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Brownian Dynamics, Molecular Dynamics, and Monte Carlo modeling of colloidal systems

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Abstract

This paper serves as an introductory review of Brownian Dynamics (BD), Molecular Dynamics (MD), and Monte Carlo (MC) modeling techniques. These three simulation methods have proven to be exceptional investigative solutions for probing discrete molecular, ionic, and colloidal motions at their basic microscopic levels. The review offers a general study of the classical theories and algorithms that are foundational to Brownian Dynamics, Molecular Dynamics, and Monte Carlo simulations. Important topics of interest include fundamental theories that govern Brownian motion, the Langevin equation, the Verlet algorithm, and the Metropolis method. Brownian Dynamics demonstrates advantages over Molecular Dynamics as pertaining to the issue of time-scale separation. Monte Carlo methods exhibit strengths in terms of ease of implementation. Hybrid techniques that combine these methods and draw from these efficacies are also presented. With their rigorous microscopic approach, Brownian Dynamics, Molecular Dynamics, and Monte Carlo methods prove to be especially viable modeling methods for problems with challenging complexities such as high-level particle concentration and multiple particle interactions. These methods hold promising potential for effective modeling of transport in colloidal systems.

Keywords: Brownian Dynamics; Molecular Dynamics; Monte Carlo; Inter-particle interaction; Diffusivity; Stochastic force; Verlet algorithm; Langevin equation; Metropolis method

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Contents

1. Introduction . . . 160
2. Background on Brownian motion . . . 161
    2.1. Defining the probability distributions for Brownian motion . . . 161
    2.2. Quantification of the distribution P_2 for discrete random walk . . . 161
    2.3. Modeling Brownian motion by a Gaussian probability distribution . . . 162
    2.4. Example of Brownian motion of a free particle . . . 162
3. Brownian Dynamics . . . 162
    3.1. Fundamental theory of Brownian Dynamics modeling . . . 163
    3.2. Incorporating inter-particle interactions . . . 164
    3.3. Numerical algorithms for Brownian Dynamics . . . 165
    3.4. Application to ionic solutions . . . 166
4. Molecular Dynamics . . . 166
    4.1. Verlet algorithm . . . 166
    4.2. Critique of the Verlet algorithm . . . 167
    4.3. Implementing a modified pair potential . . . 168

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- 4.4. Perturbation theory for MD . . . 168
  - 4.4.1. Theories of Kubo and Mori . . . 168
  - 4.4.2. Application of perturbation theory for MD . . . 168
- 5. Combined BD–MD algorithm . . . 169
- 6. Monte Carlo methods . . . 170
  - 6.1. Theory of Monte Carlo modeling . . . 170
  - 6.2. Application of Monte Carlo methods to Brownian Dynamics . . . 171
- 7. Concluding remarks . . . 172
- Acknowledgement . . . 173
- References . . . 173

1. Introduction

The purpose of this review paper is to introduce Molecular Dynamics (MD), Brownian Dynamics (BD), and Monte Carlo (MC) algorithms as alternatives for modeling colloidal transport as opposed to more conventional integral techniques such as the Ornstein-Zernike (OZ) Integral Method with Hypernetted-Chain (HNC) or Percus-Yevick (PY) closures. MD, BD, and MC algorithms offer colloidal science the advantageous capability of rigorous and meticulous accounting of discrete particle trajectories, collisions, and configurations that constitute a precise representation of the particle system at the microscopic scale [1]. Furthermore, these models deconstruct the macroscopic system behavior into individual contributions from the system's foundational, underlying constituents. Such a modeling approach strictly adheres to the actual system composition as it definitively attributes system responses to processes modeled to occur in its substructures. Therefore, the modeled system behavior can be understood and interpreted with precision and exactness. On the other hand, continuum-level modeling such as the OZ Integral Method describes the system using integrated average quantities of system properties, such as the osmotic pressure, that provide only a general representation. The macroscopic averaging of system properties is susceptible to inaccuracy or divergence when its approximations break down in the presence of complicating factors such as strong inter-particle interactions, high particle concentrations, and the onset of phase transition of the suspension [2]. In practice, the HNC and PY closures have been shown to be accurate up to a maximum particle volume fractions of 0.3–0.4 beyond which the models do not converge. Therefore, these methods are incapable of modeling the phase transition of particles that may occur at high volume fractions greater than 0.5 [3].

Furthermore, situations with inter-particle interaction at high particle volume fraction are better represented with inclusion of multi-body contributions to a given model which will again require approximations in the integral techniques [4]. On the contrary, MD, BD, and MC are capable of accounting for discrete multi-body contributions with the computationally intensive summation of all contributing particle interactions [5]. These modeling techniques have been deployed to accurately model systems of high particle volume fraction nearing the phase transition limit under the influence of particle interactions [6]. Therefore, the modeling methods are not only more fundamentally precise in their depiction of the system but also more robust when encountering complications and extreme conditions. Incorporation of these modeling methods to current modeling endeavors holds promising potential for advancing the accuracy of numerical modeling and broadening the range of applicability for theoretical understanding of colloidal transport properties.

This study will review previous modeling efforts using MD, BD, and MC as alternatives and improvements to continuum-level modeling. Of particular interest, the review will focus on algorithms for computing the thermodynamic and transport coefficients under conditions with inter-particle interaction. It will commence with a brief refreshment of the fundamental theories for Brownian motion, a critical element in the modeling of colloidal systems. The stochastic nature of Brownian motion can only be approximated by macroscopic techniques and compels rigorous, discrete accounting of individual particle trajectories to achieve a true depiction of the process. From that background, the review will proceed to first address Brownian Dynamics modeling. The fundamental theories of BD will be discussed, followed by examples of its algorithms and applications to ionic systems with inter-particle interactions. Next, the Molecular Dynamics method will be reviewed beginning with a discussion and critique of the Verlet algorithm which is considered to be the classical technique for MD modeling. The issue of modeling inter-particle interactions will again be discussed. Review of one of the more common usages of MD, perturbation theory, will ensue. Subsequently, hybrid methods that combine both BD and MD methods will be considered along with various alternative techniques. The review will then transition into a discussion of Monte Carlo techniques. Theories and variants of MC will be presented, followed by examples of applications of MC to model Brownian motion. Again, various hybrid methods combining MC and MD will be considered. The goal of this review is to bring about greater awareness of the potential for breakthroughs in modeling of colloidal transport encapsulated in MD, BD, and MC methods. It is the aspiration of the authors that MD, BD, and MC methods would undergo wider application in the field of colloidal sciences.

2. Background on Brownian motion

2.1. Defining the probability distributions for Brownian motion

To begin, a background on the fundamental theory of Brownian motion is appropriate. An excellent resource on the topic is the comprehensive review of Wang and Uhlenbeck in 1945 [1] on Brownian motion for free particles and the harmonic oscillator. In this work, Wang and Uhlenbeck [1] methodically recount the statistical properties of Brownian motion. As an introduction, trajectories of particles undergoing Brownian motion can be defined by a set of probability distributions where:

$W_1(y)\mathrm{d}y$ = probability of finding a particle in the range $(y, y+\mathrm{d}y)$ at time t.

$W_2(y_1 y_2 t)\mathrm{d}y_1\mathrm{d}y_2$ = probability of finding a particle in the range $\mathrm{d}y_1$ at time t_1 and $\mathrm{d}y_2$ at a time t $(=t_2-t_1)$ apart. (1)

and so on. More specifically, Brownian motion can be cast as a Markoff process meaning that the position of a particle at time t_n is solely dependent upon its location at the previous time t_{n-1}. In the Markoff process, the particle transitions from one location to the next by way of a conditional probability $P_2(y_1|y_2,t)\mathrm{d}y_2$ which signifies the probability that given the particle location at y_1, it will be located in the range (y_2, y_2+$\mathrm{d}y_2$) at a time t later. The conditional probability P_2 is related to the probability distributions of Eq. (1) by:

$$W_2(y_1 y_2 t) = W_1(y_1)P_2(y_1|y_2 t) \tag{2}$$

So, from Eqs. (1) and (2) it is apparent that the quantities W_2 and P_2 essentially defines the entire process. Mapping particle trajectory from Brownian motion becomes a task of defining and sampling the probability distribution P_2. A necessary property of the distribution P_2 is that it must obey the condition:

$$P_2(y_1|y_2,t) = \int \mathrm{d}y'\, P_2(y_1|y', t_0)P_2(y'|y_2, t-t_0) \tag{3}$$

where $t_0=t'-t_1$ and $t_1<t'<t_2$.

This is the well-known Smoluchowski Equation [7] which is the basis for the theory of Brownian motion. Thus, the derivation of the probability distribution that governs the Markovian process of Brownian motion is validated by its agreement with the normative Smoluchowski Equation. What remains now is to explicitly quantify the function P_2. A simple introductory example will be given in Section 2.2 to serve as the foundation for the subsequent more realistic models.

2.2. Quantification of the distribution P_2 for discrete random walk

So, it has been shown that for a Markoff process such as Brownian Motion, the system behavior is completely governed by the conditional probability P_2. A simple example involving a discrete random walk scenario will bring forth the application of the theory. In a one-dimensional discrete random walk, a particle traverses on a straight line making steps of size Δ forwards or backwards with equal probability at each time t. In this case, the conditional probability $P(n|m,s)$ that a particle positioned at $n\Delta$ at t=0 will be located at $m\Delta$ at time t=$s\tau$ (τ=time interval, s=1, 2, 3, ...) will be:

$$P(n|m,s) = \frac{s!}{\left(\frac{v+s}{2}\right)!\left(\frac{v-s}{2}\right)!}\left(\frac{1}{2}\right)^s \tag{4}$$

where v=$|m-n|$. Eq. (2) is thus readily computable and can be implemented in algorithms that model the stochastic nature of one-dimensional random walk by sampling this probability distribution.

In a more interesting scenario, this initial physical model can be advanced with the addition of the Ehrenfest transition probability [8] where the particle moves not with equal probability forward and backward but instead are more attracted to designated points. For instance, in the situation where a particle is attracted to initial point n, the transition probability distribution becomes:

$$Q(n|m,s) = \frac{R+n}{2R}\delta(m,n-1) + \frac{R-n}{2R}\delta(m,n+1) \tag{5}$$

where δ is the Kronecker delta and R is a given integer characteristic of the particular system. The particle now does not travel with equal probability forward and backward but instead with probabilities $\frac{1}{2}\left(1-\frac{n}{R}\right)$ and $\frac{1}{2}\left(1+\frac{n}{R}\right)$, respectively. The particle will then exhibit a tendency to move towards the point n. This extension mimics the influence of inter-particle interaction which is a frequent complication in colloidal transport problems. Eqs. (4) and (5) therefore offer fundamental models of one-dimensional random walk. This basic model can be applied to more complex problems involving two- and three-dimensional motion by sampling these probability distributions for particle motion in each coordinate direction. Details of this derivation are given in Wang and Uhlenbeck in 1945 [1]. Thorough discussions on random walk particle motion can be found in the classical paper by Chandrasekhar [9]. The mathematical formulation and physical depiction described above constitute the basic theory for the rigorous modeling of Brownian motion to follow.

2.3. Modeling Brownian motion by a Gaussian probability distribution

The Gaussian random process typifies the stochastic nature of many natural phenomena including Brownian motion. Wang and Uhlenbeck in 1945 [1] prove that for a Gaussian random process, the spectral density of the probability distribution represents the governing parameter of the system behavior. So, the Gaussian random probability distribution of the particle position $y(t)$ over a long time T should be written as a Fourier series of the form:

$$y(t) = \sum_{k=1}^{\infty} \left(a_k \cos 2\pi \frac{k}{T} t + b_k \sin 2\pi \frac{k}{T} t \right) \tag{6}$$

where a_k and b_k are independent random variables with Gaussian distribution. It should be noted that the summation begins at k=1 because $\langle y \rangle$=0. Wang and Uhlenbeck show that astute utilization of mathematical theorems of Gaussian distributions and applying them to the formulated Fourier series will readily generate the various types of probability functions that define Brownian motion. For instance, the mean square value of the particle velocity at a given time t will be:

$$\langle \dot{y}(t)^2 \rangle_{\mathrm{Av}} = 4\pi^2 \int_0^{\infty} f^2 G(f) \mathrm{d}f \tag{7}$$

where f=k/T and G is the spectral density of the Gaussian random variable $y(t)$. It becomes apparent here that the spectral density G is indeed the defining quantity of the Gaussian process. The spectral density can be obtained from the Langevin Equation of the particle motion as will be shown in Section 2.4.

2.4. Example of Brownian motion of a free particle

Wang and Uhlenbeck in 1945 [1] proceed to present the application of the above theory to the example of the Brownian motion of a free particle. The governing equation of motion is the well-known Langevin Equation with its general form given as:

$$\frac{\mathrm{d}\dot{y}}{\mathrm{d}t} + \beta \dot{y} = F(t) \tag{8}$$

where β is the friction coefficient and $F(t)$ is a random fluctuating force of the system. If $4D$ is taken as the spectral density of the random force $F(t)$, then in turn, the spectral density, $G_y(f)$, of the Gaussian random variable $y(t)$ becomes:

$$G_y(f) = \frac{4D}{\beta^2 + (2\pi f)^2} \tag{9}$$

From that the two-dimensional Gaussian distribution of the particle position follows as:

$$W_2(y_1 y_2 t) = \frac{\beta}{2\pi D (1-\rho^2)^{1/2}} \times \exp\left[-\frac{\beta}{2D(1-\rho^2)} \left\{ y_1^2 + y_2^2 - 2\rho y_1 y_2 \right\} \right] \tag{10}$$

where ρ=$\langle y_1 y_2 \rangle_{\mathrm{Av}} / \langle y_1^2 \rangle_{\mathrm{Av}} \langle y_2^2 \rangle_{\mathrm{Av}}$ is the correlation coefficient.

The distribution W_2 is sufficient to map the particle trajectory. Eq. (10) can be implemented into algorithms that seek to model Brownian motion. Again, extension to two- and three-dimensional motion can be attained by applying this procedure to each direction of motion.

3. Brownian Dynamics

Having re-developed the theoretical foundation of Brownian motion, the review proper will embark first on a discourse on Brownian Dynamics with its fundamental theory, algorithms, and applications. The uniqueness of BD lies in its capability to account for timescale separation, a complication problematic to MD modeling. Timescale separation depicts situations where one type of motion in the system occurs at much more rapid times than the others. Timescale separation compels MD modeling to take small time steps in order to synchronize with the rapid variations. In systems where the rapid process is not of interest, timescale separation introduces an irrelevant complication that slows the modeling procedure. So, BD offers an efficient alternative that bypasses this hindrance by considering the stochastic properties of the rapidly varying quantities in the system. Sampling the probability distributions of the stochastic processes does compromise a strict microscopic view of the system. However, discrete accounting of individual particle motion is still maintained, and so BD remains classifiable as a rigorous microscopic modeling technique. The essential theories, applications, and continuing developments of BD will be surveyed here.

3.1. Fundamental theory of Brownian Dynamics modeling

Overviews of the fundamental theories of Brownian Dynamics are given in Ermak [2], Ermak and Buckholtz [3], and Van Gunsteren and Berendsen [4]. The governing equation for BD is the Langevin Equation given here with consideration for particle interactions:

$$m\dot{v}(t) = -\gamma m v(t) + f(t) + R(t) \tag{11}$$

where m is the particle mass. Here, γ represents the friction coefficient that produces a non-conservative, non-systematic force induced by the solvent (e.g. frictional forces) and $f(t)$ adds a conservative, systematic force due to the inter-particle potential. Of particular interest here is the characteristics of the conserved random force $R(t)$ that is responsible for the Brownian motion. Referring to the discussion in Section 2, the Brownian motion is taken to be a random Gaussian process with properties given by Eq. (10). Various methods are available for integration of Eq. (11) to obtain an algorithm for the particle displacement. One possibility is given by Van Gunsteren and Berendsen in 1982 [4] for a one-component atomic system. The algorithms for particle displacement in their work are:

$$\begin{aligned} r(t_n+\Delta t) = {} & r(t_n)[1+\exp(-\gamma\Delta t)] - r(t_n-\Delta t)\exp(-\gamma\Delta t) + \frac{f(t_n)(\Delta t)^2[1-\exp(-\gamma\Delta t)]}{m\gamma\Delta t} \\ & + \frac{\dot{f}(t_n)(\Delta t)^3\left\{\frac{1}{2}\gamma\Delta t[1+\exp(-\gamma\Delta t)] - [1-\exp(-\gamma\Delta t)]\right\}}{m(\gamma\Delta t)^2} \\ & + X_n(\Delta t) + \exp(-\gamma\Delta t)X_n(-\Delta t) + O\left[(\Delta t)^4\right] \\ v(t_n) = {} & \frac{\left\{[r(t_n+\Delta t) - r(t_n-\Delta t)] + \dfrac{f(t_n)(\Delta t)^2 G(\gamma\Delta t)}{m(\gamma\Delta t)^2} - \dfrac{\dot{f}(t_n)(\Delta t)^3 G(\gamma\Delta t)}{m(\gamma\Delta t)^3} + [X_n(-\Delta t) - X_n(\Delta t)]\right\} H(\gamma\Delta t)}{\Delta t} \end{aligned} \tag{12}$$

where $f(t_n)$ is the systematic force derived from the inter-particle interaction and:

$$\begin{aligned} X_n(\Delta t) &= \frac{\int_{t_n}^{t_n+\Delta t}\{1-\exp[-\gamma(t_n+\Delta t-t)]\}R(t)\mathrm{d}t}{m\gamma} \\ G(\gamma\Delta t) &= \exp(\gamma\Delta t) - 2\gamma\Delta t - \exp(-\gamma\Delta t) \\ H(\gamma\Delta t) &= \frac{\gamma\Delta t}{[\exp(\gamma\Delta t) - \exp(-\gamma\Delta t)]} \end{aligned} \tag{13}$$

with $X_n(\Delta t)$ being a random variable that characterizes the random force $R(t)$. The random force, $R(t)$, exhibits the statistical properties:

$$\begin{aligned} &\langle R_i(0)R_j(t)\rangle = 2m_i\gamma_i k_B T\delta_{i,j}\delta(t) \\ &W(R_i) = \left[2\pi\langle R_i^2\rangle\right]^{-1/2}\exp\left\{-R_i^2/2\langle R_i^2\rangle\right\} \\ &\langle R_i\rangle = 0 \\ &\langle v_i(0)R_j(t)\rangle = 0, \quad t\geq 0 \\ &\langle f_i(0)R_j(t) = 0, \quad t\geq 0 \end{aligned} \tag{14}$$

where $\langle\ldots\rangle$ denotes the average over an ensemble, subscripts i and j classify the components of the ensemble, k_{B} is the Boltzmann's constant, T is the reference temperature, $\delta_{i,j}$ is the Kronecker delta, and $W(R_i)$ denotes the Gaussian distribution of the random force $R(t)$. The solution procedure then becomes a matter of integrating the random force, inputting the systematic and non-systematic forces, and mapping the particle trajectories according to Eq. (12). Details of the algorithm are given in Sections 3.2–3.4.

3.2. Incorporating inter-particle interactions

When applying BD modeling to colloidal systems in solution, a critical issue to consider is the role of inter-particle interactions that produce the systematic force as described by Eq. (11). The influence of inter-particle interactions becomes especially important when the system approaches high-particle concentrations nearing the phase transition limit where appreciable portions of the inter-particle potential arise from many-body contributions. In fact, Verlet in 1967 [5], in his classical work on MD modeling, remarks that the choice of the model for inter-particle interactions is among the most crucial determining factors of the accuracy and range of capability of the model. Therefore, any modeling endeavor of particle systems in liquid must place proper emphasis on representative evaluation of the inter-particle interactions occurring throughout the range of experimental conditions.

Allen in 1980 [6] presents a Brownian Dynamics model for simulating chemical reactions in a particle system in solution that includes three types of interparticle-interaction terms. In this study, Allen considers the situation where a particle B is transferred between two substrates A and C:

$$A - B\cdot\cdot\cdot C \quad \rightleftarrows \quad A\cdot\cdot\cdot B - C \tag{15}$$

where the dash (–) signifies a bond between two particles and the dotted line ($\cdot\cdot\cdot$) signifies that the two particles are detached. This scenario should be expected in highly concentrated particle suspensions and mimics the process of particle detachment and coagulation. The significance of three-body interactions is clearly evident. Allen [6] considers three contributions to the inter-particle interaction, the Lennard–Jones potential between particle pairs, the attraction between bonded pairs in the chemical reaction, and a three-body potential that facilitates the chemical reaction. Of interest here is the Lennard–Jones potential which is a commonly employed model for computing the pairwise inter-particle potential given as:

$$V^{\mathrm{LJ}}(r_{1,2}) = 4\varepsilon_{\mathrm{LJ}}\left[\left(\frac{\sigma}{r_{1,2}}\right)^{12} - \left(\frac{\sigma}{r_{1,2}}\right)^{6}\right] \tag{16}$$

where $r_{1,2}$ is the inter-particle separation, σ is the radius of the particle, and $\varepsilon_{\mathrm{LJ}}$ the characteristic potential energy minimum of the interaction between the two particles. The Lennard–Jones potential may be adequate for dilute systems where particle B experiences predominately the potential from particle A. However, in cases where particle C lies in close proximity to the pair A–B, the strictly pairwise potential of Eq. (16) should be modified to account for the third particle. Allen [6] suggests that the modeling of the inter-particle potential can be improved by replacing the Lennard–Jones potential of Eq. (16) with an improved form given in Allen [6] that utilizes the pair-distribution function $g(r_{1,2})$ in the Lennard–Jones liquid at the chosen temperature and density:

$$V^{\mathrm{g}}(r_{1,2}) = -k_{\mathrm{B}}T\ln g(r_{1,2}) \tag{17}$$

The pair-distribution function may be computed from the discrete particle locations in the suspension. Incorporating the pair-distribution function will provide additional consideration for the multi-body correlations, whether pair-wise or greater, that the potential will induce within the particle system. This approach to computing the pair-distribution function improves the inaccuracies of the pair-distribution function at high concentrations (upper limit of approximately volume fraction 0.4 [10]) when deriving it from the inter-particle potential [11]. A further improvement would be to employ a three-body potential for a colloidal triplet in an equilateral triangular configuration as given in Wu et al. [10] by first considering the contribution of three-body effects to the inter-particle force:

$$\Delta F_3 = \frac{2F_3}{3} - F_2 \tag{18}$$

where ΔF_3 is the additional three-body contribution to the inter-particle force, F_3 is the average total force between two particles in a three-body system, and F_2 is the force between two isolated particles without three-body effects. The three-body potential follows from the integration of the force. Of course, it should be noted here that Eq. (18) is valid specifically for an equilateral triangular such as when the colloidal suspension approaches a face-centered-cubic or body-centered-cubic ordered structure. So, the three-body potential derived by Wu et al. [10] may become useful in situations where the suspension approaches solidification to an ordered structure. In a modeling algorithm, Eq. (18) can be applied at each time step to compute the adjustments needed to the pair-wise potential from three-body effects.

Such an approach discretely accounts for individual particle contributions and so would not be hindered by limits of particle concentration. The detraction of a three-body potential stems from the exponential rise in the computation time that renders many such models highly impractical. Turq et al. in 1979 [11] offer a less computationally intensive method for including many-body interactions using the Ewald method. The resulting inter-particle potential is given as:

$$V_{1,2}(r_{1,2}) = \left\{\frac{e^2}{n_c}(a_1^* + a_2^*)\right\}\left\{\frac{(a_1^* + a_2^*)}{r_{1,2}}\right\}^{n_c} - \frac{e_1 e_2}{\varepsilon r_{1,2}} \tag{19}$$

where a_1^* and a_2^* are the Pauling ionic radii of the particle pair, e_1 and e_2 are the particle charges, ε is the dielectric constant of the medium, and n_c is a parameter of the system. Eq. (19) includes the influence of neighboring particles to each pairwise potential. Details of this method are given in Lewis and Singer in 1975 [12].

For a particle system in liquid, the proper choice for modeling the inter-particle interaction should be regarded as a key step in the theoretical development. In particular, for systems of high particle concentration, usage of purely pairwise potentials such as the Lennard–Jones potential should be undertaken with caution, and considerations for many-body contributions are desirable. Duly noted is that the demands for computational efficiency may dictate relaxation of a strict adherence to modeling a many-body system.

3.3. Numerical algorithms for Brownian Dynamics

Given the fundamental theories for depicting stochastic Brownian motion and inter-particle interactions presented in Sections 3.1 and 3.2, an executable numerical algorithm for mapping particle trajectories can be devised. Van Gunsteren and Berendsen in 1982 [4] present a BD algorithm that proves to be more robust than previous algorithms by allowing for a varying

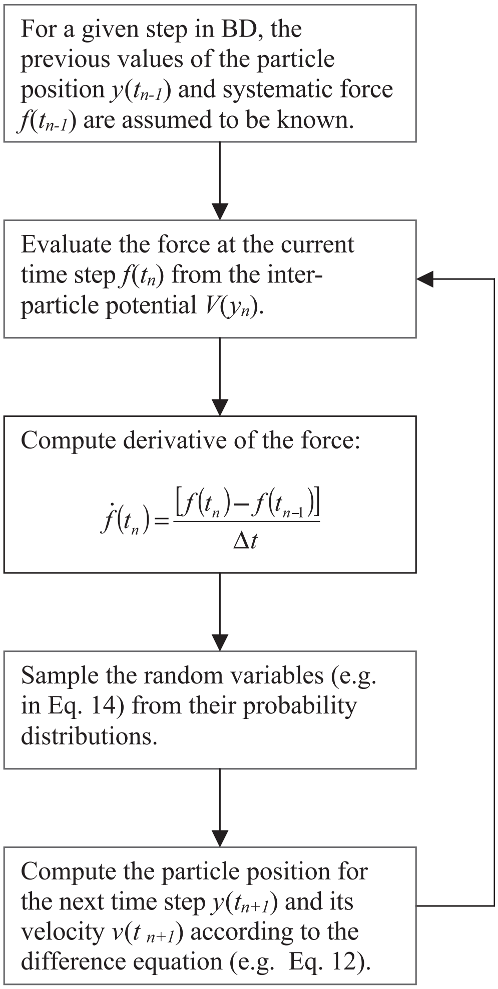


Fig. 1. Flow chart for a typical BD algorithm from Van Gunsteren and Berendsen [4].

random force within each time step and is based on the well-known Verlet MD algorithm. The modeling procedure initiates with the ordinary Langevin equation which is integrated to produce expressions for particle displacement and velocity similar to that given in Eq. (12). The solution procedure is given in Fig. 1. Details of the theoretical development and numerical algorithm are given in Van Gunsteren and Berendsen [4].

Key attributes of the algorithm of Van Gunsteren and Berenden [4] are first that it conforms to the classical Verlet algorithm in the limit of zero friction (γ=0). This convergence accords the algorithm with validation in agreement with a generally accepted and established algorithm. Secondly, the derivation of Van Gunsteren and Berenden [4] does not assume the random force to be constant within each time step of the algorithm which is the assumption used in Turq et al. [13]. Rather, the random force is integrated with consideration for its statistical properties in the form of probability distributions. The assumption of a constant random force at each time step requires that the time step be much smaller than the velocity relaxation time ($\Delta t \ll \gamma^{-1}$). Such a restriction results in much longer computation times due to the small step size. The algorithm of Van Gunsteren and Berenden [4] circumvents that restriction and delivers a faster computation scheme.

3.4. Application to ionic solutions

Having derived algorithms for BD, direct practical application to physical systems can now be examined. Turq et al. in 1977 [13] utilize BD to model the motion of interacting ions in an electrolyte solution. Their formulation aligns with the discussions given in Sections 3.1–3.3. The inter-particle potential given in Eq. (19) is selected in their model. The experimental conditions for their simulation are given in Table 1. Using their algorithm for BD such as described in Section 3.3, the trajectory of the collection of particle motion in the system is mapped. From that, the diffusivity of the system can be computed according to:

$$D = \lim_{t \to \infty} \frac{\langle r(t)^2 \rangle}{6t} \tag{20}$$

Results of their model show that the diffusivities for the cation and anion computed from BD (D_+=1.15×10^5 and D_-=1.55×10^5 cm^2/s) agree with experimental measurements (D_+=1.225×10^5 and D_-=1.795×10^5 cm^2/s). The effects of the inter-particle potential causes computed diffusivities to differ appreciably from the Stokes–Einstein diffusivities given in Table 1. So, an application of BD to successfully model particle motion in ionic solution is offered by Turq et al. [13]. Worthy of note is that the modeling is undertaken for ionic systems with electrolyte molarity of 1 M. These experimental conditions are not representative of highly concentrated particle suspensions nearing the phase transition. Furthermore, the model of the method of Turq et al. [13] is susceptible to the critique raised in Section 3.3 for their assumption of a constant random force at each time step. In fact, the restriction on the size of the time step is only loosely met in their study. The work of Turq et al. [13] offer a useful application of BD to the computation of thermodynamic and transport coefficients, but further developments to their theoretical formulation and testing of their results can still improve their model.

4. Molecular Dynamics

Molecular Dynamics takes the exhaustive approach of discrete accounting of forces exerted on each particle of the system without the approximations inherent in sampling of probability distributions as in BD. The modeling procedure casts the particle system as a system of Newtonian mechanics equations of motion. Forces that would be encountered in systems of interest to this study would include inter-particle interactions, diffusive forces, osmotic pressure, and external forces. Once the canonical equations are specified, the solution procedure becomes a matter of solving the system of N partial differential equations. The numerical method of choice has been finite difference of time.

Table 1
Experimental conditions for modeling in Turq et al. [13]

Parameters	Cation	Anion
Number of particles	32	32
Mass (atomic units)	23	35.5
Charge	1	−1
D (10^5 cm^2/s)	1.335	2.035
t_p (momentum correlation time in ps)	0.01239	0.02914

Aqueous solution with 1 M NaCl at 25 °C. D is the Stokes–Einstein diffusivity.

4.1. Verlet algorithm

The generally accepted classical algorithm for MD has been the Verlet algorithm. Verlet [5] provides exposition of his technique and categorizes it to be an “exact” method. The modeling procedure begins by casting the system in terms of its Newtonian equation of motion of each individual particle of the system:

$$m \frac{d^2 \vec{r}_i}{dt^2} = \sum_{i \neq j} \vec{F}\left(r_{i,j}\right) \tag{21}$$

where $\vec{F}$ is the inter-particle force. Verlet [5] only considers the contribution of inter-particle potential to the force term. The inter-particle potential is modeled as the Lennard–Jones type as given in Eq. (16). The solution procedure begins with integration of Eq. (21). Verlet [5] presents a simple difference equation for the integration:

$$r_i(t+h) = -r_i(t-h) + 2r_i(t) \sum_{i\neq j} F\left(r_{i,j}(t)\right) h^2 \qquad (22)$$

where h is the time step. The particle trajectory can be readily mapped from Eq. (22) with available current and past positions. The rate-limiting step in this algorithm lies in the computation of the inter-particle force, which for a system of N particles requires $N(N-1)/2$ computations at each time step. For a given particle, many of the terms in its summation of forces will be insignificant due to a large inter-particle separation with a given potential cutoff distance. So, the algorithm could be accelerated by implementing the Verlet's neighborhood list [5], which selects the nearest neighbors to include in the computation of Eq. (22). The use of the Verlet's neighborhood list derives a cut-off inter-particle separation, r_M, beyond which the force terms are negligible. Verlet [5] suggests a criterion for the cut-off separation of:

$$r_M - r_v < n\bar{v}h \qquad (23)$$

where r_v is the cut-off radius for the particle potential in units of the particle radius σ, n is chosen number of time steps, and $\bar{v}$ is a root-mean-square velocity of the particles. For a chosen n, the algorithm would proceed for $n-1$ time steps where only particles inside a distance r_M to the particle at the initial time step are included in the force term. Computational efficiency is a critical issue for MD as will be discussed further in Section 4.2.

Verlet [5] models a system of 864 argon molecules and successfully computes its thermodynamic properties such as temperature, pressure, and critical compressibility. The results of the modeling for the compressibility factor are shown in Fig. 2. The experimental values and model results are in good agreement.

Further advancements to the Verlet algorithm has led to the development of the velocity Verlet method. It is becoming the popular method of choice in recent MD models. Details of the updates to the classical Verlet algorithm using the velocity Verlet Method can be found in Swope et al. [14].

4.2. Critique of the Verlet algorithm

This apparently simple algorithm does contain a major drawback which is also associated with its greatest strength. Molecular Dynamics is commended to be an "exact" method for its meticulous accounting of all particles and forces within the system. So, for a system that involves a rapidly varying stochastic force (e.g. particle motion induced by an adjoining heat bath), that particular force must be discretely modeled as well. In these cases, the time step must be sufficiently small such that the stochastic force remains relatively constant during each time step. This constraint could greatly increase the computational demands of the algorithm. Therefore, MD is not as efficient as BD in the area of modeling timescale separation.

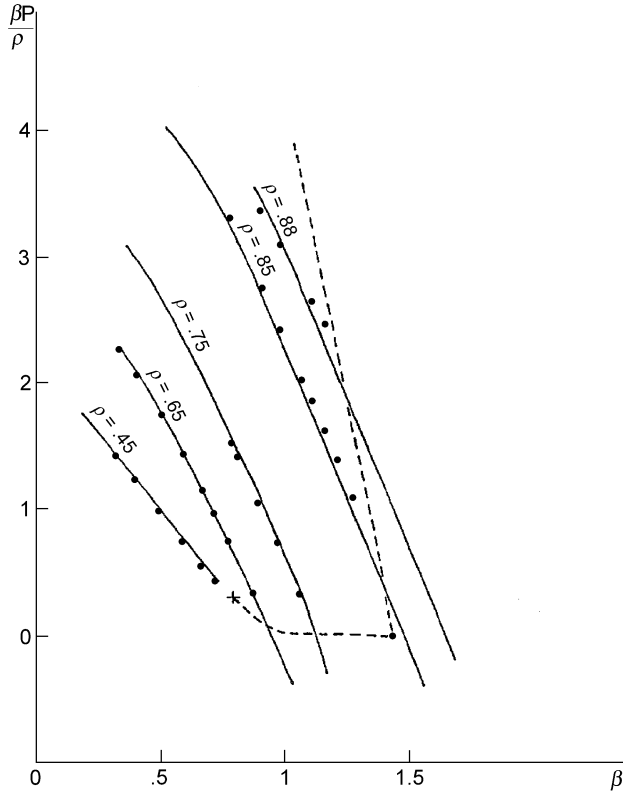


Fig. 2. The compressibility factor $\beta p/\rho$ as a function of β for the isochors β=0.88, 0.85, 0.75, 0.65, and 0.45 (solid lines), as compared with the experimental data for argon (dots). The dashed curves correspond to the gas–liquid and solid–fluid coexistence lines [5].

A second weakness of the algorithm of Verlet [5] is that it does not accurately model xenon particles which are more densely concentrated. Verlet [5] suggests that the choice of the Lennard–Jones potential may not be applicable in this case. In fact, the pair-wise approach of the Lennard–Jones potential is especially susceptible to inaccuracy in the critical regime of phase transition where multi-body forces become significant. Verlet [5] suggests that a Kihara potential would be more appropriate. Improving the inter-particle potential using Eqs. (17), (18), or (19) offers additional possibilities.

As a final note, due to the demands for computational efficiency, the use of periodic boundary conditions in the Verlet model poses an added obstacle to the simulation. Verlet [5] implements a box of length L comprising subsets of simulation cells with length a. The periodic boundary conditions restrict inhomogeneities in the system to a size within the length of one modeling cell. So, an inherent degree of order and limitation in wavelength is induced that represses the possibility of two-phase coexistence. In general, the restriction due to the periodic boundary condition is unavoidable. However, it can be controlled by proper selection of the number of particles per simulation cell and cell size.

4.3. Implementing a modified pair potential

Ermak [2] presents a modified pair potential as a more complete model of inter-particle interaction over the Lennard–Jones potential to model the motion of charged particles in ionic solution. The derivation begins with Poisson's equation and accounts for contributions from each particle in the system:

$$\nabla^2 V(r) = -\left(\frac{4\pi}{\varepsilon}\right)\rho(r) \tag{24}$$

where $\rho(r)$ is the charge distribution of particles and ions in the solution and ε is the dielectric constant of the medium. The charge distribution at each location r includes one particle of charge $-Nq$, $N+M$ counterions of charge $+q$, and M by-ions of charge $-q$. Each such system constitutes a basic modeling box of length L. This charge distribution at a given basic modeling box can be written as a Fourier series:

$$\rho(r) = \sum_{i=1}^{N_t} a_i \sum_{k=1}^{N_t} \mathrm{e}^{ik(r-r_i)}$$

$$a_i = \begin{cases} +1 \text{ for } 1 \le i \le N+M \\ -1 \text{ for } N+M+1 \le i \le N+2M \\ -N \text{ for } i = N+2M+1 = N_t \end{cases} \tag{25}$$

The potential distribution in each basic modeling box can be written in periodic form as:

$$V(r) = \frac{4\pi q}{\varepsilon v_{\text{cell}}} \sum_{i=1}^{N_t} a_i \sum_{k=1}^{N_t} \frac{1}{k^2} \mathrm{e}^{ik(r-r_i)} \tag{26}$$

where v_{cell} is the volume of the basic modeling box. The overall potential of one basic box is then:

$$U = \frac{1}{2}\int_{v_{\text{cell}}} \rho(r)V(r)dv_{\text{cell}} - \frac{q^2}{2\varepsilon}\sum_{i=1}^{N_t} a_i^2 \int_{v_{\text{cell}}} \frac{\delta(r-r_i)}{|r-r_i|}dv_{\text{cell}} \tag{27}$$

From Eq. (27), the inter-particle force is simply the gradient of the potentials. The advantage of this technique is that it reduces the number of terms in the summation of inter-particle interactions to those inside the basic box but still includes contributions from outside the box by computing the gradients of the overall potential U. The result is a great reduction in the computational demand. This strategy can be adapted to highly concentrated particle systems by grouping the particles into basic boxes such that overall potentials U in each cell can be used to compute the inter-particle potentials with a given particle i. The traditional method of Ermark given in Eqs. (24)–(27) has been updated recently by such techniques as the mesh Ewald [15,16] and the fast multiple method of Greengard [17].

4.4. Perturbation theory for MD

4.4.1. Theories of Kubo and Mori

An often-employed method of MD is perturbation theory. Perturbation theory computes transport coefficients, such as the diffusivity, as a linear response of an external field. In these situations, the external field does not induce a phase transition of the particles. Kubo [18] extensively develops the principles that govern perturbation theory and its applicability to the computation of dynamical constants such as the diffusivity. The method entails subjecting the system to a perturbing force and quantifying the system response in terms of time correlations between the perturbed and unperturbed systems. Using this idea, Kubo [18] derives the fundamental relation that the diffusivity can be computed from the time correlations of the velocities of particles in the system. The derivation of the theory is too involved to be presented here and so the reader is referred to Kubo [18] for details of the theoretical formulation.

The Kubo theory does impose a restriction in that it is only applicable to perturbations that are external to the system. Situations where the concentration gradient induces a perturbation in the form of a diffusive flux cannot be modeled by this theory. But Kubo's theory is useful for modeling interparticle interactions as the perturbation. The case of internal perturbations for a dilute system is treated by Mori [19]. Here, the diffusion caused by internal perturbations such as concentration gradients is computed from the conjugate fluxes of state variables. Again due to the lengthy derivation, the reader is referred to details given in Mori [19].

The theoretical developments of Kubo [18] and Mori [19] form the fundamental principles for MD modeling by perturbation theory. An example of the application of this modeling approach will be discussed in Sections 4.4.2 and 5.

4.4.2. Application of perturbation theory for MD

Ciccotti et al. [20] present a perturbation method for MD to compute the transport coefficients based upon the theory of Kubo [18]. The premise is that if during each step of an MD algorithm a perturbation is applied to the system (e.g. adjustments to particle coordinates or momentum), the time correlation between the system behaviors of the perturbed and unperturbed systems will yield the transport coefficients. For example, if $\alpha(r)$ is a dynamical variable of interest distributed throughout a system of N particles, then Kubo's theory yields:

$$\alpha(r) = \sum_{i=1}^{N} \alpha_i \delta(r-r_i) \tag{28}$$

Suppose the system is perturbed at time t=0 by an external field $\phi(r,t)$. The Hamiltonian of the perturbed system would be:

$$H = H_0 + H_1(t) \tag{29}$$

where H_0 and $H_1(t)$ are the Hamiltonians of the unperturbed system and the perturbation, respectively. The mean change in an observable property $\hat{O}$ of the system at time $t=\tau$ can be expressed in terms an autocorrelation function in Fourier space:

$$\langle \hat{O}(k) \rangle_\tau = \beta V \int_{-\infty}^{\tau} \mathrm{d}t' \, \langle \hat{O}(k,\tau) \hat{J}^\alpha(-k,t') \rangle_0 ik\phi(k,t') \tag{30}$$

where β=1/$k_\mathrm{B}T$, V is the volume of the system, and $\hat{J}^\alpha$ is the current corresponding to the dynamical variable α that in Cartesian coordinates satisfies:

$$\dot{\alpha}(r,t) + \nabla J^\alpha(r,t) = 0 \tag{31}$$

The general derivation given above can be clarified by a specific application. Ciccotti et al. [20] uses perturbation theory to compute the thermal conductivity λ of a particle system by introducing an energy fluctuation as the perturbation. The result for the system response is:

$$\lambda T = \beta V \int_0^{\infty} \mathrm{d}t' \, \langle \hat{J}_x^\mathrm{e}(0,t') \hat{J}_x^\mathrm{e}(0,0) \rangle_0 \tag{32}$$

where $\hat{J}_x^\mathrm{e}$ is the energy current in the x direction and satisfies the conservation given in Eq. (31) for the energy of the system. This application for computing the thermal conductivity can be readily translated to the case for calculating the transport diffusivity. Eq. (31) can be converted to an expression for mass transport by replacing the current J by mass flux of particles and the dynamical variable α by the particle mass. Eq. (32) would then become an expression for the diffusivity in terms of the autocorrelation of the mass fluxes.

The algorithm for perturbation theory would perform a typical MD simulation as given in Section 4.4.1. At each time step, the perturbation is introduced and the corresponding fluxes computed (e.g. the particle mass fluxes are computed from the particle trajectories mapped by MD). Next, the responses are computed according to Eq. (32) to yield the transport coefficients of interest at that time step. So, perturbation theory presents an alternative for computing thermodynamic coefficients using MD. It should be noted once again that the diffusivity computed here is the mutual diffusion coefficient of binary mixtures or the self-diffusion coefficient of a one component suspension. Perturbations arising from an internal concentration gradient cannot be accommodated by this method. Mori [19] addresses the issue of concentration gradient driven diffusion in a dilute system.

5. Combined BD–MD algorithm

As mentioned in Section 3, an important strength of the BD method lies in its capability of coping with high-frequency stochastic forces that confound MD methods. On the other hand, MD boasts of strengths in its comprehensive accounting of forces and simplicity of implementation as shown in Section 4. A combination of the two methods could reap the benefits of each. Ciccotti et al. [21] present a hybrid technique that employs a combined BD–MD model termed Generalized Brownian Dynamics (GBD) to extract the all-important velocity autocorrelation function of the system. From the discussion in Section 2, the spectral density of the velocity, which can be computed from its autocorrelation function, determines the particle trajectories in Brownian motion.

The strategy begins with using the Generalized Langevin Equation to model the particle Brownian motion:

$$\dot{v}_i(t) = -\int_0^t \mathrm{d}s \gamma_1(t-s)v(s) + R_1(t)$$

$$\langle R_1(t) \rangle = 0$$

$$\langle R_1(t)R_1(s) \rangle = \gamma_1(|t-s|)\langle v^2 \rangle \tag{33}$$

where R_1 is the random force producing the Brownian motion and belongs to a set $\{R_i(t),\ i=1,\infty\}$ that satisfies:

$$\dot{R}_i(t) = -\int_0^t \mathrm{d}s \gamma_{i+1}(t-s)R_i(s) + R_{i+1}(t);\ i=1,\infty \tag{34}$$

and the memory functions $\{\gamma_i(t),\ i=1,\infty\}$ are proportional to the random forces by:

$$\langle R_i(t)R_i(s) \rangle = \gamma_i(|t-s|)\langle R_{i-1}^2 \rangle;\ i=2,\infty \tag{35}$$

From Eqs. (34) and (35), it is evident that the parameters γ_i determine the velocities. The γ_i's can be found from curve-fitting with $\tilde{C}_v(p)$, the Laplace transform of the normalized velocity autocorrelation function $C_v(t)=\langle v(t)v(0) \rangle / \langle v^2 \rangle$, using Mori's continued fraction:

$$\tilde{C}_v(p) = \cfrac{1}{p + \cfrac{\gamma_1(0)}{p + \cfrac{\gamma_2(0)}{p + \cfrac{\vdots}{\cfrac{\gamma_{n-1}(0)}{p + \tilde{\gamma}_n(p)}}}}} \tag{36}$$

The fitting procedure requires prior knowledge of the velocity autocorrelation. Various methods are available for obtaining the velocity autocorrelation function including performing a preliminary MD model. However, the low-order differentiability of the numerical results of the correlation function from MD introduces large errors into the Mori's continued fraction. So, an MD correlation function should be further conditioned to render it suitable for input into Eq. (36).

The conditioning process begins by casting the Fourier transform of the MD correlation function $\widehat{C}_v(\omega)$ as:

$$\widehat{C}_v(\omega) = \frac{|P(i\omega)|^2}{|Q(i\omega)|^2}$$

$$P_m(i\omega) = \rho_0^2\left(1 + \sum_{k=1}^{m} X_k(i\omega)^k\right),\ m = 1, 2, \ldots$$

$$|Q(i\omega)|^2 = \exp\{\alpha\omega^2\} = \sum_{k=0}^{\infty}\frac{\alpha^k\omega^{2k}}{k!},\ \alpha>0 \tag{37}$$

where ρ_0 is a normalization factor of the function. The function $\widehat{C}_v(\omega)$ is then fitted against a trial function of the form:

$$\widehat{C}_T(\omega) = \rho_0^2\left(\sum_{l=1}^{m} C_1\omega^{2l}\right)\exp\{-\alpha\omega^2\}$$

$$C_1 = X_l^2 + 2\sum_{j=1}^{l}(-1)^j X_{l+j}X_{l-j}$$

$$X_k = \begin{cases} 0 \ \mathit{if}\ k<0 \text{ or } k>m \\ 1 \text{ if } k = 0 \end{cases} \tag{38}$$

The fitted trial function is now conditioned for use in Mori's continued fraction.

Ciccootti et al. [21] apply the Mori's continued fraction method to model Brownian motion of argon. Once the coefficients γ_i's are found from Mori's continued fraction, Eq. (36), the Generalized Langevin Equation can be rewritten as a system of n first-order differential equations:

$$A_0(t) = A_1(t) = v(t)$$

$$A_i(t) = -\gamma_i(0)A_{i-1}(t) + A_{i+1}(t);\ i = 1, 2, \ldots, n-2$$

$$A_{n-1}(t) = -\gamma_{n-1}(0)A_{n-2}(t) - \beta A_{n-1}(t) + \xi(t) \tag{39}$$

where n is the cut-off for the order of γ_i in Mori's continued fraction, $\beta=\tilde{\gamma_n}(p)=\tilde{\gamma_n}(0)$, and the nth random force $R_n(t)$ is taken to be a Gaussian white noise process $\xi(t)$:

$$\langle\xi(t)\rangle = 0$$

$$\langle\xi(t)\xi(s)\rangle = 2\beta\langle A_{n-1}^2\rangle\delta(t-s) \tag{40}$$

Eq. (39) can be readily integrated to derive the velocity profile $v(t)$. Results of Ciccotti et al. [21] for the fitting of the velocity autocorrelation function to a Mori's continued fraction of order n=25 is shown in Fig. 3. From these results, the velocity of particles in the model compare favorably with experimental data with error less than 1%. This combined BD–MD method offers the advantage of circumventing the process of sampling the probability distribution of the random force, as is customary in BD, while still maintaining the capability of modeling stochastic forces without approximating it as a constant value. So, the rigorousness of MD and the efficiency of BD combine to produce an overall improved algorithm.

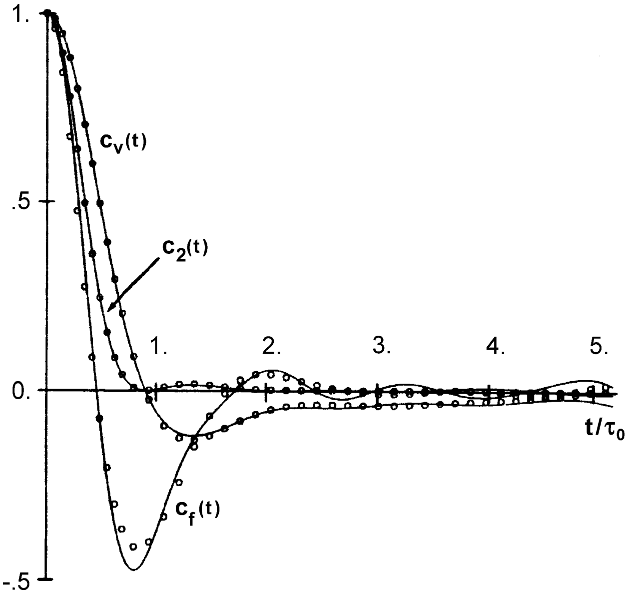


Fig. 3. Stochastic simulation of the VAT and the force ACF with a Mori chain of order n=25. Circles give the MD results for $C_v(t)$, $C_f(t)$, and $C_2(t)$. The lines show the corresponding stochastic dynamics results [21].

6. Monte Carlo methods

Monte Carlo modeling is a stochastic approach that offers similar advantages of BD with its capability to model processes occurring at rapid time scales which may confound the MD techniques. The fundamental theories and select applications of MC methods will be discussed here.

6.1. Theory of Monte Carlo modeling

A classical method to performing MC begins by casting the process as being Markovian. The system progresses from one state to the next by aid of its transition probability matrix. Metropolis et al. [22] present the now standard Metropolis method for conducting MC simulations using the energy of the system as the criterion to evaluate the acceptance or rejection of a MC step.

The Metropolis Method begins by considering a system of particles as shown in Fig. 4. The particle of interest i is initially located at r_i^m. Particle i is then proposed to be displaced randomly to a new location r_i^n using the algorithm:

$$r_i^n = r_i^m + (2a_0 - 1)\delta r_{\max} \tag{41}$$

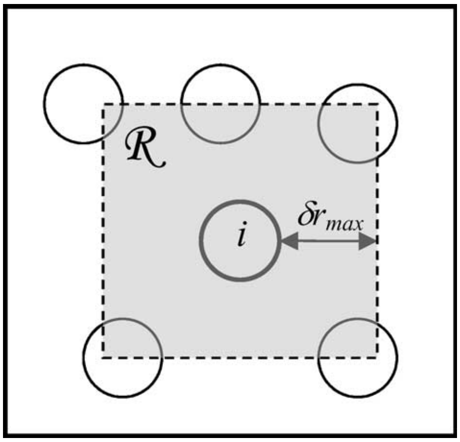


Fig. 4. State n is obtained from state m by moving atom i with a uniform probability to any point in the shaded region $\mathcal{R}$ [22].

where a_0 is a uniform random number between 0 and 1 and $\delta r_{\max}$ is the maximum allowable displacement. The proposed displacement is next evaluated for acceptance or rejection. The criterion for acceptance is the change in potential energy of the system computed as:

$$\delta V_{n,m} = \left(\sum_{j=1}^{N} V\left(r_{i,j}^{n}\right) - \sum_{j=1}^{N} V\left(r_{i,j}^{m}\right) \right) \tag{42}$$

where the potential energy is summed over all the particles within a cutoff distance r_c in relation to particle i. If $\delta V_{n,m}<0$, then the proposed move is downhill and accepted. If $\delta V_{n,m}>0$, the proposed move is uphill and is accepted with the qualification of the probability ρ_n/ρ_m which in the Metropolis method corresponds to the Boltzmann factor of the energy difference:

$$\frac{\rho_n}{\rho_m} = \frac{\exp(-\beta V_n)\exp\left(-\beta\delta V_{n,m}\right)}{\exp(-\beta V_n)} = \exp\left(-\beta\delta V_{n,m}\right) \tag{43}$$

where $\beta=1/k_B T$. In this procedure, a uniform random number between 0 and 1, ξ, is generated and compared with $\exp(-\beta\delta V_{n,m})$. If $\xi<\exp(-\beta\delta V_{n,m})$, then the uphill move is accepted. Otherwise, the proposed move is rejected for $\xi>\exp(-\beta\delta V_{n,m})$. The overall effect is that the particle proceeds with changes in potential energy $\delta V_{n,m}$ that is accepted with probability $\exp(-\beta\delta V_{n,m})$. If the uphill move is rejected, the particle remains in its original position, and the non-move is taken to be a new state nevertheless. The modeling process continues by randomly selecting successive particles for proposed displacements. Hastings [23] presents an improvement by selecting particles systematically according to their indices rather than by random selection. This step eases the number of random number generations. For the Hastings method, an important distinction should be noted, that is, it does not satisfy detailed balance. Manousiouthakis and Deem [24] prove that the Hasting method only satisfies balance. Details of Monte Carlo modeling are given in Allen and Tildesley [25], Frankel and Eppenga [26] and Frankel and Ladd [27].

6.2. Application of Monte Carlo methods to Brownian Dynamics

For physical systems such as protein structures, the motion of the molecules incurs pronounced time scale separation between the vibration of bond lengths and bond angles (on time scale of femtoseconds) versus the torsional rotation of the molecule (on time scale of nanoseconds). In these instances a purely BD or MD method meets with the difficulty of integrating both processes into the model. The problem arises from the necessities of sampling sufficiently the conformational space of the molecule and overcoming the large energy barriers that separate multiple conformations. For these cases, a method that combines the strengths of both MC and BD would be capable of overcoming this dilemma.

Guarnieri [28] applies the Monte Carlo strategy in conjunction with Brownian Dynamics to derive a dual deterministic–stochastic model of the conformation of flexible molecules. The method begins by casting the particle motion in the presence of a heat bath in the form of the Langevin Equation:

$$m\frac{dv}{dt} = f[x(t)] + R(t) - m\gamma v \tag{44}$$

where m is the particle mass, f is the systematic force, γ is the friction coefficient, and R is the random force associated with the bond length and angle vibrations. The statistical properties of the random force are:

$$\langle R(t)R(t')\rangle = 2m\gamma kT\delta(t-t') \tag{45}$$

where δ is the Dirac delta function.

Eq. (44) can be integrated to produce expressions for the displacement and velocity:

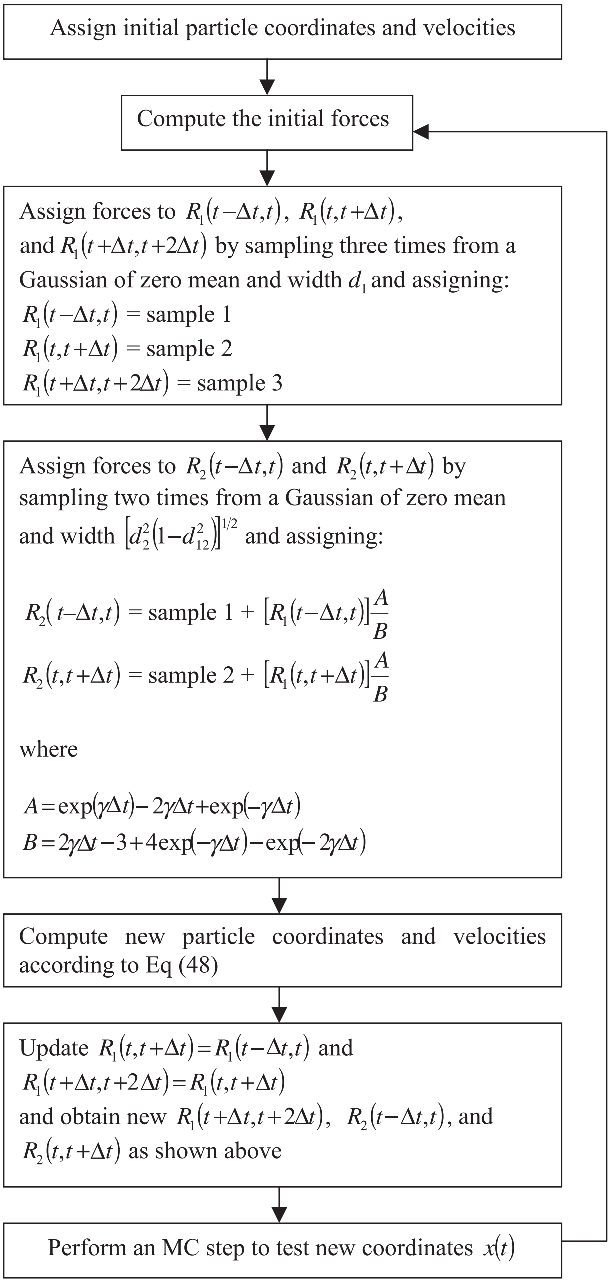
$$\begin{aligned} x(t+\Delta t) &= x(t)[1+\exp(-\gamma\Delta t)] - x(t-\mathit{\Delta} t)\exp(-\gamma\Delta t) \\ &\quad + \frac{f[x(t)]\Delta t[1-\exp(-\gamma\Delta t)]}{m\gamma} + R_1(t,t+\Delta t) \\ &\quad + R_1(t,t-\Delta t)\exp(-\gamma\Delta t) \\ v(t+\Delta t) &= v(t)\exp(\gamma\Delta t) \\ &\quad + \frac{\{f[x(t)]+f[x(t+\Delta t)]\}[1-\exp(-\gamma\Delta t)]}{2m\gamma} \\ &\quad + \frac{[R_1(t,t+\Delta t)+R_1(t+\Delta t,t+2\Delta t)]}{2\Delta t} \\ &\quad + \frac{\exp(-\gamma\Delta t)[R_2(t-\Delta t,t)+R_2(t,t+\Delta t)]}{2\Delta t} \end{aligned} \tag{46}$$

where

$$R_1(t,t+\Delta t)=\frac{1}{m\gamma}\int_t^{t+\Delta t}\mathrm{d}t'\,R(t')\{1-\exp[-\gamma(t'-t)]\}$$

$$R_2(t,t+\Delta t)=\frac{1}{m\gamma}\int_t^{t+\Delta t}\mathrm{d}t'\,R(t')\{\exp[-\gamma(t'-t)]-1\} \tag{47}$$

So, the problem now becomes a matter of Monte Carlo random samplings of R_1 and R_2 in Eq. (46) according to Gaussian distributions. Steps of the algorithm are outlined in Fig. 5.



Assign initial particle coordinates and velocities

Compute the initial forces

Assign forces to $R_1(t-\Delta t,t)$, $R_1(t,t+\Delta t)$, and $R_1(t+\Delta t,t+2\Delta t)$ by sampling three times from a Gaussian of zero mean and width d_1 and assigning:
$R_1(t-\Delta t,t)$ = sample 1
$R_1(t,t+\Delta t)$ = sample 2
$R_1(t+\Delta t,t+2\Delta t)$ = sample 3

Assign forces to $R_2(t-\Delta t,t)$ and $R_2(t,t+\Delta t)$ by sampling two times from a Gaussian of zero mean and width $\left[d_2^2\left(1-d_{12}^2\right)\right]^{1/2}$ and assigning:

$$R_2(t-\Delta t,t) = \text{sample 1} + \left[R_1(t-\Delta t,t)\right]\frac{A}{B}$$

$$R_2(t,t+\Delta t) = \text{sample 2} + \left[R_1(t,t+\Delta t)\right]\frac{A}{B}$$

where

$$A=\exp(\gamma\Delta t)-2\gamma\Delta t+\exp(-\gamma\Delta t)$$
$$B=2\gamma\Delta t-3+4\exp(-\gamma\Delta t)-\exp(-2\gamma\Delta t)$$

Compute new particle coordinates and velocities according to Eq (48)

Update $R_1(t,t+\Delta t)=R_1(t-\Delta t,t)$ and $R_1(t+\Delta t,t+2\Delta t)=R_1(t,t+\Delta t)$ and obtain new $R_1(t+\Delta t,t+2\Delta t)$, $R_2(t-\Delta t,t)$, and $R_2(t,t+\Delta t)$ as shown above

Perform an MC step to test new coordinates $x(t)$

Fig. 5. Algorithm for a combined MC–BD method. From Guarnieri [28].

The parameters of the Gaussian distributions used in Fig. 5 are:

$$d_1=\left\{\frac{kT}{m\gamma^2}[2\gamma\Delta t-3+4\exp(-\gamma\Delta t)+\exp(2\gamma\Delta t)]\right\}^{1/2}$$

$$d_2=\left\{\frac{kT}{m\gamma^2}[-2\gamma\Delta t+3-4\exp(\gamma\Delta t)+\exp(2\gamma\Delta t)]\right\}^{1/2}$$

$$d_{12}=\frac{\frac{kT}{m\gamma^2}[\exp(\gamma\Delta t)-2\gamma\Delta t+\exp(-\gamma\Delta t)]}{d_1d_2} \tag{48}$$

The method of Guarnieri [28] retains the strength of BD to accommodate rapidly varying random forces while offering a simplified numerical algorithm using MC. A similar procedure is undertaken by Ermak and Buckholz [3]. Additional examples of applications of the technique of Guarnieri [28] are given in Williams and Hall [29], Smart and McCammon [30], and Laakkonen et al. [31].

7. Concluding remarks

In this review paper, we embark on a sweeping study of the general theories and algorithms that govern rigorous, discrete modeling techniques, Brownian Dynamics, Molecular Dynamics and Monte Carlo Methods. At the outset, we perceived that the capabilities of BD, MD, and MC methods to discretely model particle trajectories at the microscopic level cast these methods as potentially more accurate and robust than the more traditional macroscopic integral approaches such as the OZ Integral Method with Hyper-Netter-Chain (HNC) or Percus-Yevick (PY) Closures. We support our hypothesis by first presenting an overview of the statistical theories underlying a critical component of colloidal transport, Brownian motion. Here we find that the fundamental equations that define random Brownian motion such as the probability distributions of particle positioning are especially conducive for modeling using the statistical elements contained in BD, MD, and MC methods.

We next proceed with differentiating the three methods according to the strengths and weaknesses of their theories and algorithms in relationship to the modeling of the major factors in colloidal transport, diffusivity and inter-particle interactions. Previous studies that engage in BD and MD modeling have shown that the inter-particle interactions play a crucial determinative role in affecting the accuracy of a proposed model. So, an important step in the development of the model involves properly diagnosing the nature of the inter-particle interactions operating in the system and then subsequently selecting the appropriate modeling techniques that would be compatible with that situation. In cases of high particle concentration, the usual pairwise interactions should be modified to account for contributions from three-body interactions. Here we review various models for the inter-particle interactions and their incorporation into the numerical algorithms.

Furthermore, we find that BD presents itself to be a more efficient modeling technique over MD because BD effectively accommodates the molecular forces that are not of significant interest to the problem using a statistically equivalent random force. The MD method does not contain such a computation-saving strategy and requires the input of all forces present in the system regardless of their significance to the problem. So, a purely discrete method that accounts for all forces in the systems remains at present to be undesirable as it is too computationally intensive. The proper balance between precisely modeling the relevant components of the problem while circumventing such requirements for the less important components of the problem produces a most effective model. With that said, we find that further improvements to the modeling effort can be attained by combining both BD and MD methods to generate hybrid techniques such as the Mori's Continued Fraction.

Our study of Monte Carlo methods reveals similar traits for this technique as BD. The MC method presents a simpler algorithm for implementation. In addition, MC incorporates the additional step of assessing the energy difference in progressing from one time step to the next step. So here, the MC method considers the physicality of the process in conjunction with its statistical properties. Therefore, MC may offer a more accurate representation of the physical attributes of the system.

Our findings and discussions contained herein serve as an introductory effort for integration of microscopic modeling techniques of BD, MD, and MC for colloidal systems. Our continuing research efforts will next build upon this study with the development of a discrete method of modeling colloidal transport and testing of the model with experimental observations.

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