Stochastic molecular dynamics: A combined Monte Carlo and molecular dynamics technique for isothermal simulations

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A hybrid Monte Carlo molecular dynamics technique is developed that gives equations of motion for an isothermal system. Test results for a Lennard-Jones fluid are shown to be in good agreement with the known equation of state. The physical interpretation of the procedure and the extension to isothermal—isobaric systems is also discussed. © 2002 American Institute of Physics.

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I. INTRODUCTION

Each of the two main simulation techniques—Monte Carlo and molecular dynamics—has its own advantage. The molecular dynamics method can be used for time-dependent phenomena because it solves the equations of motion along a trajectory. In contrast the Monte Carlo method generates a sequence of states that yields the desired probability distribution, and while this precludes the study of dynamics, it does allow the trajectory to be optimized to cover the important states of the system in an efficient manner. In recent years the molecular dynamics method has been extended beyond the constant energy systems implicit in Newton’s or Hamilton’s equations, and, for example, constant temperature or constant pressure systems may now be simulated with it.1,2 The question naturally arises as to the physical meaning of these extensions and whether the probability distributions generated by the non-Hamiltonian equations of motion are related to the standard distributions of statistical mechanics.

This paper presents a hybrid technique for simulating isothermal systems. It consists of deterministic time steps using Newton’s equations, alternated with stochastic steps based upon the Boltzmann distribution. The algorithm is very similar to that proposed by Andersen,3 with the main difference being that here the Metropolis algorithm is used, which allows the perturbation of the deterministic trajectory to be made arbitrarily small. It is proven that the standard canonical distribution is generated by the trajectory. The stochastic step represents the physical realization of a heat reservoir, and it is shown that the sign of the average change in energy at each step depends upon whether the subsystem temperature is greater than or less than that of the reservoir. A Lennard-Jones fluid is simulated and it is shown that the algorithm reproduces the standard results.

II. EQUATIONS OF MOTION

Consider a subsystem of $N$ atoms in $d$ dimensions in contact with a thermal reservoir, and denote by $\mathbf{\Gamma} = (q^{Nd}, p^{Nd})$ the coordinates of the subsystem. The subsystem evolves according to Hamilton’s equations of motion

\begin{equation}
q_{i\alpha} = \frac{\partial H^\text{total}}{\partial p_{i\alpha}} = \frac{p_{i\alpha}}{m},
\end{equation}

\begin{equation}
p_{i\alpha} = -\frac{\partial H^\text{total}}{\partial q_{i\alpha}} = F_{i\alpha} + f_{i\alpha},
\end{equation}

where $i = 1, \ldots, N$ labels the atom and $\alpha = 1, \ldots, d$ labels the coordinate. Here $F_{i\alpha} = -\partial U(q^{Nd})/\partial q_{i\alpha}$ is the force due the atoms of the subsystem only, and $f_{i\alpha}$ is the force arising from the thermal reservoir.

Obviously one has no wish to follow the motion of the atoms of the reservoir explicitly, and so one requires an expression for the effective reservoir force. By its nature the reservoir interactions represent weak perturbations on the trajectory of the subsystem that are randomly distributed according to the nature of the reservoir. In the present case of a thermal reservoir they fix the temperature of the subsystem, and they yield the canonical Boltzmann distribution of the subsystem’s coordinates in phase space,

\begin{equation}
\varphi_{\beta}(\mathbf{\Gamma}|N,V,T) = \frac{e^{-\beta H(\mathbf{\Gamma})}}{Z(N,V,T)}.
\end{equation}

Here $\beta = 1/k_{B}T$, and the Hamiltonian that appears is that of the subsystem alone.

The trajectory may be written as a Markov chain by discretizing time $t$ in steps of length $\Delta t$. The natural Hamiltonian evolution of the subsystem is

\begin{equation}
q_{i\alpha}(t + \Delta t) = q_{i\alpha}(t) + \Delta t p_{i\alpha}(t)/m,
\end{equation}

\begin{equation}
p_{i\alpha}(t + \Delta t) = p_{i\alpha}(t) + \Delta t F_{i\alpha}(t).
\end{equation}

(This has been written in the simplest form. In practice one often solves the natural motion to higher order accuracy than this.) This deterministic step is augmented by a stochastic step,

\begin{equation}
q_{i\alpha}(t + \Delta t) = q_{i\alpha}^{0}(t + \Delta t),
\end{equation}

\begin{equation}
p_{i\alpha}(t + \Delta t) = p_{i\alpha}^{0}(t + \Delta t) + \Delta t f_{i\alpha}(t + \Delta t).
\end{equation}
III. STATIONARY DISTRIBUTION

The random force \( f \) can be generated by a stochastic transition probability. In general the evolution of a probability distribution under the action of such a transition probability is given by

\[
\varphi(\Gamma_2; t + \Delta_t) = \int d\Gamma_1 \mathcal{T}(\Gamma_2; \Gamma_1) \varphi(\Gamma_1; t).
\]

(6)

Here \( \mathcal{T}(\Gamma_2; \Gamma_1) \) gives the probability of being in the state \( \Gamma_2 \) at time \( t + \Delta_t \) given that the system was in the state \( \Gamma_1 \) at time \( t \), and it is obviously normalized,

\[
\int d\Gamma_2 \mathcal{T}(\Gamma_2; \Gamma_1) = 1.
\]

(7)

For deterministic equations of motion, the transition probability is

\[
\mathcal{T}(\Gamma_2; \Gamma_1) = \delta(\Gamma_1 + \Delta_t \Gamma_1 - \Gamma_2),
\]

(8)

where \( \dot{\Gamma}_1 = \dot{\Gamma}(\Gamma_1) \). Accordingly, the probability evolves as

\[
\varphi(\Gamma_2; t + \Delta_t) = \int d\Gamma_1 \delta(\Gamma_1 + \Delta_t \Gamma_1 - \Gamma_2) \varphi(\Gamma_1; t)
\]

\[
= \frac{\varphi(\Gamma_2; -\Delta_t \dot{\Gamma}_1, t)}{|\nabla(\Gamma_1 + \Delta_t \Gamma_1)|_2}
\]

\[
=[\varphi(\Gamma_2; t) - \Delta_t \nabla \varphi(\Gamma_2; t)] \cdot \nabla \varphi(\Gamma_2; t)] + \Delta_t \nabla \varphi(\Gamma_2; t)] + O(\Delta_t^2).
\]

Taking the limit \( \Delta_t \to 0 \) gives Liouville’s theorem for the deterministic evolution of a statistical ensemble

\[
\frac{d\varphi(\Gamma_t)}{dt} + \nabla \cdot [\dot{\Gamma} \varphi(\Gamma_t)] = 0.
\]

(10)

In the stochastic case, at equilibrium, the probability of the states are proportional to their weights, which arise from the transition probabilities. If the transition from 1 to 2 is more likely than that from 2 to 1, then the state 2 is more likely than the state 1 by the same factor,

\[
\mathcal{T}(\Gamma_2; \Gamma_1) = \frac{\varphi(\Gamma_2)}{\varphi(\Gamma_1)}.
\]

(11)

Such transition probabilities are reversible,

\[
\mathcal{T}(\Gamma_2; \Gamma_1) \varphi(\Gamma_1; t) = \mathcal{T}(\Gamma_1; \Gamma_2) \varphi(\Gamma_2; t),
\]

(12)

which is to say that the forward transition is just as likely to occur as the reverse transition. [Note the distinction between \( \mathcal{T}(1; 2) \), which is the conditional probability of a particular transition, and \( \mathcal{T}(1; 2) \varphi(2) \), which is the probability of a particular transition.] In this case the equilibrium or steady state condition is automatically satisfied

\[
\varphi(\Gamma_2; t + \Delta_t) = \int d\Gamma_1 \mathcal{T}(\Gamma_2; \Gamma_1) \varphi(\Gamma_1; t)
\]

\[
= \int d\Gamma_1 \mathcal{T}(\Gamma_1; \Gamma_2) \varphi(\Gamma_2; t) = \varphi(\Gamma_2; t).
\]

(13)

Henceforth the analysis is restricted to such reversible stochastic transition probabilities.

IV. ALGORITHM

A. Isothermal system

The equations of motion (4) and (5) may be represented by the product of transition probabilities of the form

\[
\mathcal{T}(\Gamma; \Gamma_1) = \prod_{ia} \mathcal{T}(p_{ia}; p^0_{ia}) \mathcal{T}_J(\Gamma^0; \Gamma_1).
\]

(14)

The deterministic transition \( \mathcal{T}_J \) reflects Hamilton’s equations and as such it conserves energy. Accordingly, the Boltzmann distribution, Eq. (3), is invariant under its action.

One requires a similar invariance for each of the single component stochastic transition probabilities \( \mathcal{T}_{ia} \). This is easy to achieve since the Boltzmann distribution itself factors into the product of components of the momenta, and one only has to ensure microscopic reversibility for each. A convenient choice is that of Metropolis,

\[
\mathcal{T}(p_{ia}; p^0_{ia}) = a \delta(\Delta_p^i) + \frac{1}{2p^*} \theta(\Delta_p + p^*) \theta(p^* - \Delta_p)
\]

\[
\times [\theta(-\Delta_H) + \theta(\Delta_H) e^{-\beta \Delta_H}],
\]

(15)

where the rejection (same-state) factor ensures the correct normalization and is given by

\[
a = 1 - \frac{1}{2p^*} \int_{-p^*}^{p^*} d\Delta_p [\theta(-\Delta_H) + \theta(\Delta_H) e^{-\beta \Delta_H}],
\]

(16)

with clearly \( 0 < a < 1 \). Here \( \theta \) is the Heaviside step function, the change in momentum is \( \Delta_p = p_{ia} - p^0_{ia} \), the change in energy is \( \Delta_H = [p^2_{ia} - (p^0_{ia})^2]/2m \), and \( p^* \) is the maximum change in momentum, which is related to the maximum stochastic force from the reservoir, \( f_0 = p^*/\zeta \). One can readily confirm that with the Metropolis choice,

\[
\mathcal{T}(p_2; p_1) e^{-p^2_{ia} / 2m kT / \sqrt{2 \pi m kT}} = \mathcal{T}(p_1; p_2) e^{-p^2_{ia} / 2m kT / \sqrt{2 \pi m kT}}
\]

(17)

and hence that the Boltzmann distribution is stationary under the total transition probability.

The implementation of the Metropolis algorithm begins with a trial move

\[
p_{ia}^{\text{trial}} = p_{ia}^0 + \Delta_p^i,
\]

(18)

where \( \Delta_p^i = a f_{ia} \) is a random number uniformly distributed on \([-p^*, p^*]\). The change in energy of the trial move is

\[
\Delta H(\Gamma^0) = [p^2_{ia} + \Delta_p^2 - (p^0_{ia})^2]/2m,
\]

(19)

and the move is accepted if, and only if,

\[
e^{-\beta \Delta H} \geq \xi,
\]

(20)

where \( \xi \) is a random number uniformly distributed on \([0, 1]\). If the trial move is rejected one goes to the next component of momentum leaving this one unchanged from its deterministic evolution.
Note that although this stochastic step only depends upon the change in kinetic energy, the phase space probability density is not proportional to a Boltzmann factor of the kinetic energy alone because the latter is not a constant of the natural motion and so $\varphi_K$ is not an eigenvector of $T$. Also, although the stochastic transition matrix has been written as the product of successive matrices each operating on a single component of momentum, these can of course be combined into single atom or multiple atom moves.

Typically the maximum step in momentum would be related to the root mean square velocity, $p^* = \sqrt{mk_BT}$, where $\lambda = 0.1-0.01$. In practice $\lambda$ is decreased as equilibration proceeds. An acceptance rate of 98% is typical.

The algorithm was tested by simulating a Lennard-Jones fluid and comparing the results with the exact equation of state. The method works well, as is clear from Fig. 1. Particularly convincing is the heat capacity, which was obtained from the fluctuations in the energy. This demonstrates that the Boltzmann distribution is correctly generated by the trajectory.

**B. Isobaric system**

The extension of the algorithm to isobaric systems appears straightforward. One simply includes an additional stochastic step in the Markov chain to represent a change in the volume of the subsystem, and one accepts it with probability proportional to the usual Boltzmann factor. In addition to the $p\Delta V$ term, where $p$ is the reservoir pressure, one includes the change in the subsystem energy that arises from rescaling the momentum and position coordinates of the atoms. The deterministic Hamiltonian step and the stochastic isothermal momentum step remain unchanged.

A second method is based on the isenthalpic method of Andersen. Here the equations of motion are augmented with a new variable that represents the volume of the system and that is used to scale the particles’ positions and momenta. The enthalpy $E+pV$ is conserved in this approach. For an isothermal–isobaric system, the above stochastic step (in its present form or in the form suggested by Andersen), is applied to the particles’ momenta. It is not necessary, but a stochastic step on the subsystem volume could also be included.

**V. INTERPRETATION**

In the usual Monte Carlo simulation technique, a trial move that decreases energy is more likely to be accepted than one that gives an energy increase. But there are many more trial moves that lead to an energy increase than there are moves that decrease energy, and in equilibrium these tendencies are in balance. This equilibrium balance, and the precise way in which it is achieved, is manifest by temperature equality of the subsystem and the reservoir. One can see this from the macrostate transition probability, $T(E_0 + \Delta E; E_0)$, where $\Delta E$ is changed in the Hamiltonian after a full step in the Markov chain. Invoking the simplest ansatz that obeys the steady state condition, namely that this is just proportional to the probability of the destination macrostate (and is zero if $|\Delta E| > E^*/2$), one has

\[
T(E_0 + \Delta E; E_0) = \varphi(E_0 + \Delta E|T) = \frac{1}{Z'(T)} e^{S(E_0 + \Delta E)/kB - (E_0 + \Delta E)/kB T} = \frac{1}{Z(T)} e^{S(E_0 + \Delta E/T_s(E_0))/kB - (E_0 + \Delta E)/kB T} = \frac{1}{Z(E_0, E^*, T)} e^{\Delta \beta \Delta E}, \quad |\Delta E| < E^*/2, \tag{21}
\]

where the difference in the reciprocal temperature of the subsystem and the reservoir is $k_BT_s(E_0) = T_s(E_0) - T^{-1}$. This uses the fact that the macrostate probability is proportional to the exponential of the macrostate entropy. With this the average change in energy is

\[
\langle \Delta E \rangle_{E_0} = \frac{(E^*)^2}{12kB} \left( \frac{1}{T_s(E_0)} - \frac{1}{T} \right). \tag{22}
\]

This shows that if the subsystem temperature is too low, the average change in energy is toward higher energy states, and vice versa. The first term is due to the greater number of states available to the subsystem at higher energies, and the second term represents the loss of entropy by the reservoir at higher subsystem energies.

It is of interest to contrast this result for the average change in an energy macrostate with the average change in momentum for a momentum microstate. Using the Metropolis algorithm of the present method, one can show that the average change in momentum for a component of momentum $p$ at each stochastic step is

\[
\langle \Delta p \rangle_p = \frac{-(p^*)^2}{6mk_BT} p, \quad |p| > p^*/2. \tag{23}
\]

This says that provided the speed is not too small, it is most likely to decrease from its current value. This has to be the case because the Boltzmann distribution of microstates is a monotonically decreasing function of speed. Given that the system is in an unlikely state it has to favor transitions to
more likely states than to less likely states simply to maintain the steady state. This is in contrast to the transitions between energy macrostates found above which can be positive or negative because the energy probability distribution is non-monotonic due to the combination of the increase of subsystem entropy with subsystem energy and the decrease of reservoir entropy with subsystem energy. In other words, there is no internal entropy for the momentum microstate, and so the term involving the temperature of the subsystem is missing.

VI. PREVIOUS WORK

There are a number of algorithms for constant temperature molecular dynamics. One that has a stochastic element in common with the present approach was given by Andersen. In that approach at random time intervals the momentum of a particle chosen at random is replaced by a random value chosen from the Maxwell–Boltzmann distribution for the desired temperature, which to some extent mimics collisions with ghost particles of a heat bath. The present algorithm is in essence identical to that of Andersen’s in the sense that both ensure that the Boltzmann distribution is the limiting one. The main difference is in the way that this is achieved. Using the Metropolis algorithm as proposed here ensures that there is a high degree of correlation of the particles’ momenta before and after each stochastic step, whereas in Andersen’s method the pre- and post-collision momenta are uncorrelated. The perturbation of the deterministic trajectory in the present algorithm can be made arbitrarily small, and this suggests that it can be used to obtain dynamical properties. Also related to the present approach is the Nose thermostat, in the form presented by Hoover. In this deterministic, extended system approach phase space is augmented by an additional variable that represents the friction or drag coefficient whose time evolution is governed by the difference in the temperature of the subsystem and of the reservoir. Although this is superficially similar to the dependence of the average energy change per time step on the temperature difference, Eq. (22), this only occurs for energy macrostates, not for momentum microstates, Eq. (23). Other isokinetic approaches include the so-called Gaussian thermostat, in which the friction coefficient evolves in such a way that the kinetic energy is a constant of the motion.

The stochastic approach of Andersen, and the deterministic extended system approach of Nosé–Hoover, both sample the canonical ensemble (i.e., the phase space microstates are distributed according to a Boltzmann factor of the kinetic and the potential energy). These methods, and the present one, are in this aspect preferable to the isokinetic method, and to methods that involve velocity rescaling, since neither of these yield the canonical distribution.

VII. CONCLUSION

The stochastic dynamics method proposed here has several advantages over other isothermal molecular dynamics methods: it yields the correct Boltzmann distribution, the subsystem temperature is not required during the trajectory, and friction occurs implicitly and has a physical origin (i.e., it represents the perturbative forces from the thermal reservoir), rather than as an explicit, ad hoc addition to the equations of motion. It appears straightforward to generalize the present method to isobaric systems. It appears less easy to implement it for nonequilibrium systems, although in these cases the need is arguably more urgent since the current methods are based on nonphysical equations of motions and the underlying probability distributions that they generate are unknown.

5 It follows from this argument that because there are a larger number of states at higher energy, random numerical errors are likely to increase the energy of the system. This explains the small but monotonic increase in energy and temperature that is observed in conventional constant energy molecular dynamics simulations.