will provide an opportunity to gain an insight into this problem through molecular dynamics calculations. Not only can these methods work well for the present most simplified situations, but also can it be applied to other more realistic circumstances.

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