Translational and Rotational Diffusion of Ellipsoidal Particles

July 3, 2016

Abstract

We Studied Diffusion of asymmetric particles such as ellipsoidal particles in 2 dimensions. Our simulation is based on Fokker-Planck equation by using Dynamic Monte Carlo method. Our work is useful for understanding of transportation and motion of anisotropic macromolecules in membranes and also for random walk modeling micro swimmers such as E.coli. By applying a directional memory to the system, we investigated nonlinear behaviors of Mean Square Displacements (MSD) at short time and long time and crossover from anisotropic diffusion to the isotropic diffusion.

Diffusion of Ellipsoidal Particles

An ellipsoidal particle is shown in figure 1 with diameters length a and b. $\mathbf{r}$ vector is position of center of mass (CM) in Lab frame (inertial frame). θ is angle between body frame and Lab frame and the particle can rotates around it's CM point that body frame indicates the particle-fixed coordinate system.

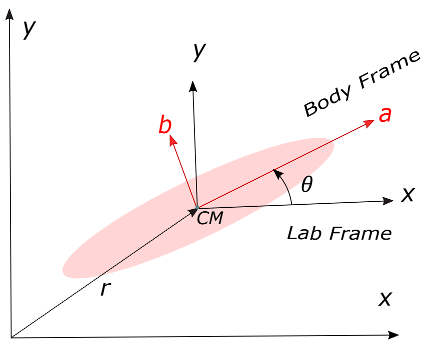

Figure 1: An ellipsoidal particle in laboratory frame and body frame.

The general form of diffusion tensor is

$$\mathbf{D} = \begin{pmatrix} D_{\parallel} & D_{\parallel}^{\perp} & D_{c}^{\parallel} \\ D_{\parallel}^{\perp} & D_{\perp} & D_{c}^{\perp} \\ D_{c}^{\parallel} & D_{c}^{\perp} & D_{R} \end{pmatrix}, \tag{1}$$

where $D_{\parallel}$ and $D_{\perp}$ are parallel and perpendicular diffusion coefficients, D_c is the rotational-translational coupling vector and D_R the rotational diffusion coefficient of particle. This tensor is diffusion matrix for the CM.

Friction tensor is determined for ellipsoidal particles [Perrin] by parameters

$$f_1 = 16\pi\eta \frac{a^2 - b^2}{(2a^2 - b^2)S - 2a}, \tag{2}$$

$$f_2 = 32\pi\eta \frac{a^2 - b^2}{(2a^2 - 3b^2)S + 2a}, \tag{3}$$

where f_1 and f_2 are translational friction coefficients along a and b axis that η is viscosity of fluid. Rotational friction coefficient perpendicular to main axis is

$$C_1 = \frac{32\pi}{3}\eta \frac{(a^2 - b^2)b^2}{2a - b^2 S}, \tag{4}$$

$$\tag{5}$$

that S for $a > b$

$$S = \frac{2}{\sqrt{a^2 - b^2}} log \frac{a + \sqrt{a^2 - b^2}}{b}, \tag{6}$$

and S for $b > a$ is

$$S = \frac{2}{\sqrt{b^2 - a^2}} arctan \frac{\sqrt{b^2 - a^2}}{a}. \tag{7}$$

Diffusion tensor can be calculated by using Einstein relation: $\frac{k_B T}{f_\alpha}$ for α either a or b, where k_B is Boltzmanns constant and T is the temperature. Also, rotational diffusion is characterized in two dimensions by a single diffusion coefficient D_R.

Finally diffusion tensor for ellipsoidal particles in body frame given by

$$\mathbf{D} = \left(\begin{array}{ccc} D_{\parallel} & 0 & 0 \\ 0 & D_{\perp} & 0 \\ 0 & 0 & D_R \end{array} \right). \tag{8}$$

By using rotational tensor $\mathbf{R}$, diffusion coefficient can be calculated in Lab frame:

$$\mathbf{D}_{lab}^{CM} = \mathbf{R}^{\dagger}\mathbf{D}^{CM}\mathbf{R} = \left(\begin{array}{ccc} \alpha & \delta & 0 \\ \delta & \beta & 0 \\ 0 & 0 & D_R \end{array} \right), \tag{9}$$

so we have

$$\alpha = D_{\parallel} cos^2\theta + D_{\perp} sin^2\theta, \tag{10}$$

$$\beta = D_{\parallel} sin^2\theta + D_{\perp} cos^2\theta, \tag{11}$$

$$\delta = -D_{\parallel} sin\theta cos\theta + D_{\perp} sin\theta cos\theta, \tag{12}$$

(13)

that α and β are diffusion coefficient along x and y axis in Lab frame and δ is diffusion coefficient along x axis and y axis simultaneously .

Fokker-Planck equation

We aim to write continuity equation for simulation of ellipsoidal particles. Continuity equation is an equation that describes the transport of some quantity. We can write down this equation for probability of density function p and particles flux $\mathbf{J}$.

The continuity equation given by

$$\partial_t p(r,\theta,t) \quad + \quad \nabla.\mathbf{J} = 0, \tag{14}$$

(15)

that ∇ is $(\frac{\partial p}{\partial x}, \frac{\partial p}{\partial y}, \frac{\partial p}{\partial \theta})$, $\mathbf{r}$ is position of center of mass and θ orientation of particle about CM. We can use Fick's law to solve this equation in body frame

$$\mathbf{J} \quad = \quad -\mathbf{D}.\nabla p, \tag{16}$$

where D is diffusion matrix for CM in Lab frame.

By using $\mathbf{D}^{CM}$, continuity equation leads to

$$\partial_t p = \alpha \frac{\partial^2 p}{\partial x^2} + \beta \frac{\partial^2 p}{\partial y^2} + D_R \frac{\partial^2 p}{\partial \theta^2} \tag{17}$$

It is not considered moving along x axis and y axis simultaneously ($\delta = 0$). Fokker-Planck equation is an equation that describes time revolution of probability density function. For modeling of random walk, discretization of differential equation can be used, thus

$$\begin{aligned} p(i,j,k)^{m+1} &= p^m_{i,j,k}[-\frac{2\alpha}{\Delta x^2} - \frac{2\beta}{\Delta y^2} - \frac{2D_R}{\Delta \theta^2} + \frac{1}{\Delta t}]\Delta t \\ &+ p^m_{i+1,j,k}[\frac{\alpha}{\Delta x^2}]\Delta t + p^m_{i-1,j,k}[\frac{\alpha}{\Delta x^2}]\Delta t \\ &+ p^m_{i,j+1,k}[\frac{\beta}{\Delta y^2}]\Delta t + p^m_{i,j-1,k}[\frac{\beta}{\Delta y^2}]\Delta t \\ &+ p^m_{i,j,k+1}[\frac{D_R}{\Delta \theta^2}]\Delta t + p^m_{i,j,k-1}[\frac{D_R}{\Delta \theta^2}]\Delta t. \end{aligned} \tag{18}$$

that i and j are position coordinates, k orientation component and $t = m\Delta t$. To determine probability, we can use coefficients of sentences of above equation, for this purpose we consider sum of probability equal to 1 :

$$\begin{aligned} &[\frac{D_\parallel}{\Delta x^2}]\Delta t && \text{right jumping} \\ &[\frac{D_\parallel}{\Delta x^2}]\Delta t && \text{left jumping} \\ &[\frac{D_\perp}{\Delta y^2}]\Delta t && \text{up jumping} \\ &[\frac{D_\perp}{\Delta y^2}]\Delta t && \text{fall down} \\ &[\frac{D_R}{\Delta \theta^2}]\Delta t && \text{clockwise-counterclockwise} \end{aligned} \tag{19}$$

There is no symmetry in two directions (x, y). Difference of probability [along x and y axis] made anisotropic diffusion. Rotational part is independent of translational part because there is no coupling between translational and rotational diffusion (coupling components of diffusion matrix (D^c) are zero).

We can use 2 method for simulation of these type of particles:
First method: Translational and rotational diffusion are decoupled and rotational part is completely random so particles just choose between 4 translational motions in Lab frame.
Second method: Particles can choose between 6 motions (4 probability of translations and 2 rotations);

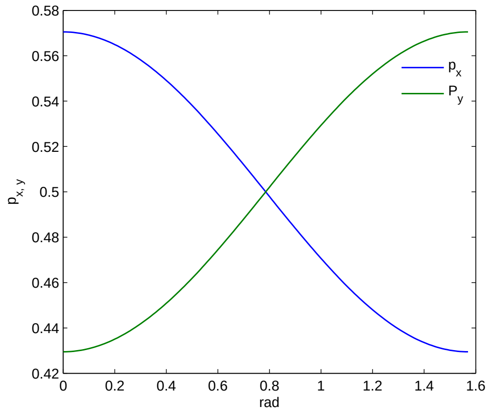

Figure 2: probability of jumping along x and y axis versus rad.

In figure 2, it can be seen that the sum of probabilities along x and y axis is equal 1. In fact, $\frac{\alpha}{\alpha+\beta}$ is probability of x axis and $\frac{\beta}{\alpha+\beta}$ probability of y axis. Diffusion coefficients change with rad. Probability of a axis at the first moment is more than b axis and at 45° are equal.

Result

Our simulation is based on Fokker-Planck theory by using Dynamic Monte Carlo method. We consider both translational and rotational random jiggling. An ellipsoidal particle is used with dimensions $a = 5.9\mu m$, $b = 1.3\mu m$ that for 200K ensemble of particles are averaged. Figures 3 and 4 representive trajectories of CM for an ellipsoidal particle at different time scales that can be seen there is no coupling between translational and rotational diffusion in long time.

Relation of MSD for rotational Brownian motion is linear $\langle [\Delta\theta(t)]^2 \rangle$ with $D_R = 0.003\frac{rad^2}{s}$ for first method and $D_R = 0.005\frac{rad^2}{s}$ for second method. The results of the two methods are similar approximately, therefore I just mention to the sencond approach. Measuring MSDs can be shown features of Brownian motion (figure 5). To recognize these features we consider initial angle $\theta_0 = 0$. In fact by consideration of this condition, we apply a

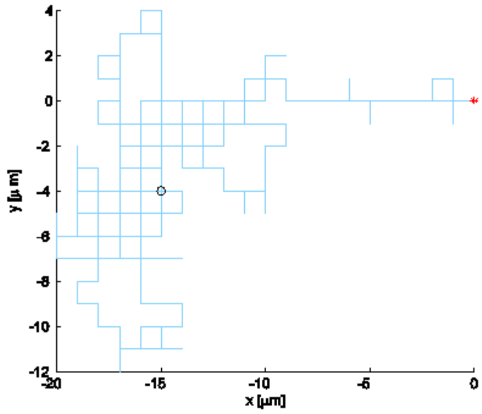

Figure 3: An ellipsoidal particle in 2 Dimensions with 100 steps.

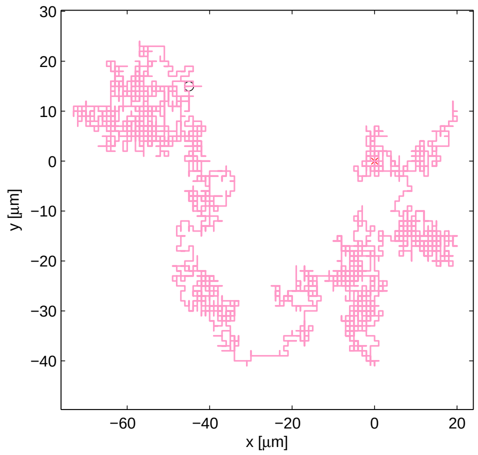

Figure 4: An ellipsoidal particle in 2 Dimensions with 1000 steps.

directional memory to the system. So there is a significant difference between short time and long time diffusion. Before propertise time τ_θ, MSDs are nonlinear and after crossover time, MSDs grow linearly with t. Slope of both lines is indentical, because at long time the directional memory is wash out.

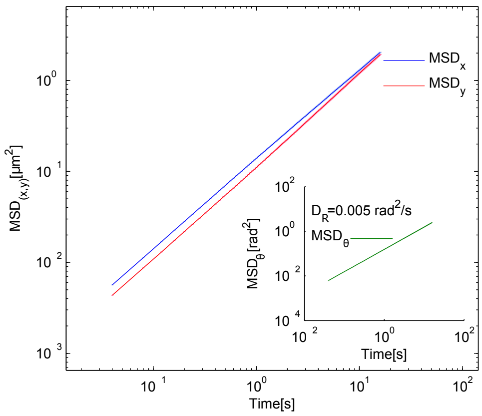

Figure 5: Mean Square Displacement for 200K of ellipsoidal particle with dimensions $a = 5.9\mu m$ and $b = 1.3\mu m$ along x and y axis and θ.

To show how the slope of curves (MSDs) change with time, we calculate slope of lines that give diffusion coefficients (D) (figure 6). We are looking for crossover from short time anistropic to the long time isotropic diffusion in Lab frame.

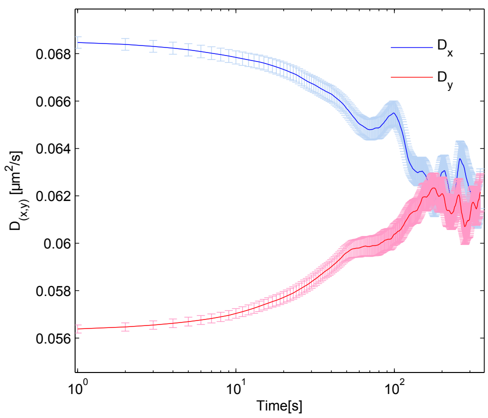

Figure 6: Diffusion coefficients for 200K of ellipsoidal particle with dimensions $a = 5.9\mu m$ and $b = 1.3\mu m$ along x and y axis.

D_x and D_y change from D_a and D_b at the first moment to the mean value for diffusion coefficient at long time. It can be seen that before τ_θ slope of line change smoothly but after that D_x fall and D_y rise rapidly to the mean value. At the long time ellipsoidal particle behaves like a spherical particle with diffusion coefficient $\bar{D}$.

References

[1] F. Perrin, *"Mouvement brownian d'un ellipsoide(I). Dispersion dielectrique pour des molécules ellipsoidales"*, J. Phys. Radium, **V** 497 (1934).
[2] Y. Han, A. M. Alsayed, M. Nobili, J. Zhang, T. C. Lubensky, A. G. Yodh, *"Brownian Motion of an Ellipsoid"*, SCIENCE **314**, 626-630 (2006).
[3] H. Risken, *"The Fokker-Planck Equation"*, Springer-Verlag , Berlin, (1989).