AIP | The Journal of Chemical Physics

Monte Carlo and event-driven dynamics of Brownian particles with orientational degrees of freedom

Flavio Romano, Cristiano De Michele, Davide Marenduzzo, and Eduardo Sanz

Citation: The Journal of Chemical Physics **135**, 124106 (2011); doi: 10.1063/1.3629452
View online: http://dx.doi.org/10.1063/1.3629452
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/135/12?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Dynamic Monte Carlo simulations of anisotropic colloids
J. Chem. Phys. **137**, 054107 (2012); 10.1063/1.4737928

Dynamic Monte Carlo versus Brownian dynamics: A comparison for self-diffusion and crystallization in colloidal fluids
J. Chem. Phys. **132**, 194102 (2010); 10.1063/1.3414827

The conformational dynamics of λ -DNA in the anti-Brownian electrokinetic trap: Brownian dynamics and Monte Carlo simulation
J. Chem. Phys. **131**, 224905 (2009); 10.1063/1.3251058

Event-driven Brownian dynamics for hard spheres
J. Chem. Phys. **126**, 134109 (2007); 10.1063/1.2719190

Isotropic-nematic spinodals of rigid long thin rodlike colloids by event-driven Brownian dynamics simulations
J. Chem. Phys. **124**, 134906 (2006); 10.1063/1.2180251

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20

Monte Carlo and event-driven dynamics of Brownian particles with orientational degrees of freedom

Flavio Romano,[1] Cristiano De Michele,[1] Davide Marenduzzo,[2] and Eduardo Sanz[2,a)]
[1]*Dipartimento di Fisica, "Sapienza" Università di Roma, P.le Aldo Moro 5, 00185 Roma, Italy*
[2]*SUPA, School of Physics and Astronomy, University of Edinburgh, Mayfield Road, Edinburgh, EH9 3JZ, Scotland, United Kingdom*

(Received 6 June 2011; accepted 5 August 2011; published online 28 September 2011)

Recently, a simple scaling argument was introduced that allows us to map, with some precautions, Brownian and Monte Carlo dynamics for spherical particles. Here, we extend the scaling to study systems that have orientational degrees of freedom and carefully asses its validity over a wide region of temperature and density. Our work allows us to devise a Brownian Monte Carlo algorithm that produces, to a good approximation, physically meaningful trajectories with a minimum programming effort, although at the expense of some sampling efficiency. © *2011 American Institute of Physics*. [doi:10.1063/1.3629452]

I. INTRODUCTION

The Metropolis algorithm,[1] which is based on the importance sampling Monte Carlo method, is among the most widely accepted and used methods to study physical systems in thermodynamic equilibrium. Monte Carlo (MC) has been used to study a large variety of physical systems and is a primary computational method in soft matter and statistical physics to study the *equilibrium* properties of physical systems.[2–4]

When the interest is on the *dynamics* of a system, on the other hand, the primary computational methods are molecular dynamics (MD) and Brownian dynamics (BD). These schemes satisfy the fluctuation–dissipation theorem, although they neglect fluid-mediated hydrodynamic interactions; these can be accounted for via computationally more expensive methods such as Lattice Boltzmann[5] or Stochastic Rotation Dynamics.[6] It is commonly believed that MC simulations simply cannot be used to study the dynamics of a physical system in any more than a very qualitative fashion. However, it has been known in the literature for some time that MC simulations only consisting of physically meaningful moves, such as small single particle displacements, may be shown to be equivalent to BD, at least in the limit in which nearly all the moves are accepted.[7–9] Some of us have recently shown[10] that the analogy between Brownian MC (BMC) and BD simulations actually holds even when the acceptance is quite small, in some cases down to 30%, for applications of physical interest such as crystal nucleation and colloidal self-diffusion in dense suspensions. Crucially, in order to map MC times to BD ones, it is necessary to take the average acceptance rate of trial moves into account.

For colloidal fluids, however, we have seen that the advantage of using BMC as opposed to BD is not obvious, as both codes are relatively easy to write. Typically, the speedup obtained in BMC due to the possibility of using a larger effective time-step is counterbalanced by the need to perform more moves when many of them get rejected by the Metropolis criterion. In this paper, we aim to explore the applicability of the time rescaling idea to a more complicated case: that of colloidal particles with rotational as well as translational degrees of freedom, such as rodlike or patchy particles. BD algorithms become quite complicated if particles have orientational degrees of freedom and even more if the interaction potential is not differentiable. Hence, it would be most useful to prove the validity of a Brownian MC scheme for particles with orientational degrees of freedom that interact via hard potentials. We have chosen to compare BMC to event driven Brownian dynamics (EDBD) (Ref. 22) because the latter is the simplest BD-type algorithm to simulate non spherical, hard bodies. Alternatives, such as Stochastic Rotation Dynamics,[6] are more complicated and incorporate hydrodynamic effects that cannot be captured with BMC. Even though MC schemes have often been used to study dynamic processes of anisotropic colloidal particles,[11–15] to the best of our knowledge the validity of MC scheme in this scenario has not yet been tested. Can we still simply use the time rescaling via acceptance introduced in Ref. 10 to map MC times to physical ones? What happens when rotational and translational motions have different acceptance rates? To answer these questions, we propose a BMC scheme for particles with anisotropic interactions and carefully test it by studying the rotational and translational dynamics of particles interacting via a patchy, square well potential.[16,17] Patchy particles are of interest to colloid physics and soft matter,[18] as they can lead to a striking variety of thermodynamically self-assembled structures and crystals.[19,20] They may also be thought of as a simple, micron-scale models for proteins,[21] which typically have non-uniform binding sites on their surface.

As we demonstrate in this paper, it is possible to formulate a simple BMC scheme which is in quantitative agreement with the EDBD simulations also in the case of systems with orientational degrees of freedom. The additional care one has to take with respect to the isotropic colloid simulations

a)Electronic mail: esanz@ph.ed.ac.uk.

 © 2011 American Institute of Physics

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20

reported in Ref. 10 is that there is a well-defined ratio between the translational and the rotational MC attempts which needs to be satisfied for Stokes' laws to hold. However, Our BMC method can handle cases in which rotations and translations are accepted with different probabilities in the MC scheme.

Our paper is organized as follows. In Sec. II we introduce our methodology. Specifically, we discuss how to quantify translational and rotational diffusion, and we present a generalization of the theory in Ref. 10 which suggests how to map time in Monte Carlo cycles to physical time. In the same section, we also sketch the way our EDBD simulations are performed and describe the primitive model of water we focus on. In Sec. III, we discuss our results and compare in detail the dynamical behavior of the system as predicted by EDBD and by BMC. Finally, in Sec. IV, we present our conclusions.

II. METHODOLOGY

We perform BMC and EDBD simulations and compare the dynamics by measuring the translational and rotational diffusion coefficients, D_t and D_r, given by

$$D_\mathrm{t} = \frac{\left\langle \frac{1}{N}\sum_i^N \| \int_0^t \mathbf{v}_i(t')\mathrm{d}t' \|^2 \right\rangle}{6t} = \frac{\left\langle \frac{1}{N}\sum_i^N \|\mathbf{r}_i(t) - \mathbf{r}_i(0)\|^2 \right\rangle}{6t} \tag{1}$$

and

$$D_\mathrm{r} = \frac{\left\langle \frac{1}{N}\sum_i^N \| \int_0^t \mathbf{w}_i(t')\mathrm{d}t' \|^2 \right\rangle}{6t}, \tag{2}$$

where $\mathbf{w}_i(t)$ and $\mathbf{v}_i(t)$ are the angular velocity and the center-of-mass velocity of particle i in the laboratory reference system at time t, $\mathbf{r}_i(t)$ is the position of particle i at time t, $\langle\cdot\rangle$ denotes averaging over the initial time and $\|\cdot\|$ denotes the Cartesian norm.

The translational diffusion both in EDBD and BMC simulations can be calculated from Eq. (1). The calculation of the rotational diffusion coefficients is somewhat less straightforward. In EDBD simulations, one can proceed as follows. Consider a particle i which undergoes N_i collisions in the time interval $[0, t]$, with $t = \sum_{k=0}^{N_i} \Delta t_{i,k}$, where $\Delta t_{i,0}$ is the time interval between $t = 0$ and the first collision occurring at a time $t_1 > 0$, $\Delta t_{i,N_i}$ is the time interval between the N_ith collision and time t, and $\Delta t_{i,k}$ is the time interval between the kth and $(k+1)$-th collisions for $k \neq 0, N_i$. With these definitions, Eq. (2) can be rewritten as

$$D_\mathrm{r} = \frac{\left\langle \frac{1}{N}\sum_i^N \| \sum_k^{N_k} \Delta\mathbf{w}_{i,k} \|^2 \right\rangle}{6t}, \tag{3}$$

where $\Delta\mathbf{w}_{i,k} = \mathbf{w}_i(t_k)\Delta t_{i,k}$. Eq. (3) can conveniently be used to calculate D_r from an EDBD simulation. Eq. (3) can also be used to calculate the diffusion coefficients from a MC simulation with the proviso that N_k is now the number of MC cycles over which we are calculating the diffusion coefficients and $\Delta\mathbf{w}_{i,k}$ is the angular displacement of particle i over the kth MC cycle (where $k = 0$ is the first MC cycle).

A. BMC with orientational degrees of freedom: mapping to physical time

Recently, some of us have studied the possibility of using MC to simulate the dynamics of particles undergoing Brownian motion with translational degrees of freedom only (spherical particles).[10] The main result was that the time corresponding to an MC cycle—consisting of N attempts (N being the number of particles) to shift a randomly chosen particle by a randomly displacement uniformly chosen in the interval $[-\delta_\mathrm{t}, \delta_\mathrm{t}]$ for each Cartesian axis—can be approximated by[10]

$$\frac{\Delta t_\mathrm{t}}{\mathrm{cycle}} \approx \frac{\delta_\mathrm{t}^2 \overline{a}_t(\delta_\mathrm{t})}{6D_\mathrm{t}^0}, \tag{4}$$

where $\overline{a}_\mathrm{t}(\delta_\mathrm{t})$ is the average acceptance ratio of the trial moves and D_t^0 is the diffusion coefficient at infinite dilution. The simplest way to derive Eq. (4) is to require that $\langle \Delta r^2 \rangle / \Delta t = 6D_\mathrm{t}^0$, the mean squared displacement per unit time at infinite dilution, is equal to the mean squared displacement in a single MC cycle

$$\frac{\langle \Delta r^2 \rangle}{\mathrm{cycle}} = \frac{3}{2\delta_\mathrm{t}} \int_{-\delta_\mathrm{t}}^{\delta_t} x^2 a_t(x)\mathrm{d}x \approx \overline{a}_\mathrm{t}\delta_t^2, \tag{5}$$

where the acceptance $a_\mathrm{t}(x)$ has been approximated by its average, $\overline{a}_\mathrm{t}$. Reference 10 provides a more detailed analysis of the dependency of $\langle \Delta r^2 \rangle$/cycle on the acceptance ratio.

Here, we are interested in using MC to simulate the dynamics of Brownian particles with orientational, as well as translational, degrees of freedom. To achieve that, we must appropriately tune the ratio between the amount of translations and rotations sampled in the MC algorithm. As we show below, it is possible to devise an MC procedure that reproduces physically meaningful trajectories by carefully choosing the ratio between δ_t and δ_r, the maximum rotation angle in a rotational trial move. We consider an MC scheme in which, on average, N rotations and N translations are attempted in each cycle. To sample the orientational degrees of freedom, we select an axis at random around which a randomly chosen particle is rotated by an angle uniformly chosen between 0 and δ_r. The mean squared rotational displacement per cycle is given by

$$\frac{\langle \Delta\theta^2 \rangle}{\mathrm{cycle}} = \frac{1}{\delta_r} \int_0^{\delta_r} a_\mathrm{r}(\theta)\theta^2 \mathrm{d}\theta, \tag{6}$$

where $a_\mathrm{r}(\theta)$ is the acceptance rate of θ-radiant rotations. As done for the translation in Eq. (5) and in Ref. 10, we approximate $a_\mathrm{r}(\theta)$ by its average $\overline{a}_\mathrm{r}$ in order to approximate the integral above

$$\frac{\langle \Delta\theta^2 \rangle}{\mathrm{cycle}} \approx \frac{\overline{a}_\mathrm{r}\delta_\mathrm{r}^2}{3}. \tag{7}$$

Now, we assume that the same procedure used for translational degrees of freedom applies to rotational degrees of freedom; that is, the infinite dilution diffusion coefficient can be used to introduce a mapping between physical time and

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20

MC cycles. By definition, one has $\langle \Delta\theta^2 \rangle = 6D_r^0 \Delta t$ that, combined with Eq. (7), gives the "rotational" time per cycle

$$\frac{\Delta t_r}{\text{cycle}} = \frac{\delta_r^2 \overline{a}_r(\delta_r)}{18 D_r^0} . \tag{8}$$

In order for time to evolve evenly for orientational and translational degrees of freedom, Δt_t and Δt_r must be equal. By equating Eqs. (4) and (8) and substituting D_r and D_0 by the Stokes-Einstein expressions for the rotational and translational diffusion [$D_r^0 = k_B T/(\pi\eta\sigma^3)$ and $D_t^0 = k_B T/(3\pi\eta\sigma)$], we find

$$\frac{\delta_t}{\delta_r} = \frac{\sigma}{3}\sqrt{\frac{\overline{a}_r(\delta_r)}{\overline{a}_t(\delta_t)}} , \tag{9}$$

which is the condition needed to map MC dynamics into BD for particles with orientational degrees of freedom. In the context of this paper, we call BMC an MC scheme that satisfies Eq. (9). In other words, by tuning δ_t and δ_r so that Eq. (9) holds, an MC run should produce dynamically meaningful trajectories. To test whether this is actually the case, we compare the long time diffusion coefficients found with this procedure with those obtained with EDBD simulations (see the Results section). In practice, δ_t and δ_r need to be iteratively tuned to satisfy Eq. (9) in a series of short MC simulations prior to any production run. We stress that acceptance rates have to be high to justify the assumption that particles diffuse according to the Stokes–Einstein equation, an assumption which is exact only in the limit of all moves being accepted.[10]

Summarizing, our recipe for BMC simulations with orientational degrees of freedom is as follows:

(i) Fix $\delta_t/\delta_r = \sigma/3$ and δ_t sufficiently small so that a high (greater than 0.7, see later in the text) acceptance ratio is obtained for both rotations and translations.

(ii) Run a short simulation to obtain an estimate of the number of steps (n_{corr}) needed for the MC scheme to produce an independent configuration.

(iii) In a series of short simulations, each longer than n_{corr} steps, iteratively adjust δ_r so that Eq. (9) is approached. Stop when Eq. (9) is satisfied within an error of a few per cent. This procedure can easily be made automatic once an estimate of n_{corr} is available.

(iv) Use the obtained value δ_r for a production run.

Since the variables upon which Eq. (9) depends are state dependent, the tuning procedure must be carried out at every state point simulated. We advise to always check *a posteriori* that Eq. (9) is satisfied to a good approximation. We also suggest that two different values of δ_t be tried for each state point to check that consistent results are obtained for both the translational and rotational diffusion properties.

We note that Eq. (9) is valid for our particular choice of exploring the configuration space with MC. If one so wishes, it can be extended to other choices by (i) performing the integrals in Eqs. (5) and (6) according to the MC scheme chosen, (ii) requiring Stokes' laws to hold, and (iii) requiring time to evolve evenly for rotational and translational degrees of freedom. In this way, one can get the equivalent of Eq. (9) for any MC algorithm.

B. Event-driven Brownian dynamics with rotations

We have performed EDBD simulations modeling particles as constant density spheres of diameter σ and mass m. The moment of inertia is diagonal and equal to $I = m\sigma^2/10$. In EDBD simulations of spherical particles, velocities are periodically reset, sampling from a Gaussian distribution, with a time interval equal to τ_t. During each interval, as described in Ref. 22, the system propagates according to Newtonian dynamics. If particles are not spherical or have anisotropic interactions,[17,23] the rotational diffusion has to be taken into account. An extension of the algorithm developed in Ref. 22 to particles with rotational degrees of freedom is quite straightforward: the center-of-mass and angular velocities are periodically reset, sampling from a Gaussian distribution with different time intervals, τ_t and τ_r, respectively. The translational and rotational diffusion coefficients D_t^0 and D_r^0 in the infinite dilution limit are

$$D_t^0 = \frac{k_B T \tau_t}{2m} ,$$
$$D_r^0 = \frac{k_B T \tau_r}{2I} . \tag{10}$$

In this limit, we expect that such diffusion coefficients obey the Stokes–Einstein (SE) and Debye–Stokes–Einstein (DSE) relations. In the present case of anisotropically interacting spherical particles with a diameter σ,

$$D_t^0 = \frac{k_B T}{3\pi\eta\sigma} ,$$
$$D_r^0 = \frac{k_B T}{\pi\eta\sigma^3} , \tag{11}$$

where η is the solvent viscosity. From Eqs. (10) and (11) it follows that

$$\tau_t = \frac{2m}{3\pi\eta\sigma} ,$$
$$\tau_r = \frac{2I}{\pi\eta\sigma^3} . \tag{12}$$

Hence, given a value for the viscosity η, the time intervals τ_t and τ_r can be readily evaluated. We note that $\tau_t/\tau_r = 10/3$, i.e., the reset intervals of the angular and center-of-mass velocities are different. For a detailed discussion of the algorithm used to propagate the Newtonian trajectory in the presence of patchy square well interactions we refer the reader to Refs. 17 and 24.

C. Model and units

We compare the dynamics obtained with BMC and EDBD for the primitive model of water (PMW) by Kolafa and Nezbeda,[16] whose equilibrium phase diagram is well characterized.[25,26] In the PMW, each particle is composed of a hard sphere of diameter σ and four additional tetrahedrally arranged sites. Two of the sites (the proton sites H) are located on the surface of the hard sphere, i.e., at distance 0.5σ from the center. The two remaining sites (the lone-pair sites, LP) are located at 0.45σ from the center. The H and LP sites of distinct particles interact via a square well (SW) potential

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20

$u_{\rm SW}$ of width $\delta = 0.15\sigma$ and depth u_0, i.e.,

$$u_{\rm SW}(r) = \begin{cases} -u_0 & r < \delta \\ 0 & r > \delta \end{cases}, \tag{13}$$

where r is here the distance between the two sites. The choice of $\delta = 0.15\sigma$ guarantees that a site cannot be involved in more than one bond. The depth of the square well potential u_0 defines the energy scale. We stress that in this model bonding between different particles is possible only for specific orientations and distances. Since the LP site is buried 0.05σ within the hard-core, the maximum center-to-center distance at which bonding is possible is 1.1σ, a value typical of the short-range colloid–colloid interactions.

We use σ as the unit of length and u_0 as the unit of energy. Temperature T is given in units of $u_0/k_{\rm B}$. We measure time in units of $\sigma^2/D_{\rm t}^0$ for the translation and of $\text{rad}^2/D_{\rm r}^0$ for the rotation. The Brownian translational time unit, $\sigma^2/D_{\rm t}^0$, corresponds to the time that a particle needs to diffuse over its own size at infinite dilution, whereas the Brownian rotational time unit $\text{rad}^2/D_{\rm r}^0$ corresponds to the time a particle needs to diffuse in angular space over 1 radiant, also at infinite dilution. In general, the two are different (both in MC steps and in real time). Translational and rotational diffusion coefficients are given in $D_{\rm t}^0$ and $D_{\rm r}^0$ units, respectively. According to the SE and DSE relations, $D_t^0/D_r^0 = 1/3$ in simulation units. To convert the number of MC cycles to time in Brownian units, we multiply the number of MC cycles by $(\delta_{\rm t}/\sigma)^2\overline{a}_{\rm t}/6$ [Eq. (4)] for the translation and by $\delta_{\rm r}^2\overline{a}_{\rm r}/18$ [Eq. (8)] for the rotation.

D. Simulation details

We have studied systems of $N = 350$ particles with periodic boundary conditions for several packing fractions $\phi \equiv (\pi/6)N/V$ (where V is the system volume in units of σ^3) and temperatures. To calculate the mean square displacement (MSD), each particle is allowed to diffuse, on average, at least ten times its diameter. In evaluating the MSD, we have taken care to subtract the center-of-mass displacement, an important correction in the long simulations at low T. At low T, simulations required more than 10^8 MC steps, corresponding to about a month of computer time. We checked that the equilibrium energy obtained is the same for BMC and EDBD for all state points studied.

III. RESULTS AND DISCUSSION

A. Square well model: EDBD and Langevin dynamics

In Ref. 22, it was shown that EDBD generates the correct long-time dynamics in agreement with true Langevin dynamics (LD) for a hard sphere system by adapting the algorithm developed in Ref. 27 for the one-dimensional case. In the present work, particles interact with both hard core and attractive interactions and it is thus essential to show that EDBD still provides correct results with respect to true LD in the presence of attractions between particles. For the sake of simplicity, for this test we consider a monodisperse system of spherical particles interacting via an isotropic square-well potential $v_{\rm SW}(r)$ defined by

$$v_{\rm SW}(r) = \begin{cases} \infty & r < \sigma \\ -u_0 & \sigma < r < \sigma + \Delta \\ 0 & r > \sigma + \Delta \end{cases}; \tag{14}$$

in our simulations, we set the interaction range to $\Delta = 0.15\sigma$.

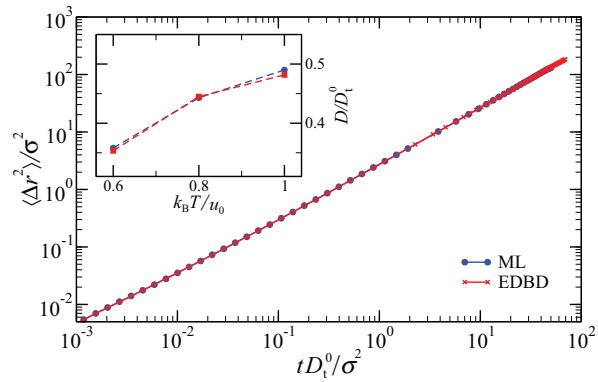

FIG. 1. Mean square displacement versus time for the same state point ($T = 0.8$, $\phi = 0.31$) simulated with EDBD and Micro Langevin (ML) dynamics. Inset: reduced diffusion coefficients as a function of the temperature for three different state points at $\phi = 0.31$. As shown, the EDBD algorithm is very reliable in giving the correct dynamics at all times.

We use an adapted version of the algorithm proposed in Ref. 27 in order to perform Langevin simulations of this system with a damping factor $\xi/m \approx 150$. The results of this comparison are shown in Fig. 1, where the MSD for the state point $\phi = 0.31$, $T = 0.8$ is plotted against the rescaled time for both EDBD and LD. This state point is chosen as a test case since it is a low-T, high-density equilibrium liquid, where the dynamics is not trivial and the system is homogeneous.[28] The behavior of the MSD is very well reproduced by EDBD. In the inset of Fig. 1, we show the diffusion coefficients obtained from EDBD and LD at $\phi = 0.31$ for a few temperatures, all showing very satisfactory agreement between the two methods. This test allows us to use EDBD as a reliable reference algorithm to test our Brownian Monte Carlo procedure.

B. Event-driven Brownian dynamics and Brownian Monte Carlo compared

To validate the use of BMC to study the dynamics of Brownian particles with orientational degrees of freedom we compare BMC with EDBD simulations. To get a correct description of dynamical processes of Brownian particles with orientational degrees of freedom, it is crucial that in the generated trajectories particles rotate and translate in the right proportion. This proportion can be quantified by the ratio between the rotational and translational mean squared displacements $\langle\Delta\theta^2\rangle/\langle\Delta r^2\rangle$, which in the diffusive regime tends to a constant whose value $D_{\rm r}/D_{\rm t}$ is state dependent. In the infinite dilution limit, for instance, $\langle\Delta\theta^2\rangle/\langle\Delta r^2\rangle = D_{\rm r}^0/D_t^0 = 3$. In Fig. 2(a) we plot $\langle\Delta\theta^2\rangle/\langle\Delta r^2\rangle$ for $T = 0.15$ and two packing fractions, $\phi = 0.31$ and 0.41, as a function of $\langle\Delta r^2\rangle$ for BMC (satisfying Eq. (9)) and EDBD simulations. As it can be seen, roughly the same value of $\langle\Delta\theta^2\rangle/\langle\Delta r^2\rangle$ is obtained for BMC

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20

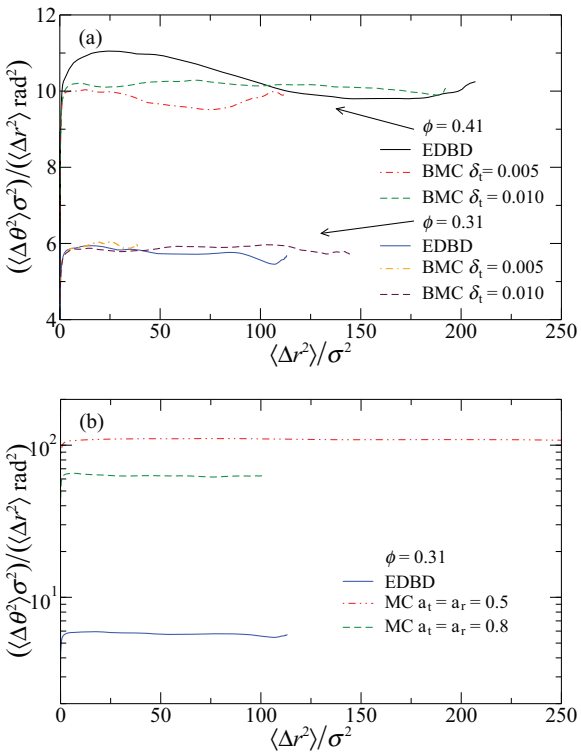

FIG. 2. (a) Ratio between the orientational and translational mean squared displacements versus the translational mean squared displacement for Brownian MC (satisfying Eq. (9)) and EDBD at $k_BT/u_0 = 0.15$ and two packing fractions: $\phi = 0.31$ and 0.41. EDBD and Brownian MC produce trajectories with the same proportion of rotation and translation. (b) Ratio between orientational and translational mean squared displacements versus the translational mean squared displacement for standard MC (where δ_t and δ_r are chosen to obtain a given acceptance rate), and EDBD at $k_BT/u_0 = 0.15$ and $\phi = 0.31$. As shown, a standard MC algorithm produces trajectories very far from physical, even if the acceptance rate is high (please note the log scale on the y axis).

and EDBD simulations. Figure 2(a) shows that increasing ϕ penalizes translation with respect to rotation, as particles can still easily rotate even though translation is hindered by collisions with other particles. The extent to which this happens is well captured by our BMC scheme. On the other hand, as shown in Fig. 2(b), a standard MC simulation in which the maximum trial displacements δ_t and δ_r are adjusted to give the same acceptance ratio produces trajectories that are very far from physical; the amount of rotation with respect to translation can be off by an order of magnitude with respect to the EDBD value. Figure 2 underlines the importance of satisfying Eq. (9) to study the dynamics of Brownian particles with orientational degrees of freedom using MC.

We now know that the trajectories produced by our BMC scheme are representative of the real dynamics of a set of Brownian particles with orientational degrees of freedom. If one wishes to obtain also the diffusion coefficients from BMC it is necessary to map the number of MC cycles to a physical time. We do that via Eqs. (4) and (8) for the translation and the rotation, respectively. From the slope of a plot of the mean squared displacement as a function of time one can get the diffusion coefficients. In Fig. 3, the mean squared displacements (both translational and rotational) from BMC and

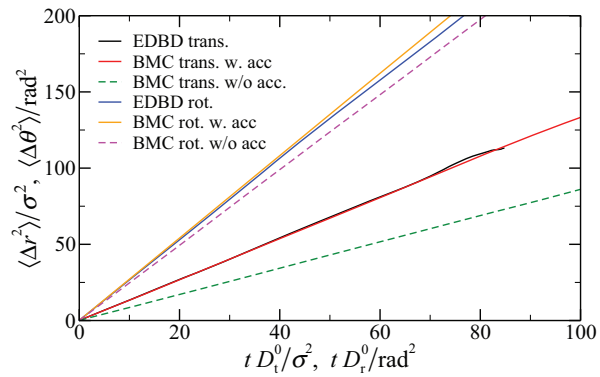

FIG. 3. Rotational and translational mean squared displacements versus time at $k_BT/u_0 = 0.15$ and $\phi = 0.15$ from BMC and EDBD simulations. Here, δ_t was fixed at 0.02, corresponding to $\overline{a}_t = 0.64$, and δ_r was chosen with the procedure introduced in Sec. II A to be 0.05036, corresponding to $\overline{a}_r = 0.91$. The solid BMC curves (w. acc.) have been obtained using $\delta_t^2\overline{a}_t/6$ and $\delta_r^2\overline{a}_r/18$ [Eqs. (4) and (8)] to convert BMC cycles to translational and rotational time, respectively. To obtain the dashed curves the same rescaling factors without including the acceptance (w/o acc.) have been used ($\delta_t^2/6$ and $\delta_r^2/18$).

EDBD at $k_BT/u_0 = 0.15$ and $\phi = 0.31$ are compared. The agreement between BMC and EDBD is good, both for rotation and translation. Dashed lines correspond to MC results without including the acceptance rate to convert MC cycles to physical time (Eqs. (4) and (8)). The agreement is much more satisfactory if the acceptance is included in the rescaling. In this way, good estimates of the diffusion coefficients can be obtained from MC even if the acceptance rate significantly deviates from 1, which is the limit for which Eqs. (4) and (8) are exact. This is useful because MC is very inefficient for acceptance rates near 1.[4] In Fig. 4, we analyze the influence of the acceptance rates on the diffusion coefficients. First, we notice that the inequality $\overline{a}_t > \overline{a}_r$ always holds. This is due to the fact that, while rotations can only be rejected due to bond breaking, translations can also be rejected because of overlap formation. Therefore, $\overline{a}_t$ is the limiting parameter in our Brownian MC simulations of the PMW. For $\overline{a}_t$ close to 1, the agreement with EDBD is excellent but the algorithm is highly inefficient. For $\overline{a}_t < 0.6$, however, BMC clearly

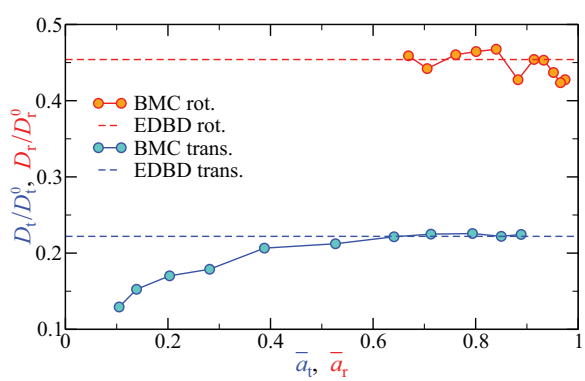

FIG. 4. Diffusion coefficients as a function of the average acceptance ratios, $\overline{a}_t$ or $\overline{a}_r$, for $k_BT/u_0 = 0.15$ and $\phi = 0.31$ (the same state point as Fig. 3). Our rescaling procedure works reliably for acceptance ratios greater than 0.7. For the case reported here, the translational moves are much more constrained than the rotational ones, but this needs not to be the case in general.

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20

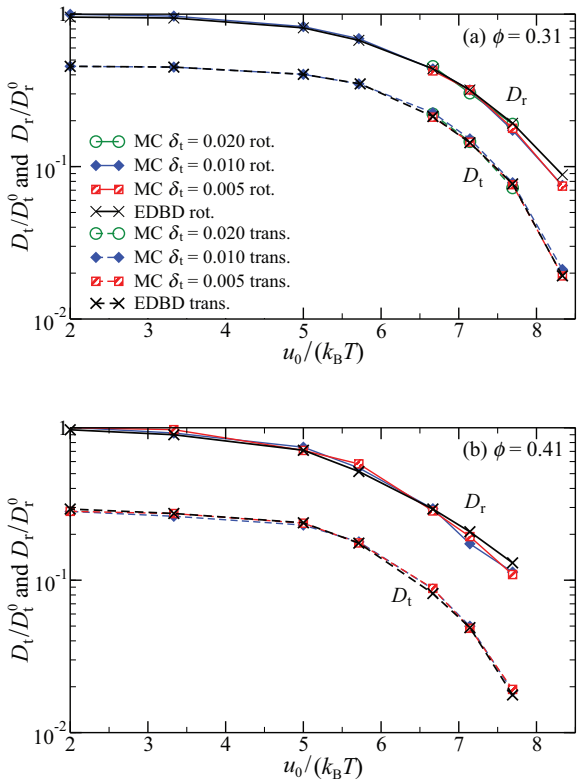

FIG. 5. Reduced rotational and translational diffusion coefficients as a function of the inverse temperature $u_0/(k_BT)$ for two packing fractions, $\phi = 0.31$ and $\phi = 0.41$. The procedure we propose works very well at high temperatures, reaching the hard sphere limit for $u_0/(k_BT)$, and retains good performance also at temperatures as low as it is possible to equilibrate within a few weeks of computer time.

underestimates D_t. We empirically find that $\overline{a}_t \simeq 0.7$ is a good compromise between accuracy (how close is BMC to EDBD) and efficiency (how long it takes to simulate a Brownian time unit). Therefore, a good recipe is to find a value of δ_t that gives $\overline{a}_t \simeq 0.7$ by following the steps described in Sec. II A.

From the slope of curves such as the ones shown in Fig. 3, we obtain the long-time diffusion coefficients, which we show in Fig. 5 for two different packing fractions and several temperatures. The agreement is excellent for both packing fractions. A comparison between Event Driven Molecular Dynamics (EDMD) and MC for the same model[17] showed that the diffusion coefficients obtained with MC can be mapped onto those obtained by EDMD using an empirical rescaling factor. Such mapping holds reasonably well for low and moderate temperatures, but it breaks down for high temperatures. Notably, in our MC–EDBD comparison the rescaling of the MC time is not empirical, but comes from the derivation shown above, and the agreement does not deteriorate with temperature.

IV. CONCLUSIONS

In this work, we have explored the possibility of studying the dynamics of suspensions of Brownian particles with orientational degrees of freedom using Monte Carlo simulations. Based on the Stokes–Einstein relations, we derived the ratio between translational and orientational maximum trial displacements that guarantees an equal time evolution for translation and rotation in a Monte Carlo simulation (Eq. (9)). Such ratio has to be iteratively achieved by tuning the maximum displacements in a series of short MC simulations. The tuning procedure needs to be done for every simulated state point. In a similar fashion we also extended the EDBD algorithm to the case of particles with rotational degrees of freedom taking into account both Stokes–Einstein and Debye–Stokes–Einstein relations. We tested our scheme with a primitive model of water, a non-differentiable potential. By comparing our Brownian Monte Carlo scheme with EDBD, we found that the dynamic Monte Carlo scheme we propose leads to a very reliable estimate of both the rotational and the translational long-time diffusion coefficients for different packing fractions and a wide range of temperatures. Given that the implementation of Monte Carlo is much simpler than that of EDBD, the scheme proposed here may prove very useful in studying dynamic processes in suspensions of Brownian particles with orientational degrees of freedom. The efficiency of our Brownian MC is limited because its accuracy breaks down if the value of the trial displacements is tuned to get acceptance rates of 0.3–0.4, as is the usual practice in MC. However, for acceptance rates grater than 0.7 we observe good agreement between BMC and EDBD dynamics. Although we have illustrated the usefulness of our Brownian BMC scheme by comparing it to EDBD for the case of a non-differentiable potential, we expect that, should a differentiable model be used, a standard BD algorithm would be usable in agreement with our Brownian MC. In principle, our scheme is devised for systems with small density heterogeneities in which the acceptance rate is roughly the same throughout the system. For instance, it would be suitable for studies of the dynamics of glass formation or crystal nucleation from a dense fluid, but not of gas–liquid phase separation, crystallization from a gas, or gel formation. A straightforward extension of the methodology proposed here would be required if one were interested in the rotation along a specific symmetry axis of the particle rather than in the overall average rotation.

ACKNOWLEDGMENTS

C.D.M. and F.R. acknowledge support from ERC (226207-PATCHYCOLLOIDS). E.S. is financed by a Marie Curie I-E fellowship.

[1] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[2] K. Binder and D. W. Heermann, *Monte Carlo Simulations in Statistical Physics*, 4th ed. (Springer, Berlin, 2002).
[3] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).
[4] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, 2nd ed. (Academic, New York, 2001).
[5] M. E. Cates, K. Stratford, R. Adhikari, P. Stansell, J.-C. Desplat, I. Pagonabarraga, and A. J. Wagner, J. Phys.: Condens. Matter **16**, S3903 (2004).
[6] A. Malevanets and R. Kapral, J. Chem. Phys. **110**, 8605 (1999).
[7] B. Cichocki and K. Hinsen, Physica A **166**, 473 (1990).
[8] K. Kikuchi, M. Yoshida, T. Maekawa, and H. Watanabe, Chem. Phys. Lett. **185**, 335 (1991).
[9] D. M. Heyes and A. C. Branka, Mol. Phys. **94**, 447 (1998).
[10] E. Sanz and D. Marenduzzo, J. Chem. Phys. **132**, 194102 (2010).
[11] A. Cuetos and M. Dijkstra, Phys. Rev. Lett. **98**, 095701 (2007).
[12] P. Pfleiderer, K. Milinkovic, and T. Schilling, EPL **84**, 16003 (2008).

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20

[13]Z. Zhang, T. Chen, and S. C. Glotzer, Langmuir **21**, 11547 (2006).
[14]F. Romano, E. Sanz, and F. Sciortino, J. Chem. Phys. **134**, 174502 (2011).
[15]E. G. Noya, C. Vega, J. P. K. Doye, and A. A. Louis, J. Chem. Phys. **132**, 234511 (2010).
[16]J. Kolafa and I. Nezbeda, Mol. Phys. **61**, 161 (1987).
[17]C. De Michele, S. Gabrielli, P. Tartaglia, and F. Sciortino, J. Phys. Chem. B **110**, 8064 (2006).
[18]D. J. Kraft, J. Groenewold, and W. K. Kegel, Soft Matter **5**, 3823 (2009).
[19]S. C. Glotzer and M. J. Solomon, Nature Mater. **6**, 557 (2007).
[20]Q. Chen, S. C. Bae, and S. Granick, Nature (London) **469**, 381 (2011).
[21]P. R. ten Wolde and D. Frenkel, Science **277**, 1975 (1997).
[22]A. Scala, T. Voigtmann, and C. De Michele, J. Chem. Phys. **126**, 134109 (2007).
[23]S. Corezzi, C. De Michele, E. Zaccarelli, D. Fioretto, and F. Sciortino, Soft Matter **4**, 1173 (2008).
[24]C. De Michele, J. Comput. Phys. **229**, 3276 (2010).
[25]C. Vega and P. A. Monson, J. Chem. Phys. **109**, 9938 (1998).
[26]F. Romano, P. Tartaglia, and F. Sciortino, J. Phys.: Condens. Matter **19**, 322101 (2007).
[27]B. G. de Grooth, Am. J. Phys. **67**, 1248 (1999).
[28]D. L. Pagan and J. D. Gunton, J. Chem. Phys. **122**, 184515 (2005).

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 157.138.110.176 On: Wed, 25 May 2016 12:04:20