Diffusion of nano-rods

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Abstract. Diffusion behaviors in nano-rods suspension in the fluid are investigated by Stochastic Eulerian Lagrangian Methods, where the degrees of freedom for coarse-grained microstructure are coupled with continuum stochastic field to capture both the relaxation of hydrodynamic modes and thermal fluctuations. The diffusion characteristics of a single rod and multi-rods are examined with hydrodynamic interaction in three dimensions. For a single rod, the mean square displacement is verified by comparing with prior experimental results. The effects of hydrodynamic interactions on the translational and rotational diffusivity with different aspect ratios are represented by velocity auto-correlation function and the orientational auto-correlation functions. For multi-rods cases, we obtained their diffusion in the ballistic and the short-time regime. The comparison between the SELM and the Langevin method confirms the hydrodynamic effect.

1. Introduction
There are rapidly growing interests in studying diffusions of micro- and nano-sized particles in solvent as they can be used to describe a rich variety of biological processes[1], and physical phenomena [2]. Besides, anisotropic particles are popular ingredients for ceramic paints and photonic materials [3]. However, the rheology and the structure arrangement of anisotropic rods differ from spherical particles [4]. In order to develop more efficient manipulation techniques for the nano-particles, it is highly desirable to get better understanding of how the nanoparticles, especially anisotropic particles, move in fluid.

The diffusion of micro- and nano-sized particles can be attributed to Brownian motion, a random motion of particles due to the collisions with fluid molecules. For spherical particles, Bian et. al. [5] summarizes its motion characteristics and corresponding theories, and introduces the experimental or simulation methods. For anisotropic particles, Han et. al. [6] studied the Brownian motion of isolated ellipsoidal particles in water confined in two dimensional channel by using digital video microscopy. Zheng and Han[7] observed the long-time and short-time diffusion coefficients of translational and rotational motions as functions of the ellipsoidal particle concentration also in two dimensions. By using a single gold nano-rod, Mehdi et. al. [8] probes nano scale rheology and anisotropic diffusion. For suspensions of anisotropic particles at high volume fraction, diffusion behaviors become even more complex and the structure patterns of the particles appear [9].

Various numerical methods are developed and applied to study the characteristics of anisotropic particles, such as molecular dynamics [10], and particle dynamics [11]. Sara and Emmanuel [12] used dynamic Monte Carlo to simulate the characteristic of disk-shaped particles. Delong et. al. [13] investigated the Brownian dynamics for three types of the rigid bodies under gravity by overdamped Langevin models.
In this paper, we investigate the diffusion characteristics of a single rod and multi-rods under hydrodynamic interaction in three dimensions. The paper is organized as follows. The “Model and simulation” section introduces the Stochastic Eulerian Lagrangian Methods (SELM)[14], and setup of the numerical model. Then, we study translational and rotational dynamics of single rod and multi-rods. The results of the simulation are validated and discussed in the “Results and discussion” section. In the last section, we will summarize the article and give an outlook for future study.

2. Model and simulation

The SELM is a numerical framework developed to simulate microstructures and fluid interactions subject to thermal fluctuations. The interaction between microstructures and fluid can be obtained by use of the interpolation technique based on the immersed boundary method [15]. And the particle-particle interactions are calculated by the LAMMPS [16], a molecular dynamics software. The motion of particles in an incompressible fluid flow satisfies the following equations:

\[\nabla \cdot \mathbf{u} = 0.\]

\[\rho \frac{\partial \mathbf{u}}{\partial t} = \mu \nabla^2 \mathbf{u} + \nabla \cdot \mathbf{p} + f_{thm}.\]

\[m \frac{d\mathbf{v}}{dt} = -\gamma (\mathbf{v} - \Gamma \mathbf{u}) - \nabla \Phi(\mathbf{X}) + F_{thm}.\]

\[\frac{d\mathbf{X}}{dt} = \mathbf{v}.\]

where \(X\) represent the microstructure, its mass and velocity denotes by \(m, v\). The fluid velocity denotes by \(\mathbf{u}, \rho\) and \(\mu\) denote fluid density and velocity. \(\gamma\) represent the operator of microstructure drag exerted by the fluid and \(\Phi\) is the potential energy associate with the microstructure. \(-\gamma (\mathbf{v} - \Gamma \mathbf{u})\) is the drag force on the microstructures and \(\nabla \Phi(\mathbf{X})\) is the drag force acting on the fluid. And the two coupling operators \(\Gamma, \Lambda\) which should be adjoint, i.e. \(\Gamma = \Lambda^∗\) [17]. We will use the specific coupling operators

\[\Gamma \mathbf{u} = \int_{\Omega} \eta (\mathbf{y} - \mathbf{X}(t) \mathbf{u}(\mathbf{y}, t))d\mathbf{y}.\]

\[\Lambda \mathbf{F} = \eta(\mathbf{x} - \mathbf{X}(t))\mathbf{F}.\]

The Peskin \(\delta\)-Function given in [18] is chosen as the kernel function \(\eta(\mathbf{x})\). \(\Omega\) is the surface of the microstructure. And the thermal forces \(f_{thm}\) and \(F_{thm}\) are introduced by the \(\delta\)-correlation Gaussian random fields with mean zero and covariances,

\[\langle f_{thm}(s) f_{thm}(t) \rangle^γ = -2k_B T(\mu \Delta - \Lambda \gamma T) \delta(t - s).\]

\[\langle F_{thm}(s) F_{thm}(t) \rangle^γ = 2k_B T \gamma \delta(t - s).\]

\[\langle f_{thm}(s) F_{thm}(t) \rangle^γ = -2k_B T \Lambda \gamma \delta(t - s).\]

\(k_B\) and \(T\) denote Boltzmann constant and temperature, respectively.

The rod model we used here is spheres connected by harmonic bonds, and the distance between the center of the spheres are set as \(\sigma\) (diameter of the particle). For a rod with aspect ratio \(a\) would have \(p\) spheres connected by harmonic bonds whose energy are set to be \(1000 k_B T\). The sphere mass is 315 \(amu\), and the temperature \(T = 298.15\ K\) with the Boltzmann constant is 0.008314 \((amu \cdot nm^2)/ps^2 \cdot K)\). The fluid viscosity \(\mu\) is set to be 602.814 \(amu\cdotnl/(ps\cdotnm)\) for water in \(T = 298.15K\). The computational domain for bulk is taken to be \(300 \times 300 \times 300\ nm^3\) resolved with a grid having cell with the mesh-width \(10\ nm\). To prevent the particles from overlapping, we adopt Weeks-Chandler-Andersen (WCA) potential as the potential between spheres:

\[\Phi(r) = \begin{cases} 4\varepsilon((\sigma/r)^{12} - (\sigma/r)^6) + \varepsilon, & r < r_c, \\ 0, & r > r_c. \end{cases}\]

where the energy \(\varepsilon = k_B T\) and \(\sigma\) and \(r\) are taken as \(10\ nm\) and \(9.5\ nm\).

3. Results and discussion

The mean squared displacements (MSDs) of a diffusion sphere can be characterized by three regimes, a ballistic regime (~\(t^0\)) when \(t < \tau_n\), a short-time diffusion (~\(t\)) when \(t \leq \tau_B\) and long-time diffusion (~\(t\)) when \(t > \tau_B\). The characteristic time scales are defined: \(\tau_n = m/6\pi\mu \sigma^2\) \((\sigma:\text{the radius of the sphere and } m:\text{the mass})\), \(\tau_B = \sigma^2/D_0\) \((D_0:\text{the diffusion coefficient of a sphere in the bulk})\).
3.1. Single rod diffusions

In the lab frame, the centroid location $X$ of the linked spheres, the polar angle $\theta$, and the azimuthal orientation angle $\phi$ give the locations of the rod. However, for rod diffusions, it would be more interest to report dynamical quantities in its body frame, relative to its unit vector $d$, which is defined as the rod long-axis direction.

For time $t = t_i$, we define the lab frame displacement $\Delta X_i = \Delta x_i \cdot e_x + \Delta y_i \cdot e_y + \Delta z_i \cdot e_z$, and the body frame displacement $\Delta r_i = \Delta r_i \cdot e_r + \Delta \theta_i \cdot e_\theta + \Delta \phi_i \cdot e_\phi$, where $e_r$, $e_\theta$, $e_\phi$ are the spherical coordinate unit vectors. And the relation between the two frames’ displacements satisfies

$$\begin{bmatrix} \Delta r_i \\ \Delta \theta_i \\ \Delta \phi_i \end{bmatrix} = \begin{bmatrix} \sin \theta_i \cos \phi_i & \sin \theta_i \sin \phi_i & \cos \theta_i \\ -\sin \phi_i & \cos \phi_i & 0 \\ -\sin \theta_i \cos \phi_i & -\sin \theta_i \sin \phi_i & \cos \theta_i \end{bmatrix} \begin{bmatrix} \Delta x_i \\ \Delta y_i \\ \Delta z_i \end{bmatrix}. \tag{11}$$

Now we can compute the $\text{MSD}_s \left< \Delta r^2 \right> \parallel$, the parallel to the unit vector $d$, and $\text{MSD}_s \left< \Delta r^2 \right> \perp$, perpendicular to the unit vector $d$. The angle brackets are ensemble averages over the initial time. In the body frame:

$$\left< \Delta r_i^2 (t) \right> = \left< \left( \sum_{i=0}^{t+1} \Delta r_i \right)^2 \right>. \tag{12}$$

$$\left< \Delta r_i^2 (t) \right> = \left< \left( \sum_{i=0}^{t+1} \Delta \theta_i \right)^2 \right> + \left< \left( \sum_{i=0}^{t+1} \Delta \phi_i \right)^2 \right>. \tag{13}$$

The long-time parallel and the perpendicular $\text{MSD}_s$ for a rod with aspect ratios $p = 3$ are given in figure 1, where $p$ is defined as $L/d$, $L$ and $d$ are the length and diameter of the rod. The results are comparable to the empirical results [19], which are given:

$$D_\parallel = \frac{k_B T \ln(2p) - 0.5}{2\pi \eta L}, \tag{14}$$

$$D_\perp = \frac{k_B T \ln(2p) + 0.5}{4\pi \eta L}. \tag{15}$$

![Figure 1. Comparison of the translation MSDs between numerical and empirical values for the rod with aspect ratio equals 3 in parallel and perpendicular directions.](image)

Next, we take the displacement of the centroid of the rods with different aspect ratios, $p = 3, 4, 5, 6$, to compute their velocity $V$ in the lab frame. Then we can get the transitional velocity auto-correlation function defined by $VACF(t) = \left< V(t) \cdot V(0) \right>$. The results are plotted in figure 2(left). We can see that the $VACFs$ decays faster with the increase of the rod length, because the longer the rod is, the more drag force is exerted by the fluid.
Figure 2. VACF(t) (left) and OACF(t) (right) of the rods with different aspect ratios, p = 3, 4, 5, 6.

The rotational motion of the rods are studied by calculating the orientational auto-correlation functions (OACF), which is defined as $OACF(t) = \langle d(t) \cdot d(0) \rangle$, where $d$ is the unit vector of the rod. The autocorrelation function decays exponentially with time, and it is in proportional to the rotational diffusion coefficient $D_{\theta}$

$OACF(t) = \langle d(t) \cdot d(0) \rangle = \exp \left( -2D_{\theta}t \right)$. \hspace{1cm} (16)

The $OACFs$ for the rods with different aspect ratios $p$, is plotted in figure 2(right). The solid lines indicate the empirical values which can be obtained by [19]

$D_{\theta} = \frac{3k_B(T \ln(2p) - 0.5)}{\pi n L^3}$. \hspace{1cm} (17)

It reveals that a shorter rod changes its direction faster than a longer one.

From figure 2, it’s not difficult to find that with the increase of the rod length, VACFs decay faster, while OACFs decay slower. Since $\tau_n \ll \tau_B$ we can see that for a given rod, VACF decays much faster than OACF which mean the VACF decays to zero within a short time period, which the orientation direction of the rod barely changed.

3.2. Multi-rods diffusions

The characteristics of rod diffusion are not only affected by its length but also influenced by the volume fraction of the rods in the solvent, where the volume fraction $k$ is defined as

$k = \frac{4\pi \rho n a^3}{3V}$. \hspace{1cm} (18)

$N$ is total rod number in suspensions and $V$ is the volume of the simulation domain. We only study the rods with the aspect ratio $p = 3$ in this section.

Figure 3. The MSDs of the Ballistic and the Short-time diffusion regime with different volume fractions $k$.
We take the displacement of the centroid of the rods with different volume fractions to compute their MSDs in the lab frame. We find that the rod diffusion can be divided into the ballistic regime and the short-time regime, which is similar to the sphere diffusion[5]. From the figure 3(left), we can see that in the ballistic regime, MSDs are not sensitive to the volume fraction, since the motion of the rod cannot "feel" the other rods around it in this time scale. When the time increase, MSDs in higher volume fractions grow slower because of the increase of the neighbouring rods. From the figure 3(right), we can see that MSDs can be fitted as straight lines at ballistic regime and short-time regime, in which two solid lines represent different volume fractions. It can be seen that the slopes of straight lines with different volume fractions can be distinguished over a long period of time.

![Figure 4. Comparison of diffusion coefficients with different volume fractions with or without hydrodynamic interaction.](image)

We compared our numerical results of normalized diffusion coefficients as function of volume fraction with the Langevin simulation in figure 4. The translational diffusion coefficients $D_t$ is calculated as $(D_{\parallel} + 2D_{\perp})/3$ and normalized by $D_t^0$ which is the single rod diffusion coefficient. With the increase of the volume fraction, the hydrodynamic effect would greatly depress the diffusion of the rods. The difference between the SELM and the Langevin model is that the Langevin model cannot capture hydrodynamic effect.

4. Conclusions

We have studied the Brownian motions of a single rod, multi-rods diffusion by using the SELM, which takes into account both hydrodynamic effects and thermal fluctuations. We have verified the characteristics of single rod diffusions by showing the diffusion coefficient in parallel direction is larger than it in perpendicular direction. For a single rod cases, the shorter the rod the less drag force exerted from the fluid, which can be concluded by the VACFs trend. In addition, its orientation barely changes in the period of the VACFs decaying to zero. For multi-rods cases, the diffusion coefficients are not sensitive to the change of the volume fractions in the ballistic regime while they can be distinguished in the short-time regime. By comparison the SELM and the Langevin model we find the hydrodynamic effect plays an important role in the calculation of rod diffusion especially in high volume fraction.

Furthermore, the SELM can be extended to study the diffusion properties of active particles, and haematite particles in the magnetic field.

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