Diffusion of an asymmetric particle in ageing viscoelastic medium

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Abstract: We have simulated the diffusion process for the spherical Brownian particle in a viscous and viscoelastic medium. We started with checking the usefulness of the commonly available Pseudo-random number generator(PNRG) for Brownian dynamics simulation. Then we attempted the simulation task by the 'fixed time step' method(Wiener process). To overcome the limitations of the Wiener process, we moved to the 'variable time step' method, which is ideal for capturing the essential features of diffusion-related experiments that last for several weeks. For simulation purposes, we are modelling the viscoelastic medium used in our experiments as per the Maxwell-Voigt model. We obtained the simulation results for the diffusive nature of spherical particles in both isotropic and anisotropic viscoelastic mediums. We also have assembled a dual trap set-up which is crucial for moving to the experimental part of the project. Currently, we are synthesizing a micron size ellipsoidal particle of the desired dimension in our lab, then we will start tracking those particles under a microscope to study diffusion.

Brownian motion is essential for studying the diffusion of a single particle. It is the random motion of particles suspended in a fluid. In terms of particle dynamics, the Brownian particle experiences different forces, such as stochastic force due to its collision with fluid particles, Stokes drag due to its movement through fluid, and maybe some external force that the particle can experience if such a potential field is present there.

Spherical particle in a viscous medium: In this case, we need to solve the following Langevin equation for the system:-

$$m \cdot \left(\frac{d^2x}{dt^2}\right) = -\gamma \cdot \left(\frac{d\ x}{dt}\right) + \xi(t)\ ;\ \gamma = 6\pi\eta a \quad (1)$$

Here, ηrepresents the viscosity of the medium, 'a' for the radius of spherical particle and $\xi(t)$ corresponds for stochastic force.

Under suitable approximation, we get the following necessary features for step length(Δx) of Brownian dynamics:- (i) random,(ii) uncorrelated, and (iii) Δx should come from a Gaussian distribution with zero mean and standard deviation, which depends on Diffusion coefficient D as given by Einstein-stokes equations-

$$D = k_b T/(6\pi\eta a) \quad (2)$$

Since we are using a pseudo-random number generator(PRNG), hence it is important to check its usefulness. We checked for its randomness and correlation as well as its power to generate Gaussian distributed numbers.

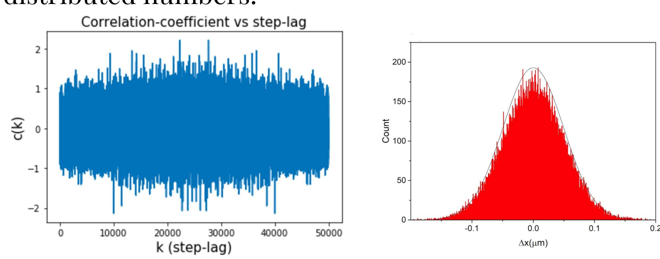

Fig. 1. [left] Autocorrelation of a Brownian trajectory showing the non-existence of correlation. [Right]Histogram of Brownian step sizes is almost Gaussian, making PRNG of *Python* useful for our simulation.

We used the Wiener process to create trajectories from computer-generated random displacement. Then we proceed to calculate the Mean square displacement (MSD) from those trajectories. From the graph of MSD with a time lag, we finally calculate the diffusion coefficient.

Wiener Process (based on a fixed time step) cannot capture a wide dynamic range of many Diffusion related experiments, which can take several days to complete. Therefore in our group, we are employing the 'variable time step' method for constructing the Brownian trajectory. This is capable of taking observation time as small as $10^{-8}s$ to large time interval of $10^{4}s$ in a single trajectory. Hence it is ideal for capturing diffusion in a system which takes several days to equilibrate.

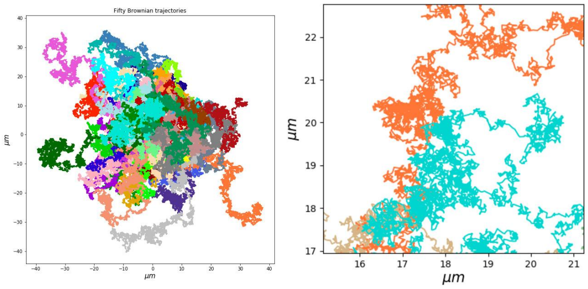

Fig. 2. [Left] Brownian trajectories for 50 particles simulated for 1000 seconds. We are taking 2 μm sized particles in water as a medium($\eta = 10^{-3} Pa \cdot s$ at T = 300 K). [Right] Zooming into trajectories clearly reveals the random walk steps taken by them.

We employ this method of simulation for 2 μm sized spherical particles suspended in water at room temperature. From trajectory, we calculated MSD using binning of all possible time-lag(τ) values in a sufficient number of bins. The Slope of MSD vs time-lag(τ) quantifies the diffusion process.

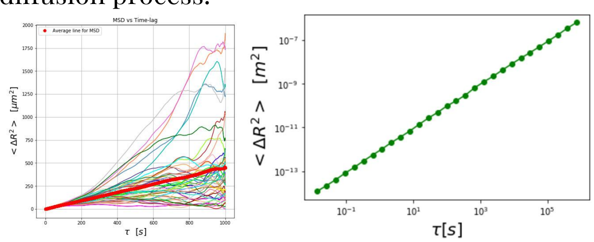

Fig. 3. [Left] Mean squared displacement (MSD) of 50 trajectories using fixed time step method with a total time of particle motion t=1000 s (or 17 minutes). [Right] MSD for a single trajectory using variable time step method with a total time of particle motion t=$10^{7}s$(~3 months). Both curves fit to $<\Delta R^2>(\tau) = 4D\tau$.

Spherical particle in viscoelastic medium:

In this case, we keep the geometry of the particle to be same as in the previous case. Our medium is viscoelastic, so we do not observe linear dependence of MSD on time lag (τ) like we get in the case of the viscous medium. Therefore we need to model our medium such that it possesses the essential feature of commonly used viscoelastic soft materials. Maxwell-Voigt model(MVM) is a successful candidate for modelling our fluid.

In this model, we get a viscously dominated response at a very high frequency ($1/\tau$) and slow viscous relaxation at a very low frequency. The maxwell part of the MVM has a low-frequency viscosity (η), and the characteristic low-frequency maxwell relaxation time $\lambda = \eta/G_p$. The Voigt part has a high-frequency viscosity η_s, and the characteristic high-frequency crossover time between elastic and viscous behavior $\lambda_B = \eta_s/G_p$. In terms of particle dynamics, a particle in the MVM is similar to a harmonically bounded Brownian particle(say, HBBP). In the HBBP, the particle feels such that it is in a medium with the viscosity of η_s and an external harmonic potential with elastic coefficient '$-k\Delta x$' where $k=6\pi a G_p$. Meanwhile, the centre of this potential well(say, HB) is also performing Brownian motion. Hence, we basically need to solve the Langevin equation for this system:-

$$m \cdot \left(\frac{d^2x}{dt^2}\right) = -\gamma \cdot \left(\frac{dx}{dt}\right) - k \cdot x + \xi(t) \qquad \textbf{(3)}$$

Under suitable approximation we get Green function, $G(x, x_0, t)$, which gives the probability of finding a particle at x position after a time interval t for the initial condition of x=x_0.

$$G(x, x_0, t) = [2\pi B(t)]^{-1/2} exp\{-\frac{[x-A(t)]^2}{2B(t)}\} \qquad (4)$$

Where, $A(t) = x_0 exp(-t/\lambda_B)$ (5)

$$B(t) = \frac{k_B T}{k}[1 - exp(-2t/\lambda_B)] \qquad (6)$$

Green function, $G(x, x_0, t)$ is Gaussian centered around A(t) and variance of B(t).

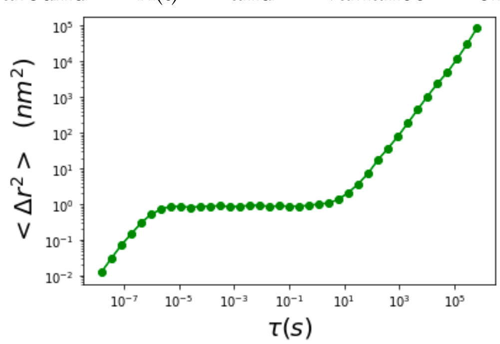

Fig. 4. MSD for a spherical particle in an isotropic viscoelastic medium modelled by the Maxwell-Voigt model. The above simulation curve is fitted to, $< \Delta r^2 > (\tau) = 4D\tau + r_0^2[1 - exp(-\tau/\lambda_B)]$ which is a good agreement with theory.

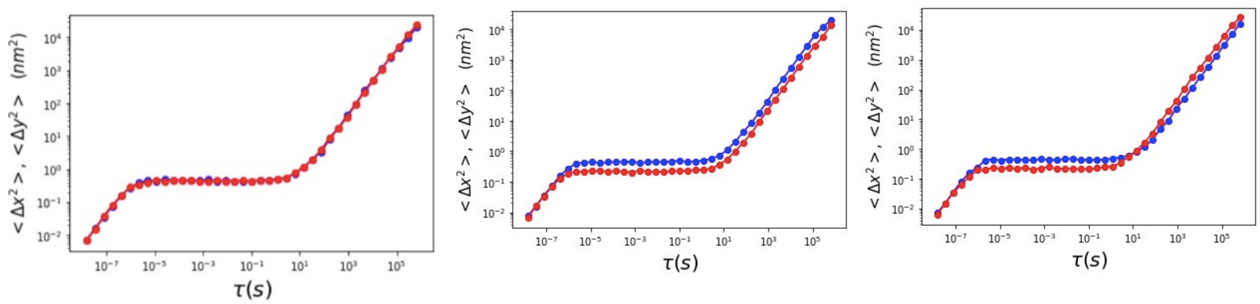

Fig. 5. MSD along the x(blue) and y(red) axis for an isotropic and two possible anisotropic cases. [Left] when the medium is isotropic, or its viscous and elastic parameters are equal in all directions, then the MSD curve for both axis overlaps as per our expectation. [Middle] In this case, elasticity and viscosity coefficient(η) along the y-axis are double those of x axis.[Right] In this case, the elastic coefficient along y is double that of the x-axis, but the viscosity coefficient(η) is half along the y-axis than that of the x-axis.

Dual trap setup: We often need an Optical trap to accompany experimental conditions for tracking Brownian particles in a viscous and viscoelastic medium. We invested a considerable amount of time in assembling a dual optical trap, which gives freedom to control a trapped particle in 3D space. It is attached to a digital microscope and computer, enabling us to collect more precise data easily.

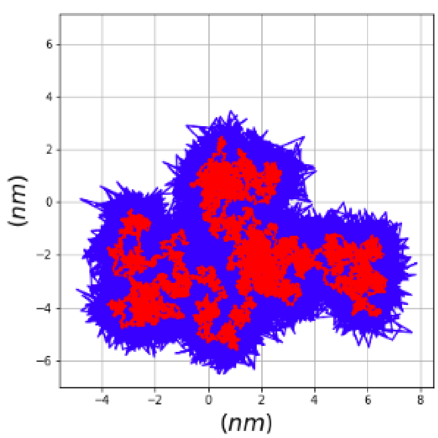

Fig.6. One of the sub-trajectory of a spherical particle in a viscoelastic medium. The blue line shows particle diffusion. The red curve refers to the diffusion of the centre of the sub-trajectory as a whole in the medium.

Particle preparation: Currently, we are putting our efforts into making probe particles for doing experiments. We are using micron-sized Polymethyl methacrylate (PMMA) beads and attach them to a thin film of polyvinyl alcohol. Then we immerse the film in a temperature-regulated oil bath and carefully stretch the film to get an ellipsoidal particle of desired shapes.

Results: Calculating the Diffusion coefficient from the simulation of spherical particles in the viscous medium using fixed and variable time step methods gives a deviation of at most 5% from the theoretical value.

References:

1. A. Einstein, R. Furth, and A. D. Cowper, Investigations on the Theory of the Brownian Movement (Methuen & Co. Ltd., London, 1926).
2. Manas khan and Thomas G. Mason, PHYSICAL REVIEW E 89, 042309 (2014)
3. Ho, C.C., Keller, A., Odell, J.A. et al. Colloid Polym Sci (1993) 271: 469.

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