

Metropolis Monte Carlo method for Brownian dynamics simulation generalized to include hydrodynamic interactions

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The Metropolis Monte Carlo method as proposed by the authors recently to be used for Brownian dynamics simulation is further extended to include the effects of hydrodynamic interactions mediated by the solvent.

1. Introduction

The Monte Carlo (MC) method is now a standard simulation technique for studying the condensed phase properties of matter [1,2]. The procedure was developed by Metropolis et al. [3] originally as a method suited to electronic computers for calculating statistical mechanical configurational integrals. Since the MC sampling is a stochastic process described by a Markovian master equation, dynamic interpretation of the method has also been done by introducing a "time" scale which actually labels the sequential order of configurations [1,2,4]. The system under consideration is assumed to be coupled to a heat bath, which induces random transitions in the system. By choosing appropriate transition probabilities, we can describe the kinetics in terms of an Ising model, which is immediately suitable for MC studies. Despite a somewhat artificial relationship between the MC "time" and physical times, MC realization of the master equation has provided reasonably approximate descriptions of the transport and relaxation phenomena in diverse physical systems, e.g., alloys, adsorbed surface layers, the helix-coil transition of a biopolymer, etc. [1,2].

While the suitability of the MC method for the study of dynamics in terms of kinetic Ising models has been amply demonstrated, in the simulation of fluids to which the application of the Ising model is less appropriate the dynamic interpretation of the MC method has not been flourishing. That the MC method generates a random walk in configuration space has been noted by many authors [5–7]. It must, however, be understood that, even in the kinetic application of the MC method to the study of a fluid, we need restrict ourselves to a part of the degrees of freedom of the system, e.g., Brownian particles embedded in a solvent continuum. In a previous paper [8] we interpreted the Metropolis MC scheme in this way and found that if we define the relationship between the MC "time" and the physical one appropriately, the MC procedure amounts to numerically solving the diffusion equation governing the motion of the Brownian particles. The relationship between the MC "time" and the physical one is so unique that the Metropolis MC method constitutes an exact (not artificial) numerical realization of the diffusion process.

The procedure we presented consists of only taking the size of the maximum allowed displacement small in the original Metropolis MC scheme and turned out to be equivalent [9] to the Brownian dynamics simulation

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method developed by Ermak and McCammon [10,11]^{#1}. Ermak and McCammon developed their method with the intention to present a parallel approach for Brownian dynamics with the molecular dynamics (MD) method. They derived their technique methodically by both the Fokker-Planck and Langevin formalisms with the inclusion of the effects of hydrodynamic interactions. In their method a Brownian trajectory is decomposed into successive displacements each of which consists of a deterministically calculated drift term, due to the sum of interparticle and external forces as well as due to the divergence of the diffusion tensor, and a stochastically calculated diffusion term due to the random force. Over a short time step the probability distribution function for the diffusive displacement is approximated by a Gaussian. On the other hand our method calculates both terms stochastically and is formulated in an integrated form so that whereas the method of Ermak and McCammon requires the calculation of the forces on the particles at each simulation step, for us it is sufficient to calculate only the potential energy change of the system.

At present our MC method is only applicable in the absence of hydrodynamic interactions. In this paper we are interested in an extension of our method to include the effects of hydrodynamic interactions.

2. Generalization of the method

The system we consider consists of N Brownian particles immersed in an incompressible solvent medium. The particles interact with one another either directly or through hydrodynamic interactions mediated by the host solvent. According to Murphy and Aguirre [12], the diffusion equation for the system is written as

$$\frac{\partial P}{\partial t} = \sum_i \sum_j \left[-\frac{\partial}{\partial X_i} \left(\frac{\partial D_{ij}}{\partial X_j} + \frac{D_{ij}}{k_B T} F_j \right) P + \frac{\partial^2}{\partial X_i \partial X_j} D_{ij} P \right], \quad (1)$$

where i and j run over the particle coordinates ($1 \leq i, j \leq 3N$), $P(\{X_i\}, t)$ is the N -particle configuration space distribution function, X_i is a position component, $D_{ij}=D_{ji}$ is the configuration dependent diffusion tensor, F_j is the sum of interparticle and external forces acting in direction j and assumed to be derivable from a potential U as $F_j = -\partial U / \partial X_j$, k_B is the Boltzmann constant and T is the absolute temperature.

Let the distribution function at time $t=t_0$ be $P(\{X_i\}, t_0) = \prod \delta(X_i - X_i^0)$, where $\delta(X)$ is the Dirac delta function. If we take $t=t_0+\Delta t$ and compute for small Δt the moments of $\Delta X_i = X_i - X_i^0$, then for $\Delta t \rightarrow 0$

$$\frac{\langle \Delta X_i \rangle}{\Delta t} = \sum_j \left(\frac{\partial D_{ij}}{\partial X_j} - \frac{D_{ij}}{k_B T} \frac{\partial U}{\partial X_j} \right), \quad (2)$$

$$\frac{\langle \Delta X_i \Delta X_j \rangle}{2\Delta t} = D_{ij}, \quad (3)$$

so that eq. (1) may also be written as

$$\frac{\partial P}{\partial t} = - \sum_i \frac{\partial}{\partial X_i} \left(\frac{\langle \Delta X_i \rangle}{\Delta t} P \right) + \frac{1}{2} \sum_i \sum_j \frac{\partial^2}{\partial X_i \partial X_j} \left(\frac{\langle \Delta X_i \Delta X_j \rangle}{\Delta t} P \right). \quad (4)$$

We assume that the hydrodynamic interactions mediated by the solvent are treated within the approximation of pairwise additivity and use, for example, the Oseen tensor [13] approximation given by

$$D_{ij} = \frac{k_B T}{6\pi\eta a} \delta_{ij}, \quad i, j \text{ on the same particle},$$

$$D_{ij} = \frac{k_B T}{8\pi\eta |\mathbf{R}_{ij}|} \left(\mathbf{1} + \frac{\mathbf{R}_{ij} \mathbf{R}_{ij}}{R_{ij}^2} \right), \quad i, j \text{ on different particles}. \quad (5)$$

^{#1} We classify the method of Ceperley et al. [7] as intermediate between ours and that of Ermak and McCammon.

Here η is the solvent viscosity, a is the sphere radius, δ_{ij} is the Kronecker delta, \mathbf{R}_{ij} is the vector from the center of sphere i to the center of sphere j , and \mathbf{I} is the unit tensor. Since the divergence of the Oseen tensor vanishes, i.e.

$$\sum_j \frac{\partial D_{ij}}{\partial X_j} = 0, \quad (6)$$

this term can be dropped from eqs. (1) and (2), simplifying greatly the calculation of the displacements.

At each simulation step we generate a set of $3N$ random numbers $\{\xi_i\}$ which conform to the following equations:

$$\langle \xi_i \rangle = 0, \quad (7)$$

$$\langle \xi_i \xi_j \rangle = D_{ij}/3D_0, \quad (8)$$

where $D_0 = k_B T / 6\pi\eta a$. They can be constructed through a linear transformation of a set of random numbers $\{x_i\}$; $-1 \leq x_i \leq 1$, $\langle x_i \rangle = 0$, $\langle x_i x_j \rangle = \frac{1}{3} \delta_{ij}$, where δ_{ij} is the Kronecker delta [11,14]. If we define ξ_i as

$$\xi_i = \sum_{j=1}^i c_{ij} x_j, \quad (9)$$

then the coefficients c_{ij} are given by

$$c_{ii} = \left(1 - \sum_{k=1}^{i-1} c_{ik}^2 \right)^{1/2},$$

$$c_{ij} = \frac{1}{c_{jj}} \left(\frac{D_{ij}}{D_0} - \sum_{k=1}^{j-1} c_{ik} c_{jk} \right), \quad i > j. \quad (10)$$

The probability distribution function for correlated random numbers $\pi(\{\xi_i\})$ is an even function of the arguments, i.e. $\pi(\{-\xi_i\}) = \pi(\{\xi_i\})$.

With these preliminaries, the generalization of our method is straightforward. We place the N Brownian particles of the system in any initial configuration. Then, we move the particles by giving random displacements along the coordinate directions such as

$$X_i \rightarrow X_i + \Delta X_i, \quad \Delta X_i = \alpha \xi_i, \quad (11)$$

where α is the maximum allowed displacement and ξ_i is a random number as specified above.

We then calculate the change in the potential energy ΔU , which is caused by the move. We choose α sufficiently small so that the change in the potential energy is

$$\Delta U = \sum_i \frac{\partial U}{\partial X_i} \Delta X_i = \sum_i \frac{\partial U}{\partial X_i} \alpha \xi_i, \quad (12)$$

i.e. the forces acting on the particles are essentially constant during the displacement. Using vector notation eq. (12) can also be written as

$$\Delta U = \boldsymbol{\xi} \cdot \nabla U, \quad (13)$$

where $\boldsymbol{\xi}$ is a $3N$ -dimensional vector whose components are $\{\xi_i\}$ and ∇ is a $3N$ -dimensional gradient operator. Likewise $\pi(\{\xi_i\})$ is written as $\pi(\boldsymbol{\xi})$. Furthermore we approximate the factor $\exp(-\Delta U/k_B T)$ in the Metropolis MC scheme by $1 - \Delta U/k_B T$. If $\Delta U < 0$, i.e. if the move would bring the system to a state of lower potential energy, we allow the move and put the particles in their new positions. If $\Delta U > 0$, i.e. if the move increases the energy, we allow the move with probability $1 - \Delta U/k_B T$. The particles remain at their original positions with probability

$$1 - \int_{\xi \cdot \nabla U < 0} d\xi \pi(\xi) - \int_{\xi \cdot \nabla U > 0} d\xi \left(1 - \frac{\Delta U}{k_B T}\right) \pi(\xi).$$

Having attempted to move the particles, we proceed similarly with the next step. Here we assume all the particles to move to their new positions in the time interval Δt .

If we calculate the mean and the covariance of the particle displacements during this time interval, we obtain to second order in α

$$\begin{aligned} \langle \Delta X_i \rangle &= \int_{\xi \cdot \nabla U < 0} d\xi \alpha \xi_i \pi(\xi) + \int_{\xi \cdot \nabla U > 0} d\xi \alpha \xi_i \left(1 - \frac{1}{k_B T} \sum_j \frac{\partial U}{\partial X_j} \alpha \xi_j\right) \pi(\xi) \\ &= \alpha \left(\int_{\xi \cdot \nabla U < 0} d\xi \xi_i \pi(\xi) + \int_{\xi \cdot \nabla U > 0} d\xi \xi_i \pi(\xi) \right) - \frac{\alpha^2}{k_B T} \sum_j \frac{\partial U}{\partial X_j} \int_{\xi \cdot \nabla U > 0} d\xi \xi_i \xi_j \pi(\xi) \\ &= -\frac{\alpha^2}{k_B T} \sum_j \frac{\partial U}{\partial X_j} \frac{1}{2} \int_{\text{all } \xi} d\xi \xi_i \xi_j \pi(\xi) \\ &= -\frac{\alpha^2}{2k_B T} \sum_j \frac{\partial U}{\partial X_j} \langle \xi_i \xi_j \rangle = -\frac{\alpha^2}{6D_0} \sum_j \frac{D_{ij}}{k_B T} \frac{\partial U}{\partial X_j}, \end{aligned} \quad (14)$$

$$\begin{aligned} \langle \Delta X_i \Delta X_j \rangle &= \int_{\xi \cdot \nabla U < 0} d\xi \alpha^2 \xi_i \xi_j \pi(\xi) + \int_{\xi \cdot \nabla U > 0} d\xi \alpha^2 \xi_i \xi_j \left(1 - \frac{1}{k_B T} \sum_k \frac{\partial U}{\partial X_k} \alpha \xi_k\right) \pi(\xi) \\ &\approx \alpha^2 \left(\int_{\xi \cdot \nabla U < 0} d\xi \xi_i \xi_j \pi(\xi) + \int_{\xi \cdot \nabla U > 0} d\xi \xi_i \xi_j \pi(\xi) \right) \\ &= \alpha^2 \int_{\text{all } \xi} d\xi \xi_i \xi_j \pi(\xi) = \alpha^2 \langle \xi_i \xi_j \rangle = \frac{\alpha^2}{3D_0} D_{ij}. \end{aligned} \quad (15)$$

In deriving eqs. (14) and (15) we used the fact that the probability distribution function $\pi(\xi)$ is an even function of the arguments so that

$$\begin{aligned} \int_{\xi \cdot \nabla U < 0} d\xi \xi_i \pi(\xi) &= - \int_{\xi \cdot \nabla U > 0} d\xi \xi_i \pi(\xi), \\ \int_{\xi \cdot \nabla U < 0} d\xi \xi_i \xi_j \pi(\xi) &= \int_{\xi \cdot \nabla U > 0} d\xi \xi_i \xi_j \pi(\xi) = \frac{1}{2} \int_{\text{all } \xi} d\xi \xi_i \xi_j \pi(\xi). \end{aligned}$$

If we determine the time scale by

$$\alpha^2 = 6D_0 \Delta t, \quad (16)$$

then eqs. (14) and (15) reduce to eqs. (2) and (3), respectively, i.e. we are simply solving eq. (1) numerically.

3. Conclusion

We have extended the Metropolis MC method as a Brownian dynamics simulation technique to the case of N interacting Brownian particles with the inclusion of the effects of hydrodynamic interactions. The hydro-

dynamic interactions were treated only in the case where the divergence of the diffusion tensor vanishes. In the more general case where it is not zero, it is only necessary to calculate their contribution deterministically as $\sum_j (\partial D_{ij}/\partial X_j)\Delta t$ and add to the mean displacement as in the algorithm of Ermak and McCammon [11].

It is consistent in principle and convenient in practice to use a single methodology to study both the equilibrium and dynamic properties of a system. For example, the Metropolis MC method allows us to simulate the relaxation process of the counterion polarization of a polyelectrolyte solution [9]. We first prepare an equilibrium distribution of the counterions around the polyion, then follow the time course of the change of the distribution upon application of an electric field pulse to the solution. In this paper the capacity of the Metropolis MC method as a Brownian dynamics simulation technique was augmented to allow us to study dynamical properties of polymers with the inclusion of hydrodynamic forces.

References

- [1] K. Binder, ed., Monte Carlo methods in statistical physics (Springer, Berlin, 1979).
- [2] K. Binder, ed., Applications of the Monte Carlo method in statistical physics, 2nd. Ed. (Springer, Berlin, 1987).
- [3] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, J. Chem. Phys. 21 (1953) 1087.
- [4] H. Müller-Krumbhaar and K. Binder, J. Stat. Phys. 8 (1973) 1.
- [5] C. Pangali, M. Rao and B.J. Berne, Chem. Phys. Letters 55 (1978) 413.
- [6] P.J. Rossky, J.D. Doll and H.L. Friedman, J. Chem. Phys. 69 (1978) 4628.
- [7] D. Ceperley, M.H. Kalos and J.L. Lebowitz, Macromolecules 14 (1981) 1472.
- [8] K. Kikuchi, M. Yoshida, T. Maekawa and H. Watanabe, Chem. Phys. Letters 185 (1991) 335.
- [9] K. Kikuchi, M. Yoshida, T. Maekawa and H. Watanabe, Proceedings of the 6th Symposium on Colloid and Molecular Electro-Optics.
- [10] D.L. Ermak and Y. Yen, Chem. Phys. Letters 24 (1974) 243.
- [11] D.L. Ermak and J.A. McCammon, J. Chem. Phys. 69 (1978) 1352.
- [12] T.J. Murphy and J.L. Aguirre, J. Chem. Phys. 57 (1972) 2098.
- [13] M. Doi and S.F. Edwards, The theory of polymer dynamics (Clarendon Press, Oxford, 1986).
- [14] J.D. Doll and D.R. Dion, J. Chem. Phys. 65 (1976) 3762.