BROWNIAN DYNAMICS SIMULATIONS WITH HYDRODYNAMICS

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Abstract

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I. MAIN RESULTS WE WILL OBTAIN

Under the following assumptions

- $\tau < \tau_a = \frac{a^2}{D_o}$
- Spherical particles of radius a.
- On colloidal time scales $\tau \gg \tau_B$ the motion of the solvent can be described by the so-called "Creeping flow equations" (aka "Stokes equations"), i.e.

$$-\nabla p(\boldsymbol{r}) + \eta_o \nabla^2 \boldsymbol{u}(\boldsymbol{r}) = 0 \tag{1}$$

$$\nabla \cdot \boldsymbol{u}(\boldsymbol{r}) = 0 \tag{2}$$

  where $p(\boldsymbol{r})$ is the pressure of the fluid at point $\boldsymbol{r}$, and $\boldsymbol{u}(\boldsymbol{r})$ is the fluid velocity in such point. This assumption implies that the Reynolds number

$$Re = \frac{\rho\ a\ v}{\eta_o} \tag{3}$$

  is low.

- Stick boundary conditions between the fluid and the surface of the particles.

we will show that:

It is possible to get the following finite difference algorithm (known as "Ermak-McCammon scheme"

$$\boldsymbol{r}_i(t_0+\tau) = \boldsymbol{r}_i(t_o) + v_i^D(\boldsymbol{X}_o)\tau + (2\tau)^{1/2}\boldsymbol{d}(\boldsymbol{X}_o)\cdot\boldsymbol{n} + o(\tau) \tag{4}$$

where

$$v_i^D(\boldsymbol{X}_o) = \sum_{j=1}^{N}[\beta \boldsymbol{D}_{ij}(\boldsymbol{X}_o)\cdot\boldsymbol{f}_j(\boldsymbol{X}_o) + \nabla_j\cdot\boldsymbol{D}_{ij}(\boldsymbol{X}_o)] \tag{5}$$

and

- $\boldsymbol{X}_o = (\boldsymbol{r}_1(t_o), ...\boldsymbol{r}_N(t_o))$
- $\boldsymbol{X} = (\boldsymbol{r}_1(t_o+\tau), ...\boldsymbol{r}_N(t_o+\tau))$
- $\beta = \frac{1}{k_B T}$
- $\boldsymbol{n}$ is a Gaussian Random vector of independently distributed components of mean zero and variance one. Usually computed using a uniform random number χ, such that $n \rightarrow R = \sqrt{12}(\chi - 0.5)$
- $\boldsymbol{d}(\boldsymbol{X})$ is square-root matrix of the positive definite matrix $\boldsymbol{D}$ which are $3N \times 3N$. $\boldsymbol{D}$ is the "translational hydrodynamic diffusivity tensor" (or the product $\beta\ \boldsymbol{D}$ is known as the translational hydrodynamic mobility tensor" (we will usually refer to them as **diffusivity tensors**.

$$\boldsymbol{D}(\boldsymbol{X}_0) = \boldsymbol{d}(\boldsymbol{X}_o)\cdot\boldsymbol{d}(\boldsymbol{X}_o) \tag{6}$$

When there is no hydrodynamics:
$\boldsymbol{D}_{ij}(\boldsymbol{X}) = D_o\ \delta_{ij}\ \mathbf{1}$

When there is hydrodynamics, $\boldsymbol{D}$ can be very complex, and obtaining analytical expressions is very difficult. If we take the approximation of just considering pairwise interactions, i.e. given a pair of spheres interacting i and j the other $N-2$ we assume do not exert any influence on the interaction between i and j, then we will show that it is possible to write

$$\boldsymbol{D}_{ij}(\boldsymbol{X}) = \boldsymbol{D}_{ij}^{far}(\boldsymbol{r}_{ij}) + \Delta\boldsymbol{D}_{ij}^{near}(\boldsymbol{X}) \tag{7}$$

where

- $\boldsymbol{D}_{ij}^{far}(\boldsymbol{r}_{ij})$ is the far-field part, valid when the distances between particles i and j is large. A usual expression for the far-field is the so know as "Rotne-Prager (RP) approximation $\boldsymbol{D}_{ij}^{RP}(\boldsymbol{r}_{ij})$ given by

$$\boldsymbol{D}_{ij}^{RP}(\boldsymbol{r}_{ij}) = \delta_{ij}\, D_o\, \mathbf{1} + (1-\delta_{ij})\, D_o \left[\frac{3}{4}\left(\frac{a}{r_{ij}}\right)[\mathbf{1} + \hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}] + \frac{1}{2}\left(\frac{a}{r_{ij}}\right)^3 [\mathbf{1} - 3\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}]\right] \quad (8)$$

  we will see later where it comes from.

- $\Delta\boldsymbol{D}_{ij}^{near}(\boldsymbol{X})$ is the near-field part (all terms not accounted in $\boldsymbol{D}_{ij}^{RP}(\boldsymbol{r}_{ij})$) plus the lubrication effects. It is important when the distances between particles i and j become smaller. We can neglect it if we have for instance a diluted system of particles that repeal each other. We cannot neglect it for instance when we have attraction between particles, or in the case of hard spheres.

Another thing we will learn is that, within the approaches we do, the static properties of a system can be computed without any need of including Hydrodyamic Interactions. So, BD without HI can be still very useful !!!

One should notice that in general:

- HI is not pairwise-additive
- They are long range, decaying as $1/r$.
- They can even diverge for certain types of motion when particles approach very closely (lubrication effects)
- Implementation of Ermak scheme is in principle $O(N^3) \rightarrow$ bottleneck in BD.
- Few particles can be simulated, typically $30 < N < 300$.

Let's proof the different results we have stated ....

II. HOW TO GET THE "FAR-FIELD": THE "ROTNE-PRAGER (RP) APPROXIMATION"

A. Steps we will do

- (1) Derive expressions for the velocity and pressure in a fluid that obeys the "Creeping flow equations" due to the action of external forces $\boldsymbol{f}^{ext}$: the Oseen tensor, and the pressure vector.

- (2) Suppose that the surface elements of the N colloidal spheres cause the external forces $\boldsymbol{f}^{ext}$ that act on the fluid, and we have stick boundary conditions on the surface of the particles.

- (3) Simplify the Oseen tensor by assuming that the distance between two particles is much larger than the diameter of the particles $2a$: the "Oseen approximation for the microscopic diffusion matrices".

- (4) Assume the two-particle level approach. Get the general form of the diffusion matrices. Show that if we stay cut the series at first order we get the "Rotne-Prager (RP) approximation".

B. Derive expressions for the velocity and pressure in a fluid that obeys the "Creeping flow equations" due to the action of external forces $\boldsymbol{f}^{ext}$: the Oseen tensor, and the pressure vector.

We assume the fluid obeys the so-called "Creeping flow equations" (aka "Stokes equations"), i.e.

$$-\nabla p(\boldsymbol{r}) + \eta_o \nabla^2 \boldsymbol{u}(\boldsymbol{r}) \;=\; 0 \tag{9}$$

$$\nabla \cdot \boldsymbol{u}(\boldsymbol{r}) = 0 \tag{10}$$

which are linear dif. equations.

If we have an external force acting on point $\boldsymbol{r}'$

$$\boldsymbol{f}^{ext} = f_o \; \delta(\boldsymbol{r} - \boldsymbol{r}'), \tag{11}$$

where the prefactor f_o is the total force acting on the fluid

$$f_o = \int d\boldsymbol{r}' \; \boldsymbol{f}^{ext}(\boldsymbol{r}'). \tag{12}$$

then, due to the linearity of the "Creeping flow equations" it is possible to show that velocity and pressure in the fluid will be proportional to f_o, ie

- $\boldsymbol{v}(r) \sim f_o$
- $p(r) \sim f_o$

and we can write this as the following equalities

- $\boldsymbol{v}(r) = \boldsymbol{T}(\boldsymbol{r} - \boldsymbol{r}') f_o$
- $p(r) = \boldsymbol{g}(\boldsymbol{r} - \boldsymbol{r}') f_o$

where

- $T(\boldsymbol{r} - \boldsymbol{r}')$ is known as the Oseen Tensor (because it seems that Oseen was the first to derive an expression for this tensor).
- $\boldsymbol{g}(\boldsymbol{r} - \boldsymbol{r}')$ is known as the pressure vector.

In short, the Oseen Tensor and the pressure vector are the Green's functions of the creeping flow equations.

Let's suppose now that our force is not just acting on $\boldsymbol{r}'$ but over the entire fluid, then, once again thanks to the linearity of the "Creeping equations" the velocity and pressure at one given point $\boldsymbol{r}$ is the sum of the contributions acting on that point that arise from all points of the fluid, i.e., we can write the velocity and pressure at point $\boldsymbol{r}$ as:

$$\boldsymbol{v}(\boldsymbol{r}) = \int d\boldsymbol{r}' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}^{ext}(\boldsymbol{r}') \tag{13}$$

$$p(\boldsymbol{r}) = \int d\boldsymbol{r}' \; \boldsymbol{g}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}^{ext}(\boldsymbol{r}') \tag{14}$$

By substituting previous expressions of $\boldsymbol{v}(\boldsymbol{r})$ and $p(\boldsymbol{r})$ into the creeping flow equations, we get (see B1.25)

$$\boldsymbol{T}(\boldsymbol{r}) = \frac{1}{8\ \pi\ \eta_o}\frac{1}{r}\left[\mathbf{1} + \frac{\boldsymbol{r}\boldsymbol{r}}{r^2}\right] \tag{15}$$

$$\boldsymbol{g}(\boldsymbol{r}) = \frac{1}{4\pi}\frac{\boldsymbol{r}}{r^3} \tag{16}$$

C. Suppose that the surface elements of the N colloidal spheres cause the external forces $\boldsymbol{f}^{ext}$ that act on the fluid, and we have stick boundary conditions on the surface of the particles.

Let's suppose we have N particles, and ∂V_j denotes the surface of the spheres. Therefore the velocity and pressure of the fluid at a point $\boldsymbol{r}$ is given by

$$\boldsymbol{v}(\boldsymbol{r}) = \sum_{j=1}^{N} \int_{\partial V_j} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_j(\boldsymbol{r}') \tag{17}$$

$$p(\boldsymbol{r}) = \sum_{j=1}^{N} \int_{\partial V_j} dS' \; \boldsymbol{g}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_j(\boldsymbol{r}') \tag{18}$$

where

- $\boldsymbol{f}_j$ is the force per unit area that a surface element dS' of the sphere j which is located at position $\boldsymbol{r}'$ exerts on the fluid.

We assume "stick boundary conditions", i.e. the velocity of the fluid at the sphere surfaces is the same than the velocity of the surfaces. This mathematically can be expressed as

$$\boldsymbol{v}_{particle} = \boldsymbol{v}_{fluid}(\boldsymbol{r}) \quad when \quad \boldsymbol{r} \in \partial V_i \tag{19}$$

$$\boldsymbol{v}_i + \boldsymbol{\Omega} \times (\boldsymbol{r}-\boldsymbol{r}_i) = \sum_{j=1}^{N} \int_{\partial V_j} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_j(\boldsymbol{r}') \quad when \quad \boldsymbol{r} \in \partial V_i \tag{20}$$

Due to symmetry (if there is no external torques) $\boldsymbol{\Omega} \times (\boldsymbol{r}-\boldsymbol{r}_i) = 0$. And we get

$$\boldsymbol{v}_i = \sum_{j=1}^{N} \int_{\partial V_j} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_j(\boldsymbol{r}') \quad when \quad \boldsymbol{r} \in \partial V_i \tag{21}$$

Now we can integrate the previous expression over the whole surface of particle ($\boldsymbol{r} \in \partial V_i$) and we get

$$\boldsymbol{v}_i = \frac{1}{4\pi a^2} \int_{\partial V_i} dS \int_{\partial V_i} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_i(\boldsymbol{r}') + \tag{22}$$

$$\frac{1}{4\pi a^2} \sum_{j \neq i}^{N} \int_{\partial V_i} dS \int_{\partial V_j} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_j(\boldsymbol{r}') \tag{23}$$

Since we now $\boldsymbol{T}$, we know that

$$\int_{\partial V_i} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') = \mathbf{1}\frac{2a}{3\eta_0} \quad for \quad \boldsymbol{r}' \in \partial V_i \tag{24}$$

and therefore

$$\int_{\partial V_i} dS \int_{\partial V_i} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_i(\boldsymbol{r}') \;=\; -\frac{1}{6\pi\eta_0 a}\boldsymbol{F}_i^h \tag{25}$$

$$\boldsymbol{F}_i^h(t) = -\int_{\partial V_i} dS' \boldsymbol{f}_i(\boldsymbol{r}') \tag{26}$$

i.e., $\boldsymbol{F}_i^h(t)$ is the total force that the fluid exerts on the particle i.

Now still we need to compute,

$$\frac{1}{4\pi a^2}\sum_{j\neq i}^{N} \int_{\partial V_i} dS \int_{\partial V_j} dS' \; \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot \boldsymbol{f}_j(\boldsymbol{r}') \tag{27}$$

Let's write it in terms of the position vectors of the centers of the spheres br_i and br_j and the local vectors $\boldsymbol{R} = \boldsymbol{r} - \boldsymbol{r}_i$ and $\boldsymbol{R}' = \boldsymbol{r}' - \boldsymbol{r}_j$, (plot B1.27), we can get for each term of the sum

$$\frac{1}{4\pi a^2} \int_{\partial V_i} dS \int_{\partial V_j} dS' \; \boldsymbol{T}(\boldsymbol{R}-\boldsymbol{R}'+\boldsymbol{r}_i-\boldsymbol{r}_j) \cdot \boldsymbol{f}_j(\boldsymbol{R}'+\boldsymbol{r}_j) \tag{28}$$

D. Simplify the Oseen tensor by assuming that the distance between two particles is much larger than the diameter of the particles $2a$: the "Oseen approximation for the microscopic diffusion matrices".

If $|\boldsymbol{R}-\boldsymbol{R}'|<2a$, then
$T(\boldsymbol{R}-\boldsymbol{R}'+\boldsymbol{r}_i-\boldsymbol{r}_j)\to T(\boldsymbol{r}_i-\boldsymbol{r}_j)$
we thus get for each term of the sum that

$$\frac{1}{4\pi a^2}\int_{\partial V_i} dS \int_{\partial V_j} dS'\ \boldsymbol{T}(\boldsymbol{r}-\boldsymbol{r}')\cdot\boldsymbol{f}_j(\boldsymbol{r}') \approx -\boldsymbol{T}(\boldsymbol{r}_i-\boldsymbol{r}_j)\cdot\boldsymbol{F}_j^h \tag{29}$$

Thus finally we get

$$\boldsymbol{v}_i = -\frac{1}{6\pi\eta_0 a}\boldsymbol{F}_i^h - \sum_{j\neq i}^{N}\boldsymbol{T}(\boldsymbol{r}_i-\boldsymbol{r}_j)\cdot\boldsymbol{F}_j^h \tag{30}$$

the diffusion matrix elements can be obtained by recalling that $\boldsymbol{D}_{ij}$ must satisfy

$$v_i = -\beta\sum_{j=1}^{N}\boldsymbol{D}_{ij}(\boldsymbol{X})\cdot\boldsymbol{F}_j^h \tag{31}$$

which leads to the "Oseen approximation for the microscopic diffusion matrices" if we just take the leading order expansion respect a/r_{ij}, namely

$$\boldsymbol{D}_{ii} \;=\; D_o\mathbf{1} \tag{32}$$

$$\boldsymbol{D}_{ij} \;\approx\; k_BT\ T(\boldsymbol{r}_i-\boldsymbol{r}_j) = \frac{3}{4}\ D_o\ \frac{a}{r_{ij}}\left[\mathbf{1}+\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}\right] \quad when \quad i\neq j \tag{33}$$

where $\boldsymbol{r}_{ij}=\boldsymbol{r}_i-\boldsymbol{r}_j$, and $D_o=k_BT/(6\pi\eta_o a)$ (the Stokes-Einstein diffusion coefficient). Remember this expression is only valid for large values of r_{ij} (i.e. small values of a/r_{ij}) otherwise we need to add more terms to the expansion.

E. Assume the two-particle level approach. Get the general form of the diffusion matrices. Show that if we stay cut the series at first order we get the "Rotne-Prager (RP) approximation"

If we assume that in the interaction between particle i and j no other of the $N-2$ particles is able to modify the interaction (i.e. low densities are assumed), then, in this two-particle approach it is possible to show that the general expressions for the diffusion matrices are

$$\boldsymbol{D}_{ii} = D_o\mathbf{1} + D_o\sum_{\substack{j=1,\\ j\neq i}}^{N}\left[A_s(r_{ij})\ \hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij} + B_s(r_{ij})\ \left[\mathbf{1} - \hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}\right]\right] \tag{34}$$

$$\boldsymbol{D}_{ij} = D_o\left[A_c(r_{ij})\ \hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij} + B_c(r_{ij})\ \left[\mathbf{1} - \hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij}\right]\right] \tag{35}$$

where the so called "mobility functions" (s=self, c=cross) are

$$A_s(r_{ij}) = -\frac{15}{4}\left(\frac{a}{r_{ij}}\right)^4 + \frac{11}{2}\left(\frac{a}{r_{ij}}\right)^6 + O\left(\left(\frac{a}{r_{ij}}\right)^8\right) \tag{36}$$

$$A_c(r_{ij}) = +\frac{3}{2}\left(\frac{a}{r_{ij}}\right) - \left(\frac{a}{r_{ij}}\right)^3 + \frac{75}{4}\left(\frac{a}{r_{ij}}\right)^7 + O\left(\left(\frac{a}{r_{ij}}\right)^9\right) \tag{37}$$

$$B_s(r_{ij}) = -\frac{17}{16}\left(\frac{a}{r_{ij}}\right)^6 + O\left(\left(\frac{a}{r_{ij}}\right)^8\right) \tag{38}$$

$$B_c(r_{ij}) = \frac{3}{4}\left(\frac{a}{r_{ij}}\right) + \frac{1}{2}\left(\frac{a}{r_{ij}}\right)^3 + O\left(\left(\frac{a}{r_{ij}}\right)^9\right) \tag{39}$$

$$\tag{40}$$

III. HOW TO GET THE "ERMAK-MCCAMMON SCHEME"

A. Steps we will do

- (1) Derivation of the Smoluchowski equation with HI
- (2) Recast the Smoluchowski equation in terms of the particle drift velocities $\boldsymbol{v}_i^D(\boldsymbol{X})$.
- (3) Assume that the time step $\tau \ll \tau_a$ and therefore the configuration has changed so little that $\boldsymbol{D}(\boldsymbol{X}) \approx \boldsymbol{D}(\boldsymbol{X}_o)$ and $\boldsymbol{v}_i^D(\boldsymbol{X}) \approx \boldsymbol{v}_i^D(\boldsymbol{X}_o)$. Get a solution for the simplified Smoluchowski equation.
- (4) Derive the finite difference algorithm.

B. Derivation of the Smoluchowski equation with HI

What we want to proof is that given a pdf $P(\boldsymbol{X},t)$ is governed by the equation

$$\frac{\partial P(\boldsymbol{X},t)}{\partial dt} = \hat{O}\ P(\boldsymbol{X},t) \tag{41}$$

$$\hat{O}\ (...) \equiv \sum_{i,j=1}^{N} \left[\nabla_{\boldsymbol{r}_i} \cdot \boldsymbol{D}_{i,j}(\boldsymbol{X}) \cdot \left(\beta\ (...)\ \nabla_{\boldsymbol{r}_j}\Phi(\boldsymbol{X}) + \nabla_{\boldsymbol{r}_j}\ (...)\right)\right] \tag{42}$$

There are different ways of getting the Smoluchowski equation with HI

- (a) Integration of the Liouville equation

$$\frac{\partial P(\boldsymbol{X},t)}{\partial dt} = \hat{L}\ P(\boldsymbol{X},t) \tag{43}$$

  where

$$\hat{L}\ (...) \equiv \sum_{j=1}^{N} \left[-\frac{\boldsymbol{p}_j}{m} \cdot \nabla_{\boldsymbol{r}_j}\ (...) + [\nabla_{\boldsymbol{r}_j}\Phi] \cdot \nabla_{\boldsymbol{p}_j}\ (...)\right] \tag{44}$$

  is the "Liouville operator". But integrating the Liouville equation respect the phase space coordinates and the momenta of the colloids is very involved (see JCP 54, 3547, (1971); JCP 57, 2098, (1972).)

- (b) As we will do ...

Let be now $\boldsymbol{X} = (\boldsymbol{r}_0,\ ...\ , \boldsymbol{r}_N)$ (only the positions). Then

$$N(t) = \int_W d\boldsymbol{X}\ P(\boldsymbol{X},t) \tag{45}$$

where W is an arbitrary volume of the positional phase space. Therefore, given that only the component of $d\boldsymbol{X}/dt$ can lead to a in-/out- flow of probability across the surface ∂W

$$\frac{dN(t)}{dt} = \int_W d\boldsymbol{X}\ \frac{\partial P(\boldsymbol{X},t)}{\partial t} = -\int_{\partial W} d\boldsymbol{S} \cdot \left[\frac{d\boldsymbol{X}}{dt}(\boldsymbol{X},t)\right] \tag{46}$$

Now using Gauss integral theorem

$$\int_W d\boldsymbol{X} \left[\frac{\partial P(\boldsymbol{X},t)}{\partial t} + \nabla_X \cdot \left[\frac{d\boldsymbol{X}}{dt} P(\boldsymbol{X},t)\right]\right] = 0 \tag{47}$$

where ∇_X is respect the 3N position coordinates. Given W is arbitrary, we get

$$\frac{\partial P(\boldsymbol{X},t)}{\partial t} = -\nabla_X \cdot \left[\frac{d\boldsymbol{X}}{dt} P(\boldsymbol{X},t)\right] \tag{48}$$

which can be rephrased as

$$\frac{\partial P(\boldsymbol{X},t)}{\partial t} = -\sum_{j=1}^{N} \nabla_{\boldsymbol{r}_j} \cdot \left[\boldsymbol{v}_j^{cg} P(\boldsymbol{X},t)\right] \tag{49}$$

where cg means coarse-grained to the diffusive time scale.

Ok. Now, what we need is an expression for the $\boldsymbol{v}_j^{cg}$.

Let's assume that in the scale we measure things the inertial forces are very small (relaxation has already passed) when compared to

- Forces arising from the total potential Φ
- The Brownian Force $\boldsymbol{F}_j^{brow}$
- forces due to the friction with the solvent $\boldsymbol{F}_j^{h}$ which make than when a fluid moves, it induces a fluid flow which affects other particles.

  Given, we assume "Creeping flow equations" to be valid, its linearity allows to say that the force acting on a sphere j must be linearly proportional to the velocities of all the other spheres, namely

  $$\boldsymbol{F}_j^{h} = -\sum_{i=1}^{N} \boldsymbol{B}_{ij} \cdot \boldsymbol{v}_j^{cg} \tag{50}$$

  where B is the "hydrodynamic friction tensor". In the case there is no hydrodynamics, then we just have

  $$\boldsymbol{B}_{ij} = \gamma\ \mathbf{1}\ \delta_{ij}^{Kronecker} \tag{51}$$

  i.e, the usual friction law.

Therefore, in the diffusive time scale, the sum of all previous forces must be zero

$$-\nabla_{\boldsymbol{r}_j}\Phi - \sum_{j=1}^{N} \boldsymbol{B}_{ij}\ \cdot\ \boldsymbol{v}_j^{cg} + \boldsymbol{F}_j^{brown} = 0 \tag{52}$$

which can be rewritten in the $3N$ momenta space notation X as

$$-\nabla_X\Phi - \boldsymbol{B}_{ij}\ \cdot\ \boldsymbol{v}^{cg} + \boldsymbol{F}^{brown} = 0 \tag{53}$$

where $\boldsymbol{v}^{cg} \equiv (\boldsymbol{v}_i^{cg},\ \ldots\ , \boldsymbol{v}_N^{cg})$, idem for $\boldsymbol{F}^{brown}$. If we define the "diffusion tensor" as

$$\boldsymbol{D} \equiv k_B T\ \boldsymbol{B}^{-1} \tag{54}$$

we can get by inverting the previous expression 53, and returning to the notation for each particle, that

$$\boldsymbol{v}_i^{cg} = \sum_{j=1}^{N} \boldsymbol{D}_{ij} \ \cdot \ \left[-\beta \nabla_{\boldsymbol{r}_j} \Phi + \beta \boldsymbol{F}_j^{brown}\right] \tag{55}$$

Thus, we get the following expression for the Smoluchowski equation

$$\frac{\partial P(\boldsymbol{X}, t)}{\partial dt} \ = \ \hat{O} \ P(\boldsymbol{X}, t) \tag{56}$$

$$\hat{O} \ (...) \ \equiv \ \sum_{i,j=1}^{N} \left[\nabla_{\boldsymbol{r}_i} \cdot \boldsymbol{D}_{i,j}(\boldsymbol{X}) \cdot \left(\beta \ (...) \ \nabla_{\boldsymbol{r}_j} \Phi(\boldsymbol{X}) + \nabla_{\boldsymbol{r}_j} \ (...)\right)\right] \tag{57}$$

aka "GSE= Generalized Smoluchowski equation with HI". Keep in mind that the previous equation you can just apply it on the Brownian time and length scales, when both particles and solvent are quasi-inertia-free.

C. Recast the Smoluchowski equation in terms of the particle drift velocities $\boldsymbol{v}_i^D(\boldsymbol{X})$.

The Smoluchowski equation

$$\frac{\partial P(\boldsymbol{X},t)}{\partial dt} = \hat{O}\ P(\boldsymbol{X},t) \tag{58}$$

$$\hat{O}\ (...) \equiv \sum_{i,j=1}^{N} \left[\nabla_{\boldsymbol{r}_i} \cdot \boldsymbol{D}_{i,j}(\boldsymbol{X}) \cdot \left(\beta\ (...)\ \nabla_{\boldsymbol{r}_j}\Phi(\boldsymbol{X}) + \nabla_{\boldsymbol{r}_j}\ (...)\right)\right] \tag{59}$$

can be recast as

$$\frac{\partial P(\boldsymbol{X},t)}{\partial t} = -\sum_{i=1}^{N} \nabla_i \cdot \left(\boldsymbol{v}_i^D(\boldsymbol{X})\ P(\boldsymbol{X},t)\right) + \sum_{i,j=1}^{N} \nabla_i \cdot [\nabla_j \cdot (\boldsymbol{D}_{i,j}\ P(\boldsymbol{X},t)] \tag{60}$$

$$\boldsymbol{v}_i^D(\boldsymbol{X}) \equiv \sum_{j=1}^{N} [\beta\ \boldsymbol{D}_{ij}(\boldsymbol{X})\ \boldsymbol{F}_j(\boldsymbol{X}) + \nabla_j \cdot \boldsymbol{D}_{ij}(\boldsymbol{X})] \tag{61}$$

where

- $\boldsymbol{v}_i^D(\boldsymbol{X})$ are the drift velocities. A new term arises due to hydrodynamics: $\sum_j \nabla_j \cdot \boldsymbol{D}_{ij}$, which physically acts as a repulsive force (tends to send particles to regions where they have more mobility).

Notice that

$$P_{eq}(\boldsymbol{X}) \equiv \frac{exp(-\beta\Phi(\boldsymbol{X}))}{Z} \tag{62}$$

where Z is the partition function, is a stationary solution of the Smoluchowski equation.

So what?

The last fact implies that Hydrodynamics do no have effect on static equilibrium properties !!! (within the approaches we have taken, keep that also in mind)

Your simulations without HI should give the correct equilibrium properties, no need of doing for them the costly HI simulations.

D. Assume that the time step $\tau \ll \tau_a$ and therefore the configuration has changed so little that $\boldsymbol{D}(\boldsymbol{X}) \approx \boldsymbol{D}(\boldsymbol{X}_o)$ and $\boldsymbol{v}_i^D(\boldsymbol{X}) \approx \boldsymbol{v}_i^D(\boldsymbol{X}_o)$. Get a solution for the simplified Smoluchowski equation.

In that case, the GSE reduces to a diffusion equation with constant coefficients, namely (in the $3N$ position space coordinates)

$$\frac{\partial P(\boldsymbol{X},\tau|\boldsymbol{X}_o)}{\partial t} \;=\; -\boldsymbol{v}^D(\boldsymbol{X}_o) \;\cdot\; \nabla P(\boldsymbol{X},\tau|\boldsymbol{X}_o) + \nabla\cdot[\nabla\cdot(\boldsymbol{D}(\boldsymbol{X}_o)\; P(\boldsymbol{X},\tau|\boldsymbol{X}_o) \tag{63}$$

It can be proof that the solution to the previous equation, if $P(\boldsymbol{X},0|\boldsymbol{X}_o) = \delta(\boldsymbol{X}-\boldsymbol{X}_o)$ is

$$P_{sol-delta}(\boldsymbol{X},\tau|\boldsymbol{X}_o) \;=\; \frac{(4\pi\tau)^{-3N/2}}{\sqrt{det(\boldsymbol{D}(\boldsymbol{X}_o))}}\; exp\left(\frac{-1}{4\tau}\right. \tag{64}$$

$$\left.[\boldsymbol{X}-\boldsymbol{X}_o-\tau\boldsymbol{v}^D(\boldsymbol{X}_o)]^T\cdot D^{-1}(\boldsymbol{X}_0)\cdot[\boldsymbol{X}-\boldsymbol{X}_o-\tau\boldsymbol{v}^D(\boldsymbol{X}_o)]\right) \tag{65}$$

which is a Gaussian.

E. Derive the finite difference algorithm.

We can see that the true solution for our system will be

$$P(\boldsymbol{X},\tau|\boldsymbol{X}_o) = P_{sol-delta}(\boldsymbol{X},\tau|\boldsymbol{X}_o) + o(\tau) \tag{66}$$

therefore we get the momentum relations

$$\langle(\boldsymbol{X}-\boldsymbol{X}_o)\rangle_o \;=\; \boldsymbol{v}_i^D(\boldsymbol{X}_o)\tau + o(\tau) \tag{67}$$

$$\left\langle(\boldsymbol{X}-\boldsymbol{X}_o)^2\right\rangle_o \;=\; 2\boldsymbol{D}_{ij}^D(\boldsymbol{X}_o)\tau + o(\tau) \tag{68}$$

which can be proof that what we have then is stochastically equivalent, in the limit $\tau \to 0$ to the "Ermak-McCammon scheme"

$$\boldsymbol{r}_i(t_0+\tau) = \boldsymbol{r}_i(t_o) + v_i^D(\boldsymbol{X}_o)\tau + (2\tau)^{1/2}\boldsymbol{d}(\boldsymbol{X}_o)\cdot\boldsymbol{n} + o(\tau) \tag{69}$$

where

$$v_i^D(\boldsymbol{X}_o) = \sum_{j=1}^{N}\left[\beta\boldsymbol{D}_{ij}(\boldsymbol{X}_o)\cdot\boldsymbol{f}_j(\boldsymbol{X}_o) + \nabla_j\cdot\boldsymbol{D}_{ij}(\boldsymbol{X}_o)\right] \tag{70}$$