Langevin Brownian dynamics simulation of Hard Spheres

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Introduction

Motivation: Colloidal Hard Spheres

Methods: Image method for reflecting boundary conditions

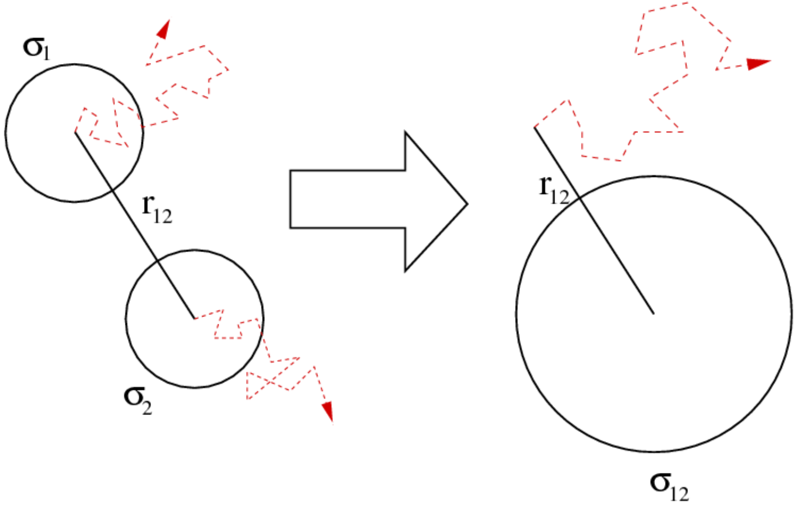
Tools: Event-Driven Molecular-Dynamics simulations

1. Integration of the Overdamped Langevin equation for Hard-Spheres
2. Integration of the Langevin equation for Hard-Spheres

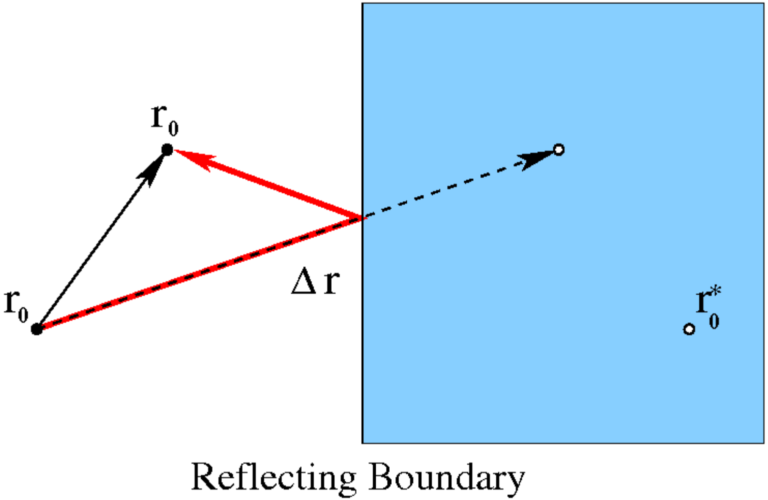
Our Main Steps to approximate Overdamped BD

1. Consider small steps such that collisions are mainly binary
2. Transform sphere-sphere collision in free diffusion + reflecting boundary problem
3. Consider steps small enough to consider the reflecting boundary flat

From two body to free diffusion with reflecting boundary



Flat Reflecting Boundary solution via Image Charge Method



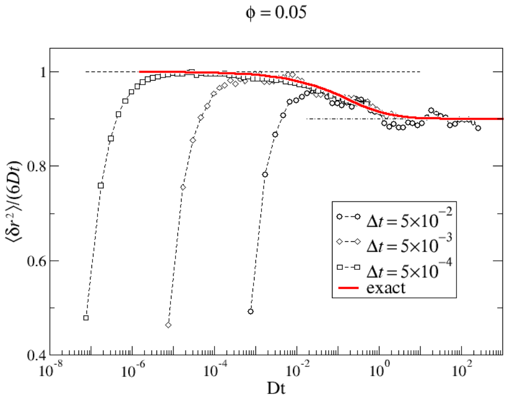
Algorithm for Overdamped BD

Use *Event Driven Molecular Dynamics* (***EDMD***) Codes !!!

- extract displacements Δr_i according to free diffusion
- define fictive velocities $v_i^{fake} = \Delta r_i / \Delta t$
- perform ***EDMD*** between t and $t + \Delta t$ using fictive velocities

For polydisperse systems, do collisions with fictive masses $\propto D_i^{-1}$
Easily implemented fixed boundaries
Easily calculated Pressure and Stress Tensor

Simulations



Tested to packing fractions up to $\phi = 0.50$

Scala - Voigtmann - de Michele , J Chem Phys 126 , 2007

Kramers Equations

The Langevin equation

$$\begin{cases} \partial_t \mathbf{v}_i & = & -\gamma \mathbf{v}_i + \mathbf{a_i} + \boldsymbol{\xi_i} \\ \partial_t \boldsymbol{r}_i & = & \mathbf{v}_i \end{cases}$$

contains singular terms in the case of ***Hard Spheres*** and standard integrators are ill defined.
We therefore start from the associated Fokker-Plank equation for the PDF $W(\mathbf{r}, \mathbf{v}, t)$

$$\partial_t W = \left[\gamma \left(\partial_{\mathbf{v}} \cdot \mathbf{v} + v_{th}^2 \partial_{\mathbf{v}}^2 \right) - \left(\mathbf{v} \cdot \partial_{\mathbf{r}} + \mathbf{a} \cdot \partial_{\mathbf{v}} \right) \right] W = \mathbf{L}_K W$$

Trotterization

We approximate the true propagator $e^{\mathbf{L}_K \Delta t} \simeq e^{\mathbf{L}_{rev} \Delta t} e^{\mathbf{L}_{irr} \Delta t}$ with the splitting $\mathbf{L}_K = \mathbf{L}_{rev} + \mathbf{L}_{irr}$:

- $\mathbf{L}_{rev} = -\left(\mathbf{v} \cdot \partial_{\mathbf{r}} + \mathbf{a} \cdot \partial_{\mathbf{v}}\right)$ is the ***Hard Spheres Liouvillian***
- $\mathbf{L}_{irr} = \gamma \left(\partial_{\mathbf{v}} \cdot \mathbf{v} + v_{th}^2 \partial_{\mathbf{v}}^2\right)$ damps and thermalizes velocities

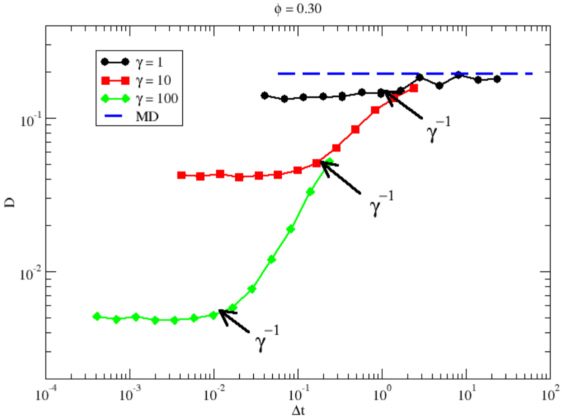
One single timestep of such *Splitted Brownian Dynamics* (***SBD***) consists in

1. $e^{\mathbf{L}_{rev} \Delta t}$: an *Event Driven Molecular Dynamic* (***EDMD***) step of length Δt
2. $e^{\mathbf{L}_{irr} \Delta t}$: the following damping and thermalization of the velocities.

SBD explores the correct ensemble for ***Hard Spheres***.

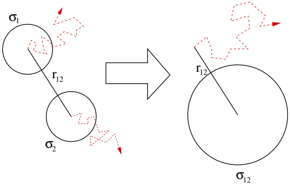
Overdamped limit for *SBD*

Effect of the damping coefficient γ on the size of the ***SBD*** simulation step Δt. The "true" value of D is obtained only for $\Delta t \ll \gamma^{-1}$. A completely analogous behavior is found at a low packing fraction $\phi = 0.10$ and an high packing fraction $\phi = 0.45$.

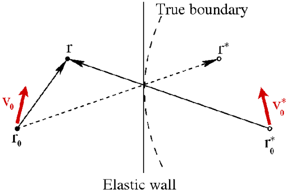


Logical steps for an *Image Method Brownian Dynamics* (***IMBD***) :

1. Consider average free displacement $\langle|\Delta r_{free}|\rangle \ll$ average distance among particles in order to consider only two body interactions
2. Map two body dynamics to one ***point*** + one ***Hard Sphere***



3. If $\langle|\Delta r_{free}|\rangle \ll$ ***Hard Sphere radius***, the point interacts with an elastic wall and the image method can be applied

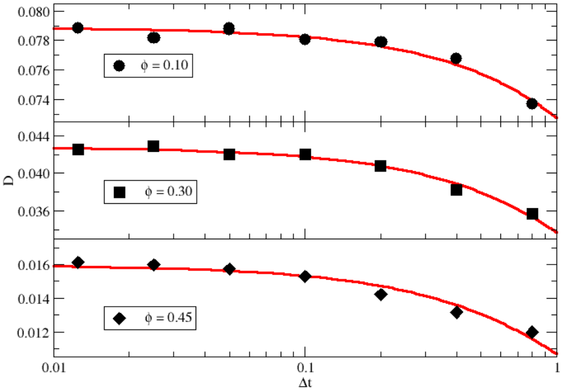


IMBD can be easily implemented from an *EDMD* code

1. Extract random displacements $\Delta \mathbf{r}_i \left(\mathbf{v}_i \left(t \right), \Delta t \right)$ according to the free particle dynamics; define ***fictive velocities*** $\mathbf{v}_i^{fake} = \Delta \mathbf{r}_i / \Delta t$
2. Use $\mathbf{v}_i^{fake}$ to perform a standard EDMD simulation for a timestep Δt ; during collisions, reflect BOTH $\mathbf{v}_i^{fake}$ and $\mathbf{v}_i \left(t \right)$
3. Thermalize: $\mathbf{v}_i \left(t + \Delta t \right) = e^{-\gamma \Delta t} \mathbf{v}_i \left(t \right) + \textit{thermal noise}$

Again, ***IMBD*** explores the correct ensemble for ***Hard Spheres***.

At difference with ***SBD***, ***IMBD*** predicts correct values of D for $\Delta t \lesssim 0.1$ regardless of damping γ and packing fraction ϕ.



To-do list

IMBD recovers the ED algorithm for OBD in the limit $\gamma \to \infty$

SBD and ***IMBD*** can be easily generalized to

1. take account of **Constant Fields**
2. take account of **Polydispersity**

IMBD should be generalized to

1. take account of **Non Constant Fields**
2. take account of **Shear**
3. take care of **non-spherical hard particles**