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From the Liouville to the Smoluchowski equation for a colloidal solute particle in a solvent

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HIGHLIGHTS

- We reach the Smoluchowski dynamics of a colloidal Brownian particle suspended in a molecular solvent starting from the microscopic Liouvillian evolution of the full classical model in the high friction limit.
- The integration of the solvent degrees of freedom goes through a multiple time scale perturbation expansion which removes the secular divergences.
- A simple dynamical Monte Carlo scheme is then proposed to solve the resulting evolution equation for the colloid solute particle.
- In particular we study the approach to the equilibrium Boltzmann distribution at late times and its resilience behavior at shorter times.

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ABSTRACT

We show how the Smoluchowski dynamics of a colloidal Brownian particle suspended in a molecular solvent can be reached starting from the microscopic Liouvillian evolution of the full classical model in the high friction limit. The integration of the solvent degrees of freedom goes through a multiple time scale perturbation expansion which removes the secular divergences. A simple dynamical Monte Carlo scheme is then proposed to solve the resulting evolution equation for the colloid solute particle. In particular we study the approach to the equilibrium Boltzmann distribution at late times and its resilience behavior at shorter times as influenced by the steepness of the external potential and the friction coefficient around their respective minima. This is very important to understand the fate of the Brownian particle's random walk and its evolution history.

1. Introduction

The dynamics of a many-body system can be given in terms of the time evolution of the probability phase space density of the chosen ensemble of particles. We must require that the total time derivative of the probability density vanishes so that the probability density as seen by an observer moving with a phase point along its phase space trajectory, is independent of time. Phase points of the statistical ensemble are neither created nor destroyed as time evolves.

The Liouvillian dynamics gives rise to the famous kinetic equation discovered by Boltzmann in 1872 (where the assumption of two body collisions only and of uncorrelated successive collisions are only valid at sufficiently low density) or to the exact Born–Bogoliubov–Green–Kirkwood–Yvon (BBGKY) hierarchical equations.

According to BBGKY the dynamics of a single particle requires the knowledge of the two-body probability density. But if we additionally require that the particle we are looking upon has mass much larger than that of all the other particles it is

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possible to expand perturbatively such dynamics so to find a closed equation for just the single massive particle probability phase space density.

A colloidal suspension is made of colloidal particles immersed in a solvent. The solvent (which may be water or other liquids) is in general a molecular liquid which can be described at a microscopic level by particles much smaller and lighter than the macromolecular colloidal particle. The problem of the dynamics of the big colloidal solute particle subject to its interaction with the smaller solvent molecules in statistical equilibrium at a given absolute temperature T is an interesting one. Starting from the observation in 1827 by Robert Brown of the motion of pollen grains in water and the interpretation of Albert Einstein in 1905 which was later verified experimentally by Jean Baptiste Perrin in 1908, the Brownian motion began to occupy an important role in non-equilibrium statistical physics. Even if the initial description of the colloid solute particle dynamics was an empirical one it soon became clear the microscopic origin of the Brownian motion. A complete microscopic description has to take into account the solvent in a proper way. The challenge is to be able to "remove" the degrees of freedom of the solvent in favor of the ones of the solute particle. So as to have a mesoscopic description of the dynamics of the colloid solute particle dressed by the solvent.

In the second half of last century it had been discovered [1] that it is indeed possible to derive the Brownian motion equations starting from the Liouvillian evolution, $\mathcal{L} \equiv i\{\mathcal{H}, \ldots\}$, with $\{\ldots\}$ the Poisson brackets and $\mathcal{H}$ the model classical Hamiltonian, of the probability density in the phase space of a model of N solvent particles and the colloidal particle, $f^{[N+1]}(t) = \exp(-i\mathcal{L}t)f^{[N+1]}(0)$, to the Fokker–Planck equation [2,3] for the dynamics of the dressed solute particle alone subject to friction. The friction coefficient ξ is expressed in terms of an equilibrium average over the phase space of the solvent in the external field of the solute particle of a particular term containing the microscopic force exerted by the solvent on the colloidal particle. At the end of last century it was shown furthermore that a high friction expansion, in turn, brings [4] to the Smoluchowski equation for the colloid solute particle or its equivalent stochastic Langevin equation. Some related literature to the present framework can be found in the following references [5–8].

It this work we outline a simple Monte Carlo scheme that may be used to solve the resulting Smoluchowski equation that we call Dynamical Monte Carlo (DynMC). The realistic case of a colloidal suspension of poly(methyl methacrylate) (PMMA) particles in water [9] is taken as an example. In particular we study the approach to the equilibrium Boltzmann distribution at late times and its resilience behavior at shorter times as influenced by the steepness of the external potential and the friction coefficient around their respective minima. This is very important to understand the fate of the Brownian particle's random walk and its evolution history. We test our new algorithm on the case of a harmonic one dimensional external potential for which the analytic exact solution of the Smoluchowski equation is known.

Of course a more realistic treatment of the molecular solvent would be through a quantum statistical mechanics description where $\mathcal{L} \equiv i[\hat{\mathcal{H}}, \ldots]/\hbar$, with $[\ldots]$ the commutator and $\hat{\mathcal{H}}$ the model Hamiltonian operator. Then we would have a mixed evolution where the solvent is treated quantum mechanically and the massive colloid solute particle is treated classically (see for example Ref. [10] or Ref. [11] where the full quantum mechanical treatment is considered). We leave this as an open future problem.

The paper is organized as follows: In Section 2 we present the reduction from the Liouville equation to the Fokker–Planck equation, in Section 3 we present the reduction from the Fokker–Planck equation to the Smoluchowski equation, in Section 4 we present the Dynamical Monte Carlo algorithm (DynMC), in Section 5 we carry on a computer experiment with the newly developed algorithm to solve for the time dependence of the mean Brownian particle position under the influence of an external harmonic potential in one spatial solution, Section 6 is for final remarks.

2. From the Liouville to the Fokker–Planck equation

In this section we will reproduce and discuss the multiple time scale perturbation expansion presented in Ref. [12] which brings from the microscopic Liouville equation for a solute particle in a solvent to its mesoscopic Fokker–Planck equation.

We consider a colloidal solute particle of diameter Σ and mass M immersed in a colloidal suspension of small solvent particles of diameter σ and mass $m \ll M$. The Hamiltonian of the system of $N+1$ particles can thus be written as

$$\mathcal{H} = \frac{P^2}{2M} + \sum_{i=1}^{N} \frac{p_i^2}{2m} + V_N(\mathbf{r}^N) + V_b(\mathbf{R}, \mathbf{r}^N), \tag{1}$$

where V_N is the total interaction energy of the N solvent particles of coordinates $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and momenta $\mathbf{p}^N = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$, and V_b is the potential energy of the solvent particles in the field of a Brownian solute particle placed at $\mathbf{R}$ with momentum $\mathbf{P}$. The Liouville operator splits naturally into a solvent and a Brownian terms: $\mathcal{L} = \mathcal{L}_s + \mathcal{L}_b$, with

$$\mathcal{L}_s = -i \sum_{i=1}^{N} \left(\frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{f}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right), \tag{2}$$

$$\mathcal{L}_b = -i \left(\frac{\mathbf{P}}{M} \cdot \frac{\partial}{\partial \mathbf{R}} + \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{P}} \right), \tag{3}$$