Momentum conserving Brownian dynamics propagator for complex soft matter fluids

Citation for published version (APA):

DOI:
10.1063/1.4904315

Document status and date:
Published: 01/01/2014

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Download date: 26. Oct. 2020
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Citation: The Journal of Chemical Physics 141, 244108 (2014); doi: 10.1063/1.4904315
View online: http://dx.doi.org/10.1063/1.4904315
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/141/24?ver=pdcov
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Momentum conserving Brownian dynamics propagator for complex soft matter fluids

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(Received 17 October 2014; accepted 4 December 2014; published online 24 December 2014)

We present a Galilean invariant, momentum conserving first order Brownian dynamics scheme for coarse-grained simulations of highly frictional soft matter systems. Friction forces are taken to be with respect to moving background material. The motion of the background material is described by locally averaged velocities in the neighborhood of the dissolved coarse coordinates. The velocity variables are updated by a momentum conserving scheme. The properties of the stochastic updates are derived through the Chapman-Kolmogorov and Fokker-Planck equations for the evolution of the probability distribution of coarse-grained position and velocity variables, by requiring the equilibrium distribution to be a stationary solution. We test our new scheme on concentrated star polymer solutions and find that the transverse current and velocity time auto-correlation functions behave as expected from hydrodynamics. In particular, the velocity auto-correlation functions display a long time tail in complete agreement with hydrodynamics. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4904315]

I. INTRODUCTION

Soft matter usually consists of deformable mesoscopic particles, either in the molten state or dissolved in appropriate solvents. Typically, the particles have sizes much larger than those of ordinary molecules but still small enough to be influenced by thermal fluctuations. The dynamics of these particles can in principle be calculated by solving the coupled deterministic equations of motion for all atoms in the system through molecular dynamics simulations. However, because of the large number of atoms needed to guarantee a faithful representation of the system (typically several orders of magnitude larger than with fluids composed of simple molecules), in practice, such calculations are not feasible. We may therefore focus on the motion of a limited set of so called coarse-grain coordinates, such as, for example, the centres-of-mass of the mesoscopic particles. Two systems with identical coarse-grain coordinates, but with slightly different values for the remaining degrees of freedom, the eliminated coordinates, in general, will have different time sequences of their coarse-grain coordinates. This behavior can be mimicked by using stochastic differential equations for the dynamics of the coarse grain coordinates. The two best-known examples are the Langevin equation and the Brownian dynamics equations.

The Langevin equation is a second order stochastic differential equation, including a friction force proportional to the velocity of the coarse-grain coordinate of the mesoscopic particle, and a random force with well-defined statistical properties. If the friction is relatively large, and the coarse-grain configuration hardly changes during the time needed to thermalize the coarse-grain velocities, we may update the coarse-grain coordinates through a first order stochastic differential equation. The latter is what we refer to as Brownian dynamics. In computer simulations of highly overdamped soft matter systems, the Brownian dynamics propagator is much more attractive than the Langevin dynamics propagator because much larger time steps may be used in the large friction limit.

The standard Langevin and Brownian dynamics propagators usually do not take into account the possibility of flow of the simulated soft matter fluid. In these cases, the equations of motion may be augmented with a term that accounts for the influence of the background fluid flow, representing the average velocity of the eliminated degrees of freedom. This is done either by assuming that the friction force is proportional to the difference between the velocity of the coarse-grain coordinate and the velocity of the background fluid (Langevin equation) or by adding the displacement of the background fluid velocity to the update of the coarse-grain position (Brownian dynamics). Usually the background flow field is assumed to be given and imposed on the particles. As a result, the coupling between the coarse-grain displacements and the background fluid is a one-way coupling: the coarse-grain motion is influenced by the fluid flow, but the fluid flow is not influenced by the interaction with the coarse-grain coordinates. This precludes the use of standard Langevin and Brownian dynamics propagators in situations where the flow of the soft matter system cannot be predicted beforehand, such as when dealing with interfaces or non-uniform flow.

In this paper, we will introduce a first order Brownian dynamics algorithm with a two-way coupling between coarse-grain motion and background fluid flow. In our previous works on Brownian dynamics simulations of soft matter systems such as wormlike micelles, core-shell particles, and telechelic polymers, we already performed a temporal
and spatial smoothing of particle displacements in flow oriented layers, with the goal to investigate possible shear banding in shear flow simulations. The method presented in the current paper is more general and can be applied to any type of flow. The algorithm is not derived from a microscopic basis, but a phenomenological description, which fulfills the constraints of Galilei invariance and local momentum conservation. In short, we suggest to keep track of an additional set of variables representing the locally averaged velocities of the eliminated degrees of freedom near the tracked particles. Because the velocity updates are Galilei invariant and momentum conserving, hydrodynamics will be preserved. We demonstrate this by obtaining time correlation functions with hydrodynamic, i.e., algebraic time tails. We leave the development of appropriate boundary conditions for future work.

II. STANDARD LANGEVIN DYNAMICS AND BROWNIAN DYNAMICS

We will first shortly review Langevin and Brownian dynamics. Usually these methods are introduced/motivated in the context of colloidal particles moving through a Newtonian fluid. We will take the same approach here, with the understanding that the “fluid” is a more general object that represents all eliminated degrees of freedom, such as in the case of a star polymer moving through a sea of polymeric arms.

Consider a mesoscopic particle \( i \) of mass \( M_i \) moving through a fluid. The particle will continually collide with the fluid molecules. Because on average, it will collide more often on the front side than on the back side, it will experience a systematic friction force proportional to its velocity. The constant of proportionality is defined as the friction coefficient \( \xi_i \), which is a system inhomogeneities (or near boundaries) possibly depends on the position \( \mathbf{R}_i \) of the particle. Besides the systematic force, the particle will experience a random force \( \mathbf{F}_i^R \) and an external force \( \mathbf{F}_i \) caused by interactions with neighbouring particles or external fields. The equation of motion is then given by the following Langevin equation:

\[
M_i \frac{d^2 \mathbf{R}_i(t)}{dt^2} = -\xi_i \frac{d\mathbf{R}_i(t)}{dt} + \mathbf{F}_i(t) + \mathbf{F}_i^R(t),
\]

where the random force \( \mathbf{F}_i^R \) has a zero average and a second moment given by

\[
\langle \mathbf{F}_i^R(t)\mathbf{F}_i^R(t') \rangle = 2k_B T \xi_i \delta_{i,j} \delta(t-t').
\]

Numerical integration of the above equations may be done through a number of schemes, ranging from a simple Verlet-like algorithm (where it should be noted that the accuracy drops due to the \( -\xi_i \frac{d\mathbf{R}_i}{dt} \) term) to a more sophisticated scheme where the equations are pre-integrated under the assumption that the external force \( \mathbf{F}_i \) is constant during one time step.\(^{1,7}\)

If the configuration hardly changes during the time needed to thermalize the velocities, i.e., in the highly overdamped limit, the computational efficiency may be increased dramatically by updating only the positions through a first order Brownian dynamics scheme. Such a scheme may be derived from the underlying Langevin equation\(^{8,9}\) and reads for a time step \( dt \)

\[
d\mathbf{R}_i(t) = \frac{\mathbf{F}_i(t)}{\xi_i} dt + k_B T \frac{\partial}{\partial \mathbf{R}_i} \left( \frac{1}{\xi_i} \right) dt + d\mathbf{W}_i^R.
\]

The second term on the right-hand side occurs naturally from the derivation presented by Ermack and McCammon.\(^8\) With the Ito approach\(^8\) adopted in this paper, it is needed to correct for spurious drifts occurring in inhomogeneous systems with position dependent friction coefficients. Notice that \( k_B T \) is in front of the derivative. Only then the generalized flux occurring in the Fokker-Planck equation (see Appendix) acquires a term proportional to the gradient of the temperature, which is needed to describe thermophoretic effects. For further details about phoretic effects, we refer to Ref. 10. The term \( d\mathbf{W}_i^R \) in Eq. (3) is an uncorrelated random displacement of particle \( i \) related to the friction through

\[
\langle d\mathbf{W}_i^R d\mathbf{W}_j^R \rangle = \frac{2k_B T}{\xi_i} \delta_{i,j} dt.
\]

We emphasize that, for a given system, the friction coefficient \( \xi_i \) in the first order Brownian dynamics update is the same as the friction coefficient \( \xi_i \) appearing in the Langevin equation. Note that with large frictions a (naive) Langevin update scales as \( \xi_i dt \), whereas the Brownian update scales as \( dt/\xi_i \). This is the reason why for highly overdamped situations, a first order Brownian propagator is more attractive than a second order Langevin propagator.

When dealing with flow, we must adapt the equations. The Langevin equation is usually altered as follows:

\[
M_i \frac{d^2 \mathbf{R}_i(t)}{dt^2} = -\xi_i \left[ \frac{d\mathbf{R}_i(t)}{dt} - \mathbf{v}(\mathbf{R}_i(t)) \right] + \mathbf{F}_i(t) + \mathbf{F}_i^R(t)
\]

leading to a similar augmentation to the Brownian dynamics propagator

\[
d\mathbf{R}_i(t) = \mathbf{v}(\mathbf{R}_i(t)) dt + \mathbf{F}_i(t) dt + k_B T \frac{\partial}{\partial \mathbf{R}_i} \left( \frac{1}{\xi_i} \right) dt + d\mathbf{W}_i^R.
\]

In both cases, \( \mathbf{v}(\mathbf{R}_i) \) is the local flow velocity at the location of particle \( i \). In the usual approach, \( \mathbf{v}(\mathbf{R}) \) must be pre-determined, for example, assuming affine flow between two moving walls. This precludes the use of first-order Brownian dynamics in situations where the flow cannot be predicted beforehand, for example, when dealing with interfaces or non-uniform flow such as shear-banding flow.

III. LOCAL VELOCITY FIELD

From a coarse-graining point-of-view, \( \mathbf{v}(\mathbf{R}_i) \) should be equal to the locally averaged velocity field of the eliminated coordinates. We will describe a way to dynamically update the local flow velocity in a simulation of a relatively dense collection of Brownian particles with a large friction with the eliminated coordinates, which we will refer to as the background fluid. The local velocity of the background fluid will homogenise through mutual friction and respond slowly
to body forces by associating a relaxation time with the background fluid. We can interpret the mutual friction and relaxation time as an effective kinematic viscosity of the background fluid.

Since we intend our method to be applicable to flowing systems, we seek for inspiration by considering the background flow to be described by the continuum equations for the velocity field \( \mathbf{v}(\mathbf{r}) \) of a Newtonian fluid

\[
\frac{D\mathbf{v}}{Dt}(\mathbf{r}) = \nu \nabla^2 \mathbf{v}(\mathbf{r}) + \mathbf{g}(\mathbf{r}). \tag{7}
\]

Here, \( D/Dr \) is the total (material) derivative, \( \nu \) is the kinematic viscosity of the background fluid, which we will assume constant in our approach, and \( \mathbf{g} \) is the acceleration due to body forces, which in this case are the forces exerted by the coarse-grain particles on the background fluid. Because we have assumed that the coupling between the coarse-grain particles and the background fluid is very large, either by a large friction (\( \xi \)) or by the very definition of the coarse degree of freedom, the force \( \mathbf{F}_i \) exerted on a coarse-grained particle, either by external fields or direct interactions with neighboring coarse-grained particles, is almost immediately transferred locally to the background fluid. The fluid acceleration due to such forces is therefore given by

\[
\mathbf{g}(\mathbf{r}) = \sum_i \mathbf{F}_i \frac{\delta(\mathbf{r} - \mathbf{R}_i)}{\rho(\mathbf{r})}. \tag{8}
\]

where \( \rho(\mathbf{r}) \) is the local mass density of the background fluid.

### A. Representation of the local velocity field

To dynamically update the background fluid velocity field, we first need to decide how we will numerically represent this velocity field. One option is to use an Eulerian grid to store the velocity values at regular positions, essentially solving a discretised version of Eq. (7). We will not use such a direct numerical simulation approach here.

Rather, inspired by Smoothed Particle Hydrodynamics (SPH), we will make use of the coarse-grain particle positions already available to us. We will associate with each coarse-grain particle \( i \) a velocity \( \mathbf{v}_i \). We emphasize that \( \mathbf{v}_i \) is not the instantaneous velocity of coarse-grain particle \( i \), but rather a representation of the average velocity of the eliminated coordinates in a volume element in the immediate vicinity of coarse-grain particle \( i \). We will use the particular representation for which \( \mathbf{v}_i \) is the extrapolation of the velocity field of the background flow to the position \( \mathbf{R}_i \) of particle \( i \). As a result, we have

\[
\frac{D\mathbf{v}}{Dt}(\mathbf{R}_i) = \frac{d\mathbf{v}_i}{dt}. \tag{9}
\]

According to the meaning of the material derivative, the left hand side is the acceleration of a background material element at position \( \mathbf{R}_i \) along its path, i.e., its Lagrangian acceleration; similarly, the right hand side is the acceleration of an embedded tracer particle. This is very similar to what experimentalists do when they visualize flow fields by dispersing observable particles in the fluid.

### B. Acceleration due to body forces

The acceleration, \( \mathbf{g}(\mathbf{R}_i) \), due to body forces acting on volume element \( i \) in the immediate vicinity of coarse-grain particle \( i \) is given by Eq. (8). We reiterate that, because of the strong coupling between coarse degrees of freedom and the background fluid, external forces \( \mathbf{F}_i \) acting on the coarse-grain particles are immediately transferred to the background fluid. Since we do not explicitly model the background fluid, we must integrate Eq. (8) over a small volume surrounding particle \( i \) to relate the external force \( \mathbf{F}_i \) to an acceleration of the background fluid at the location of coarse-grain particle \( i \), obtaining

\[
\mathbf{g}(\mathbf{R}_i) = \frac{\mathbf{F}_i}{m_i}. \tag{10}
\]

The effective mass, \( m_i \), serves as a parameter coupling the force \( \mathbf{F}_i \) to the acceleration of the background fluid. We will argue later how the effective mass can be related to the friction \( \xi_i \).

### C. Viscous damping

In a Newtonian liquid, viscous damping is proportional to the second derivative \( \nabla^2 \mathbf{v} \) of the velocity field. Brookshaw\(^{11}\) suggested a finite-difference-like form for the second derivative of any field function near the position of particle \( i \). For reasons that we will explain in Sec. IV, we have symmetrised the proposed expression resulting in

\[
\nu \nabla^2 \mathbf{v}(\mathbf{R}_i) = \nu \sum_{j=1}^{N} m_j \left( \frac{1}{\rho_i} + \frac{1}{\rho_j} \right) (\mathbf{v}_i - \mathbf{v}_j) \frac{1}{R_{ij}} \frac{dw(R_{ij})}{dr}, \tag{11}
\]

where \( w(r) \) is a normalized weight function of range \( R_c \), and \( R_{ij} = |\mathbf{R}_i - \mathbf{R}_j| \) is the distance between particles \( i \) and \( j \). As in Ref. 11, we weight the contribution from particle \( j \) with its mass \( m_j \), where now \( m_j \) is the effective mass introduced in Subsection III B. Similarly, we denote the local effective mass density near particle \( j \) as \( \rho_j \)

\[
\rho_j = \sum_{k=1}^{N} m_k w(R_{kj}). \tag{12}
\]

The sum includes the term \( k = j \). Basa et al.\(^{12}\) showed that Eq. (11) is the best among different available schemes in smooth particle hydrodynamics for approximation of the second derivatives.

The proportionality constant \( \nu \) in Eq. (11) is the kinematic viscosity of the background fluid. We define

\[
\nu = \frac{R_c^2}{28\tau}. \tag{13}
\]

where \( R_c \) is the range of the weight function \( w(r) \) and \( \tau \) is a new parameter characterizing the relaxation time for momentum diffusion in the background fluid over a length scale of the order of \( R_c \) (to be precise, the length scale is \( \sqrt{2\pi\tau} \approx 0.27 R_c \)). The appearance of the factor 28 is connected to a particular interpretation of the parameter \( \tau \) discussed in Subsection V B.
In Sec. IV, we will first state the algorithm for particle positions and local velocity updates. After this, we will give arguments for the choice of the parameters $R_c$, $\tau$, and $m_i$.

IV. UPDATE OF THE PARTICLE POSITIONS AND LOCAL VELOCITIES

A. Update of particle positions

In our new Brownian dynamics scheme, the position of particle $i$ is updated similarly to the standard Brownian dynamics algorithm described in Sec. II, where we now use an additional variable $v_i$ to store and update the flow field of the eliminated coordinates in the vicinity of particle $i$. The total displacement of particle $i$ in a time step $dr$ is given by

$$d\mathbf{R}_i(t) = v_i(t)dt + \frac{F_i(t)}{\xi_i}dt + k_BT \frac{1}{\xi_i} \frac{\partial}{\partial \mathbf{R}_i} \left( \frac{1}{\xi_i} \right) dt + dW^R_i,$$

(14)

where $dW^R_i$ is a random displacement of particle $i$ which we will specify later. As before, $\xi_i$ must be clearly identified as the friction on particle $i$ due to its motion relative to the eliminated coordinates moving with velocity $v_i$. This is conceptually in agreement with the original Brownian dynamics propagator, where the friction $\xi_i$ is due to the motion of particle $i$ relative to the fixed background velocity profile.

B. Update of local velocities

Motivated by the discussion in Sec. III, we update the velocity $v_i$ of the background fluid near particle $i$ as

$$dv_i(t) = \frac{F_i(t)}{m_i}dt + \sum_{j=1}^{N} f_{ij} (v_j(t) - v_i(t)) dr + \sum_{j=1}^{N} dW^v_{ij},$$

(15)

Below, we will argue that the effective mass $m_i$ should be chosen equal to the product of friction and relaxation time $\tau$, i.e.,

$$m_i = \xi_i \tau,$$

(16)

leaving only two parameters, $\tau$ and $R_c$, to be set.

The factor $f_{ij}$ in Eq. (15) is a dimensionless friction factor between particles $i$ and $j$, which according to Eqs. (11) and (13) is given by

$$f_{ij} = \frac{R^2_{ij}}{28} \frac{1}{R^2_{ij}} \left( \frac{1}{\rho_i} + \frac{1}{\rho_j} \right) \frac{1}{R^2_{ij}} \frac{dw}{dr} (R_{ij}).$$

(17)

It is important to note, ignoring for the moment the random velocity updates $dW^v_{ij}$, that the conservative forces $F_i$ are independent of velocities and that the velocity update Eq. (15) is therefore Galilean invariant. Also, again ignoring the random velocity updates, the velocity update conserves local momentum $\sum_i m_i dv_i = 0$. This is the reason why we symmetrized the second derivative of the velocity field in Eq. (11).

C. Fluctuating terms

We have added fluctuations $dW^v_{ij}$ in the velocity update in the last term in Eq. (15) to balance the dissipation due to the friction forces. We write the random velocity update as a pair sum because this greatly simplifies the generation of correct random terms. To conserve momentum also with these random terms, the random velocity updates must be antisymmetric when weighted by their respective effective masses, i.e., $m_i dW^v_{ij} = -m_j dW^v_{ji}$. Note that we have not included a term proportional to the gradient with respect to the velocity $v_i$ because, anticipating our results, the random velocity changes are independent of the actual velocities.

Finally, we must specify the magnitudes of the stochastic variables $dW^R_i$ and $dW^v_{ij}$. In general, for thermal systems, there is a rigorous link between the dissipative properties and the fluctuating properties, known as the fluctuation-dissipation theorem. A full derivation of the properties of the stochastic variables of our model is given in the Appendix. We start with the Chapman-Kolmogorov equation, leading to a Fokker-Planck equation for the evolution of the probability distribution of coarse-grained particle positions and velocities of the integrated out coordinates. The properties of the stochastic variables are then found by requiring the expected equilibrium distribution to be a stationary solution. The results can be summarized as follows:

$$\langle dW^R_i dW^R_j \rangle = \frac{2k_BT}{\xi_i} \delta_{ij} dr,$$

(18)

$$\langle dW^R_i dW^v_{ij} \rangle = 0,$$

(19)

$$\langle dW^v_{ij} dW^v_{ik} \rangle = \frac{2k_BT}{m_i} T_{ij} dr,$$

(20)

$$\langle dW^v_{ik} dW^v_{jl} \rangle = 0 \quad (i \neq j \land k \neq l).$$

(21)

It is important to note that the pairwise stochastic velocity updates are proportional to the friction factors $f_{ij}$. Moreover, to conserve local momentum, for a given random velocity update $dW^v_{ij}$ of particle $i$ due to the presence of particle $j$, the random velocity update of particle $j$ due to the presence of particle $i$ is given by $dW^v_{ji} = -(m_j/m_i) dW^v_{ij}$.

V. WEIGHT FUNCTION AND PARAMETERS

A. Weight function

We now must choose a particular expression for the weight function. We take from the literature on smoothed particle hydrodynamics, the following normalized weight function $w(r)$ (see Fig. 1):

$$w(r) = \frac{21}{2\pi R_c^2} \left( 1 - \frac{r}{R_c} \right)^4 \left( \frac{4}{R_c} + 1 \right) \quad (r \leq R_c).$$

(22)

This function is compact with a range $R_c$, it decreases monotonically to zero at $R_c$, and it has a derivative

$$\frac{dw}{dr} = -\frac{210}{\pi R_c^3} \left( 1 - \frac{r}{R_c} \right)^3 \frac{r}{R_c} \quad (r \leq R_c),$$

(23)
which also decreases monotonically to zero at $R_c$. For this choice of weight function, the dimensionless friction factor $f_{ij}$ is given by

$$f_{ij} = \frac{15}{2\pi R_c^3} m_j \left( \frac{1}{\rho_i} + \frac{1}{\rho_j} \right) \left( 1 - \frac{R_{ij}}{R_c} \right)^3 \quad (R_{ij} < R_c).$$

(24)

Note that the weight function $w(R_0)$, and therefore also $f_{ij}$, is zero if $R_{ij} > R_c$. Moreover, with the choice of the factor $1/28$ in the definition of the viscosity in Eq. (13) and consequently in Eq. (17), the integral of $f_{ij}$ over all space for a system with a homogeneous particle distribution is equal to unity. To speed up calculations, it is advised to use the local densities $\rho_i$ evaluated at time $t - dr$ when evaluating the friction factors $f_{ij}$ at time $t$.

B. Parameters

Let us now discuss possible choices for the new parameters introduced in our algorithm, namely, the cut-off range $R_c$ of the weight function, the relaxation time $\tau$ for momentum diffusion, and the effective masses $m_i$. We will argue here that the latter can be replaced by $m_i = \xi_i \tau$, leaving us with two adjustable parameters, namely, $R_c$ and $\tau$.

First, the range $R_c$ should be large enough to include enough neighbors to allow for a sufficiently accurate estimate of the second derivative of the velocity field at the position of a particle. In practice, this requirement is met if a sphere of radius $R_c$ contains about 10 or more particles. If the particles are randomly distributed, a range of $R_c \approx 1.4(N/V)^{-1/3}$ is sufficient. If the particles are not randomly distributed, e.g., when using repulsive particles, this range should be extended.

Second, consider the background velocity update again. We have used arguments from hydrodynamics to find a suitable form for this equation. We will now leave hydrodynamics aside and focus on Eq. (15) itself. Suppose we temporarily write the effective mass $m_i$ as the product of some friction $\xi'_i$ (not yet necessarily the same as $\xi_i$) and the relaxation time $\tau$. We may then rewrite the velocity update as follows:

$$\frac{dv_i}{dt} = \frac{F_i}{\xi_i' + \sum_{j=1}^{N} f_{ij}(v_j(t) - v_i(t))} \frac{dr}{\tau} + \sum_{j=1}^{N} dW_{ij}^v. \quad (25)$$

In order to interpret this equation, we approximate it as

$$v_i(t + dr) \approx \left[ 1 - \frac{dr}{\tau} \right] v_i(t)$$

$$+ \left[ \frac{F_i}{\xi_i' + \sum_{j=1}^{N} f_{ij}(v_j(t))} \right] \frac{dr}{\tau} + \sum_{j=1}^{N} dW_{ij}^v. \quad (26)$$

Equality holds in cases of homogeneous particle distributions; in other cases, the equation is only approximately true. We interpret this as a numerical method to smooth the background velocity, both spatially and temporally. The spatial smoothing is controlled by the dimensionless friction factor $f_{ij}$, which has been correctly normalized for this interpretation to be possible. The temporal smoothing occurs because the velocity is only fractionally updated, with a fraction given by $dt/\tau$. Because the conservative forces $F_i$ fluctuate on time scales of several times $dt$ (this is usually the limitation on the integration time step), the relaxation time $\tau$ should be larger than this fluctuation time to prevent the velocity update from drowning in fluctuating noise. In practice, we advice setting $\tau \geq 10dt$.

For consistency and stability of the method, it is important that the change in the background velocity field is much smaller than the typical “Brownian velocity” $F_i/\xi_i$ of coarse-grained particle $i$ relative to the velocity field. Because we have already ensured that $dt/\tau \ll 1$, this requirement is met if we simply set $\xi'_i = \xi_i$. With this choice, $dt/\tau$ is exactly the fraction of the Brownian velocity that is used to update the local velocity field.

Although in equilibrium, the value of $\tau$ has no upper limit, and larger values lead to a smoother velocity field, for non-equilibrium situations, the value of $\tau$ should not be too large either. In general, when the fluid is flowing with a typical velocity $v$ around an object of size $L$, inertial effects should be avoided. This means that the kinematic viscosity must be much larger than $vL$ (and therefore the Reynolds number smaller than 1). Because the kinematic viscosity is given by Eq. (13), we find that the relaxation time $\tau$ should be $\tau < R_c^2/(28vL)$.

In conclusion, we have found that the simplest choice for the effective mass is to set $m_i = \xi_i \tau$, where the relaxation time $\tau$ should be chosen in the range

$$10dt \leq \tau < \frac{R_c^2}{28vL}. \quad (27)$$

In Sec. VI, we will perform some tests of this algorithm.
VI. TESTS

A. Test system: Star polymer solution

As a test of our method, we study the flow dynamics of a solution of star polymers at overlap concentration, i.e., \( c = c^\ast \). Star polymers are now established as a class of model colloids with tunable interactions, from nearly hard to ultrasoft.\textsuperscript{13–15} They consist of a number \( f \) of linear chains (the arms) covalently joined to a common centre. As such, these colloidal star polymers interpolate between linear polymeric chains and hard colloids; the former case corresponds to \( f = 1 \) or 2 and the latter to high functionalities \( (f \to \infty) \). At intermediate functionalities, because of their nonuniform monomer density profile,\textsuperscript{16} star polymers are considered to be soft repulsive colloidal spheres with a small core and a corona consisting of grafted chains. It is their wide-ranging weakly repulsive potential that makes star polymers ideal for studying colloidal properties as function of the interactions.\textsuperscript{17}

In this paper, we will study the dynamics of a solution of high-functionality \( (f = 128 \text{ arm}) \) star polymers by tracking the motion of the centres-of-mass of each star polymer. Each pair of particles \( i \) and \( j \) at distance \( r_{ij} \) interacts through an equilibrium interaction potential \( V_{ij}(r_{ij}) \), which has been derived in the past\textsuperscript{18,19} and whose validity has been confirmed through comparison with scattering data\textsuperscript{18,20} and computer simulations.\textsuperscript{21} It reads as

\[
\beta V_{ij}(r) = \frac{5}{18} \frac{r^{3/2}}{\sigma^{3/2}} \left\{ \begin{array}{ll}
-\ln\left(\frac{r}{\sigma}\right) + \frac{1}{1 + \sqrt{r}} & \text{for } r \leq \sigma \\
\frac{\sigma}{1 + \sqrt{r}} \exp\left\{-\frac{\sqrt{r}}{2\sigma}(r-\sigma)\right\} & \text{else}
\end{array} \right.
\]

Here, \( \beta = (k_B T)^{-1} \) and \( \sigma \) is the effective corona diameter of the star. The potential shows a soft logarithmic divergence for small distances, followed by a crossover to a Yukawa form as the centre-to-centre separation grows. In the simulation, the potential is taken to be zero beyond a cut-off distance \( r_c = 2.5\sigma \), which is large enough to safely ignore the cut-off error in calculating equilibrium interaction forces, while it is small enough to keep the number of neighbour particles for each particle manageable. The role of many-body forces has been investigated by computer simulation and theory,\textsuperscript{22} where it was found that they play a negligible role for concentrations up to 4-5 times the overlap density and hence can safely be ignored in the simulations performed for this paper.

The goal of this section is to test our new Galilean invariant algorithm, without having to focus on the accuracy of the interaction model for a specific system. We realize that in general under flow conditions, the configurations of the polymer arms will be changed. However, for high-functionality \( (f = 128) \), the core of the particle is relatively dense and the deformation of the total star polymer is relatively small.\textsuperscript{23} In this work, to keep the description of the test system simple, we therefore assume we can still use the equilibrium interaction as given by Eq. (28). For the same reason, we have disabled the transient forces described in Ref. 24. At this low concentration, the transient forces have no major qualitative effect, so we simply absorb all dynamic effects of the polymer arms into an effective friction \( \xi_0 \) on each centre-of-mass.

B. Parameter settings

In the following, we will express all our measurements in units related to three of the essential parameters of the star polymer model. These are (1) the diffusion coefficient of an isolated star polymer, \( D_0 = k_B T / \xi_0 \), (2) the thermal energy \( k_B T \), and (3) the effective corona diameter \( \sigma \) of the star polymer. With this choice, the unit of time is \( \sigma^2 / D_0 \), the unit of velocity is \( D_0 / \sigma \), and the unit of pressure is \( k_B T / \sigma^3 \).

In all our simulations, we use an integration time step of \( \Delta t = 10^{-4} \sigma^2 / D_0 \). As shown in Ref. 24, at overlap concentration \( (c = c^\ast) \), the number density of star polymers is 0.24 \( \sigma^{-3} \). We use a cubic box with periodic boundary conditions, containing \( N = 512 \) polymer particles, implying a box size of 12.9 \( \sigma \).

The cut-off range \( r_c \) of the weight function in Eq. (22) is set equal to the cut-off range \( r_c \) of the interaction potential, i.e., at \( r_c = 2.5\sigma \), leading to approximately 16 neighbouring particles within a cut-off range. We investigated 4 different values of the averaging time \( \tau \): \( \tau = 3.6 \times 10^{-4} \), \( 3.6 \times 10^{-3} \), \( 3.6 \times 10^{-2} \), and \( 3.6 \times 10^{-1} \sigma^2 / D_0 \).

C. Results

Without flow, the new method should yield the same static results as classical Brownian dynamics and should give rise to hydrodynamic tails in the appropriate time correlation functions.

Focusing first on static properties, Figure 2 shows the radial distribution function \( g(r) \), which is a measure for the relative probability to find the centre of another particle at distance \( r \) from a given particle. We find no difference between

![FIG. 2. Radial distribution function of the centres of the star polymer particles using classical Brownian dynamics (black solid line) and the new Galilean invariant method for the two most extreme choices of the relaxation time for momentum diffusion (colored dashed and dotted lines).](image-url)
the radial distribution function measured in simulations using our new method and simulations using classical Brownian dynamics. Given this extremely good agreement, we expect no differences in other static properties in equilibrium either.

Next, we focus on dynamic properties. Figure 3 shows the average mean-square-displacement of the centre of a star polymer particle, defined as

\[
\text{MSD}(t) = \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle.
\]

The figure clearly shows that the equilibrium mean-square displacement of the particles is not or hardly affected by the use of the new method. Only for the smallest relaxation time, \(\tau = 3.6 \times 10^{-4} \sigma^2/D_0\), we find a slightly higher diffusivity of the particles. This is caused by fluctuations in the background velocity, which are not sufficiently damped for such short relaxation times \(\tau\).

Another characteristic dynamic equilibrium property is the shear relaxation modulus, which is a measure for the linear stress response to a small step shear strain. The shear relaxation modulus can be obtained from an equilibrium simulation by measuring the average decay of spontaneous shear stress fluctuations. The shear stress relaxation \(G(t)\) due to the particle-particle interaction forces is given by

\[
G(t) = \frac{V}{k_B T} \left( S_{xy}^{pp}(t) S_{xy}^{pp}(0) \right),
\]

\[
S_{xy}^{pp}(t) = -\frac{1}{V} \sum_{i<j} (x_i - x_j) F_{y,ij},
\]

where \(V\) is the box volume, \(S_{xy}^{pp}\) is the \(xy\)-component of the microscopic particle stress tensor, and \(F_{y,ij}\) is the \(y\)-component of the force on particle \(i\) due to its interaction with particle \(j\). In a periodic system, the microscopic stress tensor is determined by summing over each unique pair of particles, in which case \(V\) is the volume of one periodic cell. Figure 4 shows that the shear relaxation modulus due to the particle-particle interaction forces is not or hardly affected by the use of the new method. We find a slightly faster stress relaxation only for the smallest relaxation time \(\tau = 3.6 \times 10^{-4} \sigma^2/D_0\) for the same reasons as discussed before.

Finally, we investigate the equilibrium dynamic properties of the background fluid. Our derivation of the equations of motion for the background fluid was based on the Navier-Stokes equation for Newtonian fluids. Moreover, we have taken care to guarantee, besides Galilean invariance, local conservation of momentum. Therefore, we expect that fluctuations in the fluid velocity should on average decay as predicted for Newtonian fluids. Notice that all stochastic equations of motion suggested in this paper are Markovian, implying that possible memory effects should be introduced additionally, as, for example, in the RaPiD method.\(^4\)-\(^6\),\(^25\)-\(^27\)

Since hydrodynamic equations are only valid at length scales larger than individual particles, we focus on Fourier components of the velocity current, defined as

\[
\mathbf{j}(k,t) = \sum_{\alpha=1}^{N} v_{\alpha} \exp[-i\mathbf{k} \cdot \mathbf{R}_{\alpha}(t)],
\]

where \(\mathbf{k}\) is the wave vector. We then investigate the transversal current correlations

\[
C_i(k,t) = \frac{1}{N} \langle j_\alpha(k,t) j^*_\alpha(k,0) \rangle \quad (k = k_\parallel \beta, \beta \neq \alpha).
\]

According to hydrodynamic theory, the transverse current time auto-correlation function at small \(k\)-values and short times should decay exponentially with a rate determined by the kinematic viscosity of the fluid and the magnitude of the wave vector: \(C_i(k,t) = (k_B T/m) \exp[-v k^2 t]\). We note that this is only valid at large enough length scales (small wave vectors) and short times because otherwise molecular effects and collective
effects become apparent, respectively. Figure 5 (top inset) shows that our simulations agree well with the theoretical prediction at short times for small wavenumbers. For larger wave vectors, the hydrodynamic limit is no longer attained, and the transversal current correlation starts to deviate from the hydrodynamic predictions (Figure 5, bottom inset).

It is known that collective effects lead to a very slow algebraic decay in the velocity autocorrelation of particles, where the decay scales as $t^{-3/2}$ in three dimensions. Figure 6 shows the long time tail of the velocity autocorrelation of the background fluid for $\tau = 3.6 \times 10^{-4} \sigma^2/D_0$. The solid line is the prediction from mode coupling theory for hydrodynamic systems.\(^{28,29}\)

\[
\langle v_i(t) \cdot v_i(0) \rangle = -\frac{2k_B T}{\rho^m [4\pi m V]^{3/2}}, \tag{34}
\]

where $\rho^m = N/V$ is the number density. Again, we find a good agreement between simulation and theory. This proves that the background fluid behaves like a proper hydrodynamic fluid with a measured kinematic viscosity in agreement with the model parameter $\nu$.

VII. DISCUSSION AND CONCLUSION

We have developed a Galilean invariant, momentum conserving Brownian dynamics scheme for simulations of complex soft matter systems. The equations apply when only a small set of degrees of freedom is explicitly simulated, while the majority of degrees of freedom have been eliminated. The eliminated degrees of freedom may be internal degrees of freedom of complex particles and/or external degrees of freedom corresponding to solvent molecules. The interactions of the retained, coarse degrees of freedom, and the eliminated degrees of freedom are taken into account by friction forces and random displacements. In order to arrive at a Galilean invariant scheme, friction forces are taken to be with respect to moving background material. The motion of the background material is described by locally averaged velocities in the neighborhood of the dissolved coarse coordinates and carrying the same indexes as the latter. Notice that this implies that the method only applies with sufficiently large densities of retained coordinates. When writing down the equations to update the background velocities, we were guided by classical Newtonian dynamics. This automatically led us to a momentum conserving scheme.

In order to prove the usefulness of our scheme, we performed tests on concentrated star polymer solutions. Indeed, we have found that the transverse current and velocity time autocorrelation functions behave as expected from hydrodynamics. In particular, the velocity autocorrelation functions display a long time tail in complete agreement with hydrodynamics.

The background velocity updates show a strong resemblance to corresponding updates in dissipative dynamics (DPD)\(^{30}\) and SPH.\(^{31}\) Apparently, the momentum conservation laws applied in continuum hydrodynamics and implemented as in SPH almost force a DPD like update of local velocities.

We stress however that our scheme is very different from the DPD and SPH schemes. First of all, SPH is basically a solver for continuum hydrodynamic models. Generalizations to non-Newtonian, viscoelastic fluids exist,\(^{32}\) in which a posed non-Newtonian constitutive equation for the stress tensor can be incorporated in the update of the fluid velocity. In contrast, in our scheme, as well as in DPD, the viscoelasticity of the fluid arises from the interactions between the coarse particles through their interaction forces $F_i(t)$. The advantage of these methods is that such interaction forces (possibly including memory effects) have a direct link to the microscopic details of the soft matter system at hand, while such a link is
usually much more difficult to establish with constitutive models. Second, our velocities are representations of the locally averaged motion of the eliminated degrees of freedom, whereas in DPD and SPH, they represent the real velocities of the coarse particles (or fluid parcels) themselves. Moreover, from a mathematical point of view, our scheme is a first order Brownian dynamics scheme with additional variables describing the background flow, also by means of a first order scheme, whereas DPD and SPH are second order schemes written as two first order equations. Only by adhering to first order Brownian dynamics can one retain its profitable characteristic of allowing increasingly large time steps with increasing frictions.

APPENDIX: FLUCTUATION-DISSIPATION

1. Fokker-Planck equation

In this appendix, we will apply standard techniques\(^8\) to derive the statistical properties of the stochastic variables \(\text{d}W_i^m\) and \(\text{d}W_j^m\), associated with the position update and the background velocity update. We will do this by starting with the Chapman-Kolmogorov equation, leading to a Fokker-Planck equation for the evolution of the probability distribution of the positions of the coarse-grained particles and velocities of the integrated out coordinates. The properties of the stochastic variables are then found by requiring the expected equilibrium distribution to be a stationary solution.

The Chapman-Kolmogorov equation relates the distribution of particle positions and local velocities of the eliminated coordinates at different times. We will use a shorthand notation where \(\mathbf{z} = \{\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{v}_1, \ldots, \mathbf{v}_N\}\). Let \(\mathcal{G}(\mathbf{z}; \mathbf{z}_0; t)\) be the probability to find the system at time \(t\) in a state characterised by positions and velocities \(\mathbf{z}_0\), that at \(t = 0\), the system was in a state characterised by positions and velocities \(\mathbf{z}_0\). The Chapman-Kolmogorov equation then states that

\[ \frac{\partial \mathcal{G}(\mathbf{z}; \mathbf{z}_0; t)}{\partial t} = \int \mathcal{G}^{\text{eq}}(\mathbf{z}; \mathbf{z}'; \text{d}t) \mathcal{G}(\mathbf{z}'; \mathbf{z}_0; t), \]  

(A1)

i.e., a path from \(\mathbf{z}_0\) at time zero to \(\mathbf{z}\) at time \(t\) may be taken through any intermediate point \(\mathbf{z}'\) at time \(t\). As the time interval \(\text{d}t\) becomes smaller, the distribution \(\mathcal{G}(\mathbf{z}; \mathbf{z}_0; \text{d}t)\) becomes more narrow; we have \(\lim_{\text{d}t \to 0} \mathcal{G}(\mathbf{z}; \mathbf{z}_0; \text{d}t) \equiv \delta(\mathbf{z} - \mathbf{z}')\).

Going through the usual derivation,\(^8\) we arrive at the following Fokker-Planck equation:

\[ \frac{\partial \mathcal{G}(\mathbf{z}; \mathbf{z}_0; t)}{\partial t} = - \sum_i \sum_{\alpha} \frac{\partial}{\partial R_{i,\alpha}} \left( \frac{F_{i,\alpha}}{\xi_i + k_B T} \frac{\partial}{\partial R_{i,\alpha}} \mathcal{G}(\mathbf{z}; \mathbf{z}_0; t) \right) + \frac{1}{2} \sum_{i} \sum_{\beta} \frac{\partial}{\partial R_{i,\beta}} \left( \sum_{j} \sum_{\alpha} \frac{\partial}{\partial v_{j,\alpha}} \mathcal{G}(\mathbf{z}; \mathbf{z}_0; t) \right) \]

(A2)

where \(\alpha\) and \(\beta\) run from 1 to 3, corresponding to the different Cartesian components.

Note that this equation may be written as a conservation equation

\[ \frac{\partial \mathcal{G}}{\partial t} = - \frac{\partial}{\partial \mathbf{z}} \mathbf{J}(\mathbf{z}), \]  

(A3)

where \(\mathbf{J}(\mathbf{z}) = (J_{1X}, \ldots, J_{1Z}, J_{2X}, \ldots, J_{2Z})\) is a 6\(N\)-dimensional generalised flux, half of which is a “position flux” and the other half a “velocity flux.”

We will require that at equilibrium, the coordinates are Boltzmann distributed with potential energy function the one that governs the conservative forces. With coarse-grain simulations, this is the potential of mean force. We will also require that the local background velocities \(\mathbf{v}_i\) are distributed according to the Maxwell-Boltzmann distribution with effective masses \(m_i\), i.e., the equilibrium distribution must obey

\[ \mathcal{G}^{\text{eq}}(\mathbf{z}) \propto \exp \left( - \beta \Phi(\mathbf{R}_1, \ldots, \mathbf{R}_N) - \frac{1}{2} \beta \sum_i m_i \mathbf{v}_i \cdot \mathbf{v}_i \right), \]  

(A4)

where \(\beta = 1/k_BT\) and the potential energy \(\Phi\) leads to conservative forces \(\mathbf{F}_i = -\partial \Phi/\partial \mathbf{R}_i\).

At equilibrium, all occurrences of \(\mathcal{G}(\mathbf{z}; \mathbf{z}_0; t)\) in Eq. (A2) must be replaced by \(\mathcal{G}^{\text{eq}}(\mathbf{z})\). In the following, we will need the derivatives:

\[ \frac{\partial}{\partial \mathbf{R}_i} \mathcal{G}^{\text{eq}}(\mathbf{z}) = -\beta \left( \frac{\partial}{\partial \mathbf{R}_i} \Phi \right) \mathcal{G}^{\text{eq}}(\mathbf{z}) = \beta \mathbf{F}_i \mathcal{G}^{\text{eq}}(\mathbf{z}), \]  

(A5)

\[ \frac{\partial}{\partial \mathbf{v}_i} \mathcal{G}^{\text{eq}}(\mathbf{z}) = -\beta m_i \mathbf{v}_i \mathcal{G}^{\text{eq}}(\mathbf{z}). \]  

(A6)

Notice that these imply

\[ \sum_i \sum_{\alpha} \frac{\partial}{\partial R_{i,\alpha}} \mathbf{v}_i \mathcal{G}^{\text{eq}}(\mathbf{z}) + \sum_i \sum_{\alpha} \frac{\partial}{\partial v_{i,\alpha}} \frac{F_{i,\alpha}}{m_i} \mathcal{G}^{\text{eq}}(\mathbf{z}) = 0. \]  

(A7)

As a result, at equilibrium, the corresponding two terms must be removed from the conservation equation (A2). The equilibrium conditions then demand that all remaining sums between curly brackets in Eq. (A2) with \(\mathcal{G}(\mathbf{z}; \mathbf{z}_0; t)\) replaced by \(\mathcal{G}^{\text{eq}}(\mathbf{z})\) must be identically equal to zero.

We expect all second moments of random displacements and velocity updates to scale with the thermal energy \(k_BT\) and the time step \(\text{d}t\). To meet the above equilibrium conditions, we suppose that the second moments of the stochastic variables are independent of velocities \(\mathbf{v}_i\), but may still depend on the positions \(\mathbf{R}_i\), through a position dependent friction \(\xi_i\) and/or friction factor \(f_{ij}\). We will therefore write the correlations as

\[ -\frac{1}{2} \sum_i \sum_{k} \sum_{\beta} \frac{\partial}{\partial R_{i,\beta}} \left( \frac{\text{d}W_{i,k,\alpha}^m \text{d}W_{i,k,\beta}^m}{\text{d}t} \mathcal{G}(\mathbf{z}; \mathbf{z}_0; t) \right) \]

\[ -\frac{1}{2} \sum_i \sum_{k} \sum_{l} \sum_{\beta} \frac{\partial}{\partial v_{i,\beta}} \left( \frac{\text{d}W_{i,k,\alpha}^m \text{d}W_{i,l,\beta}^m}{\text{d}t} \mathcal{G}(\mathbf{z}; \mathbf{z}_0; t) \right) \]

(A2)

where \(\alpha\) and \(\beta\) run from 1 to 3, corresponding to the different Cartesian components.

Note that this equation may be written as a conservation equation

\[ \frac{\partial \mathcal{G}}{\partial t} = - \frac{\partial}{\partial \mathbf{z}} \mathbf{J}(\mathbf{z}), \]  

(A3)

where \(\mathbf{J}(\mathbf{z}) = (J_{1X}, \ldots, J_{1Z}, J_{2X}, \ldots, J_{2Z})\) is a 6\(N\)-dimensional generalised flux, half of which is a “position flux” and the other half a “velocity flux.”
\[ \langle dW_{i,a}^R dW_{j,b}^R \rangle = 2k_BT_{iab} R_{iab} \delta_{ij} dt, \]
\[ \langle dW_{i,a}^R dW_{j,b}^R \rangle = 2k_BT_{iab} R_{iab} \delta_{ij} dt, \]
\[ \langle dW_{i,a}^R dW_{j,b}^R \rangle = 2k_BT_{iab} R_{iab} \delta_{ij} dt, \]
\[ \langle dW_{i,a}^R dW_{j,b}^R \rangle = 2k_BT_{iab} R_{iab} \delta_{ij} dt, \]
\[ \langle dW_{i,a}^R dW_{j,b}^R \rangle = 2k_BT_{iab} R_{iab} \delta_{ij} dt, \]
and discard with velocity derivatives of these correlations.

Using all the above, the conditions for equilibrium may be written as
\[
\begin{align*}
\frac{1}{\xi_i} F_{i,\alpha} + k_BT \frac{\partial}{\partial R_{i,\alpha}} \left( \frac{1}{\xi_i} \right) - \sum_j \sum_\beta \left[ k_BT \frac{\partial C_{i\beta j\beta}^R}{\partial R_{j,\beta}} \right] \\
+ C_{i\beta j\beta} F_{i,\alpha} = 0, \\
\sum_j f_j \left( v_{j,\alpha} - v_{i,\alpha} \right) - \sum_j \sum_\beta \left[ k_BT \frac{\partial C_{i\beta j\beta}^R}{\partial R_{j,\beta}} \right] \\
+ C_{i\beta j\beta} F_{i,\alpha} = 0.
\end{align*}
\]

These equations will be satisfied for any set of \( R \) and \( v \) if we choose \( C_{i\beta j\beta}^R = \delta_{ij} \delta_{\alpha \beta} \xi_i \), \( C_{i\beta j\beta}^R = 0 \), and \( C_{i\beta j\beta}^\alpha = \delta_{ij} \left( f_{ij} / m_i \right) \delta_{\alpha \beta} - \left( f_{i} / m_i \right) \delta_{\alpha j} \delta_{ij} / \tau \).

In conclusion, to allow for the correct static equilibrium distribution, we must choose the stochastic variables according to
\[
\begin{align*}
\langle dW_{i,a}^R dW_{j,b}^R \rangle &= 2k_BT \xi_i \delta_{ij} dt, \\
\langle dW_{i,a}^R dW_{j,b}^R \rangle &= 0, \\
\langle dW_{i,a}^R dW_{j,b}^R \rangle &= 2k_BT m_i \delta_{ij} dt, \\
\langle dW_{i,a}^R dW_{j,b}^R \rangle &= 0 \quad (ik \neq jl \land ik \neq jl),
\end{align*}
\]
as mentioned in the main text.


