Metropolis Monte Carlo method as a numerical technique to solve the Fokker-Planck equation

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Received 20 June 1991

It is shown that the Metropolis Monte Carlo scheme contains a description of the physical diffusion process. Thus, the use of the technique is not to be restricted to its conventional application for studies of the equilibrium properties of fluids but should be extended to studies of their dynamic properties.

1. Introduction

The Metropolis Monte Carlo (MC) method is one of the simulation techniques now widely used to study the properties of fluids which may be considered as composed of many interacting molecules. It was introduced by Metropolis et al. [1] as a method suited for electronic computers to carry out a many-dimensional integral over the configuration space. In the scheme, a Markov chain of states of the liquid is constructed and the elements of the transition matrix are devised to generate a trajectory in phase space which samples a representative portion from the canonical ensemble. The method has thus been conventionally regarded as being applicable to the study of equilibrium properties. To obtain the dynamic properties, a different technique, molecular dynamics (MD), has been required.

In this report, we show that the Metropolis MC is not to be considered just as a mathematical trick but that it contains a description of the physical diffusion process. We then propose that the method should be used to study not only the equilibrium properties of fluids but also their dynamic properties although the use is somewhat restricted to the coarse level.

2. Physical interpretation of the Metropolis MC

To facilitate the discussion, we use the one-dimensional nomenclature. According to the Metropolis MC scheme, we first place the N particles of the system in any configuration. Then, we move each of the particles in succession by giving a uniform random displacement along the coordinate direction such as

$$X \rightarrow X + \Delta X, \quad \Delta X = \alpha \xi,$$

(1)

where $\alpha$ is the maximum allowed displacement and $\xi$ is a random number between $-1$ and 1. Then, after we move a particle, it is equally likely to be anywhere within a line element of length $2\alpha$ centered about its original position. On the computer, let there be a large but finite number, $Z$, of new positions for the particle. Then the probability that the move carries the particle to a new position on the line segment is written as $1/Z$.

We then calculate the change in potential energy of the system $\Delta U$, which is caused by the move. 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
particle in its new position. If $\Delta U > 0$, we allow the move with probability $\exp(-\Delta U/kT)$, where $k$ is Boltzmann's constant and $T$ the temperature.

After discriminating on $\exp(-\Delta U/kT)$, the probability that the move carries the particle to a new position is written as $1/Z$ if the move is downhill in energy and as $(1/Z) \exp(-\Delta U/kT)$ if the move is uphill. The particle remains at its original position with the probability

$$1 - \sum_{\Delta U < 0} \frac{1}{Z^2} \sum_{\Delta U > 0} \frac{1}{Z} \exp \left( -\frac{\Delta U}{kT} \right).$$

Having attempted to move a particle, we proceed similarly with the next one.

Here we consider the Metropolis MC scheme as a physical process and assume all the particles to move to their new positions in the "time" interval $\Delta t$. Since only small steps occur in the process, we can describe it by the Fokker-Planck equation.

The Fokker-Planck equation is an approximation to the master equation for Markov processes, but it is easier to handle and more directly related to physical concepts. The Fokker-Planck equation requires a minimum of detailed knowledge about any stochastic process. For example, let $X$ be the coordinate of a Brownian particle; then, it is enough to find the average change $\langle \Delta X \rangle$ and its mean-square $\langle (\Delta X)^2 \rangle$ during a small time interval $\Delta t$ to set up the equation

$$\frac{\partial P(X,t)}{\partial t} = - \frac{\partial}{\partial X} \left( \frac{\langle \Delta X \rangle}{\Delta t} P \right) + \frac{1}{2} \frac{\partial^2}{\partial X^2} \left( \frac{\langle (\Delta X)^2 \rangle}{\Delta t} P \right).$$

(2)

Let us calculate the mean displacement of the particle during this "time" interval. We assume the maximum-allowed displacement $\alpha$ is small and the change in potential energy is written as

$$\Delta U = \frac{\partial U}{\partial X} \Delta X = \frac{\partial U}{\partial X} \alpha \xi.$$

(3)

We assume, for convenience, that $\partial U/\partial X < 0$; then, to second order in $\alpha$, we have

$$\langle \Delta X \rangle = \sum_{\Delta X > 0} \frac{1}{Z} \Delta X + \sum_{\Delta X < 0} \frac{1}{Z} \exp \left( -\frac{1}{kT} \frac{\partial U}{\partial X} \Delta X \right) \Delta X \approx \sum_{\Delta X > 0} \frac{1}{Z} \Delta X + \sum_{\Delta X < 0} \frac{1}{Z} \left( 1 - \frac{1}{kT} \frac{\partial U}{\partial X} \Delta X \right) \Delta X$$

$$= \frac{1}{Z} \left( \sum_{\Delta X > 0} \Delta X + \sum_{\Delta X < 0} \Delta X \right) - \frac{1}{kT} \frac{\partial U}{\partial X} \sum_{\Delta X < 0} (\Delta X)^2$$

$$= - \frac{1}{kT} \frac{\partial U}{\partial X} \alpha^2 \sum_{\xi < 0} \xi^2 = \frac{\alpha^2}{6} \frac{\partial U}{\partial X},$$

(4)

That is, the particle gains an average drift proportional to the force $-\partial U/\partial X$ exerted by the surroundings during the "time" interval.

Similarly, the mean-square displacement is calculated to the same order in $\alpha$ as follows:

$$\langle (\Delta X)^2 \rangle = \sum_{\Delta X > 0} \frac{1}{Z} (\Delta X)^2 + \sum_{\Delta X < 0} \frac{1}{Z} \exp \left( -\frac{1}{kT} \frac{\partial U}{\partial X} \Delta X \right) (\Delta X)^2$$

$$\approx \sum_{\Delta X > 0} \frac{1}{Z} (\Delta X)^2 + \sum_{\Delta X < 0} \frac{1}{Z} \left( 1 - \frac{1}{kT} \frac{\partial U}{\partial X} \Delta X \right) (\Delta X)^2$$

$$\approx \frac{1}{Z} \left( \sum_{\Delta X > 0} (\Delta X)^2 + \sum_{\Delta X < 0} (\Delta X)^2 \right) = \alpha^2 \sum_{\xi < 0} \xi^2 \approx \frac{1}{3} \alpha^2.$$  

(5)

The mean-square displacement is independent of the force field within the approximation employed.

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It is to be noted that if we define the diffusion constant \( D \) by

\[
D = \frac{\langle (\Delta X)^2 \rangle}{2\Delta t} = \frac{\alpha^2}{6} \frac{1}{\Delta t},
\]

then the mean displacement per unit “time” is written as

\[
\frac{\langle \Delta X \rangle}{\Delta t} = -\frac{D}{kT} \frac{\partial U}{\partial X},
\]

or by using Einstein's relation, \( D/kT = 1/\zeta \), where \( \zeta \) is the friction constant, as

\[
\frac{\langle \Delta X \rangle}{\Delta t} = -\frac{1}{\zeta} \frac{\partial U}{\partial X}.
\]

We therefore obtain the Fokker–Planck equation

\[
\frac{\partial P(X, t)}{\partial t} = \frac{1}{\zeta} \frac{\partial}{\partial X} \left[ \left( \frac{\partial U}{\partial X} \right) P \right] + D \frac{\partial^2 P}{\partial X^2}.
\]

It has the same form as a diffusion equation and, in fact, it is the diffusion equation for the Brownian particles in the fluid characterized by the phenomenological constant \( D \) or \( \zeta \) as above.

We have thus shown that the physical significance of the Metropolis MC lies in the dynamic description of the system on the coarse-grained time scale. It is then clear that the scheme generates a phase-space trajectory.

Fig. 1. Change of the particle distribution function \( P(X, t) \) at three simulation steps for the Brownian motion of a harmonically bound particle with \( U = \frac{1}{2} kX^2 \). The following values were employed: \( N=10000 \), \( k=2 \), \( \alpha=0.01 \), \( kT=1.0 \) and \( \Delta t=1 \). The simulation without field yielded \( D=0.00005 \) as expected for the case where only two random numbers -1 and 1 were generated. Smooth curves represent analytical solutions.
in the canonical ensemble at \( t \to \infty \) as an equilibrium solution to the diffusion equation. Practically, it is more important that the Metropolis MC constitutes a numerical technique to solve Fokker–Planck or diffusion equations as well as to calculate configurational integrals.

3. Application

As an example, we applied the Metropolis MC to the study of the Brownian motion of a harmonically bound particle with

\[
U = \frac{1}{2} K X^2 ,
\]

where \( K \) is the force constant. Given that at \( t=0 \) the particles are all at \( X=0 \), the analytical solution at \( t>0 \) is given by [2]

\[
P(X, t) = \left( \frac{K}{2\pi kT(1-\exp[-(2K/\zeta)t])} \right)^{1/2} \exp \left( -\frac{K}{2kT(1-\exp[-(2K/\zeta)t])} \right) X^2 ,
\]

and the mean square displacement by

\[
\langle (\Delta X)^2 \rangle = \frac{kT}{K} \{ 1 - \exp[-(2K/\zeta)t] \} .
\]

The simulation without field yielded a \( D \) value consistent with the definition, eq. (6), except for the fact that it was slightly modified because, in the actual simulation, only two random numbers \(-1\) and \(1\) were generated.

Fig. 1 shows the change of the particle distribution function \( P(X, t) \) at three simulation steps or “times”. At each “time”, the mean-square displacement \( \langle (\Delta X)^2 \rangle \) was calculated.

Fig. 2 shows the plot of the mean-square displacement \( \langle (\Delta X)^2 \rangle \) against the “time”. The agreement between the results of the simulation (open circles) and the analytical solution (curve) is excellent, and \( \langle (\Delta X)^2 \rangle \) converged to the limiting value 0.5 consistent with the equipartition law.

References