Brownian Dynamics

José Morán

ME 8111 – Multiphase System Analysis

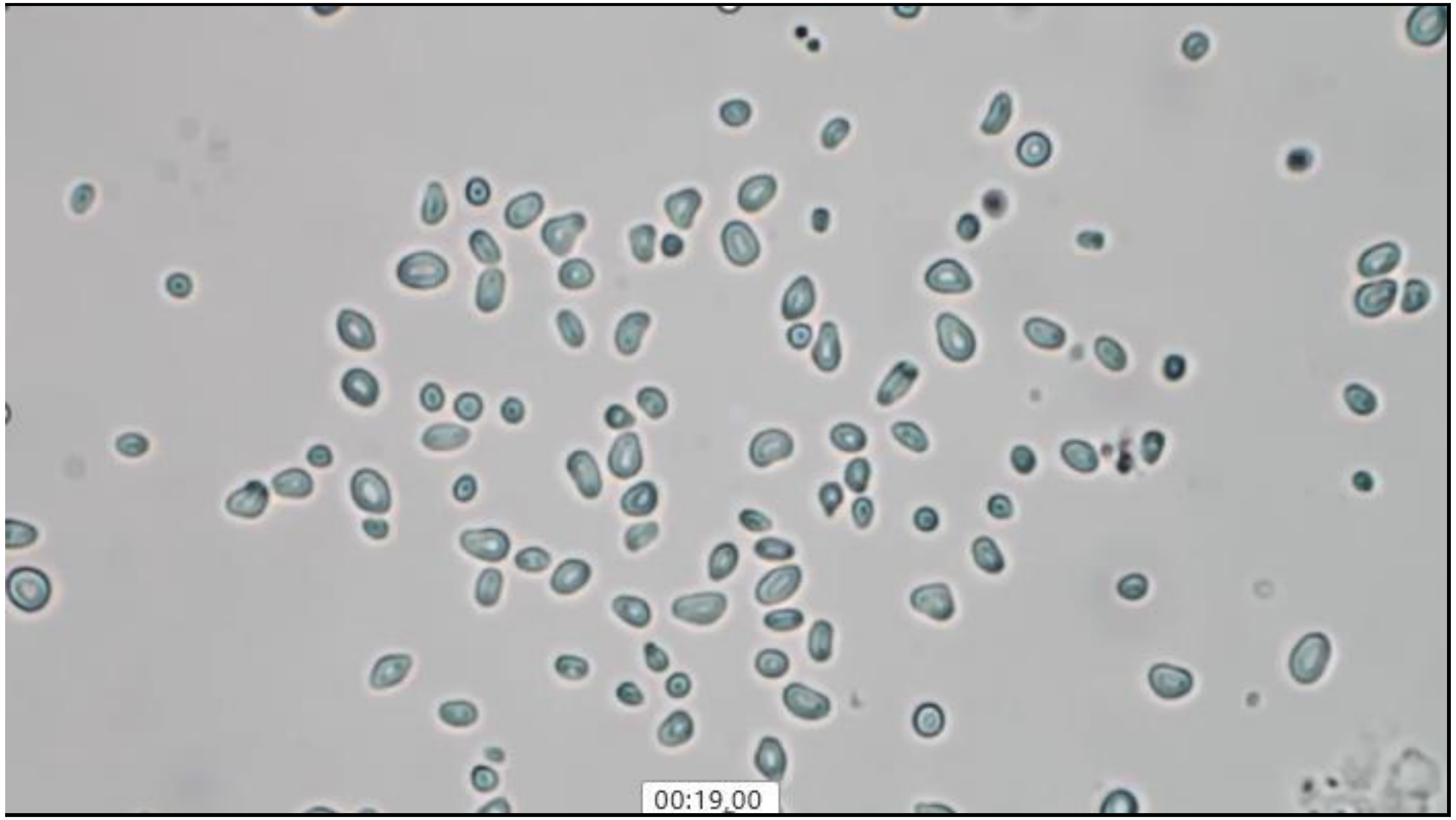
02/27/2024

Agenda

1. Brownian motion
2. The Langevin equation
3. Computational implementation
4. Examples

1. Brownian motion

https://www.youtube.com/watch?v=R5t-oA796to

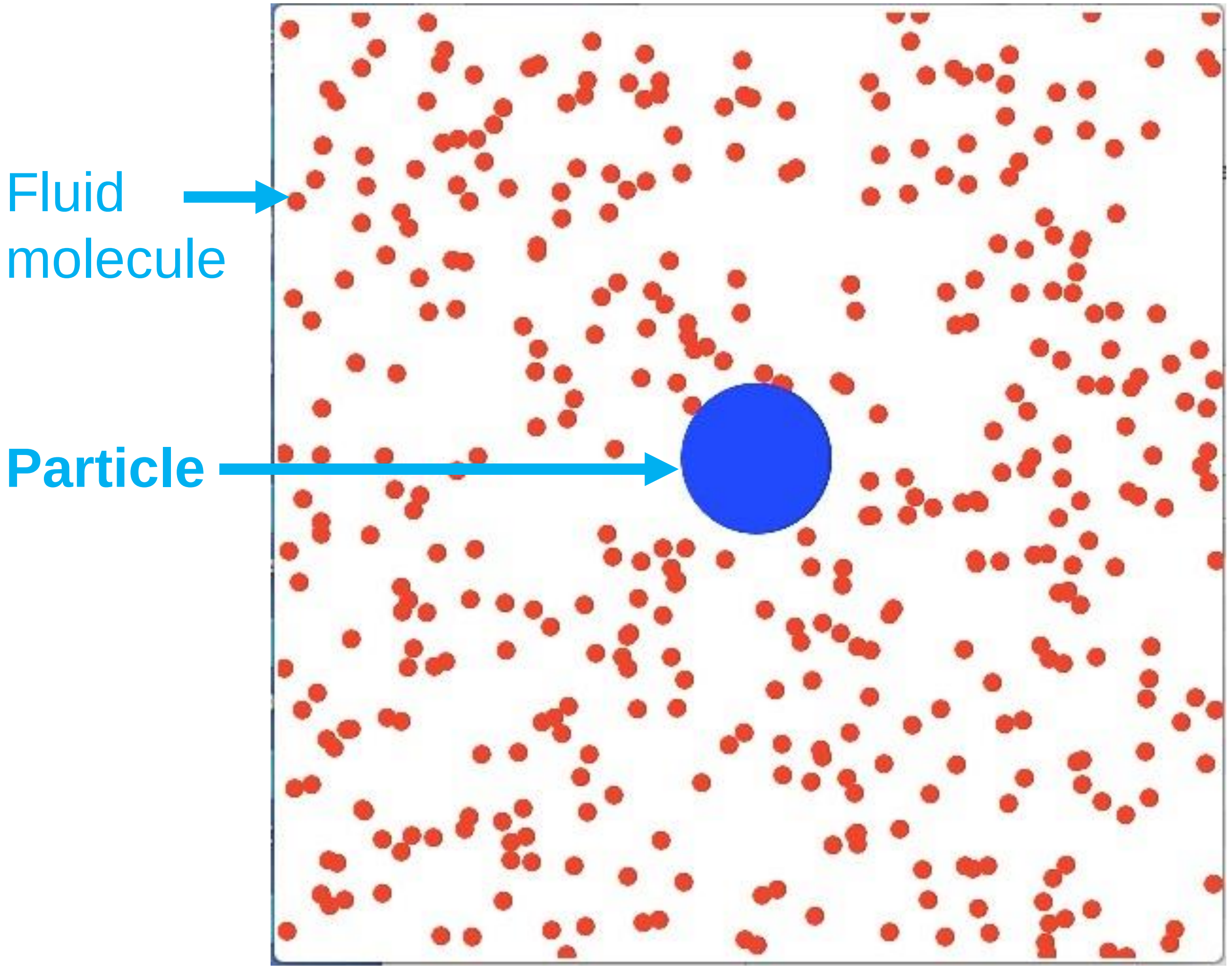


Video 1: Microscope observation of pollen grains in water

Scottish botanist Robert Brown (1773 - 1858)

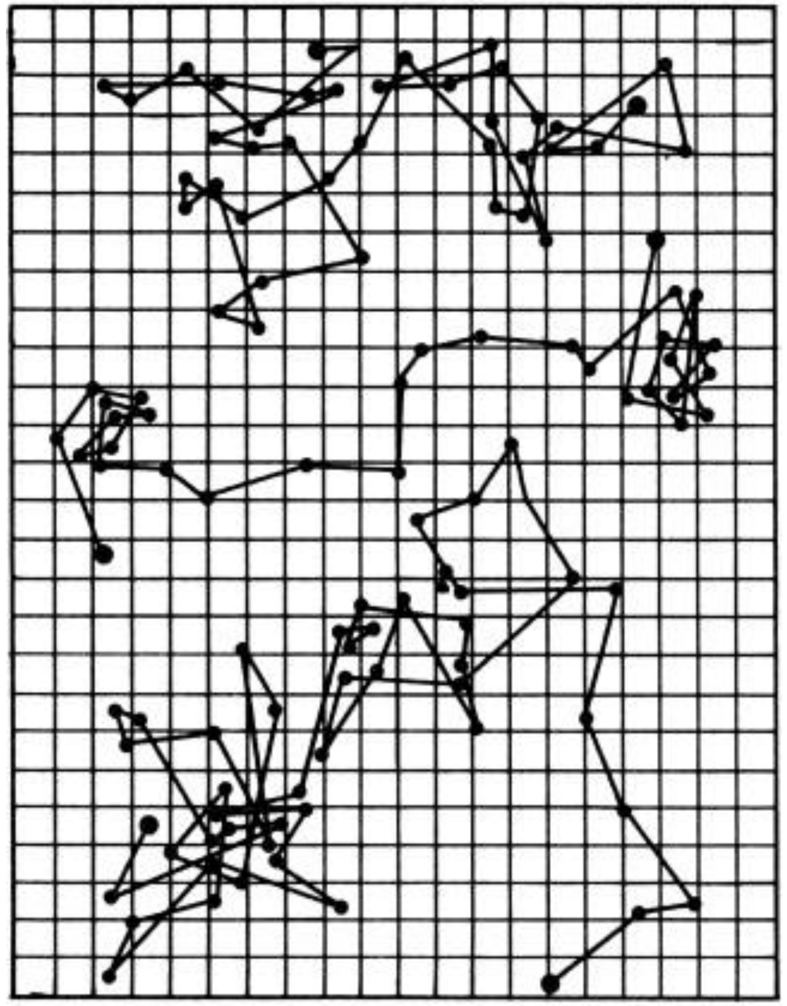
"While examining the form of these particles immersed in water, I observed many of them very evidently in motion. These motions were such as to satisfy me... that they arose neither from currents in the fluid, nor from its gradual evaporation, but belonged to the particle itself" (from p.8, D.K.C. MacDonald, 1962).

1. Brownian motion



- Random collisions between the particle and the gas molecules.
- How to model the particle-fluid interaction force?
- What is the characteristic distance and time for the particle movement?
- What trajectory will the particle follow?

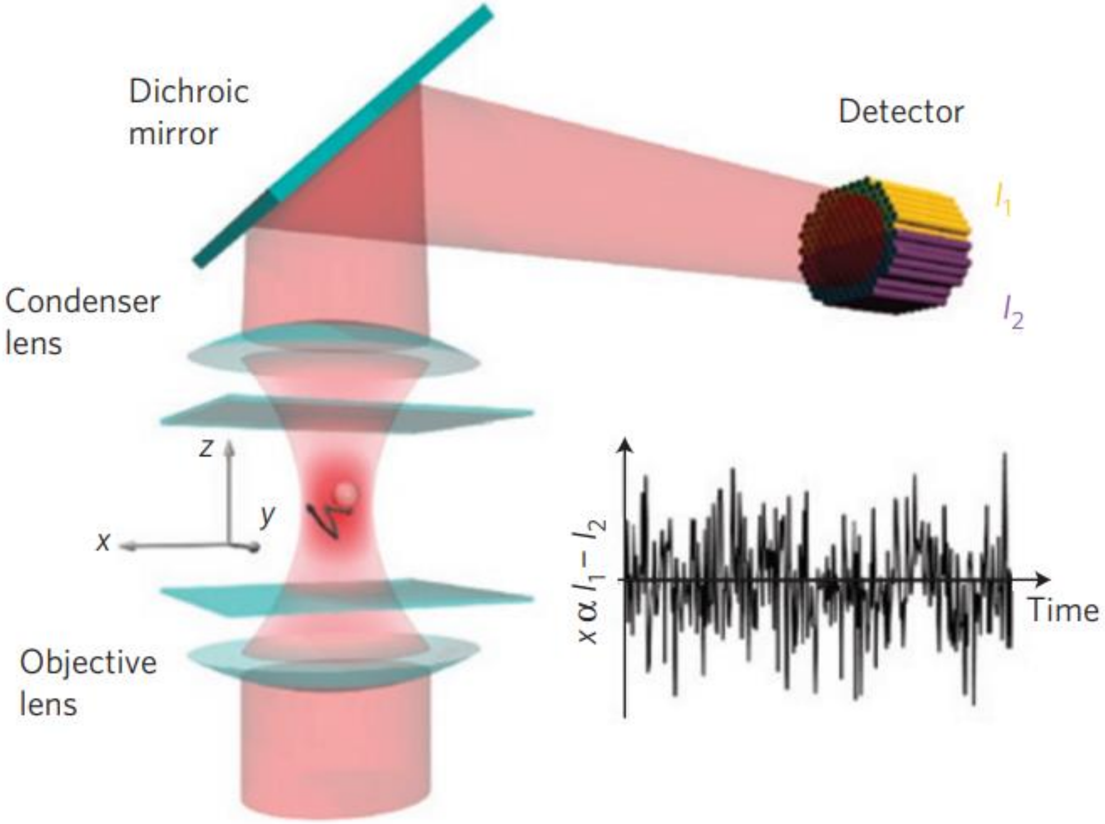
1. Brownian motion

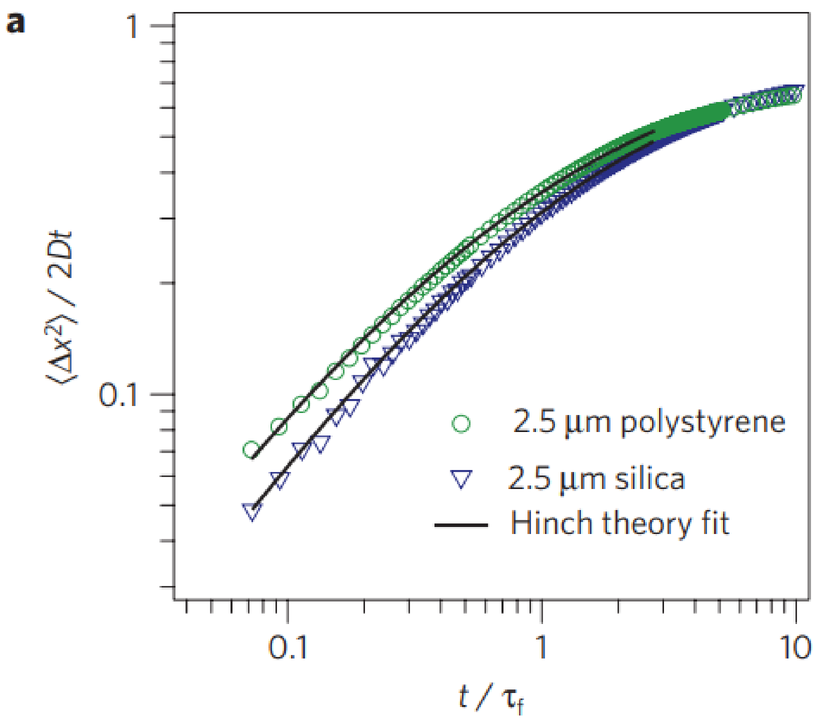


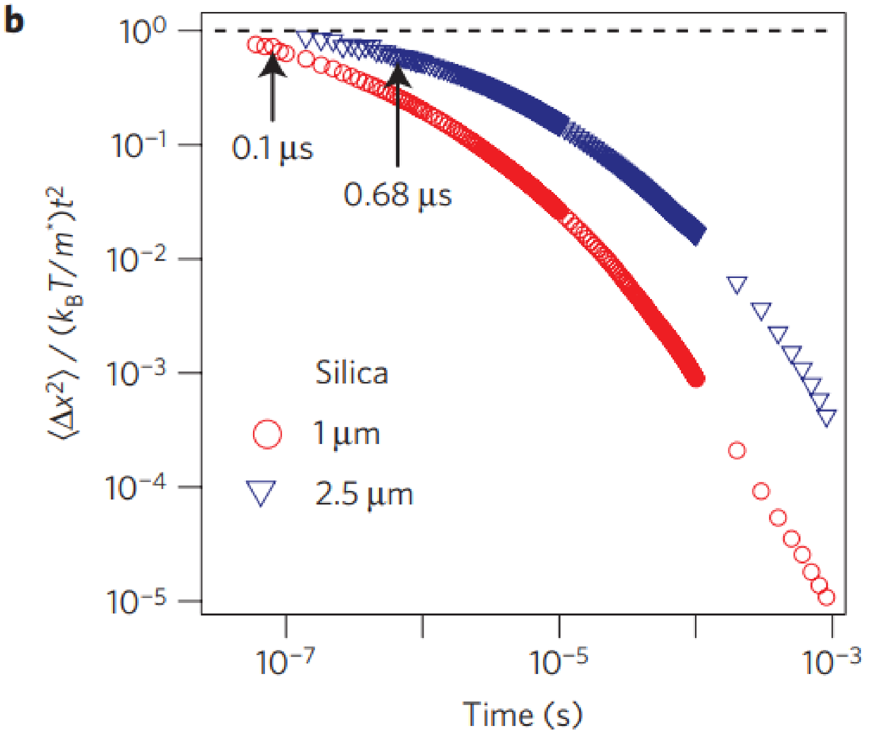
Displacement of three particles: using a camera lucida Perrin marked the successive positions of each particle at regular intervals of time (30 s), before drawing straight lines to join the dots (Perrin, 1909, p. 81)

Perrin, J. (1909). Mouvement brownien et réalité moléculaire. In *Annales de Chimie et de Physique* (Vol. 18, pp. 1-114).

1. Brownian motion





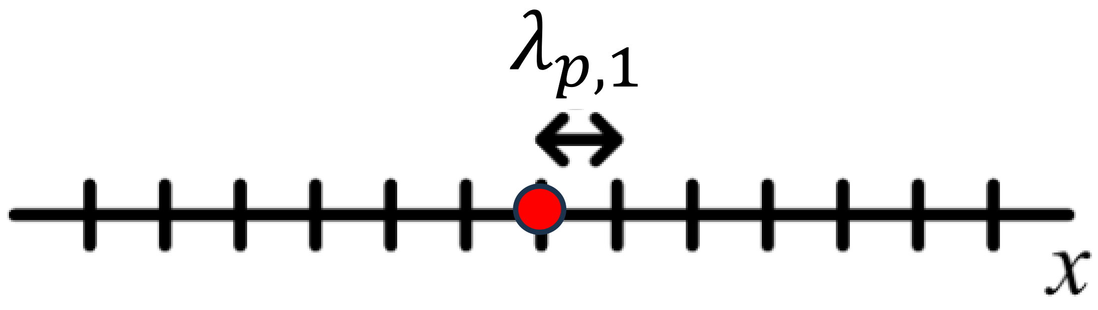


Nowadays we can use **optical tweezers** to precisely measure the displacement of particles in a fluid in the time-scale of the particle momentum relaxation

At timescales once deemed immeasurably small by Einstein, the random movement of Brownian particles in a liquid is expected to be replaced by ballistic motion.

Huang, R., Chavez, I., Taute, K. M., Lukić, B., Jeney, S., Raizen, M. G., & Florin, E. L. (2011). Direct observation of the full transition from ballistic to diffusive Brownian motion in a liquid. *Nature Physics*, *7*(7), 576-580.

1. Brownian motion



The particle moves in 1d with constant jumps of length $\lambda_{p,1}$ during a time step Δt. The probability to move right or left is the same. Where will the particle be after n time steps?

Bernoulli process:

$$f(Y=y) = q^y(1-q)^{1-y} = \frac{1}{2}, y \in \{0,1\}$$

Binomial process: $\longrightarrow$ Move $+k\lambda_{p,1}$ after n trials

$$f(K=k) = \binom{n}{k} q^k(1-q)^{n-k}$$
$$= \frac{n!}{k!(n-k)!}\left(\frac{1}{2}\right)^n, \qquad k \in [0,n]$$

Continuous form (Gaussian):

$$f(\Delta x_{n\Delta t}) = \frac{1}{\sqrt{2\pi n\lambda_{p,1}^2}} e^{-\Delta x_{n\Delta t}^2/\left(2n\lambda_{p,1}^2\right)}, n \to \infty$$

Move Δx after n time steps

Morán, J., Yon, J., & Poux, A. (2020). Monte Carlo aggregation code (MCAC) Part 1: Fundamentals. *Journal of colloid and interface science*, *569*, 184-194.

1. Brownian motion

Now, considering the time as a continuous variable $t = n\Delta t$ and introducing the so-called diffusion coefficient,

$$D = \frac{\lambda_p^2}{2\Delta t}$$

Then,

$$f(\Delta x) = \frac{1}{\sqrt{4\pi D t}} e^{-\Delta x^2/(4Dt)}, \qquad t \gg \Delta t \longrightarrow E[\Delta x^2] = 2Dt$$

As initially observed by A. Einstein (1905)

Extending this analysis to 3d we conclude: $E[\Delta r^2] = 6Dt$

2. The Langevin equation

Momentum relaxation time:

Momentum conservation

$$m\frac{dv}{dt} = -fv$$

Solution for the velocity ($v(t=0) = v_0$)

$$v(t) = v_0 \exp(-t/(m/f))$$

$\tau = m/f$: Momentum relaxation time

TABLE 5.1 Relaxation Time for Standard Density Particles at Standard Conditions

Particle Diameter (μm)	Relaxation Time (s)
0.01	7.0×10^{-9}
0.1	9.0×10^{-8}
1.0	3.5×10^{-6}
10.0	3.1×10^{-4}
100	3.1×10^{-2}

In this time-scale the particle will have a characteristic displacement of the order (persistent distance),

$$\lambda_p = \tau c \longrightarrow$$

$c = \sqrt{\frac{8k_BT}{\pi m}}$: Average Maxwellian velocity (k_B is the Boltzmann constant and T the particle temperature)

2. The Langevin equation

The model proposed by Paul Langevin,

$$m\frac{dv}{dt} = -fv + F_{\mathrm{B}}$$

Particle-fluid interaction split into a systematic and fluctuating part

Introducing a random, called Brownian, force F_B,

$$\langle F_{\mathrm{B}} \rangle = 0$$

$$\langle F_{\mathrm{B}}(t) F_{\mathrm{B}}(t') \rangle = 6 f k_{\mathrm{B}} T \delta(t - t')$$

The strength of the fluctuation depends on the friction coefficient (f) and the system temperature (T)

Important assumption: The Brownian force F_B fluctuates much faster than the particle velocity v

2. The Langevin equation

Chandrasekhar analytical solution:

$$\Psi(v; v_0) = \left[\frac{m}{2\pi k_B T(1 - e^{-2\beta t})}\right]^{3/2} \exp[-m|v - v_0 e^{-\beta t}|^2/(2k_B T(1 - e^{-2\beta t}))]$$

$$\Psi(r, v) = \frac{1}{2\pi\sigma_v\sigma_r\sqrt{1-\rho^2}} \exp\left(-\frac{\left(\frac{v-\bar{v}}{\sigma_v}\right)^2 - \frac{2\rho(v-\bar{v})(r-\bar{r})}{\sigma_v\sigma_r} + \left(\frac{r-\bar{r}}{\sigma_r}\right)^2}{2(1-\rho^2)}\right)$$

$$\bar{v} = v_0 e^{-\beta t} + \frac{F_{\text{ext}}}{m\beta}(1 - e^{-\beta t})$$

$$\bar{r} = r_0 + \frac{v_0}{\beta}(1 - e^{-\beta t}) + \frac{F_{\text{ext}}}{m\beta}(t - \frac{1}{\beta}(1 - e^{-\beta t}))$$

$$\sigma_v^2 = \frac{k_B T}{m}(1 - e^{-2\beta t})$$

$$\sigma_r^2 = \frac{k_B T}{m\beta^2}(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t})$$

$$\rho^2 = \frac{(1 - e^{-\beta t})^4}{(1 - e^{-2\beta t})(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t})}$$

Chandrasekhar, S. (1943). Stochastic problems in physics and astronomy. *Reviews of modern physics*, *15*(1), 1.

2. The Langevin equation

$$m\frac{dv}{dt} = -fv + F_B$$

Ermak and Buckholz algorithm-1:

$$v(t+\Delta t) = V + v(t)e^{-\beta\Delta t}$$

$$\underbrace{r(t+\Delta t) = R + r(t) + \frac{v(t)}{\beta}(1 - e^{-\beta\Delta t})}$$

Sampled from the bivariate probability density function $\Psi(r, v)$ obtained by Chandrasekhar

Stochastic fluctuation in velocity,

$$V = \begin{pmatrix} V_x \\ V_y \\ V_z \end{pmatrix} = \sqrt{G}\begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \end{pmatrix}$$

Stochastic fluctuation in position,

$$R = \begin{pmatrix} R_x \\ R_y \\ R_z \end{pmatrix} = \frac{H}{\sqrt{G}}\begin{pmatrix} Y_1 \\ Y_2 \\ Y_3 \end{pmatrix} + \sqrt{I - \frac{H^2}{G}}\begin{pmatrix} Y_4 \\ Y_5 \\ Y_6 \end{pmatrix}$$

$$G = \sigma_v^2; \quad I = \sigma_r^2; \quad H = \sigma_{vr} = \frac{k_B T}{m\beta}\left(1 - e^{-\beta\Delta t}\right)^2$$

$$Y_i \sim \text{Gaussian}(0, 1)$$

Ermak, D. L., & Buckholz, H. (1980). Numerical integration of the Langevin equation: Monte Carlo simulation. *Journal of Computational Physics*, *35*(2), 169-182.

2. The Langevin equation

Ermak and Buckholz algorithm-2:

$$m\frac{d\boldsymbol{v}}{dt} = -f_t\boldsymbol{v} + \boldsymbol{F}_B + \boldsymbol{F}_e$$

$$\boldsymbol{v}(t+\Delta t) = \boldsymbol{v}(t)e^{-\alpha\Delta t} + \frac{\boldsymbol{F}_e}{m\alpha}\left(1 - e^{-\alpha\Delta t}\right) + \boldsymbol{B}_1$$

$$\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \frac{1}{\alpha}\left(\boldsymbol{v}(t+\Delta t) + \boldsymbol{v}(t) - \frac{2\boldsymbol{F}_e}{m\alpha}\right)\frac{1 - e^{-\alpha\Delta t}}{1 + e^{-\alpha\Delta t}} + \frac{\boldsymbol{F}_e\Delta t}{m\alpha} + \boldsymbol{B}_2$$

$$\langle B_1\rangle = \langle B_2\rangle = 0$$

$$\langle B_1^2\rangle = \frac{3k_BT}{m}\left(1 - e^{-2\alpha\Delta t}\right)$$

$$\langle B_2^2\rangle = \frac{6k_BT}{m\alpha^2}\left(\alpha\Delta t - 2\frac{1 - e^{-\alpha\Delta t}}{1 +^{-\alpha\Delta t}}\right)$$

Ermak, D. L., & Buckholz, H. (1980). Numerical integration of the Langevin equation: Monte Carlo simulation. *Journal of Computational Physics*, *35*(2), 169-182.

3. Computational implementation

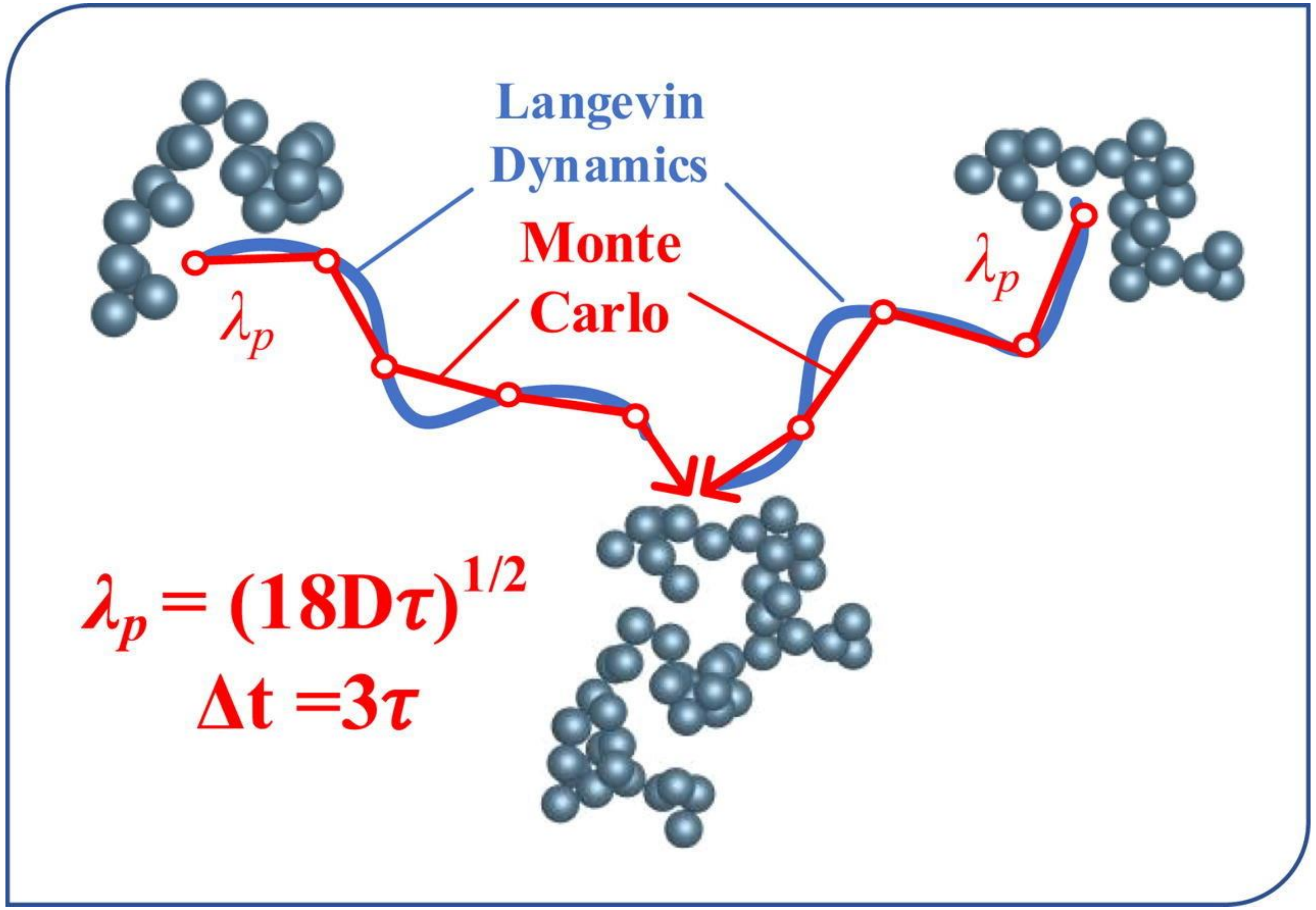
1. Solving the Langevin equation (LE) based on Ermak and Buckholz algorithm
2. Solving the LE by a 4^{th} order Runge-Kutta
3. Using a Monte-Carlo method consistent with the LE

Suresh, V., & Gopalakrishnan, R. (2021). Tutorial: Langevin Dynamics methods for aerosol particle trajectory simulations and collision rate constant modeling. *Journal of Aerosol Science*, *155*, 105746.

3. Computational implementation

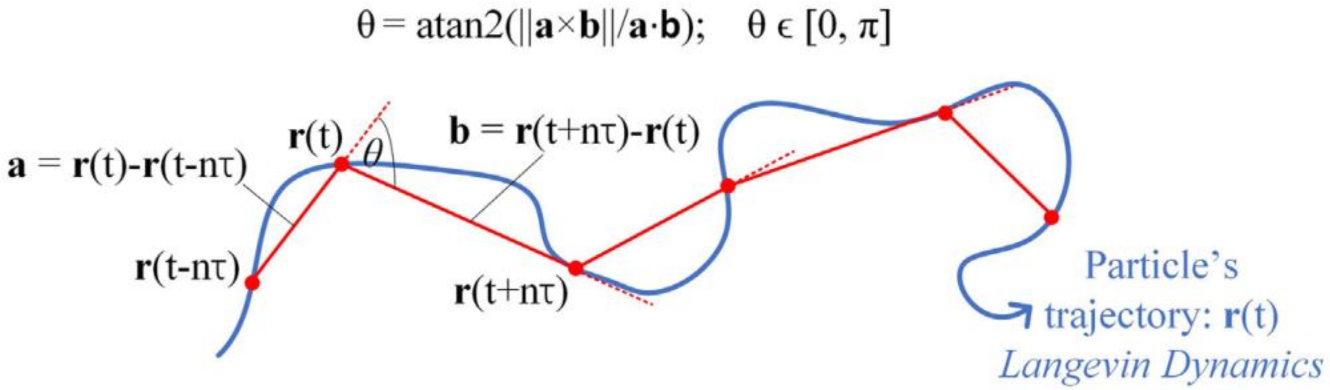
In a **Monte Carlo** approach every particle in a system is displaced individually:

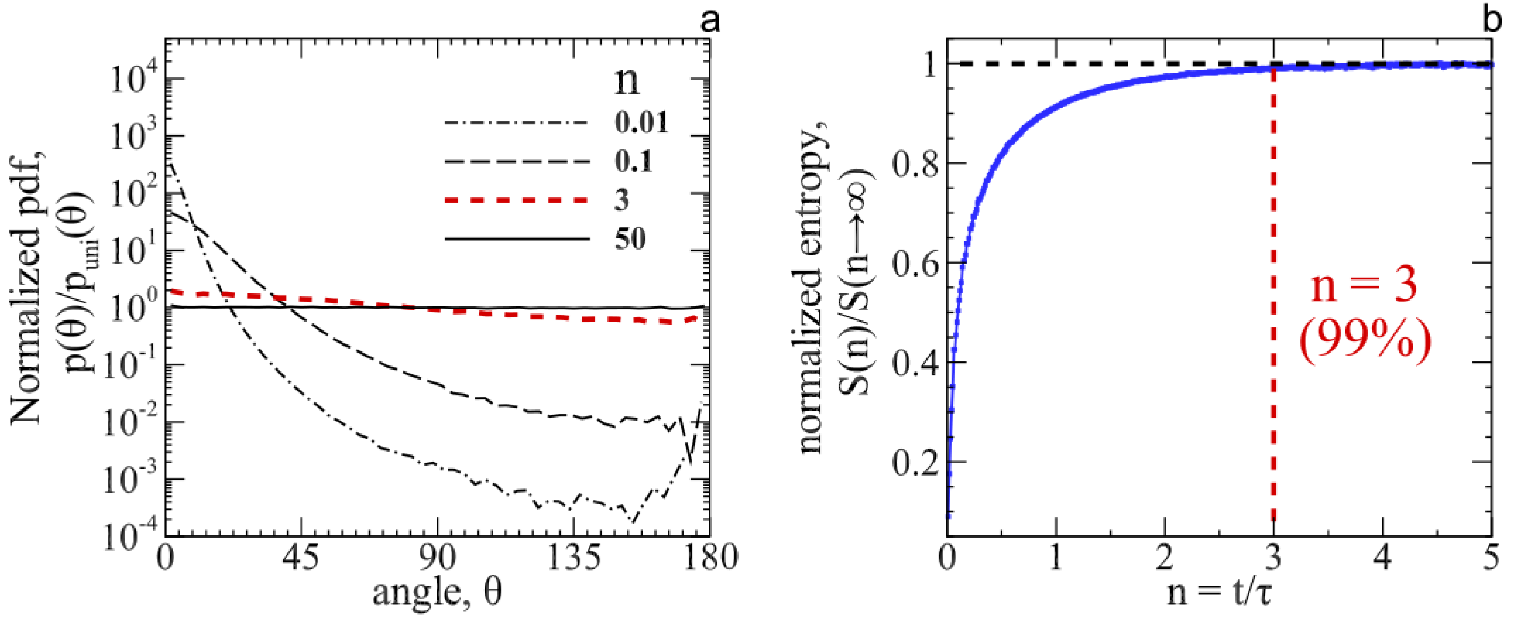
- ○ A particle moves ballistically along its persistent distance λ_p
- ○ A particle changes direction randomly after moving along λ_p
- ○ What is the time-step corresponding to λ_p to be consistent with the Langevin equation?



Morán, J., Yon, J., & Poux, A. (2020). Monte Carlo aggregation code (MCAC) Part 1: Fundamentals. *Journal of colloid and interface science*, *569*, 184-194.

3. Computational implementation

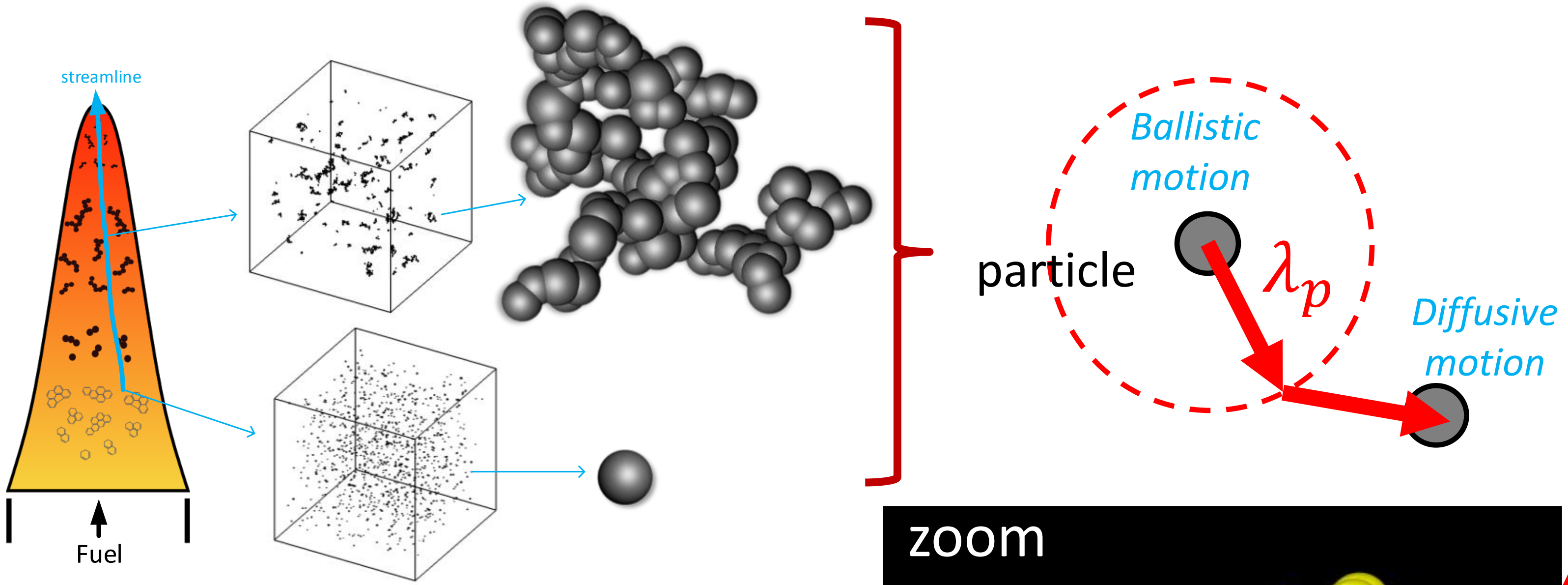


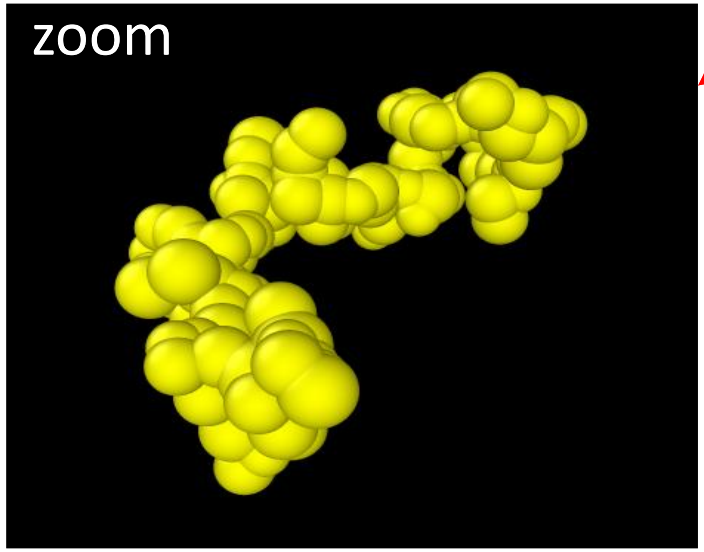


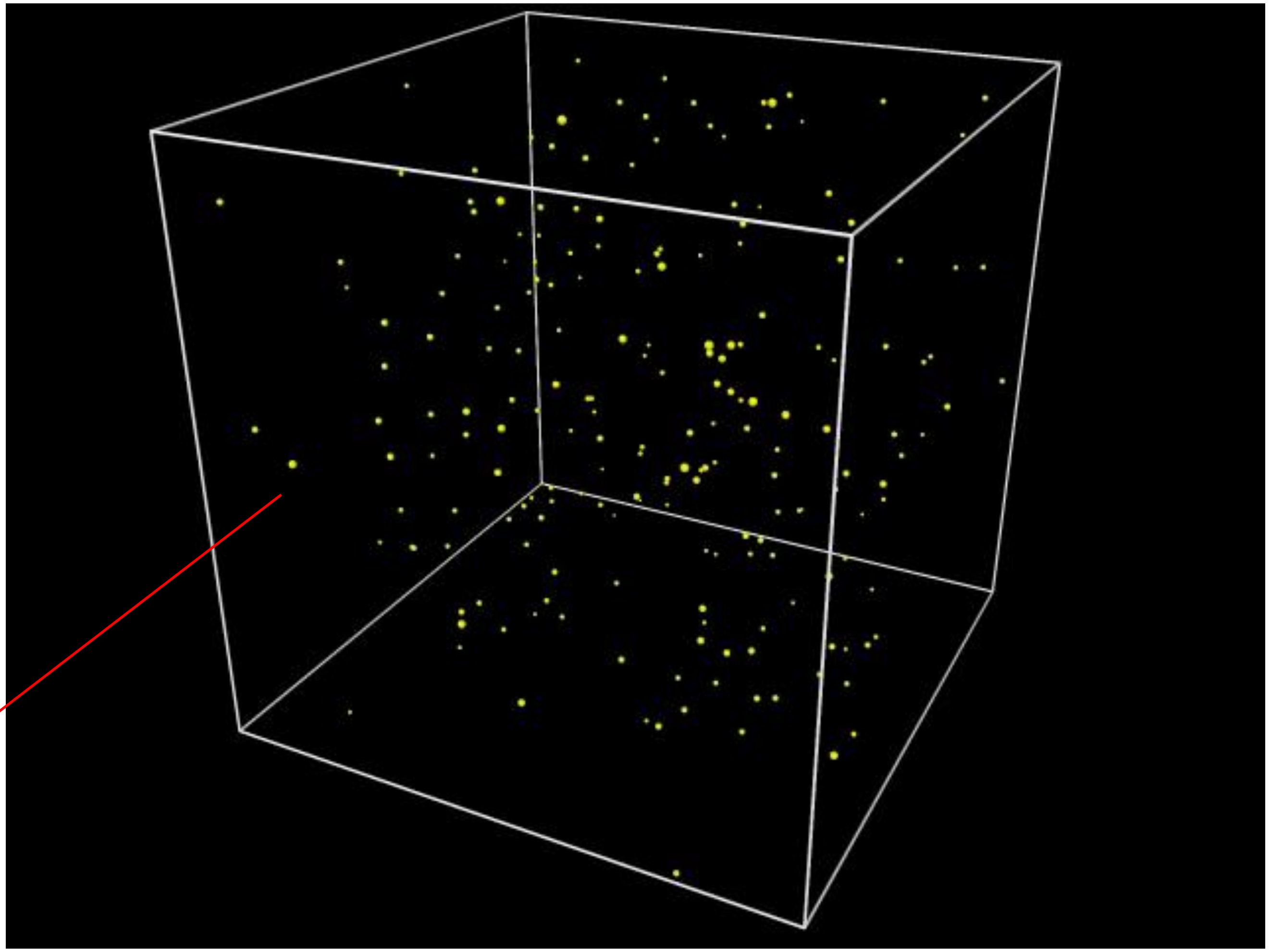
A time step of $\Delta t = n\tau$ with $n = 3$ is needed for a Brownian particle to reach a regime where it's direction changes randomly without correlation in time.

3. Computational implementation

Monte Carlo Aggregation Code[1] (MCAC),



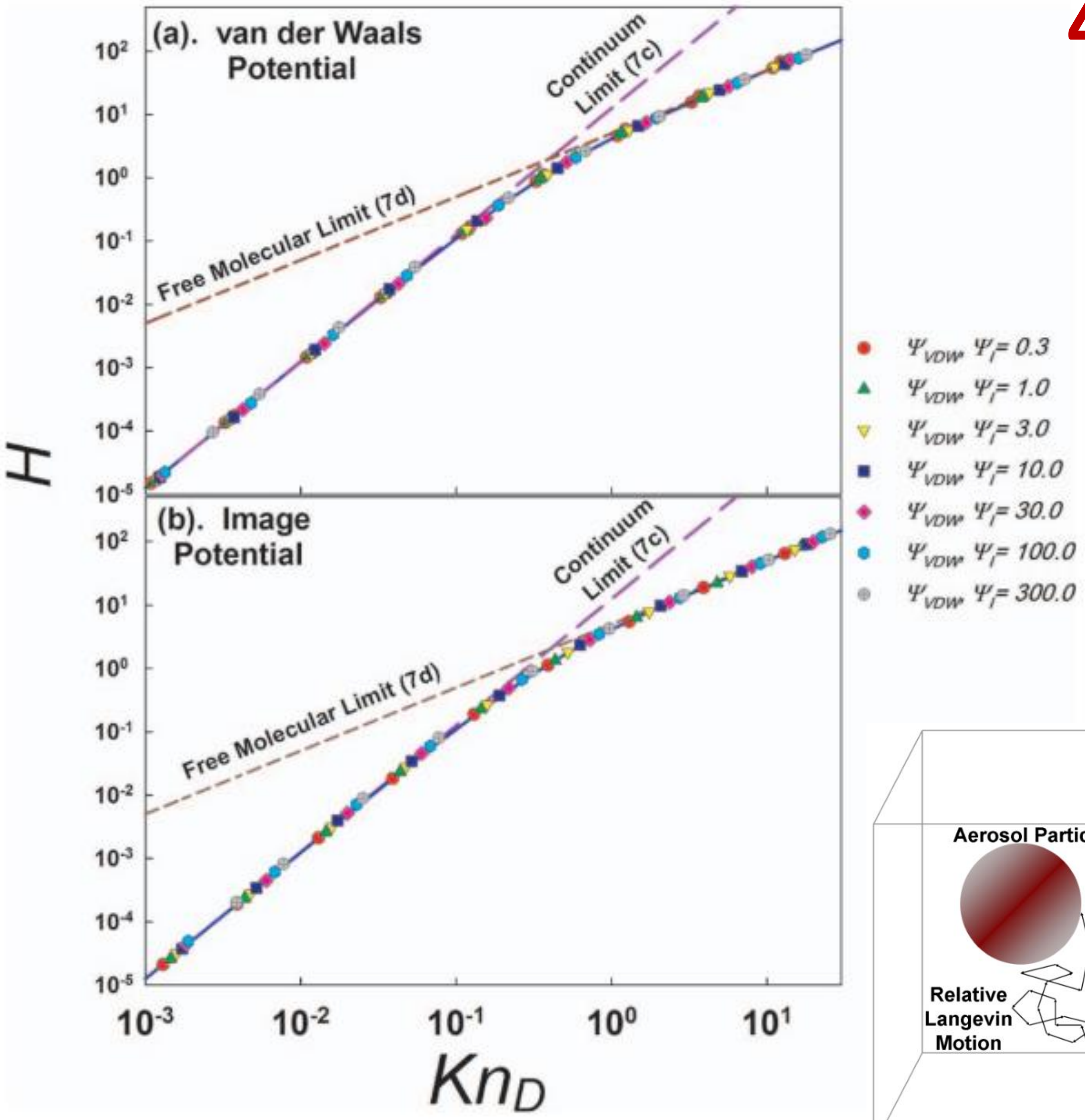


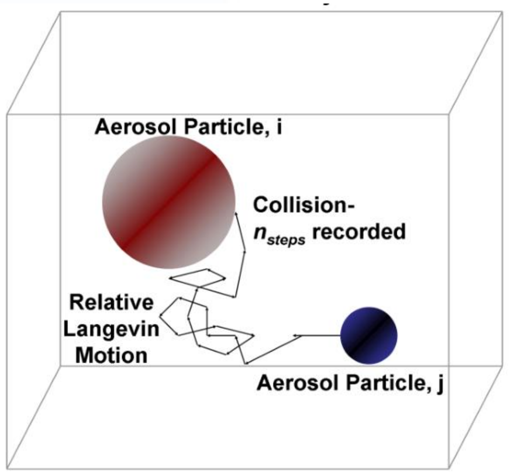


https://gitlab.coria-cfd.fr/MCAC/MCAC

[1]**Morán, J.**, Yon, J., & Poux, A. (2020). *Journal of Colloid and Interface Science*, *569*, 184-194.

4. Examples





Aerosol particle coagulation under van der Waals and image potentials

$$\tau = (f_{ij}/m_{ij})t, \qquad \vec{v}^{\,*} = \frac{m_{ij}\vec{v}}{f_{ij}(a_i + a_j)} \qquad \vec{r}^{\,*} = \frac{\vec{r}}{(a_i + a_j)}$$

Van der Waals force ($\omega = a_i/(a_i + a_j)$)

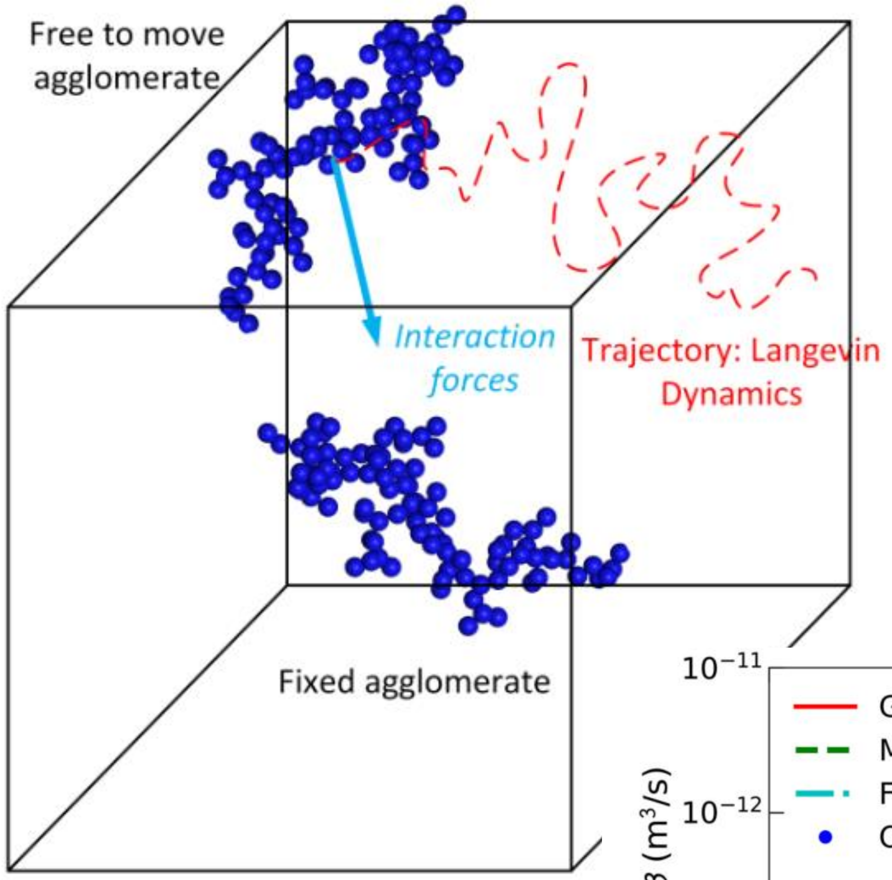
$$F^*_{VDW}[r^*, \omega] = \frac{1}{6}\left[\frac{4\omega(1-\omega)r^*}{(r^{*2}-1)^2} + \frac{4\omega(1-\omega)r^*}{\left(r^{*2}-(2\omega-1)^2\right)^2} - \frac{8\omega(1-\omega)r^*}{(r^{*2}-1)\left(r^{*2}-(2\omega-1)^2\right)}\right]$$

Image force

$$F^*_I[r^*] = \frac{(2r^{*2}-1)}{(r^{*2}-1)^2 r^{*3}}$$

Ouyang, H., Gopalakrishnan, R., & Hogan, C. J. (2012). Nanoparticle collisions in the gas phase in the presence of singular contact potentials. *The Journal of Chemical Physics*, *137*(6).

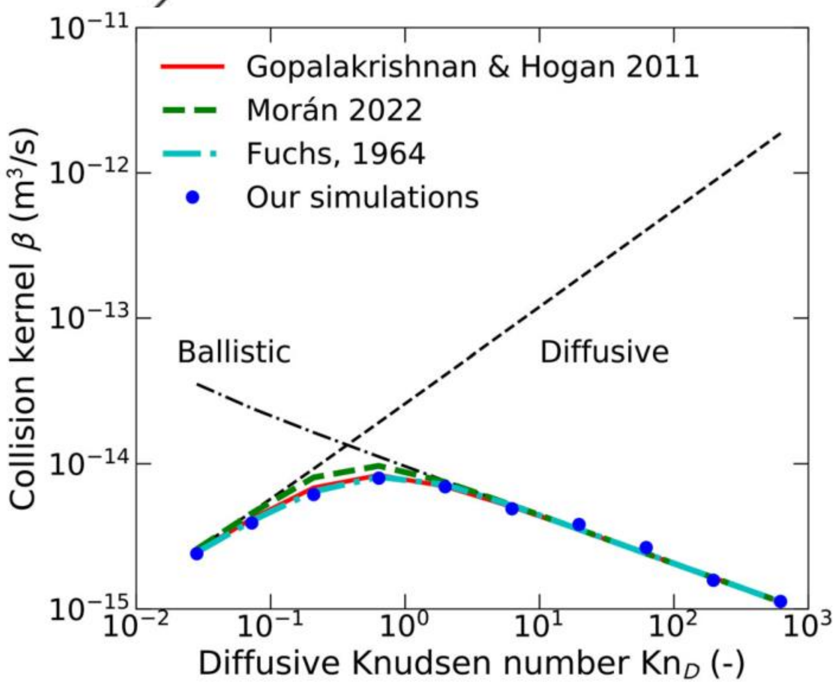
4. Examples



Collision kernel calculation[5],

$$\beta = \frac{L^3}{\mathrm{E}[t]}$$

L: Cubic domain length
E[t]: Average first-time passage (time until the first collision)



First-time passage – Collision kernels:

- Translational Langevin equation

$$\boxed{m\frac{d\boldsymbol{v}}{dt} = -f_t\boldsymbol{v} + \boldsymbol{F}_B + \boldsymbol{F}_e}$$

$$\boldsymbol{v}(t+\Delta t) = \boldsymbol{v}(t)e^{-\alpha\Delta t} + \frac{\boldsymbol{F}_e}{m\alpha}\left(1-e^{-\alpha\Delta t}\right) + \boldsymbol{B}_1$$

$$\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \frac{1}{\alpha}\left(\boldsymbol{v}(t+\Delta t) + \boldsymbol{v}(t) - \frac{2\boldsymbol{F}_e}{m\alpha}\right)\frac{1-e^{-\alpha\Delta t}}{1+e^{-\alpha\Delta t}} + \frac{\boldsymbol{F}_e\Delta t}{m\alpha} + \boldsymbol{B}_2$$

$$\langle B_1\rangle = \langle B_2\rangle = 0$$

$$\langle B_1^2\rangle = \frac{3k_BT}{m}\left(1-e^{-2\alpha\Delta t}\right)$$

$$\langle B_2^2\rangle = \frac{6k_BT}{m\alpha^2}\left(\alpha\Delta t - 2\frac{1-e^{-\alpha\Delta t}}{1+^{-\alpha\Delta t}}\right)$$

- Rotational Langevin equation

$$\boxed{\boldsymbol{I}\frac{d\boldsymbol{\omega}}{dt} = -f_r\boldsymbol{\omega} + \boldsymbol{T}_B + \boldsymbol{T}_e}$$

$$\boldsymbol{\theta}(t+\Delta t) = \boldsymbol{\theta}(t) + \boldsymbol{\omega}\Delta t$$

$$\boldsymbol{\omega}(t+\Delta t) = \boldsymbol{\omega}(t) + \frac{\Delta t}{\boldsymbol{I}}(T_e - f_r\boldsymbol{\omega}) + \frac{1}{\boldsymbol{I}}\sqrt{2k_BTf_r\Delta t\boldsymbol{\delta}}$$

Morán, J., & Kholghy, M. R. (2023). Theoretical derivation of particle collision kernels and its enhancement at high concentration from a first-time-passage approach in the diffusive regime. *Aerosol Science and Technology*, 1-23.

4. Examples

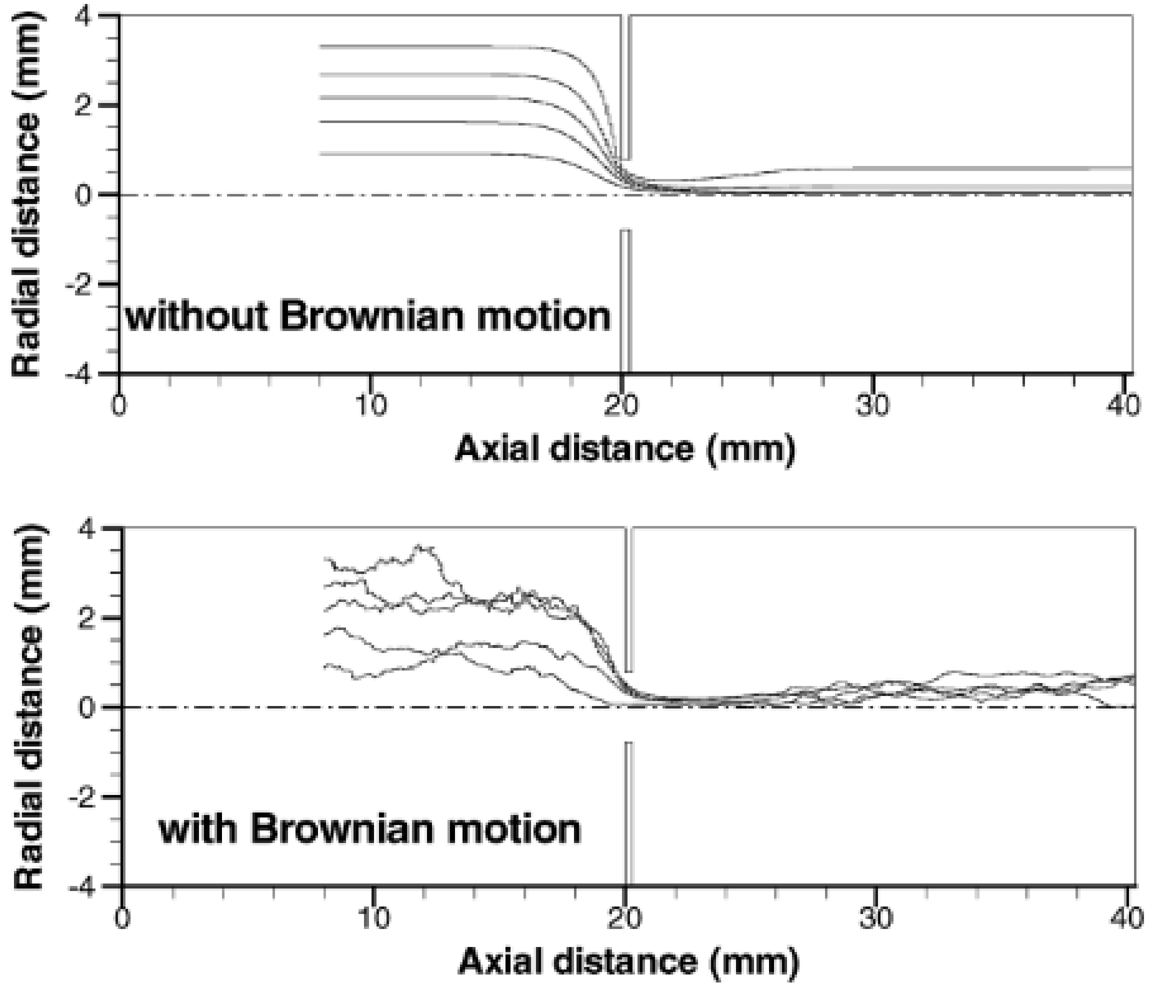


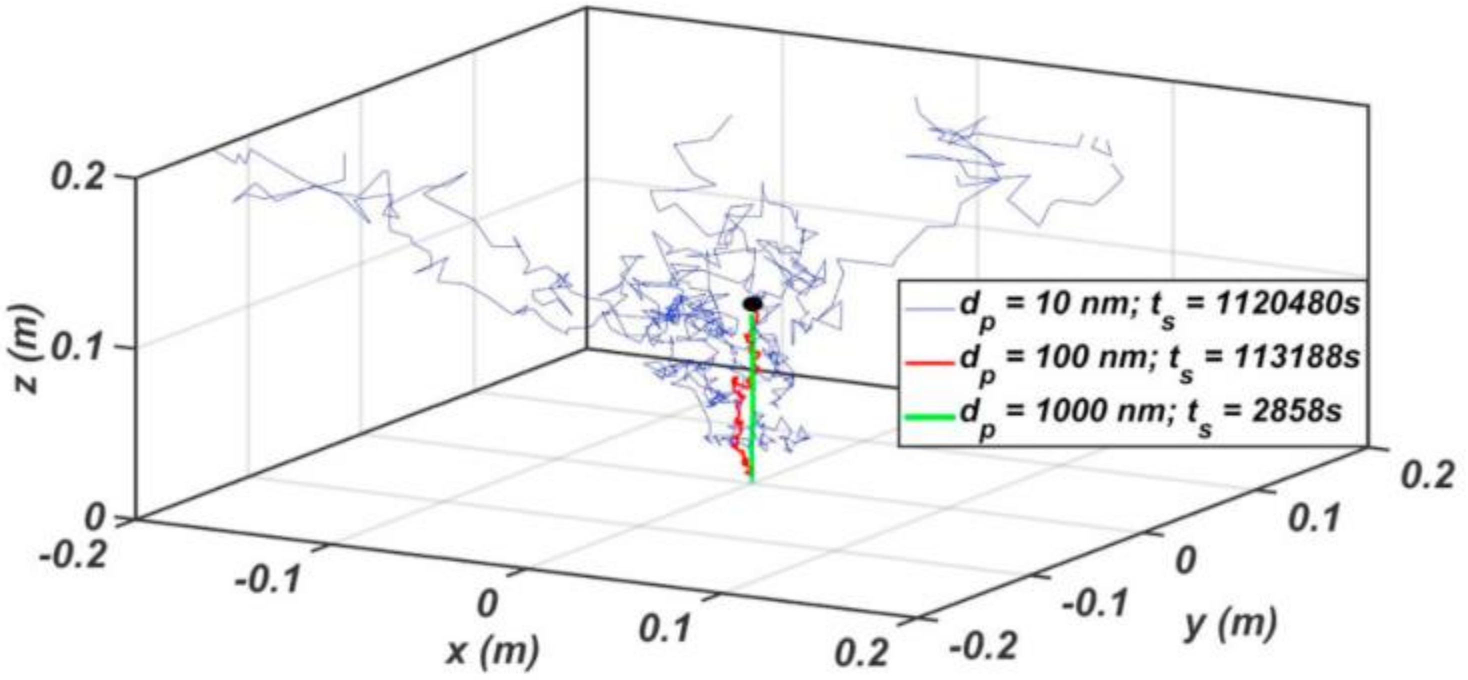
FIG. 8. Trajectories of 5 nm spherical particles of unit density in the aerodynamic lens when Brownian motion is absent or present.

Wang, X., Kruis, F. E., & McMurry, P. H. (2005). Aerodynamic focusing of nanoparticles: I. Guidelines for designing aerodynamic lenses for nanoparticles. *Aerosol Science and Technology*, *39*(7), 611-623.

Focusing lenses are devices designed for focusing particle beams along a centerline the same way we focus a beam of light.

Brownian motion becomes essential when trying to focus small nanoparticles down to 5 nm in diameter.

4. Examples

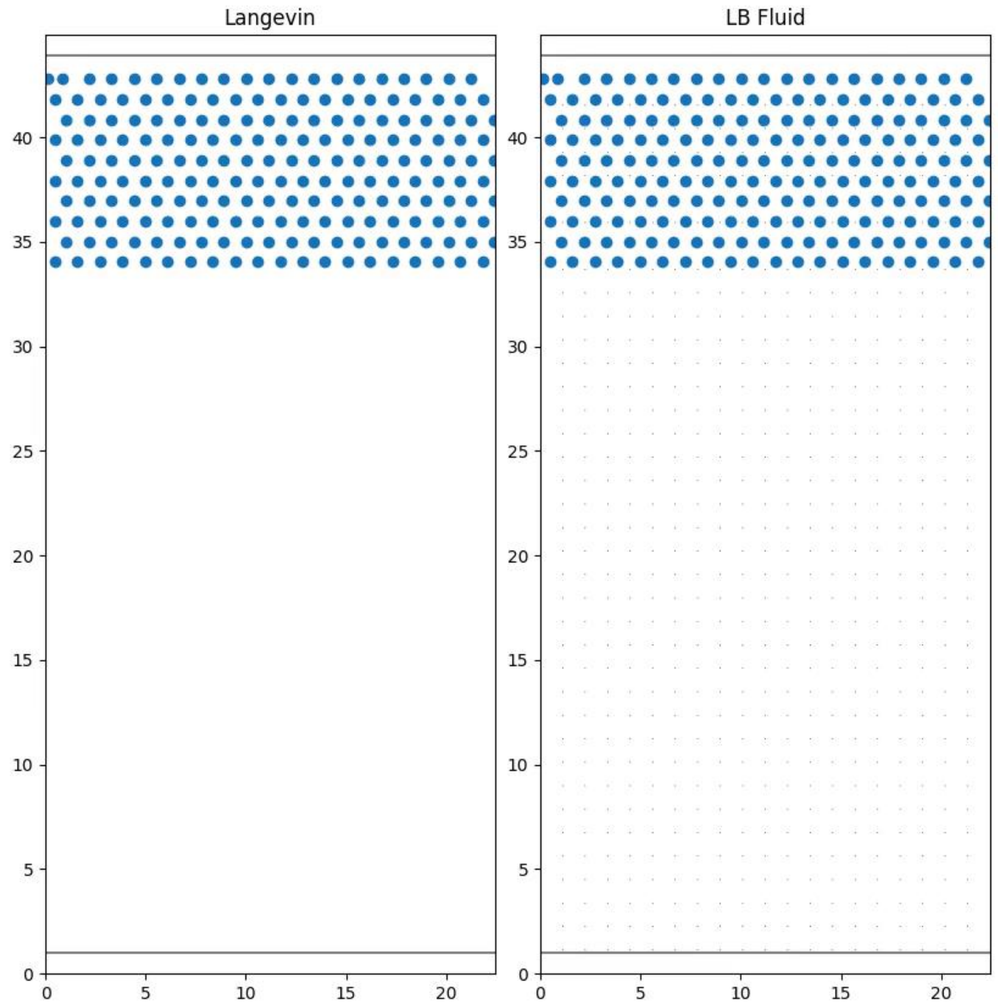


Calculated particle trajectories for the gravitational settling of 10,100,1000 nm spherical particles in still air. The starting point is indicated; it is seen that the 1000 nm particle has an average settling time 2900 s dominated by gravitation force, while the 10 nm particle wanders considerably before settling down with 10^6 s. The 100 nm particle has aspects of both deterministic settling and stochastic Brownian motion with a 10^5 s.

Suresh, V., & Gopalakrishnan, R. (2021). Tutorial: Langevin Dynamics methods for aerosol particle trajectory simulations and collision rate constant modeling. *Journal of Aerosol Science*, *155*, 105746.

4. Examples

https://youtube.com/shorts/MGqV_OSsgvc



Particle sedimentation

A simulation using ESPResSo molecular dynamics code.

Unlike the left-hand side case, the righ-hand side considers hydrodynamic interactions for particle sedimentation in a liquid.

Using Langevin equation to obtain the trajectory of particles and the Lattice Boltzmann method for the fluid flow (2-ways coupling).

4. Examples

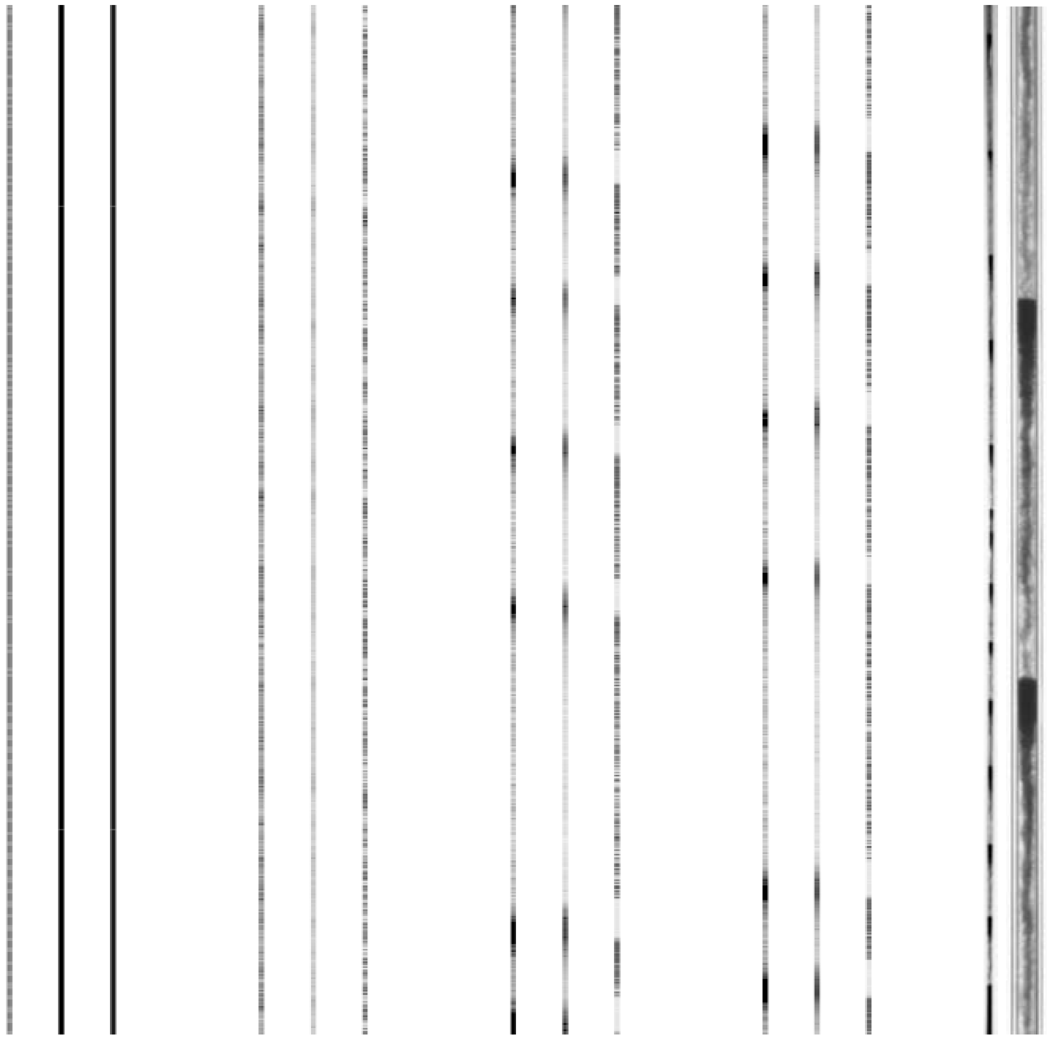


Fig. 8.1. *Left*: numerical solution of the Langevin equation for pipe flow. From *left* to *right* each sequence of three snapshots shows the density, velocity, and granular temperature for different times. The color scheme from `psplot()` has been remapped to grayscale. Dark means high density, low velocity, and high temperature. *Right*: experiment [212] and a closeup thereof.

Granular flow through a narrow pipe

$$\dot{x}_i = v_i \qquad \langle \xi_i(t) \rangle = 0$$

$$m\dot{v}_i = mg - \gamma\, v_i + \sqrt{2E\gamma}\xi_i(t) \qquad \langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta\,(t - t')$$

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x}(vp) + \frac{\partial}{\partial v}\left[\left(g - \frac{\gamma}{m}v\right)p\right] - \frac{E\gamma}{m^2}\frac{\partial^2 p}{\partial v^2} = 0$$

Riethmüller, T., Schimansky-Geier, L., Rosenkranz, D., & Pöschel, T. (1997). Langevin equation approach to granular flow in a narrow pipe. *Journal of statistical physics*, *86*, 421-430.

Suggested reading

- Bian, X., Kim, C., & Karniadakis, G. E. (2016). 111 years of Brownian motion. *Soft Matter*, *12*(30), 6331-6346.
- Chandrasekhar, S. (1943). Stochastic problems in physics and astronomy. *Reviews of modern physics*, *15*(1), 1.
- Ermak, D. L., & Buckholz, H. (1980). Numerical integration of the Langevin equation: Monte Carlo simulation. *Journal of Computational Physics*, *35*(2), 169-182.
- Suresh, V., & Gopalakrishnan, R. (2021). Tutorial: Langevin Dynamics methods for aerosol particle trajectory simulations and collision rate constant modeling. *Journal of Aerosol Science*, *155*, 105746.

Appendix: Brownian Dynamics lecture

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Under the supervision of Prof. Chris Hogan

February 28, 2024

Table of contents

1 Binomial description of Brownian motion

In this section, we try to model the movement of a particle suspended in a fluid neglecting any external force such as gravity or electric. For this purpose, we will use tools coming from modeling stochastic processes. Such tools include the Bernoulli and Binomial processes. These are general tools that can be applied for any stochastic process provided they respect the assumptions of the models (you could use them in your own research!). Indeed, I used this approach to obtain a Monte Carlo method to solve the Langevin equation in a computationally efficient way [1].

1.1 Bernoulli process

A particle moves in a 1d lattice with equal probability to move right ($+\lambda_p$) and left ($-\lambda_p$) and assuming zero probability to stay in the same position after a time step Δt (time required to move λ_p). Considering that, a Bernoulli process is stochastic with a binary outcome with a known constant probability of success (e.g., flipping a coin and observing if the head or tail is facing upwards). The outcomes of a Bernoulli process are conventionally referred to as success and failure. In the case of a particle moving along a 1d axis, we can arbitrarily and without loss of generality call the $+\lambda_p$ displacement as the success and $-\lambda_p$ the failure outcome of the Bernoulli process.

In a mathematical and short form, we can introduce the following stochastic variable,

$$Y \sim \mathrm{Be}(q)$$

meaning that Y is distributed Bernoulli with parameter $q = 1/2$ corresponding to the probability of success. Any Bernoulli process will have the following mass density function,

$$f(Y = y) = q^y(1-q)^{1-y}; \qquad q = 1/2;\ y \in \{0, 1\} \tag{1.1}$$

where the stochastic variable y can take two values, namely $y = 1$ for success ($+\lambda_p$ displacement) and $y = 0$ for failure ($-\lambda_p$ displacement). In this particular case, the mass density function of Eq. (1.1). The advantage of such a random variable is the possibility to express the displacement of the particle Δx after a realization of the Bernoulli process as,

$$\Delta x = \lambda_p y - \lambda_p(1-y) = \lambda_p(2y-1) \tag{1.2}$$

We can calculate the expected displacement as follows,

$$\begin{aligned} \mathrm{E}[\Delta x] &= \mathrm{E}[\lambda_p(2y-1)] \\ &= \lambda_p(2\mathrm{E}[y]-1) \\ &= \lambda_p(2(1/2)-1) = 0 \end{aligned} \tag{1.3}$$

In the same way, we can calculate the expected squared displacement,

$$\begin{aligned} \mathrm{E}[\Delta x^2] &= \mathrm{E}[\lambda_p^2(2y-1)^2] \\ &= \lambda_p^2(4\mathrm{E}[y^2]-4\mathrm{E}[y]+1) \\ &= \lambda_p^2(4(1/2)-4(1/2)+1) = \lambda_p^2 \end{aligned} \tag{1.4}$$

Considering the inherent isotropy of the problem, it makes sense to have a 0 expected or average displacement. It is, however, less evident that the mean-squared displacement is non-null. The definition of the Bernoulli process is a necessary step for what will come later. Also, it is not enough to describe the position of the particle after n random displacements of the particles because

Bernoulli only models the transition from one initial location to the two local neighbor lattice sites. If we want to study the particle movement after that time, then we need another model which is the binomial process described in the following section.

1.2 Binomial process

A binomial process involves a random variable counting the number of success k from a total of n realizations of the corresponding Bernoulli process. In a mathematical concise way, we can write,

$$K \sim \mathrm{Bin}(n, q)$$

meaning that the variable K is distributed Binomial with parameters n and $q = 1/2$ as previously defined. Any Binomial process will have the following mass density function,

$$f(K = k) = \left(\begin{array}{c} n \\ k \end{array} \right) q^k (1-q)^{n-k} = \frac{n!}{k!(n-k)!} q^k (1-q)^{n-k}, \qquad k \in [0, n] \tag{1.5}$$

where the random variable k can take any integer value from $k = 0$ (only failures, the particle moved $-n\lambda_p$) to $k = n$ (only successes, the particle moved $+n\lambda_p$).

Introducing a random variable for the particle displacement in n time steps as,

$$\Delta x = \lambda_p k - \lambda_p (n - k) = \lambda_p (2k - n) \tag{1.6}$$

Therefore, the expected displacement and mean squared displacement in $n\Delta t$ can be calculated as,

$$\begin{aligned} \mathrm{E}[\Delta x] &= \mathrm{E}[\lambda_p (2k - n)] \\ &= \lambda_p (2\mathrm{E}[k] - n) \\ &= \lambda_p (2(n/2) - n) = 0 \end{aligned} \tag{1.7}$$

$$\begin{aligned} \mathrm{E}[\Delta x^2] &= \mathrm{E}[\lambda_p^2 (2k - n)^2] \\ &= \lambda_p^2 (4\mathrm{E}[k^2] - 4n\mathrm{E}[k] + n^2) \\ &= \lambda_p^2 (4(n/2 + n(n-1)/4) - 4n(n/2) + n^2) \\ &= n\lambda_p^2 \end{aligned} \tag{1.8}$$

Where the moments of the distribution (1.5) are $\mathrm{E}[k] = n/2$ and $\mathrm{E}[k^2] = n/2 + n(n-1)/4$. Eq. (1.8) is of great importance to us, it states that average (or expected) squared displacement corresponds to the number of trials n times the squared displacement of a time step.

It is interesting to note that in the limit $n \to \infty$, the binomial distribution (1.5) tends to the following Gaussian distribution where $\tilde{k}$ is a continuous analogous to k,

$$f(\tilde{k}) = \frac{1}{\sqrt{2\pi n q^2}} e^{-(\tilde{k} - nq)^2/(2nq^2)}, \qquad n \to \infty,\ q = 1/2 \tag{1.9}$$

where $\mathrm{E}[\tilde{k}] = n/2$ and $\mathrm{E}[\tilde{k}^2] = n^2/4 + n/4$. Based on eq. (1.6) replacing $\tilde{k}$ by $q(\Delta x/\lambda_p + n)$ and considering the Jacobian of this change of variable q/λ_p,

$$f(\Delta x) = \frac{1}{\sqrt{2\pi n \lambda_p^2}} e^{-\Delta x^2/(2n\lambda_p^2)}, \qquad n \to \infty \tag{1.10}$$

This equation is consistent with Einstein's theory of Brownian motion when $2Dt = n\lambda_p^2$, considering $n = t/\Delta t$ obtaining $D = \lambda_p^2/(2\Delta t)$.

$$f(x) = \frac{1}{(4\pi Dt)^{1/2}} e^{-\Delta x^2/(4Dt)}, \qquad t \gg \tau$$

where $\tau = m/f$ is the particle momentum relaxation time.

Now, considering the following property of probability $P(A \cap B \cap C) = P(A)P(B)P(C)$ which means that the probability to have simultaneously the values of A, B , and C is the product of their probabilities when they are not correlated. We can assume that in Brownian motion, the movement along each axis is uncorrelated, and considering the 3d squared displacement $\Delta r^2 = \Delta x^2 + \Delta y^2 + \Delta z^2$,

$$f(\Delta r) = f(\Delta x) f(\Delta y) f(\Delta z)$$

$$f(\Delta r) = \left(\frac{1}{(4\pi Dt)^{1/2}} e^{-\Delta x^2/(4Dt)} \right) \left(\frac{1}{(4\pi Dt)^{1/2}} e^{-\Delta y^2/(4Dt)} \right) \left(\frac{1}{(4\pi Dt)^{1/2}} e^{-\Delta z^2/(4Dt)} \right)$$

$$f(\Delta r) = \frac{1}{(4\pi Dt)^{3/2}} e^{-\Delta r^2/(4Dt)}, \qquad t \gg \tau \tag{1.11}$$

Here, it is important to remember the mean displacement and mean squared displacement for a particle in 3d after a time $t \gg \tau$,

$$E[\Delta r] = 0$$

$$E[\Delta r^2] = 6Dt, \qquad t \gg \tau$$

2 Chandrasekhar analytical treatment of the Langevin equation

In this section, we will reproduce the analytical development of Chandrasekhar [2] to solve the Langevin equation. I hope to provide you here with a detailed derivation of the probability density function for the particle's velocity and position. In the notation of Chandrasekhar's work, the velocity vector of the Brownian particle is denoted in bold as $\boldsymbol{u} = (u_x, u_y, u_z)$. The Langevin equation can be written as,

$$m\frac{d\boldsymbol{u}}{dt} = -f\boldsymbol{u} + m\boldsymbol{A}(t)$$

where m and f are the particle's mass and friction coefficient, respectively. The term $m\boldsymbol{A}(t)$ is the Brownian force. We can simplify this equation by defining the momentum relaxation frequency $\beta = f/m = \tau^{-1}$,

$$\frac{d\boldsymbol{u}}{dt} = -\beta\boldsymbol{u} + \boldsymbol{A}(t) \tag{2.12}$$

We recall that Eq. (2.12) is a stochastic differential equation and thus its solution should be interpreted in terms of probability density functions (PDF). Thus, solving the Langevin equation means finding the PDF denoted as $W(\boldsymbol{u}, t; \boldsymbol{u}_0)$ representing the probability of having a velocity $\boldsymbol{u}$ at time t given a known initial velocity $\boldsymbol{u}_0$ at time $t = 0$. Once we obtain such a PDF. Similarly, we also search for the PDF $W(\boldsymbol{r}, t; \boldsymbol{r}_0)$ representing the probability of finding the Brownian particle at position $\boldsymbol{r}$ at time t given a known initial position $\boldsymbol{r}_0$ at time $t = 0$. The following sections explain in detail how Chandrasekhar obtained such PDFs.

The following assumptions are necessary for the mathematical developments presented below,

- $\boldsymbol{A}(t)$ is independent of $\boldsymbol{u}$
- $\boldsymbol{A}(t)$ changes extremely fast compared to $\boldsymbol{u}$

2.1 Velocity probability density function

We know the following boundary conditions,

$$W(\boldsymbol{u}, t) \to \delta(u_x - u_{x,0})\delta(u_y - u_{y,0})\delta(u_z - u_{z,0}), \qquad t \to 0 \tag{2.13a}$$

$$W(\boldsymbol{u}, t) \to \left[\frac{m}{2\pi k_B T}\right]^{3/2} e^{-m|\boldsymbol{u}|^2/(2k_B T)}, \qquad t \to \infty \tag{2.13b}$$

where $\delta(\dots)$ are Dirac delta functions. Eq. (2.13a) just means that the initial velocity is deterministic $(u_{x,0}, u_{y,0}, u_{z,0})$. Eq. (2.13b) indicates that the particle will be thermally equilibrated with the surrounding fluid and thus its velocity should follow the Maxwellian distribution shown in this equation where $|\boldsymbol{u}|$ denotes the magnitude of the velocity, k_B is the Boltzmann constant, and T the fluid temperature.

We can solve Eq. (2.12) by multiplying both sides of the equation by $e^{\beta t}$ and then integrating in time,

$$e^{\beta t}\frac{d\boldsymbol{u}}{dt} = -e^{\beta t}\beta\boldsymbol{u} + e^{\beta t}\boldsymbol{A}(t) \tag{2.14}$$

$$e^{\beta t}\frac{d\boldsymbol{u}}{dt} + e^{\beta t}\beta\boldsymbol{u} = e^{\beta t}\boldsymbol{A}(t) \tag{2.15}$$

The two terms on the left of this equation can be grouped using the derivative of the product rule,

$$\frac{d}{dt}(\boldsymbol{u}e^{\beta t}) = e^{\beta t}\boldsymbol{A}(t) \tag{2.16}$$

Now we integrate both sides of this equation in time,

$$\int_0^t \frac{d}{ds}(\boldsymbol{u}e^{\beta s})\, ds = \int_0^t e^{\beta s}\boldsymbol{A}(s)\, ds \tag{2.17}$$

Rearranging the left-hand side of this equation and using the fundamental theorem of calculus we obtain,

$$\frac{d}{ds}\left(\int_0^t \boldsymbol{u}e^{\beta s}\, ds\right) = \int_0^t e^{\beta s}\boldsymbol{A}(s)\, ds \tag{2.18}$$

$$\boldsymbol{u}e^{\beta t} - \boldsymbol{u}_0 = \int_0^t e^{\beta s}\boldsymbol{A}(s)\, ds \tag{2.19}$$

Dividing both sides of this equation by $e^{\beta t}$ we obtain,

$$\boldsymbol{u} - \boldsymbol{u}_0 e^{-\beta t} = e^{-\beta t} \int_0^t e^{\beta s} \boldsymbol{A}(s)\, ds \tag{2.20}$$

Taking the limit $t \to \infty$ on both sides of Eq. (2.20) we conclude that the right-hand side term should become a Maxwellian velocity distribution according to the boundary condition (2.13b). Now, owing to the difference in time scale between the fluctuations in the Brownian force compared to the fluctuations in the particle velocity, we can decompose the left-hand side of Eq. (2.20) into a sum of time intervals short enough to consider the exponential terms to be constant while $\boldsymbol{A}(t)$ will experience many variations. Based on this idea, we can use the lemma-1 from Chandrasekhar's work,

Chandrasekhar lemma 1:

$$\boldsymbol{R} = \int_0^t \psi(s) \boldsymbol{A}(s) ds \tag{2.21a}$$

$$W(\boldsymbol{R}) = \frac{1}{\left[4\pi q \int_0^t \psi^2(s) ds\right]^{3/2}} \exp\left(-\frac{|\boldsymbol{R}|^2}{4q \int_0^t \psi^2(s) ds}\right); \qquad q = \beta k_B T/m \tag{2.21b}$$

This remarkable lemma allows us to obtain an analytical expression for the probability distribution $W(\boldsymbol{R})$ of any vector $\boldsymbol{R}$ provided its value is given by a time integral like the one presented in Eq. (2.21a). This means that $W(\boldsymbol{R})$ is given by Eq. (2.21b) regardless of the distribution of $\boldsymbol{A}(s)$ given that it variates extremely fast in time (or the mathematical sum will have an infinite number of terms). Intuitively, we can say that its explanation is probably related to the central limit theorem which established that regardless of the distribution of a random variable, the sum of infinite values of such variable will have a Gaussian distribution.

Now, we use this lemma to solve the right-hand side of Eq. (2.20) so we define,

$$\boldsymbol{R} = e^{-\beta t} \int_0^t e^{\beta s} \boldsymbol{A}(s)\, ds = \int_0^t e^{\beta(s-t)} \boldsymbol{A}(s)\, ds = \int_0^t \psi(s) \boldsymbol{A}(s) ds$$

Therefore, the function $\psi(s)$ for this integral is,

$$\psi(s) = e^{\beta(s-t)}$$

Now, to obtain the PDF $W(\boldsymbol{R})$ we need to determine the following integral,

$$\int_0^t \psi^2(s) ds = \int_0^t e^{2\beta(s-t)} ds = \frac{1}{2\beta}(1 - e^{-2\beta t})$$

Now, we simply replace this expression into Eq. (2.21b) to obtain $W(\boldsymbol{R})$,

$$W(\boldsymbol{R}) = \frac{1}{[4\pi q/(2\beta)(1 - e^{-2\beta t})]^{3/2}} \exp\left(-\frac{|\boldsymbol{R}|^2}{4q/(2\beta)(1 - e^{-2\beta t})}\right)$$

Replacing the variable $q = \beta k_B T/m$,

$$W(\boldsymbol{R}) = \left[\frac{m}{2\pi k_B T(1-e^{-2\beta t})}\right]^{3/2} \exp\left(-\frac{m|\boldsymbol{R}|^2}{2k_B T(1-e^{-2\beta t})}\right)$$

According to the left-hand side of Eq. (2.20) we have $\boldsymbol{R} = \boldsymbol{u} - \boldsymbol{u}_0 e^{-\beta t}$ so we can replace it in the previous equation to obtain,

$$W(\boldsymbol{u}, t; \boldsymbol{u}_0) = \left[\frac{m}{2\pi k_B T(1-e^{-2\beta t})}\right]^{3/2} \exp\left(-\frac{m|\boldsymbol{u} - \boldsymbol{u}_0 e^{-\beta t}|^2}{2k_B T(1-e^{-2\beta t})}\right) \tag{2.22}$$

We can verify that Eq. (2.22) becomes a Maxwellian in the limit $t \to \infty$ as the exponential terms will vanish.

2.2 Position probability density function

We can use similar reasoning and make use of the same lemma-1 to obtain an analytical solution of the Langevin equation for the vector position $\boldsymbol{r}$ of the particle at time t. For that purpose, we simply express the position as the integral of the velocity,

$$\boldsymbol{r} - \boldsymbol{r}_0 = \int_0^t \boldsymbol{u}(s) ds \tag{2.23}$$

From Eq. (2.20) we know an expression for the velocity,

$$\boldsymbol{u} - \boldsymbol{u}_0 e^{-\beta t} = e^{-\beta t} \int_0^t e^{\beta s} \boldsymbol{A}(s)\, ds$$

To avoid confusion we can re-write this equation by replacing the time t with s and introducing a new variable for the integral s',

$$\boldsymbol{u}(s) = \boldsymbol{u}_0 e^{-\beta s} + e^{-\beta s} \int_0^s e^{\beta s'} \boldsymbol{A}(s')\, ds'$$

Thus, combining these two expressions we obtain,

$$\boldsymbol{r} - \boldsymbol{r}_0 = \int_0^t \left[\boldsymbol{u}_0 e^{-\beta s} + e^{-\beta s} \int_0^s e^{\beta s'} \boldsymbol{A}(s')\, ds'\right] ds \tag{2.24}$$

We can integrate the first term of the right-hand side of Eq. (2.24),

$$\int_0^t \boldsymbol{u}_0 e^{-\beta s} ds = -\frac{1}{\beta} \boldsymbol{u}_0 (e^{-\beta t} - 1)$$

Then, we replace into and re arrange Eq. (2.24),

$$\boldsymbol{r} - \boldsymbol{r}_0 + \frac{1}{\beta} \boldsymbol{u}_0 (e^{-\beta t} - 1) = \int_0^t \left[e^{-\beta s} \int_0^s e^{\beta s'} \boldsymbol{A}(s')\, ds'\right] ds \tag{2.25}$$

In the current form of Eq. (2.25) we cannot directly apply the lemma-1 and we need a strategy to simplify this equation. We can proceed to integration by parts ($\int \tilde{u} d\tilde{v} = \tilde{u}\tilde{v} - \int \tilde{v} d\tilde{u}$) considering the following change of variables,

$$\begin{cases} \tilde{u} = \int_0^s e^{\beta s'} \boldsymbol{A}(s')\, ds' \\ d\tilde{v} = e^{-\beta s} ds \end{cases}$$

where the corresponding $d\tilde{u}$ and $\tilde{v}$ are,

$$\begin{cases} d\tilde{u} = \frac{d}{ds}\left(\int_0^s e^{\beta s'} \boldsymbol{A}(s')\, ds'\right) ds = e^{\beta s}\boldsymbol{A}(s)ds \\ \tilde{v} = -\frac{1}{\beta}e^{-\beta s} \end{cases}$$

Then, the right-hand side of Eq. (2.24) becomes,

$$\begin{aligned} \int_0^t \left[e^{-\beta s}\int_0^s e^{\beta s'}\boldsymbol{A}(s')\, ds'\right] ds = & -\frac{1}{\beta}e^{-\beta s}\int_0^s e^{\beta s'}\boldsymbol{A}(s')\, ds' + \int_0^t \frac{1}{\beta}e^{-\beta s}e^{\beta s}\boldsymbol{A}(s)ds \\ = & -\frac{1}{\beta}e^{-\beta t}\int_0^t e^{\beta s}\boldsymbol{A}(s)\, ds + \frac{1}{\beta}\int_0^t \boldsymbol{A}(s)ds \\ = & \frac{1}{\beta}\int_0^t \left(1 - e^{\beta(s-t)}\right)\boldsymbol{A}(s)\, ds \end{aligned}$$

Now, we can replace back into Eq. (2.24),

$$\boldsymbol{r} - \boldsymbol{r}_0 + \frac{1}{\beta}\boldsymbol{u}_0(e^{-\beta t} - 1) = \frac{1}{\beta}\int_0^t \left(1 - e^{\beta(s-t)}\right)\boldsymbol{A}(s)\, ds \tag{2.26}$$

At this point we can directly use lemma-1 to solve Eq. (2.26) by defining,

$$\boldsymbol{R} = \frac{1}{\beta}\int_0^t \left(1 - e^{\beta(s-t)}\right)\boldsymbol{A}(s)\, ds$$

Therefore, the function $\psi(s)$ for this integral is,

$$\psi(s) = \frac{1}{\beta}\left(1 - e^{\beta(s-t)}\right)$$

Once again, we need to determine the following integral,

$$\begin{aligned} \int_0^t \psi^2(s)ds = & \int_0^t \frac{1}{\beta^2}\left(1 - e^{\beta(s-t)}\right)^2 ds \\ = & \frac{1}{\beta^2}\int_0^t \left(1 - 2e^{\beta(s-t)} + e^{2\beta(s-t)}\right) ds \\ = & \frac{t}{\beta^2} - \frac{2}{\beta^3}\left(1 - e^{-\beta t}\right) + \frac{1}{2\beta^3}\left(1 - e^{-2\beta t}\right) \\ = & \frac{1}{2\beta^3}\left(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}\right) \end{aligned}$$

Now, we simply replace this expression into Eq. (2.21b) to obtain $W(\boldsymbol{R})$,

$$W(\boldsymbol{R}) = \frac{1}{\left[4\pi q/(2\beta^3)\left(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}\right)\right]^{3/2}} \exp\left(-\frac{|\boldsymbol{R}|^2}{4q/(2\beta^3)\left(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}\right)}\right)$$

Based on the left-hand side of Eq. (2.25) we have $\boldsymbol{R} = \boldsymbol{r} - \boldsymbol{r}_0 + \frac{1}{\beta}\boldsymbol{u}_0(e^{-\beta t} - 1)$ and considering $q = \beta k_B T/m$. Therefore, we finally obtain the probability density function to have the particle at position $\boldsymbol{r}$ at time t,

$$W(\boldsymbol{r}, t; \boldsymbol{r}_0) = \left[\frac{m\beta^2}{2\pi k_B T\left(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}\right)}\right]^{3/2} \exp\left(-\frac{m\beta^2 \left|\boldsymbol{r} - \boldsymbol{r}_0 + \frac{\boldsymbol{u}_0}{\beta}\left(e^{-\beta t} - 1\right)\right|^2}{2k_B T\left(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}\right)}\right) \tag{2.27}$$

We can verify that in the limit $t \gg \beta^{-1}$ the position of the particle follows this dstribution,

$$W(\boldsymbol{r}, t; \boldsymbol{r}_0) = \frac{1}{(4\pi D t)^{3/2}} \exp\left(-\frac{\left|\boldsymbol{r} - \boldsymbol{r}_0\right|^2}{4Dt}\right); \qquad t \gg \beta^{-1} \tag{2.28}$$

where the diffusion coefficient of the particle is $D = k_B T/(m\beta)$. This is equivalent to Eq. (1.11) derived previously based on the binomial approach.

References

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